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**PREPARATION AND CHARACTERIZATION OF PHOSPHORIC-ACID
CATION-EXCHANGE RESINS**

City University of New York

Ph.D. 1982

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PREPARATION AND CHARACTERIZATION OF PHOSPHORIC-ACID
CATION-EXCHANGE RESINS

by

RUSSELL B. SELZER

A dissertation submitted to the Graduate Faculty
in Chemistry in partial fulfillment of the
requirements for the degree of Doctor of Philosophy,
The City University of New York.

1982

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RUSSELL B. SELZER

1982

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Samuel J. Howey
Chairman of Examining Committee

5 August 1982
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David C. Lebe
Executive Officer

James H. Koster
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Peter Mennit
Supervisory Committee

ABSTRACTPREPARATION AND CHARACTERIZATION OF PHOSPHORIC-ACID
CATION-EXCHANGE RESINS

by

RUSSELL B. SELZER

Adviser: PROFESSOR DARRYL G. HOWERY

Cation-exchange resins containing phosphoric-acid-monoester (PME) and phosphoric-acid-diester (PDE) groups based on a styrene/divinylbenzene copolymer matrix are prepared and characterized. These materials are used to investigate the interactions of the phosphate groups with cations.

The synthesis involves conversion of the styrene/DVB copolymer to 2-polystyrylethanol (alcohol resin) through a five-step reaction sequence. The copolymer side chain is formed through chloromethylation and nitrile formation. The nitrile resin is converted to the alcohol resin through hydrolysis and reduction. Condensation of the alcohol resin with a phosphate monoester under the action of trichloroacetonitrile produces the phosphate exchangers. Thus, reaction with monoethyl phosphate produces the PDE resin and reaction with 2-cyanoethyl phosphate produces the PME resin. The specific experimental conditions required to effect these reactions are discussed. The resins are stable under a variety of conditions.

The results of several physicochemical characterizations, including the capacities, water contents, equilibrium selectivities, infrared spectra and electrical conductivities of several ionic forms of each resin, are reported. One PME resin has a total capacity of 2.69 meq/g and consists of stronger-acid groups ($pK = 1.9$) and weaker-acid groups ($pK = 7.5$), each

accounting for fifty percent of the total cation-exchange capacity. One PDE resin consists of moderately strong-acid groups ($pK = 2.5$) and has a capacity of 1.26 meq/g. The water contents of ten ionic forms of the PME resin and six forms of the PDE resin are measured. Typical water contents (% H_2O) are: for the PME resin, 22.3 for the H^+ -form and 39.1 for the Na^+ -form; for the PDE resin, 17.9 for the H^+ -form and 28.8 for the Na^+ -form. The equilibrium isotherms for ten cation pairs for the PME resins and five cation pairs for the PDE resins are determined. The resins are highly selective for the proton and for polyvalent cations (for PME resin, $\log K_{Na}^H = 0.98$ and $\log K_{Na}^{Mg} = 1.60$; for PDE resin, $\log K_{Na}^{Mg} = 1.42$). The infrared spectra of 14 ionic forms of each resin are recorded. The IR spectra are typical of ionized phosphate groups, and the differences among the spectra are used to distinguish the mode of bonding by the various cations. Interactions are ionic for the Group IA cations while associative interactions govern the bonding in the other ionic forms. The electrical conductivities of 4 ionic forms are measured and are found to be particularly low for the Ca^{2+} - and Cu^{2+} -forms.

DEDICATION

I dedicate my thesis to the memory of my father, Irving H. Selzer, and to the memory of my brother, Martin R. Selzer.

I also dedicate this thesis to my mother, Ethel Selzer, and to my sister, Frances Yuras and family, Paul and Michele Yuras.

To Shari M. Roth I give special dedication and deepest thanks for seeing me through these years with understanding, support, friendship and love. Without you, I probably would not have made it.

I would also like to acknowledge the contribution of my mentor, Professor Darryl G. Howery, for teaching me how to be a chemist and for his patience, encouragement and unfailing confidence.

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CHAPTER ONE

INTRODUCTION

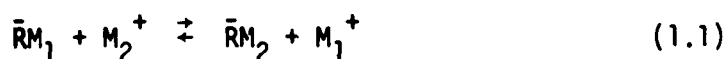
1.1 Ion Exchange and Ion-Exchange Resins.

The basic requirement for an ion-exchange material is the presence of immobile anionic or cationic groups (ionogenic groups, exchange sites), with which there are associated an equivalent amount of mobile ions of opposite charge (counterions). These mobile counterions are interchangeable with other like-charged ions present in an external solution, such that the net effect of the process is ion exchange. When the fixed ionogenic groups in the ion-exchange substance are anionic, the exchangeable counterions are cations, and the material is a cation exchanger. When the fixed ionogenic groups are cationic, the exchangeable counterions are anions, and the material is an anion exchanger. A variety of rocks, sands and soils, as well as biological materials, are known to display ion-exchange characteristics. Helfferich's book [1], considered the classic work covering all aspects of the ion-exchange field, contains an excellent historical perspective and basic introduction to ion exchange. The texts of Kunin [2] and Osborn [3] also stand as fundamental works in the field.

Ion exchangers are generally classified into two major types: the inorganic mineral exchangers and the synthetic organic ion-exchange resins. The most important inorganic exchangers are the zeolites, which are composed of an open aluminosilicate lattice possessing cation exchange properties. A large number of synthetic organic ion-exchange resins is known. The synthetic resins have fixed ionic groups attached to an inert, insoluble polymeric matrix backbone. The resins are rendered

insoluble by interconnecting the polymer chains with various kinds of chemical bridges (crosslinking). The common cation-exchange resins contain sulfonic, phenolic, carboxylic, and phosphonic groups; the common anion-exchange resins contain mono-, di- and tri-alkyl quaternary ammonium groups. Ion exchangers, both the zeolites and the synthetic resins, are used extensively in a wide variety of applications, for example, in water softening and demineralization, solvent purification, electrolyte concentration, catalysis, chromatography and oxidation-reduction [1,2,4].

The cation-exchange equilibrium reaction is represented by the following equation:



The insoluble polymeric resin matrix with its fixed anionic ionogenic groups is denoted by $\bar{R}$, and M_1^+ and M_2^+ are the exchangeable counterions (here assumed to be monovalent cations). $\bar{R}M_1$ signifies that M_1^+ is associated with the fixed charges in the resin phase (the M_1^+ -form of the resin). When the M_1^+ counterions are replaced by M_2^+ ions, the resin is said to be converted from the M_1^+ -form to the M_2^+ -form. There must be a direct quantitative correspondence between the negative charges carried by the fixed anionic groups and the total positive charge of the counterions associated with the resin phase. Thus, in the ion-exchange process, electroneutrality is strictly maintained. An ion exchanger can carry only a fixed quantity of counterions, the amount of which depends on the total charge fixed to the resin backbone. The "capacity" of an ion-exchange resin refers to the amount of counterions (usually expressed

in milliequivalents) present per unit weight of resin. The capacity, a constant for a given exchanger system, is the fundamental property for an ion exchanger.

When a cation exchanger in the M_1^+ -form is placed in an aqueous solution containing M_2^+ cations, the M_1^+ ions diffuse from the resin phase into the solution phase as they are replaced by (exchanged for) M_2^+ ions. This process continues until the equilibrium represented by equation (1.1) is established between the two phases. At equilibrium, the counterion concentration ratio in the resin phase generally differs from that in the solution phase. Thus, the exchanger is said to exhibit a selectivity for one cation over another. The selectivity is another fundamental property of all ion exchangers.

The typical cation exchanger can be viewed as a macromolecular polyanion. The polyanionic chains form a random network of charges, and the spaces between the polymeric chains (the pores or interstices of the resin) are occupied by the counterions and the solvent (water in our discussion), at least a part of which solvates the ionogenic groups and the counterions. Solvent uptake results in the swelling of the resin, the extent of which is dependent upon the degree of hydration of the counterions and on several other factors related to the nature of the resin framework. Solutes present in the external solution (electrolytes and non-electrolytes) can also be taken up by the ion exchanger, a process called sorption. Electrolyte sorption is distinguished from counterion exchange in that the former requires the resin to imbibe a cation and an anion in order to maintain electroneutrality. Sorbed electrolyte is removable from the resin pores by rinsing with excess solvent, whereas the counterions are electrochemically bound to the

resin. A unique feature of ion-exchange resins is the "ion-exclusion" phenomenon, whereby electrolytes are to a great extent prevented from entering the resin phase due to the Donnan potential [1 (p. 135)]. The theoretical aspects of the ion-exchange process are reviewed by Helfferich [1] and discussed in the volumes edited by Marinsky [5].

1.2 The Biological Ion Exchanger.

In recent years, interest in the ion-exchange characteristics of biological systems has been aroused [6-9]. In attempting to explain the physiological properties of living cells, two main schools of thought have arisen. In the traditional theory [10], the "ion-pump" located in the cell membrane is considered to be responsible for transport of ions and other species between the cellular cytoplasm and the extracellular environment. The cellular cytoplasm itself is viewed merely as a dilute aqueous solution of biopolymers and salts. According to the minority viewpoint, the cell is thought of as a relatively homogeneous ion-exchanger phase, in which the ion-exchange properties of the cytoplasm also govern the transport of nutrients. The cytoplasm is treated as a somewhat ordered aqueous phase comprised of a fixed-charge biopolymer network.

The important ion-exchange groups found in cells are the following: carboxylate groups located on proteins, phosphate monoester and phosphate diester groups on nucleic acids, and amine groups on proteins. In some cells and tissues, the total intracellular concentration of these exchange groups exceeds one molal. Damadian [11], in a detailed analysis of the ion-exchange properties of E. coli, has determined that 80 percent of the cell potassium is associated with carboxylate

and phosphate exchange sites on the cytoplasmic macromolecules. A number of physicochemical properties of cells and cell walls associated with ion-exchange properties have been measured. For example, the ion-exchange capacities of cell walls were determined as a function of pH [12-15], and other ion-exchange characteristics such as pH titration profiles [13-16] and cation affinities [17] were measured. These properties were associated with the carboxylate and phosphate groups fixed in the cell walls.

Damadian and co-workers carried out a complete characterization of the biological ion exchanger in E. coli. The investigations included determinations of capacity [8,11], selectivity [8,18], swelling [7] and pH titration measurements [11], all fundamental attributes of an ion-exchange resin. The relaxation times derived from pulsed-NMR measurements on cells and cell walls were found to correspond to those obtained on synthetic ion-exchange resins [8,19,20]. Finally, the energy requirements for operation of the traditional ion-pumps were calculated and found to exceed the available cellular energy [21,22], a point taken to justify the biological ion-exchanger model.

1.3 The Present Study.

As a result of the formulation of the biological ion-exchanger model and the supporting physicochemical evidence, synthetic ion-exchange resins containing the biologically important fixed-charge groups have been proposed as model systems for the investigation of the fundamental properties of the cellular ion exchanger. Studies of synthetic ion-exchange resins provide the particular advantage of isolating the effects of a given exchange group for detailed analysis. Since only

the immediate chemical environment about a particular group exerts any significant influences (e.g., NMR chemical shifts), the exchange groups in the synthetic and biological systems should undergo quite similar localized interactions. Further, synthetic ion-exchange resins are relatively simple, homogeneous materials amenable to detailed characterization. On the other hand, cells themselves are much too complex and heterogeneous for fundamental analysis. Internal molalities of resins range from one to ten (the order of some biological systems). The gel-like, polyelectrolyte structures of the ion-exchange resins should, therefore, have many features in common with those of the cytoplasm, as envisioned by proponents of the biological ion-exchanger model. For cytoplasmic systems and synthetic exchangers with approximately equal internal concentrations of counterions, the interactions at the ion-exchange sites and the structure of water in the regions about the exchange sites may be similar.

Howery and co-workers pioneered investigations of the biological ion exchanger with studies of the carboxylate cation-exchange resins Bio-Rex 70 and Chelex 100 [23,24]. The effect of the counterion on the structure of the resin-phase water using proton magnetic resonance spectroscopy [24] and the magnitude of the counterion-carboxylate interactions using infrared spectroscopy [23] were determined. Further studies included measurements of the electrical conductivity of various ionic forms of Bio-Rex 70 [25] and the uptake of urea on Bio-Rex 70 [26]. Cassidy [27] discussed redox polymers as models for biological systems.

Since the terminal monoester phosphate group ($-\text{OPO}_3^{2-}$) and the bridging diester phosphate group ($-\text{OPO}_2\text{O}-$), along with the carboxylate

group, constitute the major cation-exchange sites in biological systems, continuation of the fundamental study of the biological ion-exchanger model is naturally directed toward synthetic resins containing these moieties. The importance of phosphates in biological systems is well documented [28]. However, commercially available phosphorus-containing cation-exchange resins lack the structural characteristics which correspond to the biological phosphate groups. These materials are mainly monoester phosphonic acids attached to polymer backbones. Stable, homogeneous, monofunctional resins containing either phosphoric-acid-monoester groups or phosphoric-acid-diester groups are lacking.

The unavailability of well-characterized phosphate resins coupled with the need for fundamental data on phosphate ion-exchange properties provides the impetus for the present work. The preparation and characterization of ion-exchange resins with anionic monoester phosphate ($\bar{R}-OPO_3^{2-}$) and diester phosphate ($\bar{R}-OPO_2OR'^{-}$) fixed groups is desirable for a variety of reasons. The phosphorus-containing cation-exchange resins are by far the least studied of the common cation-exchanger types. Furthermore, well-defined monofunctional materials containing phosphate groups have not been reported; hence, little is known about the ion-exchange properties of phosphate groups. Considering this lack of information, preparation and characterization of phosphoric-acid-ester cation-exchange resins is significant from a purely physico-chemical standpoint. In addition, the extensive occurrence of phosphate-ester groups in living systems calls for the accumulation of this basic physicochemical knowledge toward the ultimate goal of understanding the functioning of the living cell.

In the following chapters, we describe the synthesis of two

cation-exchange resins: 2-polystyrylethylphosphoric acid and ethyl 2-polystyrylethylphosphoric acid. These materials are characterized by measuring basic physicochemical properties such as capacity, pH titration curves, selectivity, water content, infrared spectra, PMR spectra and electrical conductivity. The results are intended to contribute to a basic understanding of the physical chemistry of the ionized phosphate group and ultimately to provide a framework for understanding the function of phosphate groups in naturally occurring materials.

CHAPTER TWO

A REVIEW OF METHODS OF PHOSPHORYLATION AND SYNTHESIS OF PHOSPHORUS-CONTAINING CATION-EXCHANGE RESINS

2.1 Nomenclature of Oxy-Phosphorus Acids.

There has always been some confusion in the naming of phosphorus compounds, and, as Van Wazer [29(p. 348)] points out, this is especially so in relation to the phosphorus oxyacids, esters and salts. These discrepancies have carried over into some of the literature of phosphorus-containing ion exchangers. It is useful at the outset, then, to present the nomenclature of the types of phosphorus compounds which we shall encounter in relation to phosphorus ion exchangers.

The esters of phosphorus oxyacids are derived from orthophosphoric acid [phosphoric acid, H_3PO_4 or $\text{P}(\text{O})(\text{OH})_3$], orthophosphorous acid [phosphorous acid, H_3PO_3 or $(\text{H})\text{P}(\text{O})(\text{OH})_2$], and hypophosphorous acid [H_3PO_2 or $(\text{H})_2\text{P}(\text{O})(\text{OH})$]. The compounds which we want to prepare, a monoester phosphate $[(\text{RO})\text{P}(\text{O})(\text{OH})_2]$ and a diester phosphate $[(\text{RO})(\text{R}'\text{O})\text{P}(\text{O})(\text{OH})]$, are derivatives of phosphoric acid. These compounds are also referred to as monoalkylphosphoric acids and dialkylphosphoric acids, respectively.

Only the phosphoric acid derivatives contain the phosphate groups as they exist in biological systems. It is these ionogenic groups that we want to study in an ion-exchange resin. Other cation exchangers which are encountered contain derivatives of phosphorous and hypophosphorous acid. The "phosphonic-acid" resins are actually composed of alkylphosphonic-acid groups, $\text{RP}(\text{O})(\text{OH})_2$. Other resins contain alkylphosphonous-acid groups (or alkylphosphinic-acid groups), $\text{R}(\text{H})\text{P}(\text{O})(\text{OH})$. These

materials are characterized by direct carbon to phosphorus linkages. Most of the "phosphate" and "phosphoric-acid" resins reported are actually phosphonate and phosphonic-acid resins, in which there is direct attachment through carbon-phosphorus bonds of the oxyphosphorus groups to the polymer backbone of the resin. These materials will be discussed in more detail later.

Table 2-1 summarizes the names and structures of the oxyphosphorus groups pertinent to our subsequent discussions.

2.2 General Methods in Phosphoric-Acid Ester Synthesis.

There are a wide variety of synthetic methods for the preparation of the mono-, di- and tri-esters of phosphoric acid [29(p. 221)]. These methods are generally more complex than those used in the formation of the esters of carboxylic acids. Whereas carboxylic acids can be readily esterified by direct (catalyzed) reaction with alcohols, phosphoric acid does not form esters when direct reaction with alcohols is attempted [30,31].

Phosphoric-acid esters must be synthesized by the action of activated phosphorus compounds on alcohols or other reagents such that the adducts are convertible into the ester derivatives, e.g., by hydrolysis. Such activated phosphorus compounds include phosphorus trichloride (PCl_3), phosphorus oxychloride (POCl_3), the acid chlorides of phosphoric acid [e.g., alkylphosphodichloridates, $(\text{RO})\text{P}(\text{O})\text{Cl}_2$], phosphorus pentoxide (P_4O_{10}), phosphorus pentachloride (PCl_5) and the trialkylphosphites [$\text{P}(\text{OR})_3$]. Some of these reagents, particularly PCl_3 , POCl_3 , $(\text{RO})\text{P}(\text{O})\text{Cl}_2$, and, to a lesser extent, PCl_5 and P_4O_{10} , will react directly with alcohols to form halophosphorous- or halophosphoric-acid adducts, which then may be treated to yield the corresponding

TABLE 2-1. NOMENCLATURE OF OXYPHOSPHORUS COMPOUNDS.^a

<u>Formula</u>	<u>Structure</u>	<u>Name</u>
H_3PO_4 or $\text{P}(\text{O})(\text{OH})_3$	$\begin{array}{c} \text{O} \\ \\ \text{HO}-\text{P}-\text{OH} \\ \\ \text{OH} \end{array}$	(ortho)phosphoric acid
$(\text{RO})\text{P}(\text{O})(\text{OH})_2$	$\begin{array}{c} \text{O} \\ \\ \text{RO}-\text{P}-\text{OH} \\ \\ \text{OH} \end{array}$	alkylphosphoric acid (monoalkylphosphate)
$(\text{RO})_2\text{P}(\text{O})(\text{OH})$	$\begin{array}{c} \text{O} \\ \\ \text{RO}-\text{P}-\text{OR} \\ \\ \text{OH} \end{array}$	dialkylphosphoric acid (dialkylphosphate)
H_3PO_3 or $\text{HP}(\text{O})(\text{OH})_2$	$\begin{array}{c} \text{O} \\ \\ \text{H}-\text{P}-\text{OH} \\ \\ \text{OH} \end{array}$	(ortho)phosphorous acid
$\text{RP}(\text{O})(\text{OH})_2$	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{P}-\text{OH} \\ \\ \text{OH} \end{array}$	alkylphosphonic acid (alkylphosphonate)
H_3PO_2 or $\text{H}_2\text{P}(\text{O})(\text{OH})$	$\begin{array}{c} \text{O} \\ \\ \text{H}-\text{P}-\text{H} \\ \\ \text{OH} \end{array}$	hypophosphorous acid
$\text{R}(\text{H})\text{P}(\text{O})(\text{OH})$	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{P}-\text{H} \\ \\ \text{OH} \end{array}$	alkylphosphorous acid, alkylphosphinic acid (alkylphosphinate)

^a Reference 29, p. 348.

esters. Other activated phosphorus compounds, for example the trialkylphosphites, react with organic halides to form intermediates convertible into oxyphosphorus-acid esters. Depending on the choice and number of alkyl groups in the starting materials, various specific phosphoric esters may be prepared by these methods. Since the phosphorylation step in the reaction of these types of phosphorylating reagents is a direct reaction with the substance to be phosphorylated, i.e., the alcohol, halide or other compound, we use the term "direct phosphorylation" to describe reactions involving these reagents.

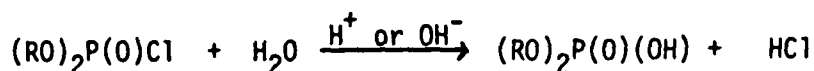
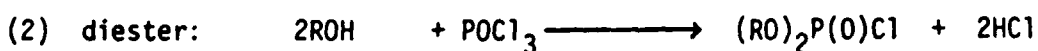
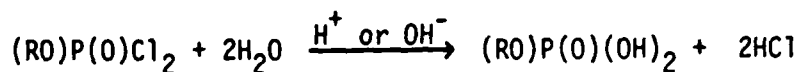
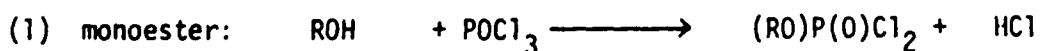
The other class of phosphorylation reactions we wish to distinguish is "condensation phosphorylation." In this type of reaction, the phosphorylating agent, generally a mono- or di-ester of phosphoric acid, is activated by one of several condensing agents. The intermediate formed from the phosphate ester and the condensing agent is the actual phosphorylating agent. This method is applicable to the phosphorylation of hydroxyl compounds. Again, the choice of alkyl groups in the phosphate ester and in the hydroxyl compound dictates the nature of the final phosphate ester product. Somewhat more control over the structure of the final product is possible with this method.

The general strategy for the synthesis of the final resins involves the introduction of phosphorus functions onto a polymer matrix which contains hydroxyl groups. Thus, we shall consider in more detail in the next two sections only those phosphorylation methods readily applicable to hydroxyl compounds.

2.2.1 Direct Phosphorylation Methods.

The direct phosphorylation methods include any reaction in which the phosphorylating agent reacts directly on contact with a hydroxyl compound (an alcoholic or phenolic compound). Since alcohols cannot be phosphorylated directly with phosphoric acid [31(p. 221)], activated phosphorus compounds must be employed. Activated phosphorus compounds used in the direct phosphorylation of alcohols are generally of the halophosphorus type. Among the more common direct-phosphorylating agents are the following: phosphorus trichloride (PCl_3), phosphorus oxychloride (POCl_3), dialkylphosphomonochloridates $[(\text{RO})_2\text{P}(\text{O})\text{Cl}]$ and alkylphosphodichloridates $[(\text{RO})\text{P}(\text{O})\text{Cl}_2]$. Phosphorus pentoxide (P_4O_{10}) and phosphorus pentachloride (PCl_5) generally give rise to mixtures of phosphate-ester reaction products [31(p. 222,226)]. Thus, P_4O_{10} and PCl_5 are not suitable in the cation-exchanger syntheses, since the final resins should be as homogeneous as possible.

The simplest preparation of phosphoric-acid esters involves the reaction of phosphorus oxychloride with an alcohol [29(p. 570),31(p. 227)]. Depending on the reaction conditions, this method can lead to the formation of all three types of phosphate esters:



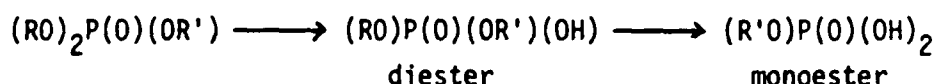
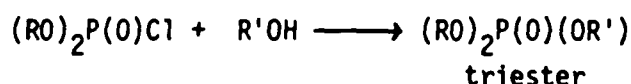
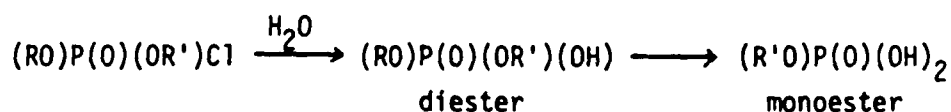
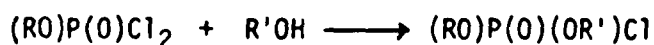


The reactions are carried out in the presence of an organonitrogen base (e.g., pyridine), which scavenges the HCl produced during the phosphorylation. However, it is difficult to obtain pure ester products. Reaction conditions, such as temperature (usually 0°C) and stoichiometric ratios, must be carefully controlled in order to produce product mixtures rich in one particular ester type.

Because of the interest of synthetic biochemists in the preparation of nucleotides and their chemical analogues [32-41], the phosphorylation reactions with POCl_3 , as well as other reagents, have been studied extensively. This work has proved invaluable for our investigations into the various phosphorylation methods, providing many details of the mechanisms of the various phosphorylation reactions, establishing starting points for the experimental conditions applied to our systems, and pointing out difficulties and how they may be circumvented. The use of POCl_3 has been applied especially in those cases in which nucleotides that are essentially phosphate monoesters were to be synthesized. For example, uridine 5-phosphoric acid was made from POCl_3 in pyridine at -40°C [32]. Guanosine-5' phosphate [34] was prepared in a similar manner, though the yield of the monoester product was low, and much inorganic phosphate was found in the product mixture.

In order to increase the selectivity and yield in the direct phosphorylation reactions, reagents related to POCl_3 can be employed. The alkylphosphodichloridates, $(\text{RO})\text{P(0)Cl}_2$, and the dialkylphosphochloridates, $(\text{RO})_2\text{P(0)Cl}$ (halophosphates), can be considered as

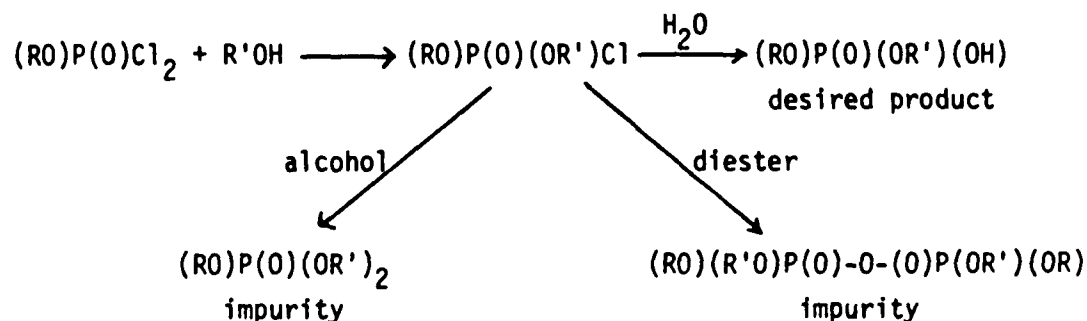
derivatives of POCl_3 in which one or two of the chlorine atoms are replaced by alkoxy groups. These compounds are prepared by reaction of POCl_3 with appropriate alcohols followed by isolation of the halophosphates. The halophosphates directly phosphorylate alcohols. Depending on the choice of alkoxy groups in the halophosphate, selected monoester phosphates and any variety of symmetrical or unsymmetrical di- and tri-ester phosphates can be synthesized. Often, the alkoxy groups of the halophosphate are chosen so as to be readily removable from the product ester without destroying the rest of the molecule [42]. The reaction sequences are:



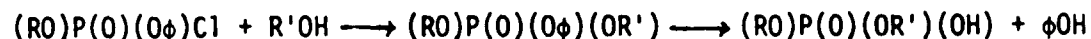
The last steps in each sequence are possible only if the $-\text{OR}$ group is removable. These kinds of reactions have been applied, for example, to the synthesis of various adenosine, guanosine, uridine and cytidine phosphates [33] and to the synthesis of various phospholipids [43].

The selectivity of these methods arises from the proper choice

of the alkyl group(s) on the halophosphate. If a protecting alkyl group is incorporated into the original halophosphate, a pure final product is assured since the phosphorylation occurs with minimal cross reaction. For example, if a specific dialkylphosphate ester is desired, use of an "unprotected" halophosphate can lead to mixed-alkyl and pyrophosphate impurities:



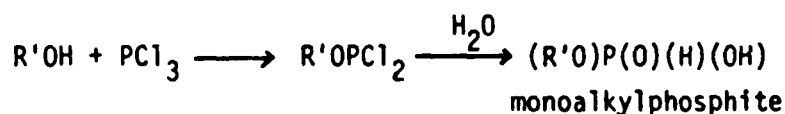
With a "protected" phosphorylating agent, only the desired ester is obtained:



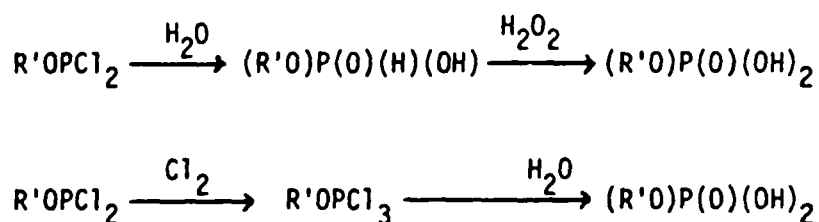
The most common protecting groups are benzyl and phenyl groups. These are readily split off by catalytic hydrogenation [31(p. 235),42-45] or other treatments [43,46]. Application of this method requires careful preparation and purification of the active halophosphate reagent. The catalytic hydrogenation step is carried out with metallized charcoal, a difficult and impractical procedure to carry out on our polymer systems.

Phosphorus trichloride, PCl_3 , can also be employed in the

phosphorylation of alcohols [30(p. 372-3)]. The reaction proceeds with the initial formation of an alkyl dichlorophosphite, which can then be hydrolyzed to a monoester of phosphorous acid:



The intermediate alkyl dichlorophosphite may be oxidized by elemental chlorine or iodine and the product hydrolyzed to form a monoester of phosphoric acid. Alternatively, the monoalkylphosphite may be oxidized to the monoalkylphosphate by hydrogen peroxide or other oxidizing agent:



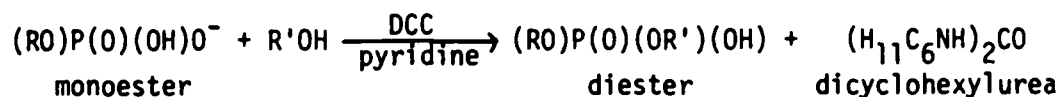
The major disadvantage associated with the phosphorus trichloride method is the nonselectivity, which gives rise to complex phosphate-ester product mixtures. Since the PCl_3 method requires the oxidation step in order to form phosphoric-acid esters, the POCl_3 method would be preferred, since it leads more directly to phosphate esters.

2.2.2 Condensation Phosphorylation Methods.

The phosphorylation of hydroxyl compounds can be accomplished with a high degree of control over the composition of the final product by application of condensation phosphorylation methods. These methods are particularly well suited for the selective preparation of specific

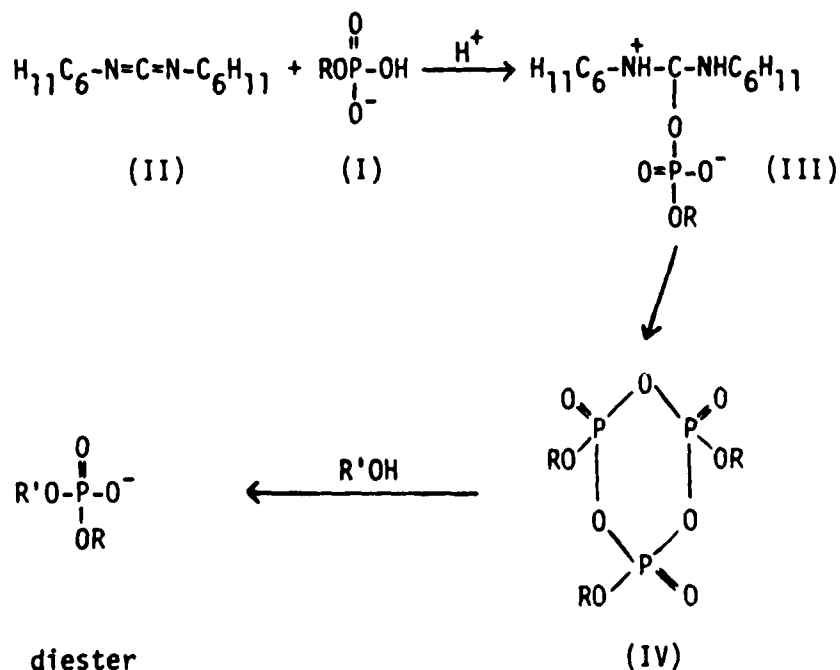
symmetrical and unsymmetrical diesters of phosphoric acid. By inclusion of appropriate protecting groups in the phosphate-ester starting compounds, selected monoesters of phosphoric acid can be obtained in high yields. In general, the technique is carried out by conversion of phosphoric acid or an ester of phosphoric acid into an activated intermediate, the phosphorylating agent, through the action of a condensing agent. Researchers with an interest in the preparation of various nucleotides [35,36,40,41,47], phospholipids [43], and synthetic analogues of natural phosphate products [43,48] have contributed to the development of these condensation methods. The condensing agents found in most common use for these applications are dicyclohexylcarbodiimide [49], trichloroacetonitrile [50], tetra-*p*-nitrophenyl pyrophosphate [51] and various arenesulfonyl halides [31(p. 231), 52]. Cramer [42] reviews many of these methods and details other aspects of phosphate-ester synthesis.

The direct formation of phosphoric-acid diesters by reaction of phosphoric-acid monoesters with alcohols is readily accomplished with dicyclohexylcarbodiimide (DCC). The reaction is normally carried out in pyridine or another organonitrogen base at temperatures around 20°C. The overall reaction can be represented as follows:

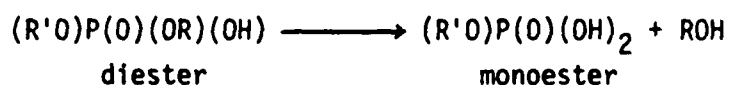


The mechanism of the DCC condensation reaction has been studied [36,49, 53,54]. The action of DCC is attributable to its ability to undergo an acid-catalyzed 1,2-addition reaction. Thus, a monoester phosphate (I)

adds to DCC (II) to form an adduct (III), which reacts further [53] to yield a trimetaphosphate (IV), the cyclic intermediate presumed to be the actual phosphorylating agent:



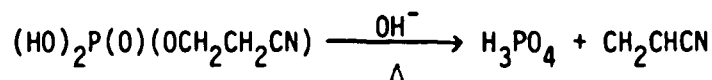
Some triester formation may accompany this reaction. If the alkyl group of the original monoester phosphate is a protecting group, then its removal from the diester product gives rise to a pure phosphoric-acid monoester:



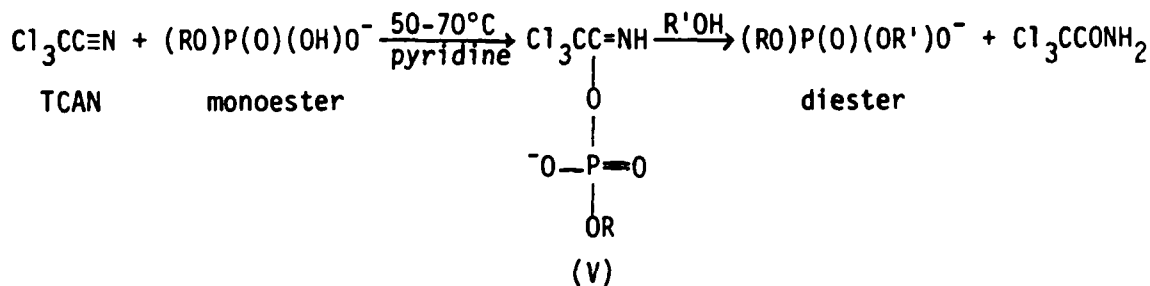
Thus, the DCC method is suitable for the preparation of both mono- and di-ester phosphates in high yield with no concomitant formation of crossed-ester products. The major impurity products are pyrophosphates, resulting from reaction of the intermediate (IV) with another phosphate

monoester molecule. Consequently, the DCC condensation method should be preferred over any of the various direct phosphorylation methods for use in the synthesis of the phosphate ion-exchange resins.

In general, selected pure monoalkyl phosphates are obtained by employing monoester phosphate reagents protected with benzyl groups. As noted previously, deprotection of benzylated compounds is performed by catalytic hydrogenation, a procedure not readily carried out on the solid polymer systems. 2-Cyanoethylphosphate (CEP) [55] was found to be a more appropriate protected monoester phosphate for our purposes. Deprotection results by treatment under mildly alkaline conditions:



Trichloroacetonitrile (TCAN) [50,56] is another condensing agent that we considered in application to the ion-exchanger syntheses. Alcohols can be phosphorylated with monoester phosphate in a manner similar to the DCC method. The active phosphorylating agent forms when the monoester phosphate adds to the nitrile group of the condensing agent. Reaction of the intermediate formed (V) with alcohol produces the phosphorylated diester product:



As in the DCC method, various protecting groups may be incorporated to

enhance the selectivity of the technique. Pyrophosphate formation is less of a concern in the use of TCAN as compared to DCC [50].

The TCAN method has found application in the synthesis of oligonucleotides [41] and synthetic analogues of natural phosphate-ester products [43,48,57,58]. In terms of the solid polymer systems to which these phosphorylation methods are to be applied, DCC has the considerable disadvantage of forming dicyclohexylurea as a reaction product. Dicyclohexylurea exhibits low solubilities in most solvents and would thus be difficult to separate from the polymer beads. TCAN, on the other hand, introduces no such difficulties.

2.3 Phosphorus-Containing Cation-Exchange Resins.

The phosphorus-containing cation-exchange materials which have been synthesized can be classified as those in which the phosphorus groups are attached to the matrix through C-P bonds and those in which the phosphorus groups are attached through C-O-P bonds. The former class constitutes the phosphonous-acid and phosphonic-acid materials and the latter comprises the phosphoric-acid materials. The naming and classification of these ion exchangers is often imprecise whenever the distinction between ion-exchanger phosphonic- and phosphoric-acid-ester groups is made. Consider, for example, the resin Duolite C-65, developed by the Chemical Process Company. This resin is described by Helfferich [1(p. 33)] as a phosphonic type while Kunin [2(p. 92)] calls it a phosphoric type. Thus, consultation of the literature requires care because many abstracts and titles incorrectly identify the nature of phosphorus cation exchangers.

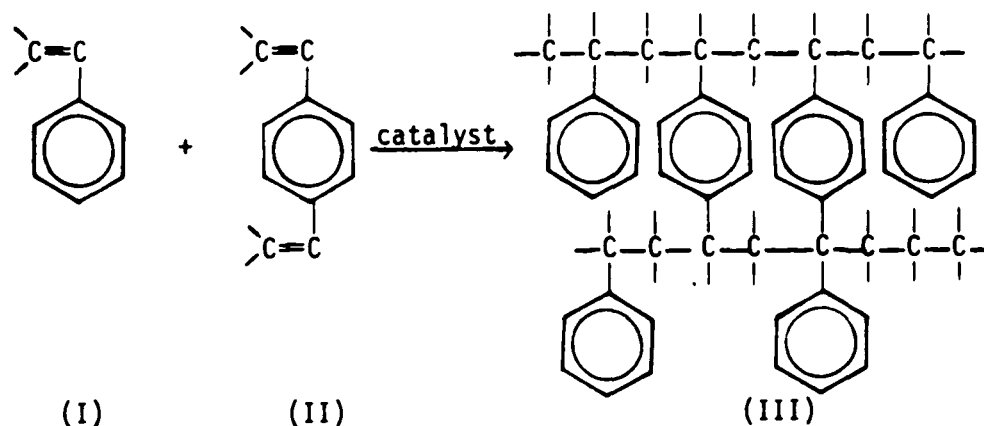
In this section, the major phosphorus-containing cation-exchange materials are reviewed. The phosphonous-acid and phosphonic-acid

exchangers are discussed together since their formulations are closely related. The phosphoric-acid ion-exchange materials include resins (relatively homogeneous polymer beads) as well as other phosphate exchangers incorporating less well defined structures (e.g., celluloses and fabrics).

There are two fundamental approaches to the preparation of these cation exchangers. One approach consists of the introduction of phosphorus functional groups onto a polymer support while the other involves polymerization or condensation of phosphorus-containing monomer molecules. A brief survey of phosphonous, phosphonic and phosphoric cation-exchange substances follows.

2.3.1 Phosphonous- and Phosphonic-Acid Cation Exchangers.

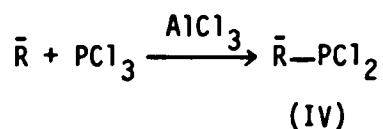
The most common phosphonic-acid cation exchange resin is polystyrylphosphonic-acid, synthesized by subjecting crosslinked polystyrene to a Friedel-Crafts phosphorylation by PCl_3 with AlCl_3 as the catalyst [59-64]. The resin matrix is formed by copolymerization of styrene (I) with a nominal percentage of divinylbenzene (II) or other divinyl aromatic crosslinking agent, usually in an aqueous suspension with benzoyl peroxide as the polymerization catalyst:



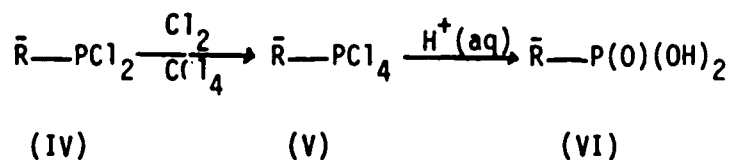
Styrene/divinylbenzene copolymers (III) (styrene/DVB) are prepared in the form of spherical beads, the sizes of which are determined by the degree of agitation of the polymerization suspension. The DVB content of a resin is specified in the name, e.g., styrene/2%-DVB is derived by reacting a monomer mixture comprised of 2% by weight of divinylbenzene.

- . - Typical resins are prepared with DVB contents of from 2 to 16%. The crosslinking agent serves to allow the porous copolymer beads to swell in a variety of solvents while remaining completely insoluble. Under the appropriate conditions, styrene/DVB copolymers undergo the same chemical reactions as do analogous monomeric benzene compounds [65]. In order to obtain a homogeneously functionalized polymer product in such reactions, such that all or most of the phenyl groups in the individual beads are reacted, it is critical that the beads be fully swollen before introduction of reactants so that the reactants can penetrate the beads uniformly.

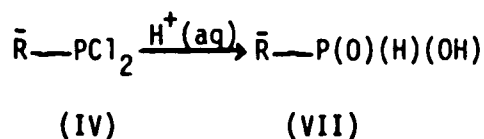
In the preparation of phosphonous- and phosphonic-acid cation-exchange resins based on styrene/DVB copolymers, the beads swell to a sufficient extent in the PCl_3 reactant such that no solvent is generally required. Addition of AlCl_3 catalyst at a temperature ranging from 50°C to the boiling point of PCl_3 causes the reaction to proceed. Using the symbol $\bar{\text{R}}$ to represent the styrene/DVB copolymer matrix (such that $\bar{\text{R}}-\text{X}$ indicates that a group X is connected to the phenyl rings in the matrix), the reaction is:



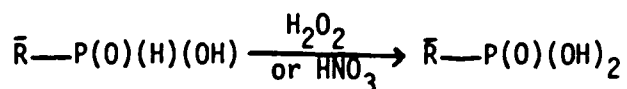
The product (IV), a dichlorophosphine, is suspended in an inert solvent and oxidized with elemental chlorine. The oxidized product (V) is then hydrolyzed in an aqueous medium to yield the phosphonic-acid resin (VI):



Alternatively, the dichlorophosphine derivative (IV) can be hydrolyzed directly to yield a phosphonous-acid resin (VII):



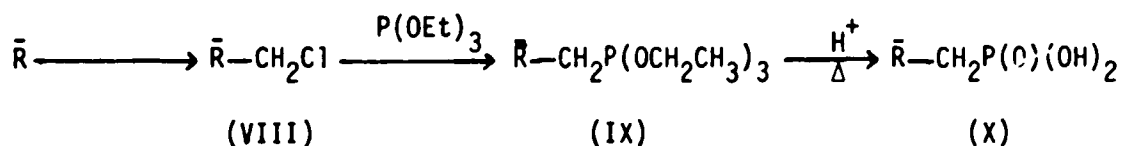
The phosphonous-acid cation exchangers have been available as commercial materials (Bio-Rex C-62, Bio-Rad Laboratories and Duolite C-62, Duolite ES-60, Chemical Process Company), and are usually synthesized and patented in conjunction with the phosphonic-acid resins [59-61]. The phosphonous-acid resins are precursors to the phosphonic-acid resins, since they can be oxidized by H_2O_2 or HNO_3 to yield the latter:



Resins prepared by these means have ion-exchange capacities from ca. 2.5 to as high as 12 meq/g. As expected, the phosphonic resins display capacities about double the capacities of the phosphonous resins from which they can be derived [60,66].

Polystyrylmethylenephosphonic-acid cation-exchange resins are

also among the more common phosphorus-containing materials [62,67,68]. The structure of these resins differs from that of the polystyrylphosphonic resins by the inclusion of a methylene group between the aromatic ring of the resin matrix and the phosphonate functional group. Preparation requires chloromethylation of the copolymer beads (chloromethylation reactions are discussed in the next chapter) and treatment of the chloromethylated polystyrene/DVB (VIII) with a trialkylphosphite, usually triethylphosphite. The dialkylphosphonate derivative (IX) produced is then hydrolyzed to the methylenephosphonic-acid resin (X) by heating in acid:



Phosphonic-acid resins of still higher capacity are produced by chloromethylation of the styrene/DVB copolymer followed by Friedel-Crafts treatment with $\text{PCl}_3/\text{AlCl}_3$ to form resins containing both "nuclear" phosphonic-acid groups (i.e., groups bonded directly to the aromatic rings) and methylenephosphonic-acid groups [69].

Other phosphonic-acid exchangers have been prepared by modifications of the techniques discussed above. For example, the action of phosphorus halides on furfural polymer backbones [70,71] produces such exchangers. Many of the phosphorus-containing cationites prepared in the Soviet Union are phosphonylated copolymers of combinations of divinyl-aromatic and vinyl-aromatic compounds other than divinylbenzene and styrene [e.g., 72]. A novel variation of the phosphonic resins is a thiophosphonic-acid exchanger [73], produced by reacting $\text{PSCl}_3/\text{AlCl}_3$

with a crosslinked polymer, followed by hydrolysis. Some phosphorus resins are actually found to be bifunctional exchangers in which the phosphonylated copolymers are sulfonated [74,75] in order to enhance the useful capacities of the materials. A condensation polymer produced from phenoxymethylenephosphonic acid and formaldehyde acts as a cation exchanger with a capacity of about 12 meq/g [76]. Recently, Czechoslovakian workers have synthesized some phosphonylated resins [77] and have studied their chromatographic properties [78]. Table 2-2 summarizes the types of commercial phosphonous- and phosphonic-acid cation exchangers which have been available. Table 2-3 shows examples of some of the Soviet-made phosphorus cation exchangers.

2.3.2 Phosphoric-Acid Cation Exchangers.

The phosphoric-acid cation exchangers generally do not have a resin-like structure. These materials were produced originally in conjunction with the phosphorylation of cotton fibers in order to impart flameproofing characteristics. Thus, many of the early phosphoric exchangers were actually phosphorylated cottons and celluloses [62,82-85]. Introduction of phosphate functions into polyvinyl alcohol also forms cation exchangers [62,86]. Commercial materials had been synthesized by polymerization of allylphosphate [87,88].

The direct phosphorylation method has been applied to convert the hydroxyl groups of cellulose and cotton [62,82-85], and of polyvinyl alcohol [62,86], to esters of phosphoric acid. Thus, phosphoryl chloride, POCl_3 , was reacted with the hydroxy-containing polymer (XI) in pyridine or pyridine/dioxane to produce a phosphodichloridate intermediate (XII), which was hydrolyzed in an aqueous medium to form the phosphoric polymer (XIII):

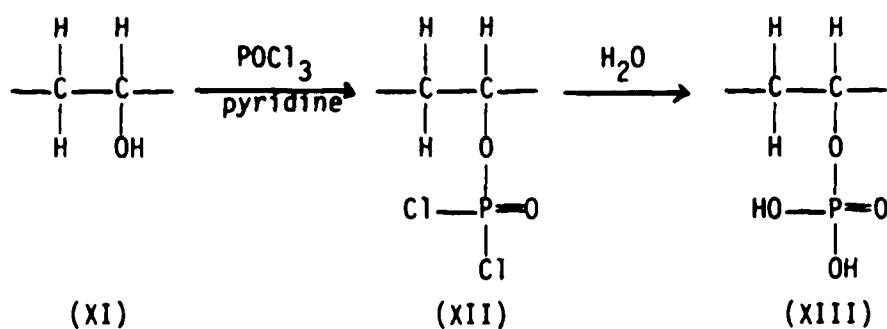
TABLE 2-2. COMMON PHOSPHORUS-CONTAINING CATION-EXCHANGE RESINS.

<u>Resin Type</u>	<u>Structure</u>	<u>Examples^a</u>	<u>References</u>
Phosphonous Acid	$\begin{array}{c} \text{O} \\ \parallel \\ \bar{\text{R}}-\text{P}-\text{OH} \\ \\ \text{H} \end{array}$	Duolite C-62, Biorex C-62	59 - 64
Phosphonic Acid	$\begin{array}{c} \text{O} \\ \parallel \\ \bar{\text{R}}-\text{P}-\text{OH} \\ \\ \text{OH} \end{array}$	Biorex C-63	59 - 64,79
Methylenephosphonic Acid	$\begin{array}{c} \text{O} \\ \parallel \\ \bar{\text{R}}-\text{CH}_2-\text{P}-\text{OH} \\ \\ \text{OH} \end{array}$	Duolite C-63	62,67 - 69
Phenolic/Phosphoric Acid	$\begin{array}{c} \text{O} \\ \parallel \\ \bar{\text{R}}-\text{OP}-\text{OH} \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	Duolite C-65	79,81

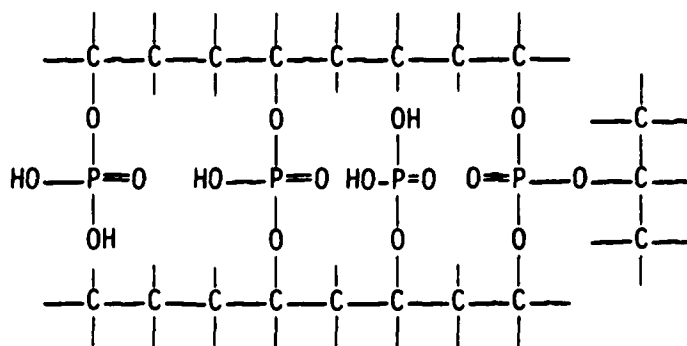
^a These resins are no longer available.

TABLE 2-3. SOME PHOSPHORUS-CONTAINING CATION-EXCHANGE RESINS
PRODUCED IN THE USSR.

<u>Resin</u>	<u>TYPE</u>
KRF, KF-1, KF-11	Phosphonic Acid
KFP	Methylenephosphonic Acid
KF-21	Mixed Phosphonic/Methylenephosphonic Acid
VKhD-9	Condensate of Vinylphosphonic Acid, Vinyl Acetate, DVB.
AF-2	Copolymer of Phenylphosphonic Acid and Acrylonitrile.



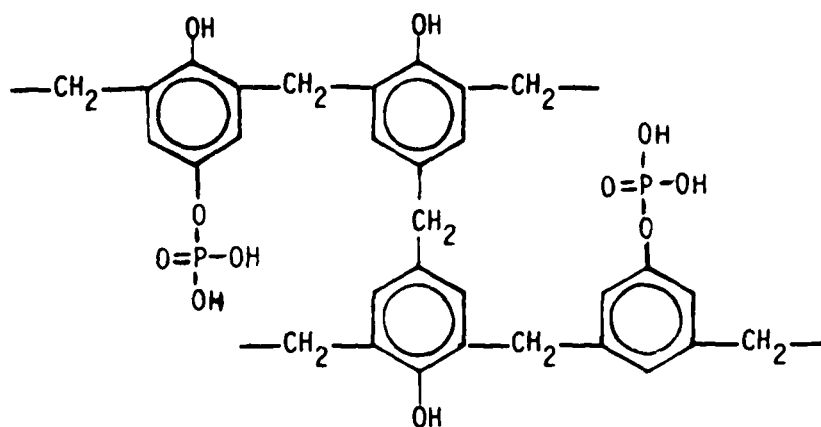
Ideally, only phosphate monoesters (XIII) would form. Actually, it was determined that a mixture of phosphate ester types was produced. These resulted from attack of the intermediate (XII) on one or two other hydroxyl functional groups. The phosphorylated product, containing crosslinkings by diester and triester phosphates, is more properly represented as:



The cotton and celluloses were also phosphorylated with $\text{H}_3\text{PO}_4/\text{P}_2\text{O}_5$ [86,89] and pentaerythrityl phosphoric acid [83]. In all cases, the phosphate exchangers were a complex mixture of esters which were not particularly stable toward hydrolysis of the phosphate-ester linkages. Such materials would not be suitable for a detailed study of the ion-exchange properties of the individual phosphate ester groups.

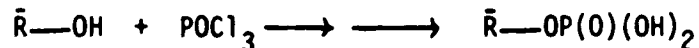
The polymerization of allylphosphates by benzoyl peroxide has been used for the synthesis of ion-exchange resins containing phosphoric-acid diester groups [87,88,90-92]. In this procedure, the polymerization produces a matrix of triester groups. Hydrolysis in aqueous NaOH yields a resin consisting of a mixture of di- and tri-esters. The product is obtained as a solid mass, which must be ground into particles of a suitable size. Again, such materials would not very useful in a detailed study of the ion-exchange properties of the individual phosphate esters.

Another phosphate resin was synthesized by condensation of mono- and di-aryl phosphates with formaldehyde [79,81]. The resulting exchangers contain phosphate groups connected to the aromatic rings of the phenolic-formaldehyde network:



Duolite C-65 was a commercial resin of this type.

Another phosphoric-acid cation exchanger was only alluded to in the literature. Abrams [59] claimed that reaction of phenolic resins with POCl₃, followed by hydrolysis, produced phenylphosphoric-acid resins:



No applications of the process could be found in the literature.

It is evident that a fundamental study of the ion-exchange properties of the phosphate group cannot be carried out with any of the materials discussed in this section. The phosphonate exchangers, which themselves have been little studied, do not contain the phosphate groups found in biological systems. The phosphate materials available cannot be conveniently handled in terms of laboratory operations, and more significantly, are not homogeneous enough to be useful for fundamental physicochemical characterization.

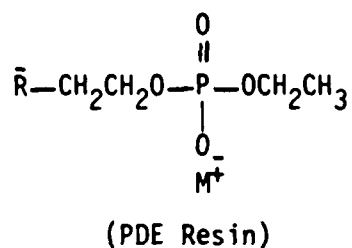
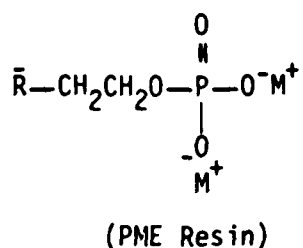
The following chapter describes the synthesis of the new phosphoric-acid-ester cation-exchange resins which we have developed.

CHAPTER THREE

SYNTHESIS OF THE PHOSPHORIC-ACID CATION-EXCHANGE RESINS

3.1 Introduction.

In this chapter, the procedures for the synthesis of our phosphoric-acid cation-exchange resins are detailed. The resins are based on a styrene/DVB copolymer matrix and contain ionogenic groups that are esters of phosphoric acid. One exchanger is composed of phosphate monoester groups (designated PME) and the other is composed of phosphate diester groups (designated PDE). In both resins, the phosphorus group is attached to the copolymer backbone through a two-carbon alkyl chain. Thus, the PME resin is the 2-polystyrylethyl ester of phosphoric acid and the PDE resin is the ethyl 2-polystyrylethyl ester of phosphoric acid. Using the symbol $\bar{R}$ to represent the styrene/DVB copolymer backbone and M^+ to denote a monovalent counterion, the structures of these resins can be represented as follows:



The specific structural attributes necessary for stable, definable cation exchangers were ascertained after numerous variations were attempted. For example, it was determined that stable phosphate linkages to the polymer formed only through a chain of at least two carbons, the polystyrylmethyl esters rapidly dephosphorylating in an aqueous medium. Analogously, although a PDE resin with a methyl group

(methyl 2-polystyrylethylphosphate) was prepared and tested, the PDE containing an ethyl group was found to be more stable. In Chapter Four, a review of all of the attempts to prepare suitable phosphoric-acid exchangers and the strategies on which they were based is given.

The general procedure for the synthesis of the resins involves the introduction of phosphate groups onto a polymeric matrix. The condensation phosphorylation method, known to be more selective and to better control the structure of the final ester product, was chosen for the phosphorylation of the polymer. This procedure requires the preparation of a polymer containing hydroxyl groups located in a suitable position on the functionalized polymer. The starting polymeric material is the styrene/DVB copolymer, generously supplied to us by the Dow Chemical Company [93]. In order to form the PME and PDE resins shown above by a condensation phosphorylation, the polymer alcohol must be 2-polystyrylethanol. Condensation of 2-polystyrylethanol with a monoester of phosphoric acid would yield the desired products: the PDE resin when the 2-polystyrylethanol is condensed with ethyl phosphate and the PME resin when the polymer alcohol is condensed with 2-cyanoethylphosphate and the 2-cyanoethyl protecting group is removed. We have found that the PDE resin also can be synthesized in an alternative manner from the PME product. This method involves condensing a monomeric alcohol (such as ethanol) with the PME resin, a procedure analogous to the other condensation reactions except that the alcohol in this case is a monomer while in the other reactions the hydroxyl group is on the polymer.

The formation of the 2-polystyrylethanol polymer reagent from the styrene/DVB copolymer starting material required careful consideration. The most direct method for the preparation of 2-phenylethanol

from benzene involves treatment of benzene with ethylene oxide (C_2H_4O) and hydrogen chloride in the presence of aluminum chloride [94]. Application of this reaction to the formation of 2-polystyrylethanol from polystyrene/DVB is not practical. The use of a solid $AlCl_3$ catalyst and gaseous HCl and C_2H_4O in a solid polymer system in conjunction with the fact that the monomeric product is reported in low yield [94] deems this process quite unattractive for our purposes.

We found that the best strategy for the preparation of 2-polystyrylethanol from the styrene/DVB copolymer consists of the application of a series of basic organic reactions. The organic-reaction sequence found to satisfactorily perform this conversion is summarized in Figure 3-1.

A one-carbon side chain is introduced onto the aromatic groups of the copolymer (I) by chloromethylation with chloromethylmethyl ether and a Lewis catalyst, titanium tetrachloride (step 1 in Figure 3-1). Although chloromethylated styrene/DVB copolymer (II) is commercially available, the choice of chlorine loadings and particle sizes is limited. Since the loading of chloromethyl groups in this material dictates the capacity (i.e., the phosphorus loading) of the final resins, it was desirable to carry out the chloromethylation so that resins with higher loadings could be produced. From this stage in the synthesis, introduction of a second carbon onto the side chain of the copolymer is readily accomplished by a nucleophilic substitution reaction with cyanide ion. Thus, treatment of (II) with sodium cyanide in acetonitrile produces polystyrylacetonitrile (III) (step 2 in Figure 3-1). Hydrolysis of III with 70% sulfuric acid yields the carboxylic-acid resin (IV) (step 3). Esterification of the latter with ethanol/

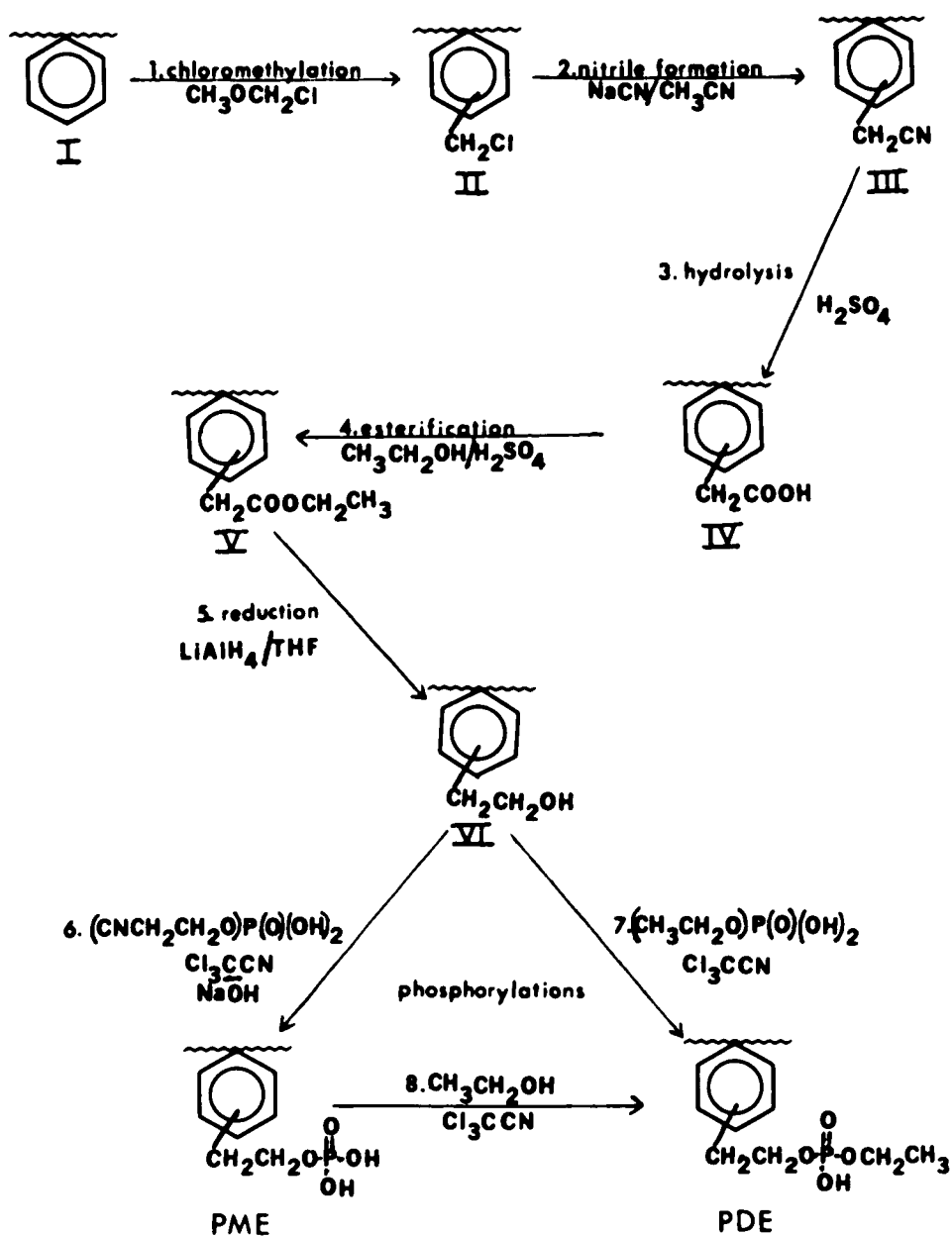


Figure 3-1
Synthetic Sequences

sulfuric acid produces ethyl 2-polystyrylacetate (V) (step 4) which can be reduced with lithium aluminum hydride in tetrahydrofuran to the desired alcohol polymer, 2-polystyrylethanol (VI)(step 5).

The phosphoric-acid cation-exchange resins are then produced by condensation phosphorylation of VI. Reaction with 2-cyanoethylphosphate in the presence of trichloroacetonitrile produces an intermediate resin which readily loses the 2-cyanoethyl group under mildly alkaline conditions to form the PME resin (step 6 in Figure 3-1). Reaction with ethyl phosphate in anhydrous N,N-dimethylformamide, employing trichloroacetonitrile as the condensing agent, gives the PDE resin (step 7). In an alternative method, the PDE resin can be synthesized directly from the PME resin by condensation with ethanol (step 8).

Application of these chemical reactions to the polymer system required the determination of the optimum reaction conditions for essentially complete conversion of the functional groups on the polymer. Temperature, solvent and reagent mole ratios were the significant variables considered. The reaction sequence was followed by measurement of the prevalent infrared frequencies characteristic of the functional groups on the polymer. Table 3-1 lists these characteristic IR bands for the various polymer intermediates in the reaction sequence.

The remainder of this chapter is devoted to a detailed discussion of each of these synthetic steps.

3.2 Chloromethylation.

In a chloromethylation reaction, an aromatic hydrogen is substituted by a chloromethyl group, $-\text{CH}_2\text{Cl}$. The reaction is applicable to a wide variety of aromatic compounds [97(p. 63)]. The chloromethylation reaction is carried out by treatment of the aromatic reagent with

TABLE 3-1. CHARACTERISTIC IR ABSORPTION BANDS.

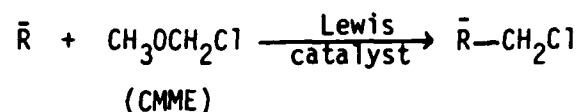
<u>Polymer</u>	<u>Frequency(cm^{-1})^a</u>	<u>Assignment</u>
$\bar{\text{R}}\text{-CH}_2\text{Cl}$	1260	C-Cl overtone [95]
$\bar{\text{R}}\text{-CH}_2\text{CN}$	2250	$\text{C}\equiv\text{N}$ stretch [96(p.295)]
$\bar{\text{R}}\text{-CH}_2\text{COOH}$	1700-1650	COOH group [96(p.)84)]
$\bar{\text{R}}\text{-CH}_2\text{COOCH}_2\text{CH}_3$	1720	C=O stretch [96(p.204)]
$\bar{\text{R}}\text{-CH}_2\text{CH}_2\text{OH}$	1030	C-O-H group [96(p.)08)]

^a Procedure for measurement of spectra given in the Appendix.

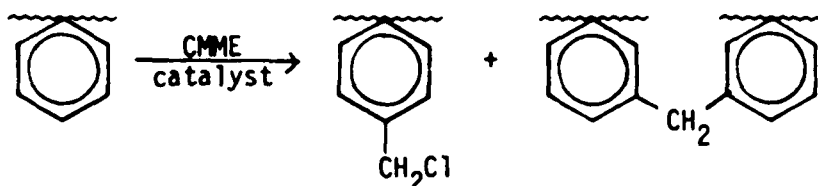
a chloromethylating agent and a Lewis catalyst. Commonly employed as chloromethylating agents are *bis*-chloromethyl ether, chloromethyl methyl ether (CMME), and a mixture of methanol, paraformaldehyde and hydrogen chloride. *Bis*-chloromethyl ether is a potent carcinogenic chemical [98(p. 332),99] and CMME is considered carcinogenic, due mainly to the presence of *bis*-chloromethyl ether as an impurity [100]. CMME has been the reagent of choice for industrial-scale chloromethylation reactions, but its use has been discontinued because of its hazardous nature. Chloromethylation with paraformaldehyde/HCl mixtures proceeds by the in situ formation of CMME, and thus avoids the direct handling of the latter substance. The Lewis catalysts most often used are anhydrous aluminum chloride, zinc chloride, and tin(IV) chloride.

The chloromethylation of polystyrene has been studied in some detail [101]. The production of chloromethylated polystyrenes is important since these materials are the supporting resins in solid-phase peptide syntheses [102-104] and are the starting points for the preparation of aminated polystyrene anion-exchange resins [1,105-107], chelating cation exchangers [108] and phosphonic-acid cation-exchange resins [62,67,68].

The chloromethylation of a styrene/DVB copolymer can be represented as:



The reaction, an electrophilic aromatic substitution, is not a clean one, being always accompanied by a side reaction in which methylene bridges form:



These methylene bridges provide additional crosslinking of the copolymer matrix, and can be qualitatively estimated by comparing the relative degrees of swelling of the chloromethylated products in suitable solvents. Bufton [109] claims that use of titanium tetrachloride as the Lewis catalyst minimizes the formation of methylene bridging. He provides qualitative evidence based on the percent swelling of chloromethylated polymers produced with AlCl_3 , ZnCl_2 and TiCl_4 .

For our chloromethylation reactions, we chose to employ TiCl_4 as the catalyst and CMME as the chloromethylating agent. Despite its hazards, CMME is a convenient reagent to use, especially on a relatively small scale.

The conversion of the styrene/DVB copolymer into chloromethylated polystyrene/DVB was monitored by observation of the change in the infrared spectrum of the reagent polymer. It was observed that a sharp, intense band at 1260 cm^{-1} appeared in the spectrum of the polystyryl-methyl chloride (see Table 3-1). The stretching frequency for the C-Cl vibration is listed at $745\text{-}645\text{ cm}^{-1}$ [95], so the 1260 cm^{-1} band in the chloromethylated-polymer spectrum is an overtone of the C-Cl stretch.

A quantitative measure of the degree of chloromethylation is obtained by determination of the chlorine content of the chloromethylated product. The procedure is adapted from the method of Schöniger [110,111] for the elemental analysis of organic compounds. The polymer is

mineralized by combustion in oxygen, followed by absorption of the combustion gases into aqueous solution. The solution is then titrated for chloride ion. The full procedure is described in the Appendix.

Our major concern was to produce a polymer having a relatively high degree of chloromethyl loadings, i.e., a polymer in which a majority of the aromatic groups contain a chloromethyl substituent. This can be expressed as a mole percent. For example, a chloromethylated polymer that is 50 mole percent has, on the average, 50 chloromethyl-substituted rings for every 100 aromatic rings. A high mole percent of chloromethyl groups is important since the capacities of the final cation exchangers depend on the degree of substitution accomplished in this first synthetic step.

The chloromethylation of a polystyrene copolymer is carried out by the addition of the catalyst to the swollen copolymer beads at temperatures ranging from about 0°C up to the refluxing temperature of the swelling agent. The swelling of the polymer beads prior to initiation of the reaction by introduction of the catalyst is crucial to the formation of a homogeneous product, i.e., one which is uniformly chloromethylated throughout each bead. Since polystyrene/DVB is swollen by CMME, no additional solvent is needed for the reaction. The reaction conditions used by Bufton [109] were employed as the starting conditions for our chloromethylations. Thus, in a preliminary experiment, 26 g (0.25 mole) of the copolymer was swollen in 95 mL of CMME (1.25 mole), followed by the addition of the 12.7 mL of TiCl_4 (0.11 mole).

The general procedure applied in all of our chloromethylation reactions is as follows: The copolymer was swollen in CMME by refluxing

(at 57°C) for 30 minutes in a resin reaction flask or in a 3-neck, round-bottom flask, equipped with a stirrer, thermometer and reflux condenser. The mixture was then cooled to 30°C, the reflux condenser replaced with a dropping funnel, and the TiCl_4 catalyst added dropwise at a rate corresponding to a total addition time of one hour. The mixture was then stirred for 15-30 minutes, and the reaction was terminated by separation of the polymer beads from the reaction mixture by filtration on a glass funnel. Washing and further treatment of the product varied according to the particular experiment. The specific reaction conditions for several chloromethylation experiments are summarized in Table 3-2.

Several important facts relating to the chloromethylation procedure were determined from these experiments. (1) It is critical that the reaction mixture be most efficiently stirred during the TiCl_4 addition and that the TiCl_4 be introduced below the surface of the CMME/polymer suspension. In a preliminary experiment (Trial, Table 3-2), the reaction mixture was agitated with a stirring bar instead of a stirring paddle, and the product was apparently very inhomogeneous (the beads were yellowed and not uniform in color). Exposure of the TiCl_4 to air/moisture should be minimized to avoid hydrolysis to TiO_2 . Thus, a Teflon tube was fixed to the stem of the dropping funnel and was directed into the center and below the surface of the reaction mixture. This set-up was used in all subsequent reaction trials. (2) The final appearance of the product beads was dependent on the post-reaction treatment. Termination of the reaction by simple filtration and washing with water and methanol resulted in beads that were yellowed and had the odor of HCl and methanol. The problem was intensified with larger

TABLE 3-2. CHLOROMETHYLATION REACTIONS.

Trial	Polymer(g) ^a	CMME(mL) ^b	TiCl ₄ (mL) ^c	Conditions	Work-Up	%Cl ^k	Mole % ^l	Product ^m
1	26 ^d	95	12.7	f	h	-	-	Cl-1
2	26 ^d	95	12.7	f	i	19.5	77	Cl-2
3	26 ^d	95	20.0	f	i	22.3	94	Cl-3
4	26 ^e	104	17.0	g	j	22.7	98	Cl-4
5	26 ^e	104	14.0	g	j	16.5	60	Cl-5
6	500 ^e	2000	380.0	f	i	24.8	>100	Cl-6

^a Styrene/DVB copolymer, 1 mole = 104 g.

^b Chloromethylmethyl ether, 1 mole = 76 mL.

^c 1 mole = 115 mL.

^d 2%-DVB copolymer from Eastman Co., Rochester, NY.

^e 2%-DVB copolymer from Dow Chemical Co., Redwood City, CA.

^f Copolymer reagent swollen for 30 min in refluxing CMME; TiCl₄ added at ca. 1 mL/5 min at 30°C; mixture then stirred for 15 min at 40°C.

^g Copolymer reagent swollen for 30 min in refluxing CMME; TiCl₄ added at ca. 2 mL/5 min at 30°C; mixture then stirred for 30 min at 30°C.

^h Product filtered and washed with H₂O, then methanol, on a glass filter; produced yellowed, odorous, inhomogeneous beads.

ⁱ Product filtered and transferred to a large volume of H₂O with stirring, followed by methanol wash; snow-white beads produced.

^j Product treated by addition of 95% ethanol to reaction mixture, followed by filtration on a glass filter and further washing with 95% ethanol; then washed with EtOH, EtOH/H₂O, H₂O, H₂O/MeOH, MeOH/HCl, MeOH/H₂O, H₂O, MeOH/H₂O and MeOH; produced snow-white beads.

^k Procedure described in the Appendix.

^l Calculated from %Cl data from the equation: mole % = 6500y/(62.3w-796y-61.3wy), where y = %Cl/100 and w = 35.5 for Cl.

^m All products exhibit a strong, sharp IR band at 1260 cm⁻¹.

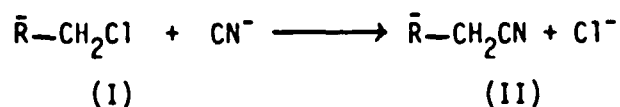
samples. This situation was improved by pouring the filtered beads into 95% ethanol, decanting, and repeating the process several times. Both CMME and TiCl_4 are soluble in 95% ethanol, so that this treatment removes a significant amount of impurities from the beads before subsequent washing. In washing, it is important to avoid abrupt changes in solvent composition. Drastic changes in copolymer swelling, which may accompany abrupt changes in solvent composition, can cause cracking and breakage of the beads. Thus, all changes in washing solvent were done gradually, altering the solvent composition in steps from one solvent to another. Products so obtained consisted of snow-white, odor-free and unbroken copolymer beads. (3) Although the results obtained for the chlorine contents of the various chloromethylated products are generally in line with the amount of TiCl_4 used in their preparations, these values should not be taken as an accurate measure of the chlorine contents of the copolymer products. Upon combustion in the Schöniger flask, a residue remained on the platinum holder for all chloromethylated polymers made. This residue was most likely a titanium compound, the dioxide and/or a chloride, which was left in the resin even after extensive washing. Further evidences for the presence of some impurities in the chloromethylated resins are that the beads discolor when heated to 70°C (as do some commercial chloromethylated polystyrenes) and that all samples exhibit a slight odor of HCl /formaldehyde after some weeks in a closed container. The chlorine contents listed in Table 3-2 are probably inflated because of these impurities. This problem is not critical, however, since, as will be discussed, subsequent treatments of the copolymer beads eliminate all major impurity residues. (4) All chloromethylated products exhibit an

intense, sharp, infrared absorption at 1260 cm^{-1} .

It can be concluded that, for our purposes, the exact reactant ratio is not critical to the nature of the product. An approximate mole ratio of 2 moles copolymer:5 moles CMME:1 mole TiCl_4 produces a sufficiently chloromethylated copolymer product.

3.3 Polystyrylacetonitrile.

In the second step of the synthesis, the chloromethylated styrene/DVB copolymer (I) is converted into polystyrylacetonitrile (II) through nucleophilic substitution by cyanide ion:



This reaction introduces an additional carbon onto the side chain of the aromatic rings of the copolymer. The substitution occurs readily in solution [112,113(p. 361)]; however, in application to the solid polymer system, a medium must be employed which will swell the copolymer beads to a sufficient extent (the chloromethylated resin is well swollen by low-polarity solvents) and provide a sufficiently high dielectric constant for dissolution of the reaction (NaCN) and product (NaCl) salts. Several solvent systems and a variety of reaction conditions were tried, as summarized in Table 3-3.

The reaction is conveniently monitored by infrared spectroscopy. Product formation is indicated by the appearance of a sharp absorption band at 2250 cm^{-1} corresponding to the $\text{C}\equiv\text{N}$ stretch and the concomitant disappearance of the $\text{C}-\text{Cl}$ band at 1260 cm^{-1} . In Table 3-3, the intensity ratio of the band at 1600 cm^{-1} , an absorption arising from

TABLE 3-3. THE CONVERSION $\bar{R}-CH_2Cl \longrightarrow \bar{R}-CH_2CN$.

Trial	Reagent ^a Resin(g)	NaCN(g)	Solvent ^b	Temp(°C)	Time(day) ^c	IR Ratio ^d	Notes	Product
1	SX-1 (5)	3.7	DMSO	40	1	2.21	f	CN-1
2	SX-1 (10)	8.0	DMSO	reflux	0.2	2.15	f,h	CN-2
3	SX-1 (5)	4.0	CH ₃ CN	reflux	1	3.13	e	CN-3
4	SX-1 (5)	5.0	1:1 H ₂ O/dioxane	50	1	-	i	CN-4
5	SX-1 (5)	4.0	1:1 H ₂ O/EtOH	reflux	2	3.25	e	CN-5
6	SX-1 (5)	4.0	3:1 CH ₃ CN/EtOH	reflux	1	2.36	e	CN-6
7	C1-2 (20)	20	1.3:1 DMF/DMSO	50	1	-	g	CN-7
8	C1-4 (5)	8.0	2:1 CH ₃ CN/95% EtOH	reflux	1	1.04	e	CN-8
9	C1-4 (10)	10	2:1 CH ₃ CN/95% EtOH	reflux	2	0.91	f	CN-9
10	C1-5 (23)	20	3:1 CH ₃ CN/95% EtOH	reflux	2	1.10	f,h	CN-10
11	C1-6 (700)	500	3:1 CH ₃ CN/95% EtOH	reflux	2	1.00	f,j	CN-11

^a Chloromethylated starting resins: SX-1=Bio-Beads SX-1, a chloromethylated styrene/1%-DVB copolymer (ca.5meq/g) from Bio-Rad Laboratories, Richmond, CA; C1-2 - C1-6 = prepared chloromethylated resins (Table 3-2).

^b Ratios are v/v. DMSO=dimethylsulfoxide, CH₃CN=acetonitrile, EtOH=absolute ethanol, 95% EtOH=95% ethanol/water, DMF=N,N-dimethylformamide. Solvent volumes (mL) generally 10-20 x polymer mass (g).

^c Reaction suspension well stirred for duration of the reaction.

^d Ratio of intensities of resin-backbone peak at 1600 cm⁻¹ and CN stretch at 2250 cm⁻¹ for product resin.

^e Product incompletely converted, based on presence of residual C-Cl band at 1260 cm⁻¹.

^f Product assumed to be completely converted since no trace of absorption at 1260 cm⁻¹ is evident.

^g Product aminated by DMF substitution of chlorine. Spectrum complicated by corresponding peaks.

^h Analyzed product found to contain no detectable chlorine. Procedure in Appendix.

ⁱ No conversion.

^j Bulk sample.

the aromatic groups in the polymer backbone and unaffected during the course of the reaction, and the CN stretch at 2250 cm^{-1} is listed for each experiment and can be used as an indication of the extent of conversion. For example, sample CN-8 (Trial 8, Table 3-3) exhibits a small absorption at 1260 cm^{-1} , while in the spectrum of sample CN-9, the absence of any absorption at 1260 cm^{-1} is an indication of no residual chloromethyl groups. The intensity ratios measured from these spectra follow this pattern, the ratio being lower for the fully converted sample (CN-9). A similar pattern holds for all of the samples in Table 3-3, although direct comparisons can only be made between nitrile-resin samples derived from the same reagent resin. In a few cases, nitrile resins for which a small residual C-Cl band persists on the IR spectra have intensity ratios for the $1600\text{ cm}^{-1}/2250\text{ cm}^{-1}$ peaks lower than ratios observed for samples assumed to be fully converted on the basis of the absence of any absorption at 1260 cm^{-1} . For example, a nitrile-resin sample derived from chloromethyl resin SX-1 under conditions similar to the preparation of sample CN-2 (Trial 2) had a $1600\text{ cm}^{-1}/2250\text{ cm}^{-1}$ peak ratio of 2.09 (compare to a ratio of 2.15 for sample CN-2), although a small peak at 1260 cm^{-1} was present on the IR spectrum. The conclusion is that the intensity ratio of the $1600\text{ cm}^{-1}/2250\text{ cm}^{-1}$ peaks and the disappearance of the 1260 cm^{-1} absorption are only general guides to the completeness of conversion, and that the substitution reaction must be carried out beyond the point of completion as deduced from these indicators to assure full reaction of all of the functional groups in the resin. The chlorine contents of the fully-converted resins were below detectable limits, confirming the spectroscopic results.

In all cases, the amount of NaCN was not critical, as long as an approximate three-fold mole excess was present in the reaction. In the early experiments, dimethylsulfoxide was found to be an excellent solvent for the reaction. Complete conversion of the chloromethylated reagent polymer could be effected under relatively mild conditions, e.g., at a temperature as low as 40°C (Trial 1, Table 3-3) and in as little as four hours (Trial 2). However, problems were encountered in subsequent treatments of the nitrile resins prepared in dimethylsulfoxide. Even after extensive washings, the distinct odor of dimethylsulfoxide from the resin beads was noted. Further reactions yielded discolored polymers (yellow/green) with sulfur-like odors. Among the other solvents tested, water/dioxane and water/ethanol (Trials 4 and 5) provided for little or no conversion, even though the NaCN was completely dissolved. These solvent mixtures are poor swelling agents for the chloromethylated-copolymer beads.

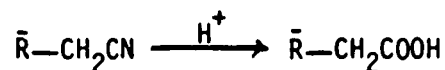
Acetonitrile, CH_3CN , is a solvent which swells the chloromethylated resin, but in which NaCN has a relatively low solubility. Thus, experiments in which only CH_3CN was the solvent resulted in incompletely converted products, even at the reflux temperature of CH_3CN (Trial 3). During these reaction trials, undissolved NaCN crystals were observed in the reaction flask. The solubility of NaCN was enhanced with a mixed solvent, composed of approximately 3:1 (v/v) CH_3CN and absolute ethanol. In this medium, nearly complete reaction was obtained (Trial 6); in other trials, full conversion resulted. Use of 95% ethanol in place of absolute ethanol afforded an even better solvent for the complete conversion of polystyrylmethyl chloride into polystyrylacetonitrile with NaCN (Trials 9, 10 and 11). In Trial 11, a bulk conversion was successfully accomplished.

In the work-up of the reaction product, which involved extensive washings with CH_3CN , ethanol and water (and intermediate mixtures of these to prevent breakage of the beads), a fine, white, water-insoluble powder was in evidence. This substance was likely TiO_2 , trapped in the copolymer beads from the chloromethylation step.

The reaction conditions for the total conversion of the chloromethylated copolymer into the nitrile resin, as deduced from these experiments, may be summarized as follows: A three-fold mole excess of NaCN over copolymer is used. The copolymer is swollen in a minimum of CH_3CN , the best solvent mixture being a 3:1 (v/v) mixture of CH_3CN and 95% ethanol. The reaction is carried out at reflux temperature for three days to insure full conversion. The product is washed with $\text{CH}_3\text{CN}/\text{EtOH}$, CH_3CN , $\text{CH}_3\text{CN}/\text{EtOH}$, $\text{CH}_3\text{CN}/\text{EtOH}/\text{H}_2\text{O}$, $\text{EtOH}/\text{H}_2\text{O}$ and H_2O . The beads are light tan to dark brown in color.

3.4 Polystyrylacetic Acid - Hydrolysis of the Nitrile Resin.

Hydrolysis of a nitrile can be accomplished with base or acid [113(p. 660),114] to produce a carboxylate salt or a carboxylic acid, respectively. For acid hydrolysis, the reaction for the conversion of polystyrylacetonitrile to polystyrylacetic acid is:



The hydrolysis reagents commonly employed are sodium or potassium hydroxide (strong solutions, often in ethylene glycol) for basic hydrolysis and concentrated sulfuric acid for acidic hydrolysis. The reactions are run at elevated temperatures. The use of concentrated sulfuric acid should be avoided in styrene/DVB copolymer systems,

especially at high temperatures, since sulfonation of the aromatic groups can easily occur [115]. Also, under such harsh conditions, oxidative degradation of the copolymer chains can ensue. On the other hand, acidic conditions would be favorable for our resins since any TiO_2 remaining in the copolymer beads would be dissolved by the H_2SO_4 . The key to hydrolysis of the nitrile resin, then, is to use an acidic medium which is not quite strong enough to induce sulfonation or degradation, yet swells the resin beads to produce a thorough hydrolysis of the nitrile functions into carboxylic functions.

As in the previous conversion processes, infrared spectroscopy is useful for following the extent of reaction. Disappearance of the CN stretching band at 2250 cm^{-1} is accompanied by the appearance of an extremely intense and somewhat broad carboxylic-acid absorption band at $1640\text{-}1720\text{ cm}^{-1}$. The product resin, polystyrylacetic acid, is itself a weakly acidic cation-exchange resin, so that its ion-exchange capacity could be measured and utilized as a further quantitative probe into the course of the synthetic sequence (as discussed in association with the bulk preparations, section 3.7). In Table 3-4, we present several experimental trials for this conversion step.

Aqueous solutions of KOH and H_2SO_4 produced no measurable hydrolysis, the nitrile-resin beads being poorly swollen by these media. A variety of mixed solvents, in which one component was the hydrolysis reagent and the other a swelling agent, were tested. For those systems in which KOH was employed (Trials 3 and 8, Table 3-4), no hydrolysis of the nitrile groups was observed. Hydrochloric-acid mixed solvents produced little or no reaction (Trials 6 and 7). In spite of the concern about sulfonation, sulfuric acid became the unavoidable choice

TABLE 3-4. HYDROLYSIS OF THE NITRILE RESIN.

<u>Trial</u>	<u>Reagent^a Resin</u>	<u>Reactants^c</u>	<u>Temp(°C)^d</u>	<u>Time(day)</u>	<u>Conversion^e</u>	<u>Product^f</u>
1	SX-2a ^b	3:1 2M H ₂ SO ₄ /dioxane	reflux	1	none ^g	-
2	CN-12	3:1 2M H ₂ SO ₄ /dioxane	reflux	1	none	-
3	CN-12	3:1 4M KOH/dioxane	reflux	1	none	-
4	CN-12	3:1 70% H ₂ SO ₄ /methanol	reflux	1	partial	COOH-1
5	CN-13	1:1:1 H ₂ SO ₄ /AA/H ₂ O	reflux	0.2	none	-
6	CN-13	1:1 HCl/dioxane	60	1	none	-
7	CN-2	1:1 HCl/EtOH	reflux	1	partial	COOH-2
8	CN-14	6:1 18M KOH/EG	reflux	1	none	-
9	CN-2	6:1 H ₂ SO ₄ /EtOH	100	1	h	COOH-3
10	CN-2	6:1 81% H ₂ SO ₄ /EtOH	100	1	h	COOH-4
11	CN-2	6:1 70% H ₂ SO ₄ /EtOH	110	1.5	total	COOH-5
12	CN-7	5:1 70% H ₂ SO ₄ /EtOH	100	1	total	COOH-6

^a Polystyrylacetonitrile samples, $\bar{R}-CH_2CN$ (Table 3-3; some samples from other preparations).

^b Derived from Bio-Rad chloromethyl resin SX-2.

^c In most trials, 5-10g nitrile resin were reacted with 25-40mL of solution per gram of resin. Ratios are v/v, and molarities refer to aqueous solutions. Percentages refer to total concentration in mixed solvent. EtOH=95% ethanol, EG=ethylene glycol, AA=glacial acetic acid, HCl=conc. hydrochloric acid, H₂SO₄=conc. sulfuric acid.

^d All reactions carried out in a round-bottom flask equipped with a reflux condenser, thermometer, trap and stirrer. Products were washed in stages with ethanol and water, with a final water wash.

^e "None"=no conversion (no COOH peaks in IR); "partial"=partial hydrolysis (some CN absorption in IR of product; further reaction produced no more conversion); "total"=full conversion (no CN band in IR of product). Product beads brown-tan in color.

^f Product resin $\bar{R}-CH_2COOH$ if fully converted.

^g Product consisted of green and black beads.

^h Sulfonated product; IR peaks at 1350, 1172 and 907 cm⁻¹.

as the hydrolysis reagent.

Preliminary experiments demonstrated that dilute sulfuric-acid solutions effected no reaction (Trials 1 and 2). As expected, reaction with concentrated sulfuric acid resulted in a product that was sulfonated to some extent (Trial 9). Reducing the sulfuric-acid concentration to 81% still led to sulfonic-acid bands on the IR spectrum of the product resin (Trial 10). Hydrolysis of the polystyrylacetonitrile resins was accomplished without simultaneous sulfonation when the sulfuric-acid concentration was reduced to below about 75% (Trials 11 and 12).

The course of the hydrolysis reaction was closely monitored by measurement of the IR spectrum of the copolymer at various intervals during the process. In Table 3-5, the variations of the intensities of the CN stretch at 2250 cm^{-1} and the COOH maximum at $1720\text{-}1680\text{ cm}^{-1}$ as a function of time are listed for the hydrolysis of a particular nitrile-resin sample. The change in the ratio of the intensities of the 2250 cm^{-1} peak (CN groups) and the 1680 cm^{-1} peak (COOH groups) reflects the simultaneous growth of the COOH band and lowering of the CN band while the changing intensity ratio of the 2250 cm^{-1} peak and the 1600 cm^{-1} peak (matrix vibration) reflects the decrease in the CN band relative to fixed matrix absorption. These data indicate that the reaction is about 90% complete after ten hours, but total conversion cannot be achieved before about twenty hours.

The optimum reaction conditions for the conversion of polystyrylacetonitrile to polystyrylacetic acid, deduced from these experiments, are as follows: A solution of 5:1 (v/v) 70% sulfuric acid/ethanol is applied at about 100°C for at least twenty hours. These conditions were found to hydrolyze all nitrile-resin samples prepared.

TABLE 3-5. COURSE OF THE NITRILE-HYDROLYSIS REACTION.

<u>Sample^a</u>	<u>Time(hr)</u>	<u>IR Ratio(2250/COOH)^b</u>	<u>IR Ratio(2250/1600)^c</u>
CN-15	0	-	0.91
CN-15a	3.5	0.61	0.54
CN-15b	6	0.17	0.26
CN-15c	10	0.06	0.10
CN-15d	15	0.02	0.05
COOH-7	20	0.00	0.00

^a CN-15 is the reagent nitrile resin. Other samples are resins withdrawn from reaction vessel at the indicated times.

^b Intensity of the CN stretch at 2250 cm^{-1} to the intensity of the COOH maximum between 1720 and 1680 cm^{-1} .

^c Intensity of the CN stretch at 2250 cm^{-1} to the intensity of the matrix peak at 1600 cm^{-1} .

The carboxylic-acid copolymer products were composed of spherical beads with a light brown to tan color. In aqueous suspension, the beads appeared translucent when held to light. Combustion of the resin in a Schöniger flask left no solids, indicating that all catalyst residues had been removed from the copolymer beads by this stage in the synthetic sequence.

3.5 Ethyl Polystyrylacetate and 2-Polystyrylethanol: Esterification and Reduction.

The final step in the synthesis of the alcohol polymer, the reagent resin in the phosphorylation reactions, involves the chemical reduction of the carboxylic-acid groups:



Among the many reducing agents known to effect this process, lithium aluminum hydride ($LiAlH_4$) is especially applicable to the reduction of carboxylic acids [116]. The reaction is typically carried out by the treatment of the carboxylic acid with an ether solution of the mixed hydride. Many acids are reduced on contact with the reducing agent, while others require elevated temperatures to sustain reaction.

There has been some work on the reduction of polymer-supported functional groups by complex metal hydrides. Lithium aluminum hydride has been employed to reduce polymer-supported nitrile, imide, oxime, lactam, hydrazide, hydrazone and carbonyl groups [117]. Polymer ketones and esters have also been reduced by this reductant [118]. Letsinger et al [119] have used $LiAlH_4$ to quantitatively reduce a carboxylic-acid styrene/DVB copolymer to polystyrylmethanol. The latter was also

prepared by reduction of an acetoxymethyl styrene/DVB copolymer resin [120]. Because of the similarity of polystyrylmethanol to the alcohol copolymer which we wished to prepare, the conditions for these reactions served as reasonable starting points in our experiments.

In preliminary experiments, we attempted to reduce the carboxylic-acid resin directly to the alcohol resin by treatment with excess LiAlH_4 in a variety of solvents. The general procedure consisted of mixing the polymer sample with an excess of LiAlH_4 /solvent and refluxing for up to twenty-four hours. In some experimental trials, the solid LiAlH_4 was added directly to the resin/ether mixture. In these reactions, the gray, insoluble component of the LiAlH_4 was difficult to separate from the product resin, the beads often retaining a gray color. In other trials, a fairly clear solution of reductant in the ether was prepared by refluxing the solid with the ether, followed by decantation of the clear reductant solution. The product resins in these reactions were less troublesome to wash. The immediate reaction product, a complex of the type $\text{LiAl}(\text{OCH}_2\text{CH}_2-\bar{\text{R}})_4$, was hydrolyzed by the slow addition, with cooling, of wet ethyl acetate (to destroy excess LiAlH_4), followed by treatment with 2 M H_2SO_4 /dioxane or 2 M NaOH /dioxane. The extent of conversion was judged by noting the infrared-spectral changes of the polymer. Reduction was indicated by the disappearance of absorptions due to carboxylate functional groups, the bands at 1720-1640, 1250 and 1150 cm^{-1} . The reduced product exhibits an intense band around 1030 cm^{-1} , due to C—O and O—H stretching vibrations. Reduction of the carboxylic-acid resin was also indicated by the loss of ion-exchange capacity. A simple qualitative test for this consisted of treatment with a $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ solution. The

reactant resin would attain a deep blue color due to exchange for $[\text{Cu}(\text{NH}_3)_4]^{2+}$ cations, whereas the reduced alcohol product would absorb almost no counterions and therefore undergo no color change. Partially converted resins take on blue colors of variable intensities.

From the results of Trials 1-3 in Table 3-6, tetrahydrofuran (THF) was determined to be the best solvent for the reaction. The solubility of LiAlH_4 in the various ethers is given [121(p. 11)] as (per 100 g solvent) 25 g in diethyl ether, 0.1 g in dioxane, and 13 g in THF. Although diethyl ether dissolves the reducing agent most efficiently, the refluxing temperature of 34.5°C is not sufficiently high to provide reaction (Trial 2). Dioxane does not dissolve enough reducing agent to provide for efficient reaction even though the boiling point is 101°C (Trial 1). With THF, an adequate reaction temperature can be maintained (reflux temperature, 67°C) at a reasonably high reductant concentration.

Reduction of an incompletely converted carboxylic-acid sample, that is, a resin containing $-\text{COOH}$ and $-\text{CN}$ functional groups, resulted in a green-colored product (Trial 4, Table 3-6). This occurred even when no significant CN absorption was observable on the IR spectrum of the reagent carboxylic-acid resin. Treatment of polystyrylacetonitrile itself with $\text{LiAlH}_4/\text{THF}$ produced a green resin, the IR spectrum of which showed peaks corresponding to the structure, $\bar{\text{R}}-\text{CH}_2\text{CH}_2\text{NH}_2$ (bands at 2180 , 1700 - 1600 cm^{-1} due to $-\text{NH}_2$ and $-\text{NH}_3^+$ groups). (This material is a weak-base anion exchanger.) Formation of green reduction products can therefore be attributed to a reagent resin which is not monofunctional and in which the presence of CN groups would limit the efficiency of conversion of the functional groups into phosphate groups. Anion-exchange groups in the final resins would also complicate the interpretation of their properties.

TABLE 3-6. REDUCTION REACTIONS WITH LiAlH_4 .

<u>Trial</u>	<u>Reagent Resin^a</u>	<u>Solvent^b</u>	<u>Conversion^c</u>	<u>Notes</u>	<u>Product¹</u>
1	COOH-1	dioxane ^d	none	i	-
2	COOH-5	ethyl ether ^d	none	i	-
3	COOH-7	THF ^d	partial	i	OH-1
4	COOH-8 ^e	THF ^d	partial	i,j	OH-2
5	COOH-9 ^f	THF ^d	total	i	OH-3
6	COOH-6	THF ^g	none	k	-
7	COOEt-1	THF ^g	total	k	OH-4
8	COOEt-2	THF ^{g,h}	total	k	OH-5

^a "COOH-" refers to carboxylic-acid resin and "COOEt-" refers to ester resin (samples from Tables 3-4 and 3-7).

^b THF=tetrahydrofuran. In typical experiments, ca.1g of LiAlH_4 per 1g of resin (mole ratio=10) in 100mL of solvent was used. The resin was pre-swollen in refluxing ether for at least 2 hr. Reaction mixtures were refluxed for up to 24 hr in a flask equipped with a reflux condenser, drying tube and stirrer. Product work-up: hydrolysis with wet ethyl acetate and 1M H_2SO_4 ; then with warm 2M H_2SO_4 /dioxane and 2M NaOH/dioxane, each for 1-24 hours.

^c Degree of conversion based on disappearance of COOH IR bands at 1720-1640, 1250 and 1150 cm^{-1} . "None"=no reduction, "partial"=some reduction, "total"=full reduction. All products retain some absorption at 1700-1600 cm^{-1} in the IR.

^d Reactions run in a flat-bottom flask with magnetic stirring bar.

^e Reagent resin contains some CN groups.

^f Scaled-up reaction using 25g of resin and 7g of LiAlH_4 in 400mL THF.

^g Reaction mixtures agitated with a stirring paddle.

^h Bulk reaction using 100g resin and 25g LiAlH_4 in 1000mL THF.

ⁱ Product resins powdered.

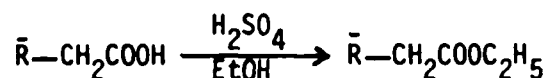
^j Product resin green.

^k Product resins in bead form.

¹ $\bar{\text{R}}\text{-CH}_2\text{CH}_2\text{OH}$ for total conversion.

The method of agitation was found to be an important experimental consideration. The reactions of Trials 1-5 in Table 3-6 were carried out in an Erlenmeyer flask set on a magnetic heater-stirrer. With this apparatus, the product resin was always in a finely-powdered form. In some experiments, reduction of the pulverized polymer could be completed in as little as one hour. The conditions created by the action of the stirring bar against the bottom of the flask in combination with the presence of the abrasive gray insoluble powder from the LiAlH_4 (presumably AlCl_3) cause this rapid destruction of the spherical beads. We found, however, that changing the agitation technique to a stirring paddle or simple periodic shaking allowed for no significant reduction of the carboxylic-acid resin, although undesirable bead breakage was eliminated (Trial 6). Even under the most extreme conditions, a 100-fold excess of LiAlH_4 with refluxing for one week, no reduction was obtained.

The esters of carboxylic acids are more easily reduced to the alcohols by LiAlH_4 than are the acids themselves [116(p. 30,34),122]. Thus, in light of the difficulty in reducing the carboxylic-acid resin, we had to consider an additional step in the synthetic sequence--the conversion of polystyrylacetic acid to its ethyl ester, ethyl polystyrylacetate:



This conversion reaction was rather easily carried out by refluxing the dry carboxylic-acid polymer with a 10:1 (v/v) solution of absolute ethanol and concentrated sulfuric acid (the esterification catalyst). Attempts to esterify with dry methanol produced no reaction. Table 3-7 summarizes the results of typical reactions. The conversion of the acid

TABLE 3-7. ESTERIFICATION REACTION.

<u>Trial</u>	<u>Reagent Resin^a</u>	<u>Treatment^{b,c}</u>	<u>Conversion^d</u>	<u>Product</u>
1	COOH-6	1g resin + 5mL H ₂ SO ₄ + 50mL MeOH	none	-
2	COOH-6	1g resin + 5mL H ₂ SO ₄ + 50mL EtOH	total	COOEt-1
3	COOH-10 ^e	100g resin + 50mL H ₂ SO ₄ + 500mL EtOH	total	COOEt-2

^a $\bar{R}-CH_2COOH$.

^b H₂SO₄=conc. sulfuric acid; MeOH=dry methanol; EtOH=dry ethanol.

^c All reactions run for one day at reflux.

^d Extent of reaction: "none"=no reaction, "total"=full reaction. Based on IR spectral changes and exchange capacities (see text).

^e Bulk reaction.

resin to the ester resin was accompanied by a change in the C=O absorption band in the infrared spectrum. The broad band ranging from 1720-1640 cm^{-1} in the spectrum of the acid resin narrowed to a sharp peak at 1720 cm^{-1} upon esterification. The conversion also caused loss of the ion-exchange capacity of the polymer. The ester resin would retain no tetraamminecopper(II)-blue color upon treatment with $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$. Trial 3 in Table 3-7 indicates that scale-up presents no problem in this reaction step.

Reduction of the esterified copolymer was possible without destruction of the spherical beads. As the results of Trials 7 and 8 in Table 3-6 show, full reduction could be accomplished by swelling the ester-resin beads in THF by refluxing for several hours, followed by application of an LiAlH_4 /THF solution at reflux for one day. Ester resins swollen in the THF without refluxing were not significantly reduced. The alcohol-resin products exhibit a minimal absorption intensity at 1700-1600 cm^{-1} in the IR and have no significant exchange capacity. Table 3-8 shows how the reduction reaction progresses, as indicated by the variation of the COOH band intensity (1720 cm^{-1}) with respect to the non-variant matrix peak at 1510 cm^{-1} (a relatively sharp, isolated peak), with the conclusion that at least twenty-four hours are required to complete the reaction.

The optimum reaction conditions for the reduction of polystyrylacetic acid to 2-polystyrylethanol are summarized as follows: Reflux polystyrylacetic acid for one day with 10:1 (v/v) dry ethanol/concentrated sulfuric acid. Wash the product with water and methanol, dry, then reflux for one day in THF. Add reductant solution prepared by refluxing excess LiAlH_4 in THF and decanting the liquid phase from the solid gray residue. Reduction is carried out for at least twenty-four hours at

TABLE 3-8. COURSE OF THE REDUCTION REACTION.

<u>Time(hr)</u>	<u>IR Ratio^b</u>
0 (ester resin) ^a	1.50
2	0.77
7	0.53
10	0.44
12	0.38
22	0.25
24 (alcohol resin)	0.19 ^c

^a Ethyl polystyrylacetate resin, sample C00Et-3.

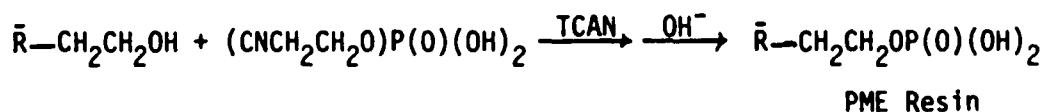
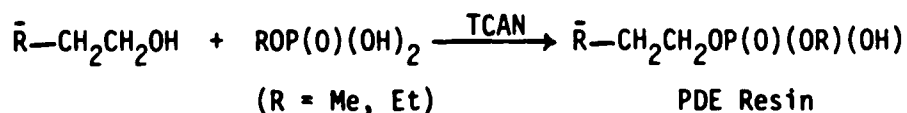
^b Ratio of intensities of the 1720 and 1510 cm^{-1} peaks.

^c Alcohol product resin always exhibits a non-zero absorption in the 1700-1600 cm^{-1} region.

reflux, and the product is treated with ethyl acetate, 1 M H_2SO_4 , then alternately stirred for twenty hours each in 2 M H_2SO_4 /dioxane and 2 M NaOH /dioxane. The product beads are brown-tan in color and leave no residue upon combustion.

3.6 Phosphorylation Reactions - Preparation of the Cation Exchangers.

The condensation of 2-polystyrylethanol with an appropriate monoester of phosphoric acid constitutes the final step in the synthesis of the phosphoric-acid cation-exchange resins. With trichloroacetonitrile (TCAN) as the condensing agent, reaction of the alcohol copolymer with monomethyl phosphate or monoethyl phosphate gives the phosphate diester resin (PDE), while reaction with 2-cyanoethyl phosphate (followed by hydrolysis) gives the phosphate monoester resin (PME):



All of the preliminary experiments involving preparation of the PDE resin utilized monomethyl phosphate as the phosphorus-ester reagent. This material, purchased from ICN Pharmaceuticals, Plainview, N.Y., was used in the reaction trials without any further treatment. Preparation of the PME resin was somewhat more complicated since the phosphorus-ester reagent, the pyridinium salt of 2-cyanoethylphosphoric acid, had to be prepared from the commercially available barium dihydrate salt of 2-cyanoethylphosphoric acid (purchased from Aldrich Chemical, Milwaukee,

WI and Eastman Chemical, Rochester, N.Y.). A solution convenient for use in the small-scale reactions containing 1 mmol of pyridinium 2-cyanoethylphosphate per 1 mL in pyridine was prepared after Tener [55] as follows: 16.4 g of $\text{Ba}[\text{O}_2\text{P}(\text{O})(\text{OCH}_2\text{CH}_2\text{CN})]\cdot 2\text{H}_2\text{O}$ were dissolved in a minimum of water (ca. 50-100 mL). Because of the salt's low solubility, the dissolution of the salt was aided by the addition of Dowex-50 (H^+ -form) and the application of mild heat. The filtered solution was then run through a column of Dowex-50 (H^+ -form) to convert the barium salt to the acid. The column was washed with water until the effluent lost acidity. This solution was lyophilized with ca. 50 mL of pyridine to a volume of 50 mL, after which 50 mL of dry pyridine (distilled over sodium) was added, followed by lyophilization down to a volume of 20 mL. The resulting viscous solution was diluted to 50 mL with dry pyridine, and contained 1 mmol/mL of the phosphate ester salt.

Anticipating the preparation of large quantities of the PME exchanger, the use of 2-cyanoethylphosphate was deemed financially impractical. A bulk phosphorylation requiring about 500 g of the barium salt would cost around \$1200 (based on the 1980 price). This reaction was made much more practical by our preparing in large quantities the barium 2-cyanoethylphosphate itself. In section 3.7.6, a description of this procedure is given.

The optimum conditions for the condensation phosphorylation reactions were determined through a series of small-scale trials. The reactions were typically set up by swelling from one to five grams of the alcohol copolymer in the reaction solvent (pyridine or N,N-dimethylformamide), followed by the addition of an excess of the phosphate ester and the TCAN. The reaction mixtures were heated in small flasks on a hot plate with periodic agitation for the smaller samples or

with a stirring paddle for the larger samples. Product work-up consisted of filtration and washing with solvent, solvent/methanol, methanol/water and water, with gradual changes in the wash-solution composition.

Phosphorylation of the copolymer was indicated by several factors. (1) The appearance of broad, intense phosphate-group absorption bands between 1250 and 1000 cm^{-1} in the infrared spectrum of the product resin. (2) The visible exchange for $\text{Cu}(\text{NH}_3)_4^{2+}$ cations, producing a color change from tan to deep blue or green, reflecting a significant cation-exchange capacity. (3) The qualitative and quantitative measurement of the phosphorus content of the product resin. The experimental details involved in these procedures are described in the Appendix.

Table 3-9 presents some representative experimental trials for the preparation of the PME resin. The reaction occurs equally well in pyridine and in *N,N*-dimethylformamide (Trials 2 and 3, Table 3-9), but will not take place below about 50°C (Trial 1). A mole ratio of 1:2:4 for resin:CEP:TCAN provides a sufficient excess of phosphate ester and condensing agent over resin to effect full reaction. The PME resin is brown to tan in color in the hydrogen form and is darker in the sodium form. Further, the resin is stable in the H^+ -form, retaining its ion-exchange capacity and infrared-spectral characteristics after oven-drying at 70°C for at least two days. Also, the resin remained unaltered after several exchange cycles consisting of alternate treatments with 1 M NaOH, 1 M NaHCO_3 , $\text{Cu}(\text{NH}_3)_4^{2+}$ and 1 M HCl.

The PDE resin is prepared under conditions similar to those for the PME resin, as Table 3-10 reveals. Phosphorylation does not take place below 50°C, even for an extended reaction time (Trial 5, Table 3-10). Condensation with monomethyl phosphate is not possible in pyridine since the two remain immiscible on mixing (Trial 1); hence,

TABLE 3-9. SYNTHESIS OF PME RESIN.

Trial	Reagent Resin(mmol) ^a	CEP (mmol) ^b	TCAN (mmol) ^c	Solvent ^d	Temp(°C) ^e	IR Max(cm ⁻¹) ^f	Capacity ^g	%p ^h	Notes	Product
1	OH-6 (5)	10	40	PY	40	-	-	-	i	-
2	OH-3 (3)	20	40	PY	55	1240	-	-	j,k	PME-1
3	OH-3 (3)	20	40	DMF	55	1240	-	-	k	PME-2
4	OH-3 (15)	30	49	PY	55	1240	1.2 (Na ⁺)	-	l	PME-3
5	OH-3 (10)	19	40	PY	60	1240	1.5 (H ⁺)	3.0	-	PME-4
6	OH-3 (14)	30	70	PY	60	1240	1.4 (H ⁺)	2.8	-	PME-5

^a 2-Polystyrylethanol, ca. 1-5 meq/g (sample OH-3 from Table 3-6).

^b CEP = 2-cyanoethylphosphate.

^c TCAN = trichloroacetonitrile.

^d DMF = N,N-dimethylformamide, PY = pyridine. Total volume ca. 15 mL/g resin.

^e Periodic agitation. All reactions run for one day. Final product obtained after heating 2 hr in 1M NaOH.

^f Maximum IR absorption in the 1250-1000cm⁻¹ range (H⁺-forms).

^g In meq/g for the indicated ionic form. Method of determination described in the text.

^h For H⁺-form. Phosphorus analysis described in the Appendix.

ⁱ Polymer not phosphorylated.

^j Sodium form has IR maximum around 1190 cm⁻¹.

^k Positive test for phosphorus. Samples PME-1 and PME-2 were first PME resins successfully prepared.

^l Resin stable to repeated exchange cycles.

TABLE 3-10. SYNTHESIS OF THE PDE RESIN.

Trial	Reagent Resin(mmol) ^a	MePO ₄ (mmol) ^b	TCAN (mmol) ^c	Solvent ^d	Temp(°C) ^e	IR Max(cm ⁻¹) ^f	Capacity ^g	%p ^h	Notes	Product
1	OH-3 (15)	30	49	PY	60	-	-	-	i	-
2	OH-3 (2)	20	40	DMF	60	1230	-	-	j	PDE-1
3	OH-3 (15)	30	49	DMF	55	1230	-	-	k	PDE-2
4	OH-3 (15)	36	49	DMF	60	1225	1.3 (Na ⁺)	-	j	PDE-3
5	OH-3 (25)	45	63	DMF	45 ^m	-	-	-	i	-
6	OH-3 (15)	36	49	DMF	60	1235	0.9 (H ⁺)	2.7	-	PDE-4
7	OH-3 (25)	63	84	DMF	70	1235	1.5 (H ⁺)	4.5	-	PDE-5
8	OH-4 (10)	20	50	DMF	65	1235	2.6 (H ⁺)	-	j	PDE-6
9	OH-5 (100)	240	400	DMF	70	1235	2.8 (H ⁺)	-	l	PDE-7

^a 2-Polystyrylethanol, ca. 1-5 meq/g (samples from Table 3-6).

^b MePO₄ = monomethyl phosphate.

^c TCAN = trichloroacetonitrile.

^d DMF = N,N-dimethylformamide, PY = pyridine. Total volume ca. 15 mL/g resin.

^e Periodic agitation. All reactions run for one day.

^f Relatively sharp IR absorption maximum for H⁺-form.

^g In meq/g for the indicated ionic form. Method of determination described in the text.

^h For H⁺-form. Phosphorus analysis described in the Appendix.

ⁱ Polymer not phosphorylated.

^j Positive test for phosphorus. Sample PDE-1 was the first PDE resin successfully prepared.

^k Resin stable to repeated exchange cycles.

^l Larger-scale sample.

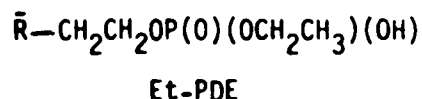
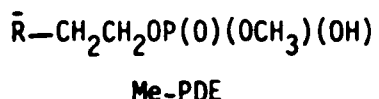
^m Reaction time = two days.

N,N-Dimethylformamide must be used for the PDE-resin preparation.

Comparison of Trials 6 and 7 in Table 3-10 indicates that a higher reaction temperature (70°C) causes enhanced phosphorylation of the copolymer. Copolymer alcohols derived from a more fully-loaded chloromethyl resin produce phosphate cation exchangers with higher capacities (Trials 8 and 9, samples from chloromethyl resin C1-3). Like the PME resin, samples of the PDE resin are stable (to dephosphorylation) after repeated exchange cycles and oven-drying at 70°C in the hydrogen form. The resin is light brown to tan in color in the hydrogen and sodium forms.

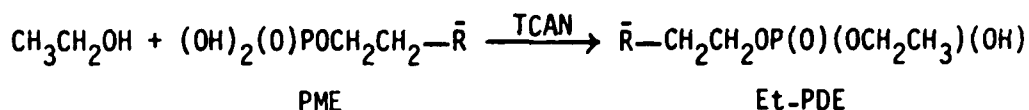
The infrared spectra of the PDE resins differ distinctly from those of the PME resins. The PDE spectra are characterized by a relatively sharp, counterion-independent band at 1230 cm^{-1} . The intermediate resin in the PME synthesis (2-cyanoethyl 2-polystyrylethyl phosphate) has a similar spectrum, with an additional small peak at 2250 cm^{-1} due to the CN groups. Hydrolysis to the PME resin produces spectra with broad, complex band structures, characterized by a strong absorption maximum between 1100 and 1240 cm^{-1} , dependent on the ionic form. The infrared spectra of the resins are discussed in detail in Chapter Six.

We also developed methods to synthesize another phosphoric-acid-ester cation-exchange resin. This material is an ethyl-PDE resin, differing from the methyl-PDE resin discussed above. The two diester resins, methyl 2-polystyrylethyl phosphoric acid and the new resin, ethyl 2-polystyrylethyl phosphoric acid, are distinguished as Me-PDE and Et-PDE, respectively:



The Et-PDE resin was synthesized by two routes. The first method parallels the production of the Me-PDE resin. Here, monoethyl phosphate (purchases from ICN Pharmaceuticals, Plainview, N.Y.) was used in place of monomethyl phosphate as the phosphate-ester reagent, all other reaction conditions being identical to those in the Me-PDE formation. The product Et-PDE resin exhibits stability and IR characteristics like those of the PME and Me-PDE resins. A representative preparation utilizes 2 g (10 mmol) of alcohol resin, 30 mmol of monoethyl phosphate and 50 mmol of TCAN in 30 mL of DMF, periodically agitated at 70°C over a period of three days.

In the second method of synthesizing the Et-PDE resin, the condensation is carried out between a polymeric phosphate ester and a simple alcohol. Here, the PME resin is converted to the Et-PDE resin by condensation with ethanol. In effect, the ethanol is phosphorylated with a polymer phosphate monoester and TCAN:



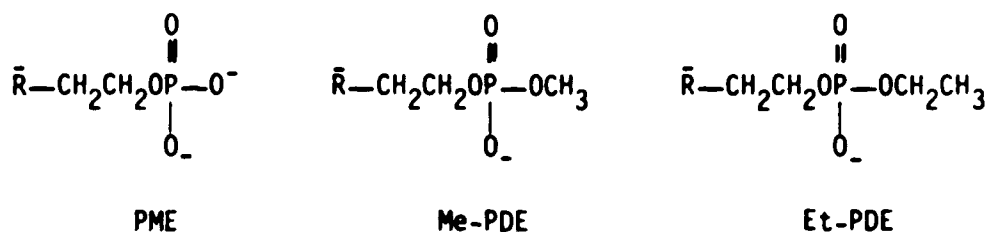
The conversion is accomplished by washing the hydrogen form of the PME resin with dry methanol, drying at 70°C for one day, swelling in dry DMF/ethanol, and adding the TCAN. The reaction is run for 1-3 days at 60-70°C. A representative preparation utilizes 1 g (5 mmol) of PME resin, 100 mmol of ethanol and 50 mmol of TCAN in 10 mL of DMF, periodically agitated at 65°C for two days. The product is identical to that obtained

from the condensation of 2-polystyrylethanol with monoethyl phosphate. The conversion in this reaction was clearly shown in the infrared spectra of the reactant and product resins. The characteristic broad absorption band around 1200 cm^{-1} in the Na^+ -form of the PME spectrum changed to a considerably sharper band at 1230 cm^{-1} upon reaction. The cation-exchange characteristics of the resins also changed with the conversion. Upon condensation with ethanol, a PME resin of capacity 1.8 meq/g in the dry hydrogen form yielded a product exchange resin of capacity 0.92 meq/g, corresponding to the approximate two-fold reduction in capacity expected on changing the dibasic exchange groups (PME) to monobasic exchange groups (PDE).

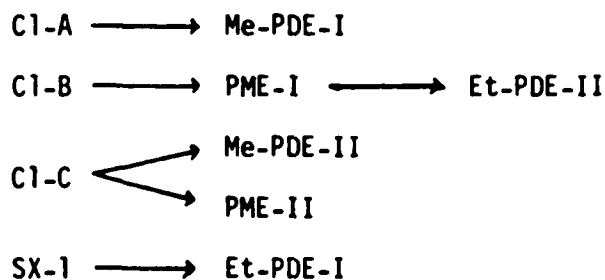
The detailed properties of all of the above cation-exchange resins will be discussed in Chapters Five and Six.

3.7 Preparation of the Resins in Bulk Quantities.

A total of six phosphoric-acid cation-exchange resins were prepared in bulk quantities. Five of these resins were the end products of three bulk conversions of styrene/DVB copolymer beads according to the reaction sequences presented previously in sections 3.2-3.6. The sixth resin was derived from a commercial chloromethylated styrene/DVB copolymer. Each of these exchangers was employed to some extent in the physicochemical characterizations, which will be discussed in Chapters Five and Six. As stated in the previous section, we distinguish among the various exchange resins by the following nomenclature: PME signifies the phosphoric-acid-monoester resin, 2-polystyrylethylphosphate; Me-PDE stands for the phosphoric-acid-diester resin, methyl 2-polystyrylethylphosphate; and Et-PDE refers to the phosphoric-acid-diester resin ethyl 2-polystyrylethylphosphate:



The following scheme summarizes the synthetic histories of the phosphate resins, C1-A, C1-B and C1-C being three bulk chloromethylated copolymers and SX-1 referring to the commercial chloromethylated polystyrene/1%-DVB, Bio-Beads SX-1 (see Table 3-2):



The remainder of this section is devoted to a description of the procedures and reaction conditions employed in the large scale synthesis of the copolymer intermediates and of the final phosphoric-acid cation-exchange resins.

3.7.1 Chloromethylation.

The starting material in all of the bulk preparations is styrene/2%-DVB copolymer obtained from the Dow Chemical Company [91]. The polymer was supplied as 45-100 mesh spherical beads. The chloromethylation procedure described here is applicable to the reaction of about one-half kilogram of the styrene/DVB copolymer.

In a 5-liter 3-neck flask equipped with a reflux condenser, thermometer and stirring paddle, reflux (ca. 57°C) 400-500 g of the copolymer beads with 2 L of chloromethylmethyl ether (CMME, purchased from Columbia Organic Chemicals, Columbia, S.C.) for one hour. Cool the mixture to 30°C and replace the condenser with pressure-equalized dropping funnel having an elongated glass stem which reaches into the center of the flask below the surface of the reaction mixture. Add 200-300 mL of titanium tetrachloride from the dropping funnel at a rate of about 3 mL/min, such that the total addition time is around 1.5 hours. Maintain the reaction temperature at 30°C by application of ice to the outside flask, and keep the reaction mixture vigorously stirred throughout the process. At the end of the addition of catalyst, the mixture is poured with stirring into 2 separate large beakers containing 1500 mL of 95% ethanol, breaking up any conglomerations of beads which may form. The alcohol is decanted, and the alcohol addition/decantation is repeated at least twice. The resin fractions are combined, transferred to a large sintered-glass funnel, and washed with ethanol, ethanol/methanol, methanol, methanol/water, methanol/4 M H₂SO₄, methanol/water and methanol. Three bulk chloromethylation reactions were carried out, the reagent quantities used in each being listed in Table 3-11(A).

3.7.2 Conversion to the Nitrile Resin.

The chloromethylated copolymer is swollen for several hours in a minimum of acetonitrile and then transferred to a 5-liter 3-neck flask equipped with reflux condenser, thermometer, and stirring paddle. Approximately 3 liters of acetonitrile, 1.1 liters of 95% ethanol and about 300 g of sodium cyanide are then added, and the mixture is maintained at 75-90°C for at least 26 hours. A small sample of resin

TABLE 3-11. SUMMARY OF BULK PREPARATIONS.

A. Chloromethylation.

<u>Bulk Reaction</u>	<u>Copolymer(g)^a</u>	<u>CMME(L)</u>	<u>TiCl₄(mL)</u>	<u>Product</u>
1	500 (4.8 mole)	2.0 (26.4 mole)	310 (2.8 mole)	Cl-A
2	400 (3.8 mole)	1.6 (21.0 mole)	180 (1.6 mole)	Cl-B
3	400 (3.8 mole)	1.6 (21.0 mole)	230 (2.1 mole)	Cl-C

B. Nitrile Formation.

<u>Bulk Reaction</u>	<u>Copolymer Reagent</u>	<u>CH₃CN(L)</u>	<u>95% Ethanol(mL)</u>	<u>NaCN(g)</u>	<u>Product</u>
1	Cl-A	3.0	1100	340	CN-A
2	Cl-B	3.0	1100	280	CN-B
3	Cl-C	2.9	1100	270	CN-C
4	SX-1 (100g)	1.0	400	50	CN-D

C. Nitrile Hydrolysis.

<u>Bulk Reaction</u>	<u>Copolymer Reagent</u>	<u>H₂SO₄(mL)</u>	<u>95% Ethanol(mL)</u>	<u>H₂O</u>	<u>Product</u>
1	CN-A				COOH-A
2	CN-B	1800	490	1300	COOH-B
3	CN-C				COOH-C
4	CN-D	750	330	750	COOH-D

D. Esterification of Carboxylic-Acid Resin.

<u>Bulk Reaction</u>	<u>Copolymer Reagent</u>	<u>Ethanol(mL)</u>	<u>H₂SO₄(mL)</u>	<u>Product</u>
1	COOH-A			COOEt-A
2	COOH-B	2500	250	COOEt-B
3	COOH-C			COOEt-C
4	COOH-D	500	45	COOEt-D

^a Styrene/DVB copolymer.

continued

TABLE 3-11. SUMMARY OF BULK PREPARATIONS.

continued

E. Reduction of the Ester Resin.

<u>Bulk Reaction</u>	<u>Copolymer Reagent</u>	<u>THF(L)</u>	<u>LiAlH₄(g)</u>	<u>Product</u>
1	COOEt-A	2.5	150	OH-A
2	COOEt-B	2.5	125	OH-B
3	COOEt-C	2.0	100	OH-C
4	COOEt-D	1.5	30	OH-D

F. PME-Resin Preparation.

<u>Reagent Resin(g)</u>	<u>2-CEP(mole)</u>	<u>TCAN(mL)</u>	<u>DMF(mL)</u>	<u>PME Resin</u>
OH-B, 290 (.70 mole)	1.84	240	1600	PME-I
OH-C, 170 (.55 mole)	1.60	230	1200	PME-II

G. Me-PDE-Resin Preparation.

<u>Reagent Resin(g)</u>	<u>MePO₄(g)</u>	<u>TCAN(mL)</u>	<u>DMF(mL)</u>	<u>Me-PDE Product</u>
OH-A, 210 (.75 mole)	180	280	900	Me-PDE-I
OH-C, 170 (.55 mole)	200	240	1200	Me-PDE-II

H. Et-PDE-Resin Preparation.

<u>Reagent Resin(g)</u>	<u>EtPO₄(g)</u>	<u>TCAN(mL)</u>	<u>DMF(mL)</u>	<u>EtOH(mL)</u>	<u>Et-PDE Product</u>
OH-D, 60 (.20 mole)	70	60	400	-	Et-PDE-I
PME-I(H ⁺), 60 (.6 mole)	-	40	80	100	Et-PDE-II

is withdrawn through a pipet, washed with acetonitrile, water and methanol, and its IR spectrum is recorded. Reaction is considered complete when no band at 1260 cm^{-1} is evident. At the completion of the reaction, the beads are allowed to settle and the acetonitrile/ethanol/NaCN solution is decanted or siphoned with caution while still hot. The beads are transferred to a large glass funnel and washed with CH_3CN /ethanol, ethanol, ethanol/methanol, methanol, methanol/water and water. 100 g of Bio-Beads SX-1 are converted by a similar, albeit scaled down, procedure. The specific reactant quantities for each preparation are shown in Table 3-11(B).

3.7.3 Hydrolysis of the Nitrile Resin.

Hydrolysis of the bulk-nitrile samples is carried out in a 5-liter 3-neck flask, fixed with a reflux condenser, thermometer and stirrer. The nitrile-resin beads (swollen with water) are heated for 12-24 hours at $100\text{-}110^\circ\text{C}$ in a solution composed of about 1800 mL of concentrated sulfuric acid, 1300 mL of water and 490 mL of 95% ethanol. The reaction was judged complete when the IR spectrum of a sample exhibited no absorption at 2250 cm^{-1} . Hydrolysis was continued for 5-6 hours beyond this point. The product was transferred to a glass filter and washed with water, water/methanol and methanol. The hydrolysis of sample CN-D was accomplished with 750 mL of concentrated sulfuric acid, 330 mL of water and 165 mL of 95% ethanol under conditions similar to those described above. Conversion of the bulk-nitrile samples CN-A, CN-B, CN-C and CN-D produced the carboxylic-acid resins COOH-A, COOH-B, COOH-C and COOH-D, respectively. The reactions are summarized in Table 3-11(C).

The ion-exchange capacities of these intermediate carboxylic-acid resins, expressed as the number of milliequivalents of hydrogen ion per gram of dry resin (meq/g), is an indication of the extent of functionalization of the styrene/DVB copolymer. The capacity was measured by determination of the amount of standard base absorbed by a given mass of oven-dried (70°C) resin. Listed in Table 3-12 are the capacities for the bulk samples COOH-A, COOH-B and COOH-C, along with the mole fraction of functionalized aromatic rings in the copolymer systems, calculated from the formula:

$$X = \frac{104c}{T-58c} \quad (3.1)$$

where X is the mole fraction loading of the copolymer and c is the ion-exchange capacity (expressed as grams H/gram dry resin). Also tabulated are the mole ratios of chloromethylation catalyst to styrene/DVB copolymer employed in the chloromethylation steps of the bulk syntheses. An increase in the relative amount of $TiCl_4$ in the chloromethylation of the copolymer produces a resin which is more highly substituted, as reflected by the ion-exchange capacities in the Table.

3.7.4 Esterification of the Carboxylic-Acid Resins.

The bulk carboxylic-acid resin samples are dried from methanol wash for 24 hours at 70°C. Esterification is carried out in a 5-liter 3-neck flask with a reflux condenser, thermometer and stirrer. About 2500 mL of absolute ethanol and 250 mL of concentrated sulfuric acid are reacted with the resin (previously swollen in ethanol) at reflux for about 20 hours. The beads are washed with ethanol, ethanol/water, water, water/methanol and methanol in a large glass funnel. The

TABLE 3-12. CAPACITIES OF THE CARBOXYLIC-ACID RESINS.

<u>Carboxylic Resin</u>	<u>Capacity(meq/g)</u>	<u>Mole Ratio^a</u>	<u>Mole Fraction^b</u>
COOH-A	3.38	0.58	43.7
COOH-B	2.33	0.42	28.0
COOH-C	3.11	0.55	39.5

^a Mole Ratio = moles TiCl_4 /moles styrene/DVB copolymer used in the chloromethylation.

^b Calculated by equation 3.1.

The esterified product resins derived from samples COOH-A, COOH-B and COOH-C are designated COOEt-A, COOEt-B and COOEt-C, respectively.

These materials exhibit a negligible ion-exchange capacity, based on uptake of standard sodium hydroxide. Resin COOH-D was reacted with 500 mL of absolute ethanol and 45 mL of concentrated sulfuric acid to produce the esterified product resin COOEt-D. The reactions are summarized in Table 3-11(D).

3.7.5 Reduction.

The bulk-reduction step proved to be difficult due to the intrinsic danger associated with handling the large quantities of lithium aluminum hydride and the LiAlH_4 /tetrahydrofuran solutions required for the reduction of the copolymers. Reduction of the bulk ester-resin samples with an excess of reductant required the use of 2500 mL of a THF solution containing 80-110 g of LiAlH_4 . We desired to use LiAlH_4 solutions containing as little of the insoluble gray solid associated with the commercial LiAlH_4 as possible. Initially, we employed a Soxhlet extractor, which is essentially a reflux condenser designed so that the refluxing liquid drips into a porous cup containing a solid, the soluble portion of the which is carried by the liquid back into the boiling vessel. This apparatus would have allowed simultaneous dissolution of the LiAlH_4 into a clear reductant solution and reduction of the copolymer in the same boiling flask. Unfortunately, the solid LiAlH_4 was found to float out of the porous cup and enter the reaction flask.

We finally settled on a rather undesirable, hazardous procedure. A relatively clear reductant solution was prepared by refluxing ca. 150 g of LiAlH_4 in 1500-2000 mL of THF for one day, after which all

solids were allowed to settle to the bottom of the flask. The clear supernate was poured off directly into the reaction flask containing the swollen (in THF) copolymer beads.

The ester-resin beads must be thoroughly dried for this reaction step. Drying from ether at 70°C for two days was sufficient. The beads were swollen by refluxing in 1500 mL of THF for one day. Reaction was initiated by pouring the reductant solution into the swollen-resin/THF mixture, and the mixture was maintained at reflux for 1-2 days in a 5-liter 3-neck flask, with a thermometer, stirrer and reflux condenser fixed with a drying tube. Small samples were withdrawn, hydrolyzed, and washed, and their IR spectra recorded to evaluate the extent of reaction. A minimum absorption (less than 5% of original absorption) in the carboxyl regions ($1720-1650\text{ cm}^{-1}$ and $1250-1150\text{ cm}^{-1}$) signified complete reaction.

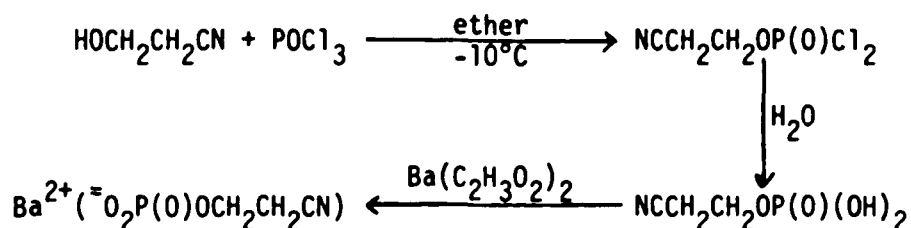
The work-up of the bulk samples began by decanting the reaction solution from the settled beads. The resin was then added in small portions to a large beaker of cold 1 M H_2SO_4 with stirring. The hydrolyzed beads were then stirred for one day in 3:1 (v/v) 2 M H_2SO_4 /ethanol. Treatment was completed by washing on a glass filter with 2 M H_2SO_4 , H_2O , 2 M NaOH, H_2O , 2 M H_2SO_4 , $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ and CH_3OH . Ester samples COOEt-A, COOEt-B and COOEt-C were reduced to the alcohol resin products OH-A, OH-B and OH-C, respectively. Resin COOEt-D was reduced with solution made from 30 g of LiAlH_4 and 1500 mL of THF to yield sample OH-D. The reactions are summarized in Table 3-11(E).

A check of the ion-exchange capacities of these ester samples (using uptake of standard base) yielded the following results: 0.06, 0.03 and 0.03 meq/g for products OH-A, OH-B and OH-C, respectively. These small values indicate essentially complete conversion of the

-COOH groups of the polystyrylacetic-acid resins into alcohol groups. Based on the capacities measured for the carboxylic-acid resins (see Table 3-12), the hydroxyl contents of the bulk-alcohol resins are calculated to be 3.55, 2.41 and 3.25 milliequivalents of OH per gram of resin for samples OH-A, OH-B and OH-C, respectively.

3.7.6 Preparation of Barium 2-Cyanoethylphosphate.

As was pointed out earlier, the production of large quantities of the monoester resin was financially practical only if we synthesized the cyanoethylphosphate reagent. The following procedure is a scale-up of Tener's method [55], by which the barium-dihydrate salt of 2-cyanoethylphosphoric acid can be made in a 60% yield. The reaction is:



Although Tener's results could be duplicated (41 g of the salt at a 60% yield), we found it more convenient to adjust the reactant quantities to produce 110-g portions of the salt in a 40% yield. In a 1-liter 3-neck flask equipped with a thermometer, stirrer and dropping funnel, a mixture of 700 mL of dry diethyl ether and 32.6 mL of POCl_3 (0.8 mole) is chilled to -10°C in a ice-salt bath. 56 mL of 3-hydroxypropionitrile (0.8 mole) in 64 mL of dry pyridine are added through the dropping funnel over a one-hour period, the temperature being maintained between -10° and -5°C . The mixture is stirred for an additional hour between -5° and 0°C after the addition is completed. The mixture is

then poured, with stirring, into a large beaker containing 1800 mL of water, 320 mL of pyridine and 600 g of crushed ice, followed by the introduction of 350 g of barium acetate in a 600 mL aqueous solution. After standing overnight, during which time the ether evaporates and the barium phosphate precipitate aggregates at the bottom of the vessel, the mixture is filtered in a large Büchner funnel. To the solution (now 2500-3000 mL total volume), chilled in an ice bath, 2500-3000 mL of 95% ethanol are added, causing the barium 2-cyanophosphate to precipitate. The product is collected in small portions in a Büchner funnel, washed twice with 50% ethanol, then with 95% ethanol, and the white, flaky crystals are air dried. The preparation furnishes 100-110 g, corresponding to an approximately 40% yield. The infrared spectrum of the product matches those of various commercial salts (Aldrich Chemical Co., Eastman Chemical Co.) and of the published spectrum [123]. Fifteen preparations were performed, producing a total of about 1300 g of barium 2-cyanoethylphosphate dihydrate.

Conversion to the water-free pyridinium salt, suitable for the phosphorylation reactions, is accomplished as follows: 150 g (0.46 mole) of the barium-dihydrate salt are dissolved in ca. 1800 mL of water with the aid of Dowex-50 (H^+ -form, about 150 mL wet-bed volume) and heat. (The resin exchanges Ba^{2+} for H^+ , forming the more soluble acid.) The solution is passed through a column of 690 mL of Dowex-50 (H^+ -form), which is then rinsed with 1600 mL of water. Pyridine (300 mL) is added to the combined eluates (now ca. 4 L total volume), and the entire mixture is then concentrated by vacuum distillation at 21° - $27^{\circ}C$ down to a volume of about 200 mL (the trap vessels are cooled with liquid nitrogen). This concentration step takes at least 24 hours. The concentrated solution is then lyophilized to a viscous oil with several

50 mL portions of dry pyridine added followed by continued lyophilization. The resulting water-free viscous oil turns to a waxy solid in a freezer and is dissolved in dry N,N-dimethylformamide for use in the phosphorylation reactions.

3.7.7 Preparation of the PME Resins.

All of the 2-polystyrylethanol resins are treated before use in the phosphorylations by heating in 3:1 (v/v) 1 M NaOH/dioxane for two days and, then in 3:1 (v/v) 1 M H₂SO₄/dioxane for two days. After thorough washing with water and methanol, the polymers are dried for two days at 70°C in a vacuum oven.

The general procedure for the formation of the PME resin involves swelling the alcohol resin (200-300 g) in 500-1000 mL of dry N,N-dimethylformamide (DMF) for one day. A quantity of pyridinium 2-cyanoethylphosphate corresponding to an approximate 3-fold mole excess over resin is dissolved in 500-600 mL of dry DMF and added to the resin/DMF mixture. A 4- to 5-fold mole excess of trichloroacetonitrile (TCAN) over resin is then added. The resulting mixture is stirred for four days at 60°-65°C in a 4-liter 3-neck flask. The resin is then separated from the reaction solution and washed with DMF, methanol and water. The resulting 2-cyanoethyl 2-polystyrylethylphosphate resin is hydrolyzed by treatment with 2 L of 0.5 M NaOH at 50°C for one day.

Two samples of PME resins designated PME-I and PME-II were prepared with the reagent quantities shown in Table 3-11(F). The resins were conditioned with three cycles of 0.5 M HCl/H₂O/0.5 M NaOH. The air-dried exchangers were run through sieves, and the 40-70 mesh and 70-140 mesh portions were kept for use. The exchangers were stored in the sodium form under water.

3.7.8 Preparation of the Me-PDE Resins.

The alcohol copolymer (ca. 200 g), pretreated as described in section 3.7.7, is swollen in 400 mL of dry DMF for one day. A 2-fold mole excess of monomethylphosphate (from ICN Pharmaceuticals, Plainview, N.Y.) in DMF is added, and the reaction is initiated by the introduction of a 3-fold excess of TCAN. After reaction for three days at 60°-65°C, the resin is filtered and washed with DMF, methanol and water. Conditioning with three cycles of 1 M NaOH/H₂O/1 M HCl, washing and air drying completes the post-reaction treatment. The 40-70 mesh beads were stored under water in the sodium form. Two methyl-diester exchangers (designated Me-PDE-I and Me-PDE-II) were prepared using the quantities of reagents listed in Table 3-11(G).

3.7.9 Preparation of the Et-PDE Resins.

The first synthetic route to this material is executed by the addition of 70 g (0.6 mole) of monoethyl phosphate (ICN Pharmaceuticals, Plainview, N.Y.) in DMF to 60 g (~ 0.2 mole) of resin OH-D swollen in DMF. Then 60 mL (0.6 mole) of TCAN are added, the total volume of DMF brought to 400 mL, and the reaction conducted for four days at 70°C. The product ion exchanger, washed with DMF, methanol and water, is conditioned with three cycles of 0.1 M HCl/H₂O/0.1 M NaOH. This Et-diester resin is designated Et-PDE-I.

Using the second approach to the synthesis of this material, 60 g (ca. 60 mmol) of resin PME-I is converted to the hydrogen form by treatment with 2 L of 0.5 M HCl, washed, and thoroughly dried at 70°C in a vacuum oven for two days. The dry resin is then swollen in 100 mL (2 moles) of absolute ethanol, and 40 mL of TCAN (0.4 mole) and 80 mL of DMF are added. The mixture is stirred for three days at 65°-70°C,

after which the resin is filtered, washed with DMF/ethanol, ethanol and water, and conditioned with three cycles of 0.2 M HCl/H₂O/0.2 M NaOH. This Et-diester exchanger is designated Et-PDE-II. These reactions are summarized in Table 3-11(H).

CHAPTER FOUR

OTHER ATTEMPTS TO SYNTHESIZE THE RESINS

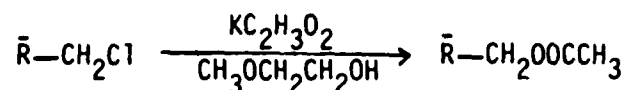
Prior to the discovery of the successful synthetic routes to the two phosphoric-acid-ester cation-exchange resins, described in Chapter Three, several other approaches to the problem were attempted. These methods, generally ineffectual, involve applications of the various phosphorylation reactions discussed in Chapter Two. Much of our earlier work focused on the introduction of oxyphosphorus groups onto a hydroxymethylstyrene/DVB copolymer matrix. Experiments were also performed with a modified hydroxymethylstyrene/DVB resin and with a polymethacrylic-acid resin. In the present chapter, these synthetic trials (and resulting tribulations) are briefly reviewed.

4.1 Polystyrylmethanol.

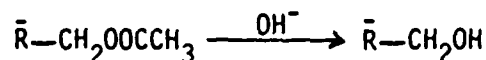
At the outset of our research, the philosophy was to find the most straightforward route to the phosphoric-acid resins. We desired a polymer backbone which was homogeneous, convenient to work with, and which required a minimum of synthetic modification in order to render it readily phosphorylatable. Hydroxymethylpolystyrene (polystyrylmethanol, $\bar{R}-CH_2OH$) fit these criteria closely. The material contains active hydroxyl functions separated from the aromatic ring, and could be easily prepared from commercially-available chloromethylated styrene/DVB copolymers via one or two simple reaction steps. Presumably, the chloromethylated polystyrenes obtained from commercial suppliers would be well characterized materials in terms of structural homogeneity and monofunctionality, since they are widely sold as "Merrifield Resins" for solid-phase peptide syntheses [102,124-126]. Unfortunately, one lot of chloromethylated polystyrene which we obtained

was found quite unsatisfactory for our purposes, producing fouled, inhomogenous and oxidized product-polymer resins.

Chloromethylated polystyrene/2%-DVB (polystyrylmethyl chloride) was obtained from Bio-Rad Laboratories, Richmond, CA. Chlorine analysis, involving combustion of a small samples (ca. 30 mg) in an oxygen flask followed by potentiometric titration (see the Appendix for details), showed the polymer to contain 17.0 ± 0.7 % chlorine, which corresponds to 65 mole % substituted aromatic rings. Conversion to polystyrylmethanol, following the method of Stewart and Young [102], consisted of two steps. After swelling in 2-methoxyethanol, the chloromethyl resin was refluxed for one day at 135°C with a two-fold mole excess of potassium acetate:



The acetoxymethylpolystyrene intermediate (polystyryl acetate) was then treated with sodium hydroxide in water/dioxane for at least one day at $25^{\circ}\text{--}30^{\circ}\text{C}$ to give the hydroxymethyl resin (polystyrylmethanol):

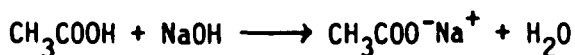
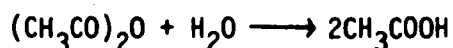
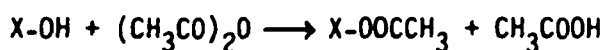


A typical chlorine analysis of the product showed less than 0.3% chlorine, indicating almost complete conversion. Comparison of the IR spectrum of the $\bar{\text{R}}-\text{CH}_2\text{Cl}$ starting resin and $\bar{\text{R}}-\text{CH}_2\text{OH}$ product resin revealed the disappearance of the band at 1260 cm^{-1} in the spectrum of the reagent resin and the appearance of the C-O-H bands ($1100\text{--}1000\text{ cm}^{-1}$) in the spectrum of the product resin. The conversion was also carried out by

the direct reaction of $\bar{R}-CH_2Cl$ with potassium hydroxide in water/dioxane at 70°-90°C for 1-2 days.

For the acetoxymethyl intermediate resin, $\bar{R}-CH_2OOCCH_3$, the expected infrared spectrum was not obtained. The spectrum did not exhibit an absorption band around 1720 cm^{-1} , indicating the absence of carbonyl groups. Instead, the spectrum closely resembled that of the hydroxymethyl resin. The acetoxymethyl resin, actually a benzyl carboxylic-acid ester, is apparently not stable in aqueous media. Upon washing, the acetoxymethyl resin hydrolyzed to acetic acid and polystyrylmethanol. The IR spectrum of an acetoxymethyl resin prepared under completely anhydrous conditions, i.e., washing with 2-methoxyethanol and dry methanol only, did exhibit a carbonyl absorption at 1730 cm^{-1} and C-O bands around 1000 cm^{-1} , further confirming the instability of the ester linkage in this resin.

Consistent with this conclusion are the results obtained for the quantitative hydroxyl analyses which were performed on the polystyrylmethanol-resin samples. In order to quantify the hydroxyl-group content of the alcohol resin, and thereby to check the extent of conversion of the chloromethylated polymer, we adopted a semi-micro procedure for the measurement of hydroxyl groups in various organic compounds [127-129]. The chemistry of the technique involves conversion of the OH groups into acetoxy groups by esterification with a quantitative excess of acetic anhydride in pyridine. The unreacted anhydride is then hydrolyzed and all acetic acid formed is titrated with standard base. Using X-OH to represent the hydroxyl compound under analysis, the reactions are:



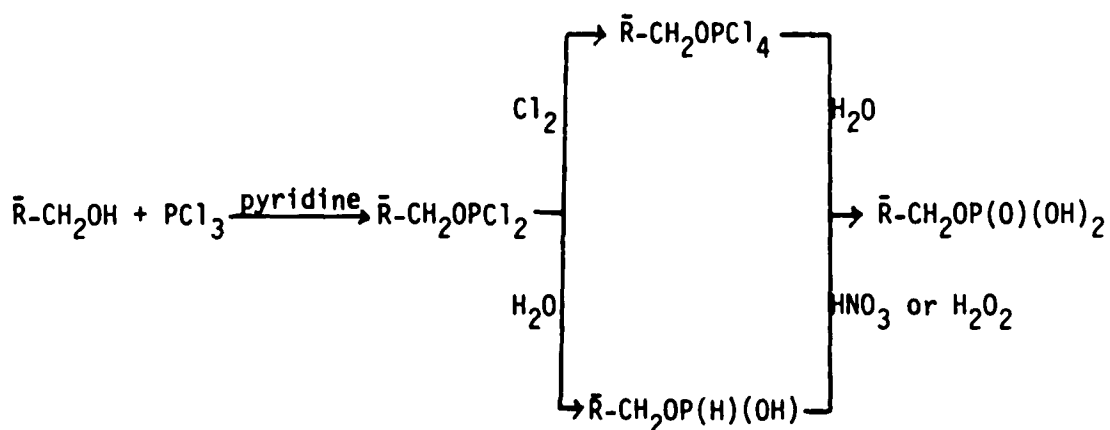
The resin is weighed into a reaction tube consisting of a small length of pyrex tubing sealed at one end and drawn out to a constricted opening at the other end. A small glass bead, to aid in agitation of the reactants, is sealed into the tube during its construction. After introduction of weighed portions of dry pyridine and excess acetic anhydride, the tube is sealed and the contents are left at a slightly elevated temperature with intermittent shaking for several days. For analysis, the tube is broken under ca. 50 mL of water and the resulting solution is titrated with standard sodium hydroxide. Blanks are run simultaneously.

The results of the hydroxyl-group analyses were difficult to interpret. The phenolphthalein endpoint in the titrations slowly but consistently faded, more so than would be expected from the effect of carbon dioxide. If the acetoxymethyl resin had indeed been hydrolytically unstable as we concluded above, then the slow hydrolysis into hydroxymethylpolystyrene and acetic acid would account for this observed increasing acidity, and thus obscure a definite determination of the hydroxyl-group content of the polymer. A check of the IR spectrum of a sample of resin taken from this analysis confirmed that the benzyl-ester resin had hydrolyzed into the alcohol resin. Actual results (for % OH) were found to vary widely and generally decreased with increasing time between breaking the reaction vessel and titrating.

In any case, the polystyrylmethanol was satisfactorily prepared and subsequently subjected to several phosphorylation attempts.

4.2 Direct Phosphorylations of Polystyrylmethanol.

Many attempts at the direct phosphorylation of polystyrylmethanol with phosphorus trichloride (PCl_3) and phosphoryl oxychloride (POCl_3) were performed. Based on the reaction scheme of Abrams [59], a straightforward route to the phosphate exchangers seemed feasible. Treatment of the alcohol polymer with PCl_3 would lead to a phosphodichloridite intermediate, which could be oxidized (with H_2O_2 or HNO_3 or Cl_2) and hydrolyzed to produce the ion-exchange resin as polystyrylmethylphosphate. The reaction scheme is:

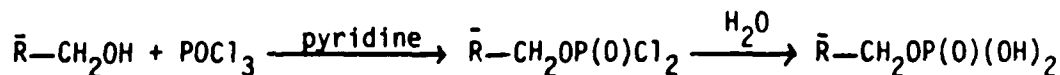


A wide variety of reaction conditions were tested. Polystyrylmethanol was treated with neat PCl_3 and with PCl_3 in the solvents methylene chloride, tetrachloroethane, perchloroethylene, dioxane, petroleum ether, diethyl ether, benzene, toluene, and in various combinations of these solvents. A small amount of pyridine was added in each experiment, serving as a scavenger for the HCl released during the phosphorylation step. The reactions were carried out at temperatures ranging from -10°C

up to the refluxing temperature of the solvent, and conducted for periods ranging from several hours to several days. In all cases, no phosphoric-acid exchanger was formed, as evidenced by the absence of characteristic $P=O$ absorptions on the IR spectra of the products and by the lack of an ion-exchange capacity for any of the products.

In a typical experiment, the resin, treated with excess PCl_3 in the particular solvent medium, was washed with methylene chloride. Introduction of water produced a strongly acidic solution, resulting from the HCl formed in the hydrolysis of the phosphodichloridite intermediate resin. This acidity indicated that phosphorylation had taken place. Since no phosphorus was detected in the hydrolyzed resin, phosphorus loss occurred during the aqueous-hydrolysis step. Samples of the phosphodichloridite resin, taken from a thorough non-aqueous wash and dried, were analyzed for their phosphorus contents using the molybdenum-blue method in the presence of chloride, described in the Appendix. Typical results ranged from 4.8 to 6.6% phosphorus, corresponding to conversion of 23 to 52% of the hydroxyl functions in the alcohol copolymer into phosphodichloridite groups. Qualitative analysis of the acidic water solution produced from the hydrolysis step showed the presence of phosphorus, confirming the hydrolysis of the phosphorus functions from the polymer matrix. Decomposition of the phosphorus-containing copolymer also ensued upon treatment with aqueous HCl , $NaOH$, $NaHCO_3$ and $Ba(OH)_2$.

Similar results were obtained in the experiments involving phosphorylation with $POCl_3$, a reagent used to phosphorylate polyvinyl alcohol [86] and cellulose [82,84]. Use of the latter compound would hopefully have produced a pentavalent phosphorus function on the resin, requiring only a hydrolysis step to form the final phosphate resin:

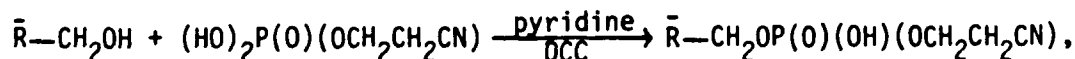


These experiments were conducted in solvents and under conditions equivalent to those used in the PCl_3 phosphorylations. We found that introduction of phosphorus functions onto the copolymer matrix was more difficult with $POCl_3$. Typical phosphorus contents for the phosphodichloridate intermediate ranged from 2.6 to 4.2% phosphorus, corresponding to only a 5 to 10% substitution of the hydroxyl groups on the alcohol copolymer, even after extended reaction periods. Again, phosphorus was lost from the polymer upon attempted hydrolysis in aqueous media.

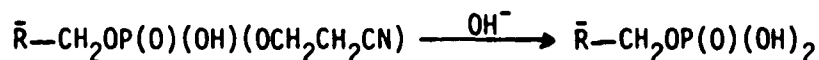
Considering the apparent instability of the benzyl-carboxylic ester in the resin system (section 4.1), it is not surprising that the benzyl-phosphate-ester linkage is even more unstable. It is known that phosphate esters are generally less stable than corresponding carboxylate esters, some mono- and di-esters being particularly unstable [31,130]. Thus, the methylene resin backbone chosen was not compatible with the formation of a stable phosphoric-acid-ester cation-exchange resin.

4.3 Condensation Phosphorylations of Polystyrylmethanol.

Blackburn et al [54] used pyridinium 2-cyanoethylphosphate and dicyclohexylcarbodiimide (DCC) to produce polystyrylmethylphosphate, although the polymer product was not subjected to aqueous media. We attempted a similar reaction scheme, condensing the alcohol copolymer (ca. 2 mmol) with excess 2-cyanoethylphosphate (ca. 6 mmol) and DCC (ca. 12 mmol):



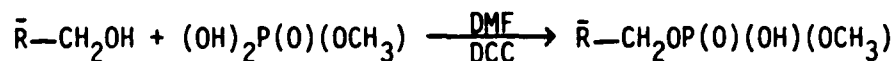
followed by splitting-off of the 2-cyanoethyl protecting group in base:



The phosphorus functions were found to hydrolyze from the copolymer with any aqueous treatment.

We attempted condensation of the alcohol copolymer (1 g) with 85% phosphoric acid (7 mL) and DCC (6 g), a method employed in the phosphorylation of cotton [86], and also condensation of the polymer with urea phosphate and DCC [131]. In both cases, the experiments failed to produce any stable phosphorus-containing materials.

Condensation of the polystyrylmethanol resin (2 mmol) with mono-methylphosphate (13 mmol) and DCC (15 mmol) should produce a phosphoric-acid-diester group on the polymer:



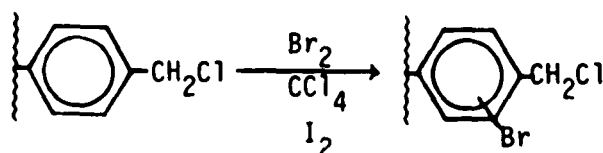
Repeated attempts at this synthesis, using a variety of reagent ratios and temperatures, yielded no stable ion-exchange resin.

Condensation reactions run with DCC were found difficult to handle in the work-up of the product. The dicyclohexylurea formed from the DCC, being extremely insoluble in most solvents, caused problems. Separation of this white solid from the resin beads was formidable, requiring many prolonged and repeated treatments with hot pyridine and hot methanol. The more convenient condensing agent, trichloroacetonitrile, produced similar unsuccessful results, no stable resins having been prepared by its use.

4.4 Phosphorylation of Modified Polystyrylmethanol.

Merrifield [124] has reported that when employing polystyrene/DVB as a solid support in peptide synthesis, a more stable carboxy-ester linkage results when the aromatic rings of the resin are destabilized. This can be accomplished by the introduction of various electron-withdrawing substituents onto the aromatic groups of the copolymer. Nitro groups can be attached by nitration with fuming nitric acid and bromo groups can be attached by bromination with bromine and iodine in carbon tetrachloride. The conditions for nitration of the chloromethyl resin were found to be too severe, treatment of the resin with excess fuming nitric acid at 0° to 10°C for two hours producing a discolored, oxidized material. Aryl bromo groups, on the other hand, were introduced under milder conditions, and their presence in the final phosphate resins would exert a minimal influence on the overall properties. This alternative was therefore pursued extensively.

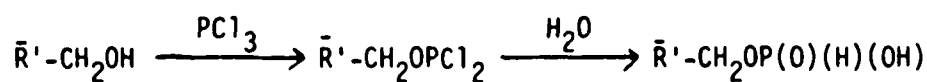
Bromination of polystyrylmethyl chloride was accomplished by stirring 10 g of the CCl₄-swollen copolymer with 7 mL of Br₂ and 150 mg of I₂ in 60 mL of CCl₄. The reaction was conducted at 25°C for two days in the absence of light:



According to Merrifield [124], this procedure results in the introduction of one bromine atom onto each aromatic ring. Results of our IR spectra for the brominated product indicate a higher bromine loading, ranging from two to five bromine atoms per ring, as evidenced by the disappearance

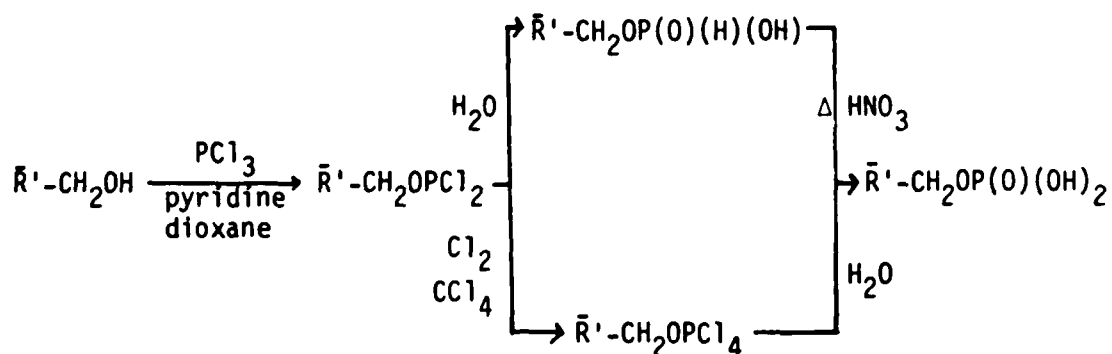
of the aromatic C-H stretch at 3030 cm^{-1} . The bromo-polystyrylmethyl chloride ($\bar{R}'\text{-CH}_2\text{Cl}$, where $\bar{R}'$ is the brominated matrix) was then converted to bromo-polystyrylmethanol ($\bar{R}'\text{-CH}_2\text{OH}$) by reaction with potassium acetate and sodium hydroxide, as described in section 4.1.

Reaction of the dried brominated alcohol copolymer with excess PCl_3 in dioxane/pyridine for two hours, followed by hydrolysis, did produce a stable phosphorylated material. A phosphorous-acid-monoester resin was formed, according to the reaction scheme:



This material was stable to repeated exchange cycles with HCl , NaOH and CuSO_4 , and its IR spectrum displayed characteristic P=O absorptions in the $1250\text{-}1000\text{ cm}^{-1}$ region. The ion-exchange capacity was measured to be in the range 1.5 to 1.7 meq/g.

The conversion of the phosphorous-acid groups to phosphoric-acid groups by oxidation was not successful. Two methods were tried, direct oxidation of the phosphorous-acid functions with aqueous nitric acid and oxidation of the intermediate phosphodichloridite functions with elemental chlorine followed by hydrolysis:

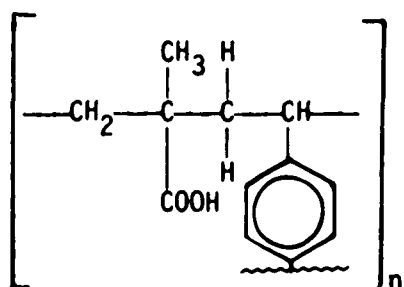


In the case of the nitric-acid treatment, the oxyphosphorus linkages were unstable to the hot oxidant solution. The material resulting from bubbling chlorine gas through a CCl_4 suspension of the resin was not significantly altered in comparison to the phosphorous-acid resin, the two materials having ion-exchange capacities of 1.5 to 1.7 meq/g. Oxidation would have been expected to produce a resin with an approximately doubled capacity, reflecting the conversion of monobasic phosphorous-acid-monoester functions into dibasic phosphoric-acid-monoester functions.

Phosphorylation of bromo-polystyrylmethanol with POCl_3 in dioxane/pyridine produced no suitable phosphate ion-exchange resin. Hydrolysis of the intermediate phosphodichloridate resin with 1 M HCl yielded a non-exchanging polymer, but hydrolysis with 1 M NaHCO_3 did result in a polymer which survived one exchange cycle with Cu^{2+} . Further attempts at exchanging the Cu^{2+} with aqueous solutions containing Na^+ , K^+ , Ca^{2+} , Ba^{2+} and H^+ ions caused decomposition of the resin. Apparently, the benzyl-phosphate-ester linkage in the brominated resin was stabilized somewhat over that in the non-brominated resin, as shown by its ability to at least survive one exchange cycle.

4.5 Use of a Polymethacrylic-Acid Backbone.

BioRex-70 (Bio-Rad Laboratories, Richmond, CA) is a polymethacrylic-acid cation-exchange resin crosslinked with divinylbenzene, having an ion-exchange capacity around 10 meq/g:



Chemical reduction of the carboxylic-acid groups to alcohol groups would result in a copolymer which, when phosphorylated, could form stable phosphate linkages. With this material, the benzyl-phosphate-ester instability is obviated, and phosphorylations could be carried out in much the same way as phosphorylations of cellulose and polyvinylalcohol. The resulting resins would be evenly crosslinked, in bead form, and have reasonable capacities and would thus have met our criteria for suitable products.

The hydrogen form of BioRex-70 was dried and refluxed in tetrahydrofuran for one day. LiAlH_4 was added, and the mixture refluxed for up to five days. The IR spectrum of the resin showed only a minimal decrease in the intensities of the carboxylate bands. To facilitate reduction, a sample of the dried hydrogen-form resin was refluxed with absolute ethanol/concentrated sulfuric acid for up to four days, in an attempt to esterify the carboxylic-acid groups. The resin produced was not fully esterified, a measurable capacity persisting. This material also could not be fully reduced to the alcohol form. Further experiments with BioRex-70 were not considered.

CHAPTER FIVE

CHARACTERIZATION OF THE RESINS I

5.1 Introduction.

Cation-exchange resins are characterized by several fundamental properties, which can be classified into two major categories. The first category covers the physical characteristics of the material, including particle size or volume [2(p. 321),132,133], porosity [1(p. 160)], density [2(p. 324)], solubility [2(p. 328)] and mechanical stability [2(p. 236)]. These properties are especially important in the application of ion-exchange processes to large scale industrial uses and other practical situations in which maximum efficiency is required over hundreds of exchange cycles. The major applications of ion-exchange technology remain today in the fields of water softening [134] and water deionization [135]. The second category of ion-exchange-resin properties is comprised of the physicochemical properties, including the ion-exchange capacity, the water content, the acid strength of ionogenic groups, the selectivity for ions, the chemical stability, the infrared spectra, the electrical conductance and the nuclear magnetic resonance spectra. The quantitative specification of each of these properties constitutes an overall characterization of the ion-exchange resin, dictating how the resin behaves under a particular set of experimental conditions and how this behavior compares with that of other ion-exchange materials.

The results of the physicochemical characterizations of the phosphoric-acid-ester cation-exchange resins prepared under the present research are given in this and the following chapter. This chapter is devoted to the capacity, acidity, stability, water content and

selectivity of the phosphate resins, while in Chapter Six the results for the infrared spectral measurements, nuclear magnetic resonance measurements and electrical conductance measurements are given and discussed.

5.2 Capacities and pH Titrations.

5.2.1 General Considerations.

The capacity of an ion-exchange resin is defined as the quantity of counterions or ionogenic groups present in a given amount of exchanger. There are several specific definitions for the capacity of an ion-exchange resin [1(Ch. 4)]. Several of these, including the apparent capacity, the sorption capacity, the useful capacity and the concentration of ionogenic groups, are a function of the particular experimental conditions to which the ion exchanger is subjected. These expressions of the ion-exchange capacity generally depend upon the pH and concentration of the external solution and upon the rate of treatment. The scientific weight capacity, however, is an inherent constant of the ion-exchange material, reflecting the specific structural and functional attributes intrinsic to the particular sample.

The scientific weight capacity is defined as the number of milliequivalents of ionogenic groups or counterions contained in one gram of dry resin, when the resin is in a specified ionic form. The resin is considered dry when it is completely free of sorbed solutes and solvent. The ionic form must be specified since the total weight of a given quantity of the resin depends on the mass of the counterion. For example, consider a hypothetical resin composed of 50 mole percent styrene units ($-\text{CH}_2-\text{CH}[\text{C}_6\text{H}_5]-$, unit mass = 104) and 50 mole percent

2-(4-vinylphenyl)-ethylphosphoric acid units

($-\text{CH}_2-\text{CH}[\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OP}(\text{O})(\text{OH})_2]$, unit mass = 228). In the hydrogen form, the capacity is calculated to be $50/[(50 \cdot 28) + (50 \cdot 228)] = 3.9 \text{ meq/g}$ (H^+ -form). In the sodium form, the capacity is found by taking into account the mass of the sodium 2-(4-vinylphenyl)-ethylphosphate units (unit mass = 272), giving $50/[(50 \cdot 28) + (50 \cdot 272)] = 3.3 \text{ meq/g}$ (Na^+ -form) for the capacity.

Typical capacities for some of the more common types of exchangers are as follows: 1-3 meq/g for the alkylammonium anion exchangers, 3-6 meq/g for the sulfonic-acid strong-acid and phosphonic-acid weak-acid cation exchangers, and up to 10 meq/g for the methacrylic-acid weak-acid cation exchangers. In industrial and laboratory ion-exchange processes, higher capacity resins require less material outlay and smaller equipment. For physicochemical measurements on the exchangers, higher capacities generally lead to larger measurable effects. Some specialized chromatographic applications make use of low capacity resins [136].

There are several techniques available for the measurement of the scientific weight capacity (hereafter referred to as "capacity"). The general procedure is to fully convert the resin into one ionic form, followed by thorough washing. The quantity of counterion held on the resin is then determined by complete removal of that ion from the exchanger and subsequent quantitative analysis using a variety of standard analytical methods. Such methods include, depending on the nature of the particular counterion, titration, colorimetric analysis, atomic absorption and isotopic labelling. The resin must be thoroughly dried and weighed at some point in the analysis.

The acid-base titration provides a convenient means for capacity determination. The resin, converted to the H^+ -form, is dried and weighed. In this state, the resin acts as an acid and can be titrated with standard base. For strong-acid exchangers, the titration can be performed directly on the resin. For weak-acid exchangers, the H^+ ions must first be liberated with an excess of salt solution or treated directly with excess standard base over an extended period to insure full reaction of all the weakly-acidic ionogenic groups. Drying the resin in the H^+ -form may lead to some difficulty, since care must be taken to insure that decomposition of the ionogenic groups does not occur during drying. Some resins are unstable in the acid form at elevated temperatures. Drying is accomplished at $100^{\circ}C$ for a few hours in a vacuum oven for the more stable resins (e.g., sulfonated polystyrene copolymers), while some of the less stable materials must be dried for longer periods at intermediate temperatures or even at room temperature over drying agents such as P_2O_5 . For newly synthesized ion-exchange resins, the stability characteristics must be ascertained in order to develop appropriate experimental procedures for the various characterization measurements.

In the characterization of a new ion-exchange resin, it is desirable to determine the capacity in more than one ionic form. In a stable, homogeneous material, the capacity values for several ionic forms will be equivalent. This correspondence indicates that all ionogenic groups are available as active exchange sites. For resins in which the ionogenic groups are comprised of elements amenable to quantitative analysis, e.g., nitrogen, phosphorus and sulfur, the

theoretical capacity can be calculated based on the elemental content. Agreement between this theoretical capacity and the measured value is also indicative of homogeneity of exchange sites. In sulfonated polystyrenes, for instance, there is good agreement between the sulfur content and the measured capacity [1(p. 74),137]. Thus, essentially every sulfonic-acid function acts as an exchange site. In resins containing nitrogen (alkylammonium anion exchangers)[138] and phosphorus (phosphonic-acid cation exchangers)[139], such good agreement is not generally found, probably due to structural inhomogeneities introduced during their syntheses.

Closely related to the capacity of a cation-exchange resin is the pH titration profile [1(p. 81)]. Analogous to the titration curves of soluble acids, the pH titration curves for strong- or weak-acid cation-exchange resins can be analyzed to evaluate the number of ionogenic groups in the resin (i.e., the capacity) and the nature of the ionogenic groups. The latter includes the number of different types of ionic groups, their degree of functionality, and the acid strengths (pK's) of the groups.

The pH titration curves for the strong-acid cation exchanger polystyrene-sulfonic acid [140,141] and the weak-acid resins composed of polymethacrylic acid [142,143] and phenolic [140,141] functions have been analyzed. The measured acid-dissociation constants (pK's) were found to correspond generally to the acid strengths of the monomeric analogues. The pK values determined fell into the ranges: < 1 for sulfonic-acid resins, 4-8 for carboxylic-acid resins, and 9-10 for phenolic resins. For the weak-acid resins in particular, the acid strengths were found to be somewhat dependent upon structural parameters, especially the

degree of crosslinking [142], and upon the degree of swelling of the resin [143]. The polymeric acids were generally weaker acids than the monomeric analogs. Titration curves for various phosphorus-containing cation exchangers have also been determined [60,85,86,88,144,145]. As expected, the curves were characteristic of dibasic phosphonic- and phosphoric-acid-monoester groups, showing a first dissociation with $pK = 2-3$ and a second dissociation with $pK = 7-8$.

For the experimental determination of a pH titration curve, the attainment of equilibrium between the resin phase and the external solution must be insured. Thus, a "direct" titration of a cation exchanger is valid only for the strong-acid types, where equilibration is rapid. Determination of the titration profile for the weak-acid exchangers is carried out by a "batch" or "indirect" method [141,142], in which several weighed samples of the H^+ -form resin are equilibrated with different amounts of standard base, the solution-volume/resin-weight ratios kept the same in each system. Analysis, after at least several days, involves measurement of the pH of each solution and indirect determination of the uptake of base by each resin sample through titration of the solution. Evaluation of the resulting profile using the method outlined by Helfferich [1(p. 84)] allows for calculation of the pK values of the ionogenic groups.

5.2.2 Experimental Procedures.

Several methods were adapted for the determination of the capacities of the phosphoric-acid-monoester and phosphoric-acid-diester resins which we have synthesized. Samples of exchangers were dried under varying conditions; it was determined that the resins were sufficiently dehydrated after 24 hours in a vacuum oven at $65^\circ C$ or after

three days in a vacuum dessicator over phosphorus pentoxide at room temperature. Standard sodium hydroxide solution was prepared by dilution of 50% (w/v) NaOH with CO₂-free water and then standardized against potassium biphthalate (dried for one day at 120°C) to the phenolphthalein endpoint. Standard hydrochloric acid was prepared by dilution of the concentrated acid and standardized against dried sodium carbonate to the methyl orange endpoint. Salt solutions were prepared from reagent-grade chlorides or nitrates, and standardized by running an aliquot through a small column of Dowex-50 in the H⁺-form, rinsing the column, and titrating the displaced protons with standard sodium hydroxide to the phenolphthalein endpoint. Magnesium was determined by EDTA titration or atomic absorption, calcium by atomic absorption, and sodium and potassium by flame photometry (see the Appendix).

The total capacity was measured by several techniques. In the method described by Helfferich [1(p. 91)], a 0.5-1.0 g sample of the dried H⁺-form resin is equilibrated with 50-100 mL of standard 0.1 N NaOH for 24-48 hours in a sealed flask. An aliquot of the solution is then back-titrated with standard HCl to the methyl orange endpoint. To account for sorption of NaOH by the resin ("Donnan uptake," the uptake of interstitial base without neutralization), an alternative procedure can be applied. The equilibrated resin and solution are transferred quantitatively to a chromatography column, the eluate solution being collected into a 250 mL volumetric flask. The resin is then rinsed with 2-3 10 mL portions of water, followed by removal of sorbed water and the remaining NaOH solution by forced-air pressure. An aliquot of the eluate is then titrated with standard HCl to the methyl orange endpoint. In still another procedure, the weighed resin, equilibrated with excess NaOH or KOH, is transferred to a column, rinsed with dilute

base (ca. 0.005 N), minimally washed (with 2-3 10 mL portions of water and forced-air pressure), and then treated with 250 mL of 1 M HCl, the eluate being collected into a volumetric flask. An aliquot of this solution is measured by flame photometry for Na^+ or K^+ ion.

The strong-acid capacity is determined by treatment of the Na^+ -form resin, prepared by equilibration in NaOH, with water for 2-4 days, until 10 mL of effluent is neutral to phenolphthalein (an "exhaustive wash"). The Na^+ remaining on the resin is eluted with 1 M HCl into a volumetric flask and determined by flame photometry.

The capacities for the ions Mg^{2+} and Ca^{2+} are determined by treatment in a column of the H^+ - or Na^+ -form of the weighed resin with excess 0.5 M $\text{Mg}(\text{NO}_3)_2$ or $\text{Ca}(\text{NO}_3)_2$ followed by a water rinse (until effluent is qualitatively free of the original counterions). Elution with 1 M HCl into a volumetric flask followed by titration of a neutralized aliquot for Mg^{2+} by the EDTA method or by atomic-absorption determination for Ca^{2+} completes the analysis.

The phosphorus contents are determined by combustion of 20-30 mg samples of the resins in a Schöniger flask, absorption of the P_2O_5 formed into aqueous solution, and colorimetric analysis for phosphorus by the molybdenum-blue or the phosphomolybdic-acid method. The detailed procedures used in the phosphorus analyses are discussed in the Appendix.

The pH titration of the resins is conducted according to Tropp Pepper [140] with some modifications. Between ten and fifteen 0.5-1.0 g samples of the oven-dried or air-dried H^+ -form resin are placed into separate flasks. A different amount of standard 0.1 N NaOH (in water or in 0.1 M NaCl) is added to each flask and the total-volume/resin-weight ratio adjusted to 125 mL/g by addition of appropriate amounts of

water or 0.1 M NaCl. To span the entire capacity range of a resin, the resin-weight/meq.-NaOH ratio is varied from 0.3 to 8.0 in a particular experiment. Equilibration times of at least three days are required, most experiments being conducted for at least five days. After this period, the pH of the solutions are measured with a glass electrode and a calomel electrode (Corning, Medfield, MA) and a Corning Model 12 pH meter, standardized with freshly prepared buffers. Aliquots of each solution are drawn off and titrated with standard NaOH (for acidic samples) or standard HCl (for basic samples). The pH titration profile is presented as a plot of the resin capacity (Na^+ uptake/gram) versus pH. For acidic samples, Na^+ uptake = meq. NaOH added + meq. H^+ found; for basic samples, Na^+ uptake = meq. NaOH added — meq. OH^- found. The capacity for each sample is found by dividing the Na^+ uptake by the sample weight.

5.2.3 Results: Capacities and pH Titrations for the Resins.

Capacities. In Table 5-1 are presented the capacities and phosphorus contents for the six phosphoric-acid-ester cation-exchange resins. The data are based on the dried H^+ -forms, and thus can be used for direct comparison of the various resins. The total capacities listed in the second column of the Table are based on treatment with excess base, such that all exchangeable protons in the resin are neutralized and thus measured. The strong-acid capacities listed in the third column of the Table are based on the observed hydrolysis of the weak-acid exchange sites for those resins which do not have monobasic ionogenic groups. When a salt form of such a resin, particularly an alkali-ion resin form, is treated in a column with water, a slow hydrolysis occurs. In the course of this hydrolysis, the salt form of the resin is

TABLE 5-1. CAPACITIES AND PHOSPHORUS CONTENTS OF THE RESINS.^a

Resin	Total Capacity(meq/g) ^b	Strong-Acid Capacity(meq/g) ^c	%P ^d	mmol (P)/g ^e
Me-PDE-I	2.05	0.90	3.50	1.13
Me-PDE-II	2.11	1.13	4.25	1.37
PME-I	2.69	1.20	4.12	1.33
PME-II	2.30	1.13	3.41	1.10
Et-PDE-I	1.00	0.95	3.40	1.10
Et-PDE-II	1.26	1.20	3.95	1.27

^a Data based on oven-dried (65°C) H⁺-forms.

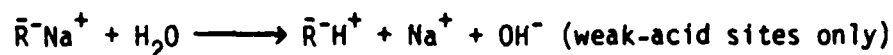
^b Total capacity based on equilibration of the H⁺-forms with excess standard base followed by back-titration. Experimental error ca. ±0.05 meq/g.

^c Strong-acid capacity based on Na⁺ eluted from the exhaustively-washed Na⁺-form resins. Experimental error ca. ±0.04 meq/g.

^d Average of five determinations. Method in Appendix. Experimental error ca. ±0.09%.

^e Based on %P.

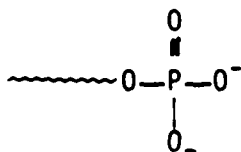
converted into the proton form and a hydroxide ion is generated:



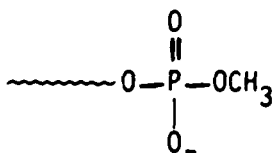
Treatment in a column with water resulted in an effluent which was basic to phenolphthalein. Complete hydrolysis of all weak-acid groups took from two to three days, corresponding to six to ten liters of water passed through the resin bed. The non-hydrolyzed exchange sites, remaining in the salt form, correspond to the strong-acid groups. In the cases for which dibasic ionogenic groups were expected, i.e., the PME resins, the water hydrolysis ("exhaustive wash") of the fully-loaded Na^{+} -forms removed a quantity of alkali ions equivalent to roughly one-half of the total capacity of the resins. This was found to be the case in repeated experiments using the Na^{+} - and K^{+} -forms with water treatments for from two to six days. Hydrolysis did not occur from divalent-ionic forms such as the Ca^{2+} -form. A similar phenomenon was noted for the commercial Duolite C-63 phosphonic-acid exchanger [69]. Because of this hydrolysis, a "minimal washing" had to be applied to the fully-loaded resins in order to measure the total capacity. Thus, base-equilibrated resins were subjected to a final treatment with very dilute NaOH (ca. 0.005 M), followed by two or three brief 10 mL water rinses with forced-air pressure removal of the interstitial water and ions. In this manner, Na^{+} hydrolysis was minimized, and any sorbed Na^{+} ion remaining in the resin would be negligible in comparison to the total capacity.

For resins PME-I and PME-II, the strong-acid capacities reported in Table 5-1 are approximately one-half the reported total capacities.

Phosphorus contents measured for these two resins (columns four and five of Table 5-1) are consistent with their phosphate-monoester structures. For resins PME-I and PME-II, the ratios of the total capacity/millimoles phosphorus per gram are 2.02 and 2.09 meq/mmol(P), respectively, reflecting two exchange sites per phosphorus atom. We take this as proof that the ionogenic groups in these resins are phosphoric-acid-monoester exchange sites:

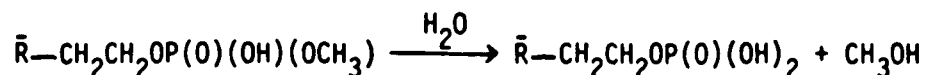


In the same regard, we would have expected that, for the methyl-PDE resins, Me-PDE-I and Me-PDE-II, the strong-acid capacities would approximately correspond to the total capacities, consistent with the presumed phosphate-diester structure of the exchange groups (i.e., one exchange site per phosphorus atom):



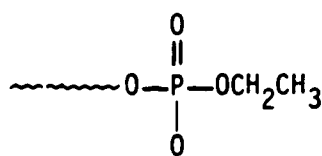
Indeed, this was not the case since the ratios of the total capacity/ millimoles of phosphorus per gram for resins Me-PDE-I and Me-PDE-II are 1.81 and 1.54 meq/mmol(P), respectively. The exchange sites in these methyl-diester resins exhibit some degree of polyfunctionality, and their structures are not in accordance with phosphoric-acid-diester groups. Since hydrolysis of phosphate esters is common [130,146], the

the methyl-alkyl portions of the phosphate diester apparently hydrolyzes to some extent:



The resulting materials are polyfunctional ion-exchange resins containing mixtures of monoester and diester groups. As such, resins Me-PDE-I and Me-PDE-II are unsuitable for study of the isolated phosphate-diester ion-exchange group. Further evidence for the conversion of the diester functions into monoester functions is presented under the discussion of the pH titration curves.

The hydrolytic instability of the methyl-PDE resins led to the development of the ethyl-PDE resins, Et-PDE-I and Et-PDE-II. The ethyl-alkyl group of the phosphate diester function was observed to form a stable linkage. From Table 5-1, the ratios of the total capacity to the millimoles of phosphorus/gram for resins Et-PDE-I and Et-PDE-II are 0.91 and 0.99 respectively. This information, along with the correspondence of the strong-acid capacities to the total capacities (Table 5-1), provides proof that the ethyl-PDE resins are essentially monofunctional, having one exchange site per phosphorus atom:



The ethyl group was found not to hydrolyze under any of the variety of experimental conditions to which the ethyl-PDE resins were subjected, the capacity remaining essentially constant throughout the treatments.

The production of resin Et-PDE-II from resin PME-I (see Chapter Three, p. 68), in which the dibasic phosphoric-acid-monoester groups were esterified into monobasic phosphoric-acid-diester groups, apparently followed an almost quantitative course, as the data of Table 5-1 infer. For resin PME-I, the total capacity equals 2.69 meq/g and there are 1.33 mmol (P)/g. Assuming that one hydrogen on each phosphorus function [total of 1.33 mmol (H)/g or 0.00133 g (H)/g] is changed to an ethyl group [total of 1.33 mmol (C₂H₅)/g or 0.03857 g (C₂H₅)/g] with a concomitant halving of the total capacity, then the capacity of the new resin would be (1.345 meq)/(1 - 0.00133 + 0.03857) g = 1.30 meq/g, and the phosphorus content would change to [1.33 mmol (P)]/(1 - 0.00133 + 0.03857) g = 1.28 mmol (P)/g. These values compare within experimental error with those actually measured for resin Et-PDE-II: 1.26 meq/g and 1.27 mmol (P)/g, respectively.

The functionality of the PME and ethyl-PDE resins was further confirmed in more direct experiments. Combustion of the sodium forms of resins PME-II, Et-PDE-I and Et-PDE-II in the Schöniger flask, followed by analysis of the resulting solutions for both sodium and phosphorus, yielded the following results. For resin PME-II, meq (Na)/mmol (P) = 2.04 (fully-loaded Na⁺-form) and 0.93 meq (Na)/mmol (P) (half-loaded Na⁺-form); for resin Et-PDE-I, meq (Na)/mmol (P) = 0.94; and for resin Et-PDE-II, meq (Na)/mmol (P) = 0.99. Simultaneous analysis for Ca²⁺ eluted from the same resins yielded these results: for resin PME-II, meq (Ca)/mmol (P) = 1.95; and for resin Et-PDE-II, 0.91 meq (Ca)/mmol (P). These results are consistent with the phosphate-monoester structure of resin PME-II and the phosphate-diester structure of resins Et-PDE-I and Et-PDE-II.

The capacities of the ion-exchangers for various counterions are presented in Table 5-2. The total capacity of four specified samples (column 2 of the Table) can be compared with the corresponding capacities for the Na^+ , K^+ , Mg^{2+} and Ca^{2+} ions. For resin Me-PDE-I, the Na^+ and Mg^{2+} capacities were obtained by exhaustively treating the H^+ -form with ca. 1 N aqueous solutions of the corresponding cation. The low Na^+ capacity (0.90 meq) relative to the total capacity of the sample (1.73 meq) indicates that only about one-half of the protons could be replaced by Na^+ ions from aqueous NaCl. This is due to the low acid strength of a portion of the exchange groups, which results in a preference of the resin for H^+ ions over Na^+ ions. In an analogous manner, the Mg^{2+} capacity was determined by displacement of resin protons by aqueous Mg^{2+} ions. The higher Mg^{2+} loading (1.40 meq) results from an increased preference by the resin for Mg^{2+} ions over Na^+ ions, although the overall preference is for H^+ ions (discussed under selectivity in section 5.5). For resin PME-I, the capacity of Na^+ ions at half conversion (i.e., the capacity of the strong-acid groups for Na^+ ions) is equal to that for K^+ ions. As with resin Me-PDE-I, excess aqueous Mg^{2+} ions could displace all strong-acid protons and only a portion of the weak-acid protons, the Mg^{2+} capacity of 1.52 meq falling between the total capacity (2.02 meq) and the strong-acid capacity (1.07 meq). The Ca^{2+} capacity, determined by treatment of the resin with excess $\text{Ca}(\text{NO}_3)_2$ and $\text{Ca}(\text{OH})_2$ (at high pH), is about the same as the total capacity. For resin PME-II, the Na^+ , K^+ and Ca^{2+} capacities reported in Table 5-2 were all determined by treatment of the resin at high pH followed by minimal washing. These capacities are essentially equivalent to each other. For resin Et-PDE-II, the capacity for the divalent ion is also equivalent to the monovalent-ion capacity. The

TABLE 5-2. CAPACITIES OF RESIN SAMPLES IN VARIOUS IONIC FORMS.^a

Resin	Total Capacity(meq) ^b	Na ⁺ Capacity(meq)	K ⁺ Capacity(meq)	Mg ²⁺ Capacity(meq) ^c	Ca ²⁺ Capacity(meq) ^d
Me-PDE-I	1.73 [±] .08	0.90 [±] .04 ^e	-	1.40 [±] .09	-
PME-I	2.02 [±] .08	1.07 [±] .04 ^f	1.06 [±] .04 ^f	1.52 [±] .09	2.13 [±] .05
PME-II	2.96 [±] .06	2.93 [±] .06 ^g	2.90 [±] .06 ^g	-	2.86 [±] .08
Et-PDE-II	1.13 [±] .05	1.13 [±] .05 ^g	-	-	1.08 [±] .06

^a For each resin, data based on an arbitrarily-weighed-out sample of the H⁺-form. Capacities are for that particular sample.

^b From treatment with excess NaOH followed by back titration or Na⁺ elution and measurement by flame photometry.

^c From treatment of the H⁺-form with excess Mg(NO₃)₂ followed by elution with HCl and EDTA titration.

^d From treatment of the H⁺-form with excess Ca(NO₃)₂/Ca(OH)₂ followed by elution with HCl and atomic absorption analysis for calcium.

^e From treatment of the H⁺-form with excess NaCl followed by titration of displaced protons.

^f From treatment of the H⁺-form with excess NaOH or KOH followed by exhaustive wash, elution with HCl, and sodium and potassium analysis by flame photometry.

^g From treatment of the H⁺-form with excess NaOH or KOH followed by minimal wash, elution with HCl, and sodium and potassium analysis by flame photometry.

conclusion from these data is that the PME and ethyl-PDE exchangers are homogeneous ion-exchange resins in which all of the phosphorus-bearing functional groups are available for exchange of counterions.

pH Titrations. The pH titration curves for the resins Me-PDE-I, Me-PDE-II, Me-PDE-III, PME-I, PME-II, Et-PDE-I and Et-PDE-II are presented as Figures 5-1 through 5-7 respectively. The first point of interest lies in the shapes of the curves for resins Me-PDE-I and Me-PDE-II (Figures 5-1 and 5-2). Both profiles display two breaks, occurring at ca. 1.4 meq/g and ca. 2.0 meq/g for Me-PDE-I and at ca. 1.1 meq/g and ca. 1.9 meq/g for Me-PDE-II. The two breaks in these curves correspond to two sets of acid groups in the resins, i.e., the presence of bifunctional ion-exchange groups. This is consistent with the capacity data (discussed above) for these two materials, further indicative of the hydrolysis of the methyl-alkyl portion of the diester phosphate to form monoester-phosphate groups. To check this hydrolysis, a fresh sample of the Me-PDE resin was prepared by reacting the 2-polystyrylethanol resin OH-D with monomethyl phosphate and TCAN, washing thoroughly with non-aqueous solvents (DMF and methanol), and conditioning only briefly with water, 0.01 M NaOH and 0.01 M HCl. The titration curve for this material, resin Me-PDE-III (air dried only), was immediately determined. Presented in Figure 5-3, this curve shows a distinct break at ca. 1.4 meq/g, and a gradually sloping increase in capacity with pH. Although not distinctly monofunctional, this freshly-prepared methyl-diester resin sample shows less bifunctional character than do resins Me-PDE-I and Me-PDE-II. The gradual slope at higher pH values may correspond to the slow hydrolysis of the methyl group or to the presence of weak-acid groups in the hydrolyzed material.

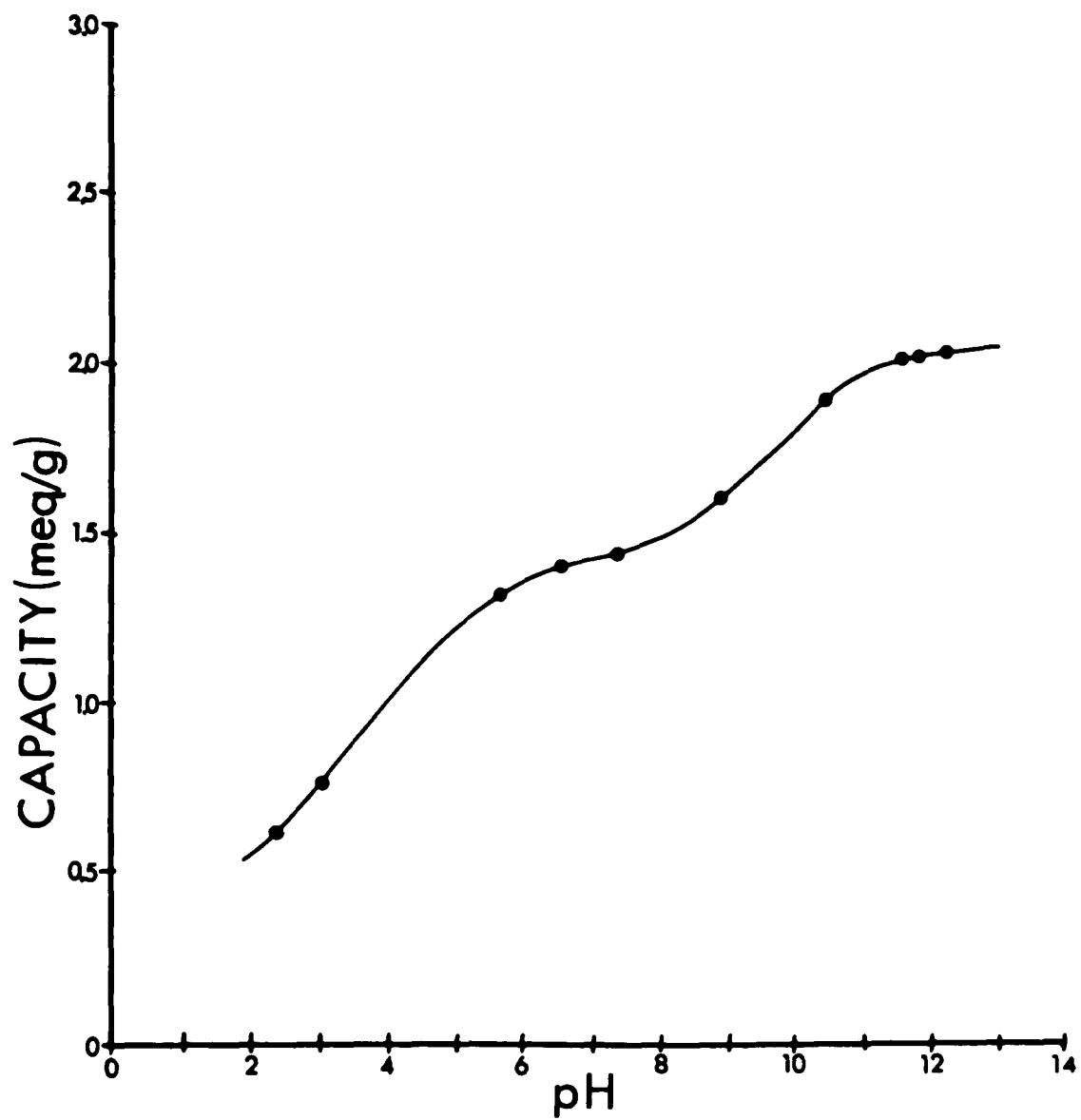


Figure 5-1
pH Titration Curve
RESIN Me-PDE-I
(0.5M NaCl)

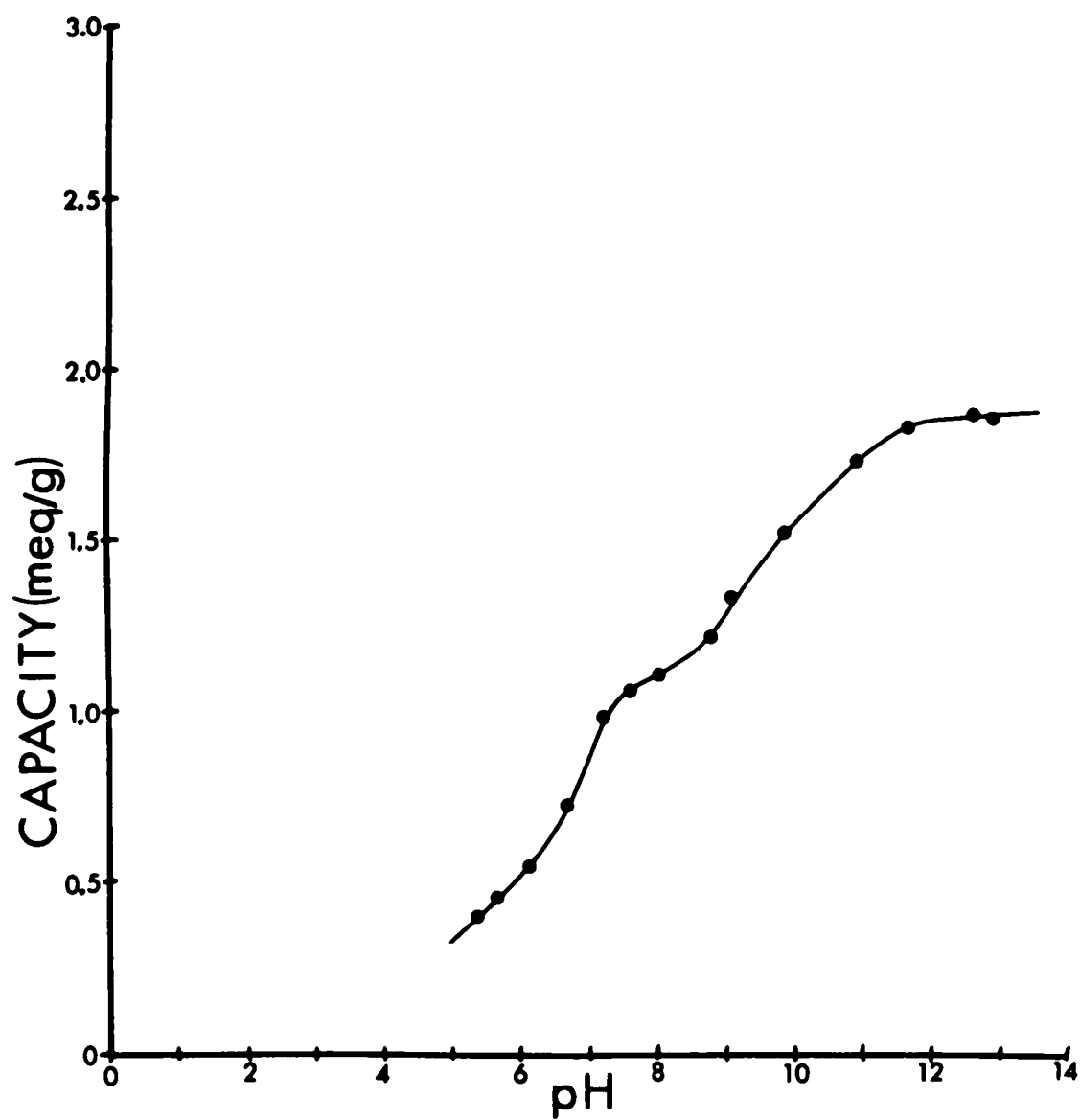


Figure 5-2
pH Titration Curve
RESIN Me-PDE-II
(no salt)

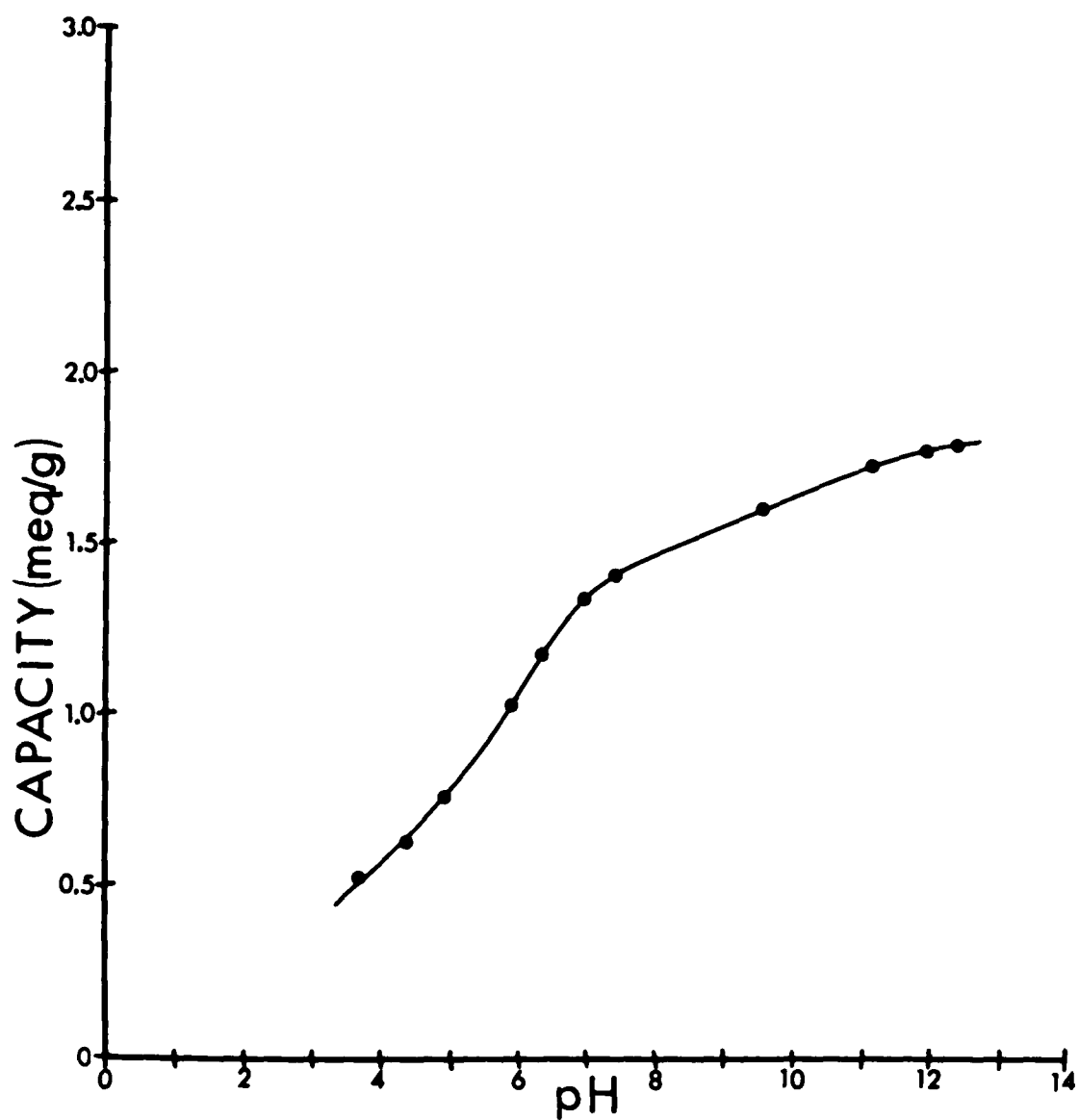


Figure 5-3
pH Titration Curve
RESIN Me-PDE-III
(no salt)

The curves for resins PME-I and PME-II (Figures 5-4 and 5-5, respectively) are characteristic of dibasic acids. For resin PME-I, the first break occurs at ca. 1.4-1.5 meq/g and the second break at ca. 2.8 meq/g, reflecting the presence of a distinct set of stronger-acid groups responsible for half the capacity below pH = 6 and a set of weaker-acid groups accounting for the other half of the capacity above pH = 6. For resin PME-II, the stronger-acid groups correspond to ca. 1.05 meq/g below pH = 6 and the weaker-acid groups contribute significantly to the capacity (another 1.05 meq/g) above pH = 6. These data are consistent with the capacity results discussed above and account for the hydrolysis of the Na^+ -loaded weaker-acid exchange sites upon treatment with aqueous NaCl (pH = 5.5) back to the H^+ -form. The relatively small slopes of these curves, especially for the second dissociations, in comparison to the slopes of the titration curves for strong-acid exchangers [1(p. 82)], are characteristic of weaker-acid ion-exchange groups. Similar curves have been reported for methacrylic-acid [140, 142,143] and phenolic [140] cation exchangers and for various phosphonic-acid resins [60,6,144,145] and phosphoric-acid exchangers, cellulose phosphate [82,85] and phosphorylated polyvinyl alcohol [86] in particular.

Comparison of the titration curves in Figures 5-4 and 5-5 with those for cellulose phosphate [82,85] and phosphorylated polyvinyl alcohol [86] point up the problem of polyfunctionality incorporated into exchangers prepared from phosphoryl chloride. The titration curves for these materials display breaks which do not correspond to the presence of simple dibasic monoester-phosphate groups, i.e., the breaks do not occur at half capacity. The authors of these reports attempted to

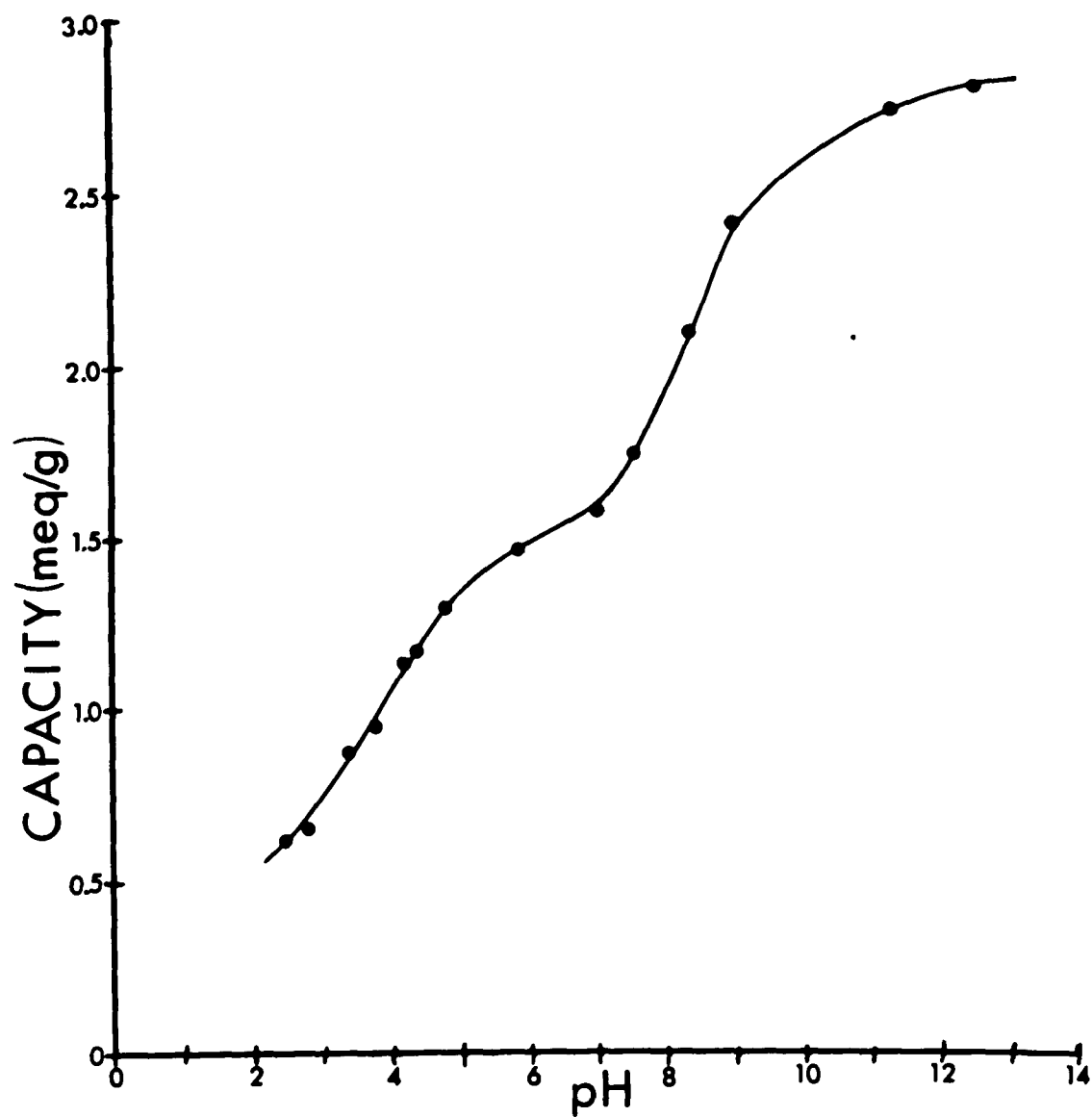


Figure 5-4
pH Titration Curve
RESIN PME-I
(0.1M NaCl)

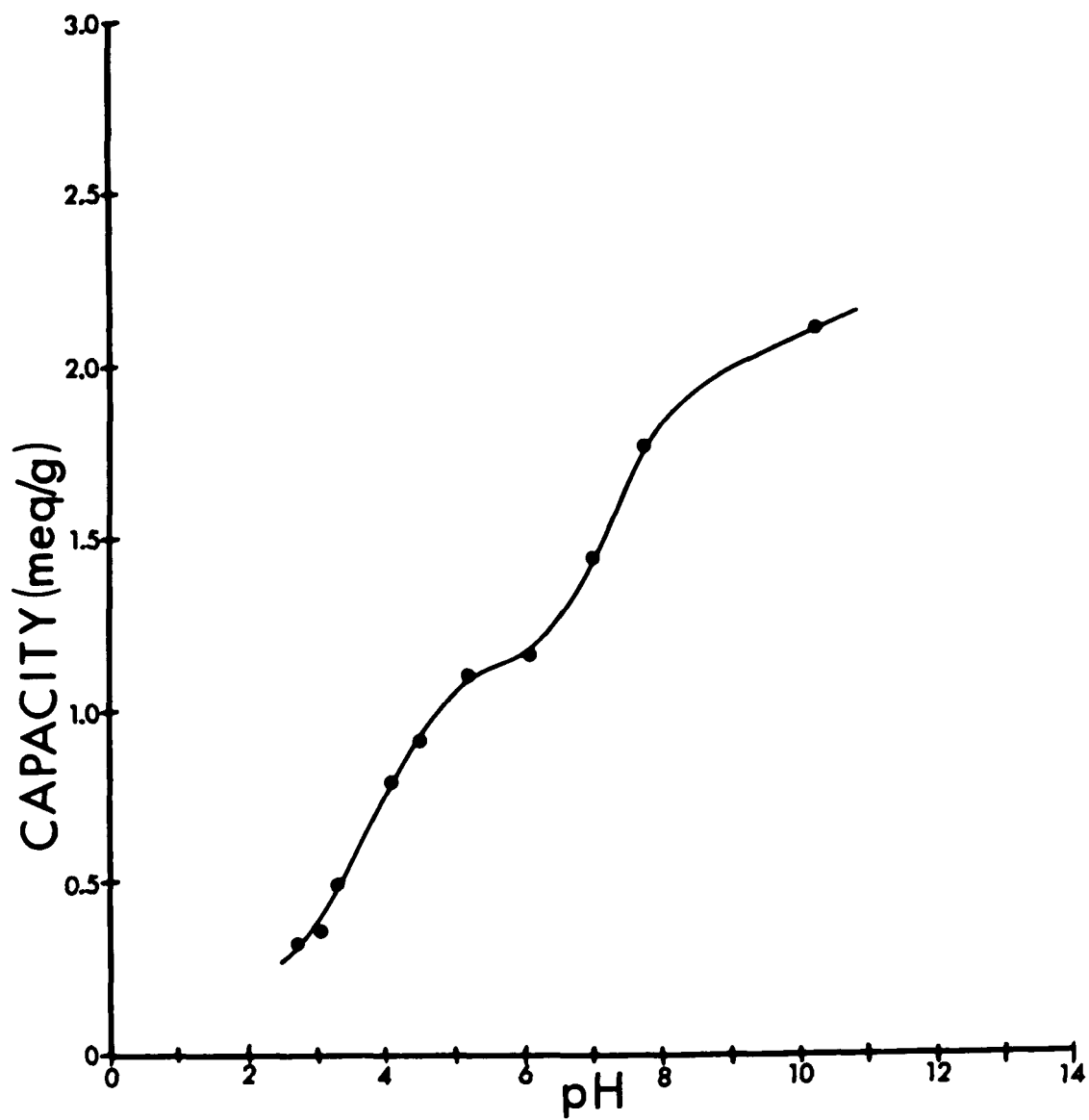


Figure 5-5
pH Titration Curve
RESIN PME-II
(0.1 M NaCl)

estimate the relative composition of the exchangers in terms of the quantity of phosphoric-acid-monoester, -diester and -triester groups. The much simpler titration curves for our resins indicate that the condensation phosphorylations applied to their syntheses resulted in monofunctional materials.

The titration curves for the ethyl-PDE resins Et-PDE-I and Et-PDE-II are shown in Figures 5-6 and 5-7, respectively. As expected, based on the capacity measurements, the curves for these resins are characteristic of monobasic weak acids, displaying only one break corresponding to the total capacity of the particular resin. For resin Et-PDE-I, this break occurs at ca. 1.05 meq/g, while it occurs at ca. 1.20 meq/g for resin Et-PDE-II. Again, we find the gradually-sloping behavior for these titration curves.

Helffferich [1(p. 85)] presents a method for approximating the pK values for the acid groups in cation exchangers. He claims this method to be more valid than application of the Henderson-Hasselbach equation to a resin system since, in the latter, the pH of the external solution is equated with the pH in the resin phase. These two pH's are quite different quantities considering the high molalities generally prevalent within the pores of an ion-exchanger bead. This problem is overcome by relating the hydrogen-ion concentration in the resin to the external pH by accounting for the internal resin concentrations. Helffferich's equation is:

$$pK = pH + \log [Na^+] - \log ([\bar{X}]/2), \quad (5.1)$$

in which the pK of the ionogenic groups is related to the external pH at half conversion (from the titration curve), the external Na^+ concen-

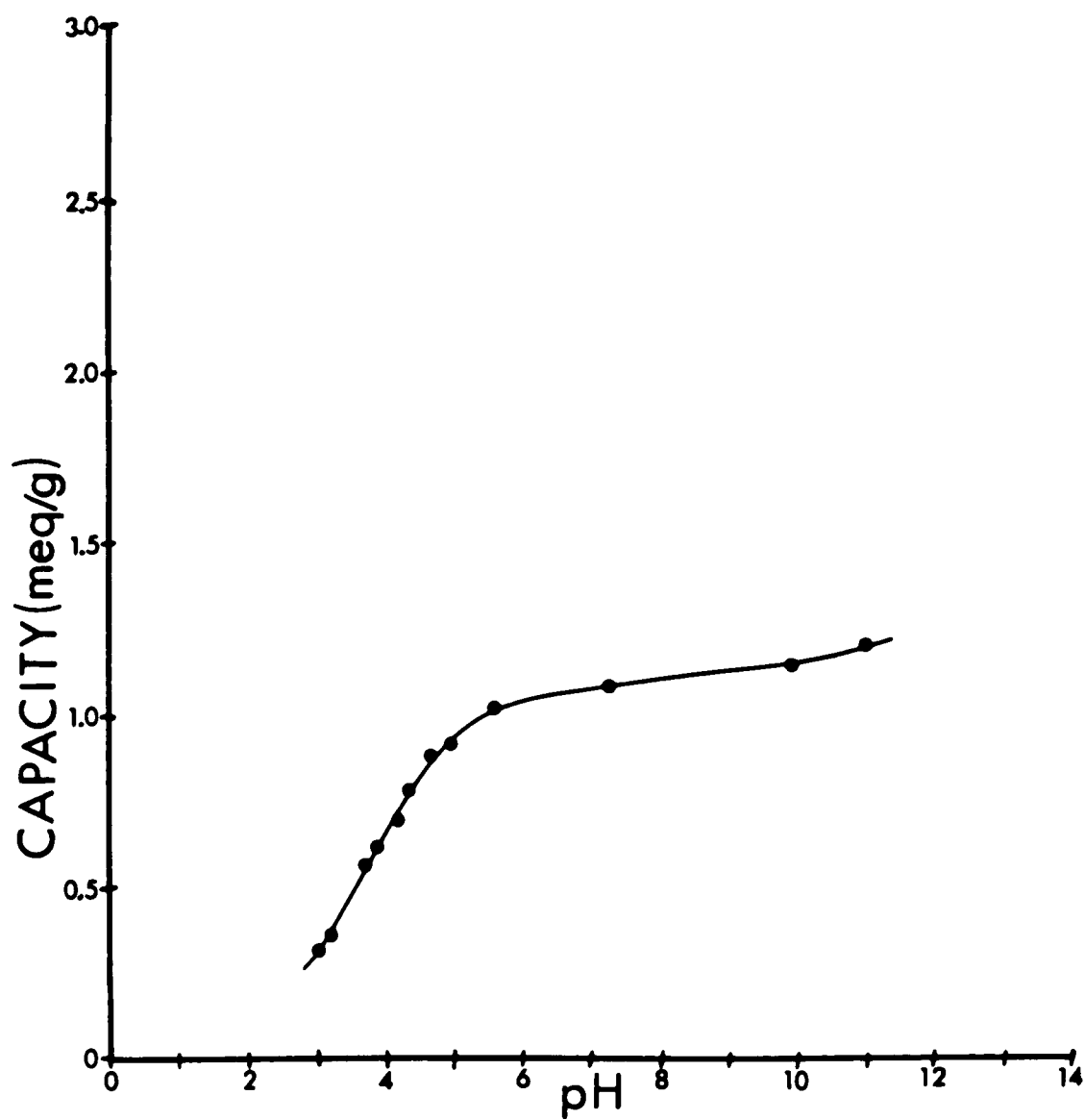


Figure 5-6
pH Titration Curve
RESIN Et-PDEI
(0.1M NaCl)

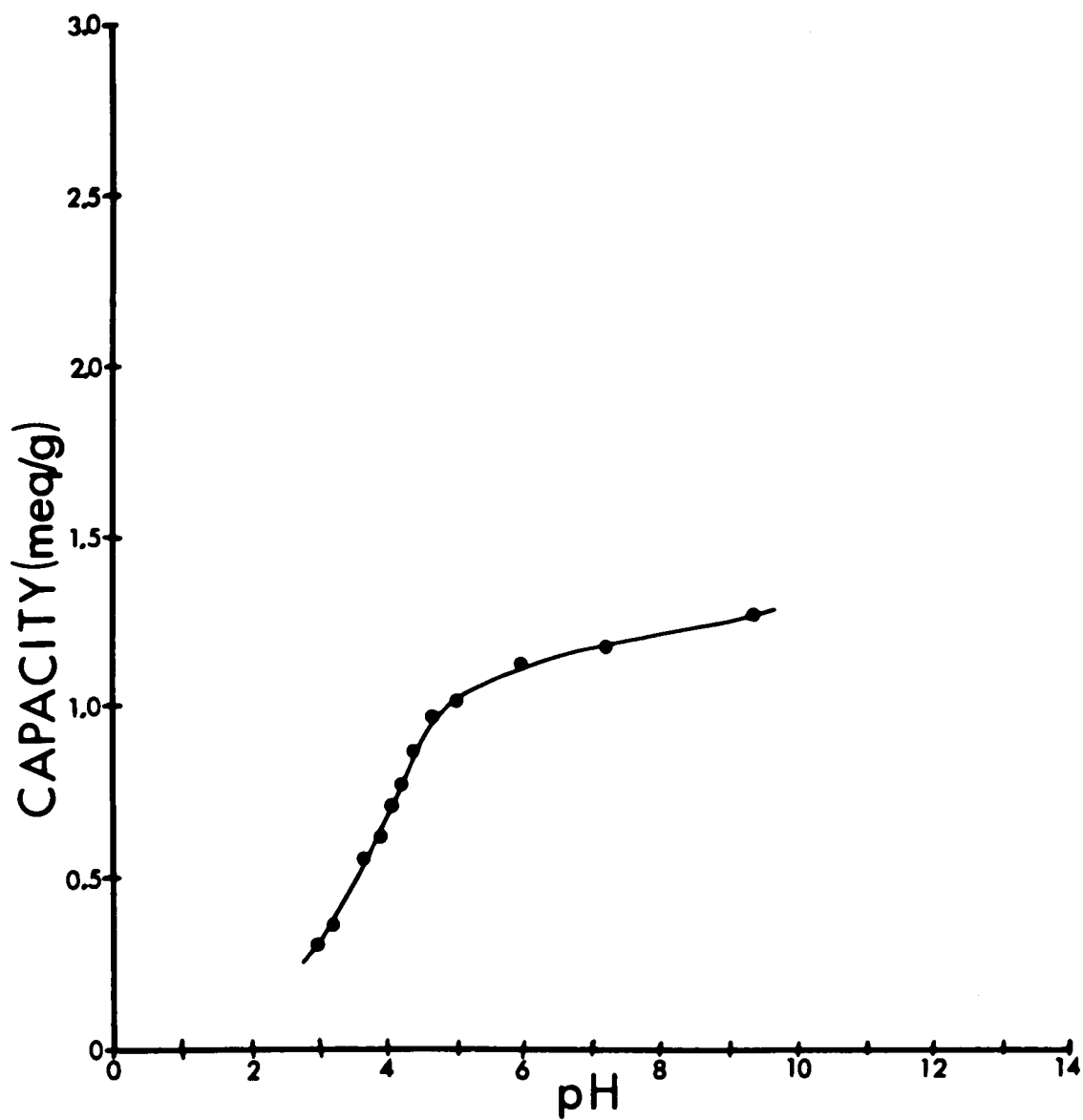


Figure 5-7
pH Titration Curve
RESIN Et-PDE-II
(0.1 M NaCl)

tration (essentially fixed for titration in 0.1 M NaCl), and the concentration of ionogenic groups at half conversion, $[\bar{X}]$. The latter is calculated from the independently-measured water content of the resin at half conversion. We applied this equation to one of the PME resins, PME-I, and to one of the ethyl-PDE resins, Et-PDE-II. Since resin PME-I contains 36.9% water at half conversion (section 5.4), we approximate the water content at half conversion (for the first dissociation, actually one-quarter total conversion of the resin) to be 27%. Thus $[\bar{X}] = (1.04 \text{ meq/g})(73 \text{ g resin}/27 \text{ g water}) = 4.05 \text{ molal}$. The pH at half conversion of the first set of acid groups is 3.20 (from Figure 5-4) and $[\text{Na}^+] = 0.1 \text{ M}$. So, $\text{pK}_1 = 3.20 + \log(0.1) - \log(4.05/2) = 1.9$. Similarly, for the second dissociation, approximating the water content at three-quarters total conversion to be 38.5% and reading pH = 8.50 from Figure 5-4, we obtain $\text{pK}_2 = 7.5$. For resin Et-PDE-II, the pH at half conversion is 3.80 (Figure 5-7) and the water content is ca. 25%, thus $\text{pK} = 2.5$.

These pK values are most reasonable. Generally, the acid strengths of groups incorporated into ion exchangers are lower than the acid strengths of corresponding monomers in solution [143]. Phenyl-phosphonic acids have $\text{pK}_1 = 1.1 - 2.1$ and $\text{pK}_2 = 6.2 - 7.6$ [147], while phosphonic-acid cation exchangers based on polystyrene/DVB have $\text{pK}_1 = 3.0 - 3.6$ and $\text{pK}_2 = 7.0 - 8.5$ [76,145], and phosphonic-acid exchangers based on α -pinene-furfural systems have $\text{pK}_1 = 2.3 - 2.6$ and $\text{pK}_2 = 7.6 - 8.7$ [144], consistent with the general principle. Monoesters of phosphoric acid have reported pK values in the ranges 1 - 2 for pK_1 and 6 - 7 for pK_2 [148,149]. Diesters of phosphoric acid have pK values around 1.5 [148]. The pK values measured for our resins therefore lie within reasonable ranges for phosphoric-acid-ester groups in resin

environments.

The gradually-sloping shapes of the titration curves imply that the ionogenic groups actually have a range of acid strengths, such that the capacities are a function of pH, especially for the weaker-acid groups. Therefore, the reported pK values for resins PME-I and Et-PDE-II should be taken as average values, representative of the overall behavior of the set of exchange groups to which they apply. This viewpoint is reinforced upon consideration of the elution profile for resin PME-II (Table 5-3). Obtained by treating the H^+ -form of the resin in a column with 1 M NaCl or 0.5 M $Mg(NO_3)_2$ and collecting and titrating the effluent in 50 mL fractions, the elution profile reveals that some of the stronger-acid groups cannot be ionized by salt solutions, unlike the case for the strong-acid sulfonic-acid exchangers. There is a gradual displacement of the weaker-acid protons as the half capacity is approached. The degree of displacement is a function of the selectivity of the resin for the cation with which it is treated. As the data in Table 5-3 show for the Mg^{2+} -treatment of the H^+ -form, a greater fraction of the strong-acid capacity is attained for a smaller volume of treatment solution, due to the stronger preference of the resin for Mg^{2+} over Na^+ . Similar results were obtained for the ethyl-PDE resins.

5.3 Stability of the Resins.

Several types of experiments were performed in order to establish the stabilities of the various cation exchangers. The stabilities of the PME and PDE resins in selected ionic forms under certain conditions were investigated. Specifically, the thermal stability of the dry H^+ -forms, and the chemical stabilities of the H^+ -, Na^+ - and Ca^{2+} -forms in various aqueous solutions and of the H^+ -, Na^+ - and mixed Mg^{2+}/Ca^{2+} -

TABLE 5-3. ELUTION PROFILE FOR RESIN PME-I.

<u>Volume(mL)^a</u>	<u>%H⁺ Displaced by 1M NaCl^b</u>	<u>%H⁺ Displaced by 0.5M Mg(NO₃)₂^b</u>
50	49	56
100	62	71
150	69	79
200	73	84
250	76	87
300	79	90
350	82	92
400	85	-
450	87	-
500	89	-

^a Volume of treatment solution collected as effluent.

^b Reported as cumulative percentage of total strong-acid capacity eluted in each fraction.

forms after several repeated exchange cycles were determined. The resin stabilities were monitored by measurement of the changes in ion-exchange capacity and phosphorus content brought about by the various treatments.

The thermal stabilities of various phosphonic-acid cation-exchange resins have been determined [150]. The resins were investigated for 80°-180°C for periods up to 20 days. Phosphorus losses of between 2% and 5% P were reported. Our resins were studied under milder conditions, approaching the conditions to which they were subjected in the various characterization experiments.

In order to determine the thermal stability of the H^+ -form resins, experiments were conducted in which a sample of resin PME-I and a sample of resin Me-PDE-I were dried and re-wetted in water, their capacities being measured after each of four such cycles. One set of H^+ -form samples was dried over P_2O_5 in a vacuum dessicator at 20°C for two days, while another set of samples was dried for one day in a vacuum oven at 65°C. The results are presented in Table 5-4. The data for the two drying methods are essentially equivalent, indicating that either drying procedure is safe for the H^+ -forms of the resins in that a significant reduction in capacity does not occur. This conclusion is of special importance since the dried H^+ -form resins are used extensively in the various resin-characterization experiments. In another test, two samples of resin Me-PDE-I in the H^+ -form were placed overnight in 50 mL of water, one sample having been dried over P_2O_5 at 20°C for 24 hours under vacuum and the other having been dried at 120°C for 24 hours in a vacuum oven. The supernate solutions were titrated with standard base, 0.05 meq (H^+)/g found for the P_2O_5 -dried

TABLE 5-4. THERMAL STABILITY.

<u>Capacities</u>	<u>Resin Me-PDE-I</u>	<u>Resin PME-I</u>
Oven Drying ^a	2.16, 2.17, 2.03, 2.07	2.04, 1.90, 1.84, 1.88
P ₂ O ₅ Drying ^a	2.20, 2.22, 2.15, 2.20	2.06, 2.07, 1.81, 1.90

^a Capacities reported (± 0.08 meq) as total milliequivalents of resin sample for each of four drying cycles.

sample and 0.29 meq (H^+)/g found for the oven-dried sample. Attributing the acidity developed to hydrolysis of the phosphate groups from the resin (as phosphoric acid), we conclude that there is significant decomposition at 120°C in the dry H^+ -form. Samples of resins PME-I and Et-PDE-I in the H^+ -form were kept in a vacuum oven at 60°C for five days, after which their phosphorus contents were measured and compared with those for similar samples dried over P_2O_5 at 20°C in vacuo. The phosphorus percentages found were (all $\pm 0.09\%$): for PME-I - 4.08% (20°C), 4.00% (60°C); and for Et-PDE-I - 3.42% (20°C), 3.37% (60°C). Again, these data indicate stability of the H^+ -form resins up to 60°C.

The hydrolysis of phosphoric-acid functions in the H^+ -, Na^+ - and Ca^{2+} ionic forms of resin Me-PDE-I in three aqueous solutions was ascertained by soaking the resin forms for 48 hours at 20°C in either 50 mL of water, 0.5 M HNO_3 or 0.5 M $NaNO_3$, followed by heating for two hours at 70°C. The phosphorus released into the supernate solutions was measured by boiling a 25 mL aliquot down to 5 mL with 5 mL of 5 M H_2SO_4 , adding 5 mL of H_2SO_4 , boiling for an additional 5 minutes, neutralizing with 19 N NaOH, and applying the molybdiphosphoric-acid analysis (see Appendix). The results are presented in Table 5-5. The H^+ -form seems to be the least stable in water, the Na^+ - and the Ca^{2+} -forms having greater and approximately equivalent stabilities. The data for all three experiments in 0.5 M HNO_3 are approximately the same, reflecting the conversion of the Na^+ - and Ca^{2+} -forms into the H^+ -form by the nitric acid. The hydrolysis in HNO_3 seems slightly repressed, while hydrolysis in a neutral-salt solution ($NaNO_3$) is the smallest. In a related experiment, the IR spectra of resins PME-II and Me-PDE-II were taken after treatment of separate samples of the H^+ -forms with 1 M

TABLE 5-5. STABILITIES IN AQUEOUS SOLUTIONS, RESIN Me-PDE-I.^a

<u>Ionic Form</u>	<u>In H₂O^b</u>	<u>In 0.5M HNO₃^b</u>	<u>In 0.5M NaNO₃^b</u>
H ⁺	4.1%	3.5%	0.9%
Na ⁺	1.2	3.1	0.6
Ca ²⁺	0.9	3.2	-

^a Reported as the percentage loss of phosphorus ($\pm 0.6\%$). Resin Me-PDE-I contains ca. 3.5% phosphorus.

^b Samples soaked in 50 mL of solution for 48 hours.

HCl and 1 M NaOH at 80°C for 6 hours. No significant changes in the spectra were noted, the intensity, position and shape of the oxyphosphorus bands remaining unaltered relative to the untreated samples. The small losses in phosphorus incurred under these conditions caused no observable spectral changes. A phosphorus loss of 4% (the maximum observed) corresponds to a capacity change of ca. 0.8%. Therefore, the maximum extent of alteration expected in the capacity properties of the resins in the various experiments in which the resins were equilibrated with salt solutions, e.g., in the selectivity-isotherm determinations (section 5.5), is expected to be less than 1%.

The loss of performance of the PME resin PME-II and the PDE resin Et-PDE-I was monitored as a function of the number of exchange cycles to which the resins were subjected. This property is significant, especially since the selectivity and capacity data were determined by repeatedly loading the resins with counterions. Samples of both resins, PME-II and Et-PDE-I, were subjected to five consecutive exchange cycles involving alternate treatments with 0.5 M NaOH/H₂O/0.5 M HCl. The capacities before the first treatment and after the last treatment were determined by neutralization of the H⁺-form with excess standard base followed by back-titration with standard acid (see p. 101). The results for the capacities before and after treatment were: for PME-II -- 2.30 vs. 2.27 meq/g, and for Et-PDE-I -- 1.00 vs. 0.97 meq/g. In a related experiment, a column of resin PME-II in the H⁺-form was loaded with Mg²⁺ and Ca²⁺ by treatment with an aqueous Mg(NO₃)₂/Ca(NO₃)₂ solution, followed by washing and elution of the counterions with 1 M HCl. The Mg²⁺ and Ca²⁺ in the eluate were determined by atomic absorption. The same column was then treated with another Mg²⁺/Ca²⁺ solution, and following

the same procedure, the total capacity for Mg^{2+} and Ca^{2+} was again measured. The process was repeated a total of five times, with the following results for the total loading of Mg^{2+} and Ca^{2+} on the PME-II sample: 3.35, 3.36, 3.28, 3.29 and 3.30 meq. The data from these two sets of experiments indicate that the resins are quite stable to repeated exchange cycles with aqueous solutions up to 1 M at room temperature.

In conclusion, the phosphoric-acid-monoester and phosphoric-acid-diester cation exchangers which we have prepared are reasonably stable materials and are not significantly altered under the experimental conditions to which they are subjected in the course of the various physicochemical characterizations.

5.4 Water Contents of the Resins.

The water content is another of the fundamental properties of an ion-exchange resin. The uptake of water by a particular exchanger is a complex function of several variables, including the ionic form, the type of functional group, the capacity, the chemical composition of the polymer matrix and the physical structure of the resin matrix (which involves the pore size, crosslinking and resin homogeneity)[1(Ch. 5)]. The water contents for PME resin PME-II and PDE resin Et-PDE-II have been determined in several ionic forms.

5.4.1 Experimental Methods.

Solvent uptake in ion-exchange resins may be found gravimetrically [132], by analysis for water by the Karl-Fischer titration [151], or from volume measurements on particles of ion exchanger using a micro-comparator [152] or a pycnometer [133]. The gravimetric method,

consisting of weighing a resin sample in the hydrated state and in the dry state, has been applied to the PME and PDE resins.

In the gravimetric method, the exchanger is equilibrated in a particular ionic form with solvent. The resin is then separated from the "external" solvent, weighed, completely dehydrated, and reweighed. The separation of the swollen exchanger from the solvent is the critical point in this procedure; the external water must be removed without the removal of the "internal" or hydration water. Among the methods employed are air drying, air suction [152] and centrifugation [132]. For the PME and PDE resins, the centrifugation technique has been applied as follows. From 0.5 to 1.0 gram of resin in a particular ionic form is equilibrated with water for at least one hour. The resin/water slurry is then transferred to a small tube fitted with a sintered-glass frit, which is placed inside a 15 mL centrifuge tube. The apparatus is sealed with Parafilm^R to prevent any excess drying of the sample due to evaporation. A small hole in the inner tube provides for pressure equalization in the system. The wet resin is spun in a centrifuge at high speed for 20 minutes. After this period, the resin beads are quickly transferred to a tared vial, weighed, and placed in a vacuum oven at 70°C for 48 hours. The dry resin is then weighed and the water content calculated from the weight loss.

Three sets of water-content determinations were performed on several ionic forms of resins PME-II and Et-PDE-II. For resin PME-II, the water contents of the H^+ -, Na^+ -, K^+ -, Mg^{2+} -, Ca^{2+} -, NH_4^+ -, Cu^{2+} -, La^{3+} -, Na^+/H^+ - and K^+/H^+ -forms were measured; for resin Et-PDE-II, the H^+ -, Na^+ -, K^+ -, Mg^{2+} -, Ca^{2+} - and La^{3+} -forms were characterized. Samples from the first set of determinations were reequilibrated with

water and reused in the second determinations to provide further evidence for the stability of the resins. The third set of determinations were carried out on fresh resin samples.

5.4.2 Results and Discussion.

Table 5-6 lists the results of the three sets of water-content determinations on resins PME-II and Et-PDE-II.

The essentially equivalent water contents obtained by repeating the measurements on the same samples of the various ionic forms of both resins provide further confirmation of the stability of these materials. The significantly lower value obtained in the second measurement on the NH_4^+ -form of resin PME-II is not indicative of capacity loss, but is the result of conversion of the NH_4^+ -form to the H^+ -form in the heated dry state. The first determination of the water content of the NH_4^+ -form correlates with those of the alkali cations, as would be expected. In the second determination, the water content of the NH_4^+ -form correlates more with that of the H^+ -form. Our infrared-spectral measurements further confirm this conversion (section 6.1). The behavior of the NH_4^+ -form of carboxylic-acid exchangers is similar [153].

The water contents of the various ionic forms follow the general pattern which would be expected on the basis of the selectivity data reported in section 5.5. The alkali-ion- and NH_4^+ -forms have the highest water contents and the lowest selectivities, implying simple electrostatic interactions with the phosphate functional groups. The relatively low water contents of the Mg^{2+} -, Ca^{2+} -, Cu^{2+} - and La^{3+} -forms provide indirect evidence for more complex interactions of the divalent counterions. Complexation, ion-pair formation or other such special interactions occur with the exclusion of hydration water. The water

TABLE 5-6. WATER CONTENTS OF RESINS PME-II AND Et-PDE-II.

Resin	Ionic Form	Percent Water			
		Sample 1	Sample 1(repeat) ^a	Sample 2	Mean ^b
PME-II	H ⁺	22.3	21.9	22.6	22.3 ^{±.4}
	Na ⁺	39.3	38.8	39.4	39.2 ^{±.3}
	K ⁺	40.5	39.8	40.3	39.7 ^{±.6}
	NH ₄ ⁺	39.7	26.3	38.3	39.0 ^{±1.0} ^c
	Mg ²⁺	32.3	32.0	32.0	32.1 ^{±.2}
	Ca ²⁺	25.4	24.5	24.8	24.9 ^{±.4}
	Cu ²⁺	24.8	24.3	24.5	24.6 ^{±.3}
	La ³⁺	22.0	22.6	22.9	22.5 ^{±.4}
	Na ⁺ /H ⁺ ^d	36.9	-	36.5	36.7 ^{±.3}
	K ⁺ /H ⁺ ^d	36.0	-	35.5	35.8 ^{±.4}
Et-PDE-II	H ⁺	17.9	17.9	17.8	17.9 ^{±.1}
	Na ⁺	29.2	28.4	28.7	28.8 ^{±.4}
	K ⁺	29.7	28.9	29.9	29.8 ^{±.5}
	Mg ²⁺	19.9	19.5	19.4	19.6 ^{±.2}
	Ca ²⁺	19.0	18.9	19.1	19.0 ^{±.1}
	La ³⁺	17.3	17.0	17.4	17.2 ^{±.2}

^a Sample from first determination re-equilibrated and re-measured.

^b Mean of three determinations [±] standard deviation.

^c Mean of first and third determination.

^d Half-converted forms.

contents for the H^+ - and La^{3+} -forms are the lowest for both resins, consistent with the high selectivities shown for the proton and polyvalent counterions.

The half-converted Na^+ - and K^+ - forms of resin PME-II (i.e., the mixed Na^+/H^+ - and K^+/H^+ -forms, prepared by exhaustively washing the fully-loaded Na^+ - and K^+ - forms) have water contents only ca. 10% lower than the respective fully-converted alkali forms. If all alkali counterions in the PME resin were bound in an equivalent manner, an approximately 30% reduction in the water contents would be expected upon replacing one-half of the alkali counterions with protons (based on the measured water content for the H^+ -form). The hydration of the PME resin is apparently determined mostly by the electrostatic interactions of the counterions with the strong-acid exchange sites. Interactions with the weak-acid exchange sites must be to some extent of a covalent or associative nature, such that the interactions of the alkali counterions with the weak-acid sites contribute only about 10% to the total water content.

The model of the PME and PDE resins suggested by the results of the capacity, pH-titration and water content data can be further elucidated by examining this water-content data more closely. From the capacity and water content of a particular resin form, the cationic hydration number, i.e., the average number of water molecules per equivalent of counterion in the resin, may be calculated using the following formula:

$$h^{\#}(M^+) = \frac{1000 w}{18c(T - w)} \quad (5.2)$$

where c = the capacity of the M^+ -form (meq/g), w = the water content of the M^+ -form/100 and $h\#(M^+) =$ the hydration number of counterion M^+ (mole H_2O /equivalent (M^+) = " H_2O/M^+ "). In Table 5-7 are listed the hydration numbers calculated for the Na^+ -, K^+ - and H^+ -forms of resins PME-II and Et-PDE-II.

According to our model, the PME resin consists of a set of "strong-acid" sites and a set of "weak-acid" sites, each contributing 50% to the total capacity. The exchange sites in the PDE resin are assumed to be approximately equivalent to the strong-acid sites of the PME resin, although actual equivalence is limited to the extent that the pK values for the two sets of exchange sites differ (pK_1 of PME resin = 1.9 and pK of Et-PDE resin = 2.5, section 5.2.3). The water content data for the mixed Na^+/H^+ - and K^+/H^+ -forms of resin PME-II provide an opportunity to check this model. From the data of Table 5-7, the water contents of these mixed forms can be predicted, and then compared to the measured values as follows.

The value ($= 7$) for the $h\#(H^+)$ for resin PME-II is actually an average of the hydration numbers for the strong-acid and weak-acid protons, according to the model. Assuming that the Et-PDE-II-resin protons [$h\#(H^+) = 10$] are equivalent to the strong-acid protons of resin PME-II, the hydration of the weak-acid protons (x) is obtained from $(x + 10)/2 = 7$, $x = 4 H_2O/H^+$. Further, assume that the Na^+ counterions of the Na^+ -form of resin Et-PDE-II [$h\#(Na^+) = 18$] are equivalent to the Na^+ counterions bound to the strong-acid sites in resin PME-II. The water content of the mixed Na^+/H^+ -form of resin PME-II, in which the Na^+ ions are assumed to occupy the strong-acid sites while the protons occupy the weak-acid sites, is found by applying these hydration numbers

TABLE 5-7. HYDRATION NUMBERS.

<u>Resin</u>	<u>Ionic Form</u>	<u>Capacity(meq/g)^a</u>	<u>h#^b</u>
PME-II	H ⁺	2.30	7
	Na ⁺	2.19	16
	K ⁺	2.12	17
Et-PDE-II	H ⁺	1.26	10
	Na ⁺	1.23	18
	K ⁺	1.20	19

^a For alkali forms, capacities based on the H⁺-form capacities (Table 5-1) with adjustments for the equivalent weights. For example, the capacity of the Na⁺-form of resin PME-II = (2.30 meq)/(1 - .0023 + .0529)g = 2.19 meq/g.

^b h# = hydration number, the number of water molecules per counterion. Calculated from equation 5.2 (moles H₂O/equivalent (M⁺)).

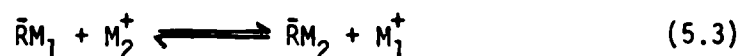
to the dry-state capacity of the mixed-ionic form. The latter is found as: capacity (Na^+/H^+) = $(2.19 \text{ meq}) / (1 + .001095 - .02519) \text{ g} = 2.24 \text{ meq/g}$. Since one gram of the dry resin contains 1.12 meq each of Na^+ and H^+ , and since hydration results in the sorption of 18 mmols $\text{H}_2\text{O}/\text{meq Na}^+$ and 4 mmols $\text{H}_2\text{O}/\text{meq H}^+$, then the one gram of dry resin picks up $(1.12)(22)(18) = 444 \text{ mg}$ of water, to give a water content of $(.444/1.444)(100) = 30.7\%$. This value is within 15% of the measured value (36.7%). Similarly, for the mixed K^+/H^+ -form of resin PME-II (dry-state capacity = 2.20 meq/g), we calculate 31.9% for the water content, which compares within 11% to the measured value (35.8%).

The discrepancies may arise from several factors, among which are: (1) the resins PME-II and Et-PDE-II were derived from different matrix backbones (see Chapter Three), (2) all protons in the mixed resin forms may not necessarily occupy weak-acid sites, and (3) the strong-acid and weak-acid sites may not be equally distributed. These results further confirm that our model provides a reasonable representation of the phosphoric-acid-ester exchangers.

5.5 Equilibrium Selectivity of the Resins.

5.5.1 General Considerations.

When a cation-exchange resin in a particular ionic form, $\bar{\text{R}}\text{M}_1$ (where $\bar{\text{R}}$ represents the insoluble resin matrix containing the anionic ionogenic groups), is placed in an aqueous solution of a different cation, M_2^+ , the M_1^+ ions will be exchanged for M_2^+ ions until an equilibrium state is achieved according to:



This process is reversible, so that the same equilibrium state will be obtained when the resin is originally in the $\bar{R}M_2$ form and the exchanging cation is M_1^+ , provided the total quantities of $\bar{R}$, M_1^+ and M_2^+ are fixed. In most cases, the resin exhibits a measurable preference or selectivity for one of the cations. Thus, the ratio of the cation concentrations on the resin will differ from the ratio of the cation concentrations in the external solution. This fundamental property of ion-exchange resins is taken advantage of in ion-exchange chromatography.

The ion-exchange equilibrium is most generally described by application of the mass-action law for the exchange reaction of equation (5.3) [154,155]. The molal selectivity coefficient is defined according to:

$$K_{M_1}^{M_2} = \frac{\bar{M}_2 \cdot M_1}{\bar{M}_1 \cdot M_2} \quad (5.4)$$

in which $\bar{M}_1$ and $\bar{M}_2$ are the molalities of the univalent cations M_1^+ and M_2^+ in the resin, and M_1 and M_2 are the respective molalities in the external solution. Equivalent fractions may also be used to define the selectivity coefficient. A rigorous thermodynamic definition of an equilibrium constant requires inclusion of activity corrections for the cations in the resin and solution phases [1(p. 1550)]. Practical limitations related to the estimation of activity coefficients for ions in solution and especially for ions associated with a resin phase dictate the routine use of the molal selectivity coefficient in presenting ion-exchange equilibrium data [155,156]. As such, the selectivity coefficient expresses in conveniently-measured terms the relative preference of a resin for one

counterion over another.

Selectivity coefficients are not constants, but are dependent on the specific experimental conditions under which they are measured. In particular, the value of the selectivity coefficient is a function of the total stoichiometric concentration of the exchangeable counterions and the capacity of the resin sample, as well as the temperature, resin structure and type of fixed ionic group on the resin [157].

Ion-exchange equilibria data are presented in the form of an ion-exchange isotherm, which is a plot showing the ionic composition of the resin versus the concentration of one of the counterions over a range of experimental conditions. From each point on the isotherm, the value of the selectivity coefficient, K , can be calculated. The data may be presented in an alternative manner, where the logarithm of the selectivity coefficient ($\log K$) is plotted as a function of the relative concentration of one of the counterions ($\bar{X}$). Several examples of such equilibrium data will be shown in section 5.5.3. The so-called integrated selectivity coefficient can be obtained by evaluation of the area under the $\log K$ vs. $\bar{X}$ plot. This "overall" selectivity coefficient is useful for comparing the equilibrium properties of different pairs of counterions on various exchangers.

5.5.2 Experimental Methods.

Determination of each point on an isotherm requires equilibration followed by quantitative analysis. The general experimental procedure for the determination of the ion-exchange isotherms and selectivity coefficients consists of equilibrating a quantity of resin in one ionic form with solutions containing various concentrations of another counterion. The solutions and resin are then analyzed for cation content

using any of a variety of analytical methods, such as titration, colorimetric analysis, atomic absorption and radio-tracer techniques.

We have applied two techniques to measure the exchange isotherms for the phosphoric-acid-ester resins. The progressive batch technique of Cosgrove and Strickland [157] provides a convenient and rapid means of obtaining the exchange isotherm. In this method, one sample of resin in a particular ionic form (say, the M_1^+ -form) is equilibrated with a succession of solutions containing the M_2^+ ion. A portion of each solution is drawn off and subjected to quantitative analysis for M_1^+ , from which the solution composition and, by material balance as described below, the resin composition can be calculated.

Specifically, to a quantity of resin with a known total capacity, c , the M_1^+ -form, Y mL of an M_2^+ -solution (of concentration m in meq/mL) diluted to 125 mL are added. After an appropriate equilibration period at 25°C, a fraction f of the solution is removed and analyzed for the number of milliequivalents, q_1 , of ion M_1^+ . To the remaining solution/resin mixture, $b \cdot Y$ mL of the M_2^+ solution are added, b representing a volume factor greater than one such that the fraction of M_2^+ present in each solution is progressively increasing. Again, after equilibration, a fraction, f , of solution is withdrawn and the milliequivalents, q_2 , of M_1^+ are measured. A total of n such experiments are conducted, where $b^{n-1} \cdot Y$ mL of the M_2^+ solution are added and q_n milliequivalents of M_1^+ are found in the fraction (f) withdrawn at the n -th step. Cosgrove and Strickland derive the following equations for calculation of the resin and solution compositions at any point in the determination:

$$\bar{X}_{M_2^+}(n) = \frac{f \left(\sum_{i=1}^{i=n-1} q_i \right) + q_n}{f \cdot c} \quad (5.5)$$

$$x_{M_2^+}(n) = 1 - \frac{t_n \cdot q_n}{m \cdot Y} \quad (5.6)$$

$$t_n = \frac{(1 - f - b)}{f[(1-f)^n - b^n]} \quad (5.7)$$

In these equations, $\bar{x}_{M_2^+}(n)$ and $x_{M_2^+}(n)$ are the equivalent fractions of M_2^+ on the resin and in the solution in the n -th experiment, respectively, f is the fraction of solution withdrawn (a constant), q_n is the milliequivalents of M_1^+ found in that fraction, c is the total capacity (in meq) of the resin sample, b is the volume factor (a constant), Y is the initial volume of the M_2^+ solution added in the first experiment and m is the normality of the M_2^+ solution. The selectivity coefficient (in terms of equivalent fractions) for each point in the determination is calculated by substituting equations (5.5) and (5.6) into equation (5.4) (using $\bar{x}_{M_1} = 1 - \bar{x}_{M_2}$ and $x_{M_1} = 1 - x_{M_2}$):

$$K_{M_1}^{M_2} = \frac{\bar{x}_{M_2} \cdot x_{M_1}}{\bar{x}_{M_1} \cdot x_{M_2}} \quad (5.8)$$

For the actual determinations on the PME and PDE resins, samples of resins corresponding to a total capacity of 4-12 meq were placed in

a 250 mL Erlenmeyer flask. The choice of the parameters b and Y depended on the capacity of the resin sample and the expected selectivity coefficient for the particular cation system, and were chosen so that 6-9 points spanning the resin-fraction range 0.1-0.9 could be found. For typical isotherms, b was 1.25, Y was 3-7 mL and the total volume was 125 mL. The concentration of the solution containing the exchanging cation (M_2^+) was standardized in the range 0.25-0.40 N, in order that the ionic strength in all systems be kept below 0.03 N. Lower ionic strengths result in reduced Donnan uptake, a factor not accounted for in this technique. A fraction $f = 0.8$ (100 mL) was withdrawn through a pipet. The method of quantitative analysis varied according to the particular cation. Titration was used for H^+ , flame photometry for Na^+ and K^+ , and atomic absorption for Mg^{2+} , Ca^{2+} and Cu^{2+} . Equilibration times ranging from 4 to 12 hours were found to yield no significant differences in the resulting isotherms. The temperature during equilibration was 20-25°C, and temperature variations within this range were not found to affect the isotherms. The capacity of the resin was measured for each individual sample by transferring the sample to a column and eluting the column with 1 M HCl. Displaced counterion was collected in a volumetric flask and the eluate was analyzed for the content of M_1^+ ion, q_e (meq), and the total sample capacity was found using:

$$c = \sum_{i=1}^n q_n + q_e \quad (5.9)$$

To check the validity of the progressive batch technique, an alternative method for the determination of the exchange isotherm was applied to a few of the systems. This second method is more rigorous, though more tedious in terms of experimental procedures. In this "column method," the resin sample is equilibrated by column treatment with solutions of known composition. For each point on an isotherm, the solution and the resin compositions for both cations are independently determined. An amount of resin in the H^+ -, M_1^+ - or M_2^+ -form is placed in a column. Three liters of a solution containing M_1^+ and M_2^+ in a known composition (total ionic strength = 0.05 N) are slowly passed through the resin. A brief washing follows, which elutes electrolyte in the resin voids but avoids any changes in composition due to hydrolysis effects. Then, the counterions are eluted from the resin with 250-500 mL of 1 M HCl into a volumetric flask. The composition of the eluate is then measured. One point on the isotherm is found with equation (5.8). The process is repeated with a new solution composition, four points being determined for each of our systems checked by this method.

5.5.3 Equilibrium Isotherms and Selectivities of the Resins.

5.5.3.1 The Data.

In order to obtain an overview of the ion-exchange equilibrium characteristics of the phosphate exchangers, equilibrium isotherms were determined for a number of systems on the PME and Et-PDE resins. For the PME resin, isotherms for the cation systems (presented as M_2/M_1) Li^+/Na^+ , K^+/Na^+ , Rb^+/Na^+ , H^+/Na^+ , Mg^{2+}/Na^+ , Ca^{2+}/Mg^{2+} , Cu^{2+}/Ca^{2+} , H^+/Cu^{2+} and Cr^{3+}/Ca^{2+} were measured; for the Et-PDE resin, the cation systems K^+/Na^+ , Mg^{2+}/Na^+ and Ca^{2+}/Mg^{2+} were measured.

The K^+/Na^+ isotherms for resin PME-I, measured at $pH \approx 5.5$ and $pH \approx 12$, are presented in Figure 5-8. For resin PME-II, the K^+/Na^+ , Mg^{2+}/Na^+ and Ca^{2+}/Mg^{2+} isotherms are shown in Figure 5-9; the Rb^+/Na^+ , H^+/Na^+ and H^+/Cu^{2+} isotherms, in Figure 5-10; and the Li^+/Na^+ , Ca^{2+}/Cu^{2+} and Cr^{3+}/Ca^{2+} isotherms, in Figure 5-11. For resin Et-PDE-I, the K^+/Na^+ , Mg^{2+}/Na^+ and Ca^{2+}/Mg^{2+} systems are presented in Figure 5-12. The cation systems K^+/Na^+ and Ca^{2+}/Mg^{2+} for resin Et-PDE-II are presented in Figure 5-13. The isotherms in Figure 5-13 can be used to illustrate how such plots are interpreted. In the upper isotherm (the Ca^{2+}/Mg^{2+} system), the resin is more selective for Ca^{2+} , the equivalent fraction in the resin phase ($\bar{x}_{M_2}$) being greater than that in the aqueous phase (x_{M_2}) over the full range of conditions. In the lower isotherm (the K^+/Na^+ system), the resin is more selective for Na^+ since the fraction of K^+ in the solution (x_{M_2}) is greater than that in the resin phase ($\bar{x}_{M_2}$) over the full range of conditions.

The majority of these isotherms were determined by the progressive batch method. Two isotherms (K^+/Na^+ for resins PME-I and Et-PDE-I) were determined in both the forward and reverse directions, and, as Figures 5-8 and 5-12 indicate, excellent reproducibility was obtained. For resin PME-II, the Mg^{2+}/Na^+ and Ca^{2+}/Cu^{2+} systems were measured by the batch method and a few points were checked by the column method. Again, agreement of the results from the two techniques was highly satisfactory. The Ca^{2+}/Mg^{2+} isotherms for resins PME-II, Et-PDE-I, and Et-PDE-II and the Ca^{2+}/Cu^{2+} and Cr^{3+}/Ca^{2+} isotherms for resin PME-II were also measured using the column method. The latter isotherm is less accurate because of the difficulty in eluting Cr^{3+} ion from the resin.

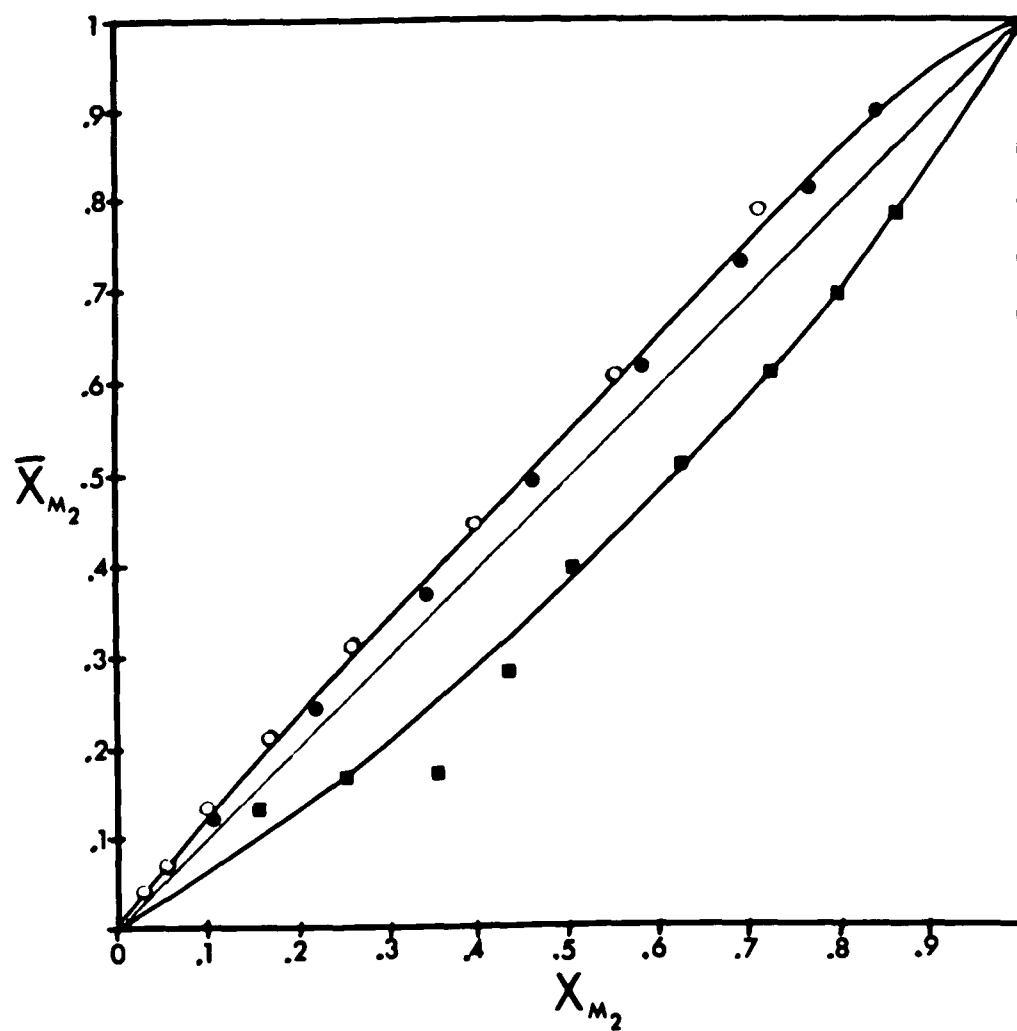


Figure 5-8

Equilibrium Isotherms

 $(M_2/M_1, 25^\circ\text{C})$

RESIN PME-I

- K^+/Na^+ , low pH (forward)
- K^+/Na^+ , low pH (reverse)
- K^+/Na^+ , high pH

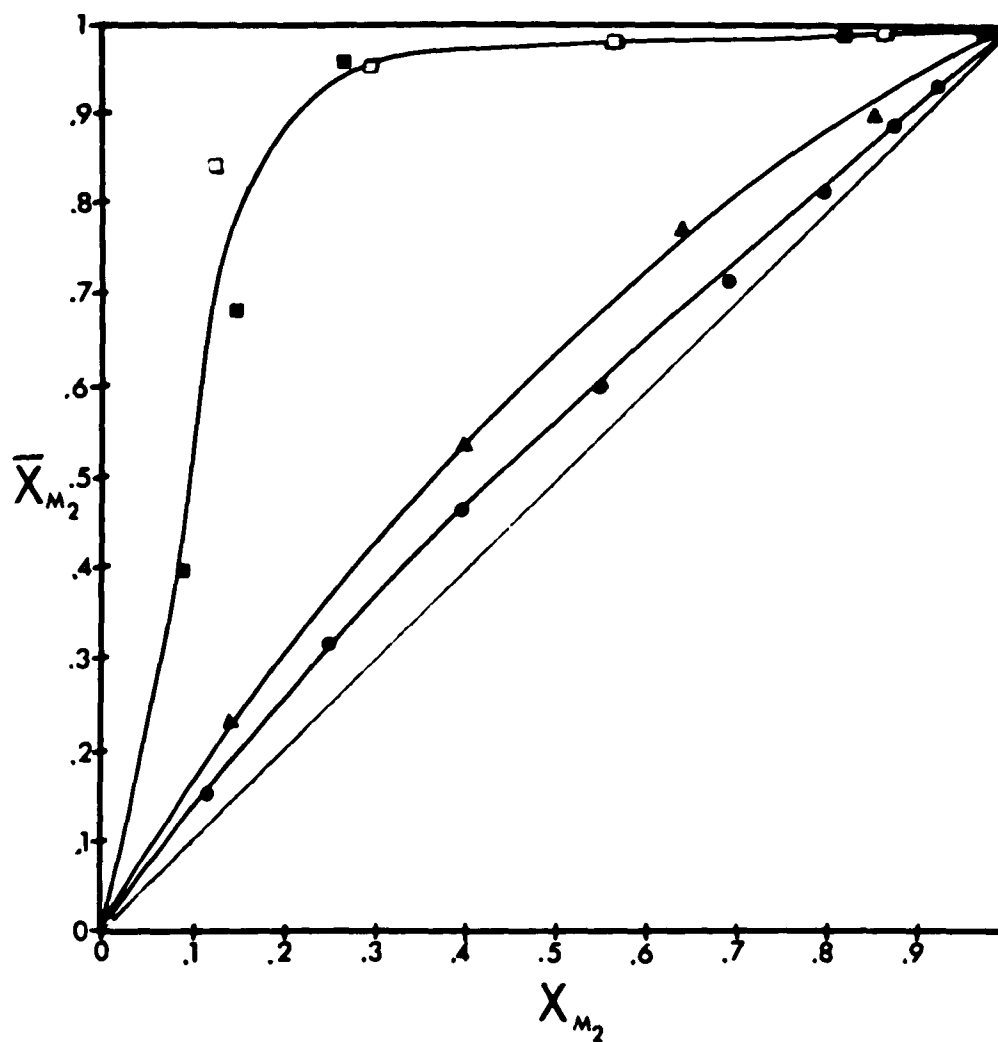


Figure 5-9
Equilibrium Isotherms
(M_2/M_1 , 25°C)

RESIN PME-II

• K^+/Na^+

■ Mg^{2+}/Na^+ (batch)

□ Mg^{2+}/Na^+ (column)

▲ Ca^{2+}/Mg^{2+}

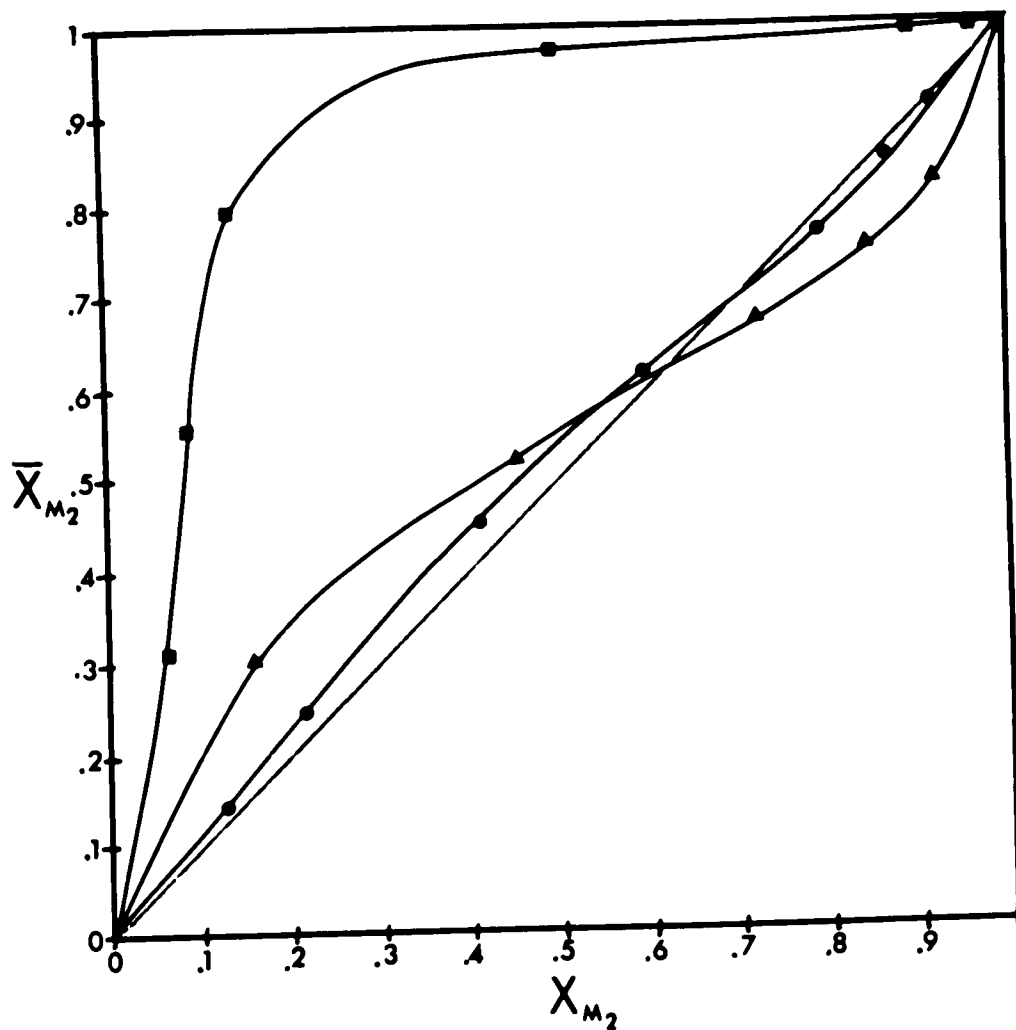


Figure 5-10
Equilibrium Isotherms
(M_2/M_1 , 25°C)

RESIN PME-II

• Rb^+/Na^+

■ H^+/Na^+

▲ H^+/Cu^{2+}

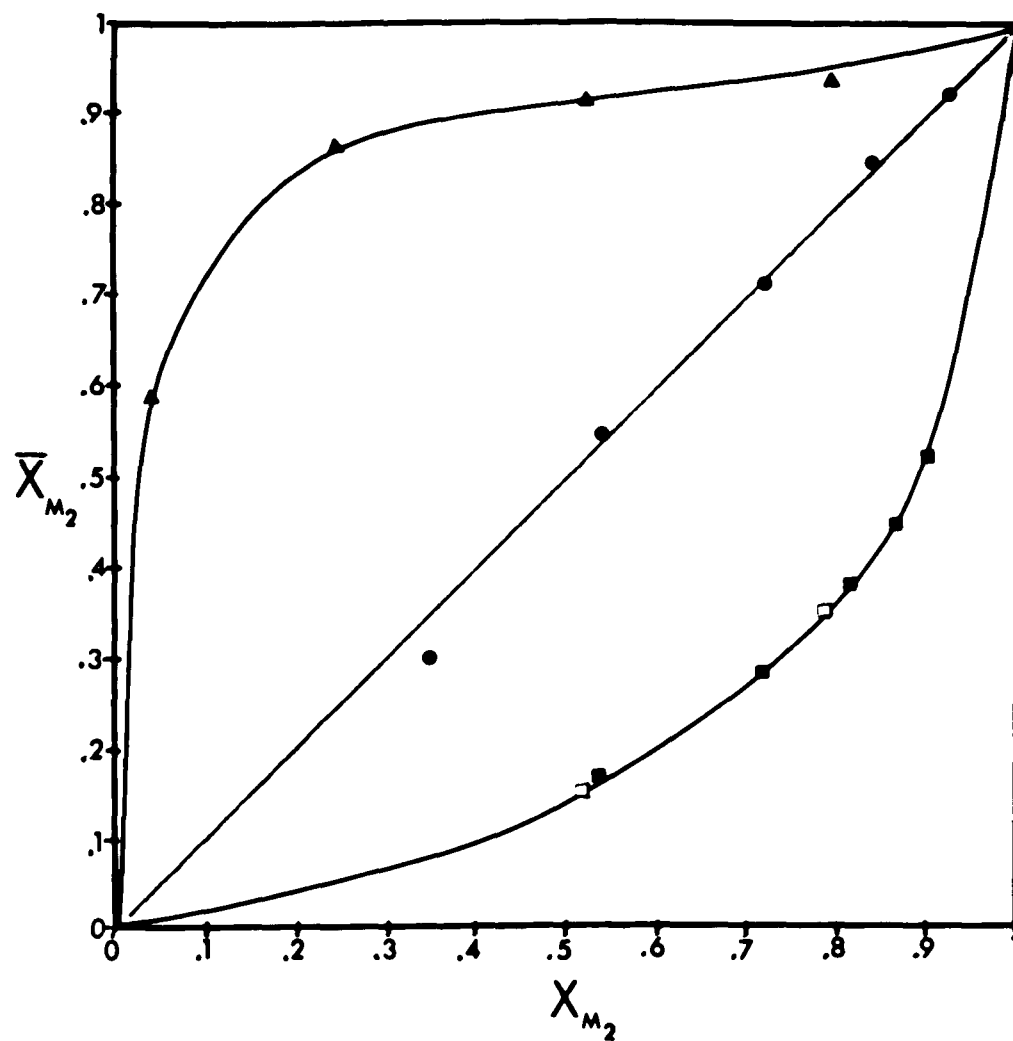


Figure 5-11
 Equilibrium Isotherms
 (M_2/M_1 , 25°C)
 RESIN PME-II
 • Li^+/Na^+
 ■ $\text{Ca}^{2+}/\text{Cu}^{2+}$ (batch)
 □ $\text{Ca}^{2+}/\text{Cu}^{2+}$ (column)
 ▲ $\text{Cr}^{3+}/\text{Ca}^{2+}$

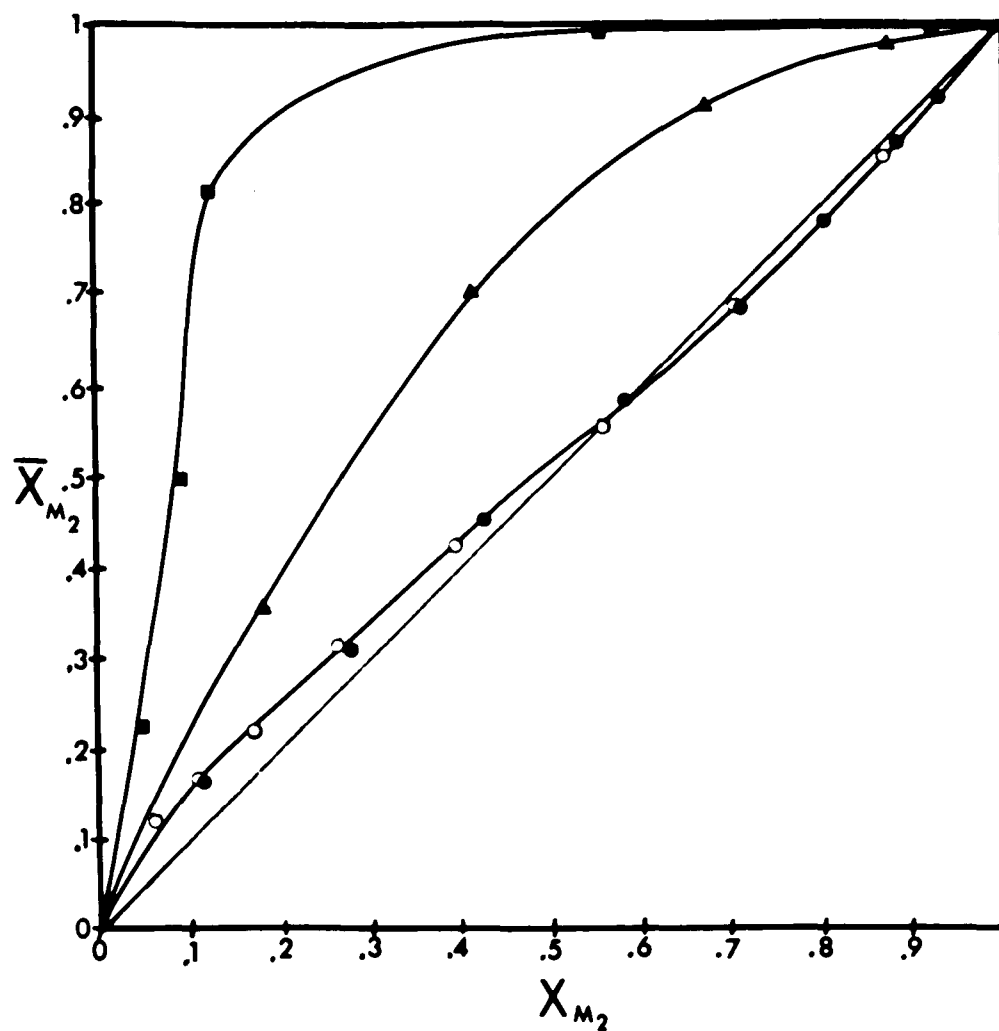


Figure 5-12
Equilibrium Isotherms
(M_2/M_1 , 25°C)

RESIN Et-PDE-I

• $\text{K}^{+}/\text{Na}^{+}$ (forward)

◦ $\text{K}^{+}/\text{Na}^{+}$ (reverse)

▪ $\text{Mg}^{2+}/\text{Na}^{+}$

▲ $\text{Ca}^{2+}/\text{Mg}^{2+}$

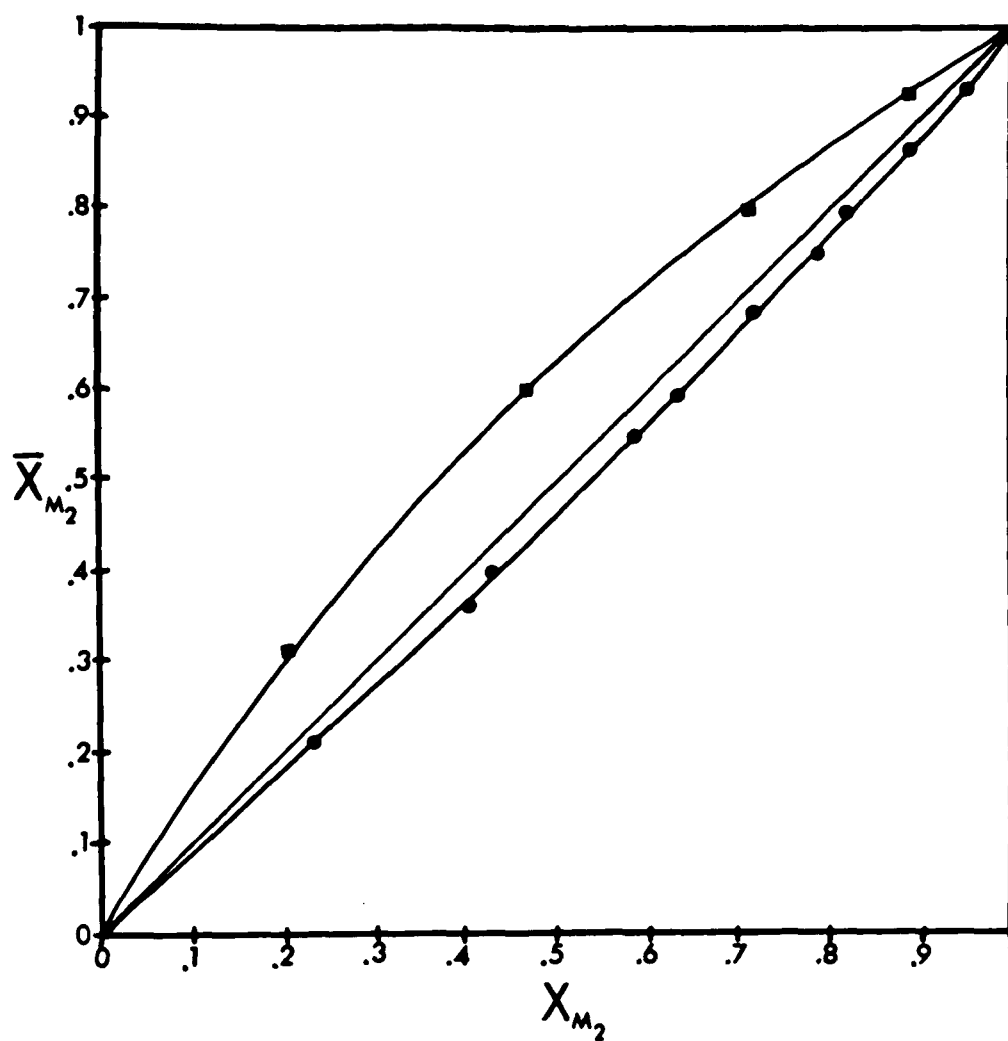


Figure 5-13
Equilibrium Isotherms
(M_2/M_1 , 25°C)
RESIN Et-PDE-II

- K^+/Na^+
- Ca^{2+}/Mg^{2+}

For the PME systems, the M_1 -cation forms were prepared by treatment of the H^+ -form in a column with the M_1 -nitrate or -chloride solution for an extended period (at least 2 L of 1 N solution for 10-24 hours). Thus, the isotherms reflect the selectivity of the strong-acid groups in the resin. For resin PME-I, the high-pH isotherm was obtained by treating the fully-loaded Na^+ -form (from a minimal wash) with KOH solutions. This isotherm reflects the selectivity of the fully-ionized strong-acid and weak-acid groups.

The general equation for the selectivity coefficient is:

$$K_{M_1}^{M_2^{z_2}} = \frac{\bar{x}_{M_2}^{z_1} \cdot x_{M_1}^{z_2}}{\bar{x}_{M_1}^{z_2} \cdot x_{M_2}^{z_1}} \quad (5.10)$$

where z_1 and z_2 are the charges on the cations in the $M_2^{z_2}/M_1^{z_1}$ system. Applying this equation to each of the data points on an isotherm, plotting $\log K_{M_1}^{M_2^{z_2}}$ versus $\bar{x}_{M_2}$, and constructing the best line through the points over the entire composition range leads to the presentations in Figures 5-14, 5-15 and 5-16 for the resins PME-I, PME-II, Et-PDE-I and Et-PDE-II. Calculation of the areas encompassed by each of these lines gives the integrated selectivity coefficients (as $\log K$) for the various cation systems. The integrated $\log K$ values for the resins are listed in Table 5-8. The experimental errors noted in the Table arise from the uncertainties in the best lines through the data points. From these integrated selectivity coefficients, the following affinity orders may be formulated:

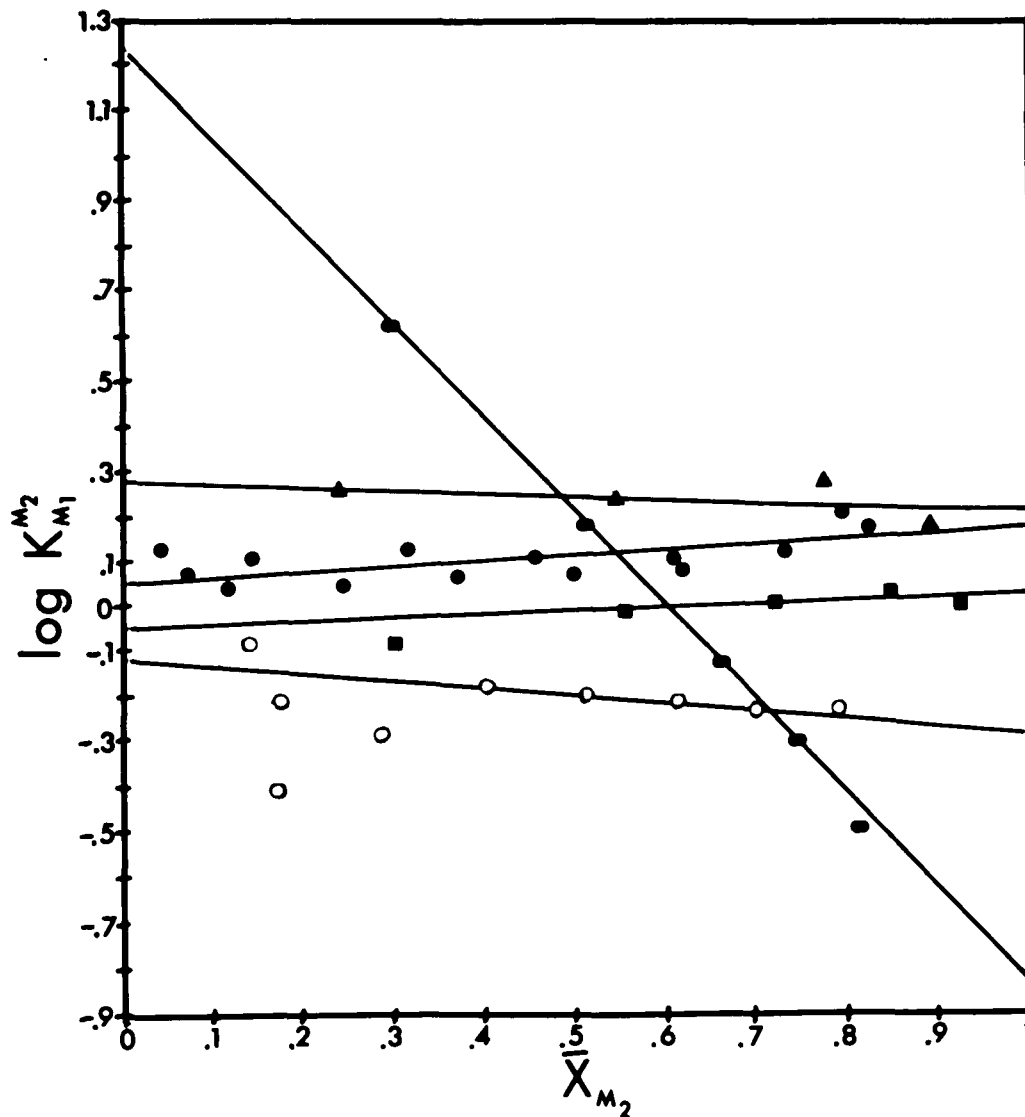


Figure 5 - 14

Log K Plots (M_2/M_1)

RESIN PME-I

● K^+/Na^+ (low pH)○ K^+/Na^+ (high pH)

RESIN PME-II

▲ Ca^{2+}/Mg^{2+} ■ Li^+/Na^+ ● H^+/Cu^{2+}

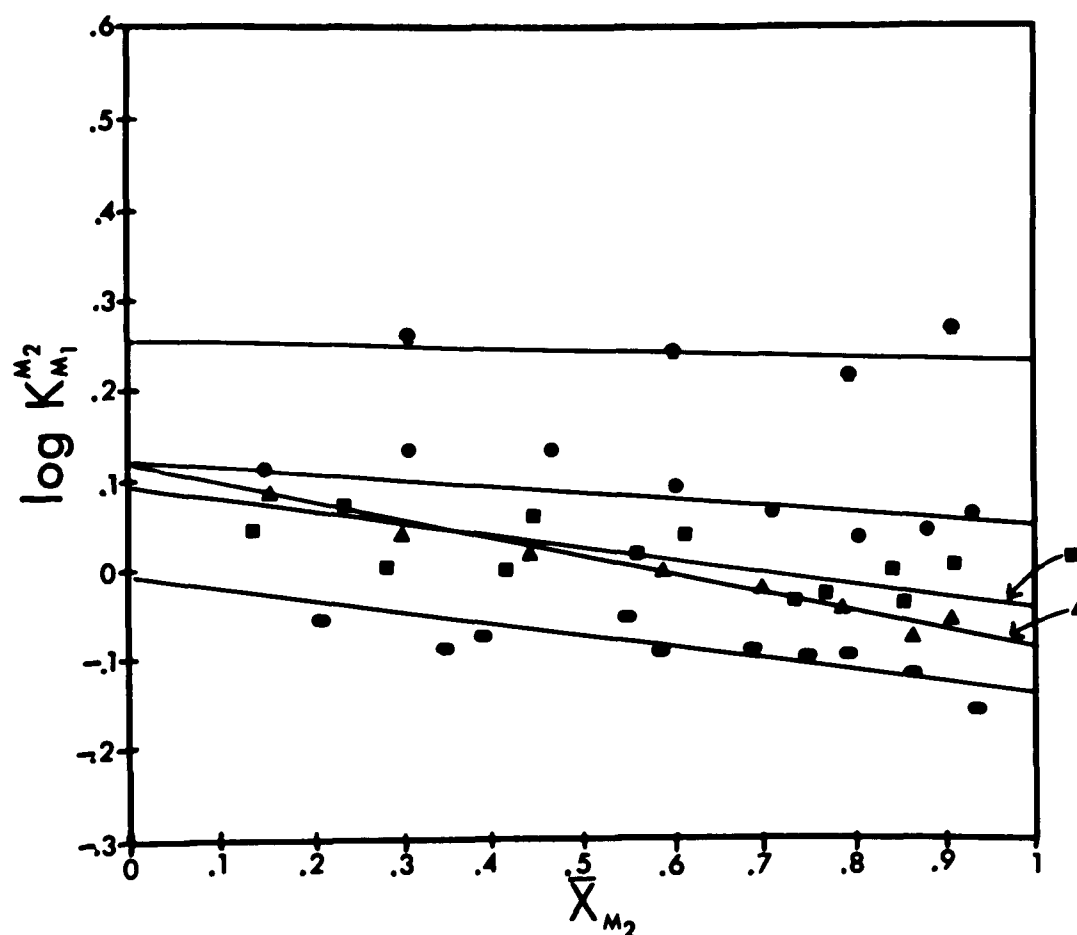


Figure 5-15

Log K Plots (M_2/M_1)

RESIN PME-II

RESIN Et-PDE-I

RESIN Et-PDE-II

 $\bullet K^+/Na^+$ $\blacktriangle K^+/Na^+$ $\bullet K^+/Na^+$ $\blacksquare Rb^+/Na^+$ $\bullet Ca^{2+}/Mg^{2+}$

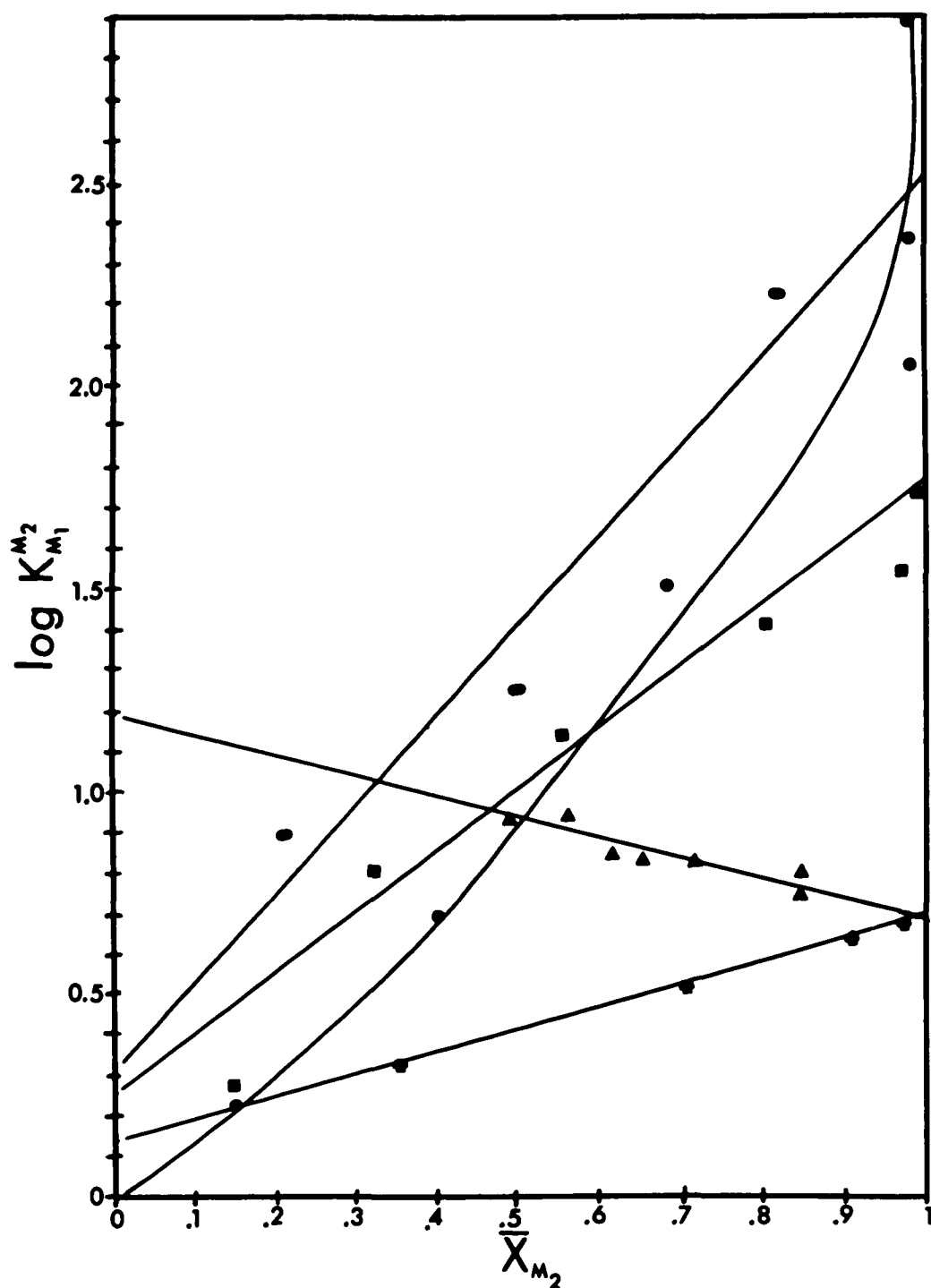


Figure 5-16
Log K Plots (M_2/M_1)

RESIN PME-II RESIN Et-PDE-I
 $\bullet Mg^{2+}/Na^+$ $\blacksquare H^+/Na^+$ $\blacktriangle Cu^{2+}/Ca^{2+}$ $\bullet Mg^{2+}/Na^+$ $\bullet Ca^{2+}/Mg^{2+}$

TABLE 5-8. SELECTIVITY COEFFICIENTS FOR THE RESINS.

Resin	(M ₂ /M ₁) System	$\log K_{M_1}^{M_2}$ ^a	Method	Error(%) ^b
PME-II	K ⁺ /Na ⁺	0.12	batch	5
	Rb ⁺ /Na ⁺	0.02	batch	15
	Li ⁺ /Na ⁺	-0.01	batch	15
	H ⁺ /Na ⁺	0.98	batch	20
	Mg ²⁺ /Na ⁺	1.60	batch + column	20
	Ca ²⁺ /Mg ²⁺	0.24	column	10
	Cu ²⁺ /Ca ²⁺	0.93	batch + column	10
	H ⁺ /Cu ²⁺	0.20	batch	10
PME-I	K ⁺ /Na ⁺ (pH 5.5)	0.12	batch ^c	10
	K ⁺ /Na ⁺ (pH 12)	-0.20	batch	10
Et-PDE-I	K ⁺ /Na ⁺	0.02	batch ^c	5
	Mg ²⁺ /Na ⁺	1.42	batch	20
	Ca ²⁺ /Mg ²⁺	0.42	column	5
Et-PDE-II	K ⁺ /Na ⁺	-0.07	batch	5
	Ca ²⁺ /Mg ²⁺	0.24	column	10

^a Integrated selectivity coefficient based on area under $\log K_{M_1}^{M_2}$ vs. $\bar{X}_{M_2}$ plot (ca. 25°C).

^b Approximate error in integrated $\log K$ based on the $\log K$ vs. $\bar{X}$ plots.

^c Both forward and reverse isotherms measured.

Resin PME-II	$\text{Cr} > \text{H} > \text{Cu} > \text{Ca} > \text{Mg} > \text{K} > \text{Rb} > \text{Na} > \text{Li}$
Resin Et-PDE-I	$(\text{H} >) \text{Ca} > \text{Mg} > \text{K} > \text{Na}$
Resin Et-PDE-II	$(\text{H} >) \text{Ca} > \text{Mg} > \text{Na} > \text{K}$
Resin PME-I	$\text{K} > \text{Na} (\text{pH} = 5.5), \text{Na} > \text{K} (\text{pH} = 12)$

The H^+ ion has been included in the affinity orders for resins Et-PDE-I and Et-PDE-II, although complete isotherms were not measured; preliminary isotherm determinations and the highly efficient column elution of all counterions by H^+ from the Et-PDE resins provide evidence that these resins are, like the PME resins, highly selective for H^+ .

5.5.3.2 Discussion.

The literature contains several reports dealing with the selectivity characteristics of phosphorus-containing cation exchangers. The high selectivity of various phosphonic-acid and phosphoric-acid exchangers for polyvalent ions such as Th^{4+} , U^{4+} , Ti^{4+} , Ce^{4+} , Fe^{3+} , Sc^{3+} , In^{3+} and UO_2^{2+} [65,85,159-161] is particularly noteworthy. The uptake of UO_2^{2+} has generated special interest concerning the separation and purification of uranium and the role of complexation in the ion-exchange mechanism [162-164]. A sodium diallylphosphate resin (a PDE resin) has been used in the separation of Be^{2+} [165].

Another unique feature of these materials is the selectivity reversal observed for the alkali cations. Typical strong-acid exchangers (i.e., the sulfonic-acid resins) have selectivity sequences for alkali cations which follow the series $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$. This so-called "normal" or Hofmeister series dictates a higher selectivity for the smaller hydrated cation, consistent with the various theoretical treatments of the ion-exchange process which attribute selectivity to an

osmotic or swelling pressure [154-156,166-169]. Such theoretical models lead to equations of the sort:

$$RT \ln \left[K_B^A \left(\frac{\gamma_A}{\gamma_B} \right) \right] = \Pi (V_B - V_A), \quad (5.11)$$

where K_B^A is the selectivity coefficient for the A^+/B^+ -cation system, γ_M is the activity coefficient for cation M in the resin phase, Π is the thermodynamic osmotic pressure and V_M is the hydrated radius of cation M. Deviations of K_B^A from unity arise in particular from differences in the counterion sizes.

Weak-acid cation exchangers generally exhibit reversed selectivity sequences [157]. This phenomenon has been noted and discussed especially for phosphonic-acid [60,157,170-172] and phosphoric-acid [171,173] cation exchangers. For example, in a study of a phosphonic-acid resin [172], only the first dissociable group of the phosphonate function was active at low pH, and the selectivity sequence corresponded to that for a monofunctional strong acid (selectivity $\text{Na} > \text{Li}$). At high pH, a reversal was observed ($\text{Li} > \text{Na}$). Similarly, a phosphoric-acid resin (Duolite C-65) exhibited the selectivity sequence $\text{K} > \text{Na} > \text{Li}$ at low pH and the sequence $\text{Li} > \text{Na} > \text{K}$ at high pH [173].

The generally accepted explanation for these phenomena centers around the polarization properties of the various species involved in the exchange process--the functional group, the counterion and water. The order of polarizability for the common cation-exchange functional groups is $\text{POO}^{2-} > \text{COO}^- > \text{H}_2\text{O} > \text{SO}_3^{2-}$ [60,157]. Thus, since the sulfonate group is less polarizable than water, it will not replace

water from the hydration sphere of the alkali cation, and the selectivity sequence will follow the "normal" order of hydrated radii, $K > Na > Li$. The more polarizable POO^{2-} groups should replace water from the hydration sphere of the more polarizing alkali cation, and the selectivity sequence would then follow the order of the crystal radii (polarizing power), $Li > Na > K$. For the phosphorus resins at low pH, where the active exchange groups is POO^- , the polarizability order is $H_2O > POO^-$ [171], so that the "normal" order of selectivity is followed. Intermediate orders of affinity have been observed for phosphate resins, such as $K > Li > Na$ [173], attributed to variations in the state of polyfunctionality of the resin-exchange groups as a function of the pH. At a particular pH, the selectivities due to the fractions of strong-acid exchange groups and weak-acid exchange groups combine to yield an overall selectivity, which might follow neither the Hofmeister nor the crystal-radii orders.

The selectivity characteristics obtained for the PME and Et-PDE resins generally correspond to those that would be expected for phosphoric-acid cation exchangers in light of the previous studies on related materials. We have not obtained any quantitative data on UO_2^{2+} exchange, although the PME resins qualitatively exhibited a high affinity for this cation, as evidenced by the difficulty encountered in eluting the UO_2^{2+} ion from the resin by H^+ . The isotherm obtained for the Cr^{3+}/Ca^{2+} system on resin PME-II (Figure 5-11) displays a high affinity for the trivalent ion; in addition, it was difficult to remove Cr^{3+} from the resin by elution with H^+ . We presume that the PME and Et-PDE resins have high selectivities for other polyvalent cations, similar to the phosphonic- and phosphoric-acid resins cited above.

Selectivity-order reversal was found for resin PME-I in

measuring the K^+/Na^+ isotherms at low (ca. 5.5) and high (ca. 12) pH (Figure 5-8). Consistent with the studies noted above, the PME resin acts as a monofunctional strong-acid resin under acidic conditions, with $K_{Na^+}^{K^+} = 1.3$ while under basic conditions, $K_{Na^+}^{K^+} = 0.63$, indicative of a modification in the nature of the exchange groups by activation of the weak-acid exchange sites. The data for resin PME-II at low pH ($K_{Na^+}^{K^+} = 1.3$ and $K_{Na^+}^{Li^+} = 0.98$) follow the expected Hofmeister sequence $K > Na > Li$, although the data for the Rb^+/Na^+ system do not fit into this trend. For the Et-PDE resins, the K^+/Na^+ systems exhibit very little selectivity. Resin Et-PDE-II shows a slight preference for Na^+ ($K_{Na^+}^{K^+} = 0.85$), and the resin Et-PDE-I undergoes a reversal in selectivity at higher K^+ loadings (overall $K_{Na^+}^{K^+} = 1.04$). Repetition of the K^+/Na^+ determination in the forward and reverse directions proved this reversal to be genuine.

The phosphate resins have a high affinity for the proton, the isotherm shown in Figure 5-10 for the H^+/Na^+ system on resin PME-II being representative of the behavior of all the resins toward H^+ . High H^+ -selectivity was found to be the case for other phosphorus-containing ion-exchange resins [85,144,145,161]. As a consequence, all univalent and divalent counterions could be efficiently eluted from the resins with acid solutions. In experiments with UO_2^{2+} - and Cr^{3+} -loaded resins, these counterions could not be totally eluted even under prolonged treatments (2-3 days) with up to 5 M acid solutions. Thus, Cr^{3+} is placed above H^+ in the affinity series presented on page 155. We presume that UO_2^{2+} and other tripositive and tetrapositive counterions would also be tightly bound to these phosphate resins and would be preferentially sorbed over H^+ .

The selectivity characteristics of the phosphoric-acid-ester resins, as reflected in the affinity orders presented above, follow the general patterns known in the field of ion-exchange selectivities [1(p. 156-169)]. The electrostatic effect is clearly evident, the selectivities for the higher-charged counterions being significantly greater than for the lower-charged counterions. As Figure 5-11 shows, resin PME-II is strikingly selective for Cr^{3+} over Ca^{2+} , while the same applies for Mg^{2+} over Na^{+} (Figure 5-9 for resin PME-II and Figure 5-12 for resin Et-PDE-I). Within a charge-type group, there is a correspondence of the selectivity to the order of hydrated-ionic size for the strong-acid functional groups in the case of resin PME-II for the univalent cations ($\text{K} > \text{Na} > \text{Li}$, Rb anomalous) and the divalent cations ($\text{Ca} > \text{Mg}$). Swelling pressures are reduced in the ionic forms of the smaller hydrated cations. Specific interactions of the multivalent counterions with the phosphate functional groups contribute to the high selectivities for these species, especially considering the complexing ability of aqueous orthophosphates [29(p. 556)] and the fact that polyvalent cations generally form insoluble phosphate salts. Some sort of ion-pair formation or association involving covalent interaction between a multivalent counterion and the phosphate functional group would be expected. Our phosphoric-acid resins provide a unique environment for the investigation of such special interactions, allowing for the isolation of the cation-phosphate system subject to a controllable degree of hydration [174]. We have probed this aspect to some extent in the analysis of the infrared spectra of several ionic forms of the resins (Chapter Six).

Perusal of Figure 5-16 reveals that for the $\text{Mg}^{2+}/\text{Na}^{+}$ and

H^+/Na^+ systems, the selectivity of the resin for Mg^{2+} and H^+ increases markedly as the loading of Mg^{2+} or H^+ increases. This behavior is unusual with respect to the common strong-acid cation exchangers [1(Ch. 5)]. Gregor [175,176] noted a similar phenomenon in anion-exchanger systems, and it was also observed for a phosphonic-acid system [172] and for H^+/NH_4^+ exchange on a polyacrylic-acid resin [177]. Increased selectivity with increased loading may be related to a reduction in resin volume which accompanies replacement of Na^+ with either H^+ or Mg^{2+} . A striking difference in the resin volume between the Mg^{2+} - and Na^+ -forms and the H^+ - and Na^+ -forms was observed during the column operations, an approximately 40-45% reduction in volume occurring upon conversion from the Na^+ -form to the H^+ - or Mg^{2+} -forms. The resin structure, to avoid increased constraint with increased loading, becomes even more selective for the counterion that can be involved in ion pairing or other specific interaction with the concomitant exclusion of hydration water. This effect occurs only in the systems for which the selectivity coefficient is relatively high (ca. > 10) and the natures of the counterions are quite different.

Selectivity coefficients for two cation systems can be used to calculate the selectivity coefficient for a third system, provided there is a cation common to the original cation systems. This may be done through the triangle rule:

$$\log K_{M_1}^{M_3} = \log K_{M_2}^{M_3} - \log K_{M_2}^{M_1}, \quad (5.11)$$

where M_1 , M_2 and M_3 are univalent cations, $K_{M_1}^{M_3}$ is the selectivity

coefficient for the new system (M_3/M_1) and $K_{M_2}^{M_3}$ and $K_{M_2}^{M_1}$ are the selectivity coefficients for the known systems (M_3/M_2 and M_1/M_2 , respectively). The equation must be slightly modified to account for cations of dissimilar charge. Application of the triangle rule to a few systems for the PME and Et-PDE resins yields the following results: for resin PME-II, $\log K_{Ca}^H = \log K_{Cu}^H - \log K_{Cu}^{Ca} = .40 - (-.93) = 1.13$, $\log K_{Mg}^{Cu} = 1.17$, $\log K_K^H = 0.86$, $\log K_{Rb}^K = 0.10$; for resin Et-PDE-I, $\log K_{Na}^{Ca} = 1.84$, $\log K_K^{Mg} = 1.40$. The values of these predicted selectivity coefficients fall in line with the affinity series presented previously (p. 155).

In summary, the phosphoric-acid-ester cation exchangers prepared in this research exhibit selectivity properties in line with those reported on previously known phosphonic- and phosphoric-acid cation exchangers. The magnitudes of the selectivity coefficients we obtained are of the same order as the few tabulated values for the other systems [178]. Further research into the equilibrium characteristics of the PDE resins would be of special interest since the phosphoric-acid-diester functional group has been subjected to almost no fundamental investigations to date. These PME and PDE resins could prove useful in chromatographic applications.

CHAPTER SIX

CHARACTERIZATION OF THE RESINS II

6.1 Infrared-Spectroscopic Study of the Resins.

The results for the measurement of the infrared spectra of 14 ionic forms of the PME and Et-PDE resins are presented in this section.

The utility of infrared spectroscopy in the characterization of ion exchangers has been noted by several authors [179-182]. The infrared spectra of the common ion-exchange substances have been recorded and discussed, including investigations of the sulfonic-acid exchangers [174,179,181,183], various carboxylic-acid exchangers [23,184], phosphonic-acid exchangers [174,185-191] and various anion exchangers [179,181,192]. From infrared spectroscopic investigations on ion-exchange resins, two major pieces of information can be obtained. First, the kinds of functional groups on the backbone matrix of the exchanger can be ascertained. The positions of the characteristic absorption bands of the chemical groups in the spectra of the polymer systems and in the spectra of the corresponding monomers are quite similar. Second, an indication of the nature of the interactive forces between various counterions and the resin functional groups can be obtained by observing the differences among the spectra of various ionic forms of the resin. We have applied these principles to our phosphate resins, and have derived additional proof of the chemical structures of the resin ionogenic groups along with some information regarding the cation-phosphate bonding in these materials.

6.1.1 Experimental Procedures.

The spectra of the H^+ -, Na^+ -, K^+ -, NH_4^+ -, Mg^{2+} -, Ca^{2+} -, Ba^{2+} -, Co^{2+} -, Cu^{2+} -, $Cu(NH_3)_4^{2+}$ -, Zn^{2+} -, Cr^{3+} -, La^{3+} - and UO_2^{2+} -forms of resins PME-I and Et-PDE-I were recorded. Samples of both resins were prepared by treating exhaustively with solutions of the appropriate cation to assure full conversion of the weak-acid sites to the particular cation form.

Specifically, the Na^+ -forms were obtained by treatment of the H^+ -forms with ca. 0.5 N NaOH followed by a minimum wash to avoid hydrolysis of the weak-acid groups back into the H^+ -form. Spectra of the Na^+ -form of resin Et-PDE-I, obtained on a sample prepared as just described and on a sample prepared by extensive washing of the Na^+ -form, were identical, indicating the presence of only stronger-acid exchange groups. The mixed Na^+/H^+ -form of resin PME-I was made by exhaustive washing of the Na^+ -form. The K^+ - and NH_4^+ -forms were obtained by treatments with excess 0.5 N KOH and 0.5 N $NH_4NO_3/10\% NH_3$, respectively, followed by minimal washing. The other ionic forms were prepared by prolonged treatment (10-24 hours) of the Na^+ -forms of resins PME-I and Et-PDE-I with 2 - 3 liters of 0.5 N salt solutions of the cations. Where possible, these were applied at pH above 7 to minimize hydrolysis. Thus, treatment with solutions of $MgCl_2/Mg(C_2H_3O_2)_2$, $Ca(NO_3)_2/Ca(OH)_2$, $BaCl_2/Ba(OH)_2$, $Zn(NO_3)_2$, $CuSO_4/Cu(C_2H_3O_2)_2$, $[Cu(NH_3)_4]SO_4$, $CoCl_2$, $Cr(NO_3)_3$, $LaCl_3$ and $UO_2(NO_3)_2$ gave the respective cation forms of the two phosphate resins.

After briefly washing until no cations could be detected in the effluents, the resin forms were dried in a vacuum oven for three days at $65^\circ C$. The KBr-disk technique [193] was employed to disperse the samples for the IR measurements. The KBr disks were prepared by mixing

ca. 100 mg of the spectroscopic-grade halide (dried at 120°C in a vacuum oven and stored over P_2O_5) with 1-2 mg of the resin sample in a steel-ball mill and agitating for two minutes on a Wig-L-Bug. The transparent disks were formed in a ½-inch Wilks die by pressing with 50 tons for five minutes. The spectra were recorded in the 4000-600 cm^{-1} region on a Beckman IR 18A infrared spectrophotometer, and spectra of at least two different samples of each ionic form were taken. The spectra were reproducible to within $\pm 8\text{ cm}^{-1}$ in the 4000-2000 cm^{-1} region and $\pm 4\text{ cm}^{-1}$ in the 2000-600 cm^{-1} region. Spectra of the H^+ - and Ca^{2+} -forms of resin PME-I were checked by the Nujol-mull technique and were found to be identical to the spectra recorded in the KBr disks in the region of interest (1300-900 cm^{-1}). Thus, ion exchange did not occur in the KBr matrix, consistent with the previous observations on Bio-Rex 70, a carboxylic-acid resin [23].

6.1.2 The Spectra.

The spectra of the PME and Et-PDE resins have the same general appearance as the spectra for the other cation-exchange resins [23,179,185]. There are absorption bands due to vibrations of the resin polymer backbone and absorption bands due to vibrations characteristic of the functional groups attached to the crosslinked resin matrix. For purposes of discussion, we divide the spectra into two regions--the region in which the styrene/DVB copolymer matrix and water absorptions appear (4000-1300 and 900-600 cm^{-1}) and the region in which the ionized phosphoric-acid-ester group vibrations appear (1300-900 cm^{-1}).

In Table 6-1, we present the major peaks present in the spectra of resins PME-I and Et-PDE-I which are due to the polymer matrix and hydration water. Several of the backbone peaks appear with different

TABLE 6-1. MATRIX AND HYDRATION-WATER BANDS IN THE SPECTRA OF RESINS PME-I AND Et-PDE-I.^a

Wavenumber(cm ⁻¹)	Description ^b	Assignment	Reference
3430-3330	vb, s	O-H stretch of hydration waters	174 (p. 54)
3020	w	aromatic C-H stretch	194 (p. 257)
2920	m	CH ₂ asymmetric stretch	194 (p. 229)
2850	sh	CH ₂ symmetric stretch	194 (p. 229)
1700-1600	w, sh ^c	hydration water	174 (p. 81)
1601	m	aromatic C-C stretches	194 (p. 260)
1505	m, sh ^d	skeleton stretching of benzene	174 (p. 6)
1490	sh, m ^d		
1450	m		
820	m, sh	skeletal vibrations	174 (p. 6-7, 12-13)
792	w ^e		
759	w, m ^{d,f}		
695	m, s ^d		

^a Major peaks in the 4000-1300 and 900-600 cm⁻¹ regions.

^b Peak descriptions: s = strong intensity, m = medium, w = weak; b = broad, sh = shoulder, v = very.

^c Peak is broad and intense in the PME-I spectra but very weak in the Et-PDE-I spectra.

^d First intensity for resin PME-I; second, for resin Et-PDE-I.

^e Et-PDE-I spectra only.

^f See p. 173 for additional possible assignment.

intensities in the spectra of the two materials. This is understandable, considering the distinct origins of the original copolymers used in the syntheses of the two resins (see Chapter Three). These backbone peaks in the spectra of resin Et-PDE-II are identical to those in the spectra of resin PME-I, as would be expected since these two resins have a common polymer precursor.

The most significant spectral region, $1300\text{-}900\text{ cm}^{-1}$, contains the bands due to the vibrations of the phosphorus groups in the resins. The peaks in this region are somewhat dependent on the counterion in the resin. Detailed descriptions of the spectra in this region are given in Table 6-2 for resin PME-I and in Table 6-3 for resin Et-PDE-I. Generally, the phosphate peaks are of high intensity and are extremely broad. For several ionic forms listed in the two tables, some absorptions are so broad that one well-defined maximum could not be distinguished. In these cases, the wavenumber range over which the maximum occurs is listed. Assignments for the absorption peaks in this spectral region are discussed in the next section. Sample spectra in the $1300\text{-}800\text{ cm}^{-1}$ region are presented for the H^+ - and K^+ -forms of resins PME-I and Et-PDE-I in Figures 6-1 and 6-2, respectively.

Measurement of the spectra of the H^+ -, Na^+ -, Ca^{2+} - and Cu^{2+} -forms of resin Et-PDE-II produced results identical to those obtained for these ionic forms of resin Et-PDE-I in the $1300\text{-}900\text{ cm}^{-1}$ region. Similarly, spectra of various ionic forms of resin PME-II were identical to those of resin PME-I. Bands given in Tables 6-2 and 6-3 are therefore independent of the particular styrene/DVB copolymer matrix and reflect the isolated interactions of the counterions with the ionogenic groups.

TABLE 6-2. INFRARED SPECTRA OF RESIN PME-I IN THE 1300-900 cm^{-1} REGION.

Ionic Form		Frequencies(cm^{-1}) ^{a,b}			
H^+	1200(b,s)	1100(sh)	1050(sh)	1015(max)	
$\text{Na}^+/\text{H}^{+c}$	1200(b,s)		1060(max)		925(m)
Na^+	1200(sh)	1110—	1065(max)	975(m)	905(w)
K^+	1200(sh)	1110—	1065(max)	980(s)	905(w)
NH_4^+	1200(b,s)	1100(sh)	1050(sh)	1015(max)	950(sh)
Mg^{2+}	1200(sh)	1110—	1060(max)	1000(w)	950—920(b,sh)
Ca^{2+}	1200(sh)	1110—	1060(max)	990(m)	920(sh)
Ba^{2+}	1200(sh)	1110—	1060(max)	970(s)	940—900(b,sh)
Co^{2+}	1200(sh)	1100(sh)	1060(max)	1000(sh)	
Cu^{2+}		1100(sh)	1060(max)	1000(sh)	
$\text{Cu}(\text{NH}_3)_4^{2+}$		1100(sh)	1060(max)	1000(sh)	
Zn^{2+}	1200(sh)	1110—	1060—	1010(max)	950(sh)
Cr^{3+}	1200—	1140(b,sh)	1100(sh)	1060—1010(max)	960(sh)
La^{3+}	1200(sh)	1100(sh)	1050(max)	1000(sh)	950—900(b,sh)
UO_2^{2+}		1100(sh)	1060—	1010(max)	920(m)

^a Peak descriptions: Intensities signified as s = strong, m = medium, w = weak, sh = shoulder. Shapes signified with b = broad and max = extremely broad, strong peak with maximum absorption at the listed frequency or frequency range (a—b).

^b All wavenumbers reproducible to $\text{ca. } \pm 4 \text{ cm}^{-1}$.

^c Half-converted (mixed H^+ and Na^+) form.

TABLE 6-3. INFRARED SPECTRA OF RESIN Et-PDE-I IN THE 1300-900 cm^{-1} REGION.

Ionic Form	Frequencies(cm^{-1}) ^{a,b}					
	1230(s)	1170(sh)		1020(s)		900(sh)
H ⁺						
Na ⁺	1220(s)		1050(s)	1020(sh)	945(m)	
K ⁺	1220(s)		1050(max)	1020(sh)	940(m)	900(sh)
NH ₄ ⁺	1220(s)		1050(sh)	1025(s)	960(sh)	900(sh)
Mg ²⁺	1220(s)		1100(sh)	1040——1020(max)	945(w)	
Ca ²⁺	1210(s)		1100(sh)	1060——1020(max)	945(w)	
Ba ²⁺	1205(s)			1045(s)	1020(sh)	945(w)
Co ²⁺	1212(s)	1160(sh)		1040(sh)	1020(s)	960(sh)
Cu ²⁺		1185(s)		1055——1020(max)	960(sh)	900(sh)
Cu(NH ₃) ₄ ²⁺		1195(s)		1040(s)	1025(sh)	955(w)
Zn ²⁺	1225(s)	1160(sh)		1050(sh)	1020(s)	900(sh)
Cr ³⁺	1220(b,m)	1165(sh)			1020(s)	900(sh)
La ³⁺	1220(s)	1160(sh)		1050(sh)	1020(s)	960(sh)
UO ₂ ²⁺	1225(s)	1160(sh)		1040——1000(max)	980(sh)	900(sh)

^a Peak descriptions: Intensities signified as s = strong, m = medium, w = weak, sh = shoulder. Shapes signified with b = broad and max = extremely broad, strong peak with maximum absorption at the listed frequency or frequency range (a——b).

^b All wavenumbers reproducible to ca. $\pm 4 \text{ cm}^{-1}$.

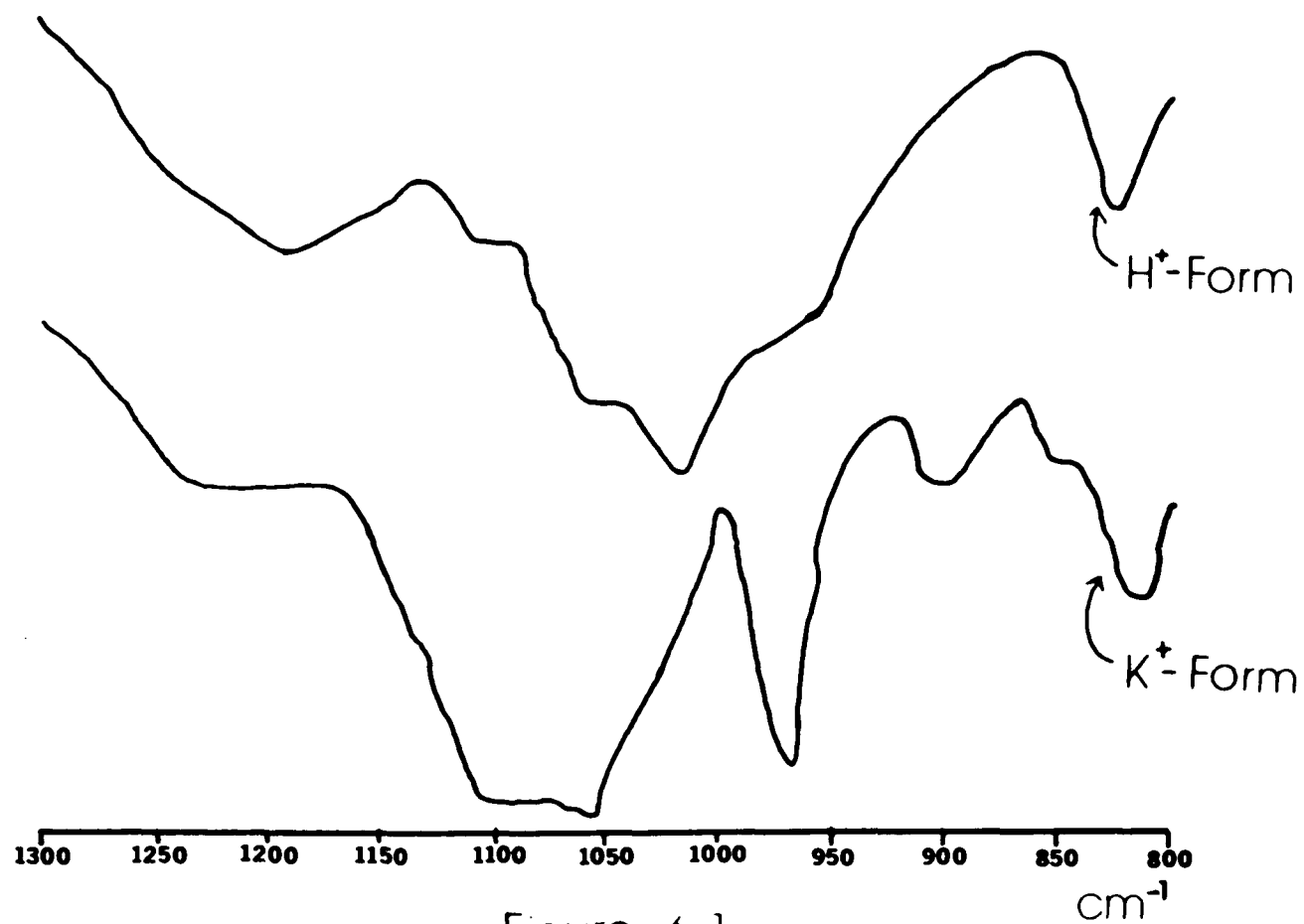


Figure 6-1
Infrared Spectra
RESIN PME-I

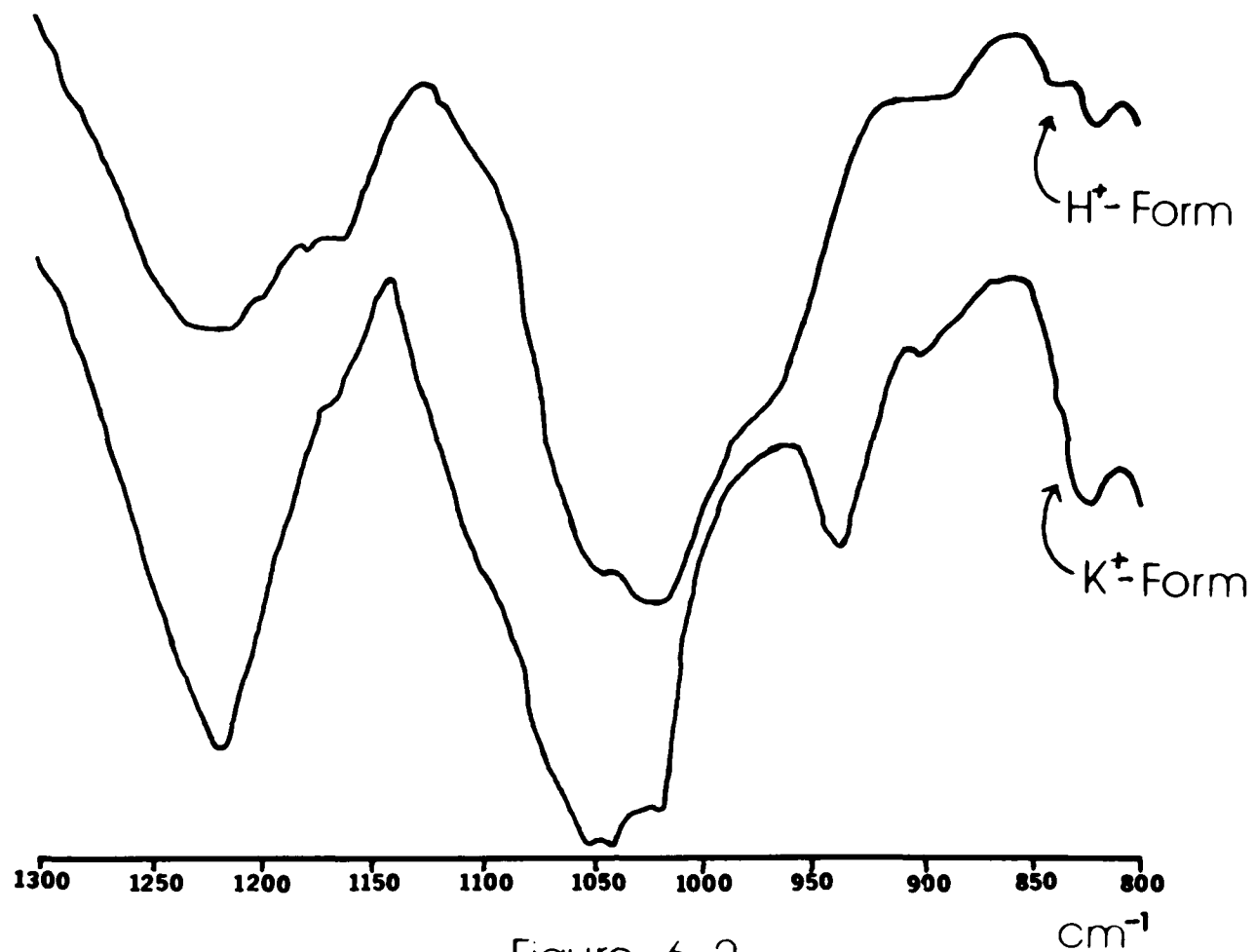


Figure 6-2
Infrared Spectra
RESIN Et-PDE-I

6.1.3 Discussion.

The general region of the infrared spectrum in which phosphoryl ($P=O$) vibrations occur is given as $1080-1400\text{ cm}^{-1}$ [66,195,196]. The oxyphosphorus ($P=O$ and $P-O$) vibrations of phosphorus-acid esters and salts appear in the $900-1300\text{ cm}^{-1}$ portion of the infrared spectrum.

Analysis of the latter wavenumber range in the spectra of the phosphate resins is therefore of particular interest in attempting to probe the interactions of the counterions with the resin ionogenic groups.

Assignments for the major peaks in the $900-1300\text{ cm}^{-1}$ region for the resins PME-I and Et-PDE-I are summarized in Table 6-4. Justifications for these assignments are presented shortly, after consideration of the factors which may complicate the spectra in this wavenumber range.

Interpretation of the spectra in the $900-1300\text{ cm}^{-1}$ region is complicated by the presence of several vibrational bands due to structural moieties other than the phosphate groups in the polystyrene/DVB-based resins. Specifically, absorption bands of aliphatic carbon-oxygen and substituted benzene rings are known to fall into the frequency range of interest [194]. The strongest interference is expected to result from the C-O stretching vibration. Consideration of the spectra of aliphatic esters of phosphoric acid (containing P-O-C linkages) must take the presence of this absorption into account since it contributes significantly to the spectral profile of these compounds [66(p. 216), 196(p. 52)]. Failure to account for C-O bands leads to erroneous interpretations of the spectra of various phosphate-diester salts [197].

The best indication as to the extent of influence of the C-O absorption on the spectra of the PME and Et-PDE resins can be obtained by comparison of the exchanger spectra with the spectrum of the synthetic

TABLE 6-4. PEAK ASSIGNMENTS IN THE 900-1300 cm^{-1} REGION.

<u>Resin</u>	<u>Wavenumber(cm^{-1})^a</u>	<u>Assignment^b</u>
PME-I	1200 (s or sh) ^c	P=O stretch
	1110-1040 (s)	P-O-C asymmetric stretch
		PO_3^{2-} asymmetric stretch
	1100 (sh)	disubstituted benzene
	1000-960 (w-m)	PO_3^{2-} symmetric stretch
Et-PDE-I	1230 (s)	P=O stretch (H^+ -form)
	1220-1200 (s)	PO_2^- asymmetric stretch
	1050-1020 (s)	P-O-C asymmetric stretch
		PO_2^- symmetric stretch

^a Intensities: s = strong, m = medium, w = weak, sh = shoulder.

^b See text.

^c s for H^+ -form, sh for other ionic forms.

precursor to the resins, 2-polystyrylethanol. The spectra of the 2-polystyrylethanol resins (samples OH-A, OH-B, OH-C and OH-D, see Table 3-11) all show a rather broad, medium-to-strong band ranging from 1020-1040 cm^{-1} . This is assigned to the C-O stretch of the primary-alcohol linkage in the polymer side chain [194(p. 137)]. As the data in Tables 6-2 and 6-3 show, a strong absorption in this wavenumber interval persists in the spectra of both phosphate resins. From a more detailed comparison of the contours of these peaks in the various spectra, it is found that the peak appears with a much higher intensity in the exchanger spectra and that for the H^+ -forms of the resins, the peak takes on a more defined, sharper maximum. In the exchanger spectra, this band does not represent a "pure" C-O vibration, but results from compound vibrations of the P-O-C groups. Complex simultaneous P-O and C-O vibrations in phosphate esters occur in the 990-1080 cm^{-1} region for the P-O-C "out-of-phase" stretch (attributed mainly to C-O vibrations) and in the 770-860 cm^{-1} range for the P-O-C "in-phase" stretch (attributed mainly to P-O vibrations)[66(p. 217)]. The peak listed in Table 6-2 and 6-3 in the 1020-1060 cm^{-1} range for the resin spectra is due in part to the P-O-C asymmetric stretch. The peak at 759 cm^{-1} listed in Table 6-1 as a matrix vibration (a sharp band of weak intensity in the PME-I spectra and of medium intensity in the Et-PDE-I spectra) may correspond to the P-O-C symmetric stretch, especially since it does not appear in the spectrum of 2-polystyrylethanol. A similar peak appears in the spectrum of diethylphosphate [196(p. 205)]. We hold this assignment as tentative since a peak at 759 cm^{-1} of variable intensity has been observed in the spectra of several other of our non-phosphorylated polymer samples.

The other interference expected in the $900\text{--}1300\text{ cm}^{-1}$ region of the exchanger spectra results from absorptions attributable to vibrations of 1,4-disubstituted benzene rings. The bands occur in the overall range of $1000\text{--}1180\text{ cm}^{-1}$ [194(p. 268)], and are found between 1097 and 1128 cm^{-1} in the spectra of various polystyrenesulfonic-acid films [174(p. 12)]. For the 2-polystyrylethanol resin, a weak absorption band is observed with a maximum at 1112 cm^{-1} . This band is present in the spectra of the various other intermediate resins encountered in the synthetic sequences. Examination of Table 6-2 and 6-3 reveals that a small shoulder persists in several of the exchanger spectra at $1100\text{--}1110\text{ cm}^{-1}$, which adds to the complexity of the large absorption bands present over the $1020\text{--}1100\text{ cm}^{-1}$ range. Rather than a reflection of the counterion-ionogenic group interaction, this small spectral feature is more likely the result of skeletal vibrations of the substituted aromatic rings in the resins.

The complexity of the infrared absorption bands of ionogenic groups in ion-exchange resins (especially the broadness of the peaks) is associated in part with the environmental inhomogeneities of the functional groups. All of the functional groups do not occupy equivalent positions in the polymer structure [23,181]. This effect also contributes to a reduction in the overall sharpness of the exchanger spectra.

Aware of the complications arising from interfering absorptions in the $900\text{--}1300\text{ cm}^{-1}$ spectral region, we now consider the spectra of the ion-exchange resins with regard to the absorptions of the phosphate groups themselves. Analysis of the spectra of the H^+ -forms of the resins, which are in effect phosphoric-acid esters, and of the spectral changes which ensue upon conversion to the ionized (salt) forms can serve to

distinguish the type of phosphate-ester groups present in the material. Comparisons among the spectra of the various ionic forms of each resin may allow for some conclusions concerning the nature of the cation-ionogenic group interactions, specifically in terms of the type of bonding involved.

The spectra for the ionic forms of resin PME-I are summarized in Table 6-2 and the assignments in the phosphate region are in Table 6-4. The H^+ -form of resin PME-I shows a relatively strong, broad absorption centered at 1200 cm^{-1} . This is assigned to the $P=O$ stretch [66,195,196], and is characteristic of phosphoryl compounds in which hydrogen bonding is involved. Hydrogen bonding causes a lowering of the position of the absorption maximum [195(p. 258),196] and a general broadening of the peak [196(p. 11)]. The large, complex absorption band centered at 1015 cm^{-1} in the spectrum of this resin results from $C-O-P$ and $P-O-H$ vibrations [195(p. 275),196(p. 41),199,200]. Conversion to the Na^+ - or K^+ -forms produces significant spectral alterations. The $P=O$ absorption at 1200 cm^{-1} is reduced to a shoulder, while the maximum of the complex band shifts to a higher frequency (1065 cm^{-1}) and is considerably broadened over a larger range. There also appears a new absorption band of medium intensity at $975-980\text{ cm}^{-1}$. Monoesters of phosphoric acid are known to behave in this manner upon conversion to salts.

Assigned to the $ROPO_3^{2-}$ group are two bands, one falling in the $1030-1170\text{ cm}^{-1}$ range and the other in the $940-1025\text{ cm}^{-1}$ range. These correspond to the asymmetric and symmetric stretching frequencies of the PO_3^{2-} group, respectively [195,196(p. 165),201]. The band for the symmetric stretch is usually of lower intensity. Disappearance of the $P=O$ stretch at 1200 cm^{-1} upon converting from the H^+ -form to the salt

forms of resin PME-I (a shoulder at 1200 cm^{-1} persists in the salt forms) is indicative of ionization of the monoester group. Overlap of the P-O-C and the PO_3^{2-} asymmetric stretching frequencies gives rise to the large, strong, complex absorption band in the $1110\text{--}1040\text{ cm}^{-1}$ frequency interval. The band of variable intensity falling between 970 and 1000 cm^{-1} in most of the PME-I salt-form spectra is unequivocally assigned to the symmetric PO_3^{2-} stretch.

The spectra of the ionic forms of resin Et-PDE-I are summarized in Table 6-3 and the assignments in the phosphate region are in Table 6-4. The spectrum of the H^+ -form of resin Et-PDE-I contains strong absorption bands at 1230 cm^{-1} and 1020 cm^{-1} . These bands are considerably sharper than the corresponding bands in the spectrum of the H^+ -form of resin PME-I. The peak at 1230 cm^{-1} is assigned to the P=O stretch and the peak at 1020 cm^{-1} is assigned to the P-O-C asymmetric stretch with some contributions from P-O-H vibrations [195(p. 275)]. Upon conversion to the salt forms, the higher-frequency peak shifts to $1200\text{--}1220\text{ cm}^{-1}$ and the lower-frequency peak broadens and becomes more complex. The spectra of the resin-salt forms correspond to the spectra of molecules containing the PO_2^- group. Salts of phosphoric-acid diesters have infrared absorptions corresponding to the asymmetric POO^- stretch in the $1124\text{--}1284\text{ cm}^{-1}$ range and the symmetric POO^- stretch in the $1052\text{--}1121\text{ cm}^{-1}$ range [195,196(p. 160),198,202]. In several studies on phosphoric-acid-diester salts, for example, the di-n-butyl [203], dimethyl, diethyl, di-iso-propyl [197], and *bis*-(2-ethylhexyl)[199] compounds, the asymmetric-stretching band was reported between 1190 and 1240 cm^{-1} and the symmetric-stretching band between 1020 and 1100 cm^{-1} . Thus, the bands around 1220 cm^{-1} in the resin spectra are assigned to

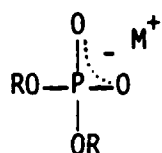
the POO^- asymmetric stretch and the bands around $1020\text{--}1050\text{ cm}^{-1}$ are assigned to the symmetric POO^- stretch coupled with the P-O-C asymmetric stretch. The weak peak or shoulder (a shoulder in most spectra, medium intensities in the Na^+ - and K^+ -form spectra) in the $940\text{--}960\text{ cm}^{-1}$ region in most of the spectra is not readily assignable, although peaks below 1000 cm^{-1} have been observed in the spectra of di-n-butyl phosphate [203] and other dialkylphosphate salts [197]. Assignment of this peak to the antisymmetrical P-O stretch of the esterified PO_2 group has been proposed [197]. The P-O-C symmetric stretch may be shifted to this frequency range in ionized ethylphosphate esters [196(p. 182)].

The infrared-spectral characteristics of the phosphate resins further confirm the structure of the ionogenic groups. It has been pointed out that the highest-frequency P-O stretching mode for salt derivatives can be used to distinguish monobasic phosphate diesters from dibasic phosphate monoesters [204]. The highest P-O frequency for monobasic salts occurs at about 1200 cm^{-1} , while that for dibasic salts occurs below 1150 cm^{-1} . This is consistent with our data for the PME and Et-PDE resins, the antisymmetric PO_2^- stretch absorbing around 1220 cm^{-1} for the Et-PDE resin forms and the antisymmetric PO_3^{2-} stretch absorbing around $1100\text{--}1040\text{ cm}^{-1}$ for the PME resin forms.

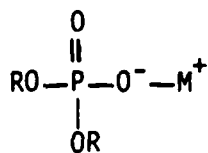
Some indication of the nature of the interaction of the cations with the phosphate groups of the resin should be derivable by noting the dependence of the positions of the symmetric and asymmetric phosphate-group frequencies as a function of the ionic form. Several correlations have been made in the literature between the cation and the relative positions of these absorption bands in simple phosphoric-acid-ester molecules [197,198,199,203], phosphinic-acid-ester molecules [205],

phosphonic-acid-ester molecules [206], and in cation-exchange resins containing phosphonic-acid-ester functional groups [185,187,188,189]. For example, in a study of 19 salts of di-n-butylphosphate, the bonding in the Na^+ and Ba^{2+} compounds was judged to be the most ionic based on the high wavenumbers for the asymmetric PO_2^- stretch in their spectra [203]. For the salts of the other cations, varying degrees of covalency and complexation were proposed based on shifts of the PO_2^- asymmetric stretch to lower wavenumbers. Also, in the study of nine salts of *bis*-(2-ethylhexyl)- and *bis*-(p-1,1,3,3-tetramethylbutyl)-phosphoric acid, a linear relationship was established between the splitting of the asymmetric and symmetric PO_2^- peaks and the ratio of charge to ionic radii of the cations [198]. For more electronegative cations (high charge/radius ratio), the splitting of the two peaks was reduced. It was proposed that more covalent interactions of the cations with the phosphate-diester groups result in increases in the positions of the higher-wavenumber PO_2^- -stretching bands. Similar results were found for salts of *bis*-(2-ethylhexyl)-phosphoric acid [199]. Other such correlations have been noted for other disubstituted phosphoric acids [196(p. 162)].

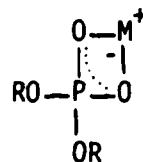
The various possible interactions of a cation M^+ with a phosphate-diester group can be schematically represented as follows:



(a)



(b)



(c)

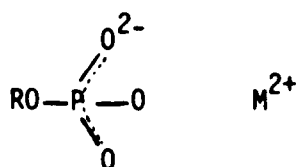
In (a), the interaction is purely ionic and symmetric and asymmetric stretching peaks would be expected in the spectrum. This would likely be the case for the alkali salts. For (b), a covalent interaction of the cation with the P=O group would increase the bond order of the P=O group and hence shift the asymmetric band to higher frequencies. The symmetric band would also be affected. For (c), complexation involving bonding of the metal to the P=O group reduces the bond order and would cause a downward shift of the asymmetric stretching peak. Similar arguments apply to bonding in the salts of phosphinic and phosphonic acids. Cases (b) and (c) probably apply to the polyvalent cation salts.

Investigators of the infrared spectra of various phosphonic-acid cation-exchange resins in different ionic forms [187] concluded that ionic interactions govern the bonding in the Na^+ -, Ca^{2+} - and Mn^{2+} -forms while changes in the positions and intensities of the significant peaks for the Cu^{2+} -, Co^{2+} -, Ni^{2+} -, Zn^{2+} -, Cd^{2+} - and Ag^+ -forms result from some degree of coordination. UO_2^{2+} ions were determined to form bidentate complexes with the phosphonate groups while Cu^{2+} and Ni^{2+} formed unidentate complexes [185,188]. Based on measurements of the electrical conductivity of various salts of organophosphorus acids, Kennedy [207,208] concluded that bonding is ionic for the Group IA and IIA ions, but is covalent for other ions. Other authors [69,80] are of the opinion that bonding is ionic only for the Group IA forms.

6.1.3.1 Effect of Counterion - Resin PME-I.

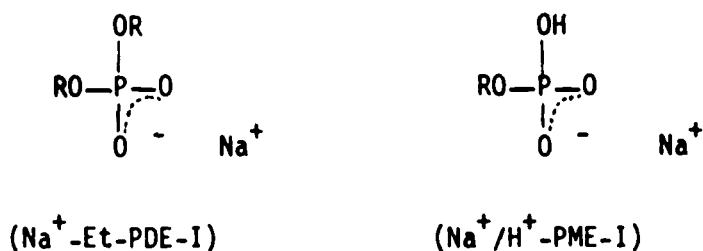
The spectra in the $900\text{--}1300\text{ cm}^{-1}$ range of the 14 ionic forms of the PME resin fall into three distinct groups: the H^+ - and NH_4^+ -form spectra; the Na^+ -, K^+ -, Mg^{2+} -, Ca^{2+} - and Ba^{2+} -form spectra; and the Co^{2+} -, Cu^{2+} -, $\text{Cu}(\text{NH}_3)_4^{2+}$ -, Zn^{2+} -, Cr^{3+} -, La^{3+} - and UO_2^{2+} -form spectra.

The H^+ -form spectrum is unique since it represents the un-ionized ROPO_3H_2 group (see p. 175). The equivalence of the NH_4^+ -form spectrum to that of the H^+ -form is the result of the conversion to the H^+ -form during drying of the NH_4^+ -form resin at elevated temperature. The similarity of these two forms was also noted from the water content data (see section 5.4). The H^+ - and NH_4^+ -spectra for carboxylic-acid resins were also found to be equivalent [23]. The similarity of the spectra of the Na^+ -, K^+ -, Mg^{2+} -, Ca^{2+} - and Ba^{2+} -forms implies that these cations bond to the resin functional groups in essentially the same manner. The NH_4^+ -form would be expected to fall into this group. All of these spectra show similarly contoured absorption maxima between 1110 and 1060 cm^{-1} , and each has a distinct, relatively sharp PO_3^{2-} symmetric stretching band below 1000 cm^{-1} , the position of which varies somewhat with ionic form. A definite trend is observed for the Group IIA ions, the symmetric-stretching band increasing in wavenumber and decreasing in intensity with increasing charge/size ratio (970 cm^{-1} (s) for Ba^{2+} , 990 cm^{-1} (m) for Ca^{2+} and 1000 cm^{-1} (w) for Mg^{2+}). A similar effect has been observed for the Group IIA cations in the salts of other phosphorus oxy-acids [69]. A similar trend (reversed) holds for the two Group IA cation forms [980 cm^{-1} (s) for K^+ and 975 cm^{-1} (m) for Na^+]. Because of the complexity of the absorption in the region of the PO_3^{2-} asymmetric stretch, shifts in this band could not be clearly judged, although changes in the contour of the peak were evident. The disappearance of the P=O stretching band and the appearance of the asymmetric PO_3^{2-} peak lead to the conclusion that the bonding in these ionic forms of the PME resins is essentially ionic, implying structures of the sort:

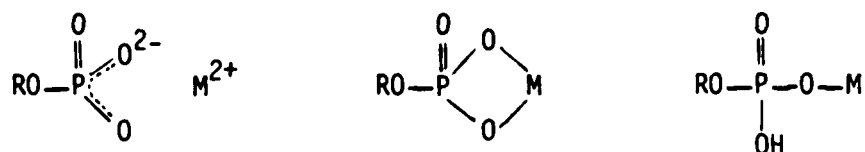


A small, broad peak at 905 cm^{-1} , present in the spectra of the Group IA-cation forms and absent in the spectra of the Group IIA-cation forms, constitutes the major difference between the spectra of the ionic forms of the two cation types. The exact assignment is uncertain, but the absorption is undoubtedly associated with the PO_3^{2-} group. Three peaks attributed to the PO_3^{2-} group were found on the spectrum of the Na^+ -form of phosphonic-acid exchangers [189]. This spectral difference may reflect some difference in the modes of interaction between the two counterion types with the monoester functional groups of the resin.

The spectrum of the mixed Na^+/H^+ -form of resin PME-I is distinct from those of the H^+ - and Na^+ -forms. The broad absorption at 1200 cm^{-1} is considerably increased in intensity and somewhat sharpened as compared to the 1200 cm^{-1} band on the H^+ -form spectrum. There is a broad peak at 935 cm^{-1} , higher in intensity than the 905 cm^{-1} peak on the Na^+ -form spectrum, and the large absorption between 1020 and 1060 cm^{-1} appears sharper than the corresponding band on the Na^+ -form spectrum. In general, the spectrum of the mixed Na^+/H^+ -form of resin PME-I resembles that of the Na^+ -form of resin Et-PDE-I. This would be expected since the structures of the functional groups in these two resin forms are analogous:



For the third group of ionic forms, the di- and trivalent transition-metal cations and the UO_2^{2+} ion, the spectra in the 900-1300 cm^{-1} region consist primarily of a single, broad, complex absorption, in most cases with distinct shoulders on the low- and high-wavenumber sides of the main peak. The bonding in these ionic forms likely involves some degree of complexation. Most importantly, the absence of the symmetric PO_3^{2-} band below 1000 cm^{-1} (although a shoulder persists in some of the spectra) and the lack of appearance of any significant increase in absorption at 1200 cm^{-1} corresponding to the P=O group rules out structures of the type:



The shoulder at 1000 cm^{-1} may correspond to a highly shifted symmetric PO_3^{2-} band; however, more definite statements cannot be made based on these data. We conclude that the bonding in these ionic forms is composed of a mixture of ionic, covalent and coordinate contributions. The spectra of the trivalent-counterion forms Cr^{3+} and La^{3+} differ slightly from those of the divalent transition cations. In the Cr^{3+} - and La^{3+} -form spectra, the shoulder at 1000 cm^{-1} is more prominent and a

broad, more distinct absorption over the 1100-1200 cm^{-1} range is evident. These characteristics are further indicative of multiple types of interactions with the resin functional groups, especially in the trivalent-ionic forms in which electroneutrality requires bonding of the counterion with more than one functional group. Additional peaks in the 900-1000 cm^{-1} region for the UO_2^{2+} -form spectrum are due to vibrations of the uranyl groups [188].

6.1.3.2 Effect of Counterion - Resin Et-PDE-I.

The spectra of the 14 ionic forms of resin Et-PDE-I in the 900-1300 cm^{-1} region are sharper than those of resin PME-I. This allows for more detailed comparisons among the individual spectra. There are two major absorptions in this region for all of the ionic forms. The band between 1020 and 1060 cm^{-1} , assigned as the combination of the symmetric PO_2^- stretch and the P-O-C symmetric stretch, comes to a relatively broad maximum which is complicated by several shoulders. The contour of this band changes with ionic form; however, its complex nature obviates a detailed analysis of these changes.

The peak around 1200 cm^{-1} is more interesting. From Table 6-3, a definite dependence of its position on the ionic form is evident. For the H^+ -form, this absorption lies at the highest frequency (1230 cm^{-1}), and corresponds to the hydrogen-bonded P=O stretch. For the other ionic forms, this peak corresponds to the asymmetric PO_2^- stretch, and is shifted to lower frequencies. That this band reflects P=O absorption in the salts has been ruled out [196(p. 159)]. For the Na^+ -, K^+ -, NH_4^+ -, Mg^{2+} -, Cr^{3+} - and La^{3+} -form spectra, the maximum of this band is at ca. 1220 cm^{-1} . For several other of the ionic forms [Ca^{2+} , Ba^{2+} , Co^{2+} , Cu^{2+} and $\text{Cu}(\text{NH}_3)_4^{2+}$], the position is shifted to even lower

wavenumbers (see Table 6-3). Covalent interactions or complex formation of the cation with the phosphoryl oxygens would lead to lowering of the frequencies of the PO_2^- vibrations. Under this assumption, we would conclude that the Co^{2+} , Cu^{2+} , Ba^{2+} and Ca^{2+} ions undergo such interactions, based on the positions of the asymmetric PO_2^- bands listed in Table 6-3 for the corresponding ionic forms. We would expect the Cr^{3+} , La^{3+} and UO_2^{2+} ions to behave similarly; however, the positions of the asymmetric PO_2^- stretching bands in their spectra are not duly affected.

Closer examination of the spectra reveals another spectral parameter which may be indicative of the cation-phosphate interactions. In Table 6-5 are listed the ratios of the intensity of the symmetric PO_2^- absorption at ca. 1020 cm^{-1} to that of the asymmetric PO_2^- absorption at ca. 1200 cm^{-1} for 12 of the Et-PDE-I spectra. Excepting the H^+ -form, the cations fall into three groups: the Group IA cations (ratios ca. 1.1 - 1.2), the Group IIA cations (ratios ca. 1.4) and the transition and UO_2^{2+} cations (ratios ca. 1.5 - 2.1). The asymmetric PO_2^- stretch is of maximum intensity in the Group IA ionic forms, in which ionic bonding is predominant. For the Group IIA ionic forms, the reduced intensity of the asymmetric PO_2^- band is indicative of a stronger association of the counterion with the PO_2^- group. For the remaining forms, this association is maximized, the asymmetric PO_2^- band exhibiting the lowest intensities for these forms. As expected, the Zn^{2+} -ionic form falls nearest the Group IIA forms.

One other feature of the Et-PDE-resin spectra in the $900\text{--}1300\text{ cm}^{-1}$ region requires mention. An absorption occurs between 940 and 960 cm^{-1} in most of the spectra, the band being strongest in the alkali cations forms, weaker in the alkaline-earth cation forms, and reduced

TABLE 6-5. RATIOS OF INTENSITIES OF SYMMETRIC/ASYMMETRIC PO_2^- STRETCH
FOR RESIN Et-PDE-1.

<u>Ionic Form</u>	<u>I_{1020}/I_{1200}^a</u>
H^+	1.7
Na^+	1.2
K^+	1.1
Mg^{2+}	1.4
Ca^{2+}	1.4
Ba^{2+}	1.4
Co^{2+}	1.9
Cu^{2+}	2.0
Zn^{2+}	1.5
Cr^{3+}	2.1
La^{3+}	1.7
UO_2^{2+}	1.8

^a Ratio of intensity of the 1020 cm^{-1} band to intensity of the 1200 cm^{-1} band. Uncertainty ca. ± 0.1 .

to a shoulder in the other ionic forms. This band is associated with the PO_2^- group, but a definite assignment is not offered.

6.1.3.3 Conclusion. The general trends observed in the spectra of the ionic forms of resin Et-PDE-I are in line with those derived for the PME-I resin ionic forms. Association to the phosphate functional groups becomes more prevalent in the series: Na^+ , K^+ < Mg^{2+} , Ca^{2+} , Ba^{2+} < Co^{2+} , Cu^{2+} , Zn^{2+} , Cr^{3+} , La^{3+} , UO_2^{2+} . These conclusions are consistent with the the selectivity data of Chapter Five, where resin selectivities increase in the series Na^+ < Ca^{2+} < Cu^{2+} < Cr^{3+} . Similar cation-functional-group interactions in the two resin types are implied.

The IR spectra of the ionic forms of the PME and Et-PDE resins have been used to further distinguish the natures of the ion-exchange groups and to obtain some general indications as to the cation-phosphate bonding. The broadness and complexity of the major absorption bands in the significant spectral region precludes a more detailed analysis of these parameters.

6.2 Electrical Conductivities of the Resins.

The determination of the electrical conductivities of packed beds of the phosphoric-acid cation-exchange resins serves as another physicochemical characterization of these materials. In this section, we present the results from the measurements of the electrical conductivities of four ionic forms of the PME and Et-PDE resins.

The conductivities for a few ion-exchange resin systems have been studied. The strong-acid polystyrenesulfonate-type exchangers have received the most attention [223-228], while data for a weak-acid polymethacrylate resin have been reported [229,230]. The conductivities

of several ion-exchanger types as a function of pH have been reported [228]. Conductivity data have been used in the formulation of models for electrical conduction through packed beds of ion exchangers [1(p. 489),225-227,231]. Ion-exchanger conductivities have also been related to the ionic mobilities [229] and the diffusion coefficients [224] of the counterions in the resin phase. Most interesting for our purposes is the relationship between the observed electrical conductivities of various ionic forms of the exchangers and the tightness of binding of the counterions to the resin functional groups [223,229,232]. Comparisons among the conductivities for the H^+ -, Na^+ -, Ca^{2+} - and Cu^{2+} - forms of the PME and Et-PDE resins further elucidate the bonding in these cation-exchange resins.

6.2.1 Experimental Procedures.

Several methods have been applied to the measurement of the electrical conductivities of ion-exchange resins. The most accurate techniques involve resins formed into rods, ribbons and membranes [1(p. 333),229,233]. Alternatively, packed beds of spherical resin particles immersed into conducting electrolytic solutions have been utilized. The so-called conductivity streaming cell has been described for this purpose [223,226,227]. Since we wished to obtain conductivity measurements from which general trends among the various ionic forms could be deduced, we adopted a less accurate but more convenient packed-bed technique.

The conductivities of packed beds of the PME and Et-PDE resins were determined by the dip cell method. The conductivity cell consists of a 2.5 cm diameter x 5 cm long weighing bottle, fitted with a Barnstead Plastic Dip Cell (#B2-03412, Barnstead Co., Boston, Mass.). The latter

is comprised of a molded epoxy body with two 3 mm diameter x 4 cm long platinized nickel electrodes, spaced 4 mm apart with 2.5 cm of rubber insulation. The body of the electrode module is fitted through a rubber stopper which is notched to fit into the weighing bottle in a reproducible manner.

The conductivities of the H^+ -, Na^+ -, Ca^{2+} and Cu^{2+} -forms of resins PME-I and Et-PDE-II were measured. Since the resin particles used in these experiments should be spherical and fairly uniform in size [224], the PME-I and Et-PDE-II resin samples were screened in the air-dried Na^+ -forms, and particles between 140 and 100 mesh were employed. The resin forms were prepared by treatments with excess HCl, NaOH, $Ca(NO_3)_2/Ca(OH)_2$ and $CuSO_4$ for the H^+ -, Na^+ -, Ca^{2+} - and Cu^{2+} -forms, respectively, followed by brief water rinses. The sample of each ionic form was then divided into portions of ca. 10 ml bed volume. Each portion was equilibrated with a solution of the appropriate cation [HCl, NaCl, $Ca(NO_3)_2$, $CuSO_4$] at a certain concentration by slowly running ca. 230 mL of the solution through the resin in a column. The resin portions were then transferred in the equilibrating (interstitial) solution to weighing bottles, covered, and equilibrated for an additional 24 hours in a constant temperature bath at 30°C. Samples of the interstitial solutions were also equilibrated at 30°C in separate weighing bottles.

The conductance measurements were made by immersing the dip cell into the equilibrated resin bed such that the level of resin was at least 0.5 cm above the exposed electrodes and the level of the interstitial solution was at least 1 cm above the resin level. The resin beds were tapped to eliminate air bubbles and to assure efficient

packing of the spheres, and the system was equilibrated for another 30 minutes at 30°C before the conductance readings were taken. A Wayne-Kerr bridge (Wayne-Kerr Laboratories, Chessington, England) was used for the electrical measurements. At least 15 minutes were required to obtain stable readings. The conductances of the interstitial solutions were taken in a similar manner.

The cell constant was obtained by measuring the conductance (L , in ohm^{-1}) of a 0.1 N KCl solution at 30°C. We found $L = 44.55 \pm .07 \times 10^{-3} \text{ ohm}^{-1}$ (average of six readings). The specific conductivity (κ , in $\text{ohm}^{-1}/\text{cm}$) of a 0.1 N KCl solution at 30°C was estimated by plotting the data of Kortüm and Bockris [234] for 0.1 N KCl at 0°C, 18°C and 25°C and extrapolating the straight line to 30°C. The result was $\kappa = 14.0 \times 10^{-3} \text{ ohm}^{-1}/\text{cm}$. The cell constant (C) is obtained from the equation:

$$\kappa = C \cdot L \quad (6.1)$$

giving $C = 0.314 \text{ cm}^{-1}$. Knowing the cell constant, all conductance values measured were converted to specific conductivities using equation 6.1. The cell constant was checked periodically during the experiments.

The inherent conductivities of the resin beads were determined by plotting the conductivity of the packed bed, which had been equilibrated with an interstitial solution of the counteranion, versus the conductivity of the interstitial aqueous solution [225,227]. For each ionic form, four such points near the isoconductance point (see below) were plotted. For the H^+ -forms, the interstitial HCl solution

concentrations ranged from 0.004 N to 0.01 N for resin PME-I and from 0.001 N to 0.004 N for resin Et-PDE-II. For the Na^+ -forms, the concentrations of the interstitial NaCl solutions ranged from 0.02 N to 0.06 N. For the Ca^{2+} -forms, the $\text{Ca}(\text{NO}_3)_2$ solutions were 0.001 N to 0.02 N for resin PME-I and 0.0007 N to 0.007 N for resin Et-PDE-II; and for the Cu^{2+} -forms, the CuSO_4 concentrations ranged from 0.0008 N to 0.01 N for resin PME-I and from 0.0002 N to 0.003 N for resin Et-PDE-II. From the curves so obtained, the unique point at which the conductivity of the packed bed of resin equals the conductivity of the interstitial solution, termed the isoconductance point, is read [1(p. 324), 225, 227, 235]. At the isoconductance point, the resin-bead conductance (our objective) equals the interstitial-solution conductance. The resin conductivities derived from the isoconductance points directly reflect the electrical-conductance characteristics of the resin bead, avoiding the necessity of applying any one of a number of models to the resin-solution system [227] in order to derive the resin conductivity.

6.2.2 Results and Discussion.

The plots of bed conductivity versus solution conductivity are presented in Figure 6-3 for the H^+ - and Na^+ -forms of resins PME-I and Et-PDE-II and in Figure 6-4 for the Ca^{2+} - and Cu^{2+} -forms. The conductivities of the four ionic forms of each resin obtained from these plots are summarized in Table 6-6 along with the equivalent conductivities of the aqueous cations. Interpretation of conductivity data for packed beds of ion exchangers is subject to several complicating factors. Primary among these are the dependence of the conductivity on the state of swelling of the resin particles [223, 229] and the influence of sorbed electrolyte [225, 227]. The latter is significant for interstitial solutions above

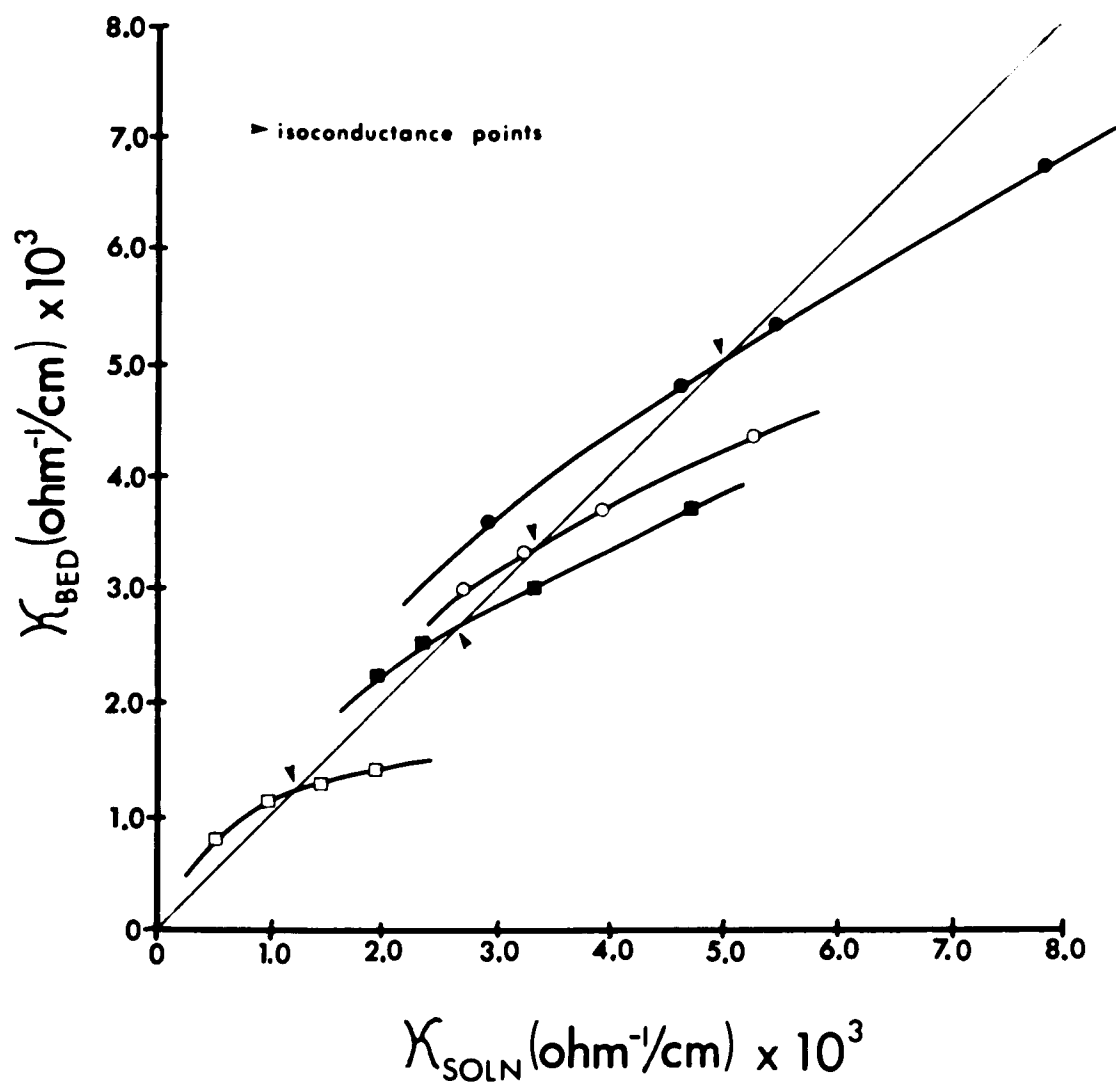


Figure 6-3
Resin Conductivities (30°C)

PME-I	Et-PDE-II
• Na ⁺ -form	◦ Na ⁺ -form
▪ H ⁺ -form	◻ H ⁺ -form

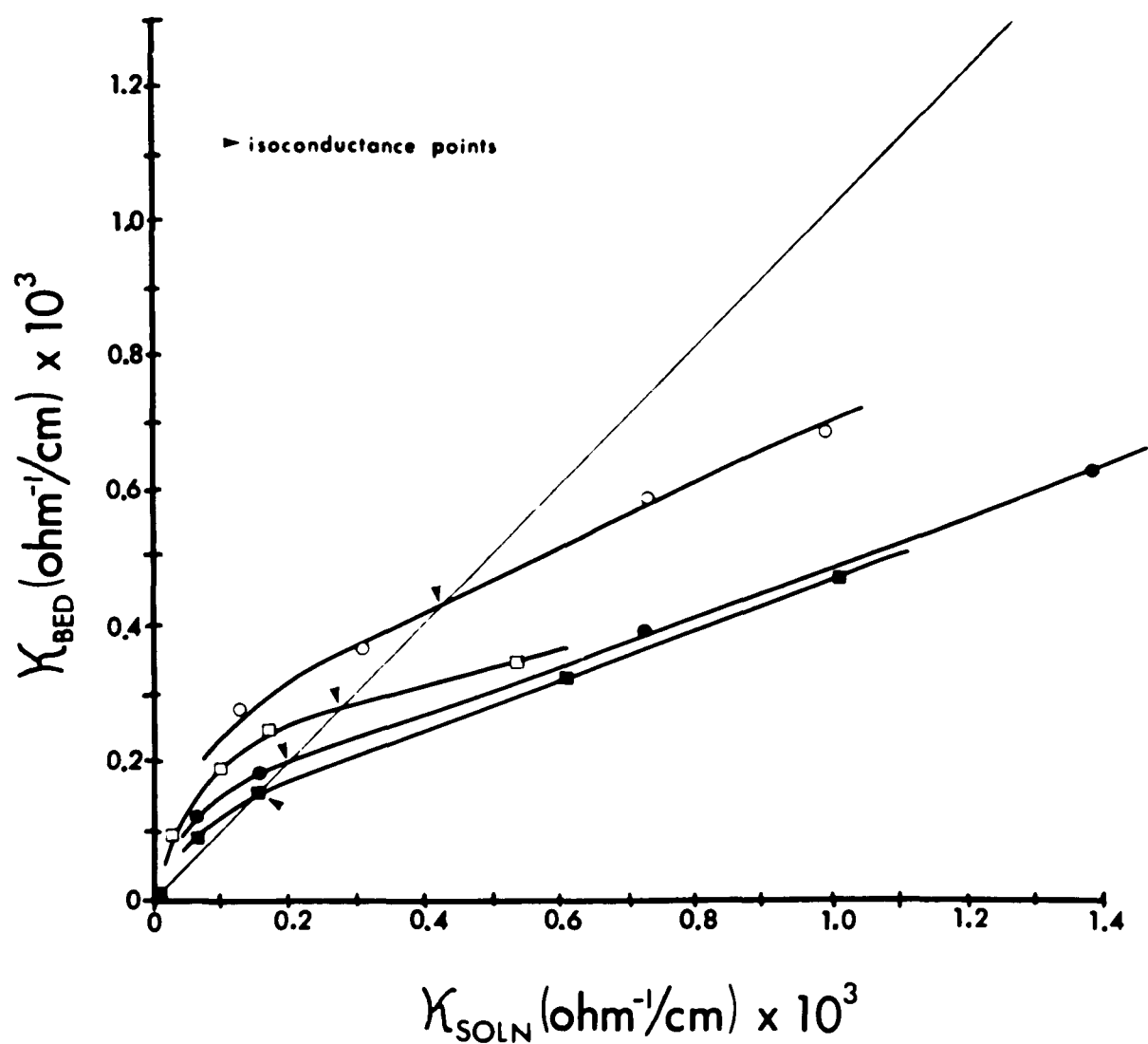


Figure 6-4
Resin Conductivities (30°C)

PME-I	Et-PDE-II
● Ca ²⁺ -form	○ Ca ²⁺ -form
■ Cu ²⁺ -form	□ Cu ²⁺ -form

TABLE 6-6. SPECIFIC ELECTRICAL CONDUCTIVITIES OF THE RESINS (30°C).

Resin	Ionic Form	Isoconductance Point ^a (ohm ⁻¹ /cm x 10 ³)	Aqueous Conductivity ^b (ohm ⁻¹ /cm)
PME-I	H ⁺	2.71 ± .06	349.8 (H ⁺)
	Na ⁺	4.97 ± .06	50.11 (Na ⁺)
	Ca ²⁺	0.210 ± .015	59.5 (Ca ²⁺)
	Cu ²⁺	0.157 ± .015	54 (Cu ²⁺)
Et-PDE-II	H ⁺	1.27 ± .06	
	Na ⁺	3.45 ± .06	
	Ca ²⁺	0.460 ± .015	
	Cu ²⁺	0.240 ± .015	

^a Obtained from Figure 6-1 for the H⁺- and Na⁺-forms and from Figure 6-2 for the Ca²⁺- and Cu²⁺-forms. Error estimates based on uncertainties in conductances for each data point and for the cell constant determinations.

^b Ref. 236.

0.1 M [227].

The relative tightness of binding of the various counteranions can be estimated by comparing the conductivity ratios for pairs of resin ionic forms with ratios calculated for the corresponding aqueous cations. Similar comparisons have been discussed for other resins [223,232]. In Table 6-7 are listed the conductivity ratios for the various pairs of ionic forms of resins PME-I and Et-PDE-II and the corresponding ratios for the aqueous cations. The patterns evident in these data are in general agreement with our results obtained in the selectivity, infrared-spectral and water-content studies. For instance, the H^+/Na^+ conductivity ratios are much lower for both resins relative to the conductivity ratio for the H^+/Na^+ aqueous cations, as expected considering the moderately weak-acid nature of the ionogenic groups. This result is also consistent with (1) the high-selectivity coefficient measured for the H^+/Na^+ system ($\log K_{Na}^H$ nearly 1 for resin PME-II), (2) the covalent bonding in the H^+ -forms versus the ionic bonding in the Na^+ -forms indicated from the IR spectra, and (3) the high water contents of the Na^+ -forms relative to the H^+ -forms (Na^+ -form contents more than 50% greater than the H^+ -form contents). The trends in the conductivity ratios are also in line with the general selectivity sequence determined for these resins, $Na < Ca < Cu$ (see Table 6-7 for $\log K$ values). The relatively high resin preference for copper over calcium ($\log K_{Ca}^{Cu} = 0.93$ for resin PME-II) is reflected in the fact that, for both resin PME-I and Et-PDE-II, the Ca^{2+}/Cu^{2+} conductivity ratios are higher than the aqueous ratio. Also, in the H^+/Ca^{2+} , H^+/Cu^{2+} , Na^+/Ca^{2+} and Na^+/Cu^{2+} systems, the conductivity ratios involving Cu^{2+} are consistently higher than the corresponding ratios involving Ca^{2+} . These results indicate lower mobilities and

TABLE 6-7. CONDUCTIVITY RATIOS.

Counterion Pair(M_2/M_1)	Resin ^a PME-I	Resin Et-PDE-II ^a	Aqueous ^a Cations	$\log K_{M_1}^{M_2}$ ^b
H^+/Na^+	0.55	0.37	6.98	0.98
H^+/Ca^{2+}	12.9	2.76	5.88	-
H^+/Cu^{2+}	17.3	5.29	6.48	0.20
Na^+/Ca^{2+}	23.7	7.50	0.84	-1.23
Na^+/Cu^{2+}	31.7	14.4	0.93	-1.76
Ca^{2+}/Cu^{2+}	1.34	1.92	1.10	-0.93

^a Data from Table 6-6.

^b Logarithm of selectivity coefficient for resin PME-II. Values for H^+/Na^+ , H^+/Cu^{2+} and Ca^{2+}/Cu^{2+} obtained from Table 5-8. Values for the Na^+/Ca^{2+} and Na^+/Cu^{2+} systems calculated using the triangle rule (see section 5.5).

hence stronger interactions of the Cu^{2+} ions with the phosphate groups.

Comparison of the $\text{H}^+/\text{Ca}^{2+}$ and $\text{H}^+/\text{Cu}^{2+}$ systems for both resins provides some insight into the differences in binding of the Ca^{2+} and Cu^{2+} counterions to the PME and PDE functional groups. For the $\text{H}^+/\text{Ca}^{2+}$ and $\text{H}^+/\text{Cu}^{2+}$ systems, the conductivity ratios listed in Table 6-7 are higher in the case of resin PME-I and lower in the case of resin Et-PDE-II than the respective conductivity ratios for the aqueous cations. In both resins, the magnitudes of the ratios correspond to Ca^{2+} and Cu^{2+} mobilities lower than the H^+ mobility. The difference lies in comparison to the aqueous systems. For resin PME-I, the higher $\text{H}^+/\text{Ca}^{2+}$ and $\text{H}^+/\text{Cu}^{2+}$ conductivity ratios (12.9 and 17.3, respectively) relative to the aqueous ratios (5.88 and 6.48) imply significant hinderance of the divalent-cation mobilities over the H^+ mobility. For resin Et-PDE-II, the somewhat lower $\text{H}^+/\text{Ca}^{2+}$ and $\text{H}^+/\text{Cu}^{2+}$ conductivity ratios (2.76 and 5.29, respectively) imply that the Ca^{2+} and Cu^{2+} ions are less hindered than the H^+ ions relative to the aqueous system. The quite low Ca^{2+} and Cu^{2+} mobilities in the PME resin may indicate a strong complexation effect between these divalent counterions and the dibasic functional groups. The lack of data on phosphate complexes in aqueous systems and the low solubilities of most phosphates obviate a comparison of these results to simpler systems. The interactions of the divalent ions in the PDE resin are less associative than the proton interaction with the monobasic PDE group. Electroneutrality requires that two functional groups of the PDE resin bond with the divalent counterion, which may inhibit the counterion associations (complexations) possible in the PME resins, and account for the higher Ca^{2+} and Cu^{2+} mobilities in the PDE resin. However, the infrared, selectivity and water-content data do point to

strong divalent cation interactions with the PDE groups, at least relative to the Na^+ -form.

The origins of the two resins used in this conductivity study allow for direct comparisons between the electrical properties of the PME and PDE materials. Since resin Et-PDE-II was prepared by esterification of the phosphoric-acid-monoester groups of resin PME-I and the capacity data reflected an essentially quantitative conversion (see Chapter Three), comparison of the conductivities of a particular ionic form of each resin directly reflects the differences in binding of the counteraction to the two types of phosphate functional groups. The conductivity of the H^+ -form of resin PME-I is about twice that of resin Et-PDE-II, an expected result for resin PME-I (which contains twice as many exchangeable protons), provided that the dissociability of the protons is the same in the two resins. The conductivity of the Na^+ -form of resin Et-PDE-II is less than that of resin PME-I, but by 31% more than the expected one-half reduction in conductivity. Apparently, the Na^+ ions associated with the stronger-acid groups of the monoester resin are responsible for a greater fraction of the electrical conductance. This result is consistent with the water contents measured for the fully-loaded Na^+ - and half-converted H^+/Na^+ -forms of the PME resin, where it was found that the Na^+ ions associated with the stronger-acid groups accounted for most of the water content (see section 5.4). The conductivities of the Ca^{2+} - and Cu^{2+} -forms of resin PME-I are lower than those of resin Et-PDE-II. Assuming similar bonding in the two resins, this would not be expected since the PME resin contains twice as many counteractions as the PDE resin. Again, there is implied a strong associative interaction of the divalent counterions with the PME functional groups.

In conclusion, our electrical conductivity data furnishes insights into the phosphoric-acid cation exchangers that fit neatly into the general characterization scheme. More careful measurements on a wider variety of ionic forms would prove fruitful in further elucidating the properties of these materials.

6.3 Proton Magnetic Resonance Spectra.

6.3.1 Introduction.

The application of proton magnetic resonance (PMR) spectroscopy to systems of ion-exchange resins has received considerable attention since the original work of Gordon [179]. A packed bed of ion exchanger in a solvent gives rise to distinct PMR spectra in which two solvent chemical shifts are usually observed. One peak is due to the solvent occupying the interstices between the resin particles (the "external" solvent), and the other peak arises from the solvent within the pores of the resin matrix (the "internal" solvent). The latter includes solvent involved in the solvation of the counterions and the ionogenic groups. The average chemical environments of the external and internal solvent are usually different and, since exchange between the external and internal solvent is slow [179,210], a separation between the internal-solvent and external-solvent PMR signals is generally produced. For the strong-acid cation exchangers swollen in water, two sharp PMR peaks are observed [179,211-214]. Broadening of the external-solvent peak is attributed to the difference in the diamagnetic susceptibilities of the solvent and the polymer beads [179]. The internal-solvent chemical shift is usually the sharper of the two signals, and appears as one line since proton exchange within the resin phase is rapid. The protons on the polymeric resin matrix are not observable due to the solid-like

environment in which they exist [24].

Several types of ion-exchange resins have been subjected to PMR spectroscopic investigations. Among these are the strongly acidic sulfonic-acid cation exchangers [179,210-222], the weakly acidic polymethacrylic-acid cation exchangers [24,212], phosphonous- and phosphonic-acid cation exchangers [212], and various strongly and weakly basic anion exchangers [210,212]. The sulfonated polystyrene resins produce the sharpest spectra, while the spectra of the polymethacrylic-acid resins generally display somewhat broader lines. Only the external water peak was observed for a phenol-sulfonic-acid resin [212], attributed to inhomogeneities in the resin particles. The phosphorus-containing cation exchangers Bio-Rex 62 and 63 gave extremely broad peaks for both solvent signals. Weakly-basic anion exchangers gave no spectra, while strongly-basic anion exchangers produced reasonable spectra. Gordon [179] originally proposed that broad signals resulted from inhomogeneities in the internal resin structure. Particle size and shape were shown not to significantly influence the spectra [211,212], although finely divided resin particles yielded somewhat broader PMR lines [212].

The PMR spectrum of an ion-exchange resin is usually described in terms of the chemical shift, defined as the displacement of the internal-solvent line from the external-solvent line. A major parameter found to correlate with the chemical shift is the internal molality of the resin (moles of counterion or ionogenic group per kilogram of solvent) [24,210-214,218], while the temperature, nature of the counterion and the nature of the resin ion-exchange group are also expected to contribute to the shift. The chemical shift increases nearly linearly with internal resin molality (from 0 to 10 m) for the sulfonated

polystyrenes [211-213]. The chemical shift also varies with the crosslinking and water content of a resin since these properties govern the internal molality. Thus, resins of higher crosslinking and lower water contents produce larger chemical shifts.

The physicochemical characterization of an ion-exchange resin can be further elucidated through PMR spectroscopy. It has been observed that the trends in chemical shifts for various ionic forms of sulfonated cation exchangers are analogous to those for aqueous systems [210,213,214]. Similar results were found for a carboxylic-acid cation exchanger [24]. These findings support the concentrated-polyelectrolyte model of ion-exchanger systems [218 and refs. therein].

PMR spectroscopy has been used particularly to study the structure of water in the strong-acid cation exchanger Dowex-50W [218]. Counteranions producing an upfield shift of the internal water peak relative to the external water peak are considered to be "structure breakers." These ions have relatively small charge/volume ratios, and tend to cause breakage of the hydrogen bonds of the solvating water molecules. Counteranions with relatively large charge/volume ratios, the "structure makers," which produce downfield shifts of the internal water peak relative to the external water peak, polarize the solvating water molecules.

A quantitative relationship between the observed chemical shift of the internal water protons and the equivalent fraction of counterions on a mixed-form resin has been observed by Howery and Kohn [215]. Thus, compositions of mixed form resins can be determined directly by PMR spectroscopy. The internal-water chemical shift in Dowex 50W has also been related to the mole fraction composition of binary aqueous solvents

[216,220]. From these measurements, solvent selectivities were determined.

Other PMR studies have been concerned with, for example, the solvation of the sulfonic-acid groups in ethanol-water solvents [219] and the calculation of volume magnetic susceptibilities for resins [217]. The ^{39}K [221] and ^{23}Na [222] pulsed-NMR spectra of cation-exchange resins have also been studied.

6.3.2 Experimental Procedures.

The resin ionic forms were prepared as previously described (see section 6.1.1). The resin samples used in the NMR experiments were carefully screened to obtain spherical beads of relatively uniform size. NMR tubes were filled with a resin-water slurry and were tapped to insure closest packing of the resin particles. A Varian T-60A spectrometer was employed.

6.3.3 Results.

A PMR spectroscopic study of our two phosphoric-acid-ester cation-exchange resins should provide additional information concerning the nature of the counterion-phosphate group interactions. Unfortunately, we observed a single combined internal-water and external-water chemical peak for all but one of the ionic forms that we tested. Only for the H^+ -form of the monoester resin (PME-I and PME-II) did we observe a low-intensity, broad, downfield chemical shift (ca. 70 Hz relative to the external-water peak). The internal molality of this ionic form is 8.0 m, significantly higher than the molalities calculated for any of the other ionic forms of either resin (molalities calculated from capacities and water contents). For example, the molalities for the Na^+ - and Ca^{2+} -forms

of resin PME-II are 3.4 and 3.5, respectively, and those for the H^+ -, Na^+ - and Ca^{2+} -forms of resin Et-PDE-II are 5.8, 3.0 and 2.6, respectively. These concentrations ordinarily would lead to observable chemical shifts. Our results may imply several conditions. The lack of a chemical shift can be due to an ordered internal water structure, internal resin inhomogeneities, or the possibility that the counterions do not influence a significant fraction of the internal water. The latter may be reasonable for polyvalent counteranions which show significant covalent interactions with the phosphate groups, but this explanation does not hold for the Group IA cations. However, the lower conductivities for the phosphate resins in comparison to those for Dowex 50 do indicate stronger associations of all counterions with the phosphate groups. These strong associations within the resin environment may obviate a measurable influence on the internal water.

APPENDIX

ANALYTICAL METHODSA.1 Digestion of Polymer Samples.

Resin intermediates encountered in the course of the synthetic sequence which contained functional groups amenable to quantitative analysis were used to monitor the degree of conversion in several reaction steps. Specifically, the polystyrylmethyl chloride, 2-polystyrylacetic acid and the final phosphoric-acid exchangers were analyzed. The 2-polystyrylacetic-acid resin was analyzed by titration (see section 3.7.3), while the chlorine- and phosphorus-containing polymers were digested into aqueous solution and analyzed.

Mineralization of these resins was accomplished by adaptation of the oxygen-flask combustion technique developed by Schöniger [110,111, 237]. The Schöniger method provides for a rapid quantitative analysis of the elemental content of solid and liquid organic compounds. The organic compounds are burned in pure oxygen, and the combustion products are absorbed into an aqueous medium and analyzed by standard methods. Among the elements that can be determined are the halogens, sulfur, phosphorus, arsenic, boron, carbon and various metals (for a review, see reference 237).

The apparatus consists of a specially-designed Erlenmeyer flask fitted with a ground-glass stopper that holds a platinum sample basket. Detailed descriptions are given elsewhere [237,238]. The flask may be purchased from SGA Scientific Co., Bloomfield, N.J. The basic procedure for analysis of a solid organic sample involves enclosing the solid in

a paper sample wrapper, fixing the latter into the platinum sample basket, introducing an absorbent solution, filling the flask with oxygen and igniting the sample. The combustion products are absorbed (digested) into the aqueous solution by shaking the flask for an appropriate time period, after which the flask is opened and the contents treated according to a standard analytical procedure.

In the specific application of the Schöniger oxygen-flask technique to our resin samples, the following procedures apply. The resin to be analyzed is ground in an agate mortar and pestle to a fine powder and dried for one to three days at 70°C in a vacuum oven. The sample wrappers are made from ashless filter paper. Pre-cut sample wrappers can be purchased from SGA Scientific Co. The pulverized resin sample (20-40 mg) is weighed into the sample wrapper, which had been trimmed down to a minimum size to avoid unnecessary consumption of oxygen during the combustion. The wrapper is then folded as described in reference 237, leaving an extended tab of paper to act as a wick. Approximately 10 mL of the absorbent solution are introduced into the flask, and the flask is filled by the downward displacement of air by oxygen. The wrapped sample is secured in the platinum sample basket, the wick is lighted by flame, and the stopper/basket assembly is quickly plunged into the flask, which is immediately inverted so that the absorbent solution seals the ground-glass joint between the stopper and the flask. When burning is complete, the flask is shaken for twenty to sixty minutes before opening and commencing the quantitative elemental analysis.

A.2 Determination of Chlorine.

We adapted a modified version of Schöniger's method [111]. Another application of the combustion technique to the determination of

of chlorine has been reported [239].

Chloromethylated copolymer samples (25-30 mg) are ground and dried as above. The digestion solution is composed of 4 mL of 2 N KOH, 2 mL of 30% H_2O_2 and 4 mL of H_2O . After combustion, the flask is shaken for 20 minutes, then opened. The stopper and sample holder are washed down, rinsing into the flask. Then, the solution is boiled for one minute to decompose any peroxides, cooled, and quantitatively transferred to a 150 mL beaker. The solution is acidified with 10 mL of 2 N HNO_3 . The total volume at this point is about 60-75 mL.

Analysis for chloride is performed by potentiometric titration [230,241], utilizing a silver electrode, a standard calomel electrode, and a Corning Model 12 meter. Silver nitrate (ca. 0.01 M) is standardized against primary sodium chloride [241].

The accuracy of the method was checked by combustion of 25-40 mg samples of a reference organochlorine compound, m-chlorobenzoic acid. The results of several analyses showed the accuracy to be within 2% and the precision to be about 4 parts per thousand. Analyses of the chlorine-containing resins were performed with precisions on the order of 7-15 parts per thousand, despite the solid residue left on the sample holder after combustion (see Chapter Three).

A.3 Determination of Phosphorus.

Two quantitative analytical methods were applied to the analysis of phosphorus in the phosphorylated resin samples. In the earlier synthetic work, the heteropoly blue (molybdenum blue) method was employed. The more convenient molybdiphosphoric acid method was used for the subsequent phosphorus analyses.

Boltz [66] gives a general overview of the methods available for the determination of total phosphorus, while Allen [242] discusses many details concerning the spectrophotometric determination of phosphorus. Several methods have been reported for the analysis of phosphorus-containing organic compounds by application of the oxygen-flask combustion technique [243-246]. Acid-digestion methods are also known [243]. Phosphorus can be indirectly determined by atomic absorption spectroscopy for molybdenum [247,248], but the method requires samples too large for our situation.

A.3.1 The Heteropoly Blue Method.

The heteropoly blue (or molybdenum blue) method for the spectrophotometric determination of phosphorus [243,244,249,250] is based on the formation of heteropoly complexes, characterized by the molybdiphosphate moiety, $[P(Mo_3O_{10})_4]^{3-}$, upon the reaction of inorganic orthophosphates with molybdates. These complexes can be reduced to a blue specie (molybdenum blue), the color intensity of which is a quantitative function of the phosphorus content.

We applied the following procedures to our resins. The reduction of the molybdiphosphate is done with hydrazine sulfate. The pulverized phosphorus-containing copolymer is dried at 70°C for one to three days. Samples containing 0.9 to 2.0 mg of phosphorus are used, corresponding to 15 to 30 mg of resin. The combustion is performed in the presence of an absorbent solution consisting of 10 mL of 10 N H_2SO_4 . The latter was found not to interfere in the subsequent analysis, whereas the nitric acid absorbent originally employed [244] oxidizes the blue complex. After a 30-minute digestion, with shaking, the flask is opened and washed down and the contents are boiled for two minutes (the boiling converts any pyrophosphates present to orthophosphate). After cooling,

the solution is quantitatively transferred to a 500 mL volumetric flask, which is diluted to the mark with water. A reference compound, diphenylphosphinic acid (10-15 mg), is also subjected to analysis.

The following solutions are prepared: standard phosphate solution (dissolve 0.1098 g of primary potassium dihydrogen phosphate, dried at 120°C for one day, in water to make 100 mL); phosphate stock solution (dilute 4 mL of the standard phosphate solution to make 250 mL of solution); 2.5% (w/v) sodium molybdate solution (dissolve 2.5 g of salt in 10 N H₂SO₄ to make 100 mL); 0.15% (w/v) hydrazine sulfate solution (dissolve 0.15 g of the compound in water to make 100 mL); reductant solution (prepare just before use by mixing 25 mL of the 2.5% sodium molybdate solution, 10 mL of the 0.15% hydrazine sulfate solution, and enough water to make 100 mL total).

In a typical analysis, 20 mL of the reductant solution, 25 mL of the sample solution (from the combustion) and sufficient water are mixed in a 50 mL volumetric flask. The mixture is then heated in a boiling-water bath for 10 minutes (to develop the color), cooled rapidly to room temperature, and adjusted to a volume of 50 mL. Calibration solutions are similarly prepared using appropriate volumes of the phosphate stock solution. The blue color is measured at 830 nm with a Beckman DU spectrophotometer, with water as the blank.

Analysis for phosphorus in the presence of chloride (for the halophosphorus intermediate resins in Chapter Four) was done by the addition of NaCl to the phosphate stock solution to give a chloride concentration of 2.56×10^{-4} M.

Accuracies within 7% were found for the reference combustions, and precisions on the order of 10 parts per thousand were obtained for

the resin analyses.

A.3.2 The Molybdiphosphoric Acid Method.

A more convenient analysis for phosphorus makes direct use of the yellow hue developed by the formation of molybdiphosphoric acid, $H_3[P(Mo_3O_{10})_4]$, in acidic solution [251]. In application of this technique to our resin samples, we also modified the combustion procedure [246] in order to eliminate the intermittent sparking and sooty fumes encountered in many of our previous combustions.

The absorbent solution consists of 10 mL of a 7 mg/mL solution of KCl. After filling the flask with oxygen, 0.5 mL of fuming nitric acid is introduced, and the combustion is commenced [246]. Digestion is carried out for one hour. The flask contents are then washed into a 150 mL beaker and boiled to dryness over a steam bath. (Using a flame or hot plate results in loss of phosphorus.) The residue is dissolved in 10-20 mL of water and washed into a 100 mL volumetric flask, then diluted to the mark.

Photometric determination of phosphorus requires the following solutions: phosphate stock solution (same as under the heteropoly blue method); 2.8 N nitric acid solution; 10% (w/v) sodium molybdate solution (dissolve 10 g of Na_2MoO_3 to make 100 mL total solution).

The yellow color is developed by mixing 20 mL of the sample solution, 5 mL of the 2.8 N HNO_3 solution, 5 mL of the 10% Na_2MoO_3 solution and sufficient water to make 50 mL total. Measurement is conducted at 420 nm. Appropriate volumes of the phosphate stock solution are used in place of the sample solution to establish a calibration curve.

Using this method, accuracies within 4% were found for the

reference compound and precisions on the order of 7 parts per thousand were obtained for the resin analyses.

A.4 Flame Photometric and Atomic Absorption Analyses.

We employed flame photometry for the analysis of sodium and potassium in the capacity and isotherm experiments. The flame photometer of the Process and Instruments Corp. (Brooklyn, N.Y.), which uses an internal lithium reference, was used. Calibration curves were established with NaCl solutions in the 0.5 to 5 mM range and KCl solutions in the 0.05 to 0.15 mM range. The volumes of all sample solutions were adjusted to produce Na^+ and K^+ concentrations within these ranges. All solutions for analysis were made 0.015 M in Li_2SO_4 .

Atomic absorption analysis for magnesium, calcium, copper, zinc and chromium was carried out with a Perkin-Elmer Model 372 atomic absorption spectrophotometer. Calibration standards were purchased from Fisher Scientific or prepared as directed in the instrument operation manual [252]. Sample-solution volumes were adjusted to give concentrations within the specified ranges [252].

A.5 Infrared Spectra.

Intermediate resins encountered in the synthetic sequence were analyzed by infrared spectroscopy. The procedures are identical to those described in section 6.1.1.

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