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STYRENE AND DIVINYLBENZENE COPOLYMER

by

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PART I

COPOLYMERIZATION KINETICS

INTRODUCTION

In 1944 a copolymerization equation[1,2,3] was developed which made it possible to determine monomer reactivity ratios. Monomer reactivity ratios are defined by the ratio of the rate constant for reaction of one type radical with its own monomer to the rate constant of that radical with some other monomer. These parameters give interesting information about copolymerization such as the nature of propagation steps, the mechanism involved, the copolymer composition and the nature of copolymer chains.

The classical methods of determining monomer reactivity ratios all involve polymerization of several initial monomer compositions to "low" conversion, isolation and purification of the polymer formed, compositional analysis, and fitting of the data to the differential form of the copolymerization equation by one of several techniques. In each case the assumption is made that the relative monomer concentrations do not change significantly from the initial conditions during the polymerization. This restriction dictates stopping the polymerization at "low" conversions in all cases which in many cases involves impractical experimental conditions.

Numerous advantages should therefore accrue from using one of the integrated forms[2] of the copolymerization equation, which permits use of the copolymerization data for high conversion copolymers. This form takes into account the drift in monomer feed and copolymer composition. This form also avoids errors encountered in the "low conversion" data, required for the differential studies, such as those arising from low molecular weight species formed by impurities and from the handling of small quantities of copolymer. However laborious calculations were required to handle the integrated form first introduced by Mayo and Lewis[2]. Nowadays a computer program[4] is available to handle the massive calculations for the integrated form.

We have, therefore, extended our studies of the differential copolymerization behavior[5,6,7] of the styrene and m-divinylbenzene, and styrene and p-divinylbenzene systems to such integral analyses with the objective of resolving some of the uncertainties presented by the data from the differential analyses. For example, the lack of intersection in the plots for the styrene and p-divinylbenzene system is particularly in need of clarification. By employing a computer program[8] it was also possible to usethe monomer reactivity ratios to calculate those aspects of copolymer structure that are related to the distribution of monomer sequences in their chain.

HISTORICAL

The most important type of addition polymerization is that of simple vinyl monomers such as ethylene, propylene, styrene, etc. In general, we now recognize four basic kinds of mechanisms[9] for polymerization of vinyl monomers — free radical, cationic, anionic, and coordination. Thermalpolymerization, photopolymerization, and polymerization initiated by peroxides, persulfates, or azo compounds, are examples of the free radical mechanisms. Acid- and base-catalyzed polymerization, initiated by sulfuric acid, boron fluoride, aluminum chloride, sodium amide, sodium alkyl or similar generalized acids and bases, proceed by an ionic (cationic or anionic) mechanism. The possibility of a fourth mechanism is essentially forced on us by the discovery of the Ziegler and other (mostly heterogenous) catalysts, which apparently do not involve "free" free-radicals, cations or anions, and which can and usually do lead to highly stereoregular polymers. In this thesis only addition polymerization by the free radical mechanism will be considered.

Free radical addition polymerization is a chain reaction, consisting of at least three steps: initiation, propagation, and termination. Polymerization initiated by peroxide proceeds by decomposition of the peroxide (I) into free radicals ($R\cdot$) which add to monomer units (M) starting the polymer chain.

$$I \longrightarrow 2R\cdot$$

$$R\cdot + M \longrightarrow M_1\cdot$$

Propagation proceeds by further addition of monomer units to this growing radical:

$$M_1\cdot + M \longrightarrow M_2\cdot$$

$$M_2\cdot + M \longrightarrow M_3\cdot$$

$$\cdots\cdots\cdots\cdots\cdots$$

$$M_x\cdot + M \longrightarrow M_{x+1}\cdot$$

Termination involves the deactivation of two growing chains by one of two different processes:

coupling,

$$M_x\cdot + M_y\cdot \longrightarrow M_{x+y}$$

or disproportionation,

$$M_x\cdot + M_y\cdot \longrightarrow M_x + M_y$$

where M_x, M_y, and M_{x+y} represent inactive polymer molecules having the numbers of units indicated by the subscript in each case.

When two different polymerizable monomers are mixed together, in the presence of an initiator, the resulting macromolecules in general contain monomer units of both types, since the growing chain free radicals can attack either type of monomer. Such a reaction is called copolymerization, and the resulting polymer is a copolymer. Alfrey, Bohrer and Mark[10] mentioned that one of the earliest works on copolymerization was carried out around 1911 by Bayer[11] who copolymerized isoprene and butadiene. Up to the early 1930's, the emphasis was placed mostly on the preparation and development of useful products, and no systematic attempt was made to elucidate the mechanism of copolymerization itself. It was, however, sometimes observed that a specific monomer would copolymerize easily with another specific monomer, whereas it would not do so with a third. In the course of numerous laboratory and pilot plant experiments to prepare various types of copolymers it was also repeatedly observed that the individual components were being used up at different rates, and that copolymer samples withdrawn at different degrees of conversions contained the two components in different ratios. In 1939 Staudinger and Schneider[12] described the fractionation of a vinyl chloride-vinyl acetate copolymer prepared from an equimolar mixture of the monomers. Chemical analysis of the fractions showed that none of them contained the monomers in a 1 : 1 ratio, but that their chemical composition varied from about 3 : 1 to 1 : 2. Norrish and Brookman[13] found that divinylbenzene produces insoluble gels with styrene, and with methyl methacrylate. They deduced from this behavior a different tendency of the divinyl monomer to enter the copolymerization reaction with the two monovinyl derivatives.

COPOLYMERIZATION EQUATION

The first published report of a mechanism for copolymerization came from Dostal[14] in 1936. In his treatment the behavior of a free radical depends on the nature of the terminal group of the radical chains and is independent of the length or overall composition of the polymer chains. Under these conditions only two types of radicals will exist in the copolymerization of any two monomers, and for long polymer chains the formation of the copolymer is determined by the four reactions:

$$\begin{array}{lll} \underline{\text{Reaction}} & \underline{\text{Rate}} & \\ M_1\cdot + M_1 \xrightarrow{k_{11}} M_1\cdot & k_{11}\,(M_1\cdot)(M_1) & \\ M_1\cdot + M_2 \xrightarrow{k_{12}} M_2\cdot & k_{12}\,(M_1\cdot)(M_2) & \\ M_2\cdot + M_2 \xrightarrow{k_{22}} M_2\cdot & k_{22}\,(M_2\cdot)(M_2) & (1) \\ M_2\cdot + M_1 \xrightarrow{k_{21}} M_1\cdot & k_{21}\,(M_2\cdot)(M_1) & \end{array}$$

where M_1 and M_2 represent the two monomers, and $M_1\cdot$ and $M_2\cdot$ represent radical chains ending in M_1 and M_2 units respectively. Dostal wrote out correct expressions for the rate of polymerization and the composition of a copolymer in these terms; but, since his expressions involved four or more unknown rate constants, he did not devise an experimental test of his conclusion.

In 1939, Norrish and Brookman[15] published an experimental study of the copolymerization of styrene and methyl methacrylate which provided the first reliable data for the theoretical analysis of a copolymerization reaction. In accordance with Dostal, they assumed that only the terminal link of a growing radical chain would be responsible for the specific rate of propagation and that the rate would be essentially independent of the length of the growing chain. To these simplifying assumptions, which have been essentially confirmed by experiment, they added another simplification — that the overall steady state radical concentration in a polymerizing mixture of the two components would depend upon catalyst concentration and not upon the composition of the mixture itself. This assumption, however, was later found to be an over simplification.

Wall[16] presented a relatively simple basis for studying copolymerizations. He defines the relative reactivity (α) of two monomers in copolymerization as the quotient of the rate constant for the individual polymerizations (k_1 and k_2, respectively): i.e.,

$$d(M_1)/d(M_2) = k_1(M_1)/k_2(M_2) = \alpha(M_1)/(M_2)$$

whereas (M_1) and (M_2) refer to concentrations of unreacted monomers. Actually Wall's equation applies only to the limiting case of ideal copolymerizations, where both radical types $M_1\cdot$ and $M_2\cdot$ have the same relative preferences for reacting with the monomers M_1 and M_2, i.e., where $k_{11}/k_{12} = k_{21}/k_{22}$. A general copolymerization equation must therefore allow for the individual preferences of certain radicals for certain monomers.

A satisfactory theoretical basis for comparing the behavior of monomers in copolymerization was published in three papers by Alfred and Goldfinger[1], Mayo and Lewis[2], and Wall[3]. This treatment may be stated as follows. In the copolymerization of the two monomers M_1 and M_2, the growing-chain radicals can be only of two kinds, those ending in an M_1 unit (designated $M_1\cdot$) and those ending in an M_2 unit ($M_2\cdot$). If we make the reasonable approximation that the reactivity of the growing-chain radical depends upon the nature of the radical end, the polymer chain is seen to be propagated by only four types of reactions (equation 1) described by Dostal[14]. In the formation of polymers of relatively high molecular weight the amount of monomer consumed in initiation may be neglected. Thus the rate of disappearance of M_1 and M_2 is

$$-\frac{d(M_1)}{dt} = k_{11}(M_1\cdot)(M_1) + k_{21}(M_2\cdot)(M_1)$$

$$-\frac{d(M_2)}{dt} = k_{12}(M_1\cdot)(M_2) + k_{22}(M_2\cdot)(M_2)$$

and the relative rate of disappearance is

$$\frac{d(M_1)}{d(M_2)} = \frac{k_{11}(M_1\cdot)(M_1) + k_{21}(M_2\cdot)(M_1)}{k_{12}(M_1\cdot)(M_2) + k_{22}(M_2\cdot)(M_2)} \qquad (2)$$

We may assume[15] that a steady state is soon reached at which the rate of conversion of $M_1\cdot$ radicals to $M_2\cdot$ radicals is equal to the rate of the reverse reaction.

$$K_{12}(M_1\cdot)(M_2) = k_{21}(M_2\cdot)(M_1) \qquad (3)$$

Substituting the value of $(M_1\cdot)$ from equation (3) into equation (2) and multiplying numerator and denominator by $(M_2)/k_{21}(M_2\cdot)$, we obtain

$$\frac{d(M_1)}{d(M_2)} = \frac{(M_1)}{(M_2)} \cdot \frac{(k_{11}/k_{12})(M_1) + (M_2)}{(k_{22}/k_{21})(M_2) + (M_1)}$$

If we define r_1 as k_{11}/k_{12} and r_2 as k_{22}/k_{21}, this becomes

$$\frac{d(M_1)}{d(M_2)} = \frac{(M_1)}{(M_2)} \cdot \frac{r_1(M_1) + (M_2)}{r_2(M_2) + (M_1)} \qquad (4)$$

The constants r_1 and r_2 are referred to as monomer reactivity ratios, since each is the ratio of the rate constant for the combination of the given type of radical with the corresponding monomer to its rate constant for combination with the other monomer. Equation (4) describes the relative rate at which two monomers enter the polymer chain in terms of their concentrations and of their monomer reactivity ratios. It may be used in the differential form shown when the relative concentration of the monomers does not change greatly. The ratio of the rates of addition of the two monomers is also the ratio of the molar concentrations of the two monomers in the resulting copolymer. This ratio will be denoted by $(m_1)/(m_2)$. We may now write the copolymer composition equation in the form:

$$\frac{(m_1)}{(m_2)} = \frac{(M_1)}{(M_2)} \cdot \frac{r_1(M_1) + (M_2)}{r_2(M_2) + (M_1)} \qquad (5)$$

It must be emphasized that the equation (5) is valid only for the composition of the initial copolymer formed at monomer concentrations M_1 and M_2. However, equation (4), in differential form, is valid at any conversion for relating the instantaneously forming copolymer with the corresponding instantaneous monomer composition.

DETERMINATION OF r_1 AND r_2

There are several methods for the determination of the relative reactivity ratios r_1 and r_2 on the basis of the differential copolymer composition equation (5). One[2] of them starts from the fact that equation (5) can be rewritten as:

$$r_2 = \frac{(M_1)}{(M_2)} \left\{ \frac{(m_2)}{(m_1)} \left[1 + \frac{(M_1)}{(M_2)} r_1 \right] - 1 \right\} \qquad (6)$$

It expresses r_2 as a linear function of r_1 with (M_1), (M_2), and (m_1), (m_2) as parameters. Any given conjugated pair of $(M_1),(M_2)$-$(m_1),(m_2)$ values represents a straight line in a r_2 versus r_1 plot. Hence, each experiment determines one straight line in the plot and the point of intersection of the lines resulting from two experiments yields the values of r_1 and r_2 for the investigated system. Three or more lines in the plot will, in general, not intersect exactly in one single point, but will define an area, which is characteristic for the errors involved in the determination of the reactivity ratios.

Another method was suggested by Fineman and Ross[17]. Substituting F for $(M_1)/(M_2)$ and f for $(m_1)/(m_2)$ into equation (5) the following results:

$$f = F\,\frac{r_1F + 1}{r_2 + F}$$

The equation is then rearranged to give:

$$(f - 1)/F = r_1 - r_2(f/F^2)$$

or:

$$y = r_1 - r_2x$$

where: $y = (f - 1)/F$

$x = f/F^2$

Each individual experiment defines one conjugated pair of x and y, and determines one point on the straight line. A series of experiments yields a set of points, which in turn define, with more or less accuracy, the straight line itself. Its intercept at the y axis is r_1, its slope is $-r_2$; the scattering of the individual points about the straight line is a measure of the errors involved in the determination of r_1 and r_2 on the basis of the available experimental data. A least square analysis can be carried out to determine the line of the best fit through the experimental points.

A third method of analyzing the data is the direct curve fitting of copolymer-monomer mixture composition plots. This is a less precise method, since the composition curve is rather insensitive to small changes in r_1 and r_2.

These methods are based on the differential form (5) of the copolymer composition equation and can only be applied if the copolymers are withdrawn at very low conversions. At these low conversions the copolymer composition is considered to be the same as the instantaneous copolymer composition.

The copolymer composition in general will not be the same as the monomer composition except for the case of an azotropic copolymer. Therefore in most cases any polymer formation changes the compositions of the monomers remaining, and there will be a continuous drift of copolymer composition with conversion. However, it is essential in practice to carry polymerizations to high conversions. If the conversions are so high that an appreciable drift in monomer concentration occurs, corrections have to be made. One way of doing it is as follows. The chemical analysis of the copolymer gives the average composition, rather than the composition of the initial copolymer. This average copolymer composition is now plotted against the average monomer composition during the reaction, rather than against the initial monomer composition. This appears to be fairly satisfactory for only small drifts in composition, but certainly cannot account for large drifts.

A more elaborate method has been developed by Mayo and Lewis[2]. They integrated equation (4), obtaining the following equation:

$$\log \frac{(M_1)}{(M_1^o)} = \frac{r_2}{1 - r_1} \log \frac{(M_1^o)(M_2)}{(M_2^o)(M_1)} - \frac{1 - r_1 r_2}{(1 - r_2)(1 - r_1)} \log \frac{(r_1 - 1)\frac{(M_2)}{(M_1)} - r_2 + 1}{(r_1 - 1)\frac{(M_2^o)}{(M_1^o)} - r_2 + 1} \qquad (7)$$

where (M_1^o) and (M_2^o) represent the initial molar concentrations of the two monomers, and (M_1) and (M_2) represent their concentrations at the time when polymerization is stopped and the sample is withdrawn. Direct application of equation (7) is very difficult, but it has been transformed into equation (8). The constants r_1 and r_2 can be evaluated graphically as follows. The molar concentrations of monomers at the start of the reaction and at the point where polymerization is stopped are determined experimentally and substituted into equation (8). Positive or negative values of P are arbitrary chosen, by trial and error, to give points in a significant region for r_2. The value of r_1 is then calculated for each of these values of P using equation (9).

$$r_2 = \frac{\log \frac{(M_2^o)}{(M_2)} - \frac{1}{P} \log \frac{(1 - P)\frac{(M_1)}{(M_2)}}{(1 - P)\frac{(M_1^o)}{(M_2^o)}}}{\log \frac{(M_1^o)}{(M_1)} + \frac{1}{P} \log \frac{(1 - P)\frac{(M_1)}{(M_2)}}{(1 - P)\frac{(M_1^o)}{(M_2^o)}}} \qquad (8)$$

where:

$$P = (1 - r_1)/(1 - r_2) \qquad (9)$$

A plot is made with r_2 as the abscissa and r_1 as the ordinate. The plot corresponding to a single experiment is a practically straight line. Another experiment (line) is necessary to give a unique solution for r_1 and r_2, represented by the intersection of the two lines. In general, Mayo and co-workers[2] have carried out three experiments for each system and have used the size of the triangle produced at the intersection to give an indication of the error involved in the values of r_1 and r_2.

Montgomery and Fry[4] have written a computer program in Fortran II for calculation of relative reactivity ratios from composition-conversion data using the integrated form of the copolymerization equation slightly modified from the original Mayo and Lewis[2] integrated equation (8). In this program the calculation of M_1 was simplified by using weight fractions and weight percent conversion rather than mole fractions and mole percent conversion. It can easily be shown that this substitution is valid if a factor, molecular weight of monomer 2 per molecular weight of monomer 1 is applied to $(M_1)/(M_2)$ and $(M_1^o)/(M_2^o)$. This integrated equation gives r_2 as a function of P. For any two distinct data points there is a unique value of P that gives identical values of r_2. The computer has therefore been programmed to accept initial monomer composition, polymer composition, and conversion for two data points and increment P in such manner as rapidly to converge r_2 for the two sets of data. This r_2 and P are then used for the calculation of r_1.

A convenient method for determining copolymer compositions and distributions is the method of graphical or numerical integration developed by Skeist[18].

$$\ln \frac{(M_1) + (M_2)}{(M_1^o) + (M_2^o)} = \int_{M_1^o}^{M_1} \frac{dM_1}{x_1 - M_1} \qquad (10)$$

where x_1 is the mole fraction of component M_1 in the monomer mixture, the symbol (M) refers to the number of moles and M refers to the mole fraction. This is the conversion-composition equation which, in combination with equation

(4), permits computation of the proportion of original monomer which is still unreacted.

In general preparation of copolymers is a relatively simple experimental procedure for peroxide initiated polymerization. The monomers to be polymerized are freed from air and sealed in an evacuated tube along with the desired initiator. The polymerizations are carried out in a constant-temperature bath, and the polymer is isolated and purified from the reaction mixture. The usual technique is precipitation of the polymers with a nonsolvent (precipitating agent), and then the polymer is dried to constant weight.

The copolymer compositions have been determined by elementary analysis[19,20]. Analysis[21] of characteristic groups may be used. Physical methods[22] such as ultraviolet and infrared absorption spectra have been used in some cases.

Analysis by the above methods has not in many cases produced reactivity ratios of the desired degree of accuracy. Elementary analysis particularly in the case of nitrogen[19,20] has not resulted in agreement of found and calculated values. The nitrogen content of polyacrylonitrile by Kjeldahl method is consistently found to be lower than expected and corrections have to be made. It has been reported[23] that infrared analysis of isoprene-butadiene copolymers was not satisfactory where the concentration of isoprene was more than 50%.

The use of C^{14}-labeled monomers[24] has been employed and is particularly applicable in determining the copolymer compositions where no other method is successful such as cases involving copolymers composed of similar monomers. The most useful procedures for the determination of the radioactivity of polymer samples prepared from labeled monomers are probably those based on combustion of the polymer to carbon dioxide, which is collected in an ionization chamber, and assayed in a vibrating reed electrometer[25,37]. This technique offers advantages in rapidity and precision in the assay but involves destruction of the sample and requires quantitative combustion of the polymer.

SIGNIFICANCE OF THE MAGNITUDE OF r_1 AND r_2

The copolymer composition equation was derived as a consequence of the introduction of the four propagation steps involved in a copolymerization reaction of two monomers. The monomer reactivity ratios r_1 and r_2 give an indication of the nature of the propagation step.

If r_1 is greater than one, radical $M_1\cdot$ prefers its own monomers. Therefore the polymer is richer in M_1 than is the monomer feed; hence the residual mole fraction of M_1 must diminish as the polymerization proceeds. For $r_1 < 1$, the opposite holds.

If $r_1r_2 > 1$, the tendency for radicals of a given kind to regenerate themselves by the addition of a like unit exceeds their tendency for alternation. Such a copolymer would contain sequences of like units in greater abundance than in a random copolymer of the same composition, and this tendency favoring sequences should be greater the larger the product r_1r_2.

The extreme case occurs where r_1 and r_2 are both equal to or close to zero. Copolymers produced from monomer pairs with reactivity ratios equal to or close to zero will have alternating units in the chain. Each radical prefers to react with the other monomer.

Case four is that in which each radical prefers to react with its own monomer. The reactivity ratios would both be greater than unity. Copolymerization occurs to only a very small degree if any, and the products would be a mixture of two polymers.

The usual product of reactivity ratios is between zero and unity. In general, it may be said that as the product of r_1 and r_2 approaches zero the copolymer units tend to alternate and as the product approaches unity the units tend to be randomly distributed.

MONOMER STRUCTURE AND REACTIVITY IN COPOLYMERIZATION

Several important factors govern the reactivity of a vinyl monomer. One factor is the extent of conjugation of the double bond with unsaturated groups in the substituents. This has been interpreted in terms of the amount of resonance stabilization of the radical adduct which is formed by the monomer with a growing chain end. Another factor is the electrical polarity of the double bond. It seems resonable to assume that an electron withdrawing group such as $-C\equiv N$ will also give a positive polarity to a free radical. A free radical with positive character will exhibit a particular preference for a monomer with a negatively charged double bond. For the electron donating groups such as $-C_6H_5$, $-CH_3$, or $-OCH_3$, the opposite will hold. A third factor is a steric effect. Monomers which possess substituents on both carbon atoms of the carbon-carbon double bond exhibit, in general, a certain reluctance to add to themselves in the growing chain, although they may add to "vinyl" free radicals quite readily.

An interesting attempt to express monomer reactivity ratios quantitatively in terms of the just mentioned has been made by Alfrey and Price[26,27]. According to these authors, the monomer reactivity ratios for a monomer pair are given by the equations.

$$\begin{aligned} r_1 &= k_{11}/k_{12} = (Q_1/Q_2)\exp -e_1(e_1 - e_2) \\ r_2 &= k_{22}/k_{21} = (Q_2/Q_1)\exp -e_2(e_2 - e_1) \end{aligned} \qquad (11)$$

where Q represents the specific reactivity of a monomer determined by the resonance effect and e represents the polar character of the radical adduct. The fundamental idea behind this scheme is to assign styrene, the reference monomer, a Q value of 1.0 and an e value of -0.8 and calculate constants for individual monomers. This would simplify the task of determining large numbers of monomer reactivity ratios for the huge number of possible monomer pairs. The Q-e scheme should be regarded as semiempirical. Although it should not, perhaps, be expected to hold accurately, it has proved useful as a basis for correlating an extensive array of otherwise incoherent data in a remarkably satisfactory fashion.

Hammett[28] has found that the effect of meta and para substituents in the benzene ring on reaction rates and equilibria in many polar reactions can be expressed by:

$$\log k/k_0 = \rho \sigma \qquad (12)$$

where k and k_0 are either rates or equilibrium constants for the side chain reactions of substituted and unsubstituted benzene rings, σ is a constant related to the substituent, and ρ a constant related to the specific type of reaction.

Walling, Mayo, and co-workers[19] have found that the relative reactivities of a series of ring-substituted styrenes with the styrene-type radical can be correlated with Hammett's σ value for the substituent. A very good straight line is obtained against the σ-values of the substituents. This is a remarkable correlation, inasmuch as the σ-values were originally obtained from polar, rather than free radical, reactions.

Recently Wiley and co-workers[29] reported that a plot of log reactivity ratios against the σ-values for the ionization of substituted benzoic acids gives a plot with two linear regions of different slope. It appears that electrostatic effects operate differently in determining the reactivity of styrene radicals with electron donor substituents than they do in determining the reactivity of styrene radicals with electron attracting substituents.

More recently attempts have been made to predict monomer reactivity ratios on the basis of Hückel molecular orbital technique[6]. It appears that these calculations, which are good only to a factor of 2 or 3, are not too useful even for prediction of the more reactive monomer of the pair.

THE DIVINYL MONOMER SYSTEM

Alfrey, Bohrer, and Mark[10] have discussed and classified divinyl monomers as being symmetrical or unsymmetrical with independent vinyl groups, intermediate vinyl groups, or extremely interdependent vinyl groups. A divinyl compound is classified symmetrical if the vinyl groups are identical and unsymmetrical if the vinyl groups are not identical. Independent vinyl groups may be defined as vinyl groups separated by long unconjugated chains and

If one group reacts the reactivity of the second group is not appreciably affected. A monomer such as isoprene is termed an extremely interdependent divinyl monomer and is unsymmetrical. While p-divinylbenzene may be classified as a symmetrical and interdependent divinyl monomer because of the conjugation between the two vinyl groups, m-divinylbenzene is an example of an independent and symmetrical divinyl monomer.

The copolymer composition equation (4) was revised by Alfrey and co-workers[10] for the vinyl-divinyl copolymerization, one of which is a symmetrical divinyl compound. The equation is

$$\frac{d(M_1)}{d(M_2)} = \frac{(M_1)}{2(M_2)} \cdot \frac{r_1(M_1) + 2(M_2)}{2r_2(M_2) + (M_1)}$$

where subscript 1 represents monovinyl compound and 2 represents divinyl monomer. At low conversions this equation can be rewritten as mentioned earlier.

$$\frac{m_1}{m_2} = \frac{(M_1)}{2(M_2)} \cdot \frac{r_1(M_1) + 2(M_2)}{2r_2(M_2) + (M_1)} \qquad (13)$$

Wiley and co-workers[5,6,7,30] have determined the reactivity ratios of the three divinylbenzene isomers copolymerized with styrene using equation (13) at low conversions. From these studies they concluded that the above equation could be used to evaluate the monomer reactivity ratios for these systems. However they always mentioned the lack of intersection in the plots for the styrene-p-divinylbenzene system.

THE CHARACTERIZATION OF SEQUENCE DISTRIBUTION IN COPOLYMERS

Theoretical predictions of sequence distribution in copolymers were included in the earliest treatments of copolymerization[1,3,31], and many theoretical papers on this subject have been published in recent years[32,33,34]. unfortunately, experimental work has not kept pace with theoretical developments, possibly due to difficulties involved in measuring sequence distributions. However, experimentalists may have been discouraged from entering this field by the relatively complex mathematical approaches taken in the theoretical treatments. There is, at present, no uniform way to express sequence distribution results and experimental results have been treated differently in almost every paper published on this subject.

In principle, the experimental determination of the sequence distribution in copolymers is simple. It is only necessary to determine the extent of any single recurring structural feature. In most chemical approaches the percentage of M_1-M_1, M_1-M_2 or M_2-M_2 linkage is determined, whereas most physical or spectroscopic approaches yield the percentage of M_1 or M_2 units present in the middle of various triads, pentads, or heptads.

The results obtained by these approaches can be compared using the concept of run number introduced by Harwood and Ritchey[35]. The run number of a copolymer is defined as the average number of uninterupted monomer sequences (or runs) which occur in a copolymer chain per 100 monomer units. This quantity can be related through elementary stoichiometric and statistical considerations to any measurable feature of copolymer structure that depends on sequence distribution. They derived an equation for the prediction of run number (R) using the propagation steps mentioned in equation (1) for the vinyl copolymerization and the steady state assumption. Thus, the rate at which monomer units are incorporated into the polymer is

$$\frac{d(M_1 + M_2)}{dt} = k_{11}(M_1\cdot)(M_1) + k_{12}(M_1\cdot)(M_2) + k_{21}(M_2\cdot)(M_1) + k_{22}(M_2\cdot)(M_2)$$

and the rate at which sequences are generated in the copolymer is

$$dS/dt = k_{12}(M_1\cdot)(M_2) + k_{21}(M_2\cdot)(M_1)$$

By dividing the above two equations and by making use of the steady state condition,

$$k_{12}(M_1\cdot)(M_2) = k_{21}(M_2\cdot)(M_1) \ ,$$

the average number of monomer units per run in the instantaneous polymer becomes

$$\frac{d(M_1 + M_2)}{dS} = 1 + \frac{r_1(\%\ M_1^o)}{2\ (\%\ M_2^o)} + \frac{r_2(\%\ M_2^o)}{2\ (\%\ M_1^o)}$$

where $\%\ M_1^o$ and $\%\ M_2^o$ refer to the molar percentages of M_1 and M_2 in the initial copolymerization mixture (feed compositions). By definition,

$$R = 100\ \frac{dS}{d(M_1 + M_2)}$$

$$R = \frac{200}{2 + r_1(M_1^o)/(M_2^o) + r_2(M_2^o)/(M_1^o)} \qquad (14)$$

This run number can be used to calculate sequence distribution in copolymers. The following equations[36] relate the run number R to molar concentration of the copolymer ($\%\ m_1$ and $\%\ m_2$) and to measurable aspects of the copolymer structure:

$\%\ M_1$-M_2 linkages (includes M_2-M_1 linkages) $= R$

$\%\ M_2$-M_2 linkages $= \%\ m_2 - (R/2)$

$M_1M_1M_1$ triads ($f_{M_1M_1M_1}$) $= \dfrac{[\%\ m_1 - (R/2)]^2}{(\%\ m_1)^2}$

$M_2M_1M_1$ (and $M_1M_1M_2$) triads ($f_{M_2M_1M_1}$) $= \dfrac{R[\%\ m_1 - (R/2)]}{(\%\ m_1)^2}$

$M_2M_1M_2$ triads ($f_{M_2M_1M_2}$) $= \dfrac{R^2}{4(\%\ m_1)^2}$

where the symbol f refers to the fraction of M_1 monomers to be found in the middle of the triads $M_1M_1M_1$, $M_2M_1M_1$, $M_1M_1M_2$, and $M_2M_1M_2$.

By applying the above considerations, Harwood[8] has recently written a Fortran program for calculating run numbers, triad distributions, and pentad distributions of initial copolymers from feed composition data and terminal reactivity ratios. We have used this approach for our systems.

EXPERIMENTAL

MATERIALS

STYRENE-β-C^{14}: This compound was supplied by Tracerlab Company with a specific activity of 0.13 millicurie/millimole. The sample contained 448.6 mg. (0.4984 ml.) with total activity of 0.5 millicurie and was stabilized with picric acid. The labeled material was diluted with 140 volumes (70 ml.) of unlabeled styrene (Baker Chemical Co.) which had been purified by a vacuum distillation in which only the middle fraction, n_D^{20} 1.5467, was collected. This diluted styrene-β-C^{14} had a specific activity of about 9.2×10^{-1} microcurie/millimole and was stored under nitrogen at below 5°C in the presence of inhibitor 2,6-ditertiary-butyl-para-cresol. Dilution[24] was carried out under nitrogen atomosphere in a polyethylene bag and a well ventillated hood.

m-DIVINYLBENZENE: Commercial m-divinylbenzene (stabilized by 1,000 ppm. of inhibitor) of about 90% purity was supplied by Shell Chemical Company, new York. This commercial monomer was fractionated[38] twice by a preparative gas chromatography (Hewlett Packard Model 776, F & M Scientific Division) and a column packed with 20% triscyanoethoxypropane on 60/80 chromosorb-W. The column temperature of 160°C and a nitrogen carrier-gas flow rate of 4.25 l/min. were used. Gas chromatographic analysis using a Perkin-Elmer R column (polypropylene glycol on chromosorb-W) with a thermal conductivity detector of the purified sample showed the substance to be 99.8+% pure (Figure 1). This material was stored until used under nitrogen below 5°C with a small quantity of 2,6-ditert-butyl-p-cresol as stabilizer and was distilled under vacuum after washing just prior to use with 1 N KOH solution to remove the inhibitor (Observed: b.p. 34°C/1 mm., n_D^{25} 1.5755; Lit:[5,39] b.p. 34°C/1 mm., n_D^{25} 1.5754).

p-DIVINYLBENZENE: p-Divinylbenzene was synthesized by the decarboxylation of p-phenylene-β,β-diacrylic acid according to the method described by Wiley and Hobson[40]. A 500 ml. three necked flask fitted with a stirrer, a distilling assembly, and an additional funnel were used to carry out the reaction. Twenty milliliters of quinoline (Baker Analyzed Reagent) and 8 g. of copper (J. T. Baker) were put in the flask. In a separate beaker, an emulsion of 8 g. of cupric acetate (Baker Analyzed Reagent), 200 ml. of quinoline, and 50 g. of diacrylic acid (Aldrich Chemicals) was made. A Wood's metal bath was heated to 260-270°C and placed under the reaction flask. Once the quinoline started distilling, small quantities of the emulsion were added through the addition funnel to insure that the reaction flask was never dry. After the complete addition of the emulsion, another 25 ml. of quinoline were added to

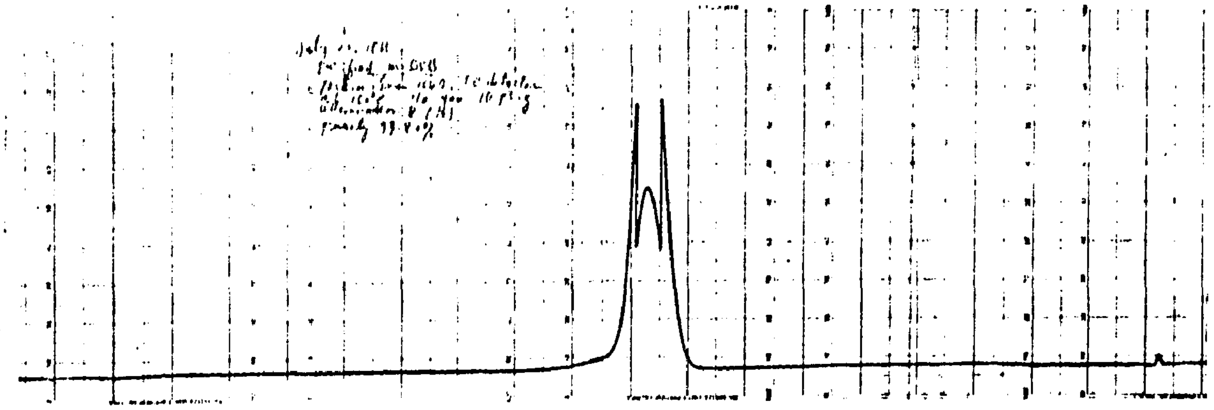


Figure 1. Analytical Gas Chromatogram of m-Divinylbenzene.

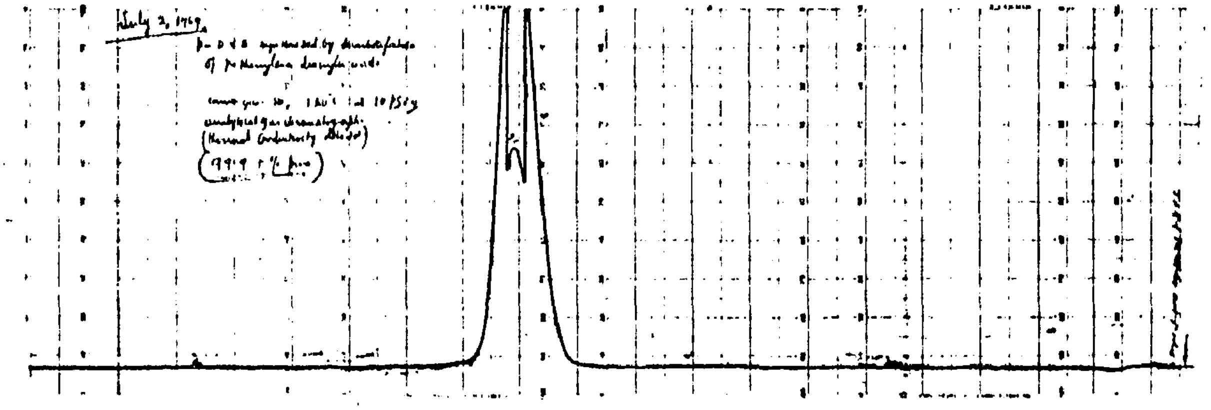


Figure 2. Analytical Gas Chromatogram of p-Divinylbenzene.

prevent the flask from drying out. The entire operation was carried out under a steady flow of nitrogen. Small quantities of the inhibitor 2,6-ditert-butyl-p-cresol were added both to the reaction flask and receiver. The distillate was kept under nitrogen in a refregerator until further treatment.

An equal volume of cold 20% sulfuric acid was added to the distillate, to which small pieces of ice had been added. The solution was put in a separatory funnel, shaken throughly, and allowed to separate. The upper layer containing divinylbenzene was washed twice more with cold 20% sulfuric acid. All the quinoline-sulfuric acid extracts were collected together and washed three times with chloroform in order to extract any divinylbenzene present. These chloroform extracts were in turn washed with 20% sulfuric acid and then combined with the original divinylbenzene fraction, which was subsequently washed with 3 N sodium hydroxide solution. The sodium hydroxide solution portion was washed with small quantities of chloroform. The combined chloroform extracts were then washed with distilled water and kept over anhydrous sodium sulfate under nitrogen. The solution was then filtered off the sodium sulfate, washing the sodium sulfate three times with chloroform. The chloroform was then evaporated under vacuum under a flow of nitrogen. The residue p-divinylbenzene portion was distilled under vacuum under a flow of nitrogen and stored under nitrogen atmosphere in a refrigerator after adding a small amount of inhibitor. The yield was 25%.

This synthesized p-divinylbenzene was further purified by a Perkin-Elmer gas chromatography (Model 154) and a Bentone column[38] (5% Ucon oil, 15% Bentone and 80% chromosorb). The column temperature of 140°C and helium carrier gas pressure of 15 psi were used. Gas chromatographic analysis using a Perkin-Elmer R column showed that this sample was 99.9+% pure (Figure 2). This material was stored under nitrogen at below 5°C with a small quantity of 2,6-ditert-butyl-p-cresol until used and was distilled under vacuum just prior to use (Observed: m.p. 30.0°C, n_D^{35} 1.5855; Lit:[5,39] m.p. 29.5-30.0°C, n_D^{35} 1.5857).

INITIATOR: Benzoyl peroxide (Fisher Scientific Co.) which was used as initiator was recrystallized from a chloroform-methanol mixture and dried under vacuum.

POLYMERIZATION PROCEDURE

All work performed with the C^{14}-labeled compounds was carried out on a large stainless steel tray with aluminum foil cover in a well-ventilated hood. Handling, cleaning of contaminated glassware, and disposal of waste were carried out according to the direction of Overman and Clark[41] on radiological safety.

The weighed pyrex reaction cell was charged with an appropriate quantity of freshly distilled divinylbenzene in nitrogen atmosphere and reweighed. Radioactive styrene was distilled into the reaction cell employing the vacuum line techniques[42] described earlier. The techniques in detail are as follow. The C^{14}-labeled monomer was placed as shown in Figure 3 in a 15 ml. graduated centrifuge tube at B and the weighed reaction cell charged with divinylbenzene at A. Each monomer was degassed in the following way. The stopcocks to the monomer tubes were closed and the contents were frozen by immersing the tubes in a bath of liquid nitrogen. The remainder of the vacuum line was evacuated and the stopcocks leading to the monomer tubes were open for about 5 minutes while keeping the monomers frozen. Closing the stopcocks the frozen monomers were allowed to thaw; this process could be hastened by immersing the tubes in a beaker of water at room temperature. The monomers were then refrozen, degassed, and remelted. The process was repeated at least four times. After degassing, finally, the stopcock at B was kept closed and the reaction cell A was immersed in liquid nitrogen. Stopcock D was closed and stopcock B was opened slowly, in order to avoid bumping, until distillation started. After the appropriate amount of monomer was distilled into the reaction cell A, stopcocks A and B were closed. After the contents of the reaction cell were allowed to melt at room temperature, the reaction cell was filled with nitrogen, and then removed from the vacuum

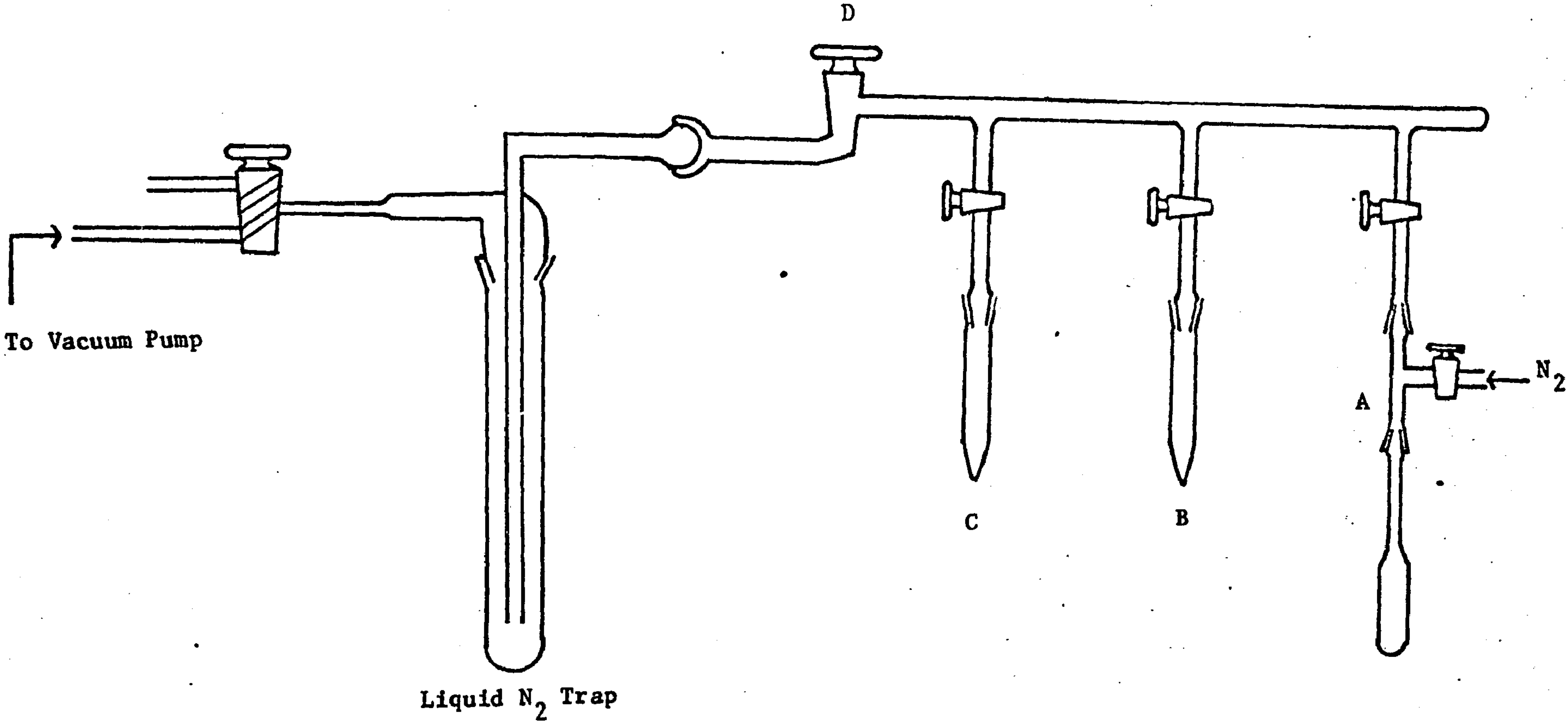


Figure 3. Vacuum Line for Distillation of Monomers into Reaction Cells.

line and stoppered. After removing the vacuum grease on the ground joint of the reaction cell with a piece of tissue paper dampened with benzene, the reaction cell was weighed. Monomer mixtures of weight ratios ranging from 0.3 to 2.5 were prepared. The total weight of the monomer mixture in each case was nearly 1 g. A solution of benzoyl peroxide in benzene (0.5 ml.), followed by benzene (0.5 to 1.0 ml.), was added to the reaction mixture in nitrogen atmosphere. The weight of benzoyl peroxide was 0.1% by weight of the monomer mixture. Then the reaction cell was connected to the vacuum line, chilled in liquid nitrogen, degassed in vacuum, and remelted. The freezing and thawing was repeated 3-4 times before the cell was sealed under vacuum with a small torch.

Polymerizations (to conversion ranges of 2-35%) were carried out in a water thermostat maintained at $75 \pm 0.1^{\circ}C$ for 30 to 200 minutes. The polymerizations were stopped by freezing the cells in dry ice-acetone mixtures at appropriate times. The polymers were recovered by precipitation by methanol. The chilled reaction cell was carefully broken, the contents of the cell were treated with 0.5 to 1 ml. of benzene containing a small amount of inhibitor and mixed with a spatula to form a uniform slurry which was then transferred to a weighed centrifuge tube. The cell was washed 3 or 4 times with benzene and the contents were again transferred to the centrifuge tube. Final washing of the cell was done with 1 ml. of methanol to make sure that no turbidity appears in the methanol washing, indicating the complete removal of polymer in earlier washings. About 5-10 ml. of methanol was added and the contents were again thoroughly stirred for complete mixing and precipitation. The tube was centrifuged for 20 minutes at 1,500 rpm. The clear supernatant liquid was carefully decanted to avoid any loss of the polymer. The reprecipitation of the polymer by (dissolving in benzene and precipitating by methanol) was carried out 3 or 4 times to ensure the complete removal of the adhering monomers and initiator. In the case of less soluble, crosslinked materials, the polymers were swollen well in benzene before treatment with methanol. After complete purification, the polymer was again dissolved in a small quantity of benzene (2-5 ml.) and the tube was gently rotated over a bed of dry ice to freeze the polymer solution uniformly on the sides of the tube. The centrifuge tube was then immediately transferred to a vacuum dessicator and evacuated for 3 to 4 hours. The centrifuge tube was then covered with an aluminum foil with holes in it and evacuated at 0.1 to 1 mm. and 45-55°C for more than 48 hours and until constant weight was obtained. The conversion was determined by dividing the weight of the copolymer produced by the total weiPolystyrene-βwo monomers used.

Polystyrene-β-C^{14} homopolymer was prepared in the same manner just mentioned. This was used as a standard C^{14}-labeled polymer for the analysis of the copolymer.

RADIOACTIVITY ASSAY

The copolymers were analyzed for styrene-β-C^{14} content using the procedure described earlier[37,43]. The weighed copolymer was completely burnt to carbon dioxide in a combustion train and then the carbon dioxide produced was collected into an evacuated ionization chamber. The radioactive content of the carbon dioxide was assayed using a vibrating reed electrometer with a recorder by determining the time required to build up a given charge.

The micro-carbon-hydrogen combustion train[44] consists of a well cleaned combustion tube filled with platinum wire, cupric oxide, lead peroxide, and silver wire; a water absorption tube containg magnesium perchlorate (Anhydron, flakes 3 to 5 mm. long); a flow meter for combustion gas; and a preevacuated, spherical ionization chamber to collect the carbon dioxide produced from combustion of the polymer, as shown in Figure 4. A combustion furnace temperature of 700°C was used and the heating mortar was operated at a preset temperature of 175-180°C.

About 2-10 mg. of the copolymer sample was accurately weighed to a microgram in a porcelain combustion boat approximately 4 mm. deep, 5 mm. wide, and 17 mm. long, and placed in a combustion train set up following the standard procedure. Medical oxygen containing 5% of carbon dioxide

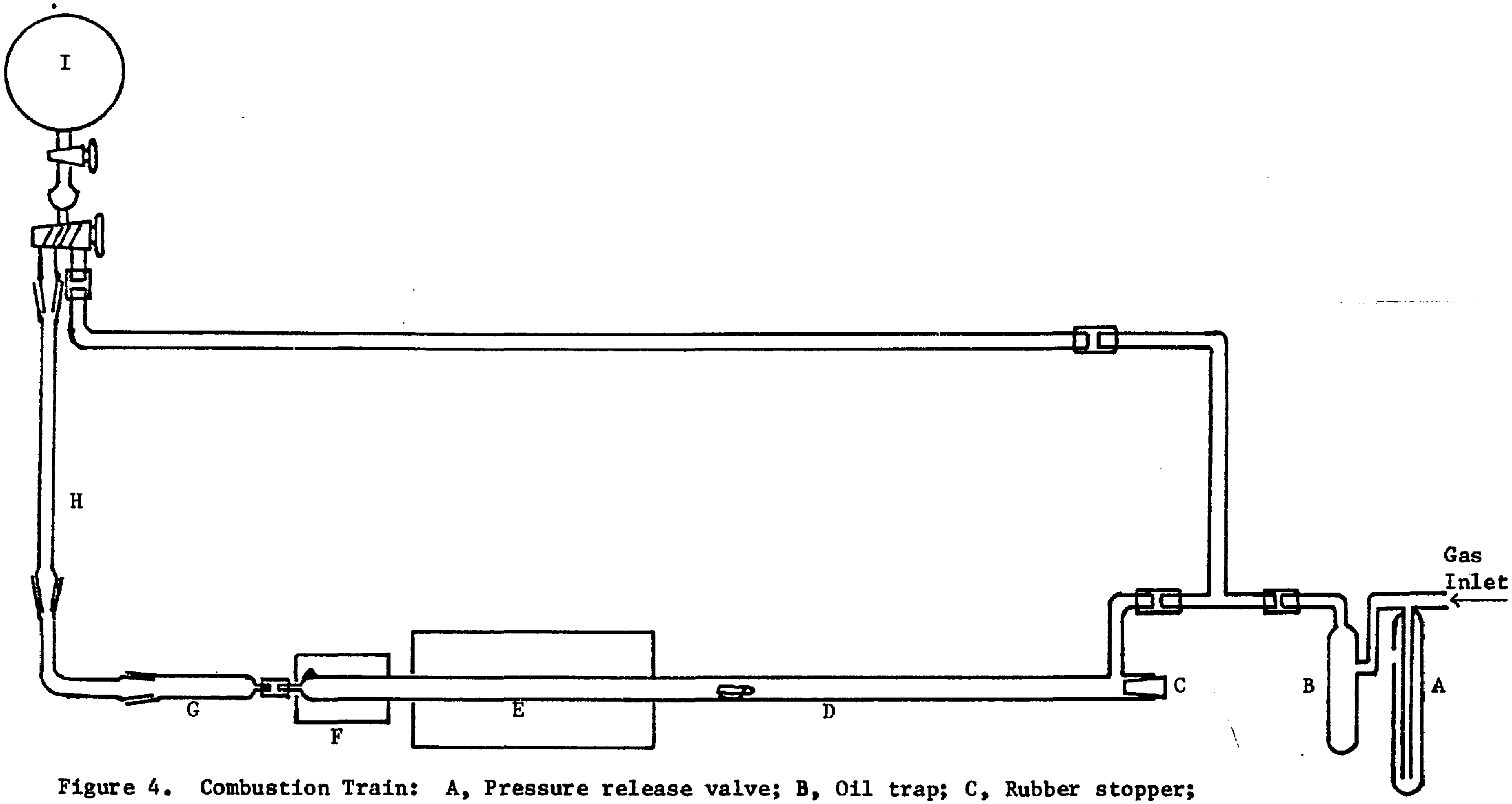


Figure 4. Combustion Train: A, Pressure release valve; B, Oil trap; C, Rubber stopper; D, Quartz combustion tube; E, Furnace; F, Heating mortar; G, Water absorption tube; H, Gas flowmeter; I, Ionization chamber.

was used for combustion at the controlled flow rate of 15 ml. per minute. This flow rate could be controlled with the needle valve in the ionization chamber. Combustion was started by gently heating the polymer with a small flame of a microburner in order to decompose it. This was done carefully since overheating caused the sample to explode. Decomposition usually required about 10 minutes. After decomposition the Bunsen burner was used to complete the combustion. The combustion products were carried by the oxygen gas through the furnace (700°C) to a pre-evacuated, Cary-Tolbert stainless steel spherical ionization chamber of about 500 ml. capacity. A total of 35-40 minutes was required to complete the entire decomposition and combustion process. During the combustion process it was necessary to reset the flowmeter by slightly opening the needle valve, because as the vacuum decreases in the ionization chamber the gas flow could decrease. The flowmeter dropped to zero at the end of combustion.

The ionization chamber was carefully moved from the combustion train to the vibrating reed electrometer head. An applied Physics Corporation Cary Model 31 Vibrating reed electrometer was used with a Honeywell Electronic 15 stripchart chromatography recorder. The ionization chamber was held in place by tightening of three hand screws on the side of the electrometer head. A negative terminal of two 90 volt "B" batteries connected in series was connected to the ionization chamber and the positive terminal was connected to the electrometer head.

A manually operated turret switch with 6 operating positions was provided on the electrometer head. The switch had a ground position, an open position, and 4 other positions in which condensers or resistors were connected in series with the feed back line on the electrometer circuit. The condensers were designed for use where large amounts of radioactivity would be encountered. Resistors were designed for radioactivity determination by the high resistance leak method. In this work it was found that the levels of activity were not sufficient to warrant use of condensers. The remainder of the condensers and the resistors were removed and the open position was used with the remainder of the copolymer analysis.

Radioactivity was determined by the rate of charge procedure. The electrometer and recorder were allowed to remain on continuously. After setting the voltage selector on the appropriate scale, as determined from the activity of the sample, the turret switch was placed on open position and the recorder pen allowed to travel from 10 to 90 as shown in Figure 5. The electrometer was then manually discharged by turning the turret switch to ground position. This caused the recorder pen to return to zero and the procedure was again repeated by placing the switch on open position. Electrometer voltage scale settings were selected to give from approximately 5 to 15

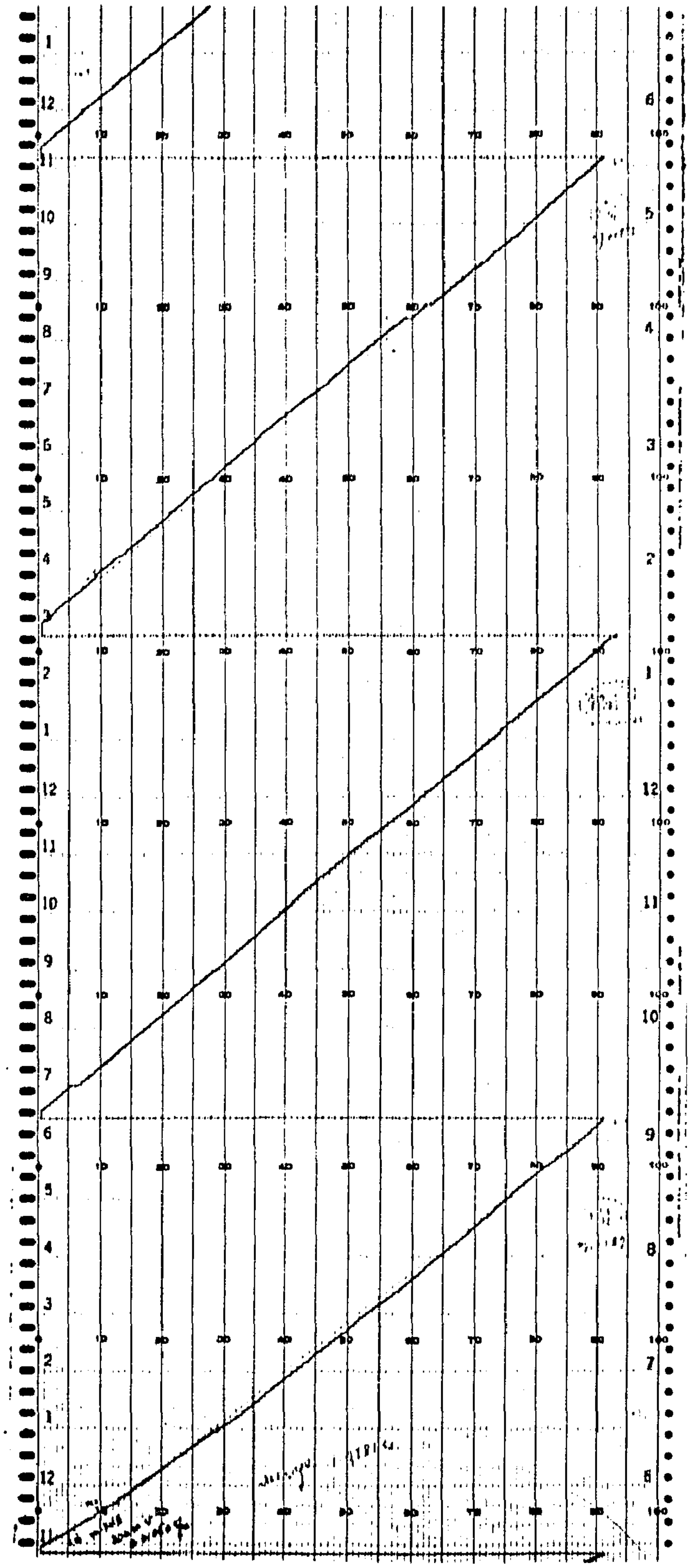


Figure 5. A Typical Chart Showing the Radioactivity Recording of a Copolymer Sample (Range 300 mV).

minutes for one recording, and the average of 5 or 6 charge rate readings on the recorder was taken. After removal of the chamber the dust cover was replaced on the electrometer head and the chamber was evacuated for at least 15 minutes before being used again. Checks by determining background after evacuation showed that 15 minutes were sufficient to remove all of the radioactive carbon dioxide. Radioactive carbon dioxide was removed from the ionization chamber by evacuation through "Ascarite" in a "U" absorption tube. At least two analyses of each copolymer were made and the analytical values were found to be within 1.4% of the average of the two analyses.

A fairly uniform background could be obtained by evacuating and filling the ionization chamber with combustion gas just prior to use. Background was always determined using the 30 millivolt scale until at least 5 uniform recording were obtained. The samples of standard polystyrene-β-C^{14} were analyzed to determine the specific activity as described above.

The copolymer composition could be calculated by comparing the specific charge rates of copolymer and of the standard polystyrene-β-C^{14}. If W equals the weight (g.) of the sample, V is millivolt electrometer scale setting, and D (inch) is the vertical distance traveled by the chart paper from the 10 division to the 90 division, then the weight fraction of styrene in copolymer would be

$$\frac{(0.8\ V_c/120\ D_c - 0.8\ V_b/120\ D_b)/W_c}{(0.8\ V_s/120\ D_s - 0.8\ V_b/120\ D_b)/W_s}$$

The subscript c stands for copolymer, s for standard, and b for background. The chart paper speed was 120 sec./ inch. The weight fraction of divinylbenzene is then found by substracting the weight fraction of styrene from unity. Actually the numerator of the equation is the specific charge rate (mev./sec./mg.) of the copolymer and the denominator that of the standard. $0.8\ V_b/120\ D_b$ is the correction term for the background. The calculated specific charge rates and the copolymer composition are given in Tables 1 and 2.

COMPUTER PROGRAM

CALCULATION OF RELATIVE REACTIVITY RATIOS: The Fortran II computer program for the integrated form of the copolymerization equation (a slightly modified version of the original Mayo and Lewis integrated equation[2]) as described by Montgomery and Fry[4] was used for treatment of the conversion and composition data to obtain r_1 and r_2 values. For any two experiments, the input data (Table 1 and 2) consist of the initial feed weight fraction of each monomer, the fractional conversion, the weight fraction of each monomer in the copolymer from the activity assay data, and the molecular weight of each monomer. For reasons given previously the equivalent weight of the

Table 1

Monomer Feed Composition, Copolymer Composition, and Conversion Data
Styrene(M_1)/m-Divinylbenzene(M_2) Copolymerization

Exp. No.	Monomer Feed(g)		Weight Fraction in Feed		Copolymer Composition[c]		Conversion (%)	Specific Charge Rate(x10^2)[d] (mV/sec/mg)	Wt. % Styrene
	M_1	M_2	M_1[a]	M_2[b]	M_1	M_2			
1	0.7006	0.2977	0.5406	0.4594	0.5086	0.4913	4.77	3.3375	50.86
2	0.5957	0.2927	0.5218	0.4781	0.5286	0.4713	18.24	3.5040	52.86
3	0.4920	0.4261	0.3660	0.6339	0.3755	0.6244	67.85	2.4895	37.55
4	0.6066	0.3924	0.4359	0.5640	0.4854	0.5146	24.47	3.2157	48.54
5	0.2991	0.8411	0.1509	0.8490	0.2236	0.7764	34.96	1.4825	22.36

a. Equivalent weight fraction of styrene in the monomer feed from the relation M_1,g/(M_1,g + M_2,2g).

b. Equivalent weight fraction of m-divinylbenzene in the monomer feed from the relation M_2,2g/(M_1,g + M_2,2g).

c. Weight fraction of M_1 and M_2 in the copolymer.

d. Specific charge rate for reference polystyrene, 6.6285 x 10^{-2}mV/sec/mg. Value is average for two determinations corrected for the background value (0.1167 mV/sec), average deviation, ±0.6%; maximum deviation ±1.4%.

Table 2

Monomer Feed Composition, Copolymer Composition, and Conversion Data
Styrene(M_1)/p-Divinylbenzene(M_2) Copolymerization

Exp. No.	Monomer Feed(g)		Wt. Fraction in Feed		Copolymer Composition[c]		Conversion (%)	Specific Charge Rate(x10^2) (mV/sec/mg)[d]	Wt. % Styrene
	M_1	M_2	M_1[a]	M_2[b]	M_1	M_2			
6	0.7313	0.3160	0.5363	0.4336	0.3897	0.6102	1.93	2.5835	38.97
7	0.6306	0.2760	0.5332	0.4668	0.4072	0.5927	14.95	2.6995	40.72
8	0.3948	0.4936	0.2855	0.7145	0.2290	0.7710	14.89	1.4775	22.29
9	0.4002	0.6669	0.2308	0.7692	0.1833	0.8166	9.04	1.2155	18.33
10	0.3810	0.8215	0.1882	0.8117	0.2475	0.7524	19.37	1.6410	24.75

a. Equivalent weight fraction of styrene in the monomer feed from the relation M_1,g/(M_1,g + M_2,2g).

b. Equivalent weight fraction of p-divinylbenzene in the monomer feed from the relation M_2,2g/(M_1,g + M_2,2g).

c. Weight fraction of M_1 and M_2 in the copolymer.

d. Specific charge rate for polystyrene 6.6285 x 10^{-2} mV/sec/mg. The value given is the average of two values, corrected for the background value (0.1167 mV/sec), average deviation ±0.8%; maximum deviation ±1.2%.

divinylmonomer is taken as half the molecular weight in calculating the monomer feed weight fraction. The program calculates r_2 in terms of the arbitrary P for each of the data points, then takes increments of P in such a manner that the two r_2 values converge to a unique value common to both points. The calculated r_2, with the corresponding P, is then used to calculate r_1. P is defined as $(1 - r_1)/(1 - r_2)$. An IBM 1620 data processing system was used.

SEQUENCE DISTRIBUTION CALCULATIONS: A Fortran IV computer program for the calculation of the sequence distribution from the terminal or penultimate reactivity ratio was used. The program is the second revision for an IBM 360 from the original program by Harwood[8]. Input was supplied on cards as follows.

First card: Read in SS1, SS2, SS3 and MUM where SS1 = +1.0 gives terminal calculation, SS2 = +1.0 prints out the conversion and the per cent of unreacted monomer A and that of B at each conversion increment, SS3 = +1.0 gives calculation at approximate conversion. If a given copolymer system is to be run at different conversions, MUM will be the number of different conversions to be calculated.

Second card: The first four positions contain either 1 or 0, depending on whether (a) diad distributions and monomer centered triad fractions, (b) tetrad distributions, (c) monomer centered pentad fractions, or (d) sequence distributions are, or are not, to be calculated. The conversion increment to be used for the calculations is specified (as a percentage) in the next ten positions according to F10.5 format.

The remaining cards contain the following information: third: copolymer system under study; fourth: molecular weight of A and B; fifth: monomer reactivity ratios of A and B; sixth: monomer feed composition in molar percentages; seventh card on: conversion expressed as a weight per cent up to and including MUM.

ANALYSIS OF EXPERIMENTAL DEVIATIONS

The radioactivity assay shows the least experimental variation in our data (±1% in duplicate analysis). Deliberate alternations of ±10% in the conversion data (Tables 3 and 4) as used in computer input calculations give an average variation of ±0.8% in styrene-m-divinylbenzene and ±2% in styrene-p-divinylbenzene except for one set of data for which the deviation is 27.5%. Deviation in the copolymer analysis caused by benzoyl or phenyl end groups is 1.0%, even for the lowest conversion copolymer, and is much less for higher conversion copolymers.

RESULTS AND DISCUSSION

The monomer reactivity ratios for the copolymerization of styrene with m-divinylbenzene and with p-divinylbenzene are one of the most significant features which distinguish these two divinyl monomers. It was noted as early as 1934 by Staudinger and Heuer[45] that styrene and divinylbenzene polymerizations are kinetically different in qualitative experiments. The quantitative determination of the reactivity ratios obtained by the differential analyses for this system was recently reported[5,6,7]. We have now repeated the determinations using the integral analyses and wish to discuss our results to provide a more useful interpretation of such results than has yet been possible, through clarification of some of the assumptions previously involved. Data for such systems are of particular significance in providing a more precise understanding of the behavior of ion exchange resins prepared from styrene-divinyl copolymer, because the ion exchange behavior is related to structural characteristics of the macromolecule.

COPOLYMERIZATION OF STYRENE AND m-DIVINYLBENZENE

m-Divinylbenzene may be considered as an example of a symmetrical divinyl monomer[10] where the two vinyl groups are approximately equal in reactivity to the vinyl compound. Therefore we introduced the idea of the revised copolymerization equation for the divinyl monomer into the calculations of initial monomer concentrations for the computer calculation input data as shown in Tables 1 and 2.

The read-out from the computer calculation using the integrated equation for the high conversions is summarized in Table 3. The average values of the monomer reactivity ratios for the styrene (M_1) and m-divinylbenzene (M_2) copolymerization at 75°C are $r_1 = 1.11$ and $r_2 = 1.00$. The conversion range for these values is from 4 to 25%. Previously observed values at 80°C are $r_1 = 0.605$ and $r_2 = 0.88$, and $r_1 = 1.27$ and $r_2 = 1.08$ from differential analyses at 0.55-3.72% and at 2.7-7.5% conversion levels, respectively.[6] A C^{14}-labeled monomer and the ionization chamber-vibration reed electrometer radioactivity technique for the differential studies as described were used. Other values[46] of $r_1 = 0.54$ and $r_2 = 0.58$ at 70°C were reported by the intersectional method. The conversion was up to 3% and the copolymer was analyzed for structural units by IR (KB_r disk samples).

The reported values indicate that at low conversions r_1 is lower than r_2, but at high conversions r_2 is lower than r_1. This trend toward higher r_1 values (up to 3.92) at higher conversions is confirmed in our integral data (Table 5) for copolymerizations up to 35% conversion having a ratio of styrene to m-divinylbenzene less than 1.

The Q and E values for m-divinylbenzene calculated

Table 3

Monomer Reactivity Ratios (r_1 and r_2) for the Styrene/m-Divinylbenzene Copolymerization

Pairs[a,b]	Average Conversion(%)	r_1	r_2
1(4.7),3(6.7)	5.7	0.95	1.00
1(4.7),2(18.2)	11.4	0.92	1.00
3(6.7),2(18.2)	12.4	1.08	1.00
1(4.7),4(24.4)	14.5	1.16	1.00
3(6.7),4(24.4)	15.5	1.31	1.00
2(18.2),4(24.4)	21.3	1.29	1.00
	Average	1.11	1.00

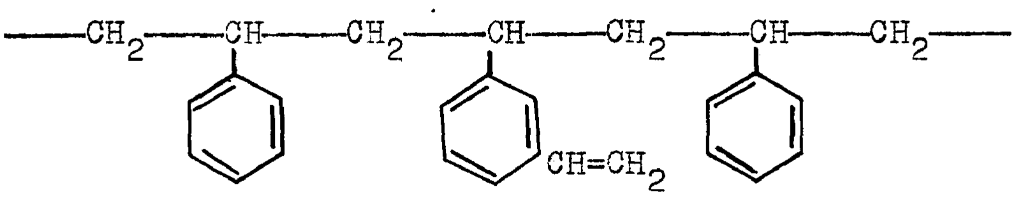
a. Data points from Table 1 used, with the conversion in parenthesis.

b. Variation of conversions by ±10% gave r_1 values (top to bottom) of 0.912, 0.920, 1.077, 1.157, 1.314, 1.292, and r_2 values of 1.00.

by the Alfrey-Price equation with reported r_1 and r_2 values[6] are Q = 1.1 and e = -0.8. These Q and e values for m-divinylbenzene are very close to those of styrene (Q = 1.0 and e = -0.8). This is also in accord with estimates based on Hückel MO calculations[6] of $r_1 = r_2 = 1$. The near equivalence of the monomer reactivity ratios at relatively low conversion in addition to these calculated values indicates that the two vinyl groups of m-divinylbenzene copolymerize independently and are equivalent in their reactivity.

However it appears, subject to clarification of the high conversion discrepancies, that the styrene and m-divinylbenzene system involves copolymerization of two monomers of approximately equivalent reactivity neither radical showing a great preference for either its own or the comonomer. Deviation from this equivalence is consistent with an increased participation of the second divinyl units in the high conversion copolymer. As the second vinyl unit becomes involved, the copolymerization system includes a substantial contribution from styrene-alkylstyrene copolymerization. Superposition of this on the styrene and m-divinylbenzene copolymerization results in a complication of the kinetics, presumably in the direction of a typical three component system involving styrene, a vinylstyrene, and an alkylstyrene. The necessary data for comparisons with such three component copolymerization systems, although readily obtainable by known techniques, are not available. The rather significant difference indicates, however, as we have suggested previously, that involvement of the second vinyl group is a important factor in evaluating these data.

There is little possibility of any considerable conjugation between the two vinyl groups in m-divinylbenzene. When a m-divinylbenzene molecule is incorporated into a copolymer chain through one of its two vinyl groups, it will inevitably be flanked on either side by a benzene ring, substituted or unsubstituted.



These benzene nuclei should have a shielding effect on the reaction of the second unreacted vinyl group of the m-divinylbenzene. There should thus be a reduction in the reactivity of this shielded group. An increased shielding effect on the second vinyl group will be expected at high conversions. This indicates the deviation from the equivalent reactivity of styrene and m-divinylbenzene is in the direction of enhanced reactivity of styrene radical towards styrene monomer and this deviation is increased at high conversions.

From these monomer reactivity ratios given above, one can predict that these ratios promise a fairly good degree of homogeneity of cross-linked polystyrene with m-divinylbenzene. This will be discussed later.

COPOLYMERIZATION OF STYRENE AND p-DIVINYLBENZENE

p-Divinylbenzene differs from the meta isomer by the virtue of the conjugation between the two vinyl groups in positions para to one another. As mentioned earlier, the behavior of the meta compound can be adequately represented by the revised copolymer composition equation for divinyl monomers, but the action of p-divinylbenzene as a cross-linking agent is not so predictable and indicates that the degree of homogeneity to be expected in these reactions is much less than that of m-divinylbenzene.

When the pure p-divinylbenzene was copolymerized with styrene to low conversions and the copolymers were analyzed by the technique described herein, it was found[6,7] that neither the differential form of ordinary copolymerization equation nor the revised equation could suitably express the monomer reactivity ratios for this reaction. For the sake of consistency, the revised composition equation for divinyl monomers was used for the calculations, but it is evident that the spread of the plots and the area of intersection by differential analyses are too large to be attributable merely to experimental errors or to variations in technique among the different samples. The reported monomer reactivity ratios for the styrene (M_1) and p-divinylbenzene (M_2) copolymerization by the differential analyses are $r_1 = 0.77$ and $r_2 = 2.08$ at 0.55-3.7%

conversion at 80°C[6], and $r_1 = 0.77$ and $r_2 = 1.46$ at 2-5.2% conversion at 70°C[7]. Values of $r_1 = 0.15$ and $r_2 = 1.22$ up to 3% conversion at 70°C from infrared spectra analyses and by the intersectional calculation method have been reported[46].

The out-put of the computer calculation for the styrene and p-divinylbenzene copolymerization is summarized in Table 4. The values of $r_1 = 0.20$ and $r_2 = 1.00$ at 75°C are obtained from the integral analysis at conversion levels in the 2-15% range. The value of r_1, as with the meta isomer, is much higher ($r_1 = 1.67$-1.76) for copolymers prepared at higher conversions (15-19%) and with less than 1 to 1 ratio of styrene and p-divinylbenzene.

It is to be noted that in the absence of simplifying assumptions the solutions of differential equation were unsatisfactory as seen in intersect plots[6,7]. It is, however, reasonably and consistently clear from all of the low conversion data that in the styrene and p-divinylbenzene system the two radicals are unlike in their behavior toward the two monomers. p-Divinylbenzene is much the more reactive monomer to either radical. This is expected by the following reason. It is known that styrene exhibits a strong tendency to add to any free radical because the resulting adduct is strongly stabilized by resonance. Because of the direct conjugation between the two vinyl groups through benzene ring, p-divinylbenzene should offer

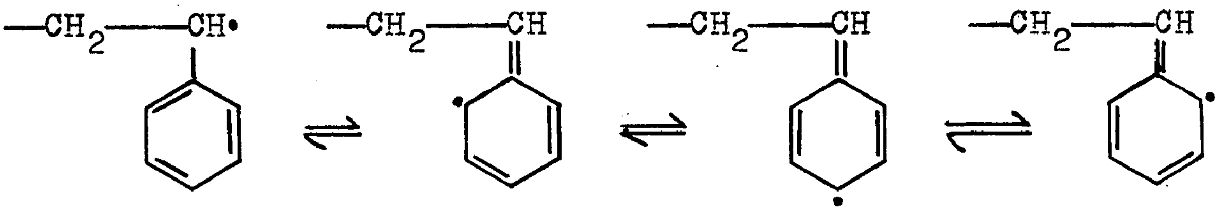
Table 4

Monomer Reactivity Ratios (r_1 and r_2) for the Styrene/p-Divinylbenzene Copolymerization.

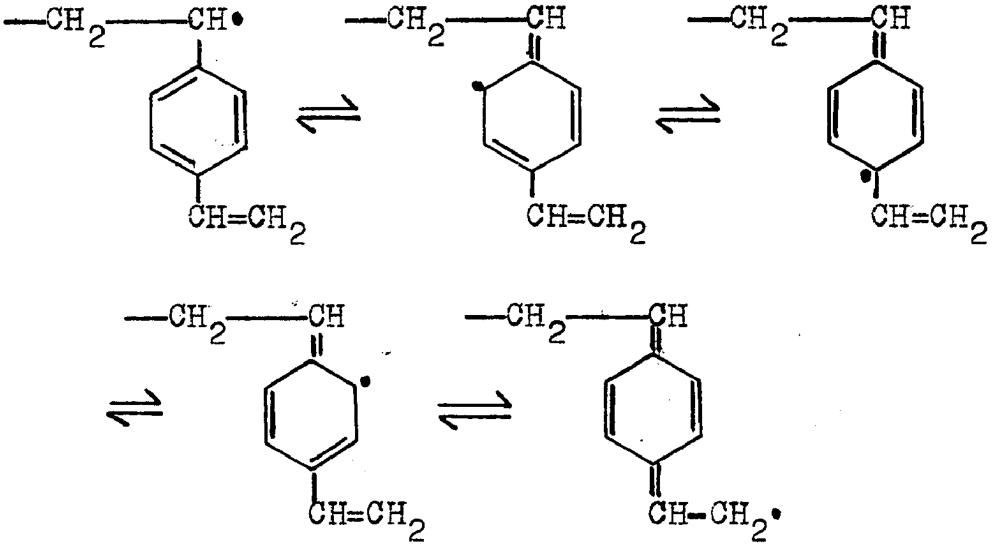
Pairs[a,b]	Average Conversion(%)	r_1	r_2
6(1.93),9(9.04)	5.48	0.15	1.00
6(1.93),8(14.89)	8.41	0.25	1.01
6(1.93),7(14.95)	8.44	0.25	1.01
7(14.95),9(9.04)	11.99	0.18	1.00
7(14.95),8(14.89)	14.92	0.21	1.00
	Average	0.20	1.00

a. Data points from Table 2 used, with the conversion in parenthesis.

b. Variation of conversions by ±10% gave r_1 values (top to bottom) of 0.149, 0.182, 0.268, 0.178, 0.209, and r_2 values of 1.00.



additional resonance structures and thus will exhibit greater reactivity in copolymerization reactions than a monomer which does not possess this conjugation, e.g., styrene.



When these two monomers compete for a free radical, the divinylbenzene will be more reactive than the styrene. p-Divinylbenzene is, as a result, incorporated more rapidly into the growing copolymer chain than styrene is. It means that divinylbenzene is consumed preferentially in the copolymerization of styrene with p-divinylbenzene.

Since the divinylbenzene is incorporated more rapidly into the growing polymer chain than styrene, it is possible to have much clustering of the divinylbenzene units in the copolymer chain because a residual or pendant vinyl group in the divinylbenzene portion of the copolymer chain will tend to favor a chain reaction. Storey[47] recently studied the initial rates and gel points for the copolymerization of styrene and p-divinylbenzene, and his results imply that intrachain cross-linking to produce microgels is an important reaction even at low crosslinker (p-divinylbenzene) levels and is the dominant reaction at moderate to high levels even before gelation.

On the other hand, it must be noted that the reactivity of a pendant double bond in the divinyl unit in the copolymer chain cannot be the same as that of a vinyl group in the unreacted divinylbenzene monomer. In the latter case, the reactivity of one vinyl group is reinforced by conjugation with the other case as discussed. As soon as one group enters into a copolymer chain, this conjugation effect will be altered and the remaining unreacted vinyl group will now possess characteristics similar to those of a vinyl group in a p-alkylstyrene molecule. The net effect will be to produce a three component copolymerization as mentioned in the meta-isomer system. The reactivities of the pendant vinyl group and the vinyl group in a p-alkylstyrene will be of similar magnitude. Wiley and co-workers[48] and Braun and co-workers[49] determined the monomer reactivity ratios for the styrene and p-isopropylstyrene system by differential analysis. They have obtained the values of r_1(styrene) = 1.22 and r_2(p-isopropylstyrene) = 0.89, and r_1 = 1.11 and r_2 = 0.54, respectively. These results indicate that p-isopropylstyrene is somewhat less reactive to the styryl radical than styrene. Therefore it is to be expected that the reactivity of divinylbenzene will be reduced by the participation of vinyl group of the p-alkylstyrene.

However, the highly enhanced r_1 values (Table 5) obtained at higher conversions and with the low monomer ratio of styrene and divinylbenzene are not explained with only this effect. The reason may be attributable to diffusion problems. At the higher levels a relatively minor involvement of the second vinyl group leads to crosslinking and this in turn inhibits ready diffusion of the more bulky divinyl monomer to the growing radical site. Comparison of the magnitude of the effect in the m-divinylbenzene (nearly four-fold) and p-divinylbenzene (over eight-fold) shows that the para isomer system shows both greater enhancement of r_1 and enhancement at lower conversion levels; i.e. 19% as opposed to 35% for the meta isomer. This is consistent with the observation that the styrene-p-divinylbenzene system crosslinks (gels) at lower conversion and shorter times that does the styrene-m-divinylbenzene system[50] and swells less[39].

The conclusion that can be reached in an analysis of these integral data is that for styrene-p-divinylbenzene copolymerization the r_2 value is considerably higher

Table 5

Monomer Reactivity Ratios (r_1 and r_2) for the Styrene/m- and p-Divinylbenzene Copolymerization.

Pairs[a]	Average Conversion %	r_1	r_2
1(4.7), 5(34.9)	19.8	3.77	1.00
3(6.7), 5(34.9)	20.8	3.92	1.00
2(18.2), 5(34.9)	26.5	3.90	1.00
8(14.89),10(19.37)	17.13	1.67	0.99
7(14.95),10(19.37)	17.16	1.76	0.99

a. Pairs of data points used, identified as experimental numbers in Table 1 and 2 with the conversion in parenthesis.

Averages

$r_1(s) = 3.86$ and $r_2(m) = 1.00$

$r_1(s) = 1.67$ and $r_2(p) = 0.99$

than the corresponding r_1 at up to moderately high conversion, but the enhanced r_1 values are obtained at higher conversions and with the low monomer ratio of styrene and divinylbenzene. It indicates that the p-divinylbenzene enters repidly into the growing polymer chain and indeed does lead to the relative bunching of crosslinkages. It is this fact which probably leads to the erratic results in the differential analyses.

SEQUENCE DISTRIBUTION

Knowledge of the composition and sequence distribution of copolymers is necessary for investigating the properties of copolymers. Unfortunately, only information on copolymer composition is easy to obtain. The run number approach[35] for studying the sequence distribution in copolymers have been introduced into the styrene-divinylbenzene copolymer system.

In the preceding sections, we have indicated that the second vinyl group in the divinyl unit in the copolymer chain is less reactive than is a vinyl in the unreacted divinylbenzene monomer. The involvement of the second vinyl group leads to the crosslinked copolymer, but it is generally known that the second vinyl group of the divinyl monomer is not involved in the reaction prior to gelation[51]. It may, therefore, be reasonable that the copolymer produced before gel point is the linear copolymer. We have calculated the sequence distribution in the copolymers produced at relatively low conversions and at the arbitrary chosen mole fraction in monomer feed, i.e., 50% styrene and 50% divinylbenzene.

The molar percentages of the unreacted monomers at each conversion increment are shown in Table 6. It is obvious the p-divinylbenzene is consumed more rapidly in the copolymerization than is the meta isomer, and the divinylbenzene content is, as a result, richer in p-divinylbenzene copolymer than in m-divinylbenzene copolymer produced at the same conversion. The copolymer composition at each conversion also indicates that the m-divinylbenzene content in copolymer is almost equal to the monomer feed composition and the copolymer composition for the m-divinylbenzene copolymer does not vary with the conversion (Table 7).

The diad and tetrad distributions, and monomer centered triad and pentad fractions in styrene-divinylbenzene copolymers produced at 5% conversion are summarized in Tables 8 and 9. In these Tables A represents styrene and B divinylbenzene. The fraction of a given type sequence for styrene is almost equal to that for m-divinylbenzene especially at these monomer feed compositions. It indicates that m-divinylbenzenes are uniformly distributed in the copolymer chain, but para isomers are not.

Figure 6 shows the moles of various sequences present per gram of copolymer formed at 5% conversion. This figure

Table 6

Molar Percentages of the Unreacted Monomers at each Conversion Increment.

I. Styrene-m-Divinylbenzene Copolymer[a]

Total Conversion(%)	Styrene(%)	m-DVB(%)
5.0	47.4	47.6
10.0	44.9	45.1
15.0	42.3	42.7
19.9	39.7	40.2
24.9	37.2	37.8
29.9	34.7	35.3

II. Styrene-p-Divinylbenzene Copolymer[a]

Total Conversion(%)	Styrene(%)	p-DVB(%)
5.1	48.1	46.9
10.3	46.2	43.8
15.4	44.3	40.7
20.5	42.3	37.7
25.6	40.3	34.7
30.7	38.3	31.7

a. Monomer feed composition, styrene 50%; DVB 50%

Table 7

Copolymer Composition at each Conversion

I. Styrene-m-Divinylbenzene Copolymer[a]

Total Conversion(%)	Styrene(%)	m-DVB(%)
5.0	51.3	48.7
15.0	51.2	48.8
29.9	51.1	48.9
54.9	50.9	49.1

II. Styrene-p-Divinylbenzene Copolymer[a]

Total Conversion(%)	Styrene(%)	p-DVB(%)
5.1	37.7	62.3
15.4	38.1	61.9
30.7	38.9	61.1
51.1	40.1	59.9

a. Monomer feed composition, styrene 50%; DVB 50%

Table 8

Sequence Distribution in Styrene and m-Divinylbenzene Copolymer.

```
 STYRENE AND META DVB SYSTEM
CI=    0.05000


MONOMER REACTIVITY RATIOS RA=  1.1100    RB=  1.0000
MONOMER FEED- A  50.000   B  50.000
COPOLYMER COMPOSITION- A  51.303   B  48.697
RUN NUMBER=  48.664            CONVERSION (WT.)=   4.986
DIAD DISTRIBUTIONS
AA= 0.26971  AB+BA= 0.48664  BB= 0.24365

TRIAD DISTRIBUTIONS
AAA= 0.27639               BBB= 0.25034
AAB= 0.49868               BBA= 0.50000
BAB= 0.22494               ABA= 0.24966

TETRAD DISTRIBUTIONS
AAAA= 0.07454              BBBB= 0.06100
BAAA= 0.13450              ABBB= 0.12183
BAAB= 0.06067              ABBA= 0.06083
AABA= 0.12783              BABB= 0.11548
AABB= 0.12801              BABA= 0.11532

AAAAA= 0.07639             BBBBB= 0.06267
BAAAA= 0.13783             ABBBB= 0.12517
BAAAB= 0.06217             ABBBA= 0.06250
ABAAA= 0.13099             BABBB= 0.11865
BAABA= 0.11817             ABBAB= 0.11849
BBAAA= 0.13117             AABBB= 0.13152
BBAAB= 0.11834             AABBA= 0.13134
ABABA= 0.05616             BABAB= 0.05616
BBABB= 0.05631             AABAA= 0.06900
BBABA= 0.11247             AABAB= 0.12450
```

A: Styrene

B: m-Divinylbenzene

Table 9

Sequence Distribution in Styrene and p-Divinylbenzene Copolymer.

```
 STYRENE AND PARA DVB SYSTEM
CI=    0.05000


MONOMER REACTIVITY RATIOS RA=  0.2000     RB=  1.0000
MONOMER FEED- A  50.000   B  50.000
COPOLYMER COMPOSITION- A  37.702   B  62.298
RUN NUMBER=  62.700           CONVERSION (WT.)=   5.137
DIAD DISTRIBUTIONS
AA= 0.06352  AB+BA= 0.62700  BB= 0.30948

TRIAD DISTRIBUTIONS
AAA= 0.02839              BBB= 0.24680
AAB= 0.28019              BBA= 0.49996
BAB= 0.69141              ABA= 0.25325

TETRAD DISTRIBUTIONS
AAAA= 0.00180               BBBB= 0.07638
BAAA= 0.01780               ABBB= 0.15473
BAAB= 0.04392               ABBA= 0.07837
AABA= 0.05317               BABB= 0.25899
AABB= 0.05247               BABA= 0.26237

AAAAA= 0.00081              BBBBB= 0.06092
BAAAA= 0.00796              ABBBB= 0.12339
BAAAB= 0.01963              ABBBA= 0.06249
ABAAA= 0.02376              BABBB= 0.20653
BAABA= 0.11725              ABBAB= 0.20920
BBAAA= 0.02345              AABBB= 0.04184
BBAAB= 0.11573              AABBA= 0.04239
ABABA= 0.17511              BABAB= 0.17509
BBABB= 0.17063              AABAA= 0.00719
BBABA= 0.34568              AABAB= 0.07096
```

A: Styrene

B: p-Divinylbenzene

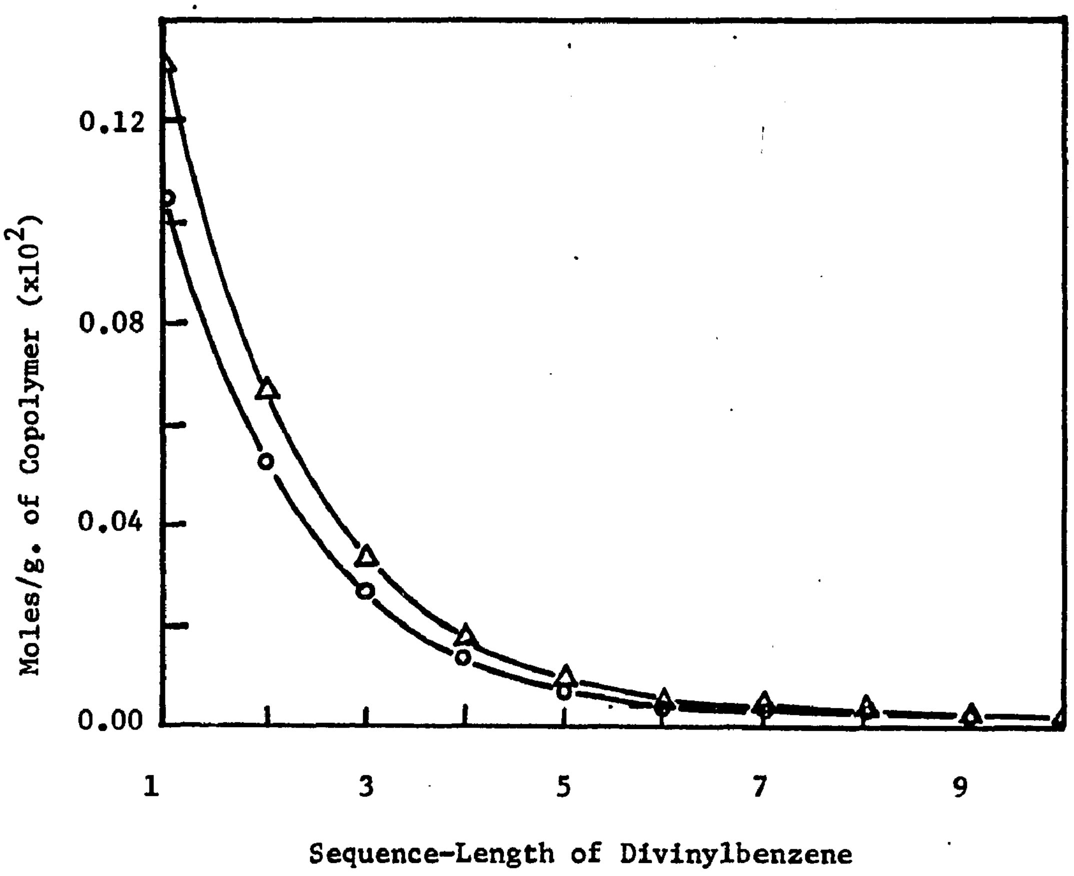


Figure 6. Sequence-length distribution curves of divinylbenzenes in the styrene-divinylbenzene copolymers obtained from 1 to 1 monomer feed compositions at the same conversion (5%);

○ for m-DVB, △ for p-DVB.

indicates that a higher mole number of p-divinylbenzene in its copolymer with styrene has longer sequence length than that of meta isomer in its copolymer at the same conversion. The number-average length[35] of a given type sequence, $\langle M_1 \rangle$ or $\langle M_2 \rangle$, is simply the total number of the given type monomer units divided by the number of runs of that type present, so that

$$\langle M_1 \rangle = \%\ M_1/(R/2)$$

and

$$\langle M_2 \rangle = \%\ M_2/(R/2)$$

The results of such calculations are $\langle$styrene$\rangle$ = 1.2 and $\langle$p-divinylbenzene$\rangle$ = 2.0 for the styrene-p-divinylbenzene copolymer, and $\langle$styrene$\rangle$ = 2.1 and $\langle$m-divinylbenzene$\rangle$ = 2.0 for meta-isomer copolymer. This indicates that the relative bunching of divinylbenzene units is of marked significance in styrene-p-divinylbenzene copolymer.

The analyses of the sequence distribution of the divinylbenzene-styrene copolymer show that the p-divinylbenzene enters into the growing copolymer chain faster than does the meta isomer. This should result in rapid exhaustion of the available p-divinylbenzene monomer long before styrene is consumed.

It appears that the copolymerization of styrene with p-divinylbenzene results in a structure with a tightly crosslinked nucleus to which long chains of polystyrene are attached and in which much more pure polystyrene may be imbedded. In comparison, the styrene-m-divinylbenzene copolymer would be expected to have a structure in which the crosslinks are more widely and more uniformly distributed than in the styrene-p-divinylbenzene copolymer, and there is presumably less pure polystyrene forming in the last stages of polymerization.

The swelling ratios[39], the rates of sulfonation[52,53] and mass spectral characteristics[54] of bead copolymers of styrene crosslinked with m- and p-divinylbenzene, the rates of peroxide-induced degradation[55] of the sulfonated bead copolymers, and the EPR spectral characteristics[56] of manganese (II) ions on sulfonated polystyrene resins crosslinked with pure divinylbenzene isomers have been reported. These data show differences which can be related to differences in the crosslinked structures produced by differences in the copolymerization characteristics of m- and p-divinylbenzenes just discussed, and are consistent with our results.

SUMMARY

The copolymerization reactivity ratios for styrene with m-divinylbenzene and with p-divinylbenzene have been determined at high conversion (up to 35%) using the integrated form of the copolymerization equation. Values of $r_1(s) = 1.11$, $r_2(m) = 1.00$ and $r_1(s) = 0.20$, $r_2(p) = 1.00$ were obtained by IBM 1620 computer calculations. These values also were used to calculate those aspects of copolymer structure that are related to the distribution of monomer sequence in styrene-divinylbenzene copolymer chain. An IBM 360 was employed to calculate the sequence distributions.

These reactivity ratios from integral analysis indicate the same relative behavior but are quantitatively different from the data obtained from differential analysis. The data confirm that the para isomer is incorporated more rapidly into the growing polymer chain than is the meta isomer. This effect leads to the relative bunching of crosslinkages in styrene-p-divinylbenzene copolymer. However, the styrene-m-divinylbenzene copolymer would be expected to have a structure in which the crosslinks are more widely and more uniformly distributed than in the styrene-p-divinylbenzene copolymer. The analysis of the sequence distribution of styrene-divinylbenzene copolymers substantiated these conclusions.

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PART II

STYRENE-DIVINYLBENZENE COPOLYMER ION-EXCHANGE RESIN —— SYNTHESIS AND EQUILIBRIUM STUDIES

INTRODUCTION

The sulfonated polystyrene crosslinked with divinylbenzene is the most widely used and studied cation-exchange resins. The commonly used divinylbenzene is a commercial material which consists of several monovinyl and divinyl monomers, as well as other compounds. A total of 11 or 12 compounds, present in variable amounts in different samples, can be distinguished by gas chromatographic analysis[1]. The complexity and variation of the structure of copolymers crosslinked by such mixtures of materials may account for some of the difficulties encountered in correlating theoretical and experimental studies of the ion-exchange resin. The properties of the resin are presumably influenced by the nature of the network, which in turn is determined by the relative polymerization reactivity of the crosslinking agent used in copolymerization.

The monomer reactivity ratios of the pure m- and pure p-divinylbenzenes with styrene are quite different as described in the first part of this thesis. The data for the sulfonation rates[2,3] of bead copolymers of styrene crosslinked with pure m- and p-divinylbenzene and for the swelling ratios[4] of the sulfonated resins show differences which can be related to differences in the crosslinked copolymer structures.

We have studied ion-exchange equilibria involving sodium, potassium, rubidium, cesium and silver ion on the sulfonated resins prepared with pure divinylbenzene isomers. The results of these equilibrium studies are correlated with compositional variations in the crosslinking network. This will provide a structural insight for the evaluation of the fundamental ion-exchange properties.

In addition, a preparation method for a new suspension agent for the synthesis of styrene and pure divinylbenzene copolymer beads is described.

HISTORICAL

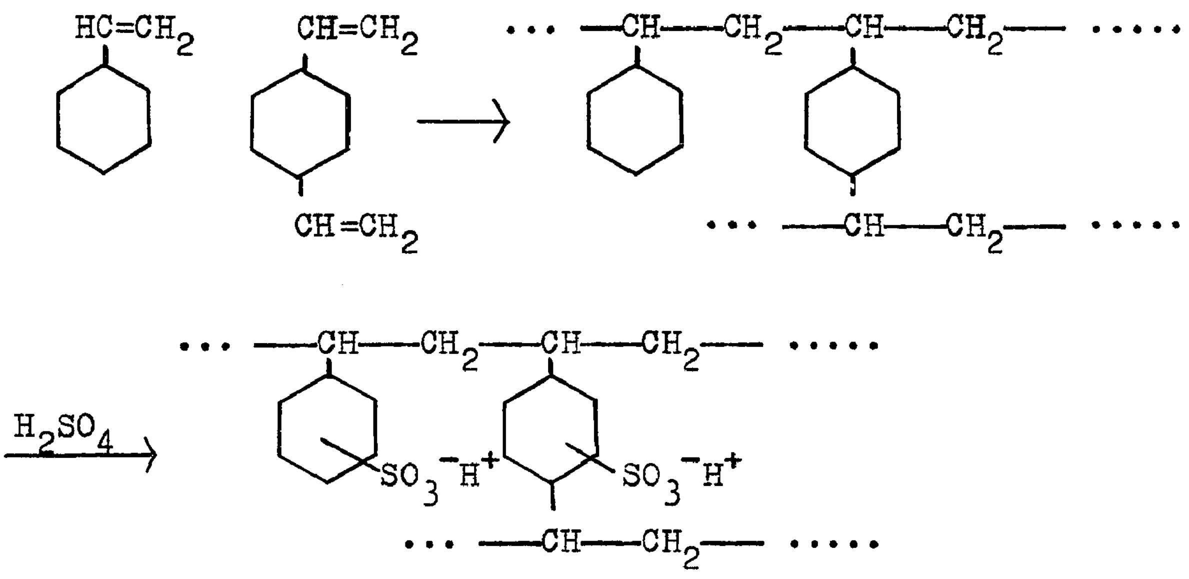
Ion exchange can be defined as anexchange of ions between a solid and a liquid in which there is no substantial change in the structure of the solid. In this definition, the "solid" is the ion exchange material or the resin particle. Ion exchange materials are of two types: inorganic and organic. The most important class of these is the organic ion-exchange resin. An ion-exchange resin particle can be visualized as an elastic, three-dimensional hydrocarbon network to which is attached a large number of ionizable groups. The nature of the hydrocarbon network affects the chemical behavior of the exchanger in degree. The nature of the ionizable groups attached to the hydrocarbon network determines the chemical behavior of an ion-exchange resin. The cation exchangers may contain $-OH$, $-COOH$, $-PO(OH)_2$, or $-SO_3H$ groups as the ionizable group, and the anion exchangers may contain primary, secondary or tertiary amino groups or quaternary ammonium groups.

Ion exchange phenomena have been recognized for a long time. The early work was principally concerned with the implications of ion exchange in soil chemistry, and this has continued to be an important field for investigation.

The study of ion exchange was greatly stimulated by the production of synthetic zeolites which not only allowed further controlled investigation, but also extended the industrial applications of these substances. An additional stimulus was provided by the development of the synthetic organic ion-exchange resins by Holmes and Adams[5] in 1935. This allowed the production of ion-exchange resins of relatively homogeneous functional types, of wide stability ranges, and of different exchange potentials[6].

The fact that within a period of approximately thirty years the utilization of ion-exchange resins for separations, recoveries, deionization, and catalysis, as well as for water softening on an industrial scale, has become a reality illustrates the importance of these resins and is indicative of the future usefulness that may be expected of them.

Resin syntheses in general can be classified as condensation polymerizations and addition polymerizations. The phenol-formaldehyde resin is a typical example of the condensation type resins. Most of the present ion-exchange resins are addition copolymers prepared from vinyl monomers. These polymers have a higher chemical and thermal stability than the condensation polymers. Crosslinked polystyrenes with sulfonic acid groups which have been introduced after polymerization by treatment with concentrated sulfuric acid or chlorosulfonic acid[7,8] are the most important resins of this type. Generally, divinylbenzene is used as the crosslinking agent.



Pure divinylbenzene is not readily accessible. Therefore the resins are usually prepared with a commercial product consisting of a mixture[1] of the different divinylbenzene isomers (about 40-55%) and ethylstyrene (about 45-60%). Ethylstyrene is incorporated into the matrix. The degree of crosslinking can be adjusted by varying the divinylbenzene content.

The so-called bead copolymerization technique[9] is used for the preparation of the copolymer beads. The monomers are mixed, and a polymerization catalyst such as benzoyl peroxide is added. The mixture is then added to a thoroughly agitated aqueous solution which is kept at the temperature required for polymerization. The mixture forms small droplets which remain suspended. The size of the droplets depends chiefly on the nature and the amount of suspension stabilizer in the aqueous phase and the speed of agitation. The copolymer is obtain in the form of spherical beads by this method.

The copolymer beads swollen[10,11] in solvents such as ethylene chloride, toluene, nitrobenzene, or dimethyl sulfoxide are transferred to another vessel where they are heated with concentrated sulfuric acid. It is advisable to transfer the sulfonated beads at first into a highly concentrated electrolyte solution which causes less swelling and then to dilute the solution stepwise to avoid rapid swelling of the resins which may cause shattering[10]. Since there exist no adequate quantitative theories that permit us to predict the necessary requirements for achieving conditions such as a fixed degree of crosslinking, a fixed particle-size distribution, a predetermined sulfonation rate or chloromethylation rate in a heterogeneous system, etc., the synthesis of ion exchange resins remains an art rather than a science[12].

For a long time, equilibria between ion exchangers and solutions have been the subject of numerous experimental and theoretical studies. Most of the earlier investigations were made with inorganic ion exchangers and centered on the study of ion-exchange equilibria, i.e., on the distritution of different competing counterionic species between the ion exchanger and a solution. In recent years, several theories for equilibria between ion exchangers and solutions have been developed. These theories may be classified[13] into two catagories. In the first catagory, a rigorous thermodynamic treatment that requires no model and no assumptions with respect to the mechanism of the phenomenon is employed. The second approach consists of the introduction of models with particular properties resembling those of the ion exchanger to permit the derivation of equations which reflect the action of various physical forces in the exchange process. A comprehensive discussion of both approaches has been described by Helfferich[13].

The first model which reflects any of the particular properties of ion-exchange resins was introduced by Gregor[14]. According to this model, the matrix of the resin is a network of elastic springs. When the resin swells, the network is stretched and exerts a pressure on the internal "pore" liquid. The "swelling pressure" in the resin affects swelling, sorption, and ion-exchange equilibria. In the thermodynamic treatment of this model, the components of the system are usually taken to be the matrix with fixed ionic groups, the various mobile ionic species, and the solvent. Solvation shells have been considered by some as being part of the ions, and by others as belonging to the solvent.

Gregor's model is purely mechanical. Swelling pressure is the only particular property considered. Electrostatic interactions are not included. Gregor's model can explain, at least qualitatively, effects in systems in which the swelling-pressure effect is not overshadowed by the action of other forces as for example the selectivity sequence of the alkali ions. This model cannot explain the striking selectivities which are often found and usually attributed to specific interactions between the fixed ionic groups and the preferred counter ion.

More recently, Lazare and Gregor[15] have suggested a refined model which includes electrostatic interactions. The matrix is represented by parallel plates which are interconnected by elastic springs and carry uniform electric surface charges. So far, the model has only been applied to swelling and electrolyte-sorption equilibria.

Both Gregor's models may be called "macroscopic". They do not involve the single ion as a discrete particle, and elasticity of the spring which represents the matrix is purely mechanical. In contrast, the models proposed by Katchalsky[16] and by Harris and Rice[17] are based on considerations on a molecular scale. In these models the matrix is represented by a crosslinked network of chains which consists of rigid, rod-shaped segments carrying one electric charge each. These models were originally developed for linear polyelectrolytes and were later extended by crosslinked gels.

The phenomena of cation exchange can be interpreted on a mass-action basis, and the mass-action law has been applied, with apparent success, to equilibria involving organic exchanger resins[18, 19]. The mass-action treatment has the advantages of simplicity and clarity and it enables a thermodynamic constant to be evaluated which should be characteristic of any exchange on a given exchanger.

Now we will consider an exchanger equilibrated with two monovalent counterions A and B, present both in the exchanger and in the solution in contact with it. We may write

$$A_R + B_S \rightleftharpoons A_S + B_R \qquad (1)$$

where subscripts R and S indicate the resin phase and the solution phase respectively. Then the selectivity coefficient[19] (or relative affinity coefficient) K_A^B may be defined

$$K_A^B = \frac{X_{B_R} \cdot X_{A_S}}{X_{A_R} \cdot X_{B_S}} \qquad (2)$$

where X_{B_R} and X_{A_R} represent the equivalent fraction of the counterions in the exchanger and X_{A_S} and X_{B_S} the corresponding equivalent fractions of these ions in the solution. $X_{A_R} + X_{B_R} = 1$ and $X_{A_S} + X_{B_S} = 1$. Clearly, if both counterions are monovalent, we could equally well use in this equation either their molar or molal concentrations in the exchanger, since only the ratio enters into the equation. Equally, we could use either the molal or the molar concentrations in the solution phase, provided that for a given phase (exchanger or solution) the amounts of the two ions are always expressed in the same concentration units.

K_A^B as defined in equation (2) represents in a quantitative way the relative ionic compositions of the resin and solution phases. Any value of K_A^B that is different from unity measures the relative difference in preference of the solution and resin phases for the two competing ions. The preference for one ion species over another in a particular phase is a measure of the relative effects of the two components on the activities in that phase. We can define another quantity K'^B_A as a corrected selectivity coefficient[19]. This quantity includes a correction for the activity coefficients in the solution.

$$K'^B_A = K_A^B(\gamma_A/\gamma_B) \qquad (3)$$

Ion-exchange equilibria are usually determined by equilibrating the ion exchanger with a solution containing both competing counterion species and analyzing the ionic composition of the ion exchanger after separation from the solution. The equilibration can be carried out in a column[20,21] or by repeated batch[22] treatment with portions of the solution.

The selectivity coefficient is usually not constant but varies with the counterion composition of the resin. This phenomenon has been investigated in terms of ion-exchange isotherms[23,24,25]. Ion-exchange isotherms can be determined point by point from a series of ion-exchange equilibrium measurements with solutions of different compositions covering the whole range of interest.

If determination of the concentrations in the solution is sufficient to calculate the equilibrium distribution, the "progressive-batch" method[26] is more convenient. Here, a sample of the ion exchanger in A form is converted stepwise to the B form by successive equilibrations with portions of a solution of the electrolyte BY. The concentrations of A and B in the solution are determined after each conversion step. The ionic composition of the ion exchangers is calculated by difference. This technique permits the whole isotherm to be obtained from successive measurements with only one sample of the ion exchanger and without separating the latter from the solution.

The equilibrium isotherm studies of the various pairs of cations have been the subject of many investigations and have led to several theories explaining the differences between the ions. It should be remembered that the divinylbenzenes in the resins used in all the ion-exchange equilibrium studies were commercial materials, which are mixtures of different components.

EXPERIMENTAL

1. PREPARATION OF ION-EXCHANGE RESINS

MATERIALS

STYRENE: This was supplied by Baker Chemical Co.. This was washed with 1 N sodium hydroxide solution and distilled water three times each. The washed styrene was dried over anhydrous calcium chloride under nitrogen atmosphere and vacuum distilled over a potassium hydroxide pellet (n_D^{20} 1.5468; Lit.[27] 1.5465).

m- AND p-DIVINYLBENZENE: The pure divinylbenzenes used for this work were prepared as described in the previous part. Gas chromatographic analyses showed m- and p-divinylbenzenes to be 99.8+% and 99.9+% pure respectively.

COMMERCIAL DIVINYLBENZENE: This was supplied by Dow Chemical Co. and was purified by vacuum distillation to obtain an inhibitor free sample (b.p. 52-3°C at 1 mm; n_D^{25} 1.5553).

INITIATOR: Benzoyl peroxide was dissolved in chloroform and was purified by precipitation with methanol.

PREPARATION OF POLYVINYL SULFATE SUSPENDING AGENT

Twenty grams of polyvinyl alcohol (Dupont, Grade 52-22) were suspended uniformly in a sulfating mixture prepared from 15 ml. of sulfuric acid (96% A.C.S. Grade, Allied

Chem.) and 100 ml. of pure ethyl alcohol at room temperature (20-25°C). The mixture was allowed to stand for 24 hours at room temperature. The paste was then diluted with 100-125 ml. of water and poured slowly into 750 ml. of methyl alcohol under fast stirring. The fine, granular precipitate was then collected on a filter and washed several times with methanol until the washings are acid free. The material was allowed to dry under vacuum at room temperature and powdered. The yield of polyvinyl sulfate was 17-18 g. and was found to contain 0.77% of sulfur. The sample was analyzed by Schwarzkopf Microanalytical Lab., Woodside, New York.

BEAD COPOLYMERIZATION

The dispersion solution was prepared by dissolving 0.75 g. of polyvinyl sulfate in 200-250 ml. of warm water with vigorous stirring. This solution was then introduced into a 500 ml., three necked flask half immersed in a constant temperature oil bath at 80°C. The flask was fitted with a nitrogen inlet, a "V" shaped stirrer, and an air condenser. The solution was stirred under a nitrogen blanket until it attained constant temperature.

At this point stirring was stopped, a 12.00 g. mixture of styrene and divinylbenzene of appropriate composition (Table 1) containing 2% by weight of benzoyl peroxide was added to the suspension solution. The solution was kept

Table 1

Experimental Data for Typical Runs of Styrene-Divinylbenzene Polymerization

Cross-Linking Monomers	Mole % of DVB	Weight of DVB (gms.)	Weight of Styrene (gms.)	Weight of Beads(gms.)		
				125μ	125-250μ	250-500μ
	2	0.648	11.388	0.9	10.0	-
c-DVB[a]	4	1.280	10.780	0.2	9.6	1.1
	8	2.543	9.603	1.5	10.0	-
	2	0.300	11.700	0.8	9.1	-
m-DVB	4	0.595	11.405	0.4	9.4	1.3
	8	1.176	10.823	2.2	9.2	-
	2	0.300	11.700	0.2	9.3	1.0
p-DVB	4	0.595	11.405	0.6	10.1	-
	8	1.176	10.823	1.3	9.6	1.0

a. Commercial divinylbenzene (Dow Chemical): Based on the analytical composition data the divinylmonomer content was calculated and used in determining the amount of crosslinking agent per unit weight of commercial divinylbenzene. c-DVB was found to contain 46.3% of divinylbenzene (31.3% of m-DVB and 15.0% of p-DVB).

stirred uniformly under an atmosphere of nitrogen. The speed of stirring was adjusted so that a stable vortex persisted in the swirling motion of the liquid and no air bubbles or foam developed.

After 20 hours of polymerization, the copolymer beads were collected and separated into different size fractions by sieving through 500, 250 and 125 micron standard screens under a constant flow of distilled water. These beads on the screens were washed with distilled water and with methanol several times, and then dried at 70°C for an hour.

The bead size distribution curves of 125-250 micron sieve cut were determined by diameter measurements of around 600 beads from each sieve size cut using a Beck Kassel microscope with a Leitz Wetzlar micrometer[28].

The yields of bead copolymerization are given in Table 1, a photomicrograph of the styrene-divinylbenzene copolymer beads is shown in Figure 1, and a typical bead size distribution curves is indicated in Figure 2.

SULFONATION OF COPOLYMER BEADS

About 8 g. of the copolymer beads in the 125-250 micron range were preswollen in 100 ml. of distilled ethylene dichloride (Fisher Certified Reagent) overnight, and the excess dichloride was removed by vacuum filtration on a sintered glass filter[3]. Concentrated sulfuric acid

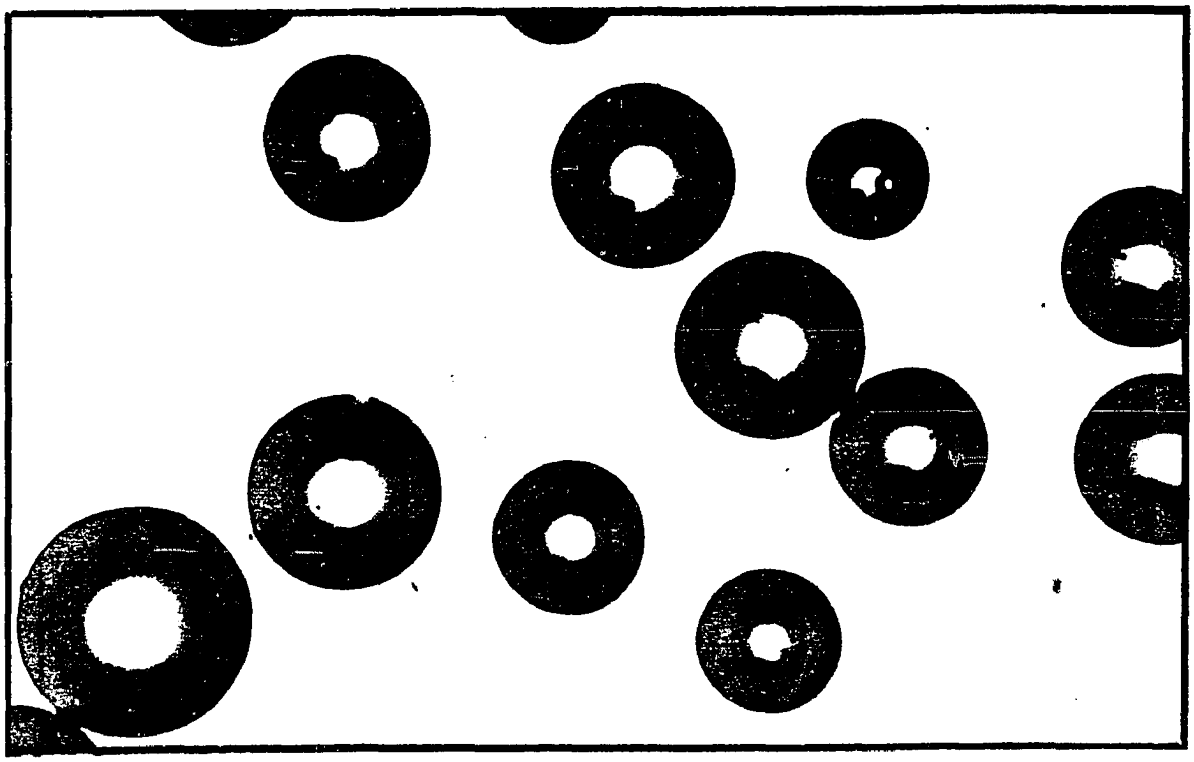


Figure 1. Photomicrograph of Polystyrene Beads Crosslinked with 4 Mole% p-Divinylbenzene (x175).

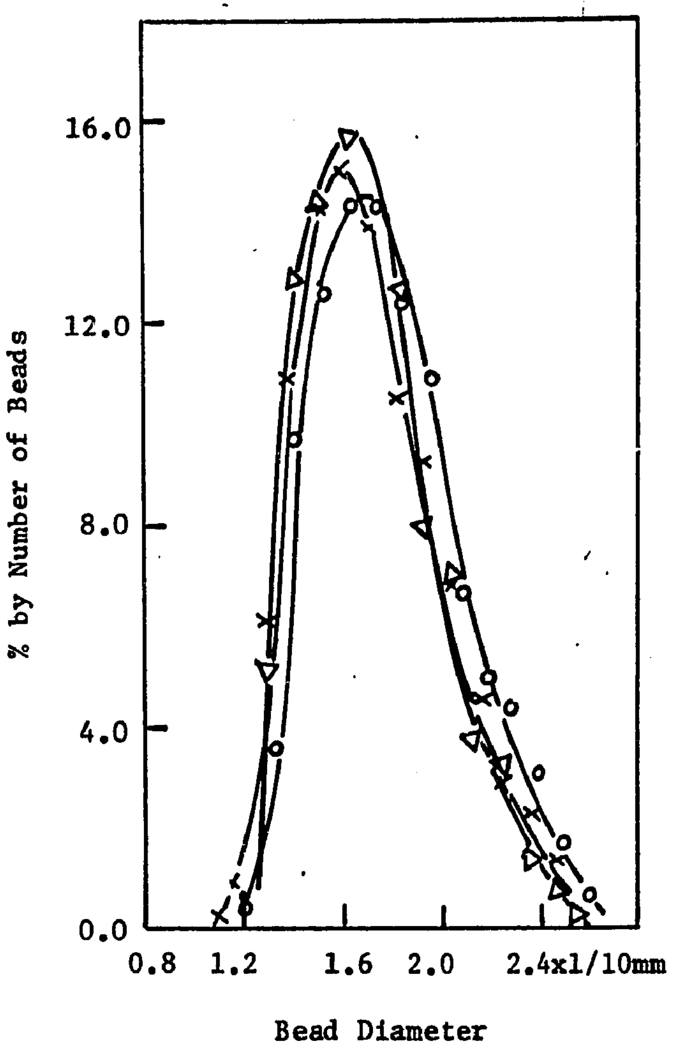


Figure 2. Size distribution curves of crosslinked bead copolymers of styrene with 4 mole% divinylbenzene: ○, c-DVB; △,m-DVB; ╳, p-DVB.

prepared from 8 parts of 95.5-96.5% sulfuric acid (Allied Chemical Co.) and 1 part of 30% fuming sulfuric acid (Allied Chemical Co.) was used for the sulfonation of copolymer beads[11]. Fifty milliliters of this sulfuric acid were used to flush the swollen beads through a wide, long-stemmed funnel into a 500 ml., three-necked round bottomed flask containing 150 ml. of the same acid maintained at a constant temperature of 100°C in an oil bath. The flask was fitted with a stirrer, a stopper, and an air condenser closed with a silica gel drying tube. After checking that all the beads are in the acid, stirring was started and the speed was so regulated that all the beads were dispersed under the surface of the liquid.

The sulfonated beads were taken out after 20-24 hours, and diluted with decreasing strengths of sulfuric acid as previously described by Wiley and co-workers[3], and finally with distilled water until the washings are free from acid. The sulfonated resins were allowed to stand in distilled water overnight, at the end of which they were washed with two or three times more with distilled water.

For the storage, the resins in the hydrogen form were washed with 0.1 M KCl solution, and then the resins in the potassium form were kept in 0.1 M KCl solution.

2. DETERMINATION OF ION-EXCHANGE ISOTHERMS

MATERIALS

RESINS: The resins in the potassium form were converted to the hydrogen form by elution with 2 l. of 2 N HCl solution (2 N HNO_3 for the resins in the silver form) at a flow rate of around 20 ml./min. on a sintered glass filter and then elution with 5 l. of distilled water ensured removal of electrolyte.

The equivalent capacities of resins were determined by the salt splitting method[29] as follow. The washed resins in H^+-form were dried in a vacuum oven at 90°C to a constant weight (usually for three days). After cooling, about 0.20-0.25 g. of the dried resins were weighed quickly and added to a 100 ml. beaker containing 50 ml. of 0.1 M KCl solution. The mixture was stirred magnetically for one hour to achieve complete equilibrium. The liberated acid was then titrated against 0.1013 N standard sodium hydroxide solution (Fisher Scientific Co. standardized with potassium acid phthalate) to an end point of pH 7, the reaction mixture being continuously stirred. The pH was followed with a Beckman pH meter (Arthur H. Thomas Co.). The equivalent capacity was calculated by following equation:

$$\text{Equivalent capacity (meq./g. of dry resin)} = \frac{\text{ml.(NaOH soln.)} \times \text{N(NaOH soln.)}}{\text{grams(dry resins)}}$$

The equivalent capacities of resins are shown in Table 2.

The water contents of resins were determined by the centrifugation method[21]. The washed resins were transferred into a glass tube fitted at one end with a sintered glass disk. The tube was then placed in a centrifuge tube. To avoid losses by evaporation, the centrifuge tube was stoppered. The spherical beads were centrifuged for 20 minutes at 1500 r.p.m.. The beads was then dried in vacuum oven at 110°C to constant weight. The difference between wet weight and dry weight of the resin gives water content. The water contents of resins are given in Table 2.

SOLUTIONS OF EXCHANGING ION: Sodium chloride (Allied Chemical Reagent Grade, 99.5%), potassium chloride (Baker Analyzed Reagent, 99.8%), rubidium chloride (Fisher, purified), cesium chloride (Fisher, certified, 99.9%) silver nitrate (Baker analyzed Reagent, 99.8%) were dried overnight at 110°C, and then used for equilibrium studies.

The 1.000 M solutions made with these dried materials were kept as stock solutions and were diluted to 0.1000M when required for the equilibrium studies.

DETERMINATION OF EQUILIBRIUM ISOTHERMS

Ion exchange isotherms were determined by the progressive-batch method[26]. A sample of 2 g. of dry resin in hydrogen form, of total exchange capacity C_R milliequivalents, was accurately weighed. An amount possessing total exchange capacity of about 10 milliequivalents was used. This was placed in a dry 250 ml. conical flask with stopper

Table 2

Equivalent Capacities and Water Contents of Resins in H^+ Form.

Crosslink Agents	Mole % of DVB	Eqv. Capacities (meq./g. dry resin)	Water Content ($g.H_2O$/g.dry resin)
	2	5.26 ± 0.005	3.29 ± 0.03
c-DVB	4	5.36 ± 0.01	1.51 ± 0.02
	8	5.18 ± 0.01	0.84 ± 0.003
	2	5.18 ± 0.005	3.56 ± 0.02
m-DVB	4	5.39 ± 0.005	1.98 ± 0.005
	8	5.24 ± 0.02	1.01 ± 0.002
	2	5.26 ± 0.005	3.34 ± 0.01
p-DVB	4	5.38 ± 0.005	1.74 ± 0.01
	8	5.22 ± 0.015	0.89 ± 0.002

and 125 ml. of distilled water were added by means of buret. The resin in water were then shaken mechanically for an hour, and 100 ml. of the water were removed by pitetting. All resin particles remain permanently in the flask during the pipetting.

Y ml. (Y = 10 ml.) of a solution of the exchanging ion M^+ were added to flask and then the solution in the flask was diluted to 125 ml. of total volume with water. The solution of M^+ used contains m milliequivalents of ion per ml. (m = 0.1 meq./ml.). The resin and solution were then shaken mechanically in a water bath thermostated at 25°C until no further exchange took place. It was found that no appreciable increase in the amount of exchange took place after shaking the resins for 3 hours. Results of duplicate experiments for different time intervals agreed within experimental error. All batch experiments were therefore assumed complete after 3 hours shaking (6 hours for silver-hydrogen system).

A fraction, f (aliquot volume = 100 ml), of the resulting solution was removed by pipetting and the number of milliequivalents of hydrogen ion, x_1, in this aliquot determined by titration with standard 0.1013 N NaOH solution (Fisher Certified) which was restandardized with potassium acid phthalate.

To the remaining solution in contact with resin, bY ml. (where b = 1.25) of standard M^+ solution were added and the volume again adjusted to 125 ml. with water. After equilibrium had been reached for the second time at the correct temperature a further aliquot (100 ml.) was removed and the number of milliequivalents of hydrogen ion now present, x_2, determined.

Similarly for the nth experiment, $b^{n-1}Y$ ml. of M^+ solution were added and the number of milliequivalents of H^+, X_n, in the nth aliquot was determined by titration. The quantity of x_n can be calculated as follows.

$$x_n = \text{Volume (ml.) of NaOH x Normality of NaOH}$$

For each experimental step, the volume of cation solution was calculated (Table 3) and was added to the mixture by means of burets. In this experiment, the determination of the constants b and f were assigned values for the reasons given by Cosgrove and Strickland[26]: "For most univalent exchanges it was found that a value of 1.25 for b gives a suitable spacing of points on an isotherm. In order to keep the total ionic strength of solutions to a minimum, so as to avoid the necessity of making activity corrections, f should be at least 0.8 (a 100 ml. portion from 125 ml.)."

CALCULATION OF SELECTIVITY COEFFICIENTS

After the nth exchange in the experiment, the molar fractions of each ion on the resin and in the solution can be calculated by the following equations.

Table 3

Volumes of Cation Solution added at each Experimental Step

Exp. No.	Vol. of 0.1 M M^+ Soln. (ml.)		Vol. of Water (ml.)
1	Y	10.00	90.00
2	$b\ Y$	12.50	87.50
3	b^2Y	15.63	84.37
4	b^3Y	19.53	80.47
5	b^4Y	24.41	75.59
6	b^5Y	30.52	69.48
7	b^6Y	38.15	61.85
8	b^7Y	47.68	52.32

i) $b = 1.25$, $Y = 10.00$ ml

ii) Volume of Water (ml.) = 100 - Volume of 0.1 M M^+ Solution (ml.)

$$X_{R_n} = f \cdot \sum_{i=1}^{i=n-1} (x_i) + x_n/f \cdot C_R \tag{4}$$

and

$$X_{S_n} = 1 - \left\{x_n(1 - f - b)/f \cdot m \cdot Y\left[(1 - f)^n - b^n\right]\right\} \tag{5}$$

where X_R = molar fraction of the cation M^+ on the resin, X_S = molar fraction of the cation M^+ in solution. The corrected f values for the water absorption by ion-exchange resins were used.

As mentioned in "Historical" section of this part, for the exchange of univalent cations on the hydrogen form of a cation-exchange resin:

$$H_R + M^+_S \rightleftharpoons M_R + H^+_S,$$

equation (2) can be written in the form

$$K_H^M = \frac{X_R}{1 - X_R} \frac{1 - X_S}{X_S} . \tag{6}$$

Therefore by using equations 5, 3 and 4 an isotherm can easily be constructed from a series of the titration experimentals.

ANALYSIS OF EXPERIMENTAL DEVIATION

It was found that, owing to the experimental errors, accurate values of K_H^M cannot be calculated from the first of the experimental steps. At low X_R a small experimental error produces a large relative error in K_H^M. The overall accuracy of the duplicate determinations of K_H^M is considered to be ±0.8% for values of X_R between 0.2 and 0.9, but the average deviation of K_H^M for the first point was ±2.8% for the cesium-hydrogen and ±5.0% for the silver-hydrogen system. The isotherms of a given pair of ions on the same mole percent divinylbenzene resins (m-, p- and commercial) for comparison were simultaneously determined to minimize the relative experimental error.

RESULTS AND DISCUSSION

There is an increasing amount of evidence to suggest that ion-exchange sites on ion-exchange resins behave nonuniformly[19]. Most of this evidence is of indirect nature. The structures obtained from the copolymerization with chemically isomeric divinylbenzenes are different because of their different copolymerizing characteristics as discussed in the earlier part. Therefore, cation-exchange equilibrium studies on the sulfonated polystyrenes crosslinked with m- and p-divinylbenzenes will give a precise understanding of the behavior of exchangers which may be related to the structural characteristics of the copolymer. First of all the preparation of the necessary resins for this study will be discussed.

PREPARATION OF COPOLYMER BEADS

In the previous studies[4], carboxymethyl cellulose ether sodium salt was employed as a suspension agent to obtain the styrene-pure divinylbenzene copolymer beads. The bead size of copolymer obtained was 20-30 mesh. It is of interest to have available beads of much smaller size for detailed studies of the ion-exchange characteristics of the sulfonated copolymers[28].

Experimental conditions for bead copolymerizations are critical and depend upon a number of factors, and optimum conditions which may vary from system to system have to be determined empirically. The most important factors influencing the bead copolymerization are the nature of the dispersion agent and the agitation of the reaction mixture[13].

The size distribution of beads can be varied by changing the speed of stirring and the position of the stirrer with respect to the liquid level. A "V" shaped stirrer with the "V" bend just below the liquid level was found to give good results in this work. The constant speed of stirring, which was adjusted so that a stable vortex persisted in the swirling motion of the liquid and no air bubbles or foam developed, was determined by trial experiments for each copolymerization run so as to give a good yield in the 125-250 micron range.

When a water-insoluble monomer is agitated in water under suitable conditions, a dispersion of monomer droplets in water is formed. For these conditions, the system attains a state of mobile equilibrium in which monomer droplets are continuously coalescing and breaking up, and the droplet size distributions is governed by the rate of agitation, and the surface tension and viscosity of the two phases. If a polymerization initiator such as benzoyl peroxide is dissolved in the monomer and the system is heated, then polymerization of the monomer droplets will take place as a large number of small bulk copolymerizations. As polymerization proceeds, the monomer becomes more viscous until it is no longer possible for droplets to coalesce and break up. At this point in the polymerization the droplets may become sticky, and in the absence of a dispersion agent the droplets may all aggregate together to form a large lump of polymer.

Several substances known as suspension agents, when added to certain dispersion systems, will prevent aggregation of monomer droplets during polymerization. However the exact mode of action of dispersion agents is not known and choice of a dispersion agent for a particular system is largely empirical. Carboxymethyl cellulose ether sodium salt is an example of a dispersion agent for the bead copolymerizations of styrene and pure divinylbenzene isomers.

It was reported[4] that using carboxymethyl cellulose ether sodium salt as a suspending agent good spherical and transparent beads in the 30-40 mesh range were obtained. However it was added that there was a tendency for beads to aggregate, which increases as the concentration of divinyl monomer in the styrene-pure divinylbenzene increases. The m-divinylbenzene systems gave severe bead aggregation at concentration greater than 4 mole % in the polymerization mixture.

One of the objectives of this study was to obtain data comparing the properties of cation-exchange resins prepared from styrene-pure divinylbenzene copolymers. With this in view, considerable care has been taken to obtain the copolymer beads to be used under as nearly identical conditions as possible so that their properties could be carefully compared.

It was, therefore, necessary to find a new suspension agent for this system. Experiments carried out have shown that polyvinyl alcohol with a low degree of sulfonation (around 2% of sulfate groups) yielded stable suspensions of fine droplets of styrene-divinylbenzene mixtures in water. High quality (spherical, free from imperfection, and transparent) polystyrene beads crosslinked with 2, 4 and 8 mole percent of commercial, pure m-, and pure p-divinylbenzenes were obtained by using polyvinyl sulfate as suspension agent (Figure 1). The yields of 125-250 micron sieve cut were 70-90% (Table 1), while the use of carboxymethyl cellulose dispersion agent under similar conditions yielded 500-800 micron size beads in 40-50% yield. The difficulty encountered previously[4] in the preparation of bead copolymers of styrene-m-divinylbenzene (especially 8%) system was also eliminated by using polyvinyl sulfate dispersion agent. Typical bead size distribution curves of 125-250 micron sieve cut are in Figure 2. This shows that the copolymer beads obtained using a new suspension agent have a narrow particle size distribution.

EQUILIBRIUM ISOTHERMS

This work has now been extended to elucidate some of the fundamental factors governing ion exchange equilibria by studying various pairs of cations. Since it was desired to eliminate as far as possible such complicating factors as ion-pairs and complex-ion formation, the study was confined to the hydrogen ion and ions of the alkali metals and silver. Therefore the ion-exchange equilibria involving sodium, potassium, rubidium, cesium, and silver ions have been studied on sulfonated polystyrene resins of 2, 4 and 8 mole % pure meta, pure para, and commercial divinylbenzene contents at a constant temperature of 25°C.

The specific ion-exchange capacity defined by the number of exchange groupings per unit amount of exchange affects the selectivity of the resins[30]. In systems involving the hydrogen ion, the effect of reducing the equivalent capacity is always to favor the uptake of the hydrogen ion by the exchanger at the expense of the other ion[19]. Therefore sulfonations of the bead copolymers were run under comparable condition to obtain resins with as nearly identical as possible values of equivalent capacities for all samples. The equivalent capacities were determined by a standard procedure and were in range of 5.2-5.4 meq./g. of dry resin in the hydrogen form (Table 2). For convenience, the experimental data for the exchange equilibrium studies are presented graphically in Figures 3-16 as a plot of selectivity coefficient (K_H^M) against equivalent fraction of cation M^+ of the resin (X_R).

The isotherm studies of commercial divinylbenzene resins prepared in this study give values comparable to results previously reported (Table 4). It will be observed that our results agree qualitatively with those previously reported. These differences in selectivity coefficient may be probably due in part to differences in the resin used. For the preparation of the resins divinyl monomer content was calculated on the basis of the analytical composition data and was used in this study, whereas previous workers reported the nominal divinylbenzene percent. Analytical data showed that the divinylbenzene content of commercial divinylbenzene (Dow Chemical) was 46.3% (meta 31.3%, para 15.0%). Therefore numerical differences in selectivity coefficient are undoubtedly due in part at least to differences in the preparation of the resin.

From Figures 3-7, one will observe the following facts. For a given pair of ions and a given resin, the selectivity coefficient varies with the cationic composition of the resin. In nearly all cases, the selectivity coefficient decreases with increasing equivalent fraction of counterion of the resin. The variation of K_H^M with the cationic composition of the resin increases markedly with the degree of crosslinking (Figures 3 and 4), and increases with the "natural" order of affinities of the cations (Figures 5-7). We may, in a loose sense, write down a "natural" order of affinities $Cs > Rb > K > Na$ as shown

Table 4

Comparison of Selectivity Coefficients at $X_R = 0.5$

System	c-DVB* (mole %)	K_H^M			
		A	B	C	D
Na-H	2	1.07	1.03		1.08
	4	1.31	1.13		1.40
	8	1.52	1.34		1.79
K-H	2				1.38
	4			1.61	1.99
	8			2.10	2.56
Rb-H	8			2.29	2.59
Cs-H	8			2.31	2.97

* In references nominal divinylbenzene percent was used.

A, Boyd and Meyer[34]

B, Soldano, Larson and Meyer[35]

C, Bonner[31]

D, Values in this study

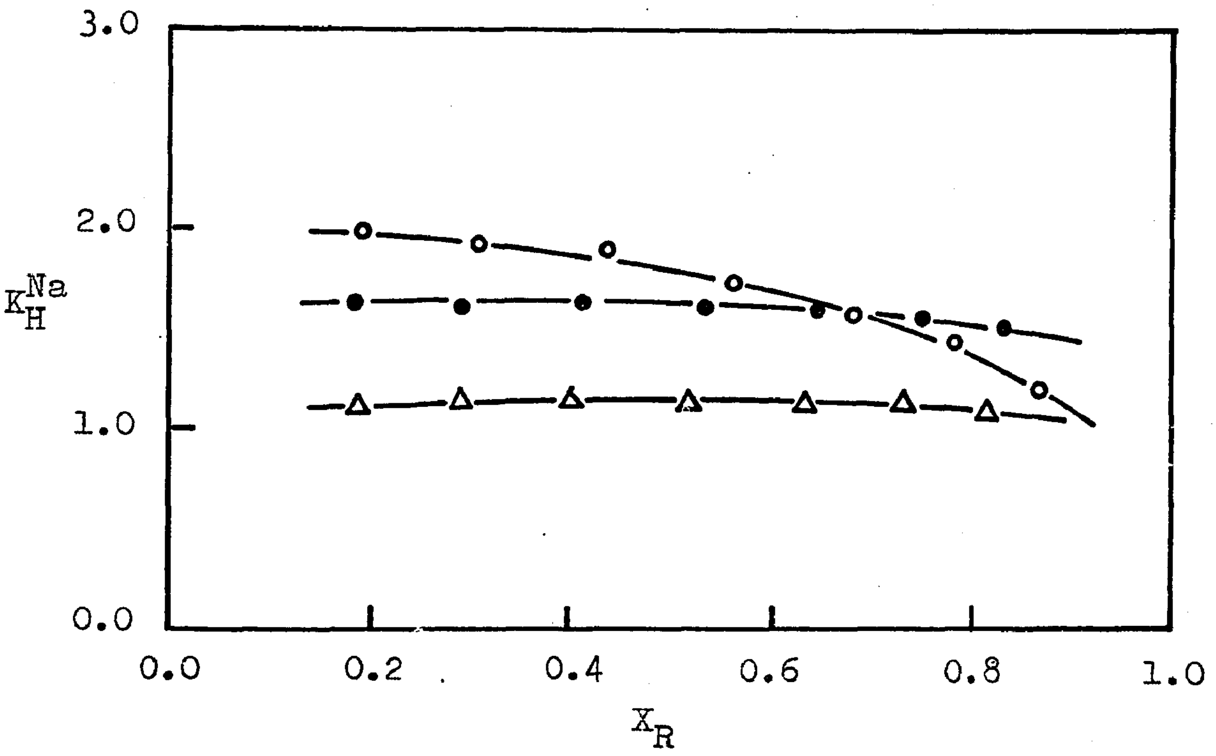


Figure 3. Sodium-Hydrogen Exchange on Commercial Divinylbenzene Resins: △ , 2% c-DVB; ● , 4% c-DVB; ○ , 8% c-DVB.

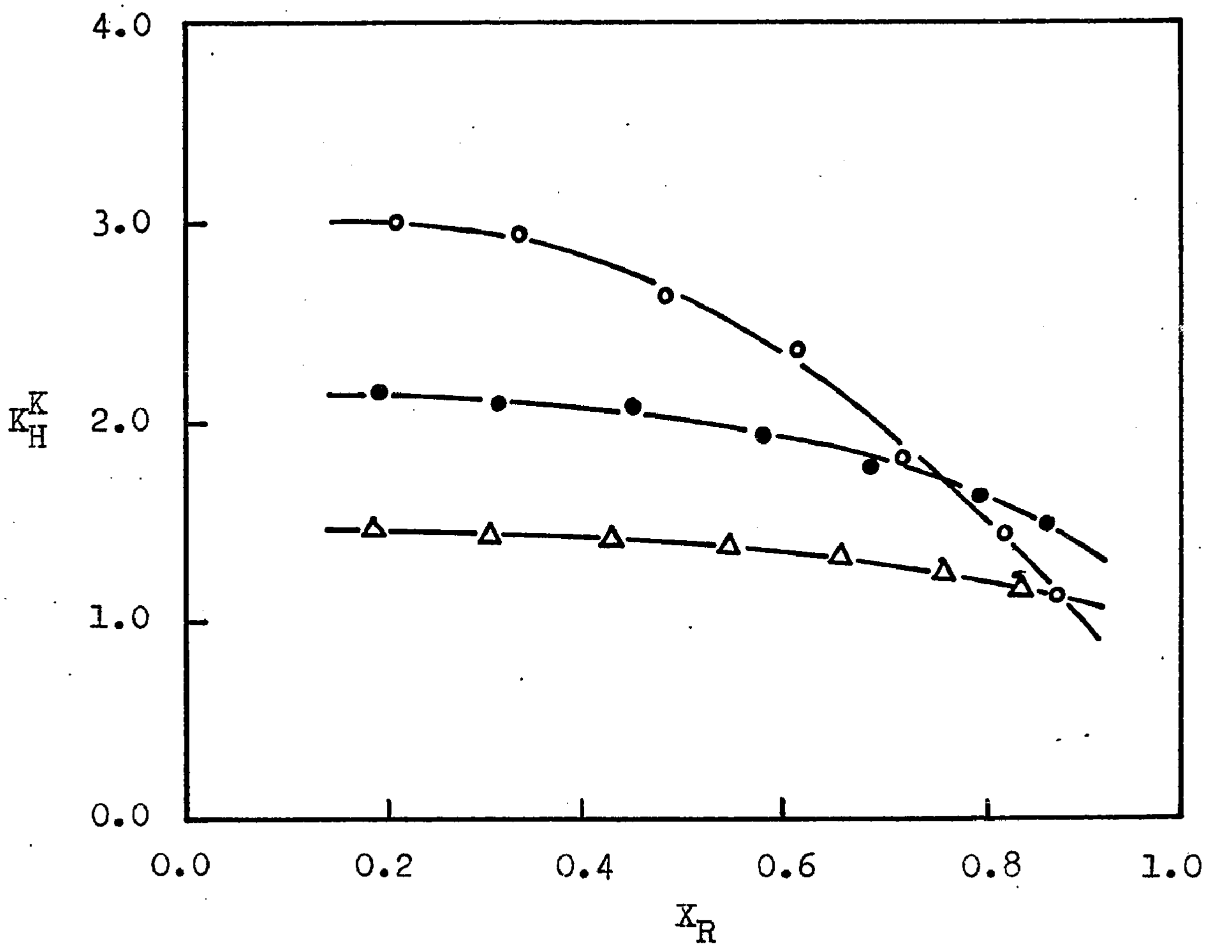


Figure 4. Potassium-Hydrogen Exchange on Commercial Divinylbenzene Resins: △ , 2% c-DVB; ● , 4% c-DVB; ○ , 8% c-DVB.

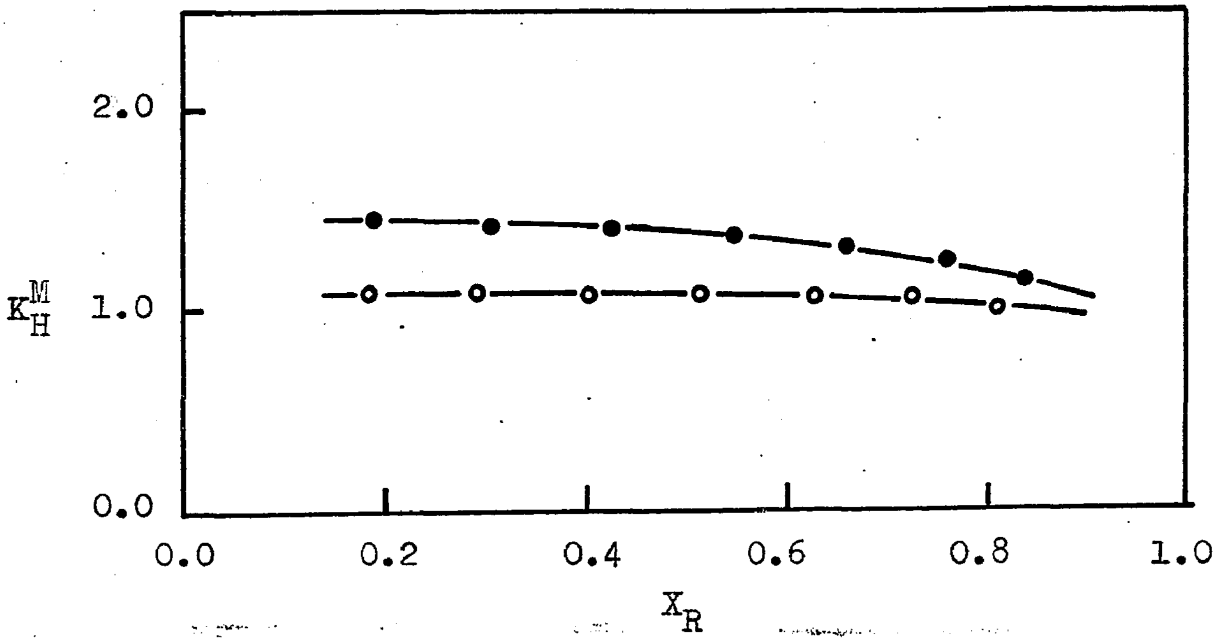


Figure 5. Sodium-Hydrogen(○) and Potassium-Hydrogen(●) Exchange on 2% Commercial Divinylbenzene Resin.

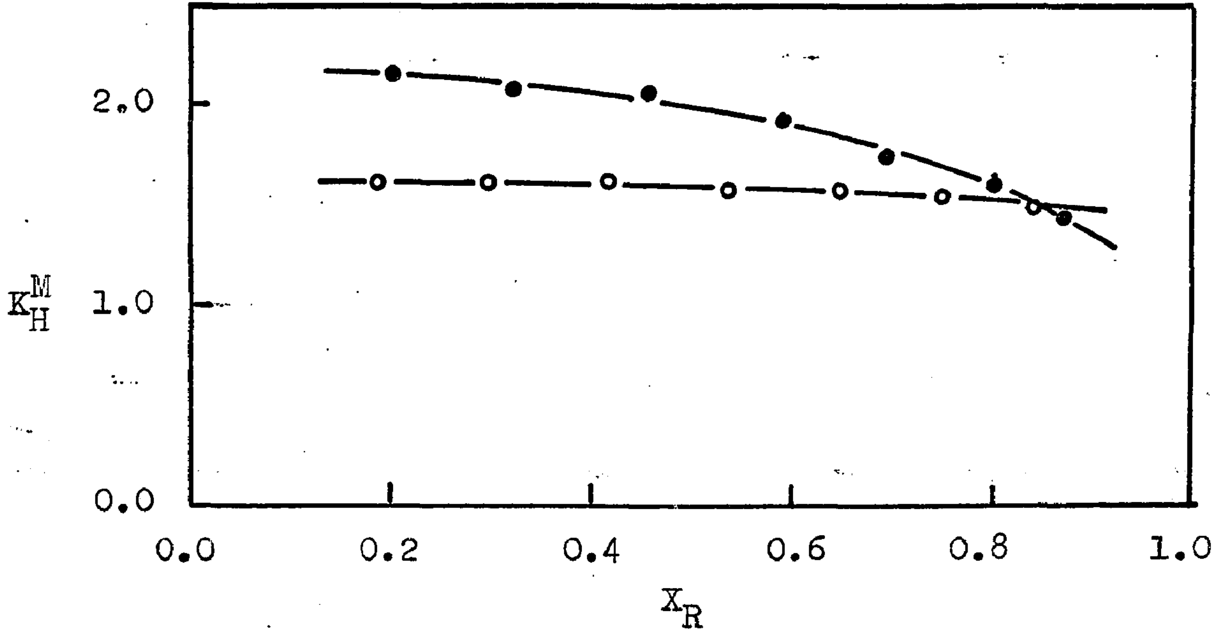


Figure 6. Sodium-Hydrogen(○) and Potassium-Hydrogen(●) Exchange on 4% Commercial Divinylbenzene Resin.

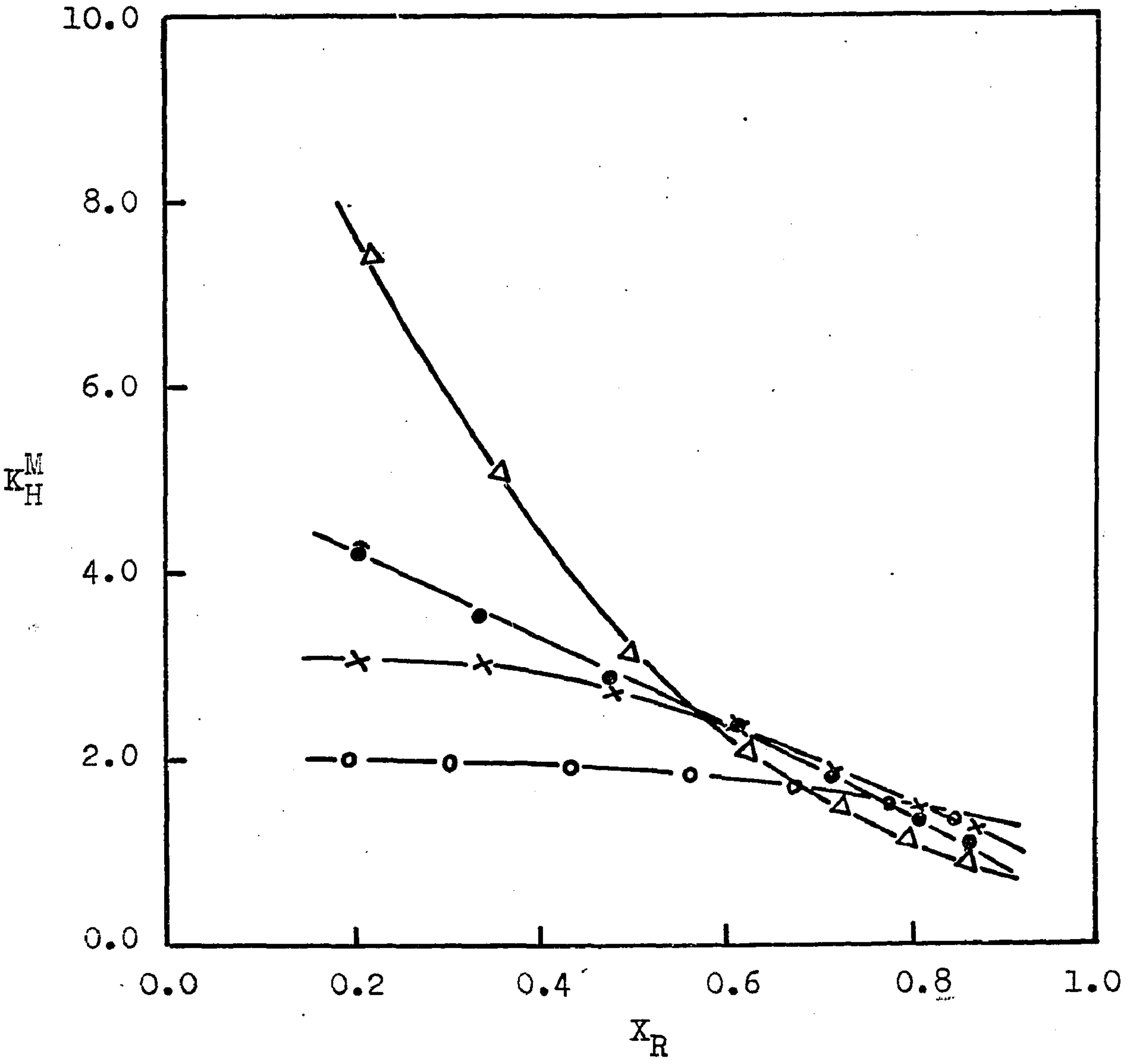


Figure 7. Sodium-Hydrogen(○), Potassium-Hydrogen(×), Rubidium-Hydrogen(●) and Cesium-Hydrogen(△) Exchanges on 8% Commercial Divinylbenzene Resin.

Table 5

Ionic Size and Hydration of Cations[a]

Ion	Naked Radii (A)	Hydrated Radii (Jenny), A	mole H_2O/eq. ion
Li	0.68	10.0	12.6
Na	0.98	7.9	8.4
K	1.33	5.3	4.0
Rb	1.49	5.09	...
Cs	1.65	5.05	...

a. Kunin[12]

in Figures 5-7. The order Cs $\rangle$ Rb $\rangle$ K $\rangle$ Na is also the order of decreasing ionic mobilities and of numerous other physicochemical properties, all of which depend on the size of the hydrated cation[12,13]. These results confirm the view that ion-exchange selectivity (at least with these simple cations) is determined primarily by the size of the hydrated ion, ions of small hydrated volume being preferred to large ions. The hydrated ionic radii of the ions of alkali metals are given in Table 5.

We will now apply Gregor's theory to this system to explain the results obtained from the commercial divinylbenzene resins. Gregor[14] postulates a model as previously described in which the exchanger is regarded as consisting of two parts, an uncrosslinked polyelectrolyte with solvent and the crosslinking. Selectivity is considered to arise primarily because of differences in the partial molar volumes of the counterions in the exchanger. According to Reichenberg[19], the mathematical expressions derivable from these postulates takes a particularly simple form if it is assumed that the ions in the exchanger are "hydrated" and that when appropriate values for the volumes of the hydrated ions are taken other kinds of interaction may be neglected. This leads to the equation

$$RT \ln K_A^B = \pi(\bar{V}_A - \bar{V}_B) \qquad (6)$$

where $\bar{V}_A$ and $\bar{V}_B$ are the values taken for the hydrated volumes of the counterions A and B in the exchanger and π

is the so-called swelling pressure or elastic counterpressure in the exchanger. It arises directly from the model, since an uncrosslinked polyelectrolyte in the presence of an ample amount of solvent would take up solvent until it dissolved completely. According to the theory, the extension of the polymer chain due to the absorption of solvent stretches the crosslinking, which in turn exerts an elastic counterpressure tending to oppose the swelling. Equilibrium is reached when the elastic counterpressure is equal to the residual osmotic pressure.

The following deductions may be derived from the simplified form (6) of Gregor's theory. (a). If $V_A > V_B$, then $K_A^B > 1$ and vice versa. In other words, of two exchangeable counterions, the one with the smaller hydrated ionic radius (and, therefore, the smaller hydrated ionic volume) will be preferred by the exchanger. If we assume the order of hydrated ionic radius given above for the alkali-metal cations, we see that this fit well with the "normal" affinity sequence. This prediction is in fair agreement with our results. (b). If $V_A > V_B$, then, as X_R increases, the resin contracts (since it is being increasingly loaded with the ion of smaller hydrated volume) and π decreases. Hence, provided $V_A - V_B$ does not change to such an extent as to nullify the effect, K_A^B will decrease. In other words, Gregor's theory predicts unambigously the decrease of affinity of the resin for an ion with increase in the amount of that ion on the resin. This prediction is in accord with nearly all our results. (c). For a given value of X_R, increase of crosslinking causes an increase of π. Hence, provided $\bar{V}_A - \bar{V}_B$ does not change to such an extent as to nullify the effect, K_A^B should increase with increase of crosslinking. As we have seen, this agrees with our results in most cases. However it fails as shown in potassium-hydrogen system on 8% divinylbenzene resin when the resin is predominantly in the ionic form of higher "natural affinity" (Figure 4). The same kind of failure[24,31] was reported for the system involving the hydrogen with resins of medium crosslinking (10% divinylbenzene).

It would appear that the experimental results on the commercial divinylbenzene resin are generally consistent, at least qualitatively, with Gregor's theory, but that a complete interpretation requires consideration of other facts. The situation is even more complicated by using commercial divinylbenzene as a crosslinking agent because it consists of several divinyl and monovinyl monomers. As described in the previous part the reactivity ratios of m- and p-divinylbenzenes with styrene are quite different. The different monomer reactivities of these crosslinking agents in copolymerization lead to the structural differences in copolymers as the precursor of the resin. The complexity and variation of the structure of copolymers crosslinked by such mixtures of materials may account for some of the difficulties encountered in theoretical studies of ion-exchange resin. Most theoretical treatments of ion-exchange selectivity assume[19] that all the fixed groups in a given exchanger behave in an identical manner with respect to their selectivity properties. Clearly the problem would be greatly complicated if this were not so. However, it appears clear that it is a gross oversimplification to consider any ion-exchange resin with a moderate to high degree of crosslinking as a homogeneous one. Therefore, to explain the resin properties it has been useful to make the assumption[24,32,33] that the ion-exchange sites in a resin are not all identical.

Reichenberg and McCauley[24] pointed out that in the preparation of crosslinked polystyrene (the precursor of ion-exchange resins), the nature of the copolymerization of styrene and divinylbenzene rendered it a virtual certainty that there would be some kind of statistical distribution of the length of chain segments between neighboring crosslinks. This implied that, after the subsequent introduction of exchange groupings, the degree of localized crosslinking around each grouping would not be constant but would vary according to some kind of statistical distribution law. Such variation would be expected to affect the selectivity properties of the groupings. Although Gregor's theory[14] predicted qualitatively a decrease of selectivity coefficient with increasing counterion composition on the resin, crude calculations[24] based on this theory indicated a much smaller decrease of the relative affinity coefficient than was found experimentally. Reichenberg and co-worker suggested that most of the actual decrease of the selectivity coefficient was due to the differing environments of the exchange sites. There is a fair amount of indirect evidence that, with ion-exchange resins, the fixed groups, within a given exchanger, are not uniform in their properties[19].

We have observed the selectivity coefficient differences which may be correlated to the structure of the resins. Figures 8-15 represent the selectivity coefficient variation with the counterion composition on the resins prepared from styrene and pure m- and p-divinylbenzenes, as well as from styrene and commercial divinylbenzene. The following facts will be observed from these data: The isotherms on pure divinylbenzene resins show the same qualitative behaviors as that on the resins from commercial divinylbenzene. The isotherms of the 2% m-divinylbenzene resin are identical with those of the 2% para isomer resin within experimental error (Figures 8 and 9). However differences in log K_H^M of a given ion pair on the m- and p-divinylbenzene resins increase with the degree of crosslinking, e.g., the differences between log K_H^{Na} of the p- and m-divinylbenzene resins are 0.00, 0.01, and 0.03 at $X_R = 0.2$ for 2, 4 and 8 mole% resins

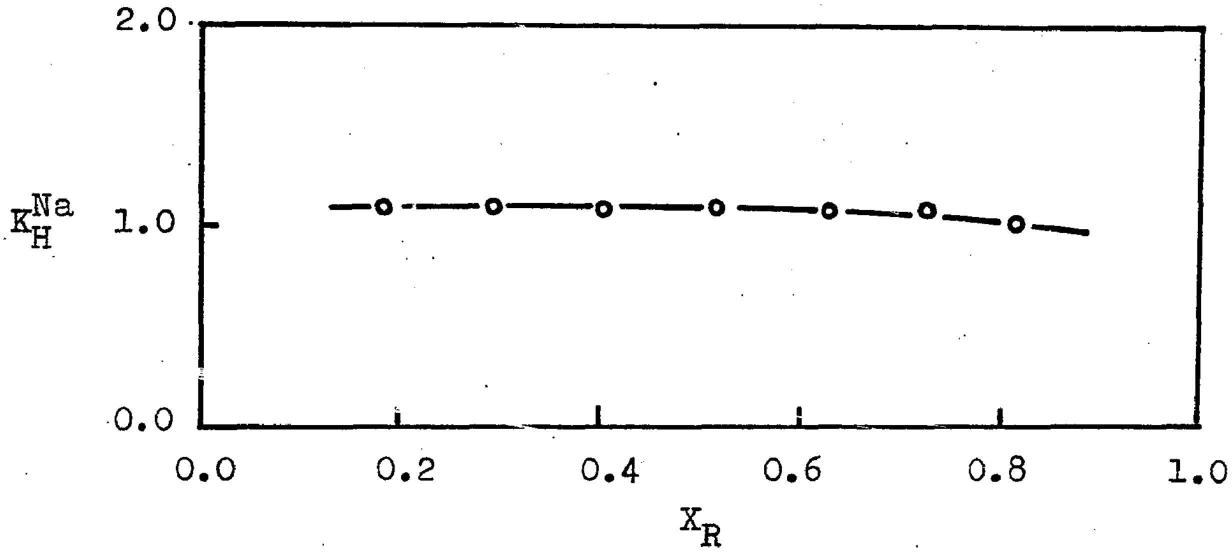


Figure 8. Sodium-Hydrogen Exchange on 2% Commercial, m-, and p-Divinylbenzene Resins.

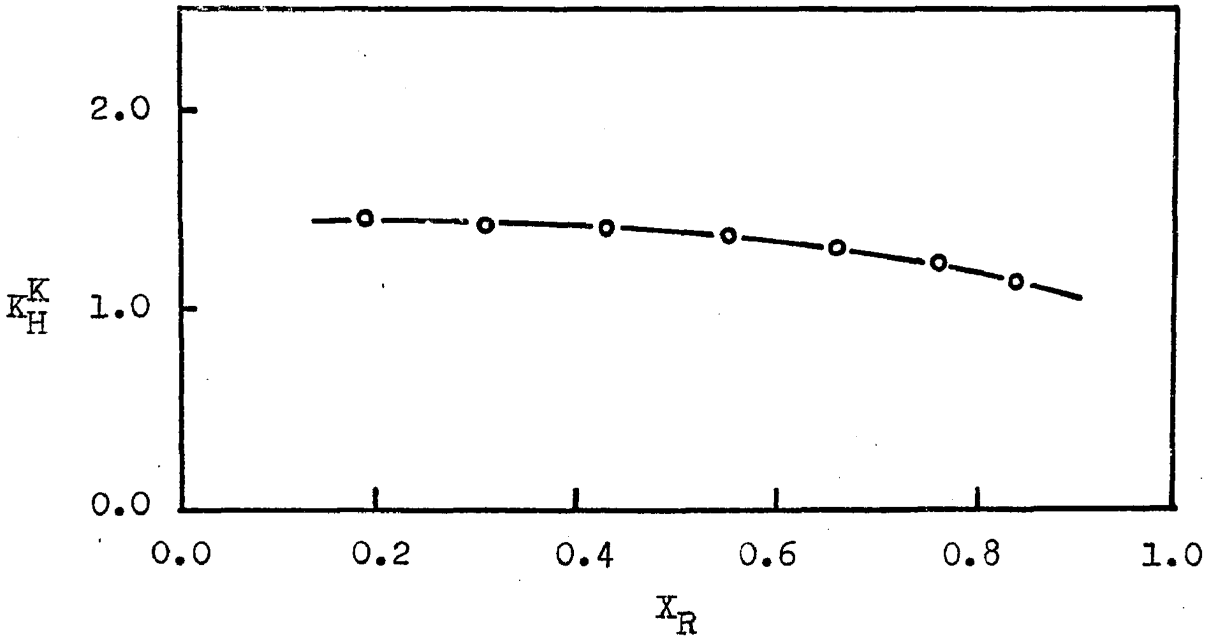


Figure 9. Potassium-Hydrogen Exchange on 2% Commercial, m-, and p-Divinylbenzene Resins.

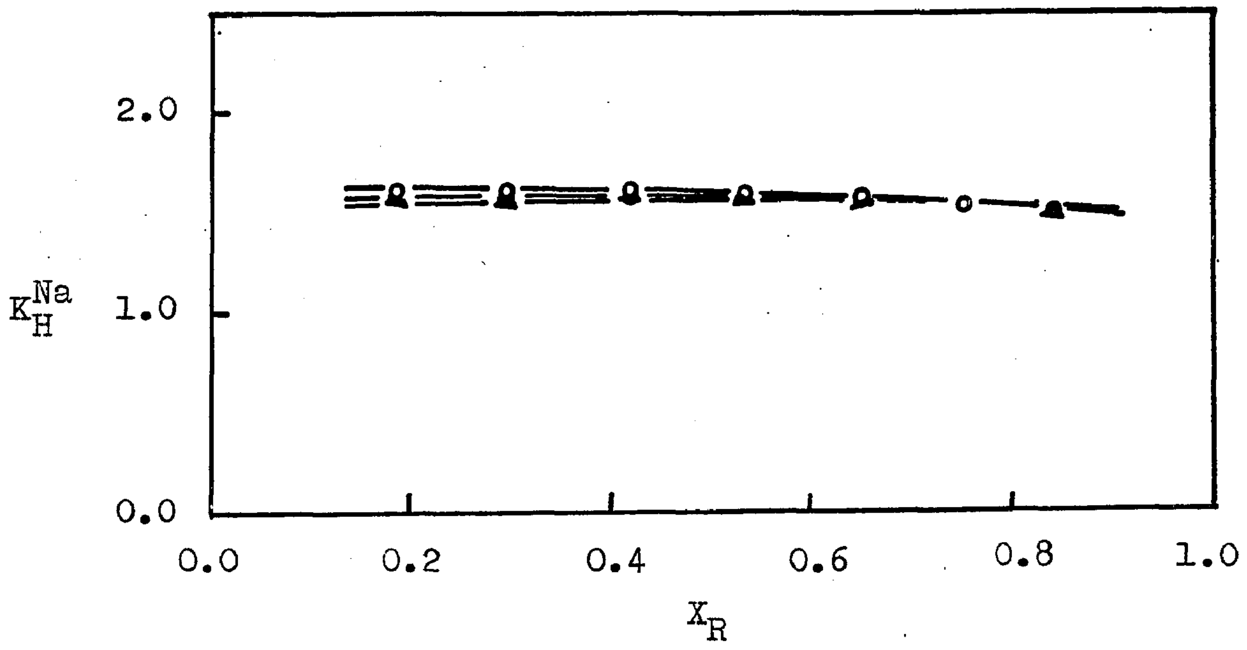


Figure 10. Sodium-Hydrogen Exchange on 4% Divinylbenzene Resins: ○ , c-DVB; △ , m-DVB; ● , p-DVB.

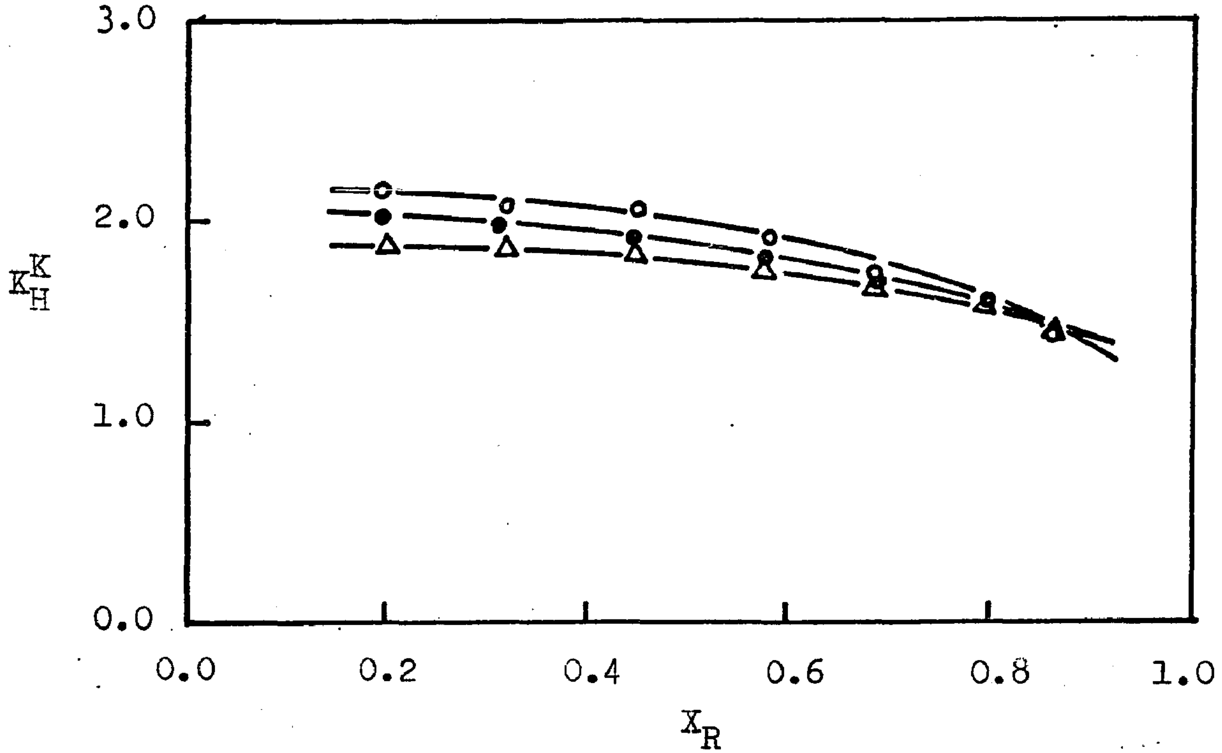


Figure 11. Potassium-Hydrogen Exchange on 4% Divinylbenzene Resins: ○ , c-DVB; △ , m-DVB; ● , p-DVB.

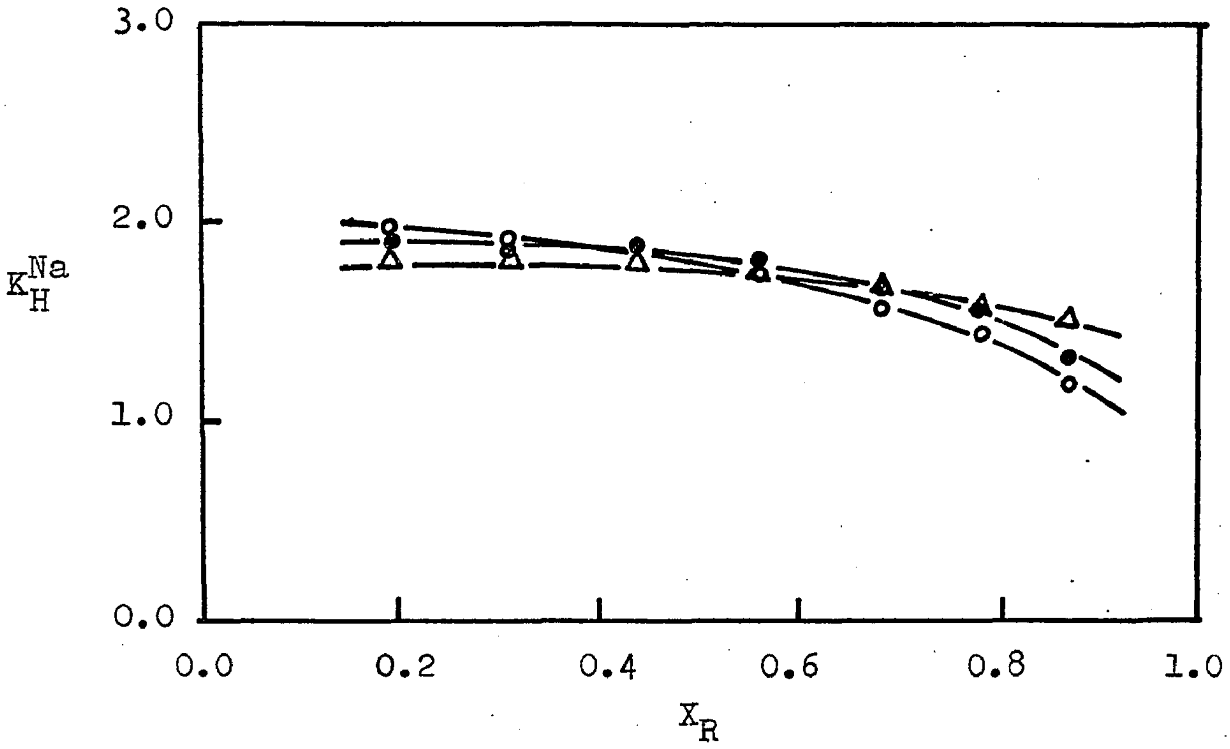


Figure 12. Sodium-Hydrogen Exchange on 8% Divinylbenzene Resins: ○ , o-DVB; △ , m-DVB; ● , p-DVB.

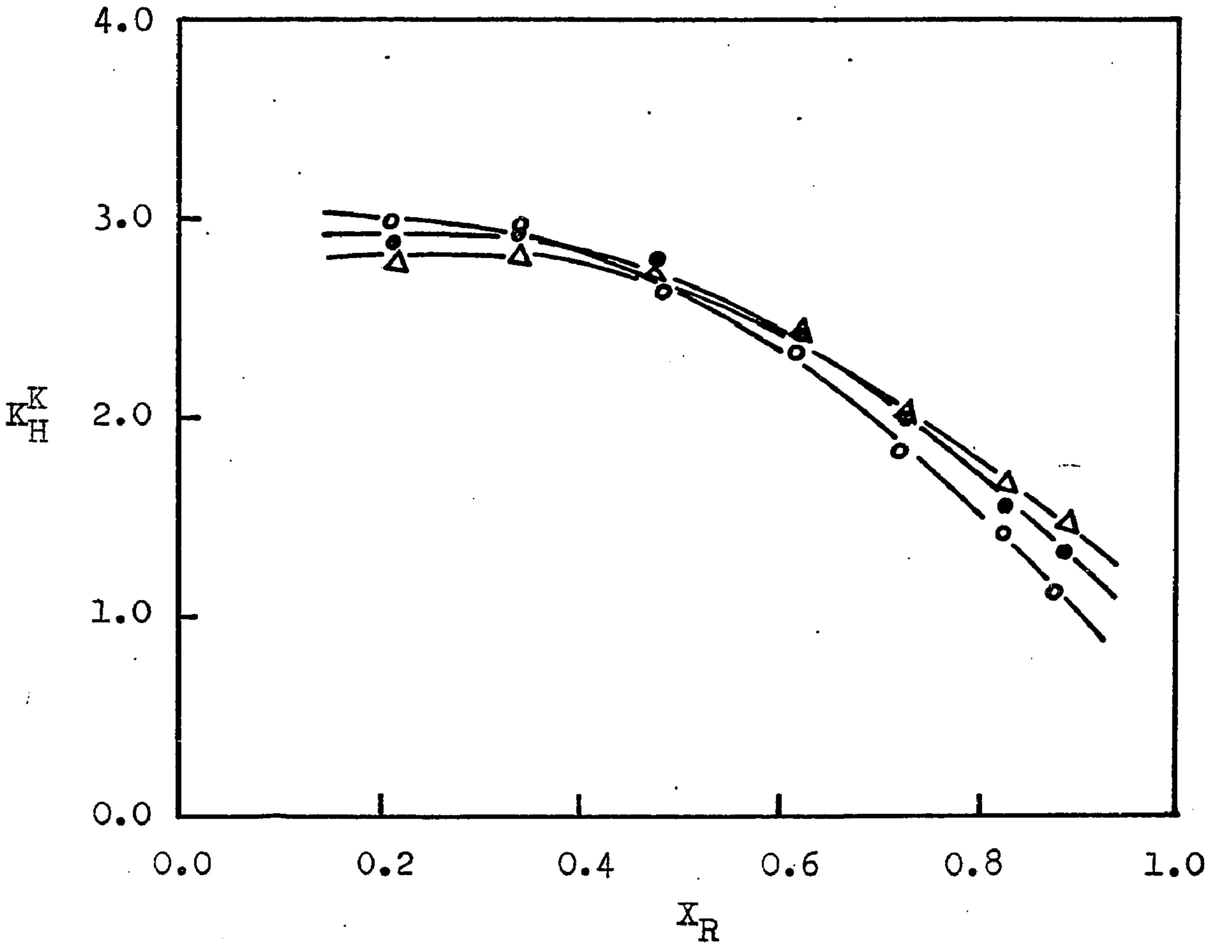


Figure 13. Potassium-Hydrogen Exchange on 8% Divinylbenzene Resins: ○ , c-DVB; △ , m-DVB; ● , p-DVB.

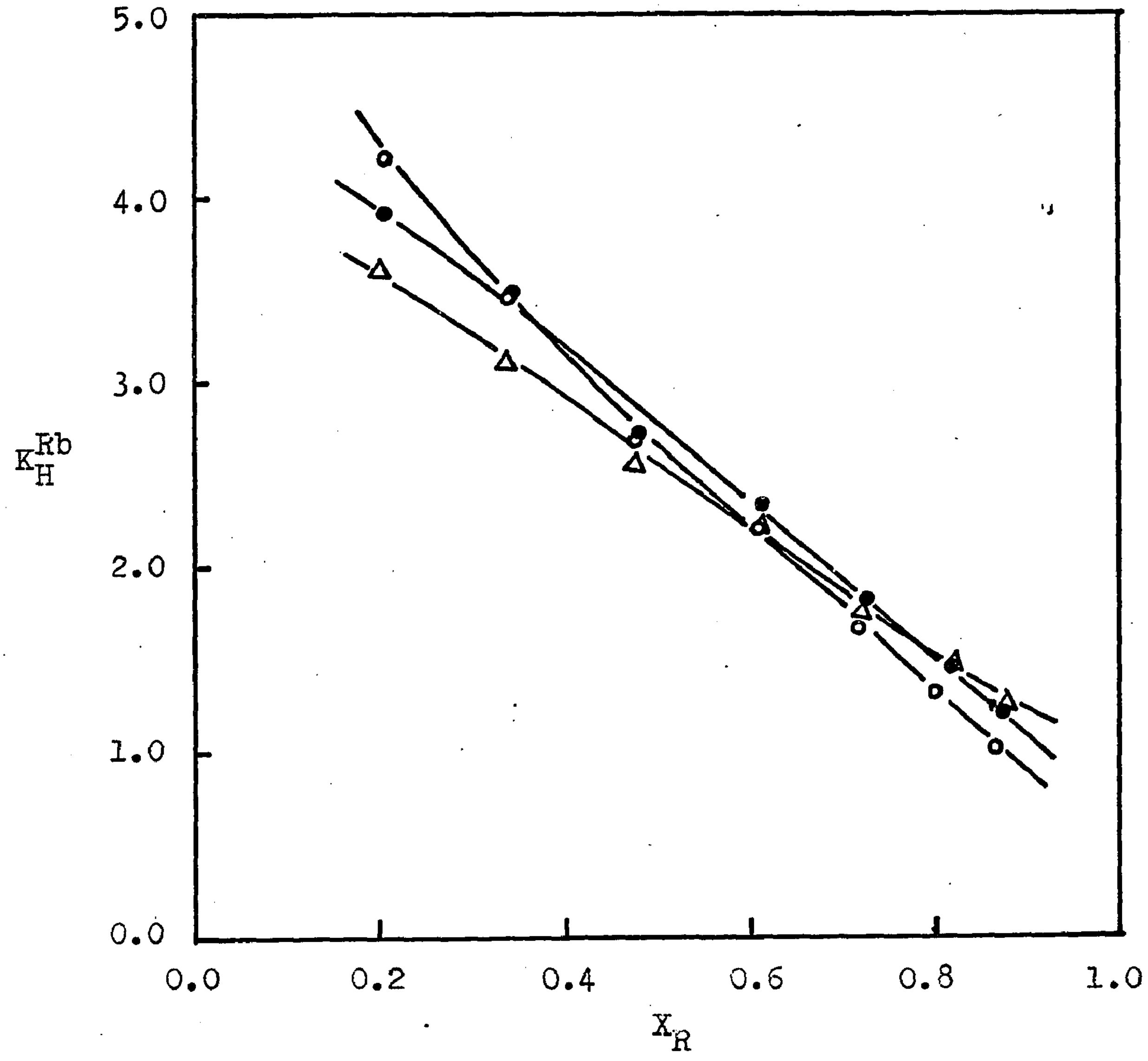


Figure 14. Rubidium-Hydrogen Exchange on 8% Divinylbenzene Resins: ○ , c-DVB; △ , m-DVB; ● , p-DVB.

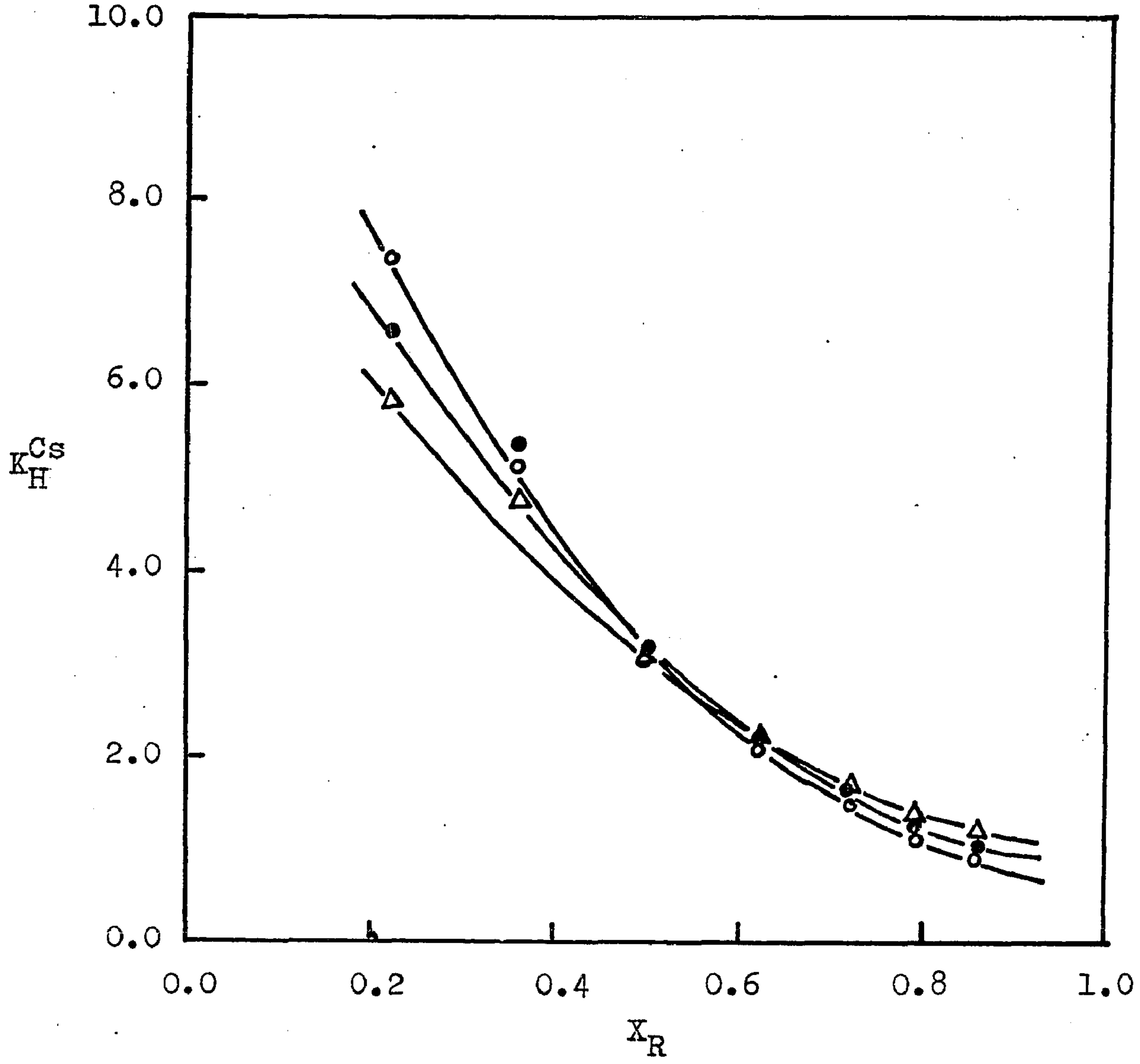


Figure 15. Cesium-Hydrogen Exchange on 8% Divinylbenzene Resins: o , c-DVB; △, m-DVB; ●, p-DVB.

respectively (Figures 8, 10 and 12). Figures 12-15 show these large affinity differences between of the 8% m- and p-divinylbenzene resins for the Na-H, K-H, Rb-H, and Cs-H systems. The values of log K_H^M of a given ion pair on the 8% p-divinylbenzene resin are higher than those on the 8% meta isomer resin when the resins are predominantly in the hydrogen form, but an intersection occurs at $X_R = 0.65-0.8$ for all systems. Figure 13, as an example, shows that log K_H^K of 8% para isomer resin is 0.43 at $X_R = 0.2$ and 0.40 for meta isomer resin at the same X_R, and the intersection point is at $X_R = 0.65$. The intersection points are at $X_R = 0.70$ for Na-H, at 0.80 for Rb-H, and at 0.73 for Cs-H system. The differences in log K_H^M on a given mole percent m- and p-divinylbenzene resins increase with the natural order of the affinity of cation. Figures 12-15 show that differences between log K_H^M of 8% p- and m-divinylbenzene resins are 0.03 for Na-H, 0.03 for K-H, 0.04 for Rb-H, 0.06 for Cs-H system at $X_R = 0.2$. However these differences vary with the cationic composition of the resin as shown in all figures. For example, the differences between log K_H^{Cs} of 8% p-divinylbenzene resin and that of 8% meta isomer resin are 0.06 at $X_R = 0.20$, 0.06 at 0.35, 0.01 at 0.50, -0.01 at 0.73, and -0.01 at 0.87 (Figure 15), where negative values mean that log K_H^{Cs} of meta isomer resin is higher than that of para isomer resin. These data also show that the variation of log K_H^M with the cationic composition of the p-divinylbenzene resin is larger than that of the meta isomer resin, e.g., log K_H^M differences of the 8% p-divinylbenzene resin between $X_R = 0.20$ and $X_R = 0.85$ are 0.18, 0.31, 0.50, and 0.80 for Na-H, K-H, Rb-H, and Cs-H systems respectively. However the differences of the 8% m-divinylbenzene resin are 0.09, 0.24, 0.47, and 0.73 for the same ion pair systems, respectively.

In order to explain these phenomena one has to consider the structural differences between m- and p-divinylbenzene resins, which are related to the difference in the degrees of crosslinking of the copolymers (or resins) obtained from the same mole fraction of divinylbenzene and the difference in the distribution of the crosslinks in the copolymers (or resins). If the selectivity differences on the resins prepared with the same molar fraction of divinylbenzene are due to the differences of the degrees of crosslinking, the degrees of crosslinking in p-divinylbenzene resins should be higher than in m-divinylbenzene resins. This is not consistent with the results of copolymerization kinetics described in previous part. The result of kinetics shows that p-divinylbenzene is incorporated more rapidly into the growing polymer chain than m-divinylbenzene during the copolymerization with styrene. This leads the relative bunching of divinylbenzene units in the styrene-p-divinylbenzene copolymer. From this fact it is expected that the reactivity of the unreacted second vinyl group of p-divinylbenzene is more reduced than that of m-divinylbenzene because perhaps of lessened freedom of movement of the monomer mixtures. In some cases, the pendant vinyl group may be completely shielded from further reaction and may not crosslink at all. It is reasonable that this effect is higher in p-divinylbenzene than in m-divinylbenzene copolymerization with styrene. Therefore the degree of crosslinking is the minor effect on the difference in the isotherms on the resins prepared from two divinylbenzene isomers.

Therefore one can consider that the most plausible cause of variation would appear the extent of crosslinking in different parts of the same resin network, some sulfonic acid groups being situated in regions of a lower degree of crosslinking than others. In principle, there will be a wide and continuous variation of the degree of localized crosslinking. According to Reichenberg and McCauley[24], the exchange sites can be divided into three groups for qualitative discussion.

1. Those situated in regions of a low degree of effective crosslinking. The fully hydrated ions of both H^+ and M^+ are available to the exchange groups but the selectivity is low.

2. Those situated in regions of a medium degree of crosslinking. If M^+ is the higher "natural" selectivity (i.e., of smaller hydrated volume), then the fully hydrated M^+ ion may still approach the exchange groups and the

selectivity is much greater than for type 1 sites.

3. Those lying in regions of high degree of crosslinking. Neither type of ion when fully hydrated can approach the exchange groups and clearly that ion will be preferred whose hydration shell can more readily be stripped to a point where the partially stripped ion is small enough to approach the exchange site.

We will consider the resin to be initially completely in the H^+-form. If we start to introduce M^+ ions into the resin, these will initially be taken up preferentially on sites of type 2 which have the greatest affinity for them and the value of log K_H^M will be accordingly high. As an increasing fraction of the type 2 sites is filled, more of the M^+ ions will have to go on to type 1 sites and hence log K_H^M will decrease. If there were no sites of type 3 there would be no intersection of the curves for resins of different degrees of crosslinking, since increase of overall crosslinking will increase the proportion of type 2 sites and thus increase the selectivity at all cation compositions. If a sufficient number of type 3 sites are present, the factors discussed should give rise not only to intersections but ultimately to inversions. By the same argument, if there were no differences in exchange sites of two divinylbenzene isomer resins, there should be no intersection of the curves and no differences in the isotherms for the resins of the same degrees of crosslinking. There are differences in the isotherms on two divinylbenzene isomer resins as described previously. It appears that the variation of log K_H^M with the resin loading will depend upon the degree of localized cross-linking around each exchange grouping. In other words, the large variation of log K_H^M with the cationic composition of the p-divinylbenzene resin shows a lack of the homogeneity of crosslinks in the copolymer. As one increases the crosslink homogeneity of the copolymer, there is less of a variation in log K_H^M with the resin loading as shown in the isotherms of the meta isomer resin.

It has already been mentioned that in the case of the alkali ions, most cation-exchange resins do indeed prefer the smaller solvated ion to the larger one. However, resins with sulfonic acid groups prefer Ag^+ and Tl^+ strongly to alkali ions, though there is little difference in the volumes of the hydrated ions. In spite of its almost identical size, Ag^+ is more strongly attracted because of its great polarizability[13,25]. Figure 16 shows the equilibrium isotherms of silver-hydrogen system on the 8% divinylbenzene resins. This isotherm shows large differences in the values of log K_H^{Ag} of m- and p-divinylbenzene resins as expected from the high affinity of silver ion. The differences of log K_H^{Ag} between $X_R = 0.21$ and $X_R = 0.88$ are 0.02 and 0.00 for p- and m-divinylbenzene resin respectively. This also indicates that there is less of a variation in log K_H^{Ag} of the meta isomer resin.

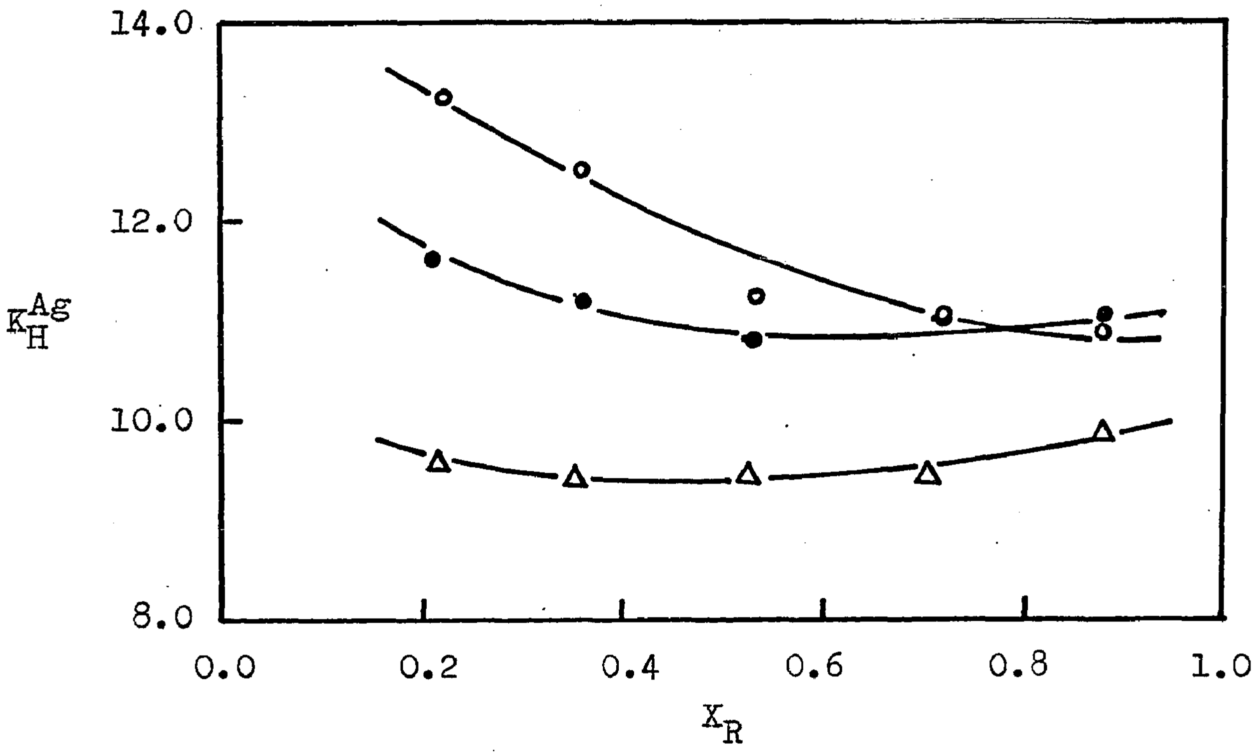


Figure 16. Silver-Hydrogen Exchange on 8% Divinylbenzene Resins: ○ , c-DVB; △ , m-DVB ● , p-DVB.

From the ion-exchange site model applied to our experimental data, it is clear that the exchange sites are more uniformly distributed in the m-divinylbenzene resins than the p-divinylbenzene resins. This may imply that the crosslinks are more uniformly distributed in the styrene-m-divinylbenzene copolymer than the styrene-p-divinylbenzene system.

SUMMARY

Equilibrium isotherms of Na-H, K-H, Rb-H, Cs-H, and Ag-H systems for a series of polystyrene sulfonated resins prepared from styrene crosslinked with commercial, m- and p-divinylbenzene have been studied at 25°C. The isotherms for a given ion pair system on 2% divinylbenzene resins are identical. However the difference between log K_H^M for the 8% m-divinylbenzene and that for the 8% p-divinylbenzene resin is relatively large, i.e., the differences are 0.03 for Na-H, 0.03 for K-H, 0.04 for Rb-H, 0.06 for Cs-H, and 0.08 for Ag-H system at $X_R = 0.2$. The values of log K_H^M of p-divinylbenzene resin are higher than those for the meta isomer resin, but an intersection always occurs for all systems at 0.65-0.8 of the mole fraction of cation on the resin. The variation of log K_H^M with the cationic composition of the p-divinylbenzene resin is larger than that of the meta isomer resin, i.e., log K_H^M differences of the 8% p-divinylbenzene resin between $X_R = 0.20$ and $X_R = 0.85$ are 0.18, 0.31, 0.50, and 0.80 for Na-H, K-H, Rb-H, and Cs-H systems respectively. However the differences of the 8% m-divinylbenzene resin are 0.09, 0.24, 0.47, and 0.73 for those ion pair systems respectively. These facts are explained in terms of variation in ion-exchange sites which are related to the network structure of the copolymers. It indicates that the p-divinylbenzene system shows less homogeneity of crosslinks. This equi-

librium study confirms the results of the copolymerization kinetics.

A new technique has been devised for the preparation of bead copolymers of small size for detailed studies of the ion-exchange characteristics of the sulfonated polymers. Polystyrene beads crosslinked with 2, 4, and 8 mole% divinylbenzene (pure meta-, para-, or commercial) of 125-250 micron size have been obtained in 70-90% yield using sulfated polyvinyl alcohol as suspending agent. Ion-exchange resins are obtained by sulfonation of these small size copolymer beads with concentrated sulfuric acid (98%) at 100°C.

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