67-17,715

FEINSTEIN, Myron Elliot, 1943-
THE EFFECT OF CHARGED INTERFACES ON THE IONIC DISTRIBUTION IN SOLUTION.

The City University of New York, Ph.D., 1967
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan

The Effect of Charged Interfaces on the Ionic Distribution in Solution

by Myron Elliot Feinstein

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

1967

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

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Preface

The work described in this dissertation was carried out in the Marlies Laboratory, Department of Chemistry, The City College of the City University of New York, during the period June 1964--June 1967. Except where otherwise indicated, the work is original and has not previously been submitted for a degree in any other university.

I wish to express grateful appreciation to my mentor, Professor H. L. Rosano, for his encouragement, advice, and invaluable friendship.

I would like to thank my associates, C. J. Cante and A. P. Christodoulou for their helpful comments on this work and further, for their immeasurable contribution to the esprit de corps which pervaded the laboratory in which we worked.

I wish, also, to thank Mrs. E. O'Connor and Mrs. J. Ulrich for their inestimable secretarial help throughout my stay at the college.

I am grateful to E. I. Du Pont de Nemours and Company for the Summer Research Assistantship of which I was the recipient for the summer of 1966 and to the City University for the University Scholarship awarded to me in June, 1967.

Finally, I would like to express my deep gratitude to Dr. E. D. Goddard, of Lever Brothers Research Division, for the sincere interest he has shown in my work and his critical comments during our many enlightening discussions.

New York, July 1967

With them the Seed of Wisdom did I sow,
And with mine own Hand wrought to make
    it grow
And this was all the Harvest that I reap'd—
"I came like Water, and like Wind I go."

Omar Khayyam

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■ K Laurate
⬡ K Myristate

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△ K Caprate

■ K Laurate

⬡ K Myristate

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pH versus ml. 2.00 x 10^{-2}M HCl added.

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▲ Na Caprate

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○ Na Myristate

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△ K Caprate

■ K Laurate

⬡ K Myristate

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Sodium ion concentration = 1.74×10^{-3}M.

Long-chain anion concentration = 1.00×10^{-3}M.

▲ Na Caprate

□ Na Laurate

○ Na Myristate

Introduction

Molecules having an aliphatic hydrocarbon "tail" of about seven or more carbon atoms and either a polar or ionic "head" differ from ordinary solutes in that they form large stable aggregates called micelles.[1,2] Micelles in ionic detergent solutions are interesting objects of research. Their structure is simple enough to be explored with present experimental techniques yet they have in common with more complex systems certain interesting features which can be studied in the simpler system of micellar solutions.[3] Because of the comparatively high purity obtainable for these systems and their thermodynamic stability, they provide excellent model systems for studying colloid chemical phenomena in general.[4]

The aggregation of single molecules containing ionic groups to form micelles causes a new situation with regard to the distribution of counterions in solution. The ionic groups form a charged layer on the external micelle surface and exert a high electrostatic field which affects the counterion distribution around them.[5] The work presented here uses the micellar solution as a model to investigate the effect of a charged interface on the ionic distribution in solution. The investigations were performed with an eye toward obtaining a better understanding of the stability of emulsions and foams, flocculation of colloidal particles, and the mechanism of the nerve impulse.

Before the commencement of the present work, it had been shown that ionic exchange can occur through a non-aqueous liquid membrane when a long-chain anionic or amphoteric compound is added to it.[6,7,8,9] For example, a M/100 solution of stearic or lauric acid dissolved in 1-pentanol separating two aqueous compartments of M/50 NaCl and M/50 KCl will exchange ions only above pH 9; below that pH the fatty acids are not ionized at the oil-water interface. Potentiometric titrations of fatty acids below and above the critical micelle concentration (c.m.c.) in presence and absence of non-aqueous solvent showed the marked influence of molecular aggregate surfaces and charged oil-water interfaces on the bulk pH.[10]

In the above study[10] pH glass electrodes were used to determine the activity of hydrogen ions. The use of cationic glass electrodes[11] in the work presented in Chapter 3, allowed the determination of the activity of sodium and potassium ions in micellar and submicellar solutions. Cationic glass electrodes have glass compositions which make them selective for a variety of cations other than the hydrogen ion. The theory describing the response of these specific ion glass electrodes is the same as that for the common pH responsive glass electrode.[11] In Chapter 4, both pH responsive and cation sensitive glass electrodes were used to simultaneously monitor the activity of hydrogen and potassium ions while titrating soap solutions (in the absence and presence of non-aqueous solvents). A theoretical approach based on an equilibrium treatment of soap solutions[12] was used to quantitatively interpret the pH behavior of the acidified soap solutions.

The possibility of using micelles as models for ionized monolayers is often little appreciated.[4] Although the charge density and the curvature of the micelle surface cannot be varied at will, this is more than offset by the reproducibitity and attainable purity of the interface and possibility of the use of some of the more reliable experimental techniques which are easily applicable to bulk solutions but difficult for ordinary interfaces. In both Chapter 3 and Chapter 4, an attempt is made to relate the results to those found by monolayer techniques.

Before a presentation of the experimental work, a chapter outlining the general considerations, and one placing the work in perspective to the literature, are presented.

CHAPTER 1

General Considerations

I. Surfactant Solutions

A surface active agent (surfactant) is an amphipatic molecule. It is comprised of an oleophilic ("oil-loving") and a hydrophilic ("water-loving") portion. The oleophilic portion is a long hydrocarbon chain and the hydrophilic portion is a polar or ionic group. In the case of an ionic surfactant, the ionic group can be either cationic (e.g. $CH_3(CH_2)_{11}N^+(CH_3)_3Cl^-$) or anionic (e.g. $CH_3(CH_2)_{11}OSO_3^-Na^+$); surface active agents may also be non-ionic (e.g. $CH_3(CH_2)_{11}OH$).

It is the amphipatic character of the surfactant molecule which accounts for its surface activity. In aqueous solutions, the preferred position for such a molecule (the position of lowest energy) is at the air-solution interface. In this way, the "head group" (ionic or polar portion of the molecule) can be immersed in the water and the hydrocarbon portion ("tail") can be oriented out of the solution, in the air. At an oil-water interface, the molecule orients itself the same way, but in this case the "tail" is in the oil instead of in the air.

A dilute solution of an ionic surfactant (e.g. sodium dodecylsulfate -- $CH_3(CH_2)_{11}OSO_3^-Na^+$) behaves very much like a dilute solution of an inorganic salt (e.g. NaCl), except for the fact that it lowers the surface tension (isothermal, reversible work to increase the surface by unit area - ergs/cm^2 = dynes/cm) of the solution.

Above a certain critical concentration of surfactant, an abrupt change in properties of the solution is observed and the surface tension (γ) no longer decreases (see Figure 1.1). This is due to the saturation of the surface and bulk solution by monomers of the surfactant ions and the formation of aggregates, called micelles, in the bulk solution. Aggregates form at this concentration (the critical micelle concentration - c.m.c.), because the electrochemical potential of the long-chain ions in the solute state is equal to the electrochemical potential of these ions in the micellar state.[13]

The exact shape and size of a micelle depends upon the surfactant and the concentration of ions in the solution.[14,15,16] A typical anionic micelle of sodium dodecylsulfate (c.m.c. $\simeq 7 \times 10^{-3}$M) contains approximately eighty monomers arranged in a sphere with the hydrocarbon tails facing inward and the ionic head groups facing the water.[3,17] The interior of the micelle, therefore, is very much like a liquid hydrocarbon; the structure of the interior of the micelle may be more organized, however, because the ionic groups are anchored on the surface. The surface of an ionic micelle is highly charged and is surrounded by counterions (gegen ions) which are attracted to it electrostatically.[3]

The measurement of any physical property as a function of concentration of surfactant can be used to determine the critical micelle concentration (refractive index, surface tension, conductivity, density, etc.). For a given head group, the critical micelle concentration is lower the longer the hydrocarbon chain length. The higher the concentration of added salt the lower is the critical micelle concentration of a given surfactant solution.[13]

II. Charged Interfaces and the Ionic Distribution in Solution

What is the effect of these charged micelle-solution interfaces on the ionic distribution in solution? In 1910, Gouy[18] first enunciated his diffuse double layer theory for charged monolayers. He assumed that the charge was uniformly spread over the monolayer-solution interface, that the monolayer was impenetrable, and that the counterions behaved as point charges (they could come right up to the plane containing the charged monolayer). Gouy further assumed that if a potential, Ψ, existed at the charged interface, the ions near this interface would obey a Boltzmann distribution under the influence of this potential. For a negatively charged interface, the relation between the concentration of monovalent ions in the surface region (${}_{s}c$) and in the bulk of solution (c) where the potential, Ψ, is zero (the distance from the interface is infinite where Ψ is zero) is:

$$ {}_{s}c_{+} = c e^{-\varepsilon\Psi/kT} \qquad (1) $$

$$ {}_{s}c_{-} = c e^{+\varepsilon\Psi/kT} \qquad (2) $$

where ε is the electronic charge

k is the Boltzmann constant

and T is the absolute temperature.

Many corrections have been made to the Gouy equation. The intent here is not to follow the historic development of the theory of the double layer, but rather to point out the approximate character[19] of equations (1) and (2).

1) Even if a plane, uniformly charged surface is assumed, there is no reason to believe that it is impenetrable.

2) The counterions are not point charges; their non-zero sizes decrease the ionic concentration near the charged surface.

3) The dielectric constant of water is probably decreased in the electrical field near the interface.

4) There is no allowance made for the polarization of water around each counterion.

5) There are coulombic interactions between the counterions which tend to increase the ionic concentration near the charged interface.

All the modifications of the Gouy equation (e.g. Stern, Grahame, etc.) retain the concept of a diffuse double layer of counterions obeying a Boltzmann distribution (exponentially decreasing concentration with increasing distance from the charged surface).

If it is assumed that Equation (1) is valid for an anionic micelle-solution interface (e.g. long-chain carboxylate anions) and that the ionization property of the head group (e.g. carboxylate) is the same in bulk and in the surface, then Equation (1) provides a relation between the surface and bulk pH (where we define pH as $-\log c_H$):

$$pH_s = pH_b + \frac{\varepsilon \Psi}{2.3\ kT}$$

Since $\frac{kT}{\varepsilon} = \frac{RT}{F}$ (per mole of ions), at 25°C.:

$$pH_s = pH_b + \frac{\Psi}{59}$$

when Ψ is in millivolts. If the potential at the anionic micelle-solution interface were -177 mv., the surface pH would be three units lower than the bulk pH.[20] This simplified treatment, then, predicts that the negatively charged micelle can very markedly alter the bulk pH by attracting hydrogen ions into the surface region. Only when $\Psi = 0$ are the bulk and surface pH equal.

This type of reasoning can be applied to cationic or anionic micelles and to any counterion (e.g. K^+ instead of H^+). It should be pointed out that the emulsion droplet-solution interface is very much like the micelle-solution interface. In an oil-in-water emulsion, the hydrocarbon chains of the surfactant ions are dissolved in the oil droplet and the head groups are in the aqueous solution and therefore, one can readily understand that these charged oil-solution interfaces also markedly affect the ionic distribution in solution.

III. The Krafft Point

If the temperature of a clear micellar soap solution is lowered sufficiently, a temperature is reached at which the solution becomes cloudy.[21] This is due to the formation of microcrystals of soap. Because of the possibility of supersaturation effects, it is better to speak of the point at which a cloudy soap solution becomes clear as the temperature is raised. This temperature is well-defined and reproducible ($\pm\frac{1}{2}$°C.) for a given soap solution. This phenomenon of an anisotropic solution of microcrystals of soap becoming an isotropic micellar solution is called the "Krafft point."[22,23] The temperature at the Krafft point varies slightly with concentration of the soap solution.

For the same alkali-metal cation, the temperature at the Krafft point increases as the chain length of the long-chain anion increases.[22] For a given long-chain carboxylate anion, the temperature at the Krafft point increases as the atomic weight of the alkali-metal cation decreases in the series K^+, Na^+, Li^+.[22] Table 1.1 illustrates these facts for carboxylate soaps and it is apparent, therefrom, that the phenomenon of the Krafft point limits the number of different soaps with which one can work conveniently at room temperature (viz. 18°C. - 30°C.).

IV. The Cationic Glass Electrode

The chemical compositions of glass electrodes are mixtures of oxides of valence +3 or greater and oxides of elements of valence +1 or +2. Cation sensitive glass electrodes generally contain Al_2O_3, Na_2O, SiO_2. The three-dimensional glass membrane formed when this mixture of oxides is heated and then cooled acts as a cation exchanger; it is almost exclusively permeable to cations (primarily of charge + 1, since these are the only significantly movable ions in the glass). This glass membrane gives rise to a Nernst potential if it is made to separate two solutions of a single salt:

Table 1.1

	C_{6}	C_{8}	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
K				<0°C		~31°C	~46°C
Na				~36°C	~53°C	~62°C	~71°C
Li	~48°C		~89°C	~124°C		~140°C	

$$V = \frac{RT}{F} \ln \frac{a_1}{a_2}$$

where a_1 and a_2 are the activities of the cation M^+.

Usually, a thin-walled glass bulb is constructed and filled with a solution of a salt (the concentration of this solution does not vary because the glass has a low water and ion permeability) and in this way, the electric potential depends only on the ionic activity in the external solution (a_1). Therefore,

$$V = \text{constant} + \frac{RT}{F} \ln a_1$$

The circuit is completed with a reference electrode and a liquid junction and the activity of the cation M^+ can now be measured in different solutions.

It is found experimentally that if more than one cation is present the electrode response is determined by the summed contributions of each cation to the transference of electricity so that for a number of cations, M_i^+ ($i = 1, 2, \ldots n,$), the potential is approximately[11]

$$V = \text{constant} + \frac{RT}{F} \ln \sum_{i=1}^{n} K_{1i}^{Pot} \; a_i$$

where K_{1i}^{Pot} is an empirical constant which gives the relative selectivity of the glass membrane for cation i vs. cation 1.

Since it has been experimentally observed that the activities of the cations govern the electrode potential it is established that glass electrodes function as perfectly reversible electrodes for cations, neither water nor anions entering importantly into the electrode reactions.

Eisenman et al. have theoretically and experimentally verified the following empirical equation for the response of cation selective glass electrodes.[24,25,26]

$$V = \text{constant} + \frac{nRT}{F} \ln \left[a_i^{1/n} + (K_{ij}^{Pot} \; a_j)^{1/n} \right]$$

where K_{ij}^{Pot} is an empirical constant describing the relative selectivity of the membrane with regard to cation j vs. cation i and n is a constant specific for a given glass and pair of cations. For K^+ and Na^+ solutions n was usually equal to one.

The selectivity constant of a glass cation exchange membrane depends upon

a) the ion-exchange equilibrium constant of the membrane-solution interfaces and

b) the mobility ratio of the ions within the membrane.

K_{ij}^{Pot} is identical to what is sometimes defined as the permeability ratio, $\frac{P_j}{P_i}$.

$$K_{ij}^{Pot} = \frac{P_j}{P_i} = K_{ij}\left(\frac{U_j}{U_i}\right)^n$$

where K_{ij} is the ion-exchange equilibrium constant of the membrane-solution interfaces,

$\frac{U_j}{U_i}$ is the ratio of the ionic mobilities in the glass,

and n is parameter describing non-ideal behavior (usually = 1 for K^+-Na^+ systems).

For potassium selective glass (composition $(Na_2O)_{27}\,(Al_2O_3)_4\,(SiO_2)_{69}$) such as the Beckman Cationic Electrode (39137) used in the present work, U_K/U_{Na} was determined to be between 0.12 and 0.23 (±30%)and $K^{Pot}_{Na/K}$ between 8.5 and 10.3.[11] From this data K_{NaK} was calculated to be between 49 and 83 (±30%). In a potassium selective glass, therefore, K^+ ions are more permeant and less mobile (more strongly bound).

When a cation sensitive glass electrode is immersed in a salt solution the electrode potential developed is composed of a phase-boundary potential contribution in the same direction as the total potential and a diffusion-potential contribution in the opposite direction.

For the system:[11]

$$\text{salt solution}' \,\big|\, \text{glass membrane} \,\big|\, \text{salt solution}''$$

$$V = V_B' + V_D + V_B''$$

where $V_B' = \text{constant} + \frac{nRT}{F} \ln \left[{a_i'}^{1/n} + (K a_j')^{1/n} \right]$

$$V_B'' = -\,\text{constant} + \frac{nRT}{F} \ln \left[{a_i''}^{1/n} + (K a_j'')^{1/n} \right]$$

V_B' and V_B'' are the boundary potentials for the two salt solutions, K is the ion exchange equilibrium constant (K_{ij}) for the $\underline{i}^{th}$ and $\underline{j}^{th}$ species, and V_D is the diffusion potential.

If a glass electrode responds with a Nernst slope to a given ion the change in potential is occurring because of changes in the phase boundary potential alone. The diffusion potential is constant in this situation.

If potassium selective glass electrodes are aged (a month is sufficient) they work much better at extremes in pH than do the fresh electrodes. Diffusion coefficients of cations in dry glass are 100 to 1,000 times smaller than in hydrated glass; furthermore, diffusion coefficients in hydrated glass are in between those for dry glass and those in free solutions. It is therefore concluded that hydration of the glass increases the ionic mobilities. It is generally believed that hydration of the glass is the principal factor in aging.

The ion exchange of glass can be represented by:

$$G^{+}(\text{glass}) + M^{+}(\text{aqueous}) \rightleftarrows M^{+}(\text{glass}) + G^{+}(\text{aqueous}) + \Delta F^{o}_{GM}$$

where M^{+}(aqueous) and G^{+}(aqueous) represent the two cations in dilute aqueous solution and G^{+}(glass) and M^{+}(glass) represent the cationic species G^{+} and M^{+} in the glass, and ΔF^{o}_{GM} is the standard free energy change of the reaction. The ionic-exchange equilibrium constant K is determined by ΔF^{o}_{GM}:

$$F^{o}_{GM} = -RT \ln K$$

where $$K = \frac{a_G^{sol} \; a_M^{glass}}{a_M^{sol} \; a_G^{glass}}$$

(where the a's are the activities of the ions in the solution and the glass).

To understand the equilibrium specificity of a glass membrane the free energy change (ΔF^{o}_{GM}) must be characterized as a function of the chemical composition of the glass. If the free energy change is described in terms of the interactions of the ions with water and with glass:

$$\Delta F^{o}_{GM} = (F_G^{Hyd} - F_M^{Hyd}) + (F_G^{glass} - F_M^{glass})$$

where, on the right-hand side of the equation, the first term is the difference in partial molal free energies of hydration of the ions G^+ and M^+ and the second term is the difference of their free energies of interaction with the glass. The partial molal free energies of hydration of ions are known experimentally with great accuracy. The free energies of interaction of the ions with the glass are a function of the chemical composition of the glass. To analyze the equilibrium specificity, the affinities of the various cations for glass must be determined as a function of its chemical composition.

It has been determined[11] that the sequence of cation specificity of a glass depends only on its oxyanion structures ("sites"). The anionic field strength of these sites is dependent on the chemical composition of the glass.

V. Specificity of a Glass

The common pH responsive glass electrodes have sodium silicate glass compositions. This glass has a structure of silicon tetrahedra (an oxygen at each corner) which are joined at their apeces by bridgingoxygen atoms (Figure 1.2a). If an alkali ion interrupts a bridging oxygen bond a cation exchange site is produced (Figure 1.2b). This is explained in the following manner: the strength of the electrostatic bond from each lattice-forming cation is defined[27] as the ratio of its oxidation state (or its charge) to its coordination number (for the silicons in Figures 1.2a and 1.2b it is $4/4 = 1$). The residual bonding strength of an oxygen atom is defined[27] as the difference between its charge (2) and the strength of the bonds from the adjacent lattice cations (silicons in Figures 1.2a and

1.2b).

When a lattice-breaking alkali cation interrupts a bridging oxygen bond the oxygen is bonded to only one adjacent silicon (Figure 1.2b) instead of the usual two. The residual bonding strength of this oxygen is the difference between its charge and the strength of the bond from the adjacent silicon $(2 - 4/4 = 1)$.

An oxygen, in the usual case, bridging two silicon tetrahedra (Figure 1.2a) has a residual bonding strength of zero $(2 - 4/4 - 4/4 = 0)$.

If a structural element introduced into the glass lattice exists in a coordination state greater than its oxidation state then an anion site is produced with a field strength determined by the residual bonding strength of the oxygen atoms. As an example: in a sodium aluminum silicate glass the aluminum has a coordination number of four but its oxidation state is three (Figure 1.2c). Since the strength of the bond from each aluminum is the ratio of its oxidation state to its coordination number its value in the case of Figure 1.2c is $3/4$. The residual bonding strength of an oxygen atom bonded to one aluminum and one silicon (bond strength, $4/4 = 1$) is $2 - 1 - 3/4 = 1/4$.

If zirconium oxides were added to a sodium silicate glass and the zirconium existed in sixfold coordination, an oxygen bonded to both a silicon and a zirconium (oxidation state = four) would have a residual strength of $2 - 1 - 4/6 = 1/3$ (Figure 1.2d).

It has been experimentally determined[11] that when the residual bonding strength of oxygen in the lattice is less than or equal to

$\frac{1}{2}$ the resulting anionic field strength leads to cation sensitivity relative to hydrogen ion.

The specificity of cation sensitive glass electrodes is merely a consequence of their different chemical compositions, which determines the field strengths of the sites. High field strength glasses are H^+ selective and low field strength glasses are selective for other cations. The pH responsive glass electrode and the cationic glass electrode used in the studies presented here are only two representatives of a continuous family of generally cation sensitive glass electrodes of differing compositions.

The Beckman Cationic Electrode (39137) has a glass composition which is $(Na_2O)_{27}(Al_2O_3)_4(SiO_2)_{69}$. It has the following decreasing order of sensitivity to univalent cations.

$$H^+ > Ag^+ > K^+ \text{ and } NH_4^+ > Na^+ > Li^+.$$

This electrode can be operated in the temperature range 0° to 80°C. and can be used to measure the activity of the above mentioned cations if their concentration is between 1.0 and 10^{-4}N. It was found experimentally that it could be used to measure K^+ and Na^+ activity in the approximate pH range of 4.5 and 13. The potassium or sodium concentration had to be approximately four factors of ten higher than the hydrogen ion concentration in order to have no hydrogen ion interference (non-Nernstian response).

VI. Calibration of the Cationic Electrode

The cationic electrodes used in the work presented were calibrated at the pH of the surfactant solutions in which they were used. The e.m.f.'s of the cationic electrode versus a reference electrode (e.g. Ag/AgCl) were determined for a series of solutions of known concentrations of the cation. These e.m.f.'s (in millivolts) were plotted against the activities of the cation in the calibrating solutions.

Activities on the molal (m) and molar (M) scales are related by[28]

$$a_M = a_m d^o$$

where d^o is the density of the solvent. At 23°C. the density of water (to three significant figures) is[29] 0.998 and at 30°C. the density of water is 0.996. The experiments in Chapters 3 and 4 were performed in this temperature range ($\sim$25 - 30°C.) where molal and molar ionic activities are identical well within the experimental error (as much as four percent).

The cation activities in the calibrating solutions were obtained by multiplying the <u>molar</u> cation concentrations by mean <u>molal</u> activity coefficients in the literature.[30] This introduced an error of less than 2%. Straight lines of approximately Nernstian slope were obtained when e.m.f. was plotted against the negative logarithm of activity. A typical calibration curve is shown in Figure 1.3.

It was found experimentally that the slope of the calibration curve was constant from day to day for a given electrode and a given set of calibrating solutions. The absolute values of the e.m.f.'s for the calibrating solutions, however, varied typically,

±1 - 3 millivolts over the same time period.

It should be mentioned that mean molal activity coefficients were used rather than single-ion activity coefficients[31] in calculating cation activities. An attempt was made to closely match the calibrating and sample solutions (as is done in pH measurements) so that the calibration curves would be valid. It was found (Chapter 3) that the activity coefficient of cations (at high pH) did not change in dilute micellar soap solutions.

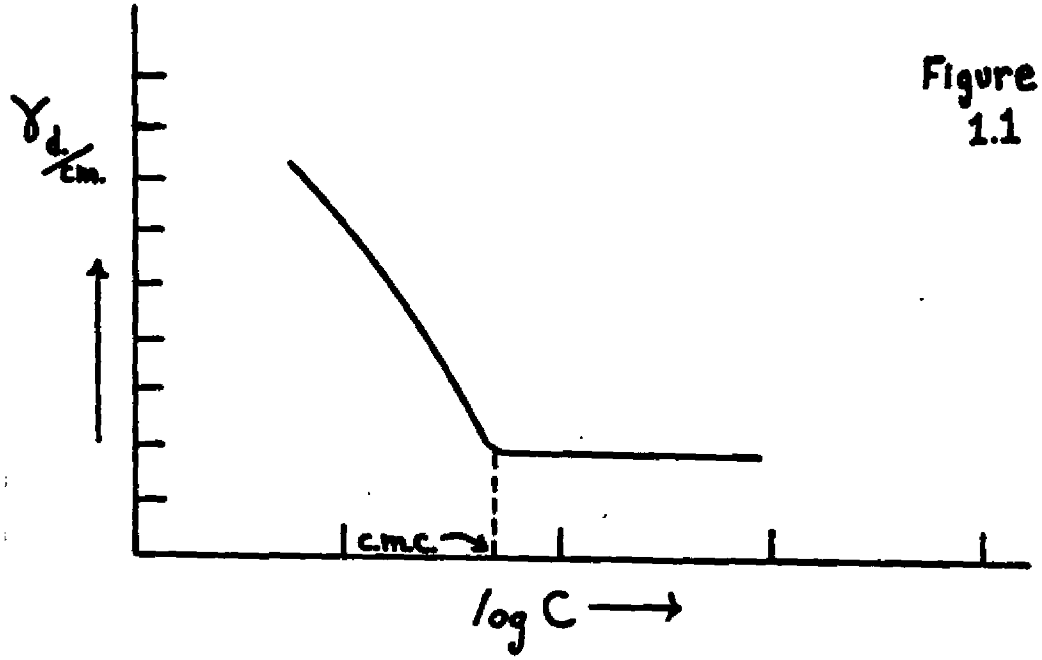


Figure 1.1

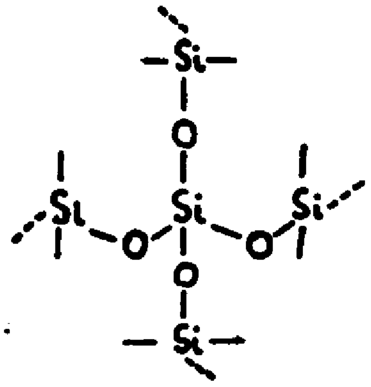


Figure 1.2a

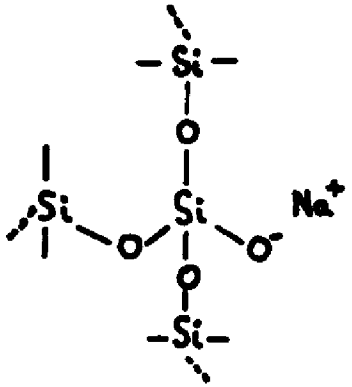


Figure 1.2b

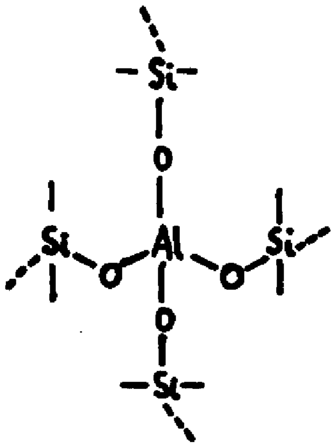


Figure 1.2c

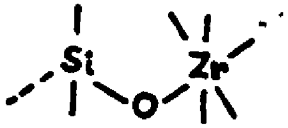


Figure 1.2d

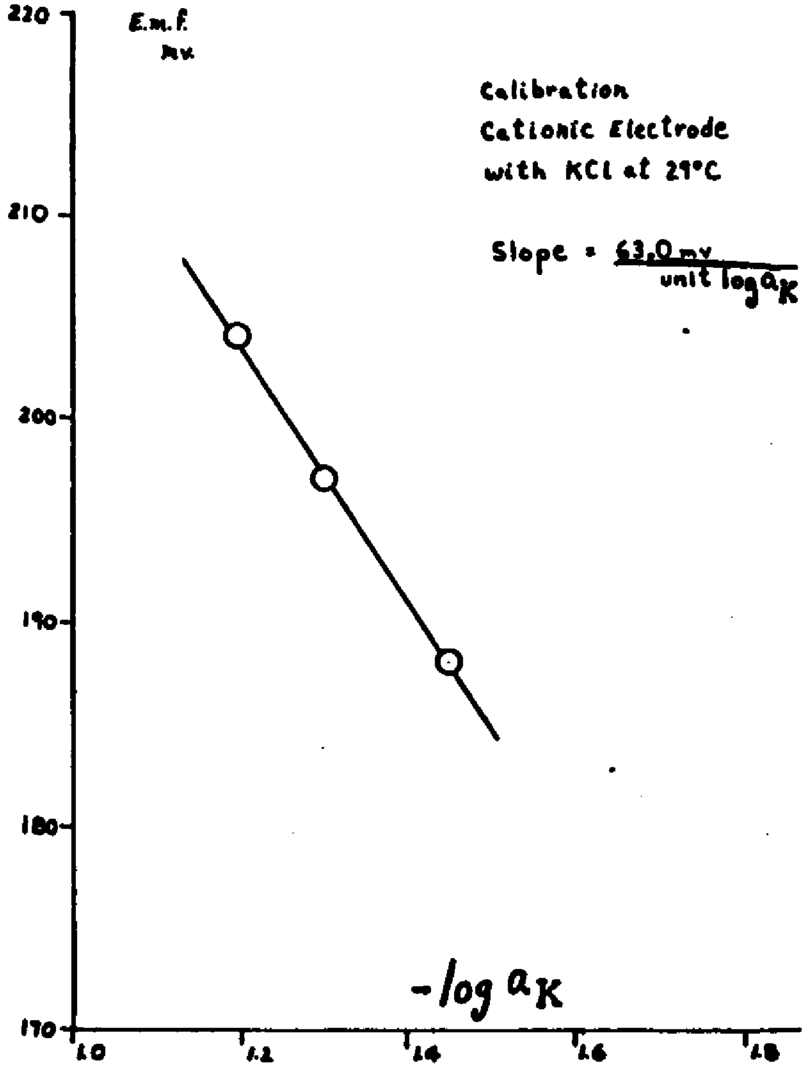

220
210
200
190
180
170
E.m.f.
mv
Calibration
Cationic Electrode
with KCl at 29°C
Slope = 63.0 mv / unit log a_K
$-\log a_K$
1.0
1.2
1.4
1.6
1.8

Figure 1.3

CHAPTER 2

Background Literature

In this brief chapter, an attempt is made to link the general considerations of Chapter 1 with the experimental investigations and results to be described in Chapters 3 and 4.

I. The Critical Micelle Concentration

Lawrence and McDonald[32] determined the critical micelle concentration of surfactants using a pH glass electrode (see later, work of Stanley and Radley[33]). A micellar solution was diluted with distilled water and the pH of the resulting solutions was plotted against concentration of surfactant; a sharp break occurred at the c.m.c. for the cases of sodium dodecylsulfate and dodecylammonium chloride.

Using a dye-solubilization technique, Corrin and Harkins[34] studied the effect of added salts on the lowering of the critical micelle concentrations of sodium dodecylsulfate, dodecylammonium chloride, decyltrimethylammonium bromide, and potassium laurate. In all cases, it was found, the logarithm of the critical micelle concentrations of the colloidal electrolyte was a linear function of the logarithm of the total concentration of the ion of opposite charge to that on the aggregate. It was conclusively demonstrated that the nature of the neben ion (ion of the same sign as that of the micelle) played no role in determining the critical micelle concentration of the surfactant. Equivalent concentrations of NaCl, Na_2SO_4, or $Na_4P_2O_7$ lowered the critical micelle concentration of a given surface active agent by the same amount. One of the experimentally determined equations given in this paper, for the logarithm of the c.m.c. of potassium laurate as a function of added salt, was used as an equilibrium condition for a micellar potassium laurate solution in Chapter 4.

II. Hydrogen Ion Concentration at a Micelle Surface

Mukerjee and Banerjee[4] determined H^+ concentrations at the surface of micelles using indicator dyes (bromophenol blue and bromocresol green). In the presence of cationic micelles of lauryl trimethylammonium chloride, and lauryl-, myristyl-, and cetyl trimethylammonium bromide, and in anionic micelles of sodium laurylsulfate, the hydrophobic parts of the dye are buried and the hydrophilic groups are exposed at the surface. The surface pK's of the dyes are higher than the bulk values, the differences increasing with increasing charge density of the micelles. This effect was attributed to the lower dialectric constant at the micelle surface.

III. Hydrolysis of Soap Solutions

Although hydrolysis in soap solutions had been investigated experimentally by measuring bulk pH with glass electrodes,[35] no quantitative interpretation was available until the recent study by Lucassen.[12] Potassium salts of C_{10}, C_{12}, C_{14}, C_{16}, and C_{18} fatty acids at 20°C. were investigated and a theory was presented which predicted pH of a partially acidified potassium soap solution as a function of the concentration of soap present. An equilibrium treatment was used, based on the possible precipitation of two out of three solid phases: fatty acid, acid soap, and neutral soap. It was further demonstrated that pH measurements could yield a simple method for the evaluation of the composition and solubility parameters of the precipitates formed in a partially acidified soap solution.

Titrations of soap solutions with HCl provide a method of investigating their hydrolysis and the nature of the precipitates formed. Rosano et al.[10,36] was the first to qualitatively describe the titrations of micellar and non-micellar potassium laurate solutions. An explanation was given for the buffering action of these systems in the presence and absence of solvent and the concept of surface pH was elucidated for these systems. In Chapter 4, a systematic study is presented which connects the studies of Lucassen to those of Rosano et al.

IV. Counterion Binding to Micelles by E.M.F. Measurements

Relatively few investigators have studied the binding of counterions to micelles by e.m.f. measurements. In 1959, Botré and co-workers[5] used membrane electrodes to determine the activity of counterions in aqueous solutions of sodium laurate, sodium laurylsulfate, and laurylaminehydrochloride. Because a sharp break occurred at the c.m.c. in the graph of activity of the cation versus concentration of detergent, it was concluded that membrane electrodes could be used to determine the c.m.c. of detergent solutions. Below the critical micelle concentration the behavior of the solutions was very much like the behavior of inorganic 1:1 electrolytes. Above the c.m.c., the activity versus concentration curves showed a steep decrease. It was concluded that the high charge density on the surface of the micelle exerts a strong electrostatic field on the counterions and they are, therefore, bound in the micelle surface region and are not detected in the bulk solution. The experimentally determined counterion activity was:

$$a = \gamma(\text{c.m.c.} + \alpha C_m). \qquad (1)$$

In this equation the contribution to the counterion activity of the unmicellized (c.m.c.) and micellized (C_m) surfactant molecules was formally separated. γ equals the activity coefficient of the counterions and α equals the degree of counterion dissociation from the micelles. It was found that α was constant in the concentration range studied.

Keh and co-workers[37] determined the degree of dissociation (α) of bromide counterions from cationic micelles of tetradecyl- and hexadecyl-trimethyl-ammonium bromide. A Ag/AgBr electrode was used to measure the bromide ion activity. The concentration of the bromide ions was related to the degree of dissociation of the micelles by equation (1). No significant difference was observed between the degrees of counterion dissociation for $C_{14}N_{+}(CH_3)_3Br^-$ (α=0.21) and $C_{16}N_{+}(CH_3)_3Br^-$ (α=0.22).

In 1960, Stanley and Radley[33] were the first to use a commercial sodium responsive glass electrode in conjunction with a saturated calomel reference electrode to determine the c.m.c. of paraffin chain salts. pNa (-log. a_{Na}) was plotted against concentration for a solution of pure NaCl and a solution of pure sodium dodecylsulfate. Below the c.m.c. of the sodium dodecylsulfate, the pNa versus concentration curve fell on the pNa versus concentration curve for NaCl. Above the c.m.c. it was noted that the activity of sodium ions increased more slowly than the total concentration of sodium dodecylsulfate.

It remained for Shedlovsky et al.[38] in 1963, to unite the techniques of Botré and Stanley. Using a treatment similar to that of Botré, Shedlovsky determined the binding of sodium counterions to micelles in aqueous solutions of sodium decyl, dodecyl, and tetradecyl sulfates. Electromotive force measurements were made using sodium responsive glass electrodes and a MacInnes-Belcher calomel half-cell and five-way stopcock reference electrode assembly.[39] It was this technique which was the basis for the e.m.f. measurements made in Chapter 3.

V. Competition of Ions at a Micelle-Solution Interface

Most recently, Pearson and Lawrence[40] have used a sodium sensitive glass electrode to measure the sodium ion activity in micellar solutions of sodium dodecylsulfate to which varying amounts of hexanol and $CaCl_2$ had been added. Hexanol added to these solutions is solubilized by the micelles and Ca^{++} ions added as $CaCl_2$ are preferentially adsorbed at the micelle surfaces. At the micelle surface the OH groups of the solubilized hexanol molecules and the doubly charged Ca^{++} ions both serve to decrease the repulsion between the ionic head groups of the detergent with the consequent release of bound sodium ions. This was a study, then, of the competition of Na^+ and Ca^{++} ions at an anionic micelle surface.

VI. Effect of Nonionic Detergent

Corkill, Goodman, and Tate[41] described the effect of a nonionic detergent, n-dodecanol + 6 ethylene oxide, on the micelle formation of sodium dodecylsulfonate. A change in the degree of dissociation of the anionic detergent (α) was brought about by its incorporation in nonionic micelles. Whereas the value of α, determined by e.m.f. and conductivity measurements, in micellar solutions of sodium dodecylsulfonate alone was 0.41, it was found to substantially increase as nonionic was added and mixed micelles were formed. It was concluded that the increase in α was due to the lower surface charge density of the mixed micelles.

VII. Polyelectrolyte Solutions

The activity coefficients of sodium ion in polyelectrolyte solutions have been extensively investigated by Ise and Okubo.[43-47] Sodium sensitive glass electrodes were used in their e.m.f. studies. These authors claimed that the single-ion activity coefficients of counterions in sodium polyacrylate solutions were almost independent of the polymer concentration in the range studied. The mean activity coefficients of sodium ions in aqueous solutions of sodium salts of polyvinyl alcohols partially acetalized with glyoxylic acid were measured electrochemically using a unique concentration cell with transference with "back-to-back" sodium glass electrodes.

CHAPTER 3

The Determination of the Apparent Binding of Counterions to Micelles by E.M.F. Measurements

I. Results

The dissociation of counterions (α) from soap micelles was determined by measuring the cation activity (with a cation sensitive glass electrode) in micellar and non-micellar soap solutions. A series of solutions of a given soap contained an excess of base and a constant cation concentration. The e.m.f. of the cationic electroce versus a calomel half-cell (Figure 3.1) was determined for each dilution of the original micellar soap solution. The concentrations of all species present were known for each dilution.

The e.m.f.'s obtained from a series of soap solutions (above and below the c.m.c) were converted to the activity of the cation using a calibration curve. The activities were divided by the known total cation concentration (Q) and in this way γ_Q, the activity coefficient of the cation in presence of the long-chain anion was obtained; $\gamma_Q = a_b/Q$. (When concentrations are in molar units it is more usual to relate the molar activity to the molarity by[28] $a_M = My$. It was decided not to use these conventional symbols since concentrations (molarity) were multiplied by mean molal activity coefficients to obtain cation activities for the calibration curves.) γ_Q for the cation was plotted against the logarithm of the molar concentration of the long-chain anion for potassium caprate, potassium laurate, potassium myristate, and sodium caprate (see Figures 3.2 and 3.3). For each series a break occurs at the c.m.c.[33] Either surface tension or refractive index measurements was used to independently determine the c.m.c. for a soap solution (see Table 3.1) since it was difficult to determine precisely the value of the c.m.c. from the break in the curve of γ_Q versus log. concentration of long-chain anion.

Before an interpretation of the experimental results is proposed, the following remarks are necessary. Since it is observed that up to the c.m.c. the e.m.f. of KOH (or NaOH) alone or KOH (or NaOH) plus soap is constant (for a given soap solution series) within the experimental error (see Figures 3.2 and 3.3), it was concluded that neither the liquid junction potential nor the activity coefficient of the cation is affected by the presence of monodispersed anion up to the c.m.c. The result is not surprising since all the soap solutions contained a large excess of KOH or NaOH and therefore were very much like the standardizing solutions.

Since the activity of the cation in a soap solution is determined by converting the cell e.m.f. to cation activity by use of a calibration curve (e.m.f. versus -log. a_b), it is assumed that the liquid junction potentials of the calibrating hydroxide solutions and soap solutions are the same. Above the c.m.c. the presence of micelles in the soap solutions may affect the liquid junction potential.

It was estimated that the method used to obtain a calibration curve for the cationic electrode (the molar cation concentrations were multiplied by mean molal activity coefficients to obtain the cation activities) introduced an error of less than 2% (see Chapter 1 - Calibration of the Cationic Electrode).

Furthermore, in our interpretation, we have held to the generally accepted view that any addition of soap above the c.m.c. merely increases the concentration of micelles.[13]

II. Experimental

The soap solutions were made by neutralizing a weighed amount of the melted fatty acid with a known amount of standardized base (KOH or NaOH) so that the pH of the resulting solution was greater than 12.3. A series of volumetric dilutions was made using a combination of standardized base (added with a buret) and distilled water. In this way a series of solutions was made to have constant cation concentrations (K^+ or Na^+), different known concentrations of long-chain anion (above and below the critical micelle concentration), and different known pH's all above 12.3. This procedure offered the following advantages: 1) high pH, in order to prevent any soap hydrolysis,[10] 2) this method of dilution did not affect the cation concentration and it was therefore possible to observe the effect of monodispersed long-chain anions or micelles on the activity of the cation.

In our study with sodium dodecylsulfate a small amount of NaOH was added to the original undiluted solution only (in order to be above pH 7) and the concentration of sodium ion was not maintained constant.

The solutions of standardized base were made from reagent grade pellets of KOH and NaOH (J. T. Baker Chemical Company, Phillipsburg, N. J.) and distilled water. The capric (C_{10}), lauric (C_{12}), and myristic (C_{14}) acids were all highest grade purity obtained from Eastman Organic Chemicals, Rochester, N. Y., and were used without further purification.

The critical micelle concentration (c.m.c.) of a soap solution series was determined either by measurement of refractive index or surface tension as a function of concentration of the long-chain anion. An Abbe refractometer (at constant temperature), Bausch and Lomb model 33-45-58, was used for the refractive index measurements. A Rosano Tensiometer (Federal Pacific Electric Company, Newark, N. J.) was used for the measurement of surface tension. The tensiometer utilizes the Wilhelmy wettable plate method and consists of a sandblasted platinum plate suspended from a Roller-Smith torsion balance. The surface tension measurements were reproducible within ±0.2 dynes.

The cell (Figure 3.1) consisted of a glass electrode sensitive to cations (Beckman 39137 Cationic Electrode, Beckman Instruments, Inc., Fullerton, Calif.) and a saturated KCl, calomel half-cell. A MacInnes-Belcher calomel half-cell and five-way stopcock assembly[39] (E. Machlett and Son, Long Island City, N. Y.) was used instead of a fiber or sleeve type calomel electrode. The cationic glass electrode was immersed in a glass cup containing the solution to be measured and this, in turn, was connected to the saturated KCl, calomel half-cell by means of the five-way stopcock. Two or three drops of the solution and then of the saturated KCl were allowed to run out of the cell to clean the junction and then the stopcock was turned so as to connect the saturated KCl with the solution to be measured. The five-way stopcock, therefore, allowed the formation of a fresh liquid junction for each measurement.

The circuit for the measurement of the cell e.m.f. consisted of the cell, a precision potentiometer (Model 2730, Honeywell Instruments, Inc., Denver, Colorado), and an electrometer (Keithly 610B, Keithly Instruments, Inc., Cleveland, Ohio) all in series. The potentiometer opposed the cell e.m.f. and the electrometer was used as a null indicator of voltage. The electrometer was set to read 10 millivolts full-scale (±0.05 millivolts with center zero) and the potentiometer was read to ±0.1 millivolt when the cell e.m.f. was of the order of 200 millivolts. The cell was in an aluminum shielded Faraday box and connections to the potentiometer and the electrometer were made with Amphenol connectors and "low-noise" (graphitized coaxial) cable. The "low-noise" cable was found necessary to eliminate stray capacitances in the wire connections.

The liquid junction was repeatedly formed and the e.m.f. read immediately after the formation of the liquid junction was reproducible within ±0.1 millivolt for a given solution.

The cationic glass electrode was calibrated with solutions of base (KOH or NaOH) of known molarity. The molarities were multiplied by mean molal activity coefficients from the literature[30] to obtain the activities of the cation (a_b). A graph of the cell e.m.f. versus the negative logarithm of the cation activity ($-\log a_b$) was a straight line which exhibited a slope within three millivolts of the theoretical value (the theoretical Nernst slope is 59.2 millivolts for a tenfold change in activity at 25° C.). The e.m.f.'s of the calibrating solutions and soap solutions were measured alternately so that the calibration could be carried out during the actual experiment.

III. Theory

The measured activity of the cation in a micellar soap solution may be formally separated into the contributions from the micellized and unmicellized soap molecules:[5,36-38,48]

$$a_b = \gamma([Q - C] + C_o + \alpha C_m) \qquad (1)$$

where

Q = constant cation concentration in the soap solution

C = total concentration of long-chain anion

$Q - C$ = stoichiometric excess cation concentration

C_o = critical micelle concentration

C_m = concentration of long-chain anion in micellar form

γ = the actual activity coefficient of the cation in the soap solution

α = degree of dissociation of the cations from the micelles

Substituting in (1) $C_m = C - C_o$ and $a_b = \gamma_Q \cdot Q$

$$\gamma_Q \cdot Q = \gamma([Q - C] + C_o + \alpha C - \alpha C_o). \qquad (2)$$

Dividing by Q and rearranging:

$$\gamma_Q = C/Q \ \gamma(\alpha - 1) + \gamma(1 + C_o/Q\,[1 - \alpha]). \qquad (3)$$

Since for each soap solution series studied a plot of γ_Q versus C/Q yielded a straight line (see Figure 3.4) one had to assume that γ and α were constant in the concentration range studied.[5] The slope

TABLE 3.1

Detergent	Constant Cation Concentration	Critical Micelle Concentration	γ_Q at c.m.c.	α
K Caprate	2.16×10^{-1} M	9.18×10^{-3} M (Ref. Ind. @ 23°C)	0.744	0.79 ± .04
K Laurate	9.00×10^{-2} M	9.12×10^{-3} M (Surf. Ten. @ 24°C)	0.764	0.69 ± .02
K Myristate	8.49×10^{-2} M	3.63×10^{-3} M (Surf. Ten. @ 25°C)	0.783	0.24 ± .02
Na Caprate	2.69×10^{-1} M	5.75×10^{-2} M (Ref. Ind. @ 26°C)	0.687	0.57 ± .02
Na Dodecyl-sulfate	J = 1.09*	7.21×10^{-3} M (Surf. Ten. @ 24°C)	0.837	0.14 ± .02

* See text

of the line was equated to $\gamma(\alpha - 1)$ for each series. The value of γ_Q at the c.m.c. was substituted for γ and the equation was solved for α. The values of α are listed in Table 3.1.

The determination of α is dependent on the value of the c.m.c. only insofar as one must know the value of γ_Q at the c.m.c. The value of γ_Q at the c.m.c. is easily determined, however, because γ_Q is essentially constant before the c.m.c.

The determination of α for sodium dodecylsulfate was undertaken in order to compare our results with those of Botré[5] and co-workers ($\alpha = 0.16$) and Shedlovsky et al.[38] ($\alpha = 0.22$). A solution of sodium dodecylsulfate (containing added NaOH) at pH 11.2, 4.94×10^{-2}M in sodium ion, and 4.54×10^{-2}M in dodecylsulfate ion was diluted volumetrically with distilled water so that the cation and anion concentrations were known for each dilution. The e.m.f.'s obtained for this series of dilutions were converted to activities of sodium ion by use of a calibration curve. A plot of γ_Q versus the logarithm of the molar concentration of dodecylsulfate ion shows a break in the curve at the c.m.c. (see Figure 3.5).

The following reasoning was used to interpret the data:

Here Q = the changing cation concentration

$$\text{again} \quad a_b = \gamma([Q - C] + C_o + \alpha C_m). \qquad (1)$$

The ratio of Q and C is a constant so that Q = JC (where J is the constant factor).

Substituting in (1)

$$a_b = Q \cdot \gamma_Q = JC\gamma_Q = \gamma(C[J - 1] + C_o + \alpha C_m). (4)$$

Upon substitution of $(C - C_o)$ for C_m and division by JC and rearranging:

$$\gamma_Q = C_o/C \cdot \gamma/J \; (1 - \alpha) + \gamma/J \; (J + \alpha - 1). \qquad (5)$$

The γ_Q's for the solutions above the c.m.c. were plotted as a function of C_o/C (see Figure 3.6) and the slope of the straight line was equated to $\gamma/J\ (1 - \alpha)$. The value of γ_Q at the c.m.c. was substituted for γ and the value 1.09 for J (obtained from the ratio of Q to C in the original undiluted solution), and the value of α was calculated (see Table 3.1). The degree of dissociation calculated in this way was 0.14. α was also evaluated at the intercept $(C_o/C = 0)$, where $\gamma_Q = 0.194$, and found to be 0.16.

IV. Discussion

The degree of dissociation of the cations from the micelle could be interpreted with the model of a micelle made of undissociated soap molecules assoiciated with ionized soap molecules. This model is most improbable because the formation of an insoluble or very slightly soluble compound (such as undissociated soap or for that matter, fatty acid) will result in a bulk precipitation.[10]

Another alternative is to assume complete dissociation but with the hydrated cations very close to the long-chain anions. In the case of soap micelles some of the cations are probably embedded in the plane of the micelle-solution interface. Goddard and collaborators[49,50] and Sears and Schulman[51] have extenxively investigated the monolayer properties of long-chain fatty acids at high pH's. These monolayers are expanded on hydroxide solutions and their behavior varies with the nature of the cation for a given long-chain anion. Small values of the surface potential indicate that the apparent surface moment of the soap molecule in the monolayer is small. This leads us to believe that either the long-chain anion and the cation are in the plane of the surface or that they are not in the plane of the surface but that the water dipoles somewhat neutralize the ion-ion dipole moment. This latter alternative is unlikely in view of the large area per molecule reported.[51] Therefore, cation size is important in characterizing soap monolayers.

Recent measurements, made by Christodoulou,[52] of surface pressure, surface potential, and surface viscosity on soap monolayers of sodium, potassium, and lithium stearate confirm the results of Sears and Schulman, and the relatively high viscosity exerted by these monolayers leads to the conclusion that some positive ions statistically alternate with long chain anions in the plane of the monolayer at these high pH's.

Goddard and Ackilli[49] have found that below pH 8.5 for stearic acid monolayers spread on aqueous substrates at various pH's, the compression surface isotherms approached the values obtained by compressing stearic acid spread on 0.1 N HCl. These authors concluded that below pH's 8.5 to 9 strong association exists between ionized and unionized forms of the fatty acid.

Because these facts were known our experiments were conducted at high pH where the competition from hydrogen ions with other cations could be neglected. Although the micelle-solution interface is probably different from a monolayer-aqueous substrate inteface an analogy between the two is reasonable and therefore the model of a soap micelle partially embedded with hydrated cations is plausible.[3] Therefore, it is concluded that the α values listed in Table 3.1 are not degrees of dissociation in the usual sense but probably are related to the extent of binding of the cations to the micelles.

In the series with potassium, α decreases with increasing chain length of the anion, myristate micelles binding more potassium than laurate or caprate (however, in our experiments the constant concentration of potassium in the caprate case was approximately twice as large as in the cases of potassium laurate or potassium myristate). Both Shedlovsky[38] and Campbell[53] found that α decreased with the chain length of the long-chain anion. Shedlovsky's α values for sodium decyl, dodecyl, and tetradecylsulfate were 0.30, 0.22, and 0.13, respectively. Campbell's values of α for sodium caprate, laurate, and myristate were 0.50, 0.35, and 0.31, respectively. It is probable that the charge density on the surface of the micelle increases with increasing chain length of the long-chain anion (because of the greater attractive forces among the associated chains); thus an increase in chain length increases the attractive forces acting on the cations. If the chain length becomes sufficiently long, precipitation of the soap occurs (Krafft point). This may explain why stearic acid (C_{18}) spread on 0.5 N NaOH (Sears and Schulman,[51] page 3531,

Figure 2) exerts a surface pressure of approximately 16 dynes/cm. at 50 A^2 per molecule while Goddard[50] (page 323, Figure 2) finds that behenic acid (C_{22}) monolayers spread on 1.0 N or 0.1 N NaOH substrates exert surface pressures between 2 and 4 dynes/cm. at an area of 50 A^2 per molecule. In the case of the behenic acid monolayers most of the monolayer may be below the "two dimensional" Krafft point.

Sears and Schulman[51] found that stearic acid monolayers spread on 0.5 N KOH were more expanded than those spread on 0.5 N NaOH and attributed this difference to the larger size of the hydrated potassium ion at the monolayer-substrate interface. Our results show a larger α value for K caprate than for Na caprate. Although it is realized that the larger total salt concentration in the Na caprate case may account for some of this difference (the greater the amount of added salt in a micellar solution, the more the dissociation of counterions is repressed, and the smaller will be the value of α), nevertheless, our results agree well with those of Campbell[53] who determined, by conductance studies, a value of 0.50 for α for sodium caprate. Furthermore, the value of determined for our potassium laurate system (0.69 - see Table 3.1) is considerably larger than the value of α determined by Botré[5] for sodium laurate (0.31). However, an explanation attributing the difference in α between sodium and potassium soaps to the larger size of the hydrated potassium ion is tenuous in light of the fact that octadecylsulfate monolayers are more expanded on a substrate of NaCl than on KCl.[54] It is clear, therefore, that the nature of the long-chain anion affects the hydration of the cation. The specific cationic-anionic system determines surface behavior.[55] So far, no adequate explanation for counterion sequence effects, and their reversal, has been proposed.

In the case of sodium dodecylsulfate, Shedlovsky et al.[38] found (at $C_0/C = 0$) an α value of 0.22 while Botré and co-workers[5] found an α value (at $C_0/C = 0$) of 0.16. Let us note that our result agrees well with these ($\alpha = 0.14$, see Table 3.1) since the addition of a small amount of NaOH (in our case) would be expected to lower the value of α.

As a result of plotting our data according to equation (3) it was concluded that the dissociation of counterions from the micelle (α) and the activity coefficient of the counterions (γ) were constant in the concentration range studied. No assumption was made with regard to the shape of the micelle or the distribution of counterions around the micelle.

As was mentioned (Chapter 2) Ise, Okubo, and Nishizaki[42,43] found that the single-ion activity coefficient of sodium ion in aqueous polyacrylate solutions was almost independent of polymer concentration. Even at zero polymer concentration the electric charges on the polymer chain cannot be separated from each other; the activity coefficient of the ionized group of the polyelectrolyte, therefore, converges to a value other than unity. In our case, up to the c.m.c., the activity coefficient is essentially constant (here only the molecularly dispersed ions are present) but beyond the c.m.c. the presence of micelles affects the measured coefficient of activity. In the hypothetical case of a purely micellar solution the activity coefficient of the cation would probably be comparable to that of the counterions in aqueous polymer solutions (where γ_Q is approximately 0.3[42]).

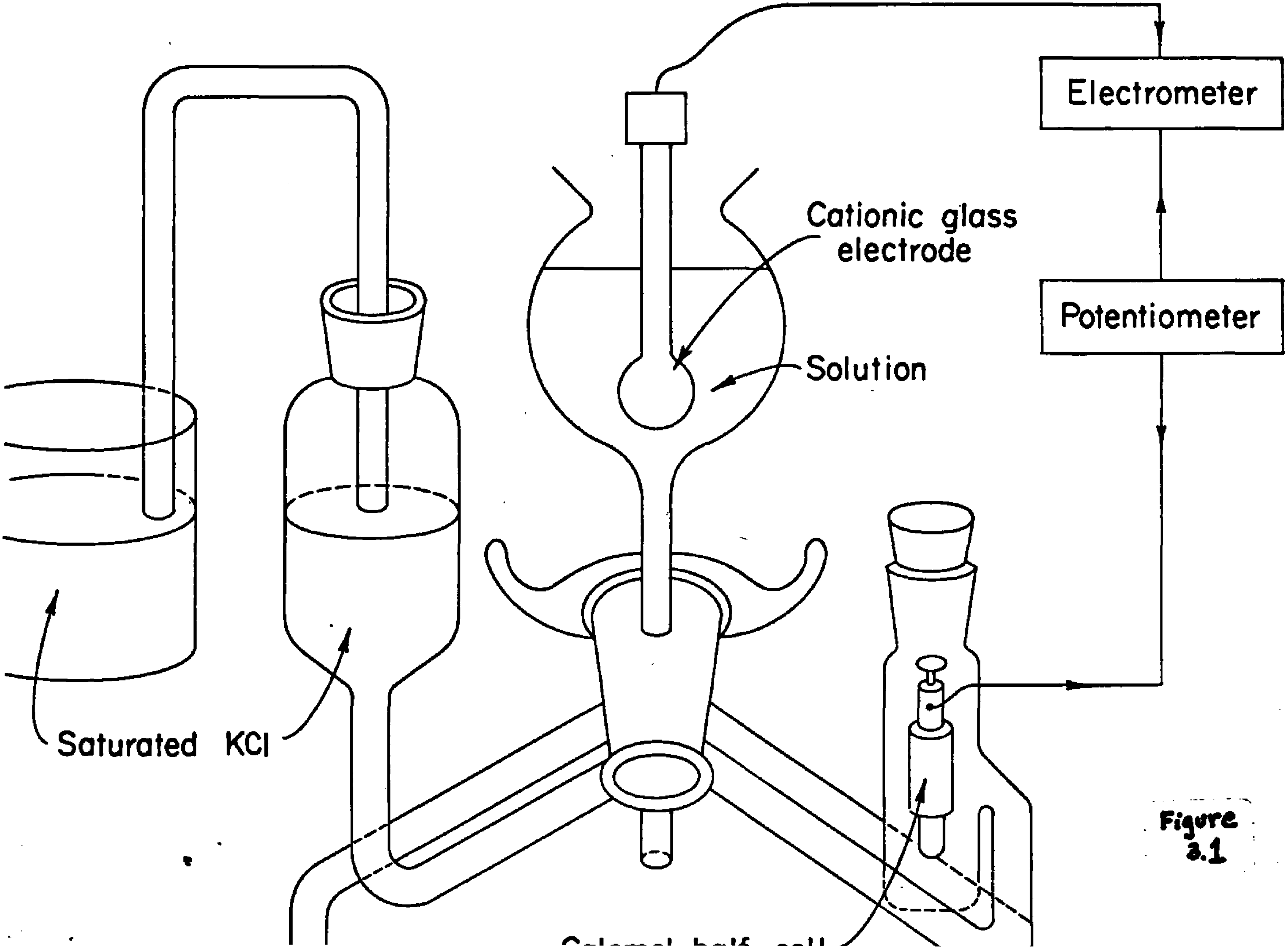
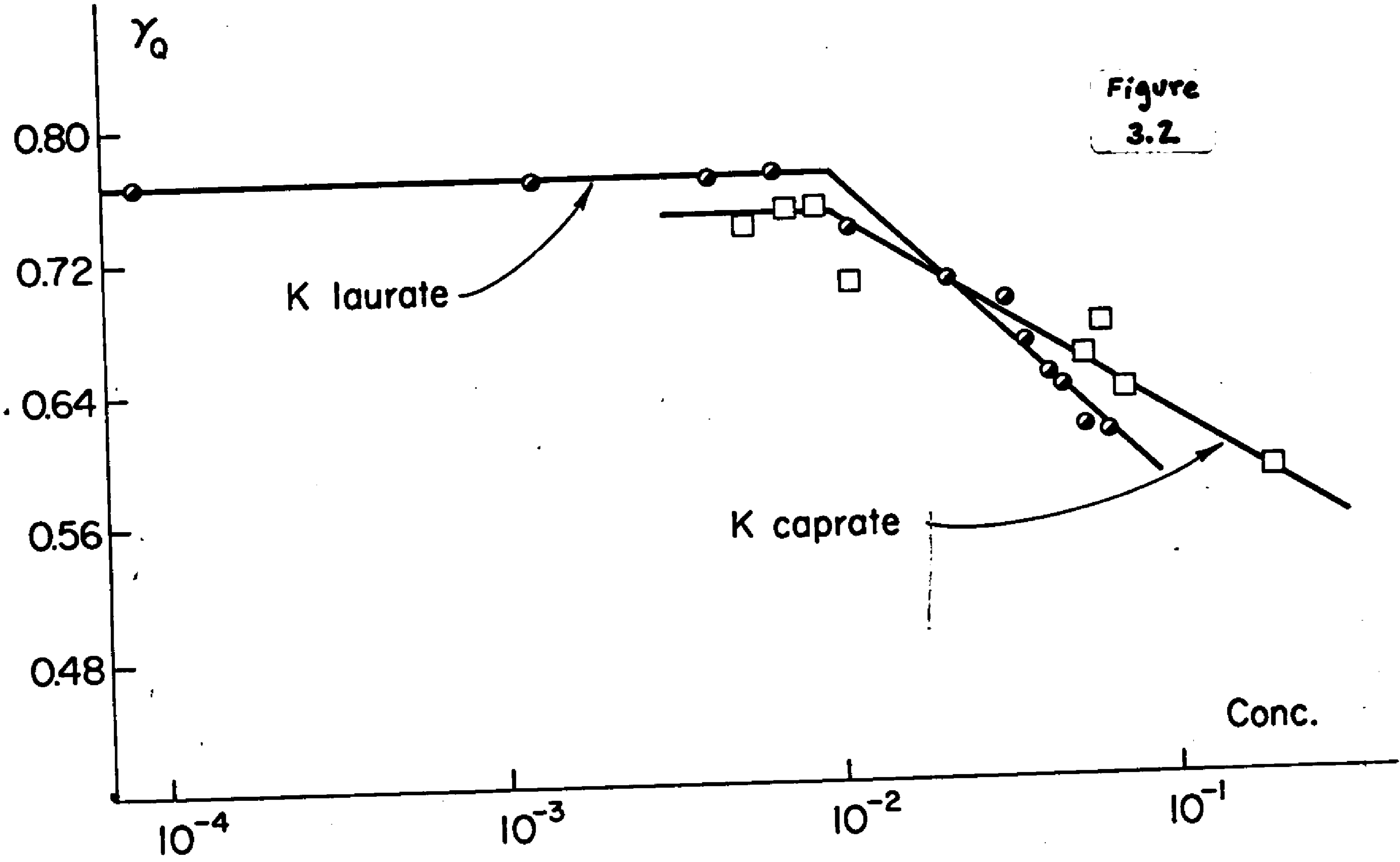
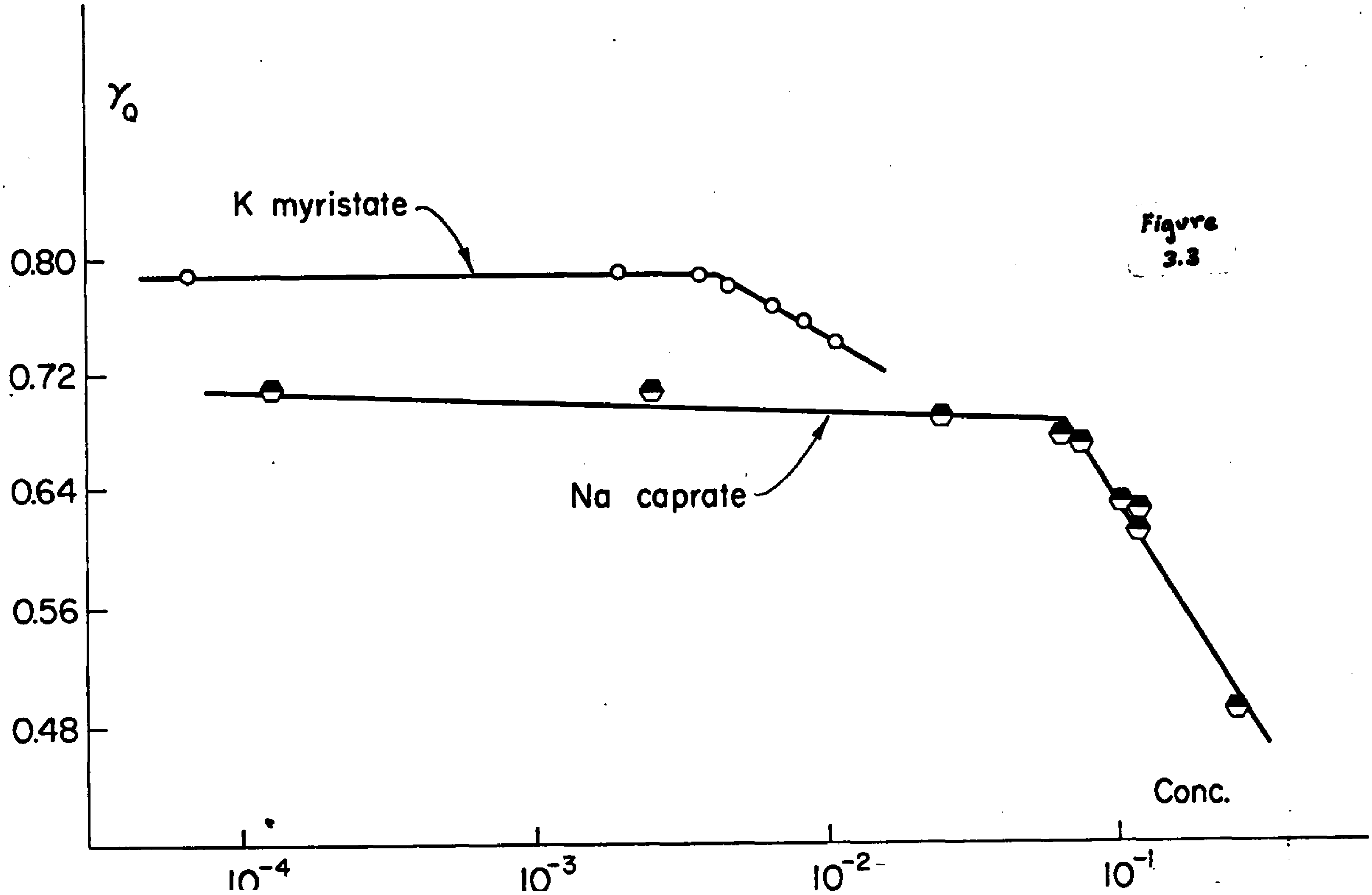

Electrometer
Potentiometer
Cationic glass electrode
Solution
Saturated KCl
Calomel half cell

Figure 3.1



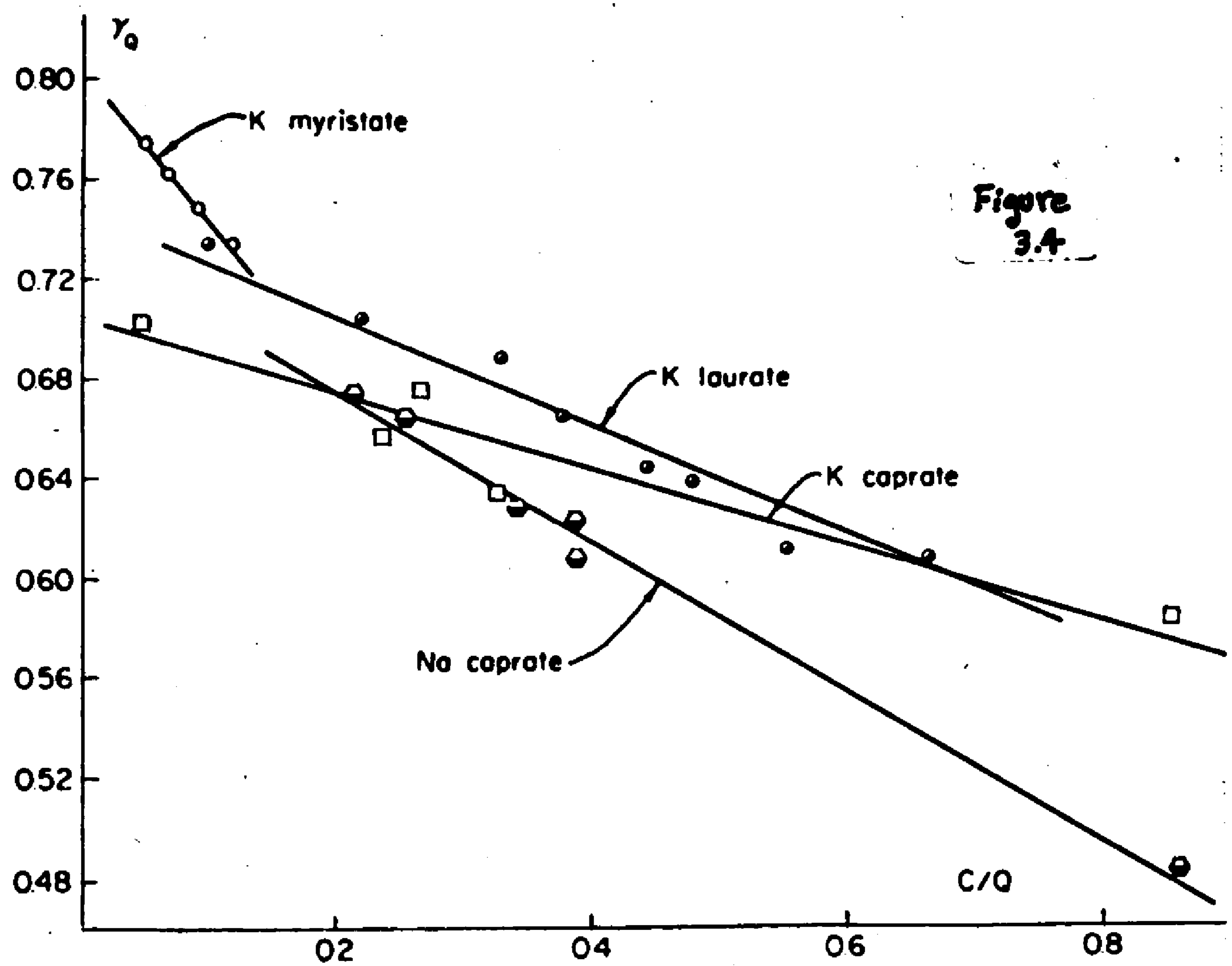
γ_Q
0.80
0.72
0.64
0.56
0.48
K laurate
K caprate
Conc.
10^{-4}
10^{-3}
10^{-2}
10^{-1}

Figure 3.2



γ_Q
0.80
0.72
0.64
0.56
0.48
K myristate
Na caprate
Conc.
10^{-4}
10^{-3}
10^{-2}
10^{-1}

Figure 3.3



γ_Q
0.80
0.76
0.72
0.68
0.64
0.60
0.56
0.52
0.48
0.2
0.4
0.6
0.8
C/Q
K myristate
K laurate
K caprate
Na caprate

Figure 3.4

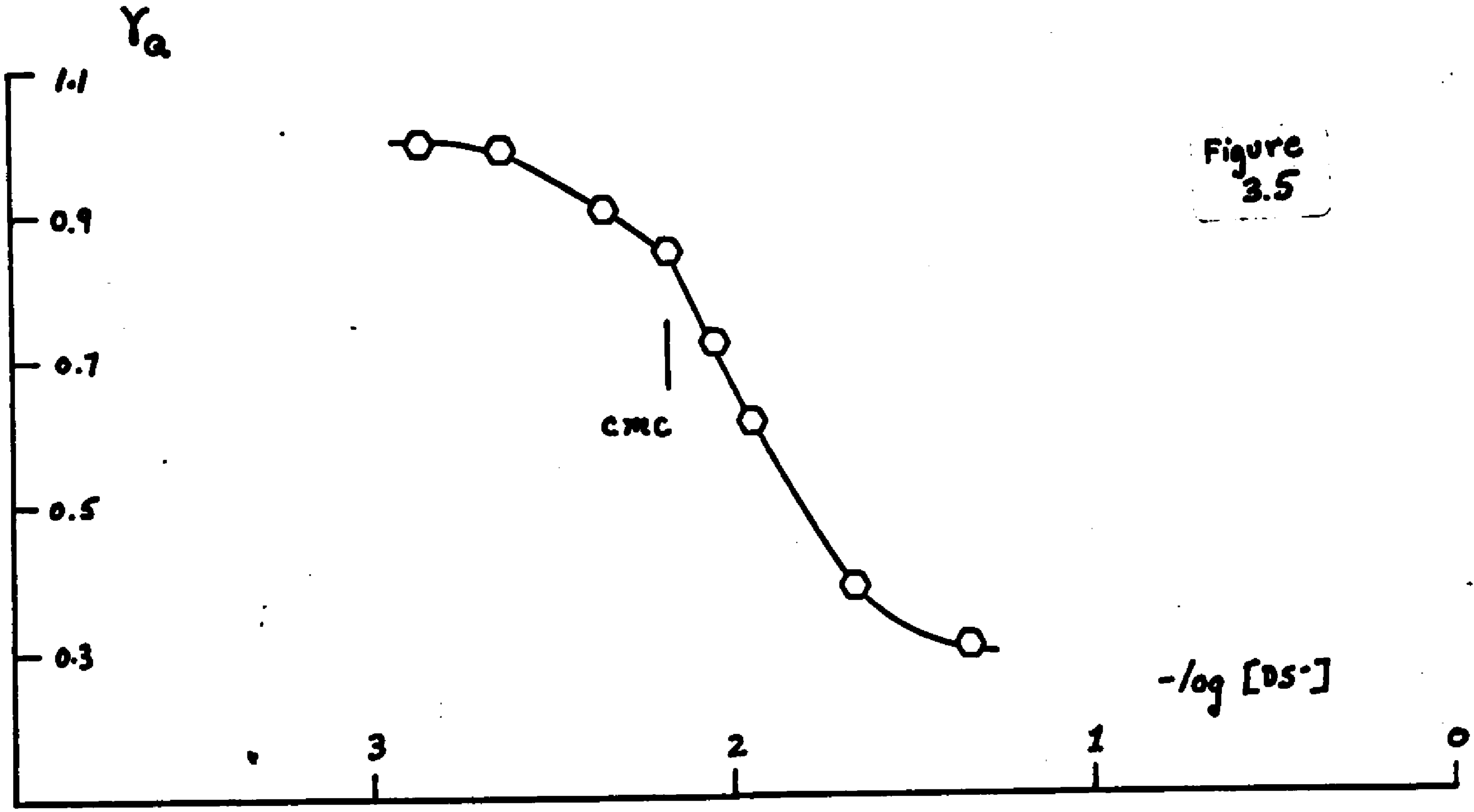
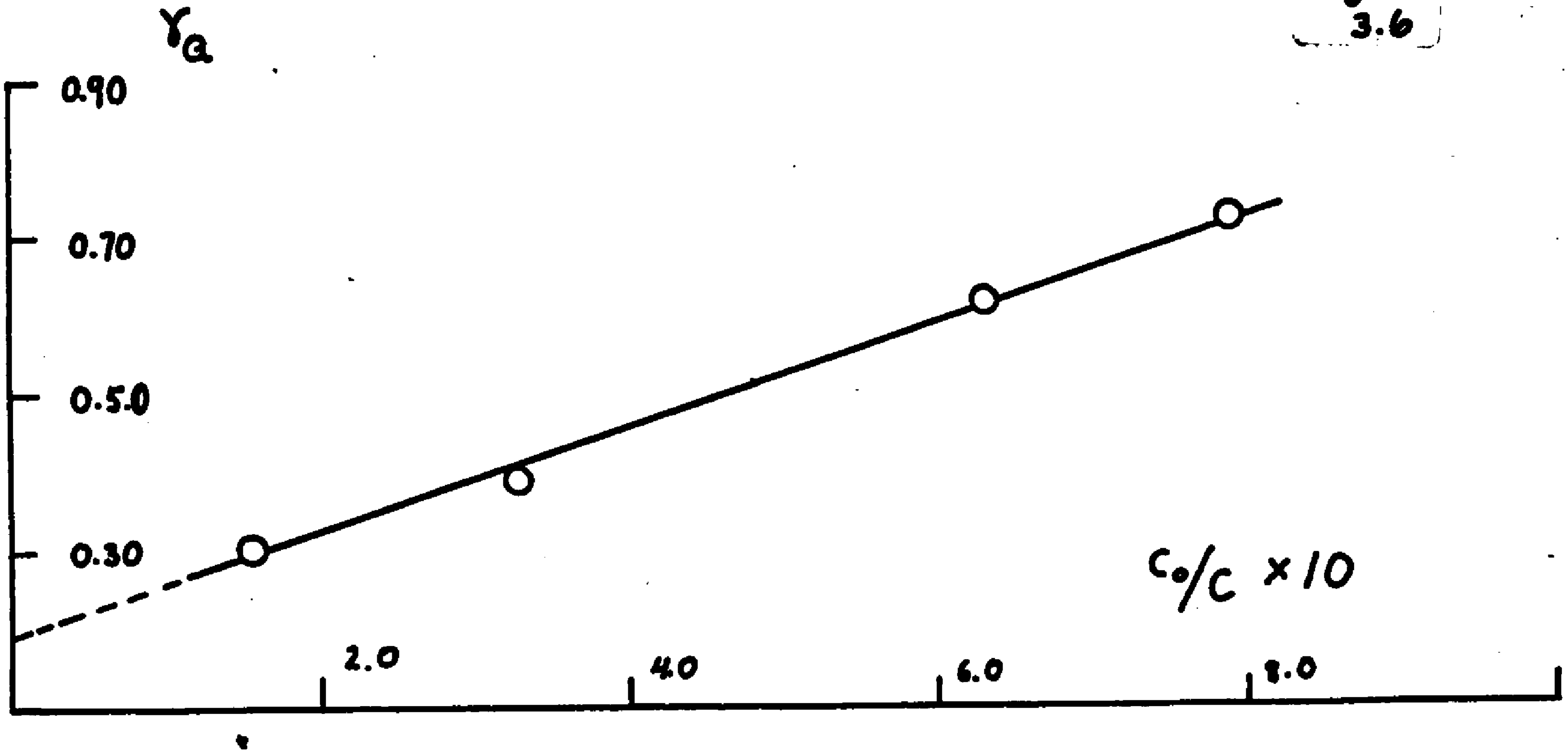


Figure 3.5

Figure 3.6



CHAPTER 4

The Influence of Micelles and Oil-Water Interfaces on Titrations of Aqueous Sodium and Potassium Soap Solutions

I. Results

Soap solutions (below and above the c.m.c. and in the presence and absence of non-aqueous solvents) containing excess base were titrated with HCl and glass electrodes were used to monitor cation activities (H^+, Na^+, K^+) during the course of the titrations. It was found that the graphs of pH versus ml. HCl added (in soap solutions below and above the c.m.c. in the absence of non-aqueous solvent) were predictable from equilibrium considerations. The pH at the surface of a micelle was inferred from the titration curves of micellar soap solutions. Simultaneous monitoring of two cations gave an insight to the physical picture of the micelle-solution interface and the oil-soap solution interface during the course of these titrations.

The titration curves of non-micellar solutions of K caprate, K laurate, and myristate are shown in Figure 4.1. Those for Na caprate, Na laurate, and Na myristate are shown in Figure 4.2. The heavy dark lines in Figures 4.1 and 4.2 represent the theoretically predicted curves of pH vs. ml. HCl added (calculated in the Theory section of this chapter) for these titrations. In all cases the concentration of the cation is 1.74×10^{-3}M and that of the long-chain anion is 1.00×10^{-3}M. Fifty milliliters of each soap solution were titrated at 29.4°C with 2.00×10^{-2}M HCl. Figures 4.1 and 4.2 are superposable within the experimental error.

In the titrations of the laurate and myristate soap solution a precipitate was first noted at approximately 1.25 ml. HCl added.

X-ray analysis[56] indicated that the precipitate was fatty acid. In the titrations of the caprates the solutions remained clear until approximately 3.20 ml. HCl added, at which point capric acid commenced precipitation.

In Figure 4.3 two titrations of micellar soap solutions are shown. Here, again, the heavy dark lines are the pH's predicted from Theory (section III this chapter). One is the titration of a potassium laurate solution (open circles) with the potassium ion concentration equal to 6.97×10^{-2}M and the laurate ion concentration equal to 5.00×10^{-2}M; the other is a titration of a potassium myristate solution (open squares) with ionic concentrations identical to those of the potassium laurate solution. In both titrations the initial solutions were clear. Upon adding HCl the pH decreased until the appearance of a precipitate in the solutions. Along this plateau of pH versus HCl added the precipitates were analyzed and found to be 1:1 acid-soap --- potassium acid laurate $\begin{pmatrix} CH_3(CH_2)_{10}COOK \\ CH_3(CH_2)_{10}COOH \end{pmatrix}_n$ or potassium acid myristate $\begin{pmatrix} CH_3(CH_2)_{12}COOK \\ CH_3(CH_2)_{12}COOH \end{pmatrix}_n$. Upon further addition of acid the pH again fell and a new plateau was reached. The precipitate was analyzed along this plateau and found to be a mixture of 1:1 acid-soap and free fatty acid --- with the percentage of fatty acid increasing at the expense of the acid-soap as more HCl was added. At the end of the titration the only precipitate present was the free acid.

Figure 4.4 shows a titration of a micellar K laurate solution in which the potassium ion concentration is equal to 6.01×10^{-2}M and the laurate ion concentration is equal to 5.00×10^{-2}M. The description of this titration is the same as that for the one in Figure 4.3 (open circles) except that a cationic glass electrode was used to monitor the potassium ion activity (plotted as the negative logarithm) at the same time that a glass electrode was used to record the pH.

Figures 4.5 and 4.6 show the titration curve of 50 ml. of the same soap solutions titrated in Figures 4.1 and 4.2, titrated in the presence of 50 ml. of chloroform (the pH is that of the aqueous layer). There are no visible significant differences between the potassium series (Figure 4.5) and the sodium series (Figure 4.6): the curves are practically superposable. It is noted by comparing the titration curves of the soap solutions with and without chloroform that the presence of the solvent markedly raises the pH.[10,36] The maximum difference in pH is found at approximately 1.60 ml. HCl added for the cases of the myristates (ΔpH $\simeq$ 1.8 units) and the laurate (ΔpH $\simeq$ 3 units) and in the region of 3.10 ml. HCl added for the caprate cases (ΔpH $\simeq$ 2.5 units).

Figures 4.7 and 4.8 show the titration curves of 50 ml. of the soap solutions in the presence of 50 ml. of n-hexane (again, the pH is that of the aqueous layer). The curves are also virtually superposable. The differences in pH between the titrations of the soap solutions with and without n-hexane are smaller than the differences when chloroform is present.

For the myristates and laurates at 1.60 ml. HCl added the

ΔpH (with and without n-hexane present) is 1.3 units and 1.8 units, respectively. For the caprates at 3.10 ml. the ΔpH is 1.7 units.

The number of milliliters of HCl used to reach the endpoint of thetitrations of the laurate and myristate soap solutions (Figures 4.1 through 4.6) and the caprate soap solutions (Figures 4.3 through 4.6) gives an average of 4.42 ml. with an average deviation from the mean of ±0.06 ml. The theoretical endpoint of these titrations is calculated (from the known volumes and concentrations of reactants) to be

$$\frac{(1.74 \times 10^{-3}\text{M})\ (50.0\ \text{ml.})}{(2.00 \times 10^{-2}\text{M})} = 4.35\ \text{ml. HCl added.}$$

The overall accuracy of the endpoints of these titrations is therefore 1.6%.

II. Experimental

The soap solutions were prepared by neutralizing a weighed amount of the melted fatty acid with a known excess of the appropriate standardized base and diluted with distilled water. The capric (C_{10}), lauric (C_{12}) and myristic (C_{14}) acids were all highest grade purity obtained from Eastman Organic Chemicals, Rochester, N. Y. Fifty milliliters of a soap solution in a beaker (with a water-jacket maintained at constant tempertaure: $\pm 0.1^{\circ}$C.) placed on a magnetic stirrer were titrated with HCl. A Thomas Combination pH electrode (NO. 4858 L-60, A. H. Thomas Company, Philadelphia, Pa.) and a cationic electrode (Beckman No. 39137, Beckman Instruments, Inc., Fullerton, Calif.) in conjunction with a Photovolt

Model 110 electronic pH meter (Photovolt Corp., New York, N. Y.; readability ±0.02 pH unit or ±1 millivolt) was used to determine the pH (or the sodium or potassium ion activity) after each addition of acid.

Some titrations were also carried out in the presence of a non-aqueous solvent. The solvents used were certified A.C.S. Spectranalyzed grade n-hexane and chloroform (Fisher Scientific Company, Fair Lawn, N. J.). After each addition of acid to 50 ml. of solvent plus 50 ml. of soap solution, the magnetic stirrer was turned up to a high enough speed to mix the two layers. It was found that stirring for three minutes and reading the pH in the aqueous layer two minutes after the stirring was stopped (and the two layers separated) gave a stable and reproducible pH.

III. Theory

Recently, Lucassen[12] has presented a quantitative equilibrium interpretation of hydrolysis in fatty acid soap solutions; theoretical pH was calculated as a function of the concentration of potassium carboxylate present. It was demonstrated that pH measurements give a simple method for evaluating the composition and solubility parameters of the precipitates formed in soap solutions - fatty acid, acid-soap, or neutral soap. We have adapted this treatment, here, for our solutions of potassium and sodium soaps and have, instead, calculated the theoretical pH as a function of the degree of acidification of the soap solution.

Non-micellar Soap Solutions

A. Precipitate of Fatty Acid:

The titrations of non-micellar soap solutions containing excess base are shown in Figures 4.1 and 4.2. It has been previously noted that a precipitate of fatty acid is formed in each case. It is the fatty acid solubility which determines the height of the pH plateaus in the figures.[12] The less soluble the fatty acid, the further to the right is the equilibrium $RCOO^- + H^+ \rightleftharpoons RCOOH$ and the lower is the hydrogen ion concentration tolerated in the solution (resulting in a higher pH plateau).

We represent the fatty acid dissociation equilibrium by

$$\frac{C_H C_Z}{C_{HZ}} = K_A \qquad (1)$$

where C_H, C_Z and C_{HZ} represent the concentration in solution of hydrogen ions, fatty acid anions, and fatty acid molecules, respectively, and K_A is the dissociation constant of the fatty acid.

The condition for electroneutrality of the solution is:

$$C_M + C_H = K_w/C_H + C_Z + XC_t + G \qquad (2)$$

where C_M = concentration of alkali metal cations in solution

$K_w = C_H C_{OH}$ = ionization constant of water

C_t = total amount of soap present in moles per unit volume

X = molar ratio between added hydrochloric acid and total amount of soap (therefore has values from 0 to 1)

XC_t, therefore, represents the concentration of chloride ions added to the solution as a consequence of acidification of the soap present with HCl.

G = concentration of chloride ions added to the solution in neutralizing the excess base present with HCl.

In all our soap solutions an excess of base was originally present and we can write

$$C_t = KC_M \qquad (3)$$

where K is a constant smaller than 1.

The concentration of fatty acid molecules in the solution equals the solubility of the fatty acid (S_{HZ}) and therefore

$$C_{HZ} = S_{HZ} \qquad (4)$$

When equation (1), (3), and (4) are substituted in the equation for the electroneutrality for the solution (2) the result is

$$C_H = \frac{K_w + K_A S_{HZ}}{C_t(1/K - X) + C_H - G} \qquad (5)$$

(see Appendix p. 67)

In Figures 4.1 and 4.2

$$C_t = 1.00 \times 10^{-3}M$$
$$1/K = 1.74$$
$$G = 7.4 \times 10^{-4}M$$

For the cases of the myristates and the laurates since $C_t(1/K - X) \geq 7.4 \times 10^{-4}$ and $C_H < 10^{-6}$ (pH is always greater than 6 for these cases - see Figures 4.1 and 4.2; and X can never be greater than 1) we can write $C_H \ll C_t(1/K - X)$ and taking negative logarithms in equation (5) we obtain

$$pH = -\log(K_w + K_A S_{HZ}) + \log\left[10^{-3}(1.74 - X) - 7.4 \times 10^{-4}\right] \qquad (6)$$

When the values for K_w, K_A, and S_{HZ} are substituted in equation (6)

$$K_W = 1.47 \times 10^{-14} \text{ (given at } 30^\circ\text{C.)}^{57}$$

$$K_A = 1.25 \times 10^{-5}$$

$$S_{HZ} = 1.05 \times 10^{-5} \text{ for } C_{12} \text{ acid}$$

$$= 5.25 \times 10^{-7} \text{ for } C_{14} \text{ acid}$$

(where it is assumed that the values of the dissociation constant of the fatty acid, K_A, and the solubility of the fatty acid, S_{HZ}, reported by Lucassen[12] for 20°C. is valid in our systems containing excess base and maintained at 29.4°C.) K_W (1.47×10^{-14}) is seen to be $\ll K_A S_{HZ}$ (1.31×10^{-10} for C_{12}, 5.51×10^{-12} for C_{14}). Therefore, from equation (6) we obtain

$$\text{pH} = 8.18 + \log (1 - X) \text{ for myristate} \tag{7}$$

$$\text{pH} = 6.88 + \log (1 - X) \text{ for laurate} \tag{8}$$

Equations (7) and (8) provided theoretical values of pH as a function of the degree of acidification (X from 0 to 1) drawn in Figures 4.1 and 4.2 as a heavy solid line.

For the case of caprate[12] $S_{HZ} = 2.09 \times 10^{-4}$ and again

$$K_W \ll K_A S_{HZ} \quad (1.47 \times 10^{-14} \ll 2.61 \times 10^{-9});$$

equation (5) becomes

$$C_H = \frac{(1.25 \times 10^{-5})\,(2.09 \times 10^{-4})}{10^{-3}\,(1.00 - X) + C_H} \tag{9}$$

Equation (9) (solved by successive approximations) provided the theoretical values of pH as a function of acidification for the caprate cases drawn in Figures 4.1 and 4.2 as a heavy solid line.

B. No Precipitate is Present:

In the titrations of the caprates (Figures 4.1 and 4.2) it was previously noted that a precipitate of capric acid did not form until approximately 3.20 ml. of HCl were added. Consequently, to predict the pH as a function of the degree of acidification up to the point where a precipitate starts to form a different equation was used which is valid for the case when no precipitate is present.

In this case

$$C_t = C_Z + C_{HZ} \tag{10}$$

and equations (1), (2), (3), and (10) combine to give (see Appendix p. 68)

$$C_t = \frac{(K_w - C_H^2 + GC_H)\ (K_A + C_H)}{C_H \left[(1/K - X)C_H + K_A(1/K - X - 1)\right]} \tag{11}$$

But $K_w \ll C_H^2$ (e.g. at pH 6, $C_H^2 = 10^{-12}$ and $K_w = 1.47 \times 10^{-14} \ll 10^{-12}$) and $K_w \ll GC_H$ (e.g. at pH 6, $GC_H = (7.4 \times 10^{-4})\ (10^{-6}) = 7.4 \times 10^{-10}$ and $K_w = 1.47 \times 10^{-14} \ll 7.4 \times 10^{-10}$) and substituting the values given above for the caprate cases in Figures 4.1 and 4.2:

$$10^{-3} \approx \frac{(-C_H^2 + 7.4 \times 10^{-4} C_H)\ (1.25 \times 10^{-5})}{C_H \left[(1.74 - X)\ C_H + 1.25 \times 10^{-5}\ (0.74 - X)\right]} \tag{12}$$

Equation (12) (solved by successive approximations) provided values of pH as a function of the degree of acidification, X, when no precipitate was present (dashed line in Figures 4.1 and 4.2).

In our treatment of non-micellar soap solutions, activity coefficients have been omitted since the solutions were dilute (the order of magnitude of the concentrations was 10^{-3}M).

Micellar Soap Solutions

The titration curve of a micellar soap solution exhibits two plateaus when pH is plotted as a function of added acid.[10,36] The plateau at the higher pH is due to the coexistence of micelles and acid soap and the plateau at the lower pH results from the conversion of acid-soap to free fatty acid. In the systems studied here, only 1:1 acid-soap was formed, and it is therefore apparent that after half of the total number of long-chain anions in micellar form have been neutralized (along the plateau at higher pH), the conversion of micelles to acid-soap is complete, and any further addition of acid results in a steadily decreasing pH as the monomeric long-chain anions (which represent the critical micelle concentration) are converted to acid-soap. At half neutralization of the soap, all the carboxylate anions are in the form of acid-soap and upon adding more HCl, a new equilibrium is established between acid-soap and free fatty acid.

A. K Laurate - Coexistence of Acid-Soap and Fatty Acid:

Along the plateau where acid-soap and fatty acid coexist, (plateau at lower pH) the relevant equilibria are represented by equation (1) and

$$C_M C_H C_Z^2 = K_{MHZ_2} \qquad (13)$$

where K_{MHZ_2} is the solubility product of the 1:1 acid-soap.

When equations (1), (4), and (13) are substituted in the equation for the condition of electroneutrality (2) so as to eliminate C_M and C_Z, the following equation is obtained (see Appendix p. 70):

$$K_{MHZ_2} \; C_H^2 = (K_A S_{HZ})^2 \; \left[K_W + K_A S_{HZ} + XC_H C_t + GC_H - C_H^2 \right]. (14)$$

However K_w (1.47×10^{-14}), $K_A S_{HZ}$ $[(1.25 \times 10^{-5})\ (1.05 \times 10^{-5}) = 1.31 \times 10^{-10}]$, and $C_H^2 (\simeq 10^{-14})$ are all considerably smaller than XC_HC_t $[X(10^{-7})\ (5 \times 10^{-2})]$ so that taking negative logarithms and rearranging yields:

$$pH = \log K_{MHZ_2} - 2 \log K_A S_{HZ} - \log (XC_t + G). \qquad (15)$$

For potassium acid laurate[12] $K_{MHZ_2} = K_{KHL_2} = 6.31 \times 10^{-15}$. pH is plotted as a function of X (from 0.5 to 1) in Figure 4.3 (heavy solid line) for the case of a K laurate solution where $[K^+] = 6.97 \times 10^{-2}M$ and $[L^-] = 5.00 \times 10^{-2}M$.

B. K Laurate - Coexistence of Micelles and Acid-Soap:

In laurate solutions for the case where soap micelles coexist with acid soap (plateau at higher pH), equation (13) and[34]

$$0.57 \log C_M + \log C_Z = -2.617 \qquad (16)$$

are combined with the equation of electroneutrality (2) to give

$$10^{-37.4}\left(\frac{C_H}{K_{MHZ_2}}\right)^{7.15} + C_H = K_w/C_H + 10^{18.7}\left(\frac{K_{MHZ_2}}{C_H}\right)^{4.075} + XC_t + G \qquad (17)$$

(see Appendix p. 72)

When $C_H \approx 10^{-9}$ the terms C_H and K_w/C_H can be neglected, and when the value of K_{MHZ_2} is substituted in (17) the following result is obtained:

$$10^{-37.4}\left(\frac{C_H}{(6.31 \times 10^{-15})}\right)^{7.15} = 10^{18.7}\left(\frac{6.31 \times 10^{-15}}{C_H}\right)^{4.075} + XC_t + G. \qquad (18)$$

Equation (18) provided the pH values (by successive approximations) plotted (as a heavy solid line) in Figure 4.3 for values of the degree of acidification, X, from 0 to 0.5.

C. K Myristate

For the case of the micellar solutions of K myristate containing excess base, no equation of the form of equation (16) is available. Consequently, no prediction could be made as to the pH along the plateau where micelles are converted to acid soap. The experimental titration curve obtained, however, is shown in Figure 4.3 for a K myristate solution where $[K^+] = 6.97 \times 10^{-2}$M and $[M^-] = 5.00 \times 10^{-2}$M.

For the plateau corresponding to the conversion of potassium acid myristate to myristic acid, equation (15) with[12] $K_{MHZ_2} = K_{KHM_2} = 1.58 \times 10^{-17}$ gives good agreement with the experimental results (Figure 4.3). The theoretically predicted pH's (from equation (15) heavy solid line in Figure 4.3) are the same for both cases shown in Figure 4.3.

It should be mentioned that:

a) Figure 4.3 illustrates that the plateau at pH 7 is longer than the plateau at pH 9 or 10; this is because at the higher pH micelles are converted to acid-soap and then as the monomers are converted to acid-soap, the pH begins to decrease. It is therefore not expected that micelles are converted to acid-soap in the range X (degree of acidification of soap) from 0 to 0.5, but rather in some smaller range (viz. all the micelles are converted to acid-soap before the point X = 0.5 is reached).

The difference between the end of the plateau at higher pH and the beginning of the one at the lower pH represents the critical micelle concentration. This is much smaller in the case of K Myristate than in the case of K Laurate.

b) activity coefficients for hydrogen ion were not available for solutions of the compositions and concentrations studied here, and therefore, the negative logarithm of the hydrogen ion concentration was equated to pH. The agreement with the experimental results is, nonetheless, considered good.

Titrations Using a Cationic Glass Electrode

A. Nonmicellar Soap Solutions

For the titrations of sodium and potassium laurates and myristates shown in Figures 4.1 and 4.2 the use of cationic glass electrode reveals no change in activity of the cation throughout the course of the titration (e.m.f. of cationic electrode vs. calomel electrode did not change by more than ±1 millivolt). This was not done for the caprate cases shown in Figures 4.1 and 4.2 because low pH prohibits the use of the cationic glass electrode (interference from hydrogen ion). A cationic glass electrode was, however, used in the titration of a potassium caprate solution ($[K^+] = 1.98 \times 10^{-2}$M, $[\text{caprate}^-] = 1.85 \times 10^{-2}$M) and a sodium caprate solution ($[Na^+] = 8.68 \times 10^{-2}$M, $[\text{caprate}^-] = 7.53 \times 10^{-2}$M) where x-ray analysis revealed capric acid as the only precipitate, and again the activity of the cation was found to remain constant throughout the titrations (the pH plateau of these titrations did not fall below 6).

In all the above mentioned titrations the use of a cationic glass electrode confirms the fact that free fatty acid is the only precipitate, for if acid-soap or neutral soap precipitated one would detect a decrease in the bulk cation activity.

B. Micellar Laurate Solution

Figure 4.4 shows a titration of a micellar K laurate solution in which the potassium and hydrogen ion activities were monitored simultaneously. The cationic electrode was calibrated with KCl solutions at pH 7 and was used in soap solutions between pH 5 and 9 where it was assumed the KCl calibration was valid.

We note that when all the long-chain anions have been converted to acid-soap (1.62 ml. HCl added), it is expected that the maximum amount of potassium ions would have been removed from the solution and indeed the potassium ion activity is seen to be at a minimum here. The apparent concentration of free potassium ions at this point can be calculated from the measured activity of potassium ions (3.08×10^{-2}M) and the activity coefficient of a KCl solution of this apparent concentration:

$$a \simeq M\gamma$$

$$3.08 \times 10^{-2} M \simeq M\,(0.836)^{30}$$

$$3.68 \times 10^{-2} M \simeq M$$

The apparent concentration of potassium ions bound in the form of acid-soap is equal to the total analytical concentration of potassium ions at this point,

$$\frac{50.00 \text{ ml.}}{51.67 \text{ ml.}} \times 6.01 \times 10^{-2} M = 5.82 \times 10^{-2} M$$

minus the apparent concentration of free potassium ions and is therefore equal to $5.82 \times 10^{-2}M - 3.68 \times 10^{-2}M = 2.14 \times 10^{-2}M$. Since this amount of potassium ions is bound in the form of 1:1 potassium acid laurate, the amount of laurate ion in this precipitate is $2 \times 2.14 \times 10^{-2}M = 2.28 \times 10^{-2}M$. The predicted concentration of laurate ion in the form of acid-soap at this point of half neutralization is equal to one half the total analytical concentration of laurate ions at this point:

$$\frac{1}{2} \times \frac{50.00 \text{ ml.}}{51.67 \text{ ml.}} \times 5.00 \times 10^{-2}M = 2.42 \times 10^{-2}M$$

As potassium acid laurate is converted to lauric acid (plateau at $pH \leq 7$), the potassium ions are returned to the bulk solution and the activity increases until the theoretical maximum is reached when all the laurate is in the form of lauric acid.

The open hexagon in Figure 4.4 indicates the measured activity of potassium ions in the K laurate solution with no HCl added ($pH = 11.70$; the cationic electrode was calibrated with KOH for this measurement) and the dotted line indicates how the potassium ion activity must increase as HCl is added to the solution and the hydrogen ions displace the potassium ions from the micelle-solution interface.

No experimental points are given for $-\log a_K$ versus ml. of HCl added for pH's between 11.7 and 9.1. In this region the cationic electrode cannot be calibrated with KOH (calibration is valid for potassium ion activity measurements made at high pH) or KCl (calibration is valid for potassium ion activity measurements made in the pH range near 7) alone. It should be mentioned that, in general, activity coefficients of potassium ion are larger for KOH solutions of a given concentration than for KCl solutions of the same concentration.[30] Therefore, in a solution of constant potassium ion molality one would expect the potassium ion activity ($a = m\gamma$) to decrease slightly as the pH was changed from 11.7 to 9.1. During the course of the titration shown in Figure 4.4, the e.m.f. of the cationic electrode versus the reference electrode (Ag/AgCl) increased slightly in this pH range. This indicates that the bulk activity of potassium ion is increasing in this region. Since $\underline{a} = m\gamma$ and γ is known to decrease in this region; since $\underline{a}$ increases, m (molality of potassium ion) must be increasing.

This fact (slight increase in bulk potassium ion concentration in pH region 11.7 to 9.1) and the fact that the potassium ion activity does not decrease steadily as soon as acid-soap precipitate begins to form (pH = 9.1) indicates that a compensating effect is operating. Potassium ions are released into the bulk of the solution from the charged interfaces as the micelles are destroyed (converted to acid-soap) and potassium ions are removed from the solution by the formation of the acid-soap precipitate. Consequently, $-\log a_K$ of the solution does not change drastically until most of the micelles are destroyed (see Figure 4.4).

C. Nonmicellar Soap Solutions in Presence of Solvent

The course of a titration of a non-micellar laurate solution (as in Figures 4.1 and 4.2) was interrupted at approximately the middle of the pH plateau (concentration of $H^+ \simeq 2 \times 10^{-7}$M) and 50 ml. of a non-aqueous solvent (n-hexane or chloroform) was added and the titration was continued as above. In one case (laurate with chloroform added) upon addition of the solvent followed by vigorous stirring for three minutes, though the pH (measured in the aqueous layer two minutes after the stirring was stopped and the layers had separated) changed by almost three units, the e.m.f. of the cationic electrode vs. calomel changed by less than one millivolt. This shows that although the sodium or potassium ion concentration was approximately 10^4 times as great as the hydrogen ion concentration before addition of the solvent $\left(\frac{1.74 \times 10^{-3} M\ K^+}{2 \times 10^{-7} M\ H^+} \simeq 10^4\right)$, upon addition of the chloroform the hydrogen ion activity changed a thousandfold while the sodium or potassium ion activity did not change significantly. It appears, then, that in the pH range 7 to 10 neither sodium nor potassium ion can compete effectively with hydrogen ion at the oil-soap solution interface.

Furthermore, the cation activity (K^+ or Na^+) was monitored in the titrations shown in Figures 4.5, 4.6, 4.7, and 4.8. In no case did the e.m.f. of the cationic electrode versus the reference electrode change by more than one or two millivolts during the course of the titration. It was indicated, therefore, that the counterion environment at the negatively charged oil-soap solution interface was primarily hydrogen ions, because although the presence of solvent greatly altered the bulk pH (compare Figures 4.1, 4.5, and 4.7 and 4.2, 4.6, and 4.8), the bulk (and therefore the surface) cation activity was not affected.

IV. Discussion

Although a valid quantitative description of hydrolysis in potassium soap solutions has been given by Lucassen[12] (wherein the pH of a partially acidified potassium soap solution was determined from the soap concentration), little qualitative description was offered. Rosano et al.,[10,36] on the other hand, gave a qualitative description of titrations of soap solutions but did not attempt to give a theoretical quantitative description of their systems. It has been shown, in the present work, that Lucassen's treatment (i.e. equilibrium consideration) can be adapted to predict pH as a function of acidification for micellar and non-micellar soap solutions containing excess base, and that, in the case of non-micellar soap solutions, this treatment is valid for both potassium and sodium soaps.

Furthermore, the only precipitate which appears in a titration of a non-micellar soap solution (potassium or sodium, caprate, laurate, or myristate) is the free fatty acid. This is contrary to the prior contention of Rosano et al.[10,36] that when a non-micellar K laurate solution was titrated with HCl, the precipitate was K acid laurate up to half-neutralization and a mixture of this acid-soap and free lauric acid past this point. It was claimed that the buffering action of this system was due to the presence of acid-soap. It has now been confirmed that it is the fatty acid solubility alone which determines the buffering action in the systems studied here.

In our titrations of micellar solutions of potassium laurate and potassium myristate, we have found that both the quantitative treatment of Lucassen and the qualitative description of Rosano et al. are valid (Figures 4.3 and 4.4). For example, as acid is added to a micellar potassium laurate solution (Figure 4.4), hydrogen ions displace potassium ions from around the negatively charged micelles and the bulk potassium ion activity increases. When potassium acid laurate begins to precipitate (bulk pH $\simeq$ 10.3), it indicates that the surface hydrogen ion concentration around the micelles has reached a certain critical value at which lauric acid can form. This lauric acid formed at the micelle surface precipitates as a 1:1 acid-soap. Since the micelles are converted stoichiometrically to acid-soap, this is, in fact, a surface titration. As previously noted, the fact that the plateau at this pH is shorter than the one at the lower pH indicates that the concentration of hydrogen ions near the micelle surface must be greater than that in the bulk of solution -- the monomers in the solution (hydrogen ion environment is determined by the bulk pH) are precipitated as acid-soap only after all the micelles have been neutralized. Since free fatty acid can exist in the bulk of solution only when the pH has fallen to approximately 7 (plateau at lower pH), this must give an indication of the pH at a micelle surface when micelles are being converted to acid-soap at the plateau at higher pH. Formation of acid-soap requires that hydrogen ions discharge on carboxylate head groups at the micelle surface -- the environment at the micelle surface must be pH 7, even though the bulk pH is two or three units higher (Figures 4.3 and 4.4). It is therefore just as natural to attribute the buffering action of a micellar soap solution to the surface effect[10,36] as it is to interpret it on the basis of solubilities of the precipitates present.[12]

When half the number of long-chain anions have been neutralized, the bulk potassium ion activity reaches a minimum. Further addition of acid at this point results in the conversion of this acid-soap to free fatty acid. In Figure 4.4 the bulk potassium ion activity is seen to increase as the acid soap is converted to free acid. The bulk potassium ion activity reaches its predicted theoretical maximum when all of the long-chain anion is in the form of fatty acid.

$$\left(\frac{50.00 \text{ ml.}}{52.92 \text{ ml.}}\right) \quad (6.011 \times 10^{-2}M) = 5.69 \times 10^{-2}M$$

but $\gamma_{\pm} = 0.808$ for $5.69 \times 10^{-2}M$ KCl[30]

$$-\log a_K = -\log (5.69 \times 10^{-2}M)(0.808) = 1.34$$

The pH at this plateau is determined by the solubility of the coexisting precipitates (fatty acid and acid-soap). Equation (15) predicts the same pH for a micellar potassium laurate or myristate solution of the same concentration. This is because the longer the chain length of the anion the less soluble is the acid and the corresponding acid soap. The first two logarithmic terms on the right in equation (15), therefore, change with the chain length of the anion in such a way so as to just compensate each other and the resulting pH is the same whether the system is laurate or myristate.

The presence of a solvent in the titration of a non-micellar soap solution markedly raises the pH (compare Figures 4.1, 4.5 and 4.7; 4.2, 4.6, and 4.8). Upon addition of HCl, any long-chain acid formed dissolves into the solvent present. The solvent is, therefore, always in contact with a non-micellar solution and although there is no precipitate present, the solution is buffered. In a titration of a micellar soap solution any acid-soap formed in the aqueous phase is destroyed if there is a solvent present.[10,36] Here, again, the solution is buffered at a higher pH than in the absence of solvent.

Long-chain anions at the oil-soap solution interface act as a reservoir for hydrogen ions added to the aqueous phase. This charged interface acts as a buffer because beyond a certain surface hydrogen ion concentration the hydrogen ions discharge on the carboxylate head groups and the fatty acid formed is removed by dissolving in the solvent. Only after all the long-chain anions have been neutralized can the pH abruptly decrease. For the systems studied the behavior was the same (for a given long-chain anion and a given solvent) whether a potassium or sodium soap was titrated. If the sodium or potassium ions comprised a sizeable portion of the couterion environment near the charged interface a difference in behavior might be expected. The fact that this was not the case and further, that measurements of bulk cation activity indicated that little if any potassium or sodium ions were removed from the bulk to the surface region, indicates that in the systems studied neither potassium nor sodium ions could effectively compete with hydrogen ions for the negatively charged oil-aqueous soap solution interface.

It is also noted that the structure of the interface (solvent used and chain length of the anion) markedly affects the negative charge density and therefore the buffering action of the system. For example, for a given non-micellar soap solution titration, the pH is seen to be higher when chloroform is the solvent than when n-hexane is used. A possible explanation is that n-hexane molecules can fit between the hydrocarbon chains of the carboxylate anions at the oil-soap solution interface, thereby increasing the distance between the charged polar groups, decreasing the negative charge density at the interface, with a consequent decrease in surface hydrogen ion concentration and a lower bulk pH. It is known from surface potential studies of monolayers of long-chain fatty acids at high pH, the more condensed the monolayer, the more hydrogen ions are attracted to the monolayer-substrate interface.[50,52] These monolayer studies have also demonstrated that the longer the chain length of the fatty acid, the more effective is the monolayer in attracting cations.[52] The titrations of non-micellar soap solutions in the presence of a solvent demonstrate this effect, too. The longer the chain length of the anion, the higher is the buffered pH (Figures 4.5, 4.6, 4.7, and 4.8).

The technique of simultaneous monitoring of cation activities during a titration thus affords one of a method of obtaining a qualitative (as well as quantitative) physical picture of what occurs at the interfaces in solution and enables one to illustrate the competition of ions at a charged interface.

V. Conclusions

It is concluded that charged interfaces markedly affect the ionic distribution in aqueous solutions of surfactants. The monitoring of univalent cation activity (H^+, Na^+, K^+) in the bulk, during the course of titrations of soap solutions (below and above the critical micelle concentration, in the presence and absence of non-aqueous solvents), provides a method of inferring cation activities in the surface regions of charged interfaces. The simultaneous use of a pH glass electrode and a cation sensitive glass electrode during a surface titration (at a micelle-solution interface or an oil-solution interface) is a unique method for studying the competition of ions at a charged interface (see Figure 4.4).

Cationic glass electrodes can be used to determine the amount of counterion dissociation (α) of anionic soap micelles (in solutions where there is negligible soap hydrolysis; pH greater than 12.3). These determinations of α in micellar soap solutions at high pH can be compared to isotherms of long-chain fatty acid monolayers spread on substrates of high pH. The soap micelle-solution interface and the fatty acid monolayer-substrate interface provide complementary models for the understanding of the effect of charged interfaces on counterion distribution. For potassium carboxylate soap micelles, the amount of counterion dissociation decreases with increasing hydrocarbon chain length of the long-chain anion (see Table 3.1). Alpha (α) decreases in the series K caprate

(C_{10}), K laurate (C_{12}), K myristate (C_{14}). Also, K caprate micelles are more dissociated than Na caprate micelles. These results are consistent with those found, by other workers, in monolayer studies. It is concluded (Chapter 3) that the greater the hydrocarbon chain length of the anion the greater is the charge density at the micelle surface and the smaller is the degree of counterion dissociation. Also, the specific interaction between the cation (counterion) and the anion (in the micelle) affects the degree of dissociation of the micelle (α) and it is, therefore, incorrect to interpret differences in α (for a given long-chain anion) simply on the basis of differences in cation hydration.

For titrations of non-micellar and micellar soap solutions (in the absence of a non-aqueous solvent), graphs of pH versus milliliters of HCl added can be theoretically predicted from equations given in Chapter 4. The equations are derived from equilibrium considerations of hydrolysis in soap solutions. Although the method of analysis has been previously described, its application to titrations of sodium and potassium carboxylate soap solutions is original.

In titrations of non-micellar soap solutions (potassium and sodium caprate, laurate, and myristate) with HCl, the more insoluble is the free fatty acid formed, the higher is the pH at which the solution is buffered (see Figures 4.1 and 4.2). Since the only precipitate present during these titrations is the fatty acid, the buffering action of the solution is not due to a surface effect.

The titrations of micellar solutions of potassium laurate and potassium myristate with HCl look like the titration of a diacid (see Figure 4.3). The two plateaus in pH versus milliliters of HCl added can be quantitatively interpreted in terms of the equations developed in Chapter 4 (hydrolysis in soap solutions) and in terms of a surface effect. The negatively charged carboxylate micelles electrostatically attract cations into the region of the micelle surface. Bulk pH measurements allow one to infer the hydrogen ion activity in the surface region. The hydrogen ion activity at the K laurate micelle surface appears to be approximately one hundred times as great as that in the bulk. The hydrogen ion activity at the K myristate micelle surface is approximately one thousand times that in the bulk. Again it is concluded (Chapter 4), that the longer the hydrocarbon chain length of the long-chain carboxylate anion, the greater is the negative surface charge density of the micelle (and, therefore, the lower the pH in the surface region).

Titrations of non-micellar soap solutions in the presence of non-aqueous solvents (chloroform and n-hexane) demonstrate that oriented surfactant ions at the oil-aqueous solution interface can raise the pH of the bulk by two or three units because of the high negative charge density at the interface. The neutralization of these interfaces (by interfacial titration) by HCl is very much like the neutralization of the micelle-solution interface except that the fatty acid formed is dissolved by the non-aqueous solvent. The structure of the interface (type of solvent used) is found to be an important factor in its ability to alter the bulk pH.

The titration, with HCl, of a micellar potassium laurate solution with simultaneous monitoring of the H^+ and K^+ ion activities provides a physical description of the competition of the cations for the negatively charged micelle surfaces. A quantitative analysis is also possible (see Figure 4.4).

It has been demonstrated, by using surfactant solutions and cation sensitive glass electrodes, that charged surfaces can greatly alter the ionic activity in solution by attracting counterions and sustaining activities in interfacial regions as much as three powers of ten greater than that in the bulk. The marked effect of charged interfaces on the ionic distribution in solution is established.

Figure 4.1

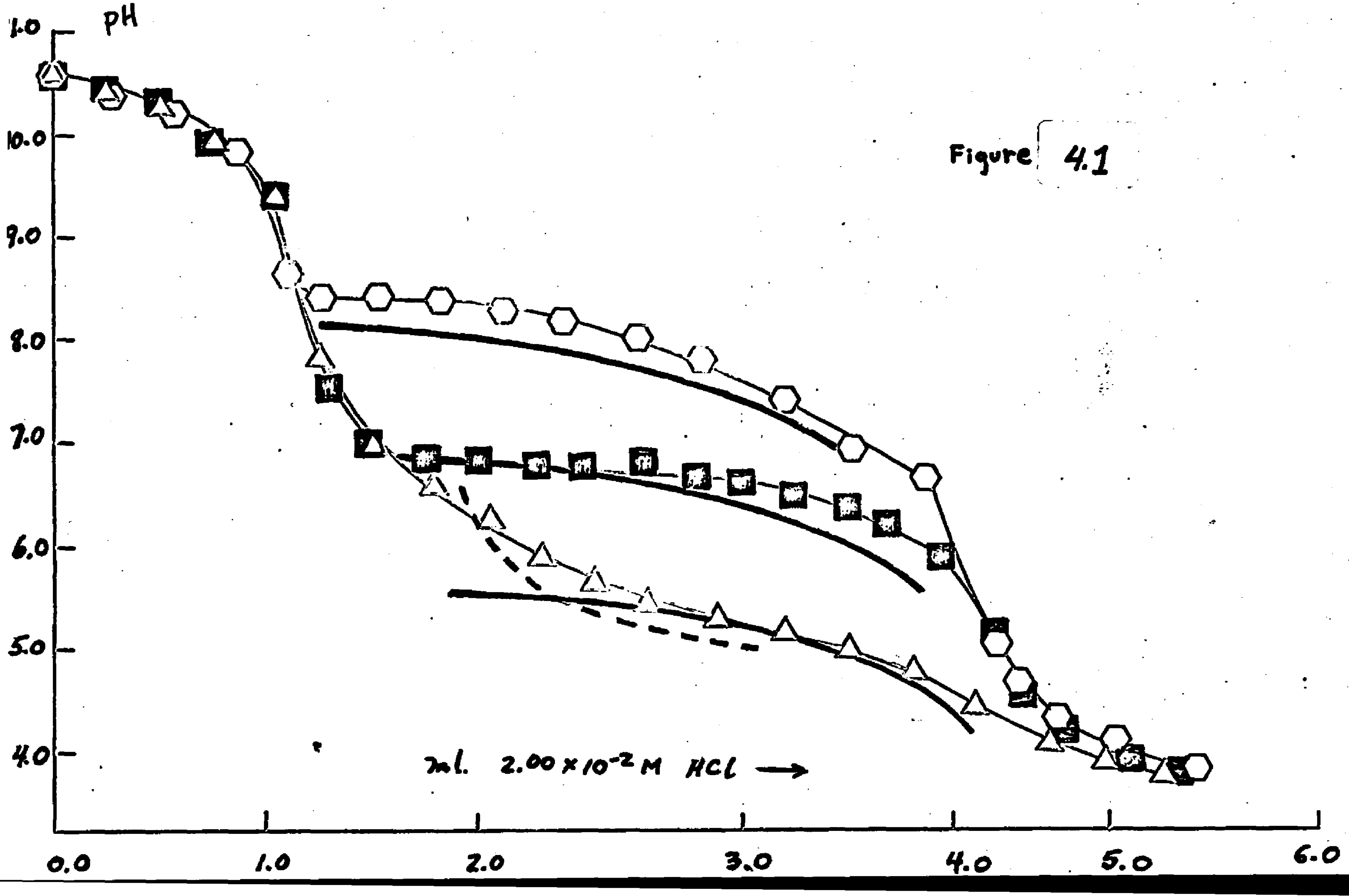
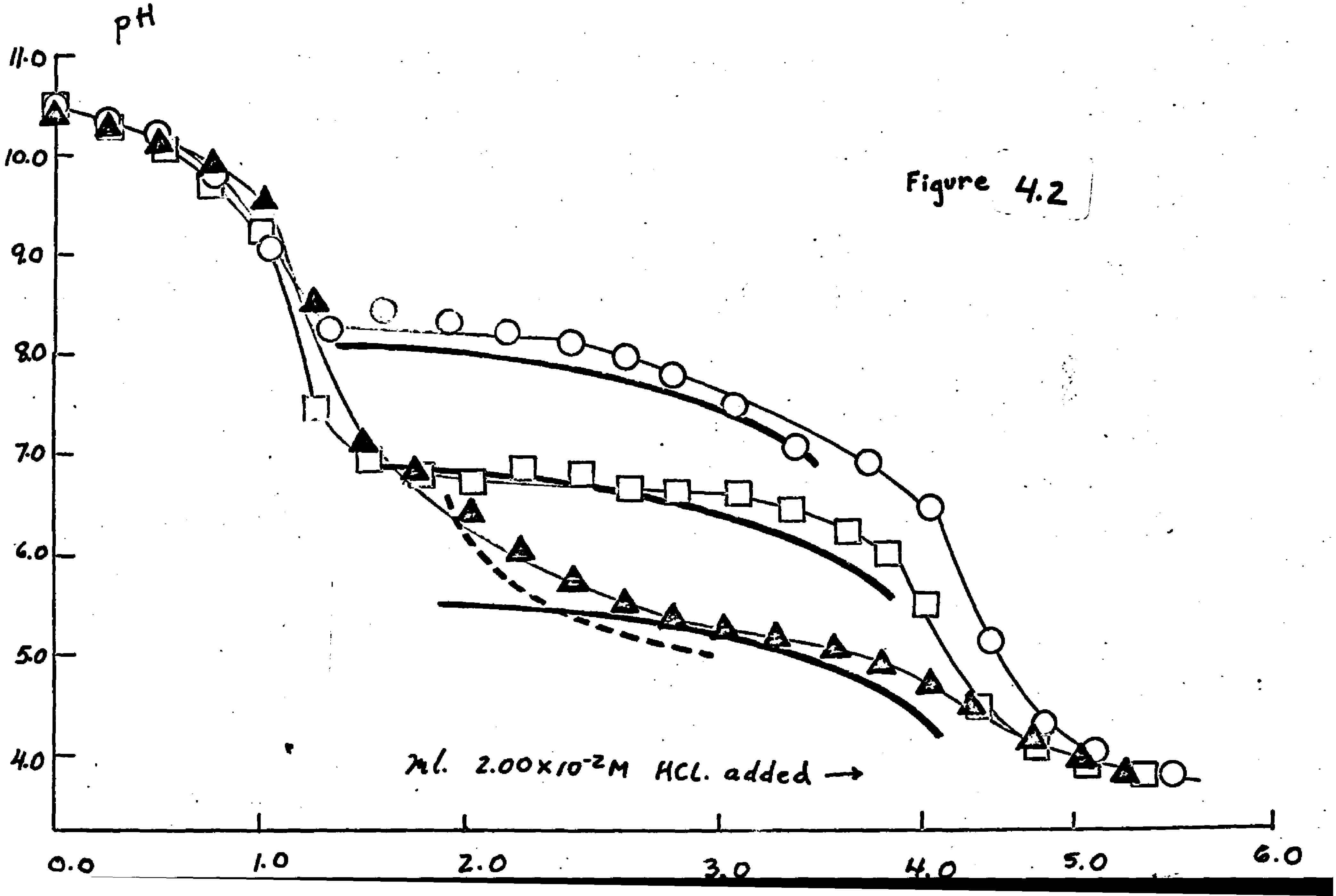


Figure 4.2


pH
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
ml. 2.00×10⁻²M HCL. added →

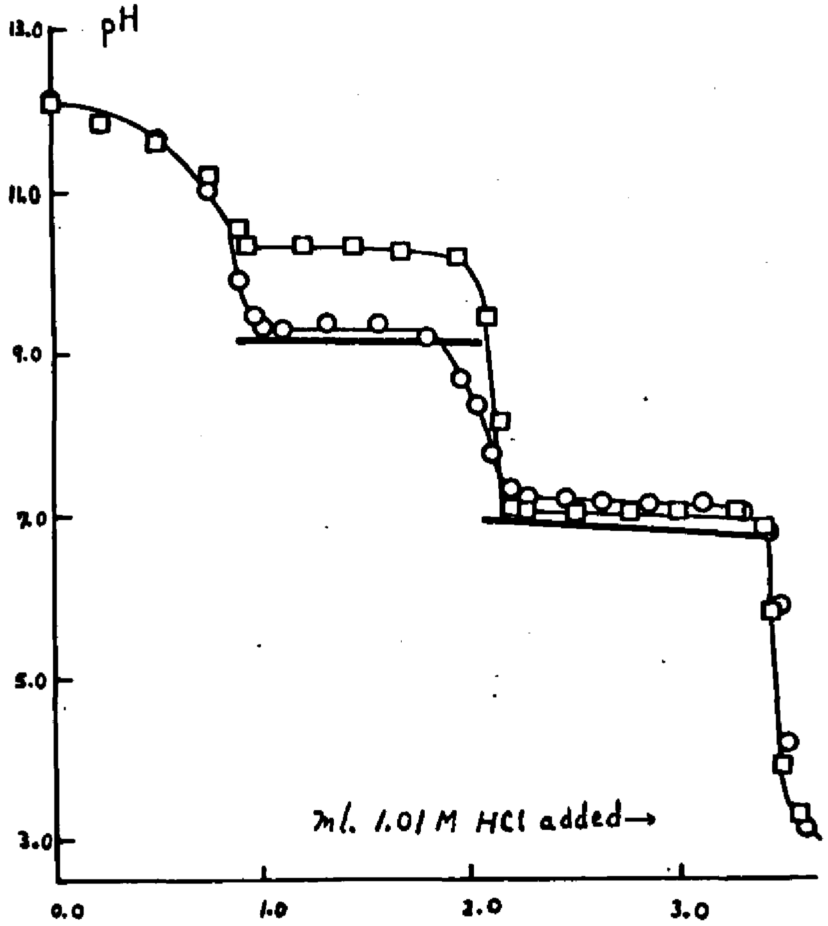


Figure 4.3

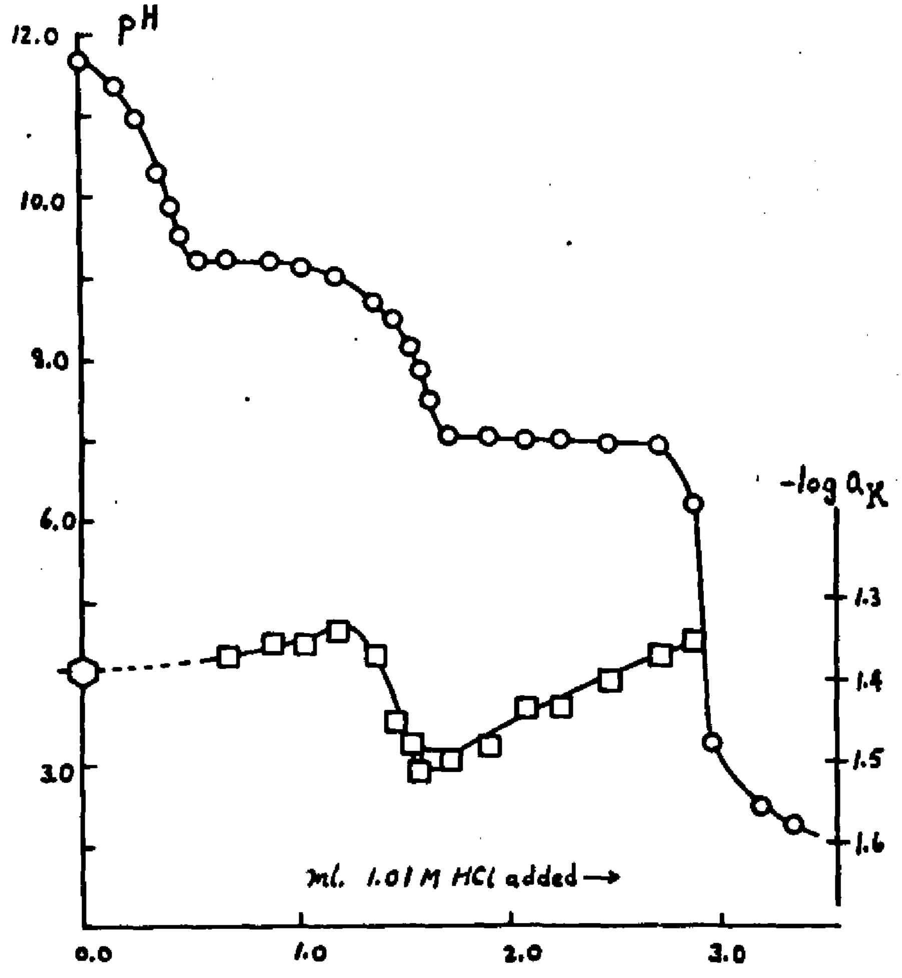


Figure 4.4

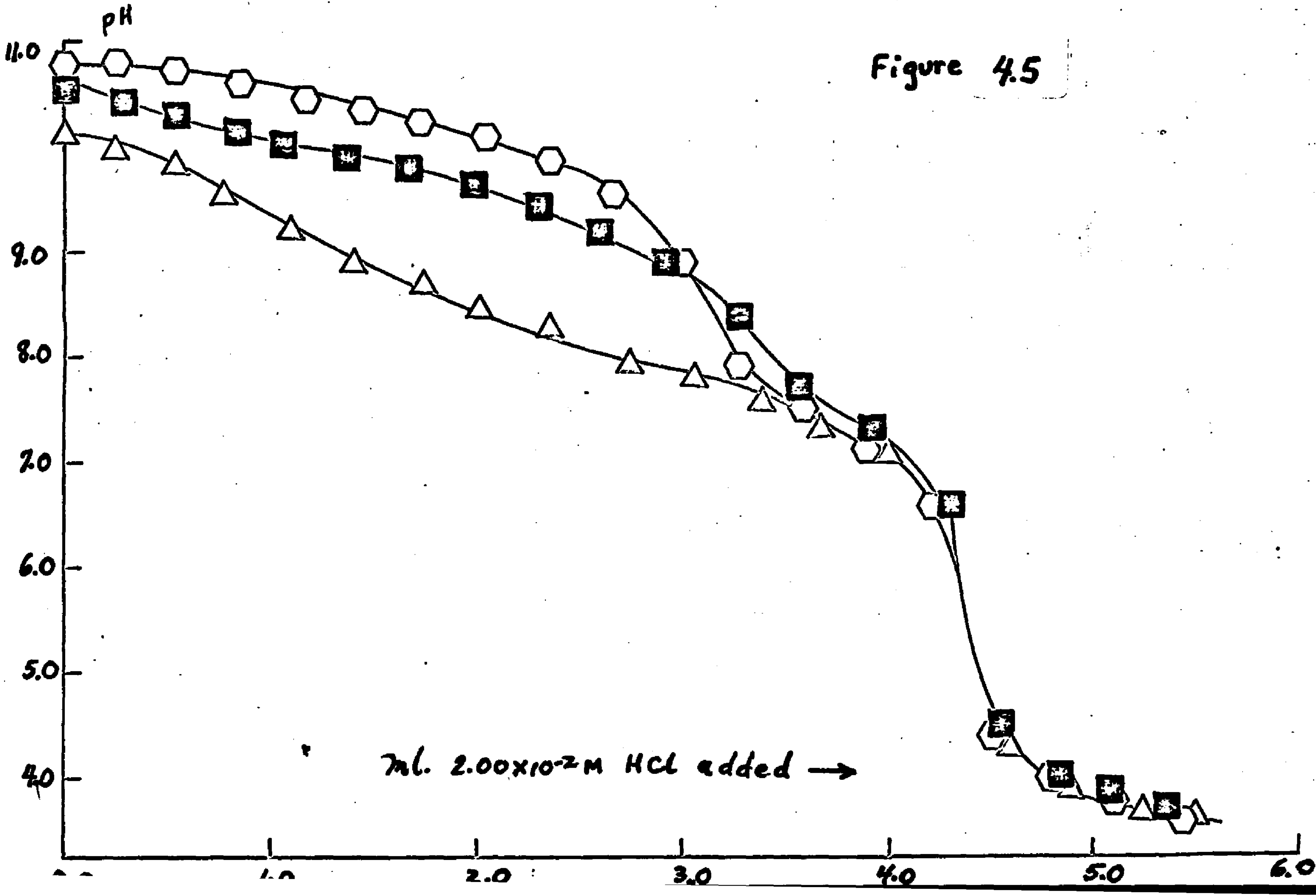
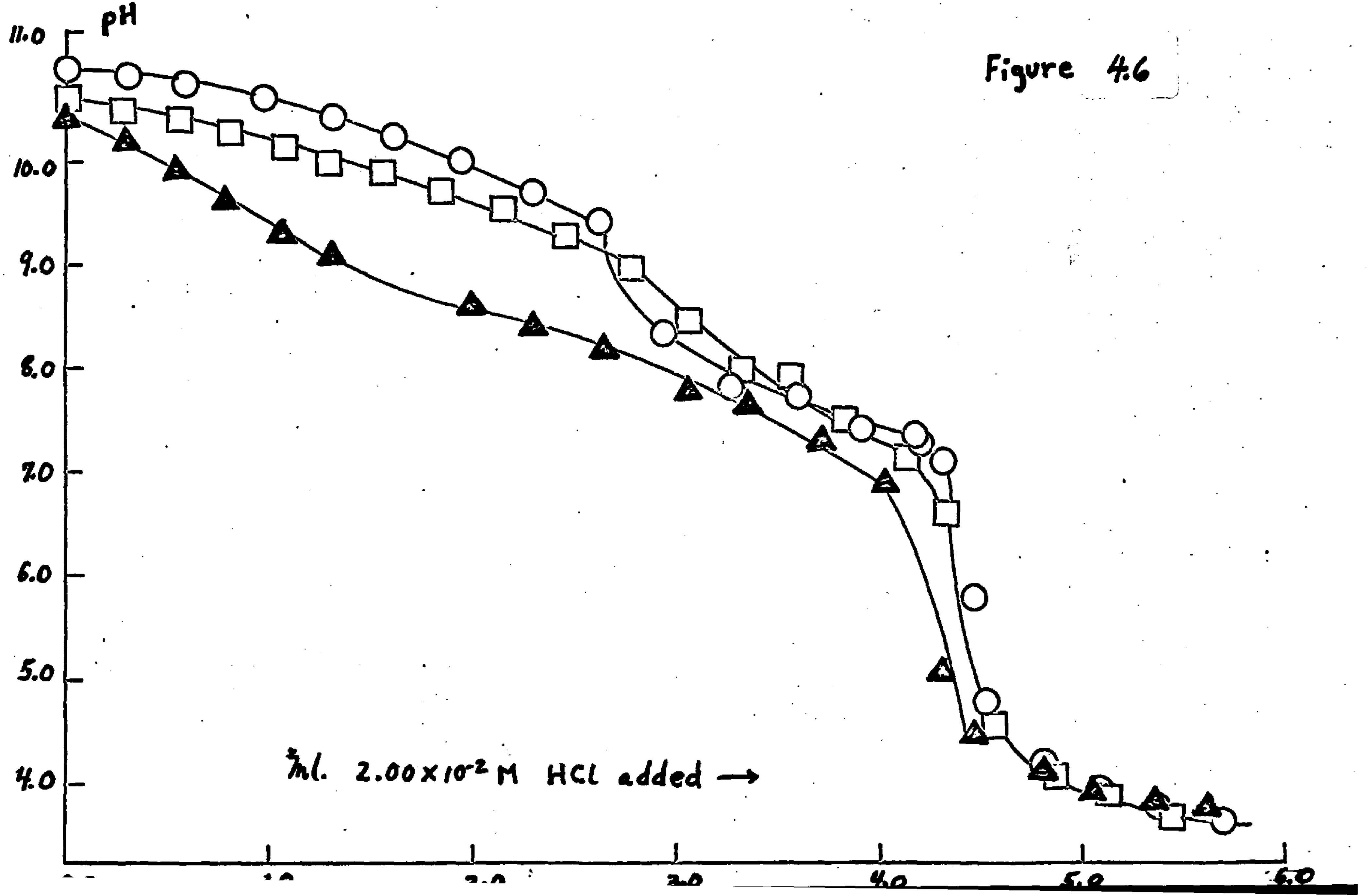


Figure 4.5

Figure 4.6



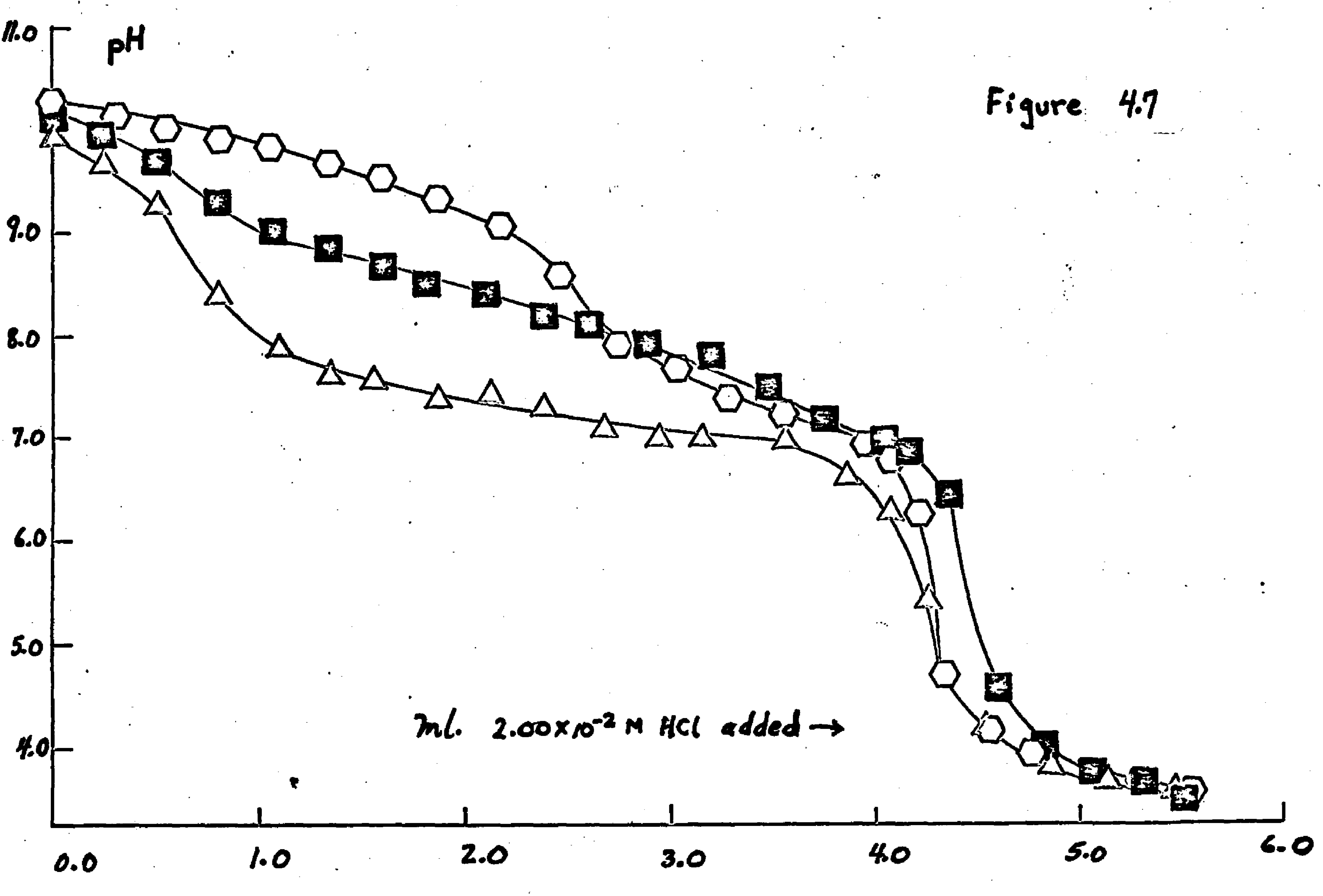


Figure 4.7

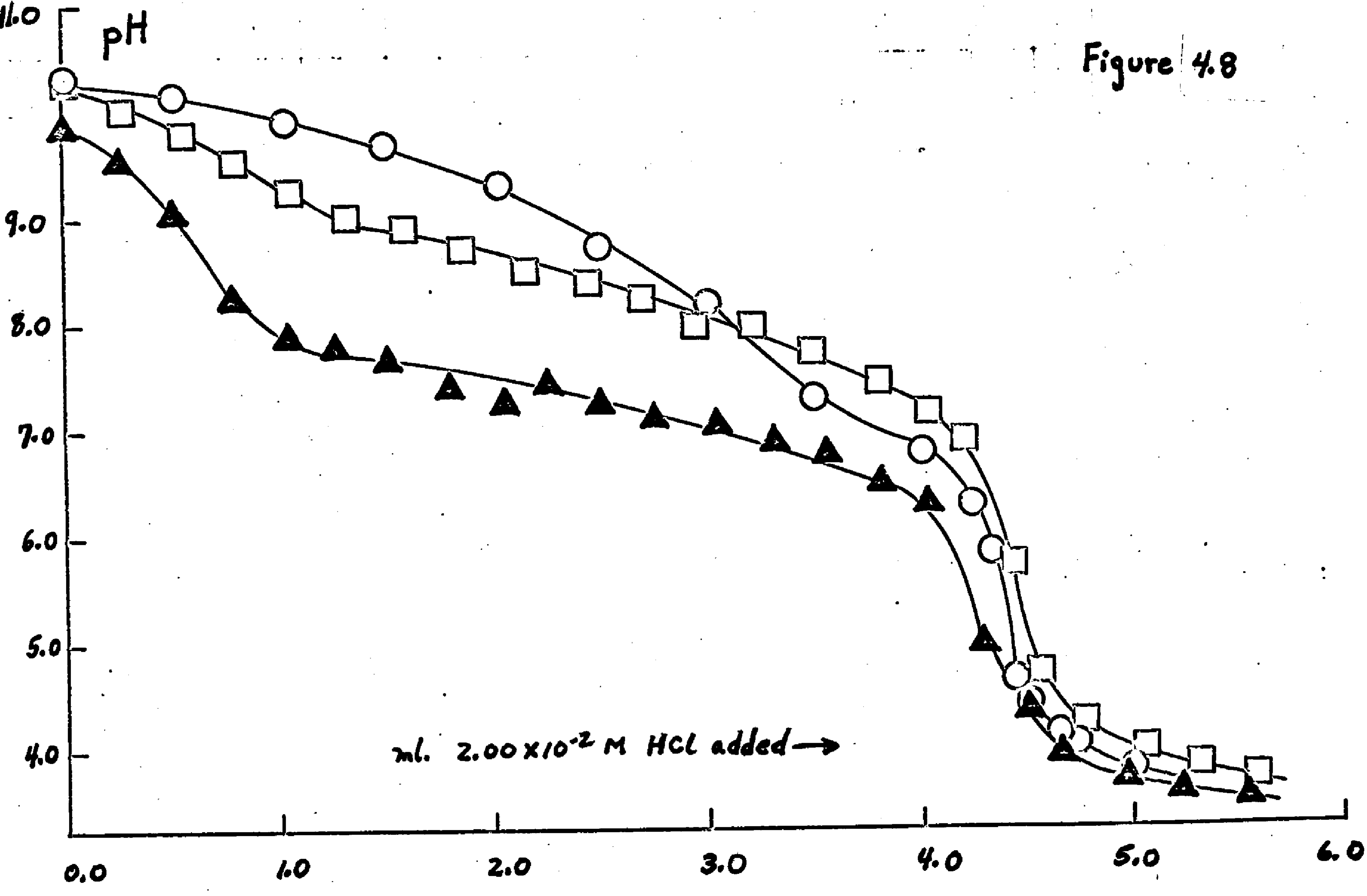


Figure 4.8

APPENDIX for CHAPTER 4

Non-micellar Soap Solutions:

Fatty Acid Precipitates

(1) $$\frac{C_H C_Z}{C_{HZ}} = K_A$$

(3) $$C_t = KC_M$$

(4) $$C_{HZ} = S_{HZ}$$

(2) $$C_M + C_H = \frac{K_w}{C_H} + C_Z + XC_t + G$$

From (3)

(A) $$C_M = \frac{C_t}{K}$$

From (1) and (4)

(B) $$C_Z = \frac{K_A C_{HZ}}{C_H} = \frac{K_A S_{HZ}}{C_H}$$

Substituting (A) and (B) in (2)

$$\frac{C_t}{K} + C_H = \frac{K_w}{C_H} + \frac{K_A S_{HZ}}{C_H} + XC_t + G$$

Multiplying by C_H and rearranging

$$C_H \left[\frac{C_t}{K} - XC_t + C_H - G \right] = K_w + K_A S_{HZ}$$

$$C_H \left[C_t \left(\frac{1}{K} - X \right) + C_H - G \right] = K_w + K_A S_{HZ}$$

(5) $$C_H = \frac{K_w + K_A S_{HZ}}{C_t \left(\frac{1}{K} - X \right) + C_H - G}$$

Non-micellar Soap Solution:

No Precipitate is Present -- Potassium and Sodium Caprate

(1) $$\frac{C_H C_Z}{C_{HZ}} = K_A$$

(3) $$C_t = KC_M$$

(10) $$C_t = C_Z + C_{HZ}$$

(2) $$C_M + C_H = \frac{K_w}{C_H} + C_Z + XC_t + G$$

From (3)

(A) $$C_M = \frac{C_t}{K}$$

From (1)

(B) $$C_{HZ} = \frac{C_Z C_H}{K_A}$$

Substituting the value of C_{HZ} from (B) in (10)

$$C_t = C_Z + \frac{C_Z C_H}{K_A} = C_Z\left(1 + \frac{C_H}{K_A}\right)$$

(C) $$C_Z = \frac{C_t}{\left(1 + \frac{C_H}{K_A}\right)}$$

Substituting (A) and (C) in (2)

$$\frac{C_t}{K} + C_H = \frac{K_w}{C_H} + \frac{C_t}{\left(1 + \frac{C_H}{K_A}\right)} + XC_t + G$$

Rearranging and factoring

$$C_t\left[\frac{1}{K} - \frac{K_A}{(K_A + C_H)} - X\right] = \frac{K_w}{C_H} - C_H + G$$

Multiplying by $C_H(K_A + C_H)$

$$C_tC_H\left[\frac{K_A + C_H}{K} - K_A - X(K_A + C_H)\right] = (K_w - C_H^2 + GC_H)(K_A + C_H)$$

Rearranging and factoring

$$C_tC_H\left[\left(\frac{1}{K} - X\right)C_H + K_A\left(\frac{1}{K} - X - 1\right)\right] = (K_w - C_H^2 + GC_H)(K_A + C_H)$$

$$(11) \quad C_t = \frac{(K_w - C_H^2 + GC_H)(K_A + C_H)}{C_H\left[\left(\frac{1}{K} - X\right)C_H + K_A\left(\frac{1}{K} - X - 1\right)\right]}$$

Micellar Soap Solutions:

Coexistence of Acid-Soap and Fatty Acid

(1) $$\frac{C_H C_Z}{C_{HZ}} = K_A$$

(4) $$C_{HZ} = S_{HZ}$$

(13) $$C_M C_H C_Z^2 = K_{MHZ_2}$$

(2) $$C_M + C_H = \frac{K_W}{C_H} + C_Z + XC_t + G$$

From (1) $$C_Z = \frac{K_A C_{HZ}}{C_H}$$

Substituting for C_{HZ} from (4)

(A) $$C_Z = \frac{K_A S_{HZ}}{C_H}$$

From (13) $$C_M = \frac{K_{MHZ_2}}{C_H C_Z^2}$$

Substituting for C_Z from (A)

(B) $$C_M = \frac{K_{MHZ_2}}{C_H\left(\frac{K_A S_{HZ}}{C_H}\right)^2} = \frac{K_{MHZ_2} C_H}{(K_A S_{HZ})^2}$$

Substituting (A) and (B) in (2)

$$\frac{K_{MHZ_2} C_H}{(K_A S_{HZ})^2} + C_H = \frac{K_w}{C_H} + \frac{K_A S_{HZ}}{C_{HZ}} + XC_t + G$$

Subtracting C_H and multiplying by $(K_A S_{HZ})^2 C_{HZ}$

$$(14) \quad K_{MHZ_2} C_H^2 = (K_A S_{HZ})^2 \left[K_w + K_A S_{HZ} + XC_H C_t + GC_H - C_H^2 \right]$$

Micellar Soap Solution:

Coexistence of Micelles and Acid-Soap -- Potassium Laurate

(1) $$\frac{C_H C_Z}{C_{HZ}} = K_A$$

(13) $$C_M C_H C_Z^2 = K_{MHZ_2}$$

(16) $$0.57 \log C_M + \log C_Z = -2.617$$

(2) $$C_M + C_H = \frac{K_w}{C_H} + C_Z + XC_t + G$$

From (13)

(A) $$C_Z = \left(\frac{K_{MHZ_2}}{C_M C_H}\right)^{\frac{1}{2}}$$

From (16)

$$\log C_M^{0.57} + \log C_Z = \log 10^{-2.617}$$

$$\log C_M^{0.57} C_Z = \log 10^{-2.617}$$

$$C_M^{0.57} C_Z = 10^{-2.617}$$

Substituting for C_Z from (A)

$$C_M^{0.57} \left(\frac{K_{MHZ_2}}{C_M C_H}\right)^{\frac{1}{2}} = 10^{-2.617} = \left(\frac{K_{MHZ_2}}{C_H}\right)^{\frac{1}{2}} C_M^{0.07}$$

$$C_M^{0.07} = 10^{-2.617}\left(\frac{C_H}{K_{MHZ_2}}\right)^{\frac{1}{2}}$$

$$\text{(B)} \quad C_M = 10^{-37.4}\left(\frac{C_H}{K_{MHZ_2}}\right)^{7.15}$$

Substituting in (A) the value of C_M from (B)

$$C_Z = \left(\frac{K_{MHZ_2}}{C_H}\right)^{\frac{1}{2}}\left[\left(\frac{K_{MHZ_2}}{C_H}\right)^{7.15} 10^{37.4}\right]^{\frac{1}{2}}$$

$$\text{(C)} \quad C_Z = 10^{18.7}\left(\frac{K_{MHZ_2}}{C_H}\right)^{4.075}$$

Substituting (B) and (C) in (2)

$$\text{(17)} \quad 10^{-37.4}\left(\frac{C_H}{K_{MHZ_2}}\right)^{7.15} + C_H = \frac{K_W}{C_H} + 10^{18.7}\left(\frac{K_{MHZ_2}}{C_H}\right)^{4.075} + XC_t + G$$

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