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PROPERTIES OF SODIUM DEOXYCHOLATE.

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# SURFACE, MICELLAR, AND SOLUBILIZATION PROPERTIES OF SODIUM DEOXYCHOLATE

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

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By

DAVID CHARLES THOMAS

Norman, Oklahoma

1978

SURFACE, MICELLAR, AND SOLUBILIZATION

PROPERTIES OF SODIUM DEOXYCHOLATE

APPROVED BY

DISSERTATION COMMITTEE

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# I. SUMMARY AND DISCUSSION OF RESULTS

## CHAPTER 1

## INTRODUCTION

The bile acids have been studied as biological surfactants and for their solubilizing power for over one hundred years. M. E. L. McBain and E. Hutchinson discussed early work in a monograph on the theories of solubilization developed by James W. McBain[1]. Their monograph treats the solubilization of water-insoluble materials by surfactants of all kinds but points out that a remarkable amount of early work was done with bile acids.

In 1868, Küehne showed that cholesterol was soluble in solutions of bile salts. Pflüger (1899) traced the adsorption of fat in animal tissues using oil-soluble dyes and found that the dyes were soluble in aqueous soap solutions and bile salt solutions. Early in this century many workers studied the solubilizing properties of bile salts without an understanding of the mechanism.

Wieland and Sorge attempted to explain the behavior

of bile salts by the formation of coordination compounds and may have laid the foundation for the idea of association between bile salt molecules. Later, Vergar suggested that the solubilizing, or protective, action of bile salts might be due to a protective ring of bile salt molecules around the fat or other molecules being solubilized. The functional groups of the bile acid were believed to be oriented outward from the fat molecules. Eventually, scientists realized that the bile salts were not unique and that they belonged to the class of colloidal electrolytes known as association colloids.

The bile acid salts are important because they are the digestion-promoting constituents of bile. They emulsify fats, can activate lipases, and play a leading role in the digestion and absorption of fats by the body. Bile acids are synthesized in the liver by modification of cholesterol to the specific bile acids. Deoxycholic acid is produced from cholic acid by the action of intestinal bacteria. The most important bile acids are the taurine and glycine derivatives of cholic acid, deoxycholic acid, and chenodeoxycholic acid. The bile acids are the end products of the metabolism of cholesterol. Approximately twenty to thirty grams of bile acids are secreted per day in the human body and of that amount about 90% remains in circulation[2].

Much more recently, Florence[3] pointed out the importance of bile acids saying: "There are several well-

known examples of biologically important micellar behavior in living organisms. Probably the best known is the involvement of the bile salts in the absorption of fats, in which a micellar phase can be identified." Small[4] listed the biological properties of the bile acids in his review on the physical chemistry of cholanic acids. They solubilize the insoluble components of bile (lecithin and cholesterol), aid in the digestive process by solubilizing the products of pancreatic hydrolysis (the monoglycerides and fatty acids) and are believed to control the synthesis of cholesterol in the intestines.

The bile acid salts also have value as model colloidal systems for the study of micellization. Their properties differ significantly from ordinary aliphatic detergents in that they are restrained sterically to a rigid structure with a hydrophobic side and a hydrophilic side. They form no liquid crystal phases, form small micelles, and have excellent solubilizing properties for various amphiphilic compounds like lecithin and monoglycerides. In contrast, long-chain aliphatic detergents form liquid crystal phases, form large micelles, and have poor solubilizing capacities for amphiphilic compounds[5].

This research has attempted to provide new information about the micellar properties of sodium deoxycholate by studying its solubilization of hydrocarbons, benzene and cyclohexane. Hopefully, the solubilization data will shed a

little more light on the properties of these biologically important compounds. Simultaneously, the bile acid salt has been used as a model compound to test a mass-action model for micelle formation developed here and the surface tension method of estimating micellar properties. Similar mass-action models have been used by others to explain micellar properties; however, none of the earlier studies fit the entire surface tension curve to a single model as was done in the present study. The results of the research are summarized in this section of the dissertation and are discussed individually in later sections. This format was chosen to help the reader to see the inter-relationship of the research sections and to examine the results without having to wade through experimental detail.

# CHAPTER 2

## LITERATURE SURVEY ON BILE ACID SURFACE CHEMISTRY

In 1921, E. Joël[6] measured the surface tension of various body fluids, including bile, using the viscostalagmometer developed by Traube. This is the earliest reference to surface tension measurements on bile salts that was found. E. Gilbert[7] showed that sodium salts of various bile acids gave characteristic surface tension curves that changed when other bile acids were added. Krajewskey and Wvedensky[8] measured the surface tension of sodium taurocholate and sodium glycocholate at various temperatures and found that the bile acids had great surface activity at low concentrations but that the "limit of adsorption" was reached rapidly (This may be the first detection of the micellar properties of bile acids.).

Von Kuthy[9] studied a series of five bile acids for their solubility and surface tensions. He suggested that the solution might be an emulsion or a micellar system. Boutaric and Berthier[10] measured the surface tension properties of bile acids as a function of time and fit their

data to an exponential function:

$$\gamma - L = (\gamma_o - L)e^{-at^n}$$

where L, a, and n were constants, and t was time. Later, they generalized that for bile salts n and a vary inversely with concentration and solution pH[11]. Dasher[12] studied the effect of pH in bile acid surface tension by the drop weight and pendant drop methods and found that a maximum in surface tension occurred at pH 6.8.

Ekwall[13] measured micelle formation by solubilization of p-xylene. He observed the critical micelle concentration (usually abbreviated CMC) for sodium deoxycholate as 0.007M in water. Crawford[14] found the CMC of sodium deoxycholate in water to be 0.0063M by measuring the solubilization of cholesterol. Below the CMC very little cholesterol is solubilized while above the CMC a rapid increase in solubility occurs. Ekwall and Ekholm[15] studied films of bile acids using a surface balance and determined that sodium deoxycholate has an area of 85$\mathring{A}^2$ per molecule in a tightly packed film.

Loos and Ruysson[16] studied the effect of salt concentration on the micellar molecular weight of sodium deoxycholate. They found the addition of salt increased the micellar molecular weight from 1250 to about 4000 in 0.1M NaCl. Moerloose and Ruysson[17] estimated the micelle

molecular weights of sodium cholate (2020) and sodium deoxycholate (5320) in 0.1M NaCl by light scattering techniques.

The literature described above was mentioned because it shows the development of the ideas about the surface activity of the bile acids from the first measurements of their effects on surface tension up to more recent research which discusses measurement of the micelle molecular weight. The literature through 1971 has been reviewed and discussed carefully by Small[4] in a book describing the chemistry of the bile acids. His review has been used extensively in this work. Other work of importance is discussed below.

Kratohvil and DelliColli[18] studied the effects of salt on micelle size and CMC with sodium taurodeoxycholate and sodium glycodeoxycholate using surface tension and light scattering techniques. They found that the CMC decreased with increasing salt concentration and that the micelle size increased with increasing salt concentrations.

Fontell[19-23], in an extensive series of papers, studied the micellar behavior of bile acid salts. He studied the osmotic activity and vapor pressure of aqueous solutions of sodium cholate, sodium deoxycholate, and sodium dehydrocholate over a broad range of concentrations. He found that an association process occurred in the range 0.004-0.005 molal for sodium deoxycholate. He estimated the

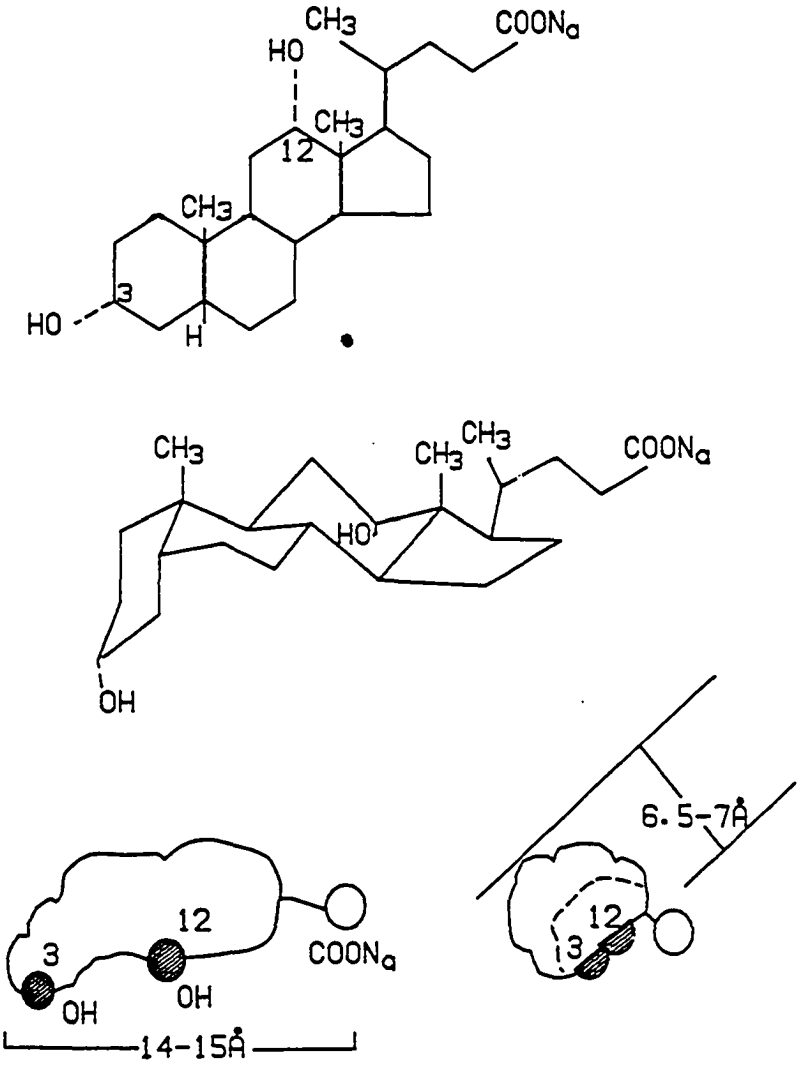
aggregate size as 5-6 molecules for sodium deoxycholate in water. Sodium cholate associated between 0.011-0.013 molal in an aggregate of 3-4 molecules[19]. Using light scattering on the same systems he found that association began above 0.013M for the cholate and was complete above 0.045M. The micelle molecular weight for sodium cholate was between 1300 and 3000. Sodium deoxycholate began association above 0.004M and was complete above 0.009M with a micelle molecular weight of 3000 to 4000. He also found that an upper limit beyond which light scattering was inaccurate existed - 0.1M for sodium cholate and 0.045M for sodium deoxycholate[20]. His viscosity measurements using capillary viscometers showed that, at high concentrations, there may be a secondary structure in which the micelles are interlinked. He states that the micelle shape up to 0.48M (sodium cholate) and 0.30M (sodium deoxycholate) is spherical or near spherical. Beyond these concentrations the micelle shape changes due to the formation of secondary structures[21]. He used low angle x-ray scatterings to confirm the above-mentioned results and estimated that the sodium deoxycholate micelle has a radius of about 20Å above 0.065M or an aggregation number of 24. Sodium cholate has a micellar radius of about 17Å above 0.085M or an aggregation number of 16[22]. The last paper in the series discussed mixtures of bile acid salts, n-decanol, and water[23]. His phase diagrams show a continuous transition from homogeneous solutions of

bile acid salt in water to homogeneous solutions of bile acid salt and water in decanol. At high decanol concentrations inverted micelles formed with decanol as the exterior phase. Fontell mentions papers to be published that will discuss the mixed solubility of n-decanol and p-xylene in bile acid micelles. He stated that the addition of decanol above a critical content reduces the system capacity for solubilizing xylene. As far as I have been able to determine, this work was never published. Fontell's comment about the interaction of solubilized species is the only such statement that I have found.

Holzbach and coworkers[24] used quasielastic laser spectrometry to study pure and mixed micelles of bile salts. Their results indicated that solubilization of lecithin and cholesterol from low levels to super-saturation did not affect the micelle size.

FIGURE I-1

SODIUM DEOXYCHOLATE STRUCTURE



## CHAPTER 3

## PHYSICAL AND CHEMICAL PROPERTIES OF SODIUM DEOXYCHOLATE

Sodium deoxycholate is a $C_{24}$ carboxylic acid salt with a cyclopentenophenanthrene nucleus. It is a saturated molecule with two hydroxyl groups at the 3 and 12 carbon atoms. The systematic name for the compound is: the monosodium salt of 3α, 12α-dihydroxy-5β-cholen-24-oic acid. The Chemical Abstracts Registry Number is 302-95-4. The apparent molar volume is 524 $\mathring{A}^3$/molecule and the apparent partial specific volume is 0.765 $cm^3/gm$[25]. The crystal structure is orthorhombic with principal refractive indices of 1.550, 1.538, and 1.533[26]. The structure and conformation of sodium deoxycholate are shown in Figure I-1 along with a diagramatic representation of the molecule in longitudinal cross-sectional views. The most biologically important bile acids are glycodeoxycholic acid ($C_{23}H_{37}(OH)_2CONHCH_2CO_2H$) and tawrodeoxycholic acid ($C_{23}H_{37}(OH)_2CONHCH_2CH_2SO_3H$). They were not used in this study.

# CHAPTER 4

## MICELLIZATION OF SODIUM DEOXYCHOLATE

Sodium deoxycholate forms relatively small micelles of up to forty molecules in the presence of sodium chloride. Since the deoxycholate ion has one side that is definitely hydrophobic while the other side has two hydrophilic hydroxyl groups, it is reasonable to assume that, in aqueous media, the hydrophobic regions of the ions associate so that the hydrophilic regions are oriented outward. Small and coworkers[27] showed that the NMR spectral peak of the C-18 proton on sodium cholate is broadened on micelle formation indicating association. They use their data to confirm the hypothesis of back-to-back or hydrophobic interaction. Oakenfull and Fisher[28] take the opposite view and postulate that the primary interaction between bile acid molecules is through hydrogen bonding. They base their interpretation on the drop in partial molar volume of the bile acid salts on micellization. They estimate that the hydrophobic interaction between two bile salt molecules is similar to that between two C-12 chains and that the volume of interaction

would be +100 ml/mol.

Dimers may occur in a premicellization equilibrium that covers a very narrow range of concentration[19]. As the concentration increases association increases to form the final micelle. Recent work[29] supports the idea that primary micelles of a few molecules (usually estimated at about four) form and then larger micelles form from these units.

Figure I-2 is a sketch of a possible primary micelle unit for sodium deoxycholate formed through hydrophobic interactions on the hydrocarbon side. Chen and coworkers[30] use a similar model for the primary unit in their work on the permeability of gas molecules into the micelle. It is likely that in alkaline media, such as used in the present research, secondary micellization would occur through hydrogen bonding between hydroxyls or between hydroxyls and carboxylic acid groups because virtually all the carboxylic acid groups should be ionized. Hydrogen bonding between hydroxyls on adjacent primary micelles would produce a compact bundle of micellar groups that when large would probably be disc-shaped. Hydrogen bonding between the hydroxyl proton and a carboxylic acid group would produce a string-like structure (Figure I-3) that could extend indefinitely. Mazer and coworkers[29] suggest this possibility from their measurement of hydrodynamic radii of bile salt micelles.

The mass action model of micelle formation and the

major observations made during this research are described below in summary form. The details of the work are provided in the later sections.

Micelles are assumed to form using the single micelle species mass action model which states for sodium deoxycholate (NaDC):

$$n\ DC^- \overset{K_n}{=\!=} (DC^-)_n \qquad (1)$$

where $K_n$ is the association constant for the formation of sodium deoxycholate micelles of aggregation number n. The total sodium deoxycholate concentration $C_T$ is given by:

$$C_T = C_m + n\ K_n\ C_m^n \quad . \qquad (2)$$

The Gibbs adsorption equation relates the change in surface coverage to the change in monomer concentration, $C_m$. The general Gibbs adsorption equation

$$\frac{-\ d\ \gamma}{RT\ d\ \ell n\ a_2} = \Gamma_2 - \frac{X_2}{X_1}\Gamma_1$$

reduces to

$$\frac{-\ d\ \gamma}{RT\ d\ \ell n\ a_2} = \Gamma_2 \qquad (3)$$

when $X_2/X_1$ is much less than 1. The activity $a_2$ can be

replaced by $C_2$ when sufficient excess electrolyte is present. Equation (3) further reduces to

$$d\gamma = -\Gamma_2 RT\, d\, \ell n\, C_2$$

where $\gamma$ is the surface tension, $\Gamma$ is the amount of surfactant adsorbed in moles/cm$^2$. $\Gamma$ can be related to $\Gamma_m$, the amount of surfactant adsorbed at monolayer coverage through the Langmuir adsorption isotherm which can be stated:

$$\Gamma = \Gamma_m\, C_m/(\alpha + C_m) \qquad (4)$$

where $C_m$ is the surfactant monomer concentration and $\alpha$ is the surfactant concentration at which $\Gamma = \Gamma_m/2$.

Equations (3) and (4) are combined to give

$$d\gamma = -\Gamma_m RT \frac{d\, C_m}{\alpha + C_m}$$

which on integration gives:

$$\frac{\gamma_o - \gamma}{\Gamma_m RT} = \ell n\, (1 + C_m/\alpha) \qquad (5)$$

where $\gamma_o$ is the electrolyte surface tension. Equation (5), which was first stated by Szyszkowski as a semi-empirical equation, describes the change in surface tension of a solution with concentration of the monomer. Equation (2)

describes the change in monomer concentration with total concentration during micellization. The fact that the surface tension continues to change beyond the CMC has been well established (see Section III). Figure I-4 is an example from data taken during this study. The change in surface tension beyond the CMC could only be caused by a change in $\Gamma_m$ or $C_m$. Since $\Gamma_m$ is believed to be constant beyond the CMC, the change in surface tension must be related to the change in monomer concentration.

Ellipsometric measurements of the thickness of the surfactant film at the air-water interface were used to confirm that $\Gamma_m$ remains constant beyond the CMC. An example of the data obtained is shown plotted in Figure I-4. The rest of the data are shown in tabular form in Section II of this dissertation. From these data it is concluded that $\Gamma_m$ is constant beyond the CMC and that the change in surface tension is caused by a change in monomer concentration in accordance with the model set out above. The results of this study are summarized in Table I-1.

The ellipsometric data are remarkably constant for the very thin film found. The film thickness, 6.3Å compares well with the estimated cross-sectional diameter for the deoxycholate ion of 6.9Å (Figure I-1) and the molecular area agrees with reported areas for sodium deoxycholate of $85Å^2$ (see Sections II and III). The molecular area calculated from $\Gamma_m$ shows more variation; however, the average area for

sodium deoxycholate from the ellipsometric data ($83.6\text{Å}^2$) is the same as the average from the surface tension data.

The micelle aggregation number, n, determined from the surface tension data agrees well with published values measured by light scattering techniques (see Figure III-2). The aggregation state of the micelle increases slowly with increasing salt concentration to a maximum of around forty molecules. If such a micelle were formed as shown in Figure I-3, it would be about 140Å long which is about twice the length suggested by Mazer and coworkers[29]. It is likely then that the micelle is a mixture of the linear polymer and the "bundles" of primary micelles. The smaller micelle seen at low salt concentration[12-14] may be a group of three primary micelles in a bundle while the larger micelle of around forty molecules may be three to four bundles hydrogen-bonded together.

If the primary micelle unit configuration changed radically from small micelles to large micelles, one would expect a change in solubilization capacity per deoxycholate ion. Solubilization experiments were carried out as a part of this study to determine whether or not the smaller micelles (n=14) absorbed hydrocarbon differently than did larger micelles (n=40). The solubilization data are summarized in Tables IV-14 and IV-15. The data were used to calculate thermodynamic quantities for the solubilization of benzene and cyclohexane by micelles of varying sizes. The

average results are shown in Table I-2. The differences between free energies of solubilization for large and small micelles are clearly insignificant. The free energy of solubilization as defined here is the change in free energy that occurs when the hydrocarbon is solubilized from the aqueous phase (reference state) into a mole of deoxycholate ions in micellar form. It can be concluded that large and small micelles take up benzene and cyclohexane in the same way. It is, therefore, unlikely that there is a significant change in the deoxycholate ion environment as the salt concentration increases.

An effect of increasing salt concentration is evident in Table IV-17. The total solubility of both benzene and cyclohexane in the micelle is reduced as the ionic strength increases. The ratio of intramicellar solubility in the low ionic strength to high ionic strength case is an average of 1.10. If no effect of salt concentration occurred, this ratio would be 1.00. The effect probably occurs because of an electrostriction of the micelle wherein at higher salt concentrations the negative carboxylic acid groups and the polar hydroxyl groups can come closer together. Interestingly enough, the ratio of solubilities appears to follow the Setchenow equation which predicts a ratio of 1.17 for the solubility of benzene in salt solutions[31].

If the number of molecules of hydrocarbon

solubilized (benzene + cyclohexane) per micelle is calculated and used to estimate the ratio of hydrocarbon molecules to deoxycholate anion, one can see that about two deoxycholate anions are required to solubilize one hydrocarbon molecule. There is an apparent interaction of benzene and cyclohexane that shows up at low benzene mole fraction as can be seen in Figure IV-7. The hydrocarbon to deoxycholate ratio is increasing up to 0.5 mole fraction of benzene and then is constant. The smaller micelle ($n \sim 14$) solubilizes slightly more hydrocarbon per molecule of deoxycholate than the larger ones as discussed above.

Mixtures of benzene and cyclohexane were solubilized by sodium deoxycholate micelles to determine the effects of mixed hydrocarbons on micellar solubility. A previously unsuspected result was found: The solubilized benzene and cyclohexane mixtures have the same relative concentrations in the micelle as they have in the contacting solution. That is, the interior of the micelle is sufficiently hydrocarbon-like that the same activity/concentration relationships hold in the micelle as in the contacting solution. Figure IV-1 shows these results graphically. These observations suggest that the complex problem of mixed solubilization into micelles could be simplified by assuming that, at equilibrium, the saturated micelle will contain hydrocarbon molecules in the same relative concentrations as the insoluble contacting solution. Only at low benzene

concentrations does any discrepancy occur; in these systems, the proportion of benzene in the micelle is slightly higher than in the contacting solution. Longer equilibration times and better analytical procedures may show that the relationship is obeyed across the whole concentration range.

# CHAPTER 5

## SUGGESTIONS FOR FUTURE WORK

This research has stimulated several ideas for future work that I felt should be mentioned.

1. Ellipsometry is a powerful tool for studying adsorption at interfaces. The present work has extended it to air-water interfaces. It could be used with more conventional surfactants like stearic acid to study the buildup of films through wide spreading pressure ranges. When used in conjunction with a Langmuir film balance, ellipsometry should give direct information about the orientation of surfactant molecules at the interface. It could also be used as was done here to determine the molecular area of a packed film for comparison to the values predicted by the Gibbs adsorption equation.

2. The surface tension measurement of micellar size, molecular area, and micelle association constant portion of this work could be extended to other surfactants. It could be used with aliphatic surfactants to see whether or not the model is appropriate for larger micelles. I

believe that the model is reasonable but think that the accuracy of surface tension measurements beyond the CMC will be the limiting factor in application of the method to larger micelles. The techniques used here constitute a good way to directly obtain micellar association numbers and should be extended to other systems to give more direct information on micellar sizes. The effects of temperature, salt concentration, and pH can be readily studied. It may be feasible to use the data fitting technique to study micellar sizes in the very concentrated micellar solutions used in tertiary oil recovery.

It would also be interesting to try to apply the model to a mixed surfactant system with data fitting over the entire concentration range. It may be possible to better calculate the surface tension curve for a mixed surfactant system. These calculations would have application to tertiary oil recovery work where mixed, poorly characterized surfactant systems are the rule rather than the exception.

3. The solubilization of hydrocarbons into micellar solutions is a very timely area for research. Many industrial concerns are actively pursuing tertiary oil recovery using micellar fluids. They should be concerned with the solubilization of hydrocarbon by their fluids.

Solubilization studies on hydrocarbons in biologically active micelles like the bile acid-lecithin system

should give new insight into the micelle's role in fat and cholesterol solubilization.

## REFERENCES


1. M. E. L. McBain and E. Hutchinson, Solubilization and Related Phenomena, Academic Press, New York (1955) Ch. 1 and references cited therein.

2. P. Karlson, Introduction to Modern Biochemistry, translated by C. H. Doering, Academic Press, New York (1965) p. 244.

3. A. T. Florence, in Micellization, Solubilization, and Microemulsions, Vol. 1, K. L. Mittal, ed., Plenum Press, New York (1977), p. 55.

4. D. M. Small, "The Physical Chemistry of Cholanic Acids," in Bile Acids, P. P. Nair, ed., Plenum Press, New York (1971), p. 249.

5. D. M. Small, J. Am. Oil Chem. Soc., 45, 108 (1968).

6. E. Joël, Biochem Z., 119, 93 (1921).

7. E. Gilbert, Z. ges. expl. Med., 48, 255 (1925).

8. N. A. Krajewskey and N. Wvedensky, Biochem. Z., 191, 241 (1927).

9. A. von Kúthy, Biochem. Z., 237, 380 (1930) and 240, 308 (1932).

10. A. Boutaric and P. Berthier, Compt. rend., 220, 730 (1945).

11. A. Boutaric and P. Berthier, J. Chim. Phys., 42, 117 (1945).

12. G. F. Dasher, Jr., Science, 116, 660 (1952).

13. P. Ekwall, Cong. Intern. Biochem. Résumés Communs. 2nd Cong. Paris, 126 (1952).

14. N. Crawford, J. Med. Lab. Technol. (London), 13, 351 (1956).

15. P. Ekwall and R. Ekholm, Proc. Intern. Cong. Surface Activity, 2nd, London, Vol. 1, Butterworths, London (1957), p. 23.

16. R. Loos and R. Ruysson, Mededel. Kominkl. Vlaam. Acad. Wetenschap. 20, No. 4 (1958).

17. P. D. Moerloose and R. Ruysson, J. Pharm. Belg., 14, 95 (1959).

18. J. P. Kratohvil and H. T. DelliColli, Can. J. Biochem., 46, 945 (1968).

19. K. Fontell, Kolloid-Z. u. Z. Polymere, 244, 246 (1971).

20. K. Fontell, Kolloid-Z. u. Z. Polymere, 244, 253 (1971).

21. K. Fontell, Kolloid-Z. u. Z. Polymere, 244, 614 (1971).

22. K. Fontell, Kolloid-Z. u. Z. Polymere, 244, 710 (1971).

23. K. Fontell, Kolloid-Z. u. Z. Polymere, 250, 825 (1972).

24. R. T. Holzbach, S. Y. Oh, M. E. McDonnell, and A. M. Jamieson, in Micellization, Solubilization, and Microemulsions, Vol. 1, K. L. Mittal, ed., Plenum Press, New York (1977), p. 403.

25. Ref. 4, p. 266.

26. V. J. Barczak, Personal Communication, January 5, 1977.

27. D. M. Small, S. A. Penkett, and D. Chapman, Biochim. Biophys. Acta, 176, 178 (1969).

28. D. G. Oakenfull and L. R. Fisher, J. Phys. Chem., 81, 1838 (1977).

29. N. A. Mazer, R. F. Kwasnick, M. C. Carey, and G. B. Benedek, in Micellization, Solubilization, and Microemulsions, Vol. 1, K. L. Mittal, ed., Plenum Press, New York (1977), p. 384.

30. M. Chen, M. Grätzel, and J. K. Thomas, J. Am. Chem. Soc., 97, 2052 (1975).

31. M. B. King, Phase Equilibrium in Mixtures, Pergamon Press, New York (1969), pp. 325-27.

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TABLE I-1

Summary of Ellipsometric and Surface Tension Results
on the Micellar Properties of Sodium Deoxycholate
in Sodium Chloride Solutions

| Data Set: | A | B | C | D | E |
|---|---|---|---|---|---|
| Electrolyte | | | | | |
| NaOH, M | 0.01 | 0.01 | 0.001 | 0.01 | 0.10 |
| NaCl, M | | 0.15 | 0.50 | 0.50 | 0.50 |
| Ellipsometric Data: | | | | | |
| Ave. Film Thickness, Å | 6.9 | 6.1 | 6.1 | 6.2 | 6.2 |
| Molecular Area, $Å^2$/mol. | 76 | 86 | 86 | 85 | 85 |
| Surface Tension Data | | | | | |
| Micelle Size, n | 12.4 | 14.5 | 40.4 | 40.0 | 42.3 |
| $K_n$, $M^{1-n}$ | $2.39 \times 10^{23}$ | $4.51 \times 10^{34}$ | $1.6 \times 10^{116}$ | $1.89 \times 10^{116}$ | $2.8 \times 10^{124}$ |
| $\Gamma_m$ m/$cm^2$ | $2.0 \times 10^{-10}$ | $1.7 \times 10^{-10}$ | $2.2 \times 10^{-10}$ | $2.0 \times 10^{-10}$ | $2.1 \times 10^{-10}$ |
| Molecular Area, $Å^2$/mol. | 83.1 | 97.7 | 75.5 | 84.0 | 77.5 |
| $\alpha$, $\mu$M | 78.5 | 4.09 | 4.71 | 2.67 | 4.14 |
| CMC, M | 0.0064 | 0.002 | 0.0011 | 0.0009 | 0.0009 |

TABLE I-2

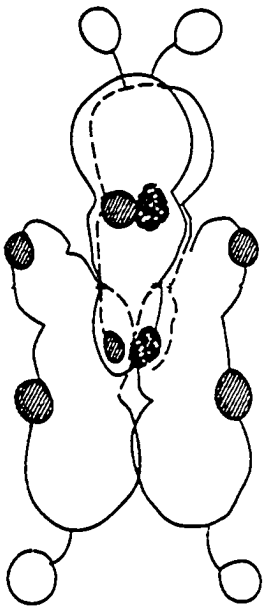
Average Free Energy* of Solubilization of Benzene and Cyclohexane in Sodium Deoxycholate Micelles of Differing Sizes

| | $\Delta G_S$, Benzene Kcal/$m_{BZ}$ $m_{NaDC}$ | $\Delta G_S$, Cyclohexane Kcal/$m_{CH}$ $m_{NaDC}$ |
|---|---|---|
| $n \sim 14$ | -1.86 | -3.60 |
| $n \sim 40$ | -1.83 | -3.70 |

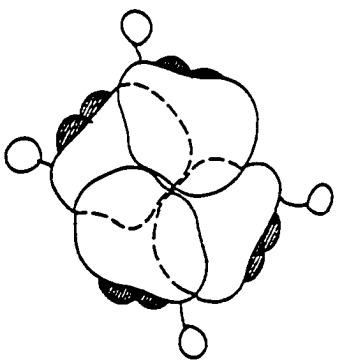
*$\Delta G_S$ is the free energy of solubilization of the hydrocarbon in the micelle from aqueous solution.

FIGURE I-2

POSSIBLE CONFORMATION OF A FOUR-UNIT SODIUM DEOXYCHOLATE PRIMARY MICELLE



SIDE VIEW



END VIEW

FIGURE I-3

POSSIBLE HYDROGEN BONDING INTERACTION
TO PRODUCE A SECONDARY BILE SALT MICELLE

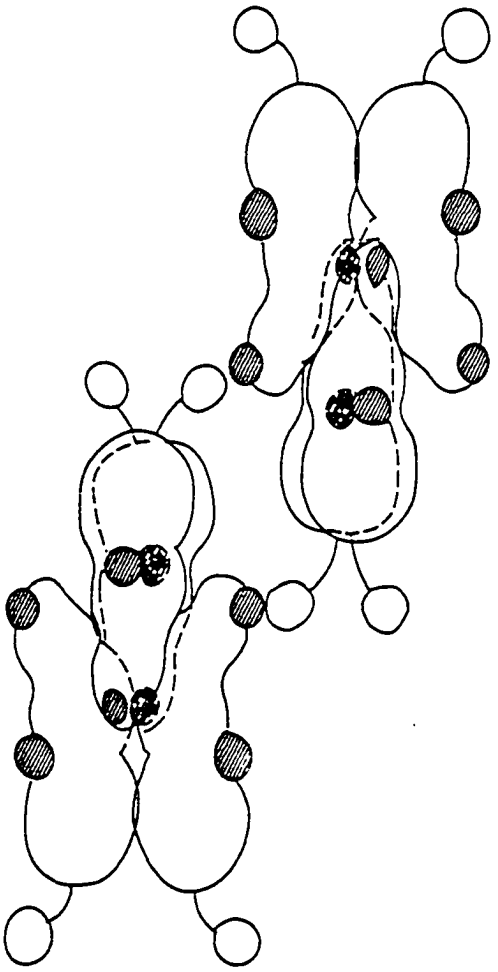
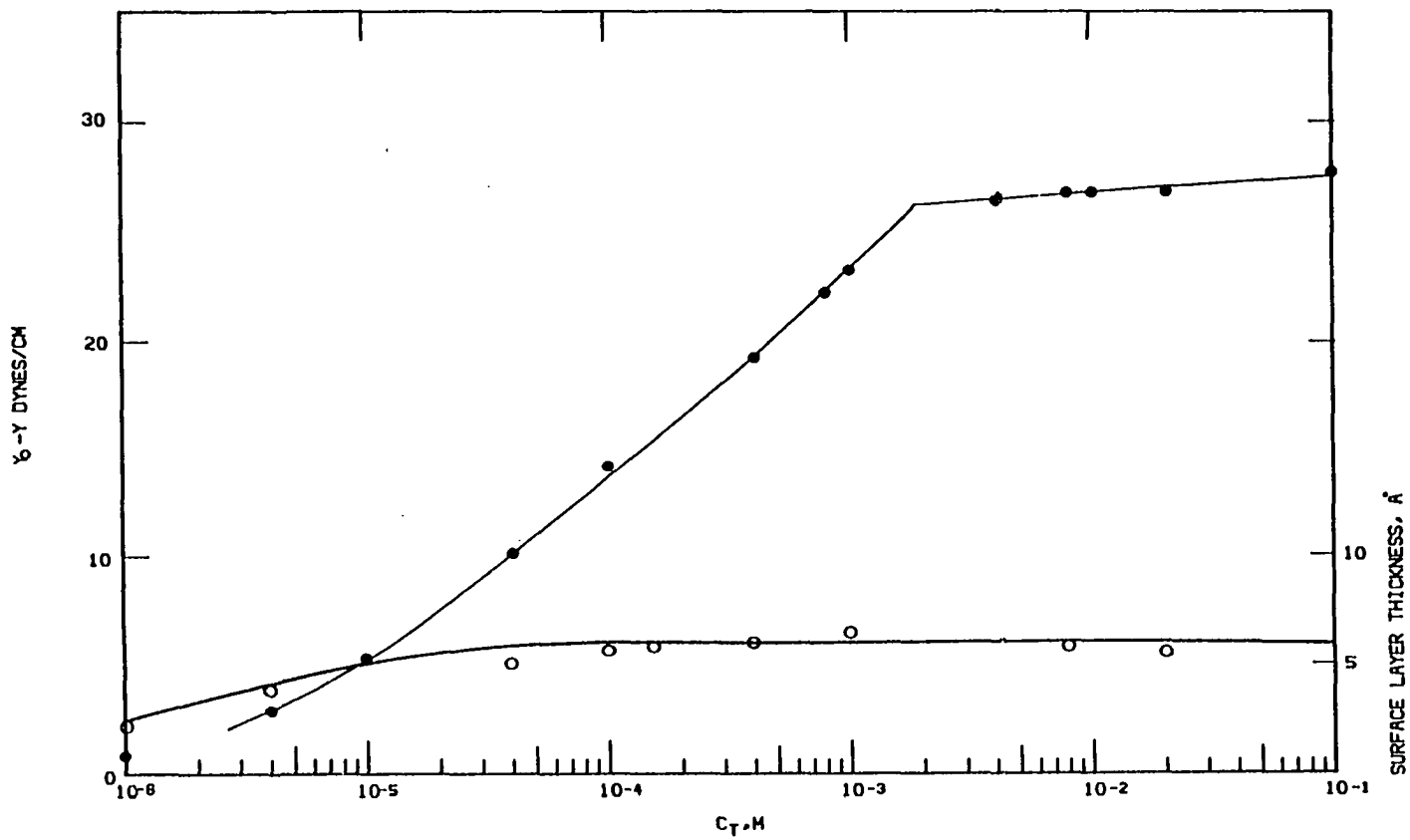


FIGURE I-4
SURFACE TENSION AND ELLIPSOMETRIC DATA FOR
SODIUM DEOXYCHOLATE IN 0.01M NaOH AND 0.15M NaCl



# II. THE MOLECULAR AREA AND SURFACE ADSORPTION OF SODIUM DEOXYCHOLATE FROM ELLIPSOMETRIC MEASUREMENTS

## CHAPTER 1

## INTRODUCTION

Ellipsometry is the study of the effects of reflection on polarized light. It can be used to determine optical properties of an adsorbed film on a surface. The optical constants measured are the refractive index, $n$, and the absorption coefficient, $\kappa$. If the films examined are sufficiently thin (less than 1000Å), the thickness of the film on the substrate can be determined. The present work uses ellipsometry to determine the thickness of a very thin layer of deoxycholate anions at the air-electrolyte interface. These experiments were intended to determine whether or not multilayer formation occurred beyond the critical micelle concentration and to determine if the deoxycholate anion changes orientation as its concentration increases. The measurements were used to verify that the Langmuir adsorption isotherm is a valid model for surface layers of soluble surface active materials.

Ellipsometry is well suited for the desired measurements as evidenced by its use by Hall[1] to measure the thickness of an adsorbed water layer (less than 7Å) on quartz. Hall refers to the work of Bayh and Pflug[2] measuring water vapor layers of 3.6Å thickness adsorbed on alkali halides. Steiger[3] measured the build-up of successive layers of arachidic acid on gold in the 50 to 600Å thickness range. He also measured the thickness of tripalmitolglycerine multilayers in the 25 to 300Å range.

Tennyson Smith[4] described a method to measure simultaneously film thickness, surface tension, and contact potential of adamantane carboxylic acid at a mercury-gas interface. He reports film thicknesses in the 3 to 30Å range. He showed excellent agreement between surface tension and ellipsometric measurements for estimating film thicknesses and molecular areas.

# CHAPTER 2

## ELLIPSOMETRY THEORY

Analysis of ellipsometric data to obtain a film thickness requires solution of the fundamental equation of ellipsometry (Equations 6 and 9 below). A derivation of this equation and a discussion of the data required are presented below. The derivation follows one given by Archer[5] in his "Manual on Ellipsometry".

When light is reflected from a surface its intensity is diminished because some of the light is transmitted into the surface film and the substrate. The ratio of the electric field vector of the reflected wave, R', to the electric field vector of the incident wave, E', is the Fresnel reflection coefficient, r.

$$r = \frac{R'}{E'} \quad . \tag{1}$$

In terms of the amplitudes of the reflected and incident waves and of the phase change, $\beta$, caused by reflection, the coefficient becomes

$$r = \frac{R}{E} e^{i\beta} \quad . \tag{2}$$

The reflection coefficient depends on the orientation of the wave relative to the plane of incidence. The wave is resolved into two components: s, normal to the plane of incidence and p, in the plane of incidence. The net reflection coefficient is the ratio of the reflection coefficients of the component waves.

$$r = \frac{r_p}{r_s} = \frac{R_p E_s}{R_s E_p} e^{i(\beta_p - \beta_s)} \quad . \tag{3}$$

The phase change between the p and s components, $\Delta$, is one of the fundamental measurements taken in ellipsometry. The second measurement, $\Psi$, is the arctangent of the factor by which the amplitude ratio changes.

$$\Delta = (\beta_p - \beta_s)_{reflected} - (\beta_p - \beta_s)_{incident} \tag{4}$$

$$\Psi = \arctan \frac{R_p E_s}{R_s E_p} \quad . \tag{5}$$

When Equations (4) and (5) are substituted into Equation (3), the fundamental relationship between reflection coefficients and ellipsometric measurements results.

$$r = \frac{r_p}{r_s} = \tan\Psi e^{i\Delta} \quad . \tag{6}$$

Light reflected from the surface of a film, shown in Figure II-1 as $R'_I$ is unchanged. Light refracted through the film, reflected off the substrate back through the film (of thickness d) and into the medium ($R'_{II}$) undergoes a relative phase change of $2\delta$ where

$$\delta = \frac{360}{\lambda} d \left(\eta_1^2 - \sin^2 \Phi_1\right)^{1/2} . \qquad (7)$$

Subsequent internal reflections give phase changes of $2\delta$ for each reflection. Figure II-1 shows four of the infinite number of reflected beams. Medium 0 is assumed to be air with a refractive index $\eta_0$ of 1.000.

Medium 1 is the film with a refractive index, $\eta_1$, of 1.540 for sodium deoxycholate. Medium 2 is the substrate, water, with a refractive index, $\eta_2$, of 1.333.

The reflection coefficient, r, for the film is given by

$$r = \frac{R'}{E'}$$

but R' is the sum of all the component reflections,

$$R' = R'_I + R'_{II} + R'_{III} + R'_{IV} + \ldots + R'_n$$

and

$$R'_I = E' r_{01}$$

$$R'_{II} = E' \, t_{01} \, t_{10} \, r_{12} \, r_{10} \, e^{-2i\delta}$$

$$R'_{III} = E' \, t_{01} \, t_{10} \, r_{12}^{2} \, r_{10} \, e^{4i\delta}$$

$$R'_{IV} = E' \, t_{01} \, t_{10} \, r_{12}^{3} \, r_{10} \, e^{-6i\delta}$$

$$\vdots \qquad\qquad \vdots$$

$$R'_{N} = E' \, t_{01} \, t_{10} \, r_{12}^{(N-1)} \, r_{10} \, e^{-2(N-1)\delta}$$

The transmittance coefficients $t_{10}$ and $t_{01}$ are related to the reflection coefficient $r_{01}$ by

$$t_{10} \, t_{01} = (1 - r_{01})^{2} \quad .$$

The reflection coefficient between Medium 0 and Medium 1, $r_{01}$, is the negative of the reflection coefficient from Medium 1 to Medium 0

$$r_{01} = -r_{10} \quad .$$

The above relationships can be combined to give:

$$r = \frac{R'}{E'} = r_{01} \, (1-r_{01})^{2} \, r_{12} \, e^{-2i\delta} - (1-r_{01})^{2} \, r_{01} \, r_{12}^{2} \, e^{-4i\delta}$$

$$+ \ldots = \frac{r_{01} + r_{12} \, e^{-2i\delta}}{1 + r_{01} \, r_{12} \, e^{-2i\delta}} \quad . \qquad (8)$$

The mathematical development is identical for both wave components. When appropriate superscripts are added and Equations (6) and (8) are combined, the fundamental equation of ellipsometry results:

$$\tan\Psi\, e^{i\Delta} = \frac{r_{01}^{p} + r_{12}^{p}\, e^{-2i\delta}}{1 + r_{01}^{p}\, r_{12}^{p}\, e^{-2i\delta}} \cdot \frac{1 + r_{01}^{s}\, r_{12}^{s}\, e^{-2i\delta}}{r_{01}^{s} + r_{12}^{s}\, e^{-2i\delta}} \quad . \tag{9}$$

The Fresnel reflection coefficients needed in Equation (9) can be calculated from

$$r_{12} = \frac{\eta_1 \cos\phi_2 - \eta_2 \cos\phi_1}{\eta_1 \cos\phi_2 - \eta_2 \cos\phi_1} \quad . \tag{10}$$

Equation (10) as stated by Jenkins and White[6] is general and can be modified to give the appropriate reflection coefficient by substitution of the correct values for the refractive index, $\eta$, and for the angle of incidence $\phi$. The angle of incidence ($\phi_1$) inside the film and the angle of refraction ($\phi_2$) into the substrate can be calculated using Snell's law[7]:

$$\eta_1 \sin\phi_1 = \eta_2 \sin\phi_2 \quad . \tag{11}$$

# CHAPTER 3

## ELLIPSOMETRIC MEASUREMENTS

The measurement procedure, following Archer[5], used to determine $\Delta$ and $\Psi$ is adjustment of the polarizer and analyzer so that the reflected beam intensity is minimized. There are two polarizer orientations that give minima:

$$\Delta_1' = +\Delta \quad \text{and} \quad \Delta_2' = -\Delta \quad .$$

$\Delta_1'$ and $\Delta_2'$ give distinct minima in which the polarizer settings differ by 90°.

The phase difference between the components, $\Delta'$, is given by

$$\Delta' = (\beta_p - \beta_s)_{\text{incident}} \quad .$$

$\Delta'$ is given by

$$\tan \Delta' = \sin \delta \tan (2P - 90°)$$

where $\delta$ is the phase shift induced by the Babinet-Soleil compensator and P is the polarizer angle. The second measurement, $\Psi$, is given by defining

$$\tan L = \frac{E_p}{E_s}$$

where $E_{p,s}$ is the amplitude of the electric field vector (p or s) of the transmitted beam. L is given by

$$\cos 2L = -\cos\delta \cos 2P \quad .$$

The reflected beam intensity will be minimized when the analyzer setting, $A_0$, satisfies the following equation:

$$\tan \Psi = \cot L \tan (-A_0) \quad .$$

When the polarizer setting is $P_0'$ ($= P_0 \pm 90°$),

$$\tan \Psi = \cot L' \tan A_0'$$

and

$$\cot L' = \tan L \quad ;$$

$$\tan^2 \Psi = \tan A_0' \tan (-A_0) \quad .$$

If the compensator is a quarter wave plate, or is set as such, $\delta = 90°$ and $\Delta$ and $\Psi$ are given by the much simpler

relationships:

$$\Delta = 90° - 2P_0 = 270° - 2P_0' \qquad (12)$$

and

$$\Psi = -A_0 = A_0' \quad . \qquad (13)$$

Equations (6), (7), (8), (9), (10), (11), (12), and (13) must be simultaneously solved to get values for the film thickness, d, on a given substrate. McCrackin developed a computer program to solve these equations and to allow data analysis in many ways[8]. This program was put on the University computer by Dr. Eric Enwall as MACRAC II. The use of this program greatly simplified interpretation of the experiments described here.

A table (Table II-1) of polarizer settings versus film thickness for sodium deoxycholate was generated and used to make Figure II-2. Figure II-2 allows one to determine the film thickness directly from the polarizer settings if the film refractive index is known. The value of $\Psi$, calculated from the analyzer angle, is insensitive to film thickness variations; therefore, an average polarizer setting, P, is all that is required to estimate a film thickness. With ideal compensators and perfect reflectors, the two polarizer settings $P_1$ and $P_2$ differ by exactly 90°. In practice, they deviate significantly so the program calculates a $\Delta$ and $\Psi$ value for each pair of polarizer and analyzer

settings and, then, averages them before calculating a film thickness value. The same film thickness is obtained if the two polarizer settings are used to calculate an average setting (Ex: $[45.60° + (136.40 - 90.00)]/2 = 46.00$).

As mentioned earlier, the analyzer setting (see $\Psi$ value in Table II-1) is insensitive to film thickness; therefore, the average analyzer setting for the first three sodium deoxycholate solutions tested was used as the correct setting for the rest of the measurements in that experiment. This technique was used to save experimental time and to reduce the exposure of the solutions to contamination.

The solution refractive index increased slightly as the sodium deoxycholate concentration increased. Table II-2 shows the effect of increasing the solution refractive index at a constant film thickness of 6Å on the polarizer and analyzer settings. Over the refractive index range used (1.3333 to 1.3344) the polarizer angle changed only 0.01° while the analyzer angle changed 0.06°. The use of a single refractive index for the solution (1.3333) introduced very little error into the film thickness measurements.

The film measurements are quite sensitive to the refractive index of the film-forming material. Since no literature value could be found, the refractive index was calculated from the molar refractivity of sodium deoxycholate. The best values obtained were 1.576 and 1.602. The solubility of sodium deoxycholate is too low to give a large

enough change in solution refractive index for accurate measurements. The refractive indices of sodium deoxycholate were determined by a standard geological technique, matching the crystal's refractive index to that of an oil of accurately known refractive index under a polarizing microscope. The observations showed sodium deoxycholate to have an orthorhombic crystal structure with principal refractive indices of 1.550, 1.538, and 1.533[10]. The geometric mean refractive index of 1.540 was used in this work, as recommended by Bauer and Fajans[11], with good success. Den Engelson and de Koning[12] show that solid state refractive indices can be used to estimate film thicknesses and optical properties for insoluble monolayers on water.

The importance of using the correct refractive index for the film is shown in Table II-3. The polarizer settings for a film 6Å thick vary rapidly with film refractive index. The correct refractive index can be calculated from ellipsometric measurements if the film is relatively thick, say above 50Å. However, with very thin films little information can be obtained unless the film refractive index is known. The films of interest in this research are in the 0-10Å range so the film refractive index is necessary for accurate film thickness measurements.

# CHAPTER 4

## INSTRUMENT AND EXPERIMENTAL DETAILS

A Gaertner Model L119 Ellipsometer mounted for use with liquid surfaces on an Accessory Stand (Model L118HV) was used in these experiments. A schematic view of an ellipsometer is shown in Figure II-3[13].

Light from a mercury vapor lamp passes through a narrow band pass filter that serves as a monochromator. The emitted light, the 5461Å mercury line passes through a collimator into a polarizer. The polarizer, a Glan-Thomson prism system plane-polarizes the light. The Glan-Thomson prism is similar to a Nicol prism but gives higher performance over a wider wavelength range. The prism is aligned to a divided circle that can be read with a precision of 0.01°. The plane polarized light then passes through a Babinet-Soleil compensator which is made of two crystal quartz wedges with their optical axes parallel to their faces and to each other. A plane parallel crystal quartz plate with its optical axis perpendicular to the optical axes of the wedges completes the compensator. Changing the relative

position of the wedges causes a relative retardation of one component of the incident beam to the other. This retardation, a "quarter-wave" or 90°, can be set for a wide range of wavelengths. Details of the construction, accuracy, and calibration of the compensator are given in the instrument manual[14].

Elliptically polarized light from the compensator, set with the major axis at +45° to the plane of incidence, falls on the film and surface to be examined. The reflected light, re-plane-polarized, passes through a second Glan-Thomson prism (the analyzer) to a photomultiplier for analysis.

Accurate determinations of the polarizer and analyzer settings corresponding to the extinction minima were made by the following procedure that is described and justified by Archer[15]. A rough estimate of the minimum was found by sequentially adjusting the polarizer and analyzer position to produce the deepest minimum. Once the rough minimum was found, the analyzer was rotated a few degrees in either direction and an accurate angle measurement was made at a set intensity. The analyzer was rotated back through the minimum to the same intensity reading (usually 20 to 40 units on the microammeter scale). The two accurately known analyzer settings were averaged to obtain the analyzer setting corresponding to the deepest intensity minimum. With the analyzer set to its minimum, the procedure was

repeated with the polarizer. The second set of readings was determined in the same way. This technique is quite precise, usually reproducing to within 0.01°.

The sample cell and holder are shown in Figure II-4. The solution to be analyzed was transferred by pipet to a cell made from a small glass bottle. The bottle was about 4 cm square and 10 cm high. When cut on an angle to minimize reflection interference it held about 12 cc of sample. The cell was overfilled so that the fluid surface bulged above the top of the cell and a few drops were removed by pipet until the light spot seen through the ellipsometer's viewing telescope (replaces photomultiplier in the instrumental arrangement) was round and sharp at the edges. This technique ensured that the level of the fluid was the same in each experiment and that the surface was flat. A single drop made a detectable difference in spot sharpness.

The cell holder was made by machining an aluminum block to produce a thermostatted cell that was held at 25 $\pm$0.1°C. The entire cell and cover were sandblasted to reduce stray reflections of light. The apparatus was durable and convenient to use. The same glass cell was used for all the measurements.

# CHAPTER 5

## DISCUSSION

The ellipsometric data were used to calculate the film thickness and molecular areas for sodium deoxycholate solutions of varying salt content. The data are summarized in Table II-4 and shown in detail in Tables II-5 to II-10. The film thickness was measured as discussed above and the area per molecule calculated using Djavanbakht, Kale, and Zana's value for the molal volume at infinite dilution of sodium deoxycholate, 315.8 $\pm$1 $cm^3$/mole[16]. This value gives a molecular volume of 524.3 $\mathring{A}^3$/molecule which divided by the film thickness yields the projected area per molecule.

Small reports experimental values for deoxycholic acid at pH 2 in 3M NaCl of 85 $\mathring{A}^2$/molecule[17]. Ekwall and Ekholm found about 85 $\mathring{A}$ per molecule in film balance studies[18]. Small estimated that free bile acid molecules are 20-21 $\mathring{A}$ long and about 6-7 $\mathring{A}$ at the narrowest and widest diameters. This estimate gives a molecular volume of 565 to 808 $\mathring{A}^3$/ molecule, which is substantially greater than the 524 $\mathring{A}^3$/ molecule reported earlier. The lower value is assumed to be

correct because of the excellent agreement between ellipsometric data ($84\text{Å}^2$/molecule), surface tension ($84\text{Å}^2$/molecule), and literature values ($85\text{Å}^2$/molecule).

In most of the experiments an increase in film thickness occurs just before the critical micelle concentration and subsides slightly above the CMC. The increase from 6 to 10Å is not large enough to be an orientation change from parallel to perpendicular to the interface which would require a shift to a 14Å film. The film thickness increase was probably due to an insoluble impurity present in very low concentration in the solutions or equipment. As micelles formed, it apparently was solubilized leaving a "clean" deoxycholate film for examination.

The main conclusions drawn in this work are:

1. No multilayers of sodium deoxycholate form at any concentration at alkaline pH, in the salt concentration ranges examined.

2. No shift in orientation from parallel to perpendicular to the interface occurs as the sodium deoxycholate concentration is increased.

3. Ellipsometry is a valuable tool for the study of surface films at air-water interfaces. The experimental problems, especially the constant threat of contamination, are formidable; however, the information gained by this direct method is very valuable.

## REFERENCES


1. A. C. Hall, J. Phys. Chem., 74, 2742 (1970).

2. W. Bayh and H. Pflug, Z. Angew. Phys., 25, 328 (1968).

3. R. Steiger, Helvetica Chimica Acta, 54, 2645 (1971).

4. Tennyson Smith, J. Coll. Interf. Sci., 26, 509 (1968).

5. R. J. Archer, "Manual on Ellipsometry," Gaertner Scientific Corporation, Chicago, Ill.

6. F. A. Jenkins and H. E. White, Fundamentals of Optics, McGraw-Hill (1957), pp. 509-512.

7. Ibid, p. 5.

8. F. L. McCrackin, "A FORTRAN Program for Analysis of Ellipsometer Measurements," NBS Technical Note 470, April 1969.

9. S. Glasstone, Textbook of Physical Chemistry, 2nd Ed., Van Nostrand Co., Inc. (1946), pp. 528-32.

10. V. J. Barczak, Personal Communication, January 5, 1977.

11. N. Bauer and K. Fajans, "Refractometry," in Physical Methods of Organic Chemistry, A. Weissberger, Ed., Interscience (1945), pp. 669-70.

12. D. den Engelson and B. de Koning, J. Chem. Soc., Faraday Trans. I, 70, 1603 (1974).

13. Adapted from R. F. Spanier, "Ellipsometry, A Century-Old New Technique," Industrial Research, September 1975, p. 74.

14. "Instrument Manual 7109-C-116-RO for Ellipsometers L118 and L119 Series," Gaertner Scientific Corporation.

15. Ref. 5, p. 8.

16. A. Djavanbakht, K. Kale, and R. Zana, "Ultrasonic Absorption and Density Studies of the Aggregation in Aqueous Solutions of Bile Acid Salts," submitted to J. Coll. Interf. Sci.

17. Donald M. Small, "The Physical Chemistry of Cholanic Acids," in Bile Acids, P. P. Nair, ed., Plenum Press, New York, 1971, pp. 249-357.

18. P. Ekwall and R. Ekholm, Proc. Intern. Conf. Surface Activity, 2nd, London, Vol. 1, Butterworths, London (1957), p. 23.

TABLE II-1

POLARIZER AND ANALYZER SETTINGS GENERATED BY McCRACKIN'S PROGRAM
FOR SODIUM DEOXYCHOLATE FILMS OF VARIOUS THICKNESSES

ANGLE OF INCIDENCE: 55.33°
COMPENSATOR ORIENTATION: +45.00°
PHASE ANGLE OF COMPENSATOR: +90.00°
REFRACTIVE INDEX, $n$, OF AIR 1.0000
REFRACTIVE INDEX, $n$, OF FILM: 1.540
REFRACTIVE INDEX, $n$, OF WATER: 1.3333

WAVELENGTH: 5461Å
TRANSMISSION OF COMPENSATOR: 1.0000

ABSORPTION COEFFICIENT, $\kappa$, OF AIR: 0.0000
ABSORPTION COEFFICIENT, $\kappa$, OF FILM: 0.0000
ABSORPTION COEFFICIENT, $\kappa$, OF WATER: 0.0000

| Film Thickness, Å | Delta, Δ | psi, Ψ | $P_1$ | $A_1$ | $P_2$ | $A_2$ |
|---|---|---|---|---|---|---|
| 0 | 0 | 3.57 | 45.00 | -3.57 | 135.00 | 3.57 |
| 2 | - .79 | 3.57 | 45.39 | -3.57 | 135.39 | 3.57 |
| 4 | -1.57 | 3.57 | 45.79 | -3.57 | 135.79 | 3.57 |
| 6 | -2.36 | 3.57 | 46.18 | -3.57 | 136.18 | 3.57 |
| 8 | -3.15 | 3.57 | 46.57 | -3.57 | 136.57 | 3.57 |
| 10 | -3.94 | 3.57 | 46.97 | -3.57 | 136.97 | 3.57 |
| 12 | -4.72 | 3.57 | 47.36 | -3.57 | 137.36 | 3.57 |
| 14 | -5.51 | 3.57 | 47.75 | -3.57 | 137.75 | 3.57 |
| 16 | -6.29 | 3.58 | 48.15 | -3.58 | 138.15 | 3.58 |
| 18 | -7.08 | 3.58 | 48.54 | -3.58 | 138.54 | 3.58 |
| 20 | -7.86 | 3.58 | 48.93 | -3.58 | 138.93 | 3.58 |

TABLE II-2

EFFECT OF REFRACTIVE INDEX OF THE SOLUTION ON POLARIZER AND ANALYZER SETTINGS AT CONSTANT FILM THICKNESS (6Å)

| $\eta_{solution}$ | Delta, $\Delta$ | psi, $\Psi$ | $P_1$ | $A_1$ | $P_2$ | $A_2$ |
|---|---|---|---|---|---|---|
| 1.3333 | -2.36 | 3.57 | 46.18 | -3.57 | 136.18 | 3.57 |
| 1.3339 | -2.36 | 3.55 | 46.18 | -3.55 | 136.18 | 3.55 |
| 1.3345 | -2.37 | 3.53 | 46.18 | -3.53 | 136.18 | 3.53 |
| 1.3351 | -2.37 | 3.51 | 46.19 | -3.51 | 136.19 | 3.51 |

REFRACTIVE INDEX MEASUREMENTS ON SODIUM DEOXYCHOLATE SOLUTIONS

| Conc. NaDC, M | $\eta_{25°C}$ |
|---|---|
| 0.0001 | 1.3334 |
| 0.001 | 1.3338 |
| 0.005 | 1.3341 |
| 0.01 | 1.3344 |

TABLE II-3

EFFECT OF FILM REFRACTIVE INDEX ON POLARIZER AND ANALYZER SETTINGS AT CONSTANT FILM THICKNESS (6Å)

| $n_{Film}$ | Delta, $\Delta$ | psi, $\Psi$ | $P_1$ | $A_1$ | $P_2$ | $A_2$ |
|---|---|---|---|---|---|---|
| 1.540 | -2.36 | 3.57 | 46.18 | -3.57 | 136.18 | 3.57 |
| 1.576 | -2.90 | 3.57 | 46.45 | -3.57 | 136.45 | 3.57 |
| 1.6024 | -3.32 | 3.57 | 46.66 | -3.57 | 136.66 | 3.57 |

TABLE II-4

SUMMARY OF FILM THICKNESS DATA
FROM ELLIPSOMETRIC EXPERIMENTS

| NaDC in Electrolyte | Estimates From Plotted Data | | All Values Used Averaged | |
|---|---|---|---|---|
| | Film Thickness, Å | Molecular Area, Å$^2$/mol | Film Thickness, Å | Molecular Area, Å$^2$/mol |
| 0.01M NaOH | 6.9 | 76 | 6.63 | 79 |
| 0.01M NaOH, 0.15M NaCl | 6.1 | 86 | 5.89 | 89 |
| 0.01M NaOH, 0.30M NaCl* | 7.4 | 71 | 7.04 | 74 |
| 0.001M NaOH, 0.50M NaCl | 6.1 | 86 | 6.66 | 79 |
| 0.01M NaOH, 0.50M NaCl | 6.2 | 85 | 6.20 | 85 |
| 0.1M NaOH, 0.50M NaCl | 6.2 | 85 | 6.05 | 87 |
| Averages | 6.3 | 83 ±4 | 6.29 | 84 ±5 |

*Deleted in Average calculations because of impurities from a cracked water line in water distillation unit.

TABLE II-5

ELLIPSOMETRIC MEASUREMENTS ON
SODIUM DEOXYCHOLATE IN 0.01M NaOH

| NaDC Solution Conc., M | $P_1$ | $A_1$ | $P_2$ | $A_2$ | $\bar{P}$ | $\bar{A}$ | Film Thickness Å |
|---|---|---|---|---|---|---|---|
| 0.0001 | 45.46 | 356.51 | 136.15 | 3.64 | 45.82 | 3.57 | 4.1 |
| 0.0004 | 46.05 | 356.51 | 136.48 | 3.66 | 46.27 | 3.58 | 6.4 |
| 0.001 | 46.27 | 356.49 | 136.30 | 3.63 | 46.29 | 3.57 | 6.5 |
| 0.002 | 46.18 | 356.52 | 136.49 | 3.62 | 46.39 | 3.55 | 7.0 |
| 0.004 | 46.43 | 356.55 | 136.37 | 3.69 | 46.40 | 3.57 | 7.1 |
| 0.005 | 47.41 | 356.69 | 136.26 | 3.59 | 46.84 | 3.45 | 9.3 |
| 0.008 | 46.55 | 356.59 | 136.21 | 3.58 | 46.38 | 3.50 | 7.0 |
| 0.01 | 46.32 | 356.59 | 136.13 | 3.62 | 46.23 | 3.52 | 6.3 |
| 0.02 | 46.33 | 356.60 | 136.04 | 3.54 | 46.19 | 3.47 | 6.0 |

TABLE II-6

ELLIPSOMETRIC MEASUREMENTS ON SODIUM DEOXYCHOLATE IN 0.01M NaOH AND 0.15M NaCl

| NaDC Solution Conc., M | $P_1$ | $A_1$ | $P_2$ | $A_2$ | $\overline{P}$ | $\overline{A}$ | Film Thickness A |
|---|---|---|---|---|---|---|---|
| $1 \times 10^{-6}$ | 45.45 | 356.60 | 135.53 | 3.80 | 45.49 | 3.60 | 2.5 |
| $4 \times 10^{-6}$ | 45.70 | 356.60 | 135.80 | 3.80 | 45.75 | 3.60 | 3.8 |
| $1 \times 10^{-5}$ | 45.99 | 356.60 | 136.02 | 3.80 | 46.01 | 3.60 | 5.1 |
| $4 \times 10^{-5}$ | 45.96 | 356.60 | 136.10 | 3.80 | 46.03 | 3.60 | 5.3 |
| $1 \times 10^{-4}$ | 46.12 | 356.60 | 136.21 | 3.80 | 46.16 | 3.60 | 5.9 |
| $4 \times 10^{-4}$ | 46.21 | 356.60 | 136.23 | 3.80 | 46.22 | 3.60 | 6.2 |
| $8 \times 10^{-4}$ | 46.27 | 356.60 | 136.09 | 3.80 | 46.18 | 3.60 | 6.0 |
| $1 \times 10^{-3}$ | 46.24 | 356.60 | 136.38 | 3.80 | 46.31 | 3.60 | 6.6 |
| $4 \times 10^{-3}$ | 46.15 | 356.60 | 136.19 | 3.80 | 46.17 | 3.60 | 6.0 |
| $8 \times 10^{-3}$ | 46.08 | 356.60 | 136.29 | 3.80 | 46.19 | 3.60 | 6.1 |
| $1 \times 10^{-2}$ | 46.03 | 356.60 | 136.22 | 3.80 | 46.13 | 3.60 | 5.8 |

TABLE II-7

ELLIPSOMETRIC MEASUREMENTS ON SODIUM DEOXYCHOLATE
IN 0.01M NaOH AND 0.30M NaCl*

| NaDC Solution Conc., M | $P_1$ | $A_1$ | $P_2$ | $A_2$ | $\bar{P}$ | $\bar{A}$ | Film Thickness Å |
|---|---|---|---|---|---|---|---|
| $1 \times 10^{-6}$ | 45.26 | 356.77 | 135.26 | 3.69 | 45.23 | 3.46 | 1.2 |
| $4 \times 10^{-6}$ | 45.82 | 356.77 | 135.81 | 3.69 | 45.82 | 3.46 | 4.2 |
| $1 \times 10^{-5}$ | 45.95 | 356.77 | 135.96 | 3.69 | 45.96 | 3.46 | 4.9 |
| $4 \times 10^{-5}$ | 46.16 | 356.77 | 136.12 | 3.69 | 46.14 | 3.46 | 5.8 |
| $1 \times 10^{-4}$ | 46.34 | 356.77 | 136.29 | 3.69 | 46.32 | 3.46 | 6.7 |
| $4 \times 10^{-4}$ | 46.58 | 356.77 | 136.61 | 3.69 | 46.59 | 3.46 | 8.1 |
| $8 \times 10^{-4}$ | 46.67 | 356.77 | 136.69 | 3.96 | 46.68 | 3.46 | 8.5 |
| $1 \times 10^{-3}$ | 46.74 | 356.77 | 136.72 | 3.69 | 46.73 | 3.46 | 8.8 |
| $2 \times 10^{-3}$ | 46.79 | 356.77 | 136.68 | 3.69 | 46.74 | 3.46 | 8.8 |
| $4 \times 10^{-3}$ | 46.39 | 356.77 | 136.53 | 3.69 | 46.46 | 3.46 | 7.4 |
| $6 \times 10^{3}$ | 46.31 | 356.77 | 136.42 | 3.69 | 46.37 | 3.46 | 7.0 |
| $8 \times 10^{-3}$ | 46.50 | 356.77 | 136.54 | 3.69 | 46.52 | 3.46 | 7.7 |
| $1 \times 10^{-2}$ | 46.42 | 356.77 | 136.45 | 3.69 | 46.44 | 3.46 | 7.3 |
| $2 \times 10^{-2}$ | 46.39 | 356.77 | 136.49 | 3.69 | 46.44 | 3.46 | 7.3 |
| $1 \times 10^{-1}$ | 45.93 | 356.77 | 136.47 | 3.69 | 46.20 | 3.46 | 6.1 |

*Deleted in average calculations because of impurities from a cracked water line in water distillation unit.

TABLE II-8

ELLIPSOMETRIC MEASUREMENTS ON SODIUM DEOXYCHOLATE
IN 0.01M NaOH AND 0.50M NaCl

| NaDC Solution Conc., M | $P_1$ | $A_1$ | $P_2$ | $A_2$ | $\bar{P}$ | $\bar{A}$ | Film Thickness Å |
|---|---|---|---|---|---|---|---|
| $1 \times 10^{-6}$ | 45.95 | 356.55 | 135.53 | 3.40 | 45.74 | 3.43 | 3.8 |
| $4 \times 10^{-6}$ | 46.36 | 356.55 | 135.58 | 3.40 | 45.97 | 3.43 | 4.9 |
| $1 \times 10^{-5}$ | 46.62 | 356.55 | 135.73 | 3.40 | 46.18 | 3.43 | 6.0 |
| $4 \times 10^{-5}$ | 46.67 | 356.55 | 135.81 | 3.40 | 46.24 | 3.43 | 6.3 |
| $1 \times 10^{-4}$ | 46.75 | 356.55 | 135.77 | 3.40 | 46.26 | 3.43 | 6.4 |
| $4 \times 10^{-4}$ | 46.80 | 356.55 | 136.34 | 3.40 | 46.59 | 3.43 | 8.0 |
| $8 \times 10^{-4}$ | 46.83 | 356.55 | 136.18 | 3.40 | 46.51 | 3.43 | 7.7 |
| $1 \times 10^{-3}$ | 46.69 | 356.55 | 136.17 | 3.40 | 46.43 | 3.43 | 7.4 |
| $2 \times 10^{-3}$ | 46.65 | 356.55 | 136.01 | 3.40 | 46.33 | 3.43 | 6.8 |
| $4 \times 10^{-3}$ | 46.50 | 356.55 | 135.81 | 3.40 | 46.16 | 3.43 | 5.9 |
| $6 \times 10^{-3}$ | 46.43 | 356.55 | 135.76 | 3.40 | 46.09 | 3.43 | 5.6 |
| $8 \times 10^{-3}$ | 46.51 | 356.55 | 135.89 | 3.40 | 46.20 | 3.43 | 6.1 |
| $1 \times 10^{-2}$ | 46.32 | 356.55 | 135.55 | 3.40 | 45.94 | 3.43 | 5.8 |
| $2 \times 10^{-2}$ | 46.63 | 356.55 | 135.79 | 3.40 | 46.21 | 3.43 | 6.2 |

TABLE II-9

ELLIPSOMETRIC MEASUREMENTS ON SODIUM DEOXYCHOLATE
IN 0.001M NaOH AND 0.50M NaCl

| NaDC Solution Conc., M | $P_1$ | $A_1$ | $P_2$ | $A_2$ | $\bar{P}$ | $\bar{A}$ | Film Thickness Å |
|---|---|---|---|---|---|---|---|
| $1 \times 10^{-6}$ | 45.08 | 356.56 | 136.49 | 3.59 | 45.79 | 3.52 | 4.0 |
| $4 \times 10^{-6}$ | 45.43 | 356.55 | 136.73 | 3.62 | 46.08 | 3.53 | 5.5 |
| $1 \times 10^{-5}$ | 45.53 | 356.55 | 136.82 | 3.62 | 46.18 | 3.53 | 6.0 |
| $4 \times 10^{-5}$ | 45.73 | 356.55 | 136.76 | 3.62 | 46.25 | 3.53 | 6.3 |
| $1 \times 10^{-4}$ | 45.79 | 356.55 | 136.99 | 3.62 | 46.39 | 3.53 | 7.0 |
| $4 \times 10^{-4}$ | 46.02 | 356.55 | 137.27 | 3.62 | 46.65 | 3.53 | 8.4 |
| $8 \times 10^{-4}$ | 46.26 | 356.55 | 137.48 | 3.62 | 46.87 | 3.53 | 9.5 |
| $1 \times 10^{-3}$ | 46.16 | 356.55 | 137.38 | 3.62 | 46.72 | 3.53 | 8.7 |
| $2 \times 10^{-3}$ | 45.82 | 356.55 | 137.12 | 3.62 | 46.47 | 3.53 | 7.4 |
| $4 \times 10^{-3}$ | 45.40 | 356.55 | 136.96 | 3.62 | 46.18 | 3.53 | 6.0 |
| $6 \times 10^{-3}$ | 45.40 | 356.55 | 136.96 | 3.62 | 46.18 | 3.53 | 6.0 |
| $8 \times 10^{-3}$ | 45.36 | 356.55 | 136.91 | 3.62 | 46.14 | 3.53 | 5.8 |
| $1 \times 10^{-2}$ | 45.46 | 356.55 | 136.90 | 3.62 | 46.18 | 3.53 | 6.0 |

TABLE II-10

ELLIPSOMETRIC MEASUREMENTS ON SODIUM DEOXYCHOLATE
IN 0.1M NaOH AND 0.50M NaCl

| NaDC Solution Conc., M | $P_1$ | $A_1$ | $P_2$ | $A_2$ | $\bar{P}$ | $\bar{A}$ | Film Thickness Å |
|---|---|---|---|---|---|---|---|
| $1 \times 10^{-6}$ | 45.32 | 356.63 | 136.68 | 3.43 | 46.00 | 3.40 | 5.1 |
| $1 \times 10^{-5}$ | 45.52 | 356.68 | 136.84 | 3.46 | 46.18 | 3.39 | 6.0 |
| $4 \times 10^{-5}$ | 45.56 | 356.66 | 136.88 | 3.45 | 46.22 | 3.40 | 6.2 |
| $1 \times 10^{-4}$ | 45.69 | 356.66 | 136.83 | 3.45 | 46.26 | 3.40 | 6.4 |
| $4 \times 10^{-4}$ | 45.84 | 356.66 | 136.76 | 3.45 | 46.30 | 3.40 | 6.6 |
| $8 \times 10^{-4}$ | 45.65 | 356.66 | 137.10 | 3.45 | 46.38 | 3.40 | 7.0 |
| $1 \times 10^{-3}$ | 45.78 | 356.66 | 137.13 | 3.45 | 46.42 | 3.40 | 7.2 |
| $2 \times 10^{-3}$ | 45.72 | 356.66 | 136.71 | 3.45 | 46.22 | 3.40 | 6.2 |
| $4 \times 10^{-3}$ | 45.62 | 356.66 | 136.63 | 3.45 | 46.13 | 3.40 | 5.8 |
| $6 \times 10^{-3}$ | 45.31 | 356.66 | 136.89 | 3.45 | 46.10 | 3.40 | 5.6 |
| $8 \times 10^{-3}$ | 45.37 | 356.66 | 136.90 | 3.45 | 46.14 | 3.40 | 5.8 |
| $1 \times 10^{-2}$ | 45.29 | 356.66 | 136.77 | 3.45 | 46.03 | 3.40 | 5.2 |
| $2 \times 10^{-2}$ | 45.25 | 356.66 | 136.89 | 3.45 | 46.07 | 3.40 | 5.5 |

FIGURE II-1

MULTIPLE REFLECTION OF LIGHT FROM A FILM COVERED SURFACE

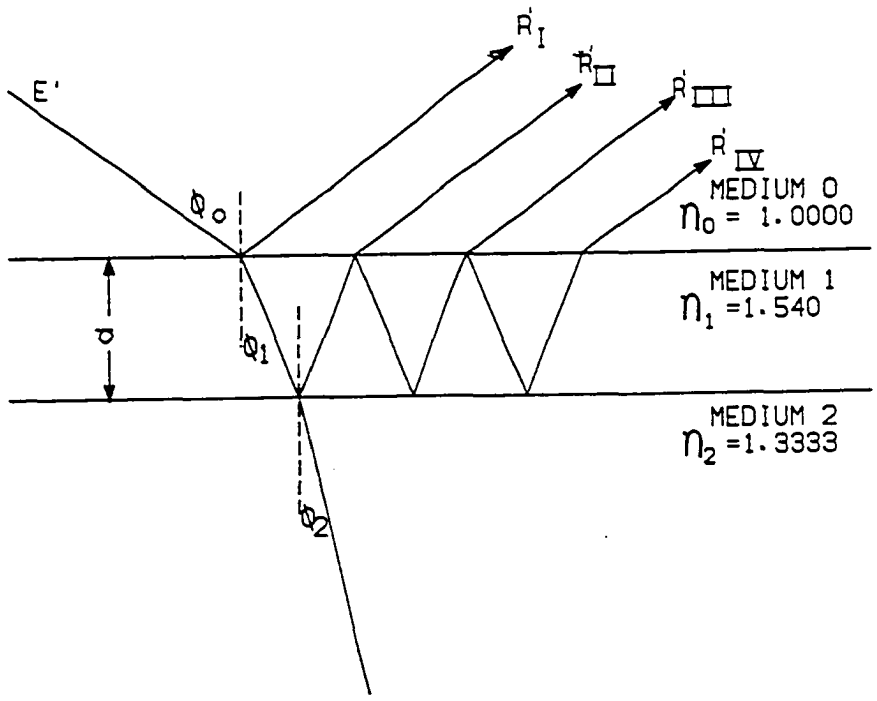


FIGURE II-2

CALCULATION OF FILM THICKNESS
FROM POLARIZER SETTINGS

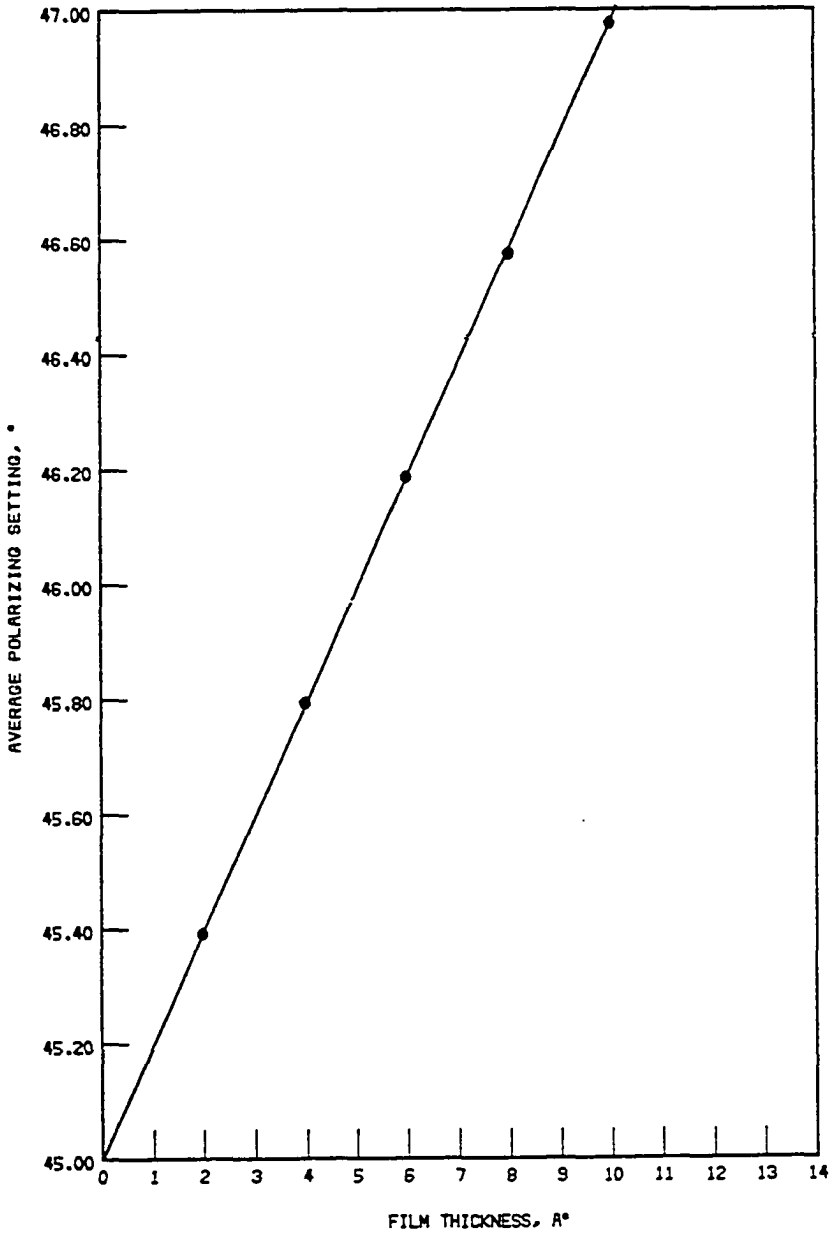


FIGURE II-3

SCHEMATIC VIEW OF AN ELLIPSOMETER

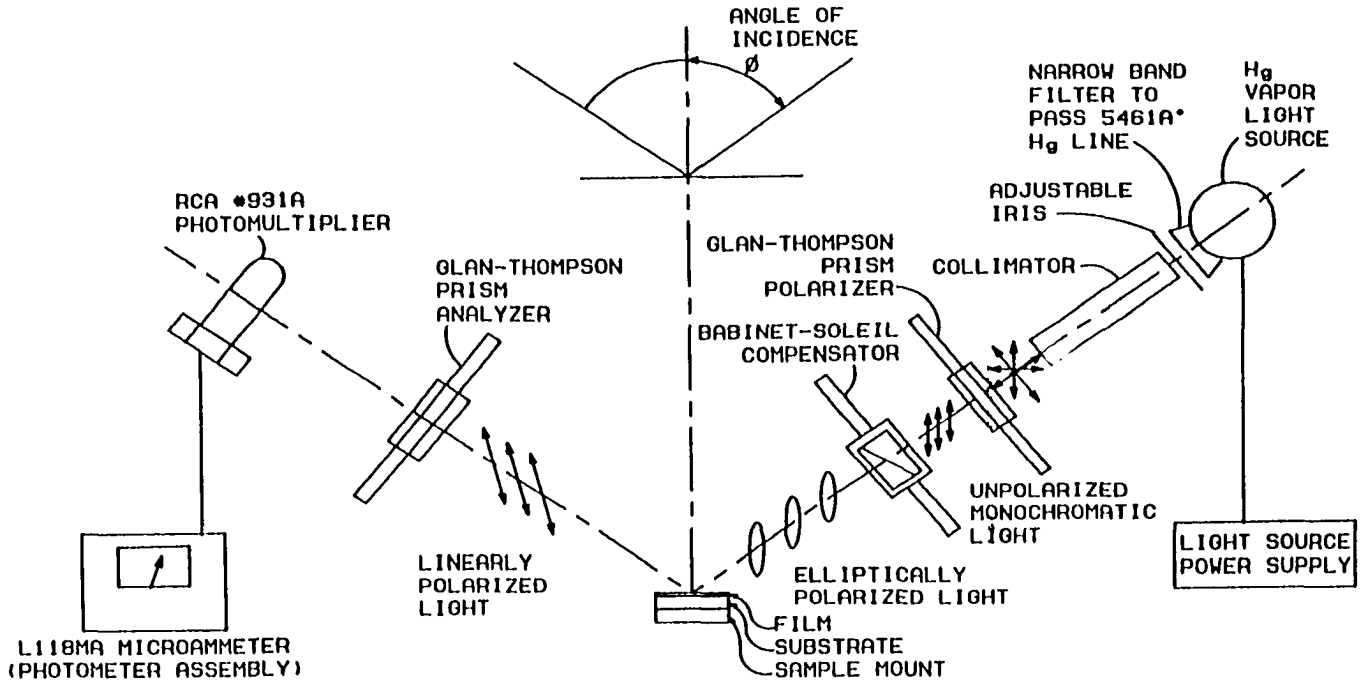
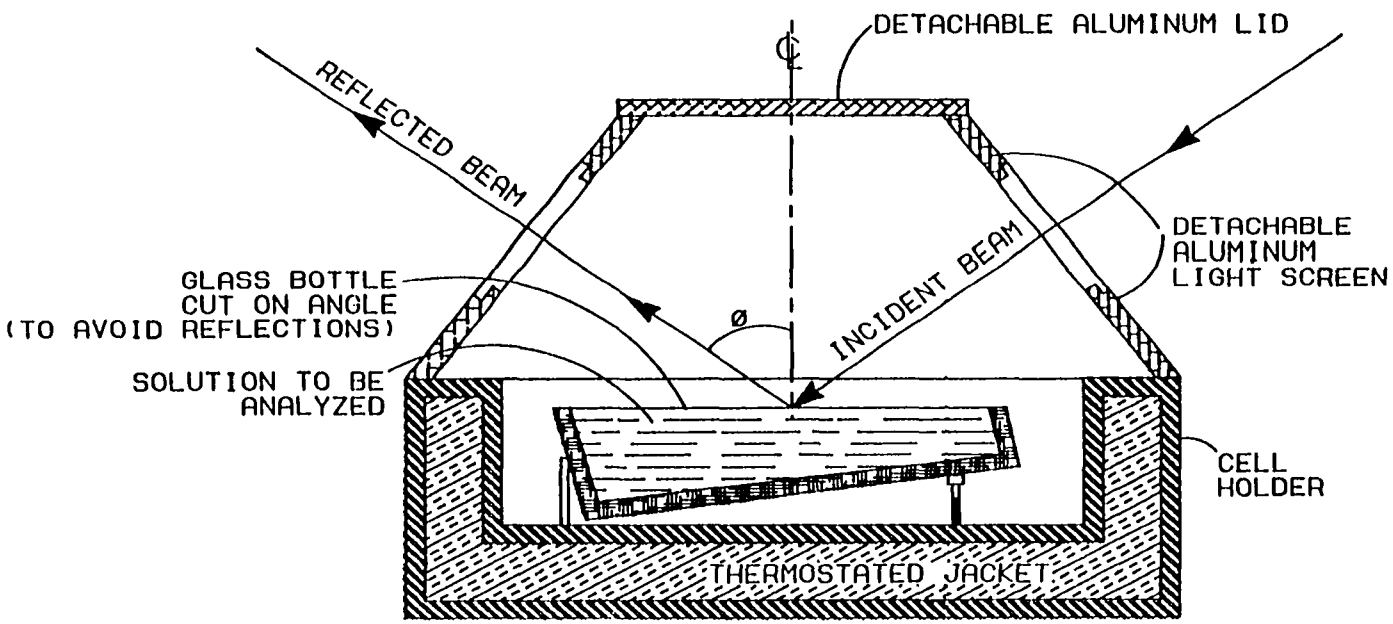


FIGURE II-4

CROSS SECTION VIEW OF THE ELLIPSOMETRY CELL AND CHAMBER



# III. ESTIMATION OF MICELLAR PROPERTIES FROM SURFACE TENSION MEASUREMENTS

## CHAPTER 1

## INTRODUCTION

Micellar properties such as size, equilibrium constants, and free energy of micellization are hard to measure. The critical micelle concentration (CMC), the most easily obtained and most studied micelle property, can be measured by light scattering, surface tension, conductimetric and numerous other methods. Shinoda lists twenty-one techniques used to measure critical micelle concentrations of surface active materials[1]. Micelle sizes or aggregation numbers have been measured by several methods: light scattering, electrophoretic mobility, small angle x-ray diffraction, diffusion - viscosity, and osmotic pressure are examples[2]. The best and most powerful technique for estimation of micellar size is light scattering[3,4].

Light scattering was first used for micelle size determination by Debye and Anacker[5]. It takes advantage of the fact that light scattering turbidity, measured at 90°,

is a function of surfactant concentration. Above the CMC, a strong increase in turbidity with concentration is noted. Debye states that the turbidity versus concentration curve above the CMC is given by:

$$\frac{HC'}{T'} = \frac{1}{M_m} + 2BC'$$

where $C' = C - C_o$ ($C$ = concentration and $C_o$ = CMC), $M_m$ is the micelle molecular weight, B is the second virial coefficient, $T' = T - T_o$ ($T$ = solution turbidity and $T_o$ = solvent turbidity), and H is a constant defined as:

$$H = [32\pi\eta_o^2 (\eta - \eta_o)^2/c^2] \, 3\lambda^4 N \quad .$$

N is Avogadro's number, $\eta$ is the solution refractive index, $\lambda$ is the wavelength of incident light, and $\eta - \eta_o/c$ is the concentration gradient of the refractive index. If the monomer molecular weight is known, the aggregation number of the micelle can be calculated. The ratio of scattering at other angles to that at 90° can be used to estimate the shape and dimensions of micelles.

The present study introduces and develops another way to estimate aggregation numbers of relatively small micelles. Surface tension measurements above the CMC are used to measure the change in surfactant activity which is fitted to the Gibbs adsorption isotherm and a mass action model to find values for the aggregation numbers.

# CHAPTER 2

## A MASS ACTION MODEL OF MICELLIZATION

Discussion of Literature on Micellization Models.

Two major models of micelle formation have been used to explain the properties of micellar solutions. The earlier phase-separation model treated micellization as the formation of a separate hydrocarbon phase as small "droplets" - or micelles - in the bulk aqueous phase. The model predicts that the surface tension of a micellar solution is constant above the CMC. The Gibbs equation $d\gamma = -\Gamma RTd\ln a$, gives a constant surface tension above the CMC only if both $\Gamma$ and the surfactant activity, a, remain constant. The surfactant concentration at the interface, $\Gamma$, is believed to remain constant above the CMC. Ellipsometric measurements, Part II, confirm this prediction. The presence of a separate surfactant phase requires that the surfactant activity, a, be constant.

Mukerjee[6] gives numerous references supporting the phase separation model and then points out some problems with the theory. It predicts that an abrupt change in

properties occurs at the CMC. Experimental results show that a smooth change in properties occurs through the CMC region and that the monomer activity slowly increases beyond the CMC.

Corkill and co-workers, in a series of papers[7,8,9], studied the thermodynamics of micellization and models of micelle formation for nonionic surfactants. Their vapor pressure data on micellar systems show that the activity of the monomer continues to increase above the CMC, in agreement with the mass action model. The earliest paper in the series[7] attributed the vapor pressure depression to a decrease in micellar size. Later light scattering studies of higher molecular weight nonionic surfactants[9] indicate that the micelles first have comparatively low aggregation numbers just above the CMC and increase over a narrow concentration range (about five times the CMC). Above this concentration, $C_L$, the micelle remains constant in size until the effects of interparticle interference ruin the accuracy of light scattering techniques.

The work described above supports the mass action model of micelle formation. Stigter and Overbeek[10] addressed the question of the micelle size distribution for spherical micelles by considering the competing effects of electrical charge and the hydrophobic interactions in micellization. They show that minimization of the total free energy ideally requires a monosized micelle while in a real

system a narrow size distribution is predicted. They estimated a range of aggregation numbers from 80 to 130 with mean of 105 for a highly charged spherical micelle of sodium lauryl sulfate in 0.05M NaCl.

Clayfield and Matthews[11] show that the surface tension decreases significantly above the CMC for sodium dodecylsulfate. They attribute the change to an activity coefficient effect and show the surface tension data plotted against activity calculated from the Debye-Hückel equation and from osmotic coefficient data. The Debye-Hückel calculations show a decrease in surface tension with increasing activity while the osmotic coefficient data (from freezing point depression) show virtually no change in activity at higher concentrations. The data were obtained for solutions with no added electrolyte. The authors support the phase separation model and claim the change in surface tension seen by others is due to non-equilibrium measurements or activity coefficient effects.

Elworthy and Mysels[12] made a very precise study of sodium dodecylsulfate solutions both below and above the CMC to conclusively show that the surface tension decreased and, hence, that the monomer activity increased beyond the CMC. They concluded that the phase separation theory of micellization did not apply in this case while a simple mass action model fit their data well. Their work showed that activity coefficient effects would cause the surface tension to

decrease beyond the CMC even more than observed.

Hall and Pethica[13] discussed the thermodynamics of micellization using Hill's small system method of statistical thermodynamics. They combined the phase separation approach and the mass action approach to produce an integrated description of micelle formation. They indicate that the mass action model is appropriate when relatively small micelles form. When large micelles form they favor the phase separation model.

More recent work by Tanford[14], Aniansson et. al.[15], Ruckenstein and Nagarajan[16,17], and P. Mukerjee[18] support the mass action approach to micellization as a stepwise association of monomers to form an aggregate like:

$$2M_1 \overset{K_2}{\rightarrow} M_2 \; ; \; M_2 + M \overset{K_3}{\rightarrow} M_3 \; ; \; \ldots \; ; \; M_j - 1 + M \overset{K_j}{\rightarrow} M_j$$

or

$$j\,M \overset{B_j}{\rightarrow} M_j$$

where $K_j$ is the stepwise association constant and $B_j$ is the overall association constant.

Ozeki and co-workers[19] recently combined application of the Gibbs adsorption equation and the Langmuir model of adsorption to the surface adsorption and surface tension of dodecyldimethyl ammonium chloride solutions. They worked at salt concentrations from 0 to 0.94M sodium chloride in their attempt to account for the positive and negative

adsorption of sodium and chloride ions. They showed that the surfactant cation formed a soluble monolayer while the chloride formed a diffuse layer near the interface. They detected no change in surface tension above the CMC; however, their data by the drop weight method showed large fluctuations ($\pm$0.5 dynes/cm) in the CMC region. They fit their data to the Gibbs adsorption equation to calculate the amount adsorbed and then used the Langmuir isotherm as the model for surface adsorption.

The preceding survey of the literature demonstrates that the mass action model of micellization is believed to best explain the appearance and properties of micelles for a great variety of systems. It also shows that formation of a soluble monolayer can be explained using the Langmuir isotherm and that surface tension versus concentration data can be explained using the Gibbs adsorption equation above and below the CMC.

The research reported here used all three of these ideas to correlate properties of sodium deoxycholate solutions. The validity of the Langmuir isotherm for the formation of the soluble monolayer was confirmed by the ellipsometric measurements reported in Section II of this dissertation.

Mass Action Model of Micellization. The Gibbs adsorption equation relates the change in surface coverage to the change in monomer concentration[20]. The Gibbs

adsorption equation

$$\frac{-d\gamma}{RTd\ln a_2} = \Gamma_2 - \frac{X_2}{X_1}\Gamma_1$$

reduces to:

$$\frac{-d\gamma}{RTd\ln a_2} = \Gamma_2 \qquad (1)$$

when $X_2/X_1$ is much less than 1. The activity, $a_2$, can be replaced by the molar concentration when an excess of electrolyte with a common ion is present. Equation (1) further reduces to

$$d\gamma = -\Gamma_2 \, RTd\ln c_2$$

where $\gamma$ is the surface tension and $\Gamma$ is the amount of surfactant adsorbed in moles/cm$^2$. $\Gamma$ is related to, $\Gamma_m$, the surfactant concentration at monolayer coverage through the Langmuir isotherm:

$$\Gamma = \Gamma_m \frac{C_m}{\alpha + C_m} \qquad (2)$$

where $C_m$ is the surfactant monomer concentration and $\alpha$ is the surfactant concentration at which $\Gamma = \Gamma_m/2$. Equations (1) and (2) are combined to give:

$$d\gamma = - \Gamma_m RT \frac{d\, C_m}{\alpha + C_m}$$

which when integrated gives:

$$\frac{\gamma_o - \gamma}{\Gamma_m RT} = \ln\ (1 + \frac{C_m}{\alpha}) \qquad (3)$$

where $\gamma_o$ is the electrolyte surface tension. Equation (3) was first presented by Szyszkowski as a semiempirical equation.

The micelle is assumed to form by the single micelle species mass action model proposed by Tanford and many others[14-18]. Stated for sodium deoxycholate the association equation is:

$$n\ DC^- \xrightarrow{K_n} (DC^-)_n$$

where $K_n$ is the association constant for the formation of sodium deoxycholate micelles of aggregation number, n. The total sodium deoxycholate concentration $C_T$ is given by

$$C_T = C_m + nK_n C_m^{\,n} \quad . \qquad (4)$$

The association constant, $K_n$, was rewritten $K^n$ for convenience in computation. As the micelle aggregation number increased, $K_n$ became larger than the numerical range of the IBM computer system. The entire surface tension versus

concentration curve was fitted to Equations (3) and (4) using Marquardt strategy in a program written by Eric Enwall[21]. Trial values of n, $\alpha$, $\Gamma_m$, and K were chosen and the program executed. The procedure adjusts the variable parameters to solve Equation (3) for $C_m$ using the trial values and experimental surface tension values. Then $C_T$ is calculated and compared to the actual value for each point. The procedure seeks to minimize the sum of the differences between the actual $C_T$ and the calculated $C_T$.

# CHAPTER 3

## EXPERIMENTAL DETAILS

Chemicals. Sodium deoxycholate obtained from Sigma Chemical Company was used in all experiments. Initially it was purified by precipitation as the acid and recrystallized from ethanol; however, when no difference in results was detected with the unpurified material no further purification was attempted because of poor yields. Reagent grade sodium hydroxide and sodium chloride were used without further purification. Ellipsometric measurements served as a very sensitive detector of contamination as the smallest amount of surface active contaminant gave a detectable film. Water was doubly distilled with the second distillation being done in an all-glass still that ran continuously. Even with stringent precautions contamination problems were frequently encountered.

Equipment. An Ainsworth Chain-O-Matic (Model DLB) analytical balance was modified for use as a Wilhelmy plate surface tension balance. Although two similar balances were used (Serial No. 30928 and 36350), the second was used for

the bulk of the work. The pans and pan arrest mechanism were removed and a Wilhelmy plate attached to the left arm of the balance. A counterweight of a small plastic vial filled with glass beads was used to balance the weight of the plate.

The plates used were made by carefully sandblasting each side of thin platinum sheets with very fine (<44μm) alumina powder. Hanger wires made of 1mm platinum wire were pressure welded to the plate. In use the bottom edge of the plate was leveled to the liquid surface by carefully bending the hanger wire so that the reflection of light from the plate and liquid surface showed that the plate was accurately leveled. The sandblasting roughened the plate so that dewetting would be less likely. Jordan and Lane[22] showed that a roughened surface reduced dewetting and improved accuracy in surface tension measurements.

The plate dimensions are shown in Table III-1. Plate 2 was used with Balance 36350 for most of the work. The equipment arrangement is shown schematically in Figure III-1. The solution to be measured was put into a 100 mm Petri dish on an aluminum heat exchanger. A large diameter (125 mm) glass tube about 70 mm long was used as a shield against air currents and dust. The lid was a plate glass disc split into two pieces and drilled to fit around the hanger wire without touching. A Haake FK2 Constant Temperature Circulator brought the whole system to 25.0 $\pm$0.1°C in

about twenty minutes. The procedure used was to put the sample to be measured in the dish and to allow at least twenty minutes for temperature stabilization before measuring the surface tension.

The "maximum pull" technique which measures the force necessary to detach the plate from the liquid surface was used. This technique avoids contact angle effects by assuming a zero contact angle at the instant of detachment. The measurements were corrected to equilibrium by deducting the force required to pull the liquid below the plate edge to the maximum height above the equilibrium surface level. LaMer and Robbins[23] made this correction by calculating the volume so lifted. This volume is given by:

$$V = t \times l \times h$$

where t is the plate thickness, l is the plate edge length, and h is the height that the plate reached above the equilibrium position. A thin plate, as used in this work, is best because the correction required is small.

The most difficult part of this correction method is estimation of the height above equilibrium that the plate reached. This problem was solved by calibrating the vertical displacement of the plate edge to the balance pointer travel with a precision cathetometer. Both balances used had similar displacements per unit of pointer travel as

shown in the calibration data (Table III-2).

The correction required was virtually constant for all measurements (+3 units or 0.98 mm). Each solution's surface tension was calculated using LaMer and Robbins' equation:

$$\gamma_{corr} = (g/p)\ (M_{max} - \rho_{H_2O}\ V) \qquad (5)$$

where g is the gravitational constant (979.65 $cm/s^2$ corrected to Oklahoma City), p is the plate perimeter (7.6133 cm for plate 2), $M_{max}$ is the mass required to pull the plate from the liquid surface, $\rho_{H_2O}$ is the density of water (0.9970 $gm/cm^3$ at 25°C), and V is the volume of the extra liquid lifted above the equilibrium surface level $8.29 \times 10^{-4}$ $cm^3$/unit).

Pure water was tested repetitively to measure the precision and accuracy of the equipment. The value obtained for pure water at 25°C was 72.44 $\pm$0.06 dynes/cm slightly higher than the accepted value of 72.02 dynes/cm[24]. No correction was applied to the experimental data because the difference between the electrolyte and solution surface tension was used in all computations. The error should be nearly constant and minimized by using this technique. The surface tension data are presented in Tables III-3 through III-7. Both the corrected values and the maximum pull values are shown.

# CHAPTER 4

## DISCUSSION

The surface tension versus concentration data were used to calculate the adjustable parameters in the Gibbs/ Langmuir adsorption equations. The non-linear least squares regression method used minimizes the sum of the square of the difference (sum del. sq.) between calculated and actual concentrations. One data set (0.01M NaOH and 0.50M NaCl) would not converge on a best fit unless the micelle size, n, was fixed. The best minimum was found by increasing n to find the minimum sum. del. sq. and root mean square deviation. Analysis of the other data sets yielded unique minima without manipulation.

The parameters evaluated were the micelle size, n; the concentration, $\alpha$, at which a half monolayer has formed; $\Gamma_m RT$ which allows calculation of $\Gamma_m$, the surface deoxycholate concentration required to form a complete monolayer; and the micelle association constant $K_n$. The results of the data fitting are shown in Table III-9.

The micelle sizes obtained were compared to the

values tabulated by Small in his review on the physical chemistry of cholanic acids[25]. Figure III-2 shows the comparison graphically. My data show that at low salt concentrations a micelle of twelve to fourteen molecules forms and maintains that size over the range of 0.01 to 0.16 M total salt concentration. All my experiments were performed in 0.01M NaOH to ensure complete dissociation of the bile acid. The literature results at low salt concentrations were done in the pH 7 to 9 range. At higher salt contents, the micelle size appears to level off at about 40-42 molecules.

The small micelle size (four molecules) inferred from literature data at low salt concentration may occur because undissociated deoxycholic acid molecules that are insoluble in water are solubilized by deoxycholate anions.

The micelle association constants were initially calculated as a function of micelle size in micromolar units for convenience in computation. When recalculated in molar units, the association constants are on the order of $10^{23}$ to $10^{124}$ ($M^{1-n}$ units) depending on the total salt concentration. The free energy of micellization per monomer, $\Delta G_m$, was calculated using

$$\Delta G_m = \frac{\Delta G}{n} = \frac{-RT\ln K_n}{n} = -RT\ln K \quad .$$

The symbols are defined by Equation (4) and the discussion

following it. The free energy values obtained agree well with values for sodium taurocholate and sodium taurodeoxycholate (-3.43 and -3.79 Kcal/M at 20°C, respectively)[26]. The free energies are plotted versus salt concentration in Figure III-3. The free energy of micellization becomes more negative and then appears to level off with increasing salt concentration. Larger micelles are therefore favored because the free energy per micelle becomes more negative.

The sodium deoxycholate concentration at monolayer coverage, $\Gamma_m$, is obtained from $\Gamma_m RT$ when RT is eliminated. The data in Table IX are virtually constant at $2.00 \pm 0.17 \times 10^{-10}$ moles/cm$^2$. The molecular area in $\mathring{A}^2$ per molecule agrees closely with the molecular areas obtained from ellipsometric measurements and with literature values. The surface tension data give an average of $83\mathring{A}^2$/molecule compared to an average of $83.6\mathring{A}^2$/molecule from ellipsometry. Ekwall and Ekholm reported $85\mathring{A}^2$/molecule for deoxycholic acid on 3M NaCl at pH 2.0 from film balance experiments[27]. The agreement between these three different methods is excellent.

The fourth parameter obtained from the curving fitting was $\alpha$, the concentration at which a half monolayer has formed. The concentrations are quite low - on the order of $10^{-6}$M except at very low salt concentrations.

The values measured by ellipsometry are lower than those calculated from surface tension data by a factor of

five to ten. I believe the surface tension data are more accurate because of the difficulty in measuring sub-monolayer films with the ellipsometer. The slightest contamination could significantly affect the film thicknesses observed.

The critical micelle concentration corresponding to each electrolyte concentration was determined from the surface tension data. The CMC drops with increasing salt concentration in agreement with literature data reviewed by Small[28]. He reports values of 2-5 mM in physiological saline. These results agree fairly well with my data in Table III-9. Beyond 0.3M NaCl there is a small drop in CMC while below 0.3M the drop is more rapid.

# CHAPTER 5

## CONCLUSIONS

The experimental data are adequately correlated to the single species mass action model used in this work. Good agreement on micelle size and the free energy of micellization per monomer with literature values was found for sodium deoxycholate. I believe that this model and method can be applied to other surfactant systems that form relatively small micelles (less than 50 molecules). The data fitting technique, using data obtained over the entire concentration range, from far below the CMC to well above it, allows estimation of association constants and micelle size from readily obtained surface tension data.

A change in sodium deoxycholate micellar behavior occurs between 0.15 and 0.30M sodium chloride concentrations. Interestingly, the isotonic salt concentration seen in human body fluids lies in this range (about 0.17M NaCl). It is possible that the shift in micelle size seen here could be related to changes in salinity in the body. Small

suggests that a shift from primary to secondary micellization occurs as salinity increases[29]. The present work was done under conditions that are far from physiological so the apparent correlation in micelle size shift is probably accidental.

## REFERENCES


1. K. Shinoda, "The Formation of Micelles," in Colloidal Surfactants, K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, Academic Press, New York (1963), p. 9-15.

2. Ibid., p. 20-21.

3. Ibid., p. 21-23.

4. P. Becher in Nonionic Surfactants, Vol. I, M. J. Schick, ed., Marcel Dekker, Inc., New York (1968), pp. 478-515.

5. P. Debye and E. W. Anacker, J. Phys. Chem., 55, 644 (1951).

6. P. Mukerjee, J. Phys. Chem., 66, 1375 (1962).

7. J. M. Corkill, J. F. Goodman, and R. H. Ottewill, Trans. Faraday Soc., 57, 1627 (1961).

8. J. M. Corkill, J. F. Goodman, and S. P. Harrold, Trans. Faraday Soc., 60, 202 (1964).

9. R. R. Balmbra, J. S. Clunie, J. M. Corkill, and J. F. Goodman, Trans. Faraday Soc., 60, 979 (1964).

10. D. Stigter and J. T. G. Overbeek, Proc. Intern. Cong. Surface Activity, 2nd, London, Vol. 1, Butterworths, London (1957), p. 311.

11. E. J. Clayfield and J. B. Matthews, Proc. Intern. Cong. Surface Activity, 2nd, London, Vol. 1, Butterworths, London (1957), p. 172.

12. P. H. Elworthy and K. J. Mysels, J. Coll. Interf. Sci., 21, 331 (1966).

13. D. G. Hall and B. A. Pethica in Nonionic Surfactants, Vol. I, M. J. Schick, ed., Marcel Dekker, Inc., New York (1967), pp. 516-557.

14. C. Tanford, Proc. Nat. Acad. Sci. USA, 71, 1811 (1974).

15. E. A. G. Aniansson, S. N. Wall, M. Almgren, H. Hoffmann, I. Kielmann, W. Ulbricht, R. Zana, J. Long, and C. Tondre, J. Phys. Chem., 80, 905 (1976).

16. E. Ruckenstein and R. Nagarajan, J. Phys. Chem., 79, 2622 (1975).

17. E. Ruckenstein and R. Nagarajan, J. Coll. Interf. Sci., 57, 388 (1976).

18. P. Mukerjee in Micellization, Solubilization, and Microemulsions, Vol. 1, K. Mittal, ed., Plenum Press (1977), p. 171.

19. S. Ozeki, M. Tsunoda, and S. Ikeda, J. Coll. Interf. Sci., 64, 28 (1978).

20. B. A. Pethica, Trans. Faraday Soc., 50, 413 (1954).

21. E. Enwall, NLLSQ, The University of Oklahoma, September 1975.

22. D. O. Jordan and J. E. Lane, Aust. J. Chem., 17, 7 (1964).

23. V. K. LaMer and M. L. Robbins, J. Phys. Chem., 62, 1291 (1958).

24. G. Loglio, A. Ficalbi, and R. Cini, J. Coll. Interf. Sci., 64, 198 (1978).

25. D. M. Small, "The Physical Chemistry of Cholanic Acids," in Bile Acids, P. P. Nair, ed., Plenum Press, NY (1971), p. 318.

26. Ibid., p. 315.

27. P. Ekwall and R. Ekholm, Proc. Intern. Cong. Surface Activity, 2nd, London, Vol. 1, Butterworths, London (1957), p. 23-30.

28. Ref. 25, p. 305.

29. Ref. 25, pp. 324-325.

TABLE III-1

DIMENSIONS OF PLATES USED IN MEASUREMENTS

A. Plate 1 Used With Balance 30928

| | |
|---|---|
| WIDTH: | 3.216 cm |
| LENGTH: | 2.520 cm |
| MASS: | 0.93177 gm* |
| THICKNESS: | 0.00536 cm |
| PERIMETER: | 6.443 cm |

B. Plate 2 Used With Balance 36350

| | |
|---|---|
| WIDTH: | 3.800 cm |
| LENGTH: | 1.880 cm |
| MASS: | 1.0198 gm* |
| THICKNESS: | 0.00665 cm |
| PERIMETER: | 7.6133 cm |

*Mass of plate before attaching hanger wire

TABLE III-2

VERTICAL DISPLACEMENT PER UNIT OF POINTER TRAVEL

| Balance #30928 | | |
|---|---|---|
| Pointer Position | Cathetometer Reading | Δ Per Unit |
| +10 (left) | 884.18mm | |
| + 5 | 882.46 | 0.34 |
| + 4 | 882.22 | 0.24 |
| + 3 | 881.90 | 0.32 |
| + 2 | 881.51 | 0.39 |
| + 1 | 881.10 | 0.41 |
| 0 | 880.90 | 0.20 |
| - 1 | 880.56 | 0.44 |
| - 2 | 880.20 | 0.36 |
| - 3 | 879.84 | 0.36 |
| - 4 | 879.62 | 0.22 |
| - 5 | 879.22 | 0.40 |
| -10 (right) | 877.62 | 0.32 |

Average Displacement: 0.333mm/unit

| Balance #36350 | | |
|---|---|---|
| Pointer Position | Cathetometer Reading | Δ Per Unit |
| +10 (left) | 912.95 | |
| + 5 | 911.30 | 0.33 |
| + 4 | 911.00 | 0.30 |
| + 3 | 910.65 | 0.35 |
| + 2 | 910.35 | 0.30 |
| + 1 | 910.00 | 0.35 |
| 0 | 909.70 | 0.30 |
| - 1 | 909.35 | 0.35 |
| - 2 | 909.00 | 0.35 |
| - 3 | 908.70 | 0.30 |
| - 4 | 908.35 | 0.35 |
| - 5 | 908.05 | 0.30 |
| -10 (right) | 906.40 | 0.30 |

Average Displacement: 0.328mm/unit

TABLE III-3

SURFACE TENSION DATA

FOR SODIUM DEOXYCHOLATE IN 0.01M NaOH

| Conc. M | Corr. Surface Tension, dynes/cm | Max. Pull, gm | Height Above Equilibrium |
|---|---|---|---|
| 0.0 | 72.00 | 0.4738 | 1.31mm |
| 0.0001 | 67.71 | 0.4458 | 1.31mm |
| 0.0002 | 66.12 | 0.4353 | 1.31mm |
| 0.0003 | 63.87 | 0.4204 | 1.31mm |
| 0.0004 | 62.51 | 0.4114 | 0.98mm |
| 0.0005 | 62.34 | 0.4099 | 0.98mm |
| 0.0006 | 61.37 | 0.4042 | 1.08mm |
| 0.0007 | 60.79 | 0.4013 | 1.31mm |
| 0.0008 | 60.08 | 0.3957 | 1.15mm |
| 0.0009 | 59.89 | 0.3944 | 0.98mm |
| 0.001 | 58.91 | 0.3880 | 1.15mm |
| 0.002 | 56.15 | 0.3702 | 1.15mm |
| 0.003 | 53.74 | 0.3538 | 1.15mm |
| 0.004 | 52.76 | 0.3473 | 1.15mm |
| 0.005 | 50.89 | 0.3355 | 0.98mm |
| 0.006 | 50.62 | 0.3337 | 1.15mm |
| 0.007 | 50.45 | 0.3321 | 0.98mm |
| 0.008 | 50.25 | 0.3309 | 1.15mm |
| 0.009 | 50.27 | 0.3311 | 1.15mm |
| 0.010 | 50.27 | 0.3310 | 0.98mm |
| 0.012 | 49.84 | 0.3285 | 1.15mm |
| 0.014 | 49.60 | 0.3267 | 1.15mm |
| 0.016 | 49.49 | 0.3259 | 1.15mm |
| 0.018 | 49.39 | 0.3253 | 1.15mm |
| 0.020 | 49.25 | 0.3243 | 1.15mm |

Plate 1 and Balance 30928

TABLE III-4

SURFACE TENSION DATA

FOR SODIUM DEOXYCHOLATE IN 0.01M NaOH, 0.15M NaCl

| Conc. M | Corr. Surface Tension, dynes/cm | Max. Pull, gm | Height Above Equilibrium, mm* |
|---|---|---|---|
| 0.0 | 73.37 | 0.5726 | 0.98 |
| 0.000001 | 72.58 | 0.5665 | 0.98 |
| 0.000004 | 69.58 | 0.5449 | 0.98 |
| 0.00001 | 68.23 | 0.5327 | 0.98 |
| 0.00004 | 63.75 | 0.4978 | 0.98 |
| 0.0004 | 54.20 | 0.4237 | 0.98 |
| 0.0008 | 51.02 | 0.3989 | 0.98 |
| 0.001 | 50.10 | 0.3918 | 0.98 |
| 0.004 | 46.91 | 0.3670 | 0.98 |
| 0.008 | 46.56 | 0.3643 | 0.98 |
| 0.010 | 46.54 | 0.3641 | 0.98 |
| 0.020 | 46.29 | 0.3622 | 0.98 |
| 0.100 | 45.75 | 0.3580 | 0.98 |

Plate 2 and Balance 36350

*The height pulled above equilibrium was not detectably different on any measurement from +3 units or 0.98mm.

TABLE III-5

SURFACE TENSION DATA

FOR SODIUM DEOXYCHOLATE IN 0.01M NaOH, 0.30M NaCl

| Conc. M | Corr. Surface Tension, dynes/cm | Max. Pull, gm | Height Above Equilibrium, mm |
|---|---|---|---|
| 0.0 | 73.64 | 0.5747 | 0.98 |
| 0.000001 | 73.31 | 0.5721 | 0.98 |
| 0.00001 | 67.34 | 0.5255 | 0.98 |
| 0.00004 | 61.90 | 0.4835 | 0.98 |
| 0.0001 | 57.90 | 0.4524 | 0.98 |
| 0.0008 | 48.04 | 0.3758 | 0.98 |
| 0.001 | 46.50 | 0.3638 | 0.98 |
| 0.002 | 45.50 | 0.3560 | 0.98 |
| 0.004 | 45.71 | 0.3577 | 0.98 |
| 0.006 | 45.70 | 0.3576 | 0.98 |
| 0.008 | 45.75 | 0.3581 | 0.98 |
| 0.010 | 45.65 | 0.3572 | 0.98 |
| 0.020 | 45.41 | 0.3553 | 0.98 |
| 0.100 | 45.06 | 0.3526 | 0.98 |

Plate 2 and Balance 36350

TABLE III-6

SURFACE TENSION DATA

FOR SODIUM DEOXYCHOLATE IN 0.001M NaOH, 0.50M NaCl

| Conc. M | Corr. Surface Tension, dynes/cm | Max. Pull, gm | Height Above Equilibrium, mm |
|---|---|---|---|
| 0.0 | 74.44 | 0.5810 | 0.98 |
| 0.000001 | 73.59 | 0.5743 | 0.98 |
| 0.00004 | 61.70 | 0.4819 | 0.98 |
| 0.0001 | 57.99 | 0.4531 | 0.98 |
| 0.0004 | 50.48 | 0.3947 | 0.98 |
| 0.0008 | 46.25 | 0.3619 | 0.98 |
| 0.001 | 45.14 | 0.3531 | 0.98 |
| 0.002 | 44.75 | 0.3502 | 0.98 |
| 0.004 | 44.79 | 0.3505 | 0.98 |
| 0.006 | 44.62 | 0.3492 | 0.98 |
| 0.008 | 44.58 | 0.3489 | 0.98 |
| 0.010 | 44.40 | 0.3475 | 0.98 |
| 0.020 | 44.13 | 0.3454 | 0.98 |

Plate 2 and Balance 36350

TABLE III-7

SURFACE TENSION DATA

FOR SODIUM DEOXYCHOLATE IN 0.01M NaOH, 0.5M NaCl

| Conc. M | Corr. Surface Tension, dynes/cm | Max. Pull, gm | Height Above Equilibrium, mm |
|---|---|---|---|
| 0.0 | 73.63 | 0.5746 | 0.98 |
| 0.000001 | 72.92 | 0.5690 | 0.98 |
| 0.000004 | 69.49 | 0.5424 | 0.98 |
| 0.00001 | 65.15 | 0.5087 | 0.98 |
| 0.00004 | 60.22 | 0.4704 | 0.98 |
| 0.0001 | 55.56 | 0.4342 | 0.98 |
| 0.0004 | 49.68 | 0.3885 | 0.98 |
| 0.0008 | 45.23 | 0.3539 | 0.98 |
| 0.0020 | 44.80 | 0.3507 | 0.98 |
| 0.0040 | 44.72 | 0.3499 | 0.98 |
| 0.008 | 44.59 | 0.3490 | 0.98 |
| 0.010 | 44.53 | 0.3486 | 0.98 |
| 0.120 | 44.43 | 0.3477 | 0.98 |
| 0.10 | 44.20 | 0.3459 | 0.98 |

Plate 2 and Balance 36350

TABLE III-8

SURFACE TENSION DATA

FOR SODIUM DEOXYCHOLATE IN 0.10M NaOH, 0.50M NaCl

| Conc. M | Corr. Surface Tension, dynes/cm | Max. Pull, gm | Height Above Equilibrium, mm |
|---|---|---|---|
| 0.0 | 74.39 | 0.5804 | 0.98 |
| 0.00004 | 61.61 | 0.4812 | 0.98 |
| 0.0001 | 57.41 | 0.4466 | 0.98 |
| 0.0004 | 50.36 | 0.3939 | 0.98 |
| 0.0008 | 46.14 | 0.3611 | 0.98 |
| 0.001 | 45.56 | 0.3565 | 0.98 |
| 0.002 | 45.47 | 0.3558 | 0.98 |
| 0.004 | 45.16 | 0.3534 | 0.98 |
| 0.006 | 45.21 | 0.3539 | 0.98 |
| 0.008 | 45.14 | 0.3532 | 0.98 |
| 0.010 | 45.01 | 0.3522 | 0.98 |
| 0.020 | 44.88 | 0.3512 | 0.98 |
| 0.100 | 44.76 | 0.3503 | 0.98 |

Plate 2 and Balance 36350

TABLE III-9

SUMMARY OF SURFACE TENSION EXPERIMENTAL RESULTS

| ELECTROLYTE | | | | | | |
|---|---|---|---|---|---|---|
| NaOH, M | 0.01 | 0.01 | 0.01 | 0.001 | 0.01 | 0.10 |
| NaCl, M | ---- | 0.15 | 0.30 | 0.50 | 0.50 | 0.50 |
| MICELLE SIZE | | | | | | |
| Molecules/ | 12.4 | 14.5 | 34.7 | 40.4 | 40 | 42.3 |
| Micelle | $\pm$4.1 | $\pm$5.2 | $\pm$27.8 | $\pm$30.4 | ---- | $\pm$12.8 |
| K* | 2.34 | 6.37 | 1.01 | 9.89 | 1.14$\pm$ | 1.10 |
| Micellar Assn. Constant | $\pm$.50x $10^{-4}$ | $\pm$1.3x $10^{-4}$ | $\pm$.19x $10^{-4}$ | $\pm 1.3\times10^{-4}$ | $.01\times10^{-3}$ | $\pm$.01x $10^{-3}$ |
| Kn, $M^{1-n}$ | $2.39\times10^{23}$ | $4.51\times10^{34}$ | $2.8\times10^{98}$ | $1.6\times10^{116}$ | $1.89\times10^{116}$ | $2.8\times10^{124}$ |
| $\Delta G_m$, Kcal/m | -2.57 | -3.26 | -3.87 | -3.92 | -3.96 | -4.11 |
| $\Gamma_m RT$ | 4.95 $\pm$0.12 | 4.21 $\pm$0.09 | 5.00 $\pm$0.19 | 5.45 $\pm$0.14 | 4.90 $\pm$.14 | 5.31 $\pm$0.09 |
| $\Gamma_m$, $M/cm^2$ | $2.0\times10^{-10}$ | $1.7\times10^{-10}$ | $2.0\times10^{-10}$ | $2.2\times10^{-10}$ | $2.0\times10^{-10}$ | $2.1\times10^{-10}$ |
| Molecular Area $A^{\circ 2}$/molecule | 83.1 | 97.7 | 82.3 | 75.5 | 84.0 | 77.5 |
| $\alpha$ µM | 78.5 $\pm$5.6 | 4.09 $\pm$.39 | 4.21 $\pm$0.63 | 4.71 $\pm$0.51 | 2.67 $\pm$0.32 | 4.14 $\pm$0.30 |
| CMC, M | 0.0064 | 0.002 | 0.0011 | 0.0011 | 0.0009 | 0.0009 |
| RMSD dynes/cm | 0.2838 | 0.2963 | 0.4991 | 0.3009 | 0.4498 | 0.1854 |

*Sodium Deoxycholate (NaDC) concentrations expressed in µM units for computation purposes. See Equation (4) and the following discussion.

FIGURE III-1

WILHELMY PLATE SURFACE TENSION BALANCE

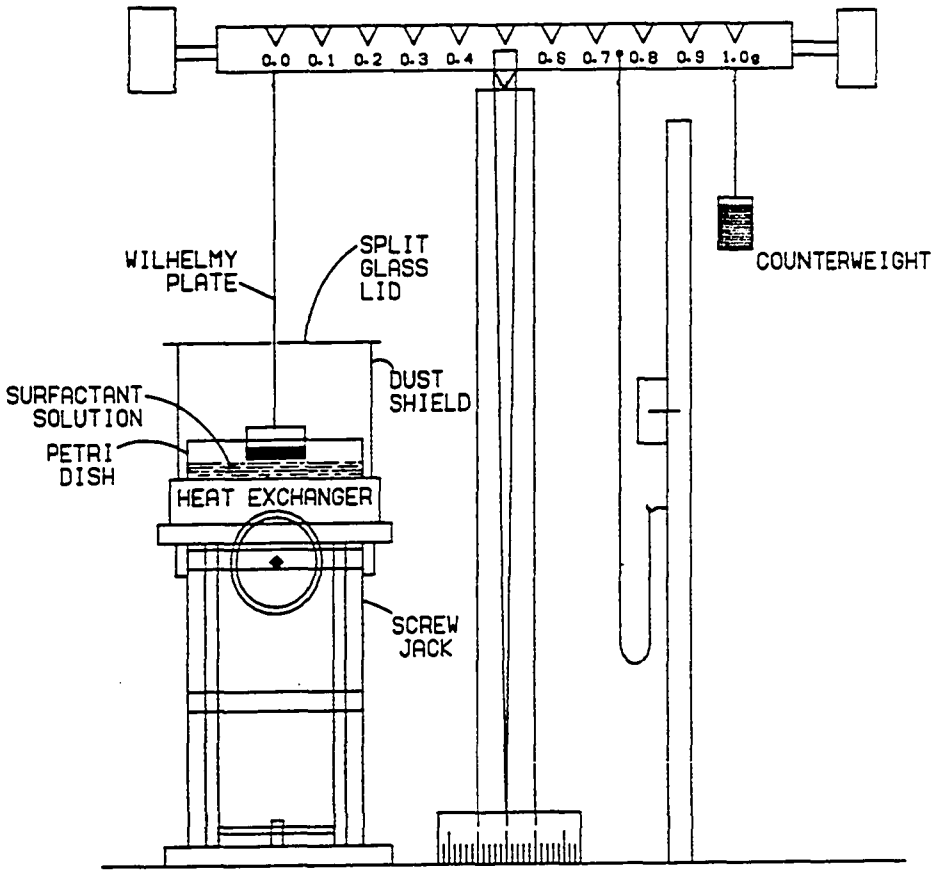


FIGURE III-2

COMPARISON OF LITERATURE RESULTS
TO EXPERIMENTALLY DETERMINED
MICELLE AGGREGATION NUMBERS
AT VARIOUS SALT CONCENTRATIONS

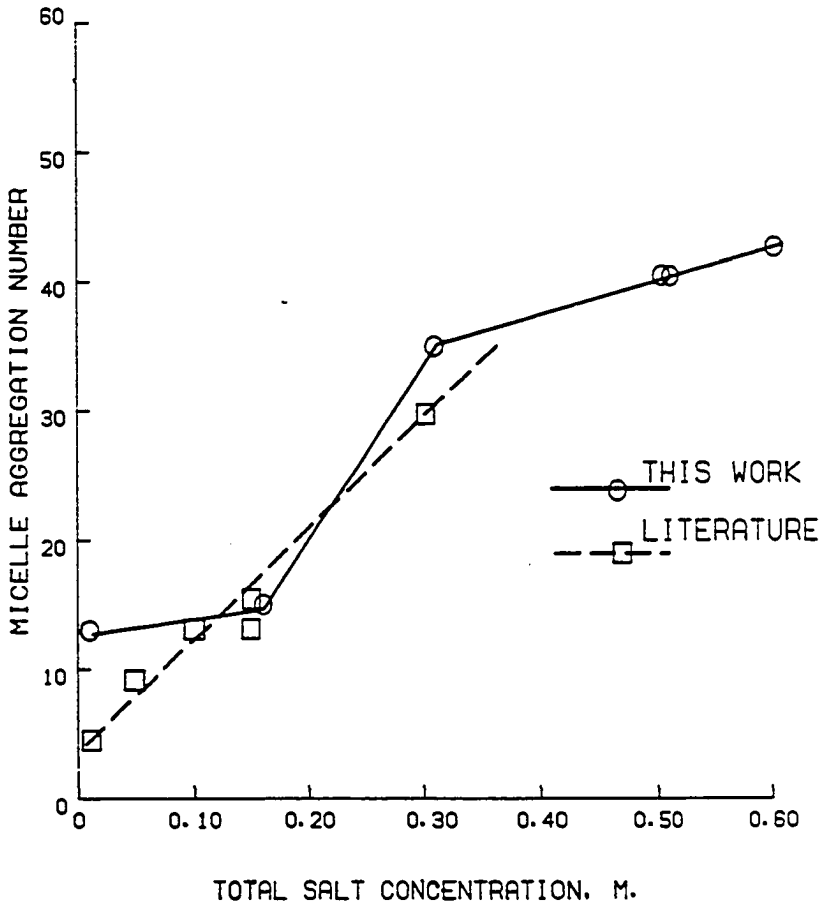
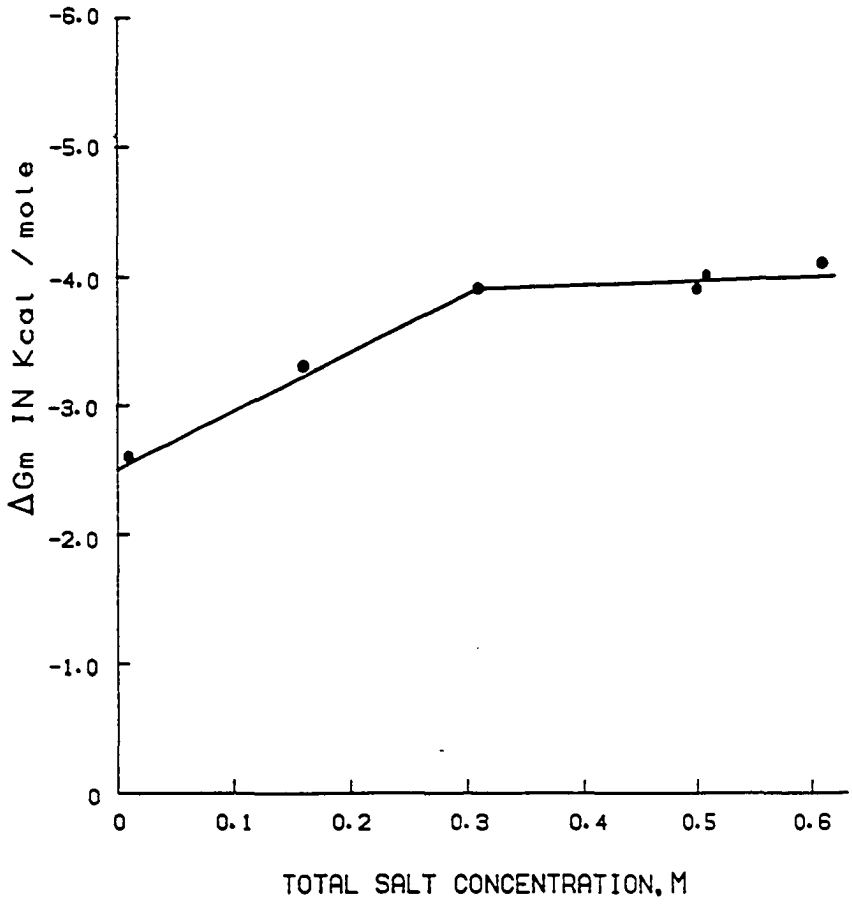


FIGURE III-3

FREE ENERGY CHANGE PER MONOMER ON MICELLE FORMATION AS A FUNCTION OF SALT CONCENTRATION



# IV. SOLUBILIZATION OF BENZENE AND CYCLOHEXANE BY SODIUM DEOXYCHOLATE MICELLES

## CHAPTER 1

## INTRODUCTION

Micelles solubilize water-insoluble compounds, like hydrocarbons into their hydrocarbon-like interiors by absorption. If a micelle-forming species formed micelles of different sizes by change in micelle configuration, one would expect the amount of hydrocarbon solubilized to change. This work has established that sodium deoxycholate forms micelles of different sizes as the salt content changes; therefore, the solubilization of cyclohexane and benzene by sodium deoxycholate micelles was studied to determine whether or not the larger micelles absorbed hydrocarbons differently than did the smaller ones. Other experiments were performed to determine the effect of mixing hydrocarbons on their solubilization in the micelle.

# CHAPTER 2

## BACKGROUND AND LITERATURE

Most intramicellar solubilization studies have concerned themselves with the absorption of pure hydrocarbons into the micelle. Mixtures of surfactants are frequently studied to look for synergistic solubilization effects. I was able to find no published studies of mixed hydrocarbons being absorbed into a micelle where an attempt to estimate the composition of the intramicellar phase was made.

Wishnia[1] studied the solubilization of ethane, propane, butane, and pentane in solutions of sodium dodecylsulfate. His data, obtained using manometric and radioactive tracer techniques, support a liquid hydrocarbon model for the micelle interior. He estimated the hydrophobic contribution to $\Delta G$, $\Delta H$, and $\Delta S$ of micellization. The average $\Delta G$ of transfer of a methylene group from water to a sodium dodecylsulfate is -0.76 Kcal/mol.

Rehfield[2,3] discussed the solubilization of benzene by sodium dodecyl sulfate and cetyltrimethyl ammonium

bromide (CTAB). He used differential ultraviolet absorption spectroscopy to determine the amount of benzene dissolved in the micellar solutions. The concentration of dissolved benzene varied linearly with sodium dodecyl sulfate concentration over the 0.006 to 0.05M range. He concluded that most of the benzene dissolved in sodium dodecyl sulfate solutions is in the hydrocarbon interior rather than near the micelle surface. His data for CTAB solutions are similar with the amount of benzene solubilized fitting the equation $S = 0.99mM + 2.55m$ where m is the CTAB concentration in mmol/l. Rehfield's data support the liquid hydrocarbon model of solubilization.

Mukerjee and Cardinal[4] used ultraviolet spectroscopy to study solubilization of benzene and benzene derivatives by Triton X-100 micelles. They used a two-state model for the solubilized species with distribution of the solubilizate between a nonpolar (dissolved) state in the hydrocarbon core and a polar (adsorbed) state associated with the micelle-water interface. They postulate that adsorption at the interface is more important at low benzene concentrations than at high benzene concentrations where most of the benzene is solubilized.

Brady and Huff[5] studied the vapor pressure of benzene over solutions of sodium dodecyl sulfate and dodecylpyridinium chloride at two surfactant concentrations and three temperatures. They calculated the heat of solubilization

and activity changes for all three components. They explain the solubilization as a cooperative rather than an adsorption process. They found that only 75% of the benzene was available for solubilization. The other 25% was apparently bound differently. Their data may be explained using Mukerjee and Cardinal's distribution mechanism.

Eriksson and Gillberg[6] presented results of NMR studies of the solubilization of aromatic compounds in cetyl trimethylammonium bromide (CTAB) that showed at low concentrations that benzene is adsorbed in the interface between the aqueous phase and the micelle.

Birdi[7], in a review paper on the thermodynamics of micellization shows that solubilization of a water-insoluble compound can be treated as a pseudo-two-phase system and concluded that micellar hydrophobic interactions are the main forces responsible for solubilization and are independent of ionic strength and the aggregation number.

# CHAPTER 3

## EXPERIMENTAL

Chemicals. Spectral grade benzene and cyclohexane obtained from Mallinckrodt were used in all experiments. The water used to prepare the sodium deoxycholate solutions was distilled in an all-glass still following deionization. The sodium chloride and sodium hydroxide used were reagent grade materials obtained from Fisher. All the chemicals used were the same as used in the rest of this study.

Extraction Experiments. The extraction procedure followed was to mix the appropriate hydrocarbon mixture with the micellar or electrolyte solution by shaking vigorously for a minute. The solution was allowed to equilibrate for a minimum of three days. Early experiments showed that one day was sufficient for equilibration. After three days, an aliquot of the water layer was pipetted carefully into a known volume of carbon tetrachloride for extraction. The solution was shaken vigorously and allowed to stand for twenty-four hours after which a sample of the carbon tetrachloride layer was extracted for analysis.

Early experiments used a Beckman DK-2 Spectrophotometer. Cyclohexane was analyzed with its near-IR hand at 3.42μm while benzene was analyzed at 3.29μm. The accuracy of the measurements was poor because of the instrument's age and condition, so after literally hundreds of measurements this technique was abandoned in favor of direct analysis of the solutions by mass spectrometry in the Routine Testing Laboratory at Amoco Production Company (M. L. Dunton, Supervisor). The help of Dr. Dunton and Ralph George, mass spectrometer operator, is gratefully acknowledged.

A small sample (1-5μℓ) of sample was injected into the mass spectrometer's ionizing chamber. The ions are analyzed and collated as the total mass of the compound from the known fragments. The data acquisition and analysis were completed in the Laboratory Automation Computer that is directly linked to the instrument. The data, Table IV-1, are reported as weight percent in the solution. Table IV-2 shows the data calculated in molar units in the aqueous phase corrected for the dilution ratios used. Table IV-3 shows the data reduced to enhancement of concentration by solution in the micelles, and as the number of hydrocarbon molecules solubilized per micelle. Table IV-3 also shows that the mole fraction of benzene in the micelle at equilibrium is the same within experimental error as the mole fraction of benzene in the contacting solution.

Direct contact of the hydrocarbon mixture and the micellar solution might produce an emulsion that makes any estimates of the total solubility of hydrocarbons in the micelle questionable. Other work in progress in the laboratory on the solubility of benzene and cyclohexane in sodium deoxycholate micelles was used to check for emulsion formation.

Vapor Pressure Experiments. Linda and Donna Smith of this laboratory are using vapor pressure measurements to study the uptake of benzene and cyclohexane by sodium deoxycholate. Their data were used to estimate the composition of the micellar solution at saturation by extrapolation from lower benzene concentrations. Their data were fit to an empirical equation:

$$C_T = A + BP + CP^2 \qquad (1)$$

where $C_T$ is the total concentration of benzene added, P is the vapor pressure of benzene and cyclohexane above the solution, and A, B, and C are arbitrary constants determined by the curve-fitting process.

The data are reproduced here as Tables IV-4 through IV-10. They were obtained using vapor pressure measurement apparatus and techniques developed in this laboratory[8-12]. The Mensor Quartz Bourdon-Tube Pressure Gauge readings were

corrected to true pressure readings using the following polynomial equation:

$$P\ (\text{mm Hg}) = 1.02379 \times G - 4.92097 \times 10^{-5} \times G^2 + 1.98329 \times 10^{-6} \times G^3 - 1.93916 \times 10^{-8} \times G^4 \times 7.11193 \times 10^{-11} \times G^5 - 8.99632 \times 10^{-14} \times G^6 \quad .$$

Additional corrections for the solubility of air in benzene and in cyclohexane were made to yield accurate pressure measurements.

# CHAPTER 4

## DATA ANALYSIS AND DISCUSSION

The solubilization data obtained by directly contacting benzene-cyclohexane mixtures with the micellar solutions show (Table IV-2) that the relative enhancement of cyclohexane solubility is much greater than that of benzene. However, when cyclohexane and benzene solubilities in the interior of the micelle are calculated in terms of mole fractions, a previously unexpected observation is made. The relative concentrations of benzene and cyclohexane in the intramicellar solution are the same as in the contacting solution. This observation has not been made previously for any system. It is valuable because it can be used to help simplify the complex problem of solubilization of mixed hydrocarbons. The micelle interior appears to act as a separate hydrocarbon phase in which the aqueous phase solubilities are unimportant. One could consider the aqueous phase as a membrane through which the hydrocarbons pass but that does not affect the final equilibrium composition. The micelle size does not significantly affect the composition of the intramicellar solution as can be seen in Figure

IV-1. The data for both micelle sizes are the same within experimental error.

Extraction experiments involved directly shaking the micellar solution with the hydrocarbon contacting solution so that the micelle would be saturated when sampled. These conditions could easily result in an emulsion where artificially high solubilities would be found. Vapor pressure measurements on solutions well below saturation at all times were used to check for emulsion formation[13]. The experiments were performed by introducing small amounts of benzene into a micellar solution containing a known amount of cyclohexane and sodium deoxycholate. The data were analyzed by a rather complicated procedure that used the premise that the equilibrium intramicellar solution has the same composition as the contacting solution. Before discussing the calculation procedure in detail, I will give a brief overview of the steps involved:

1. The vapor pressure data for the unsaturated micellar solution were analyzed to obtain an equation relating the total amount of benzene added to the total hydrocarbon vapor pressure.

2. An estimated mole fraction composition of the saturated micelle was guessed.

3. A total pressure was calculated using Scatchard's data and the Redlich-Kister equations for the activity coefficients.

4. The total pressure was used to calculate the total amount of benzene added at saturation. The individual benzene and cyclohexane pressures predicted from the Scatchard data were used to account for the benzene and cyclohexane in the vapor phase.

5. The Setchénow equation and Henry's law were used to calculate the amount of hydrocarbon in the electrolyte solution.

6. The amount of each hydrocarbon in the intramicellar solution was calculated to give the estimated mole fraction benzene in the micelle.

7. The initial guess and the estimated mole fraction were averaged and the calculations repeated until the difference between the two was less than 0.000001 mole fraction.

The procedure used to calculate the composition of the micellar solution from vapor pressure data was to first estimate the mole fraction of benzene corresponding to the amount of cyclohexane added and the amount of benzene needed to reach saturation. The Redlich-Kister equations truncated to three terms were used to estimate activity coefficients for benzene and cyclohexane[14]:

$$\log Y_B = X_C^2 \left[B+C(3X_B-X_C)+D(X_B-X_C)(5X_B-X_C)\right] \qquad (2)$$

$$\log Y_C = X_B^2 \left[B+C(3X_C-X_B)+D(X_C-X_B)(5X_C-X_B)\right] . \qquad (3)$$

The data of Scatchard and coworkers[15] for the composition of benzene and cyclohexane mixtures at 40°C and 70°C were used to calculate values for B, C, and D at 25°C. The values obtained are shown in Table IV-11. The vapor pressure of each component was calculated from

$$P_B = P_B^\circ X_B \gamma_B \text{ and } P_C = P_C^\circ X_C \gamma_B \quad . \tag{4}$$

The data were used to prepare the vapor pressure versus liquid composition diagram shown as Figure IV-2.

The total pressure was used to calculate the moles of benzene added at saturation using Equation (1). Each set of data (Tables IV-4 through IV-10) was used to calculate the required constants (Table IV-12) for Equation (1). The calculated total benzene concentration, the total cyclohexane concentration and the vapor pressures of each were used to calculate the composition of the vapor phase and of the aqueous phase. The vapor phase was assumed to be ideal so the ideal gas law, in the form:

$$n/V = P/RT \tag{5}$$

could be used to calculate the vapor composition.

The solubility of benzene and cyclohexane in the electrolyte solution was calculated using the Setchénow equation[16]

$$\log_{10} (S^{o}/S) = K_{s1} C_{e1} + K_{s2} C_{e2} \qquad (6)$$

where $S^{o}$ is the solubility of the non-electrolyte in water, $K_{s1}$ is the salting-out coefficient (0.256) for benzene in sodium hydroxide ($C_{E1}$ = 0.01M), and $K_{s2}$ is the salting-out coefficient (0.198) for benzene in sodium chloride ($C_{E2}$ = 0.15 or 0.50M). The same salting-out coefficients were assumed to apply for cyclohexane for lack of actual data. Cyclohexane solubility in the electrolyte is small so the error from this assumption is unimportant. The salting-out coefficients obtained were: 1.0771 for 0.01M NaOH and 0.15M NaCl, and 1.263 for 0.01M NaOH and 0.50M NaCl. Tucker's[17] newly determined solubility of benzene in water (0.0226M) at 25.000°C was used. Pierotti and Liabastre's[18] value (0.0011M) at 25.0°C for the solubility of cyclohexane in water was used.

The amount of benzene or cyclohexane in the electrolyte solution is given by Henry's law which was written for convenience in the form:

$$P = C_{M}H \qquad (7)$$

where P is the pressure in mm Hg, $C_{M}$ is the molar hydrocarbon concentration, and H is the Henry's law constant in mm Hg/M unit. This relationship was used to calculate the hydrocarbon concentration in the electrolyte solution from

the vapor pressure. The values used are shown in Table IV-13.

The net concentration of hydrocarbon in the micelle was taken to be the difference between the total aqueous concentration calculated earlier and the solubility in the electrolyte. The intramicellar solution composition was used to calculate the mole fraction of benzene in the micelle. This calculated mole fraction was compared to the estimated mole fraction initially chosen and by an iterative program the calculations repeated until the difference between the estimated and calculated mole fractions was less than 0.000001. The resulting composition was taken to be the equilibrium composition of the intramicellar solution at saturation.

The aqueous phase compositions calculated at these mole fractions are compared to the observed compositions in Tables IV-14 and IV-15. The observed compositions were estimated from composition diagrams constructed using the extraction experimental data. The diagrams used are shown as Figures IV-3 to IV-6. The agreement between the calculated and observed compositions is good. The vapor pressure data are probably more accurate because of the number of liquid transfers and extractions involved in the direct measurement methods.

The free energy of solubilization for benzene and cyclohexane in sodium deoxycholate micelles was calculated

following Birdi[19]. Hydrocarbon molecules in aqueous solution are in equilibrium with hydrocarbon molecules in the micelle. The equilibrium constant for the solubilization process can be stated as

$$K_s = C_m/(C_{aq}C_{NaDC}) \quad .$$

A free energy of solubilization can then be calculated using

$$\Delta G_s = -RT \ln K_s \quad .$$

$C_m$ is the amount of hydrocarbon solubilized in the micelle and $C_{aq}$ is the concentration of hydrocarbon in the electrolyte. The calculated free energies are shown in Table IV-16. The average free energies of solubilization shown in Table IV-17 are the same for both micelle sizes. This indicates that the hydrocarbon is solubilized in the same way regardless of the micelle size. These observations are interpreted to mean that the structure of the small micelle is not radically different from that of the large micelle and that the large micelles may be groups of smaller primary micelles.

There is an effect of ionic strength on micellar solubilization. The larger micelle solubilizes slightly less hydrocarbon per deoxycholate than the smaller micelle. The data are shown in Table IV-17 and in Figure IV-7 for

comparison. The ratio of micellar solubility in the smaller micelle to the larger micelle is 1.10 $\pm$0.09. The intramicellar space for hydrocarbon may be smaller in the large micelle because of electrostriction effects. That is, the micelle is compressed because of the neutralizing effects of the high salt concentration on the charged carboxylic acid groups allowing these changes to move closer together than they would in lower ionic strength solutions.

# CHAPTER 5

## CONCLUSIONS

1. At equilibrium, the intramicellar solution has the same composition as the contacting hydrocarbon solution. That is, the micelle interior acts as a container in which the activity relationships between benzene and cyclohexane are the same as in a simple mixture of the two.

2. The hydrocarbons are taken up by both small and large micelles in the same way. There is no effect of micelle size on solubilization in this case. There is, however, an effect of ionic strength on solubilization. Higher ionic strength reduces the capacity of the micelle to solubilize hydrocarbon molecules.

## REFERENCES


1. A. Wishnia, J. Phys. Chem., 67, 2079 (1963).

2. S. J. Rehfield, J. Phys. Chem., 74, 117 (1970).

3. S. J. Rehfield, J. Phys. Chem., 75, 3905 (1971).

4. P. Mukerjee and J. R. Cardinal, J. Phys. Chem., 82, 1620 (1978).

5. A. P. Brady and H. Huff, J. Phys. Chem., 62, 644 (1958).

6. J. C. Eriksson and G. Gillberg, Proc. Scand. Symp. Surface Activ., 2nd, Stockholm, 1964, p. 148-56, C.A. 66: 33360h.

7. K. S. Birdi, "Thermodynamics of Micellization," in Micellization, Solubilization, and Microemulsions, Vol. 1, K. L. Mittal, ed., Plenum Press, New York, 1977, pp. 151-169.

8. E. E. Tucker, PhD Dissertation, The University of Oklahoma, 1969.

9. V. Cheam, PhD Dissertation, The University of Oklahoma, 1971.

10. C. Lin, PhD Dissertation, The University of Oklahoma, 1964.

11. A. A. Taha, PhD Dissertation, The University of Oklahoma, 1965.

12. E. H. Lane, PhD Dissertation, The University of Oklahoma, 1977.

13. L. Smith and D. Smith, Personal Communication, 1978.

14. M. B. King, Phase Equilibrium in Mixtures, Permagon Press, New York, 1969, pp. 325-327.

15. G. Scatchard, S. E. Wood, and J. M. Mochel, J. Phys. Chem., 43, 119 (1939).

16. Ref. 14, p. 260.

17. E. E. Tucker, unpublished work.

18. R. A. Pierotti and A. A. Liabastre, "The Structure and Properties of Water Solutions," Dept. of Interior, Office of Water Resources Research Report, W72-12099, June 1972.

19. Ref. 7, p. 154.

TABLE IV-1

RAW DATA FROM EXTRACTION OF BENZENE AND CYCLOHEXANE INTO MICELLES

| Solution | Mole Fraction Benzene in Contacting Solution | $CCl_4$ wt % | $C_6H_6$ wt % | $C_6H_{12}$ wt % |
|---|---|---|---|---|
| $H_2O$ | 0.00 | 99.973 | 0.00 | 0.027 |
| | 0.25 | 99.754 | 0.194 | 0.052 |
| | 0.50 | 99.597 | 0.386 | 0.017 |
| | 0.75 | 99.478 | 0.510 | 0.009 |
| | 1.00 | 99.412 | 0.588 | 0.00 |
| 0.01M NaOH | 0.00 | 99.968 | 0.00 | 0.032 |
| 0.15M NaCl | 0.25 | 99.791 | 0.189 | 0.020 |
| | 0.50 | 99.702 | 0.286 | 0.012 |
| | 0.75 | 99.523 | 0.469 | 0.008 |
| | 1.00 | 99.459 | 0.541 | 0.00 |
| 0.10M NaDC | 0.00 | 99.801 | 0.00 | 0.199 |
| in | 0.25 | 99.718 | 0.103 | 0.179 |
| 0.01M NaOH | 0.50 | 99.640 | 0.211 | 0.149 |
| 0.15M NaCl | 0.75 | 99.607 | 0.306 | 0.087 |
| | 1.00 | 99.603 | 0.395 | 0.002 |
| 0.01M NaOH | 0.00 | 99.983 | 0.001 | 0.016 |
| 0.50M NaCl | 0.25 | 99.812 | 0.153 | 0.035 |
| | 0.50 | 99.709 | 0.281 | 0.010 |
| | 0.75 | 99.561 | 0.429 | 0.010 |
| | 1.00 | 99.421 | 0.579 | 0.00 |
| 0.10M NaDC | 0.00 | 99.796 | 0.00 | 0.204 |
| in | 0.25 | 99.728 | 0.096 | 0.172 |
| 0.01M NaOH | 0.50 | 99.679 | 0.184 | 0.137 |
| 0.50M NaCl | 0.75 | 99.649 | 0.278 | 0.073 |
| | 1.00 | 99.638 | 0.362 | 0.00 |

TABLE IV-2

REDUCED DATA FROM EXTRACTION OF BENZENE AND CYCLOHEXANE INTO MICELLES

| Solution | Mole Fraction Benzene in Contacting Solution | $C_6H_6$ M in $CCl_4$ | $C_6H_{12}$ M in $CCl_4$ | Conc. in Aqueous Phase, M | |
|---|---|---|---|---|---|
| | | | | $C_6H_6$ | $C_6H_{12}$ |
| $H_2O$ | 0.00 | 0.00 | 0.0051 | 0.00 | 0.00102 |
| | 0.25 | 0.0395 | 0.00983 | 0.0079 | 0.00197 |
| | 0.50 | 0.0785 | 0.00321 | 0.0157 | 0.00064 |
| | 0.75 | 0.1036 | 0.0017 | 0.0207 | 0.00034 |
| | 1.00 | 0.1194 | 0.00 | 0.0239 | 0.00 |
| 0.01M NaOH | 0.00 | 0.00 | 0.00606 | 0.00 | 0.00121 |
| 0.15M NaCl | 0.25 | 0.0385 | 0.00378 | 0.0077 | 0.000755 |
| | 0.50 | 0.0582 | 0.00227 | 0.0116 | 0.00045 |
| | 0.75 | 0.0953 | 0.00151 | 0.0191 | 0.00030 |
| | 1.00 | 0.1099 | 0.00 | 0.0220 | 0.00 |
| 0.10M NaDC | 0.00 | 0.00 | 0.0376 | 0.00 | 0.0376 |
| in | 0.25 | 0.02096 | 0.0338 | 0.0210 | 0.0338 |
| 0.01M NaOH | 0.50 | 0.04291 | 0.0281 | 0.0429 | 0.0281 |
| 0.15M NaCl | 0.75 | 0.06223 | 0.0164 | 0.0622 | 0.0164 |
| | 1.00 | 0.0803 | 0.00038 | 0.0803 | 0.00038 |
| 0.01M NaOH | 0.00 | 0.0002 | 0.00303 | 0.00 | 0.00061 |
| 0.50M NaOH | 0.25 | 0.03117 | 0.00662 | 0.00623 | 0.00132 |
| | 0.50 | 0.05720 | 0.00189 | 0.0114 | 0.000378 |
| | 0.75 | 0.08722 | 0.00189 | 0.0174 | 0.000378 |
| | 1.00 | 0.1176 | 0.00 | 0.0235 | 0.00 |
| 0.10M NaDC | 0.00 | 0.00 | 0.0386 | 0.00 | 0.0386 |
| in | 0.25 | 0.0195 | 0.0325 | 0.0195 | 0.0325 |
| 0.01M NaOH | 0.50 | 0.0374 | 0.0259 | 0.0374 | 0.0259 |
| 0.50M NaCl | 0.75 | 0.0566 | 0.0138 | 0.0576 | 0.0138 |
| | 1.00 | 0.0737 | 0.00 | 0.0737 | 0.00 |

TABLE IV-3

ENHANCEMENT AND MOLECULAR ABSORPTION DATA FOR
EXTRACTION OF BENZENE AND CYCLOHEXANE INTO MICELLES

| Micellar Solution | Mole Fraction Benzene in Contacting Solution | Enhancement of Conc. in Micelles | | Molecules Micelle | | | Mole Fraction Benzene in Micelle |
|---|---|---|---|---|---|---|---|
| | | $C_6H_6$ | $C_6H_{12}$ | $C_6H_6$ | $C_6H_{12}$ | Total | |
| n = 14 | 0.00 | 0.00 | 0.0364 | 0.0 | 5.10 | 5.10 | 0.00 |
| 0.10M NaDC | 0.25 | 0.0133 | 0.0330 | 1.86 | 4.62 | 6.48 | 0.287 |
| in | 0.50 | 0.0313 | 0.0277 | 4.38 | 3.87 | 8.25 | 0.532 |
| 0.01M NaOH | 0.75 | 0.0431 | 0.0161 | 6.03 | 2.25 | 8.28 | 0.728 |
| 0.15M NaCl | 1.00 | 0.0583 | 0.00 | 8.16 | 0.0 | 8.16 | 1.00 |
| n = 40 | 0.00 | 0.00 | 0.0380 | 0.0 | 15.2 | 15.2 | 0.00 |
| 0.01M NaDC | 0.25 | 0.0133 | 0.0312 | 5.31 | 12.47 | 17.78 | 0.298 |
| in | 0.50 | 0.0260 | 0.0255 | 10.38 | 10.21 | 20.59 | 0.496 |
| 0.01M NaOH | 0.75 | 0.0392 | 0.0134 | 15.66 | 5.37 | 21.03 | 0.746 |
| 0.50M NaCl | 1.00 | 0.0502 | 0.00 | 20.08 | 0.0 | 20.08 | 1.00 |

TABLE IV-4

VAPOR PRESSURE MEASUREMENT OF BENZENE SOLUBILITY
IN 0.10M NaDC, 0.01M NaOH, AND 0.15M NaCl

| Vol. Benzene Added | Gauge Units | |
|---|---|---|
| 0.00 | 22.757 | (23.292 mm Hg) |
| 0.0270 | 26.229 | |
| 0.05784 | 29.514 | |
| 0.08839 | 30.751 | |
| 0.11984 | 36.045 | |
| 0.15085 | 39.295 | |
| 0.18220 | 42.569 | |
| 0.21279 | 45.574 | |
| 0.24394 | 48.559 | |
| 0.27502 | 51.553 | |
| 0.30603 | 54.498 | |
| 0.33675 | 57.393 | |
| 0.36707 | 60.159 | |
| 0.39745 | 62.882 | |
| 0.42836 | 65.630 | |
| 0.47889 | 70.075 | |
| 0.50988 | 72.721 | |
| 0.54120 | 75.399 | |
| 0.59155 | 79.597 | |
| 0.64268 | 83.871 | |
| 0.69329 | 87.923 | |
| 0.74364 | 90.770 | |
| 0.82507 | 96.532 | |
| 0.90571 | 102.594 | |
| 0.98603 | 107.789 | |
| 1.08625 | 113.283 | |

Temp.: 25.000 ± 0.0006°C
Liq. Vol.: 98.30 ml

TABLE IV-5

VAPOR PRESSURE MEASUREMENT OF BENZENE SOLUBILITY IN 0.10M NaDC, 0.01M NaOH, AND 0.15M NaCl WITH CYCLOHEXANE ADDED (20% OF SATURATION)

| Vol. Benzene Added | Gauge Units | |
|---|---|---|
| 0.00 | | (23.276 mm Hg) |
| 0.20225 ml Cyclohexane | 44.562 | (45.635 mm Hg) |
| | | 22.359 mm Hg Cyclohexane |
| 0.00 ml $C_6H_6$ | 44.562 | |
| 0.02984 | 47.417 | |
| 0.05979 | 50.355 | |
| 0.08979 | 53.307 | |
| 0.11972 | 56.283 | |
| 0.15027 | 59.093 | |
| 0.18185 | 60.186 | |
| 0.21278 | 62.862 | |
| 0.24360 | 65.170 | |
| 0.29396 | 69.566 | |
| 0.34531 | 74.266 | |
| 0.39565 | 79.239 | |
| 0.44730 | 83.281 | |
| 0.49841 | 87.608 | |
| 0.54888 | 91.852 | |
| 0.59918 | 95.967 | |
| 0.64963 | 100.048 | |
| 0.70036 | 103.864 | |
| 0.78108 | 109.992 | |
| 0.83185 | 113.354 | |

Temp.: 25.001 ± 0.001°C
Liq. Vol.: 97.45 ml

TABLE IV-6

VAPOR PRESSURE MEASUREMENT OF BENZENE SOLUBILITY IN 0.10M NaDC, 0.01M NaOH, AND 0.15M NaCl WITH CYCLOHEXANE ADDED (40% OF SATURATION)

| Vol. Benzene Added | Gauge Units | |
|---|---|---|
| 0.00 | | (23.456 mm Hg) |
| 0.36099 ml Cyclohexane | 58.950 | (60.400 mm Hg) |
| 0.00 ml $C_6H_6$ | 58.950 | 36.944 mm Hg Cyclohexane |
| 0.03060 | 60.958 | |
| 0.06080 | 63.538 | |
| 0.09115 | 67.540 | |
| 0.12263 | 69.921 | |
| 0.15299 | 72.576 | |
| 0.18359 | 75.365 | |
| 0.21434 | 78.107 | |
| 0.24445 | 81.095 | |
| 0.29470 | 85.416 | |
| 0.34666 | 91.011 | |
| 0.39720 | 94.766 | |
| 0.44742 | 98.867 | |
| 0.49781 | 103.096 | |
| 0.54831 | 107.609 | |
| 0.62898 | 113.204 | |

Temp.: 25.000 ± 0.001°C
Liq. Vol.: 97.45 ml

TABLE IV-7

VAPOR PRESSURE MEASUREMENT OF BENZENE SOLUBILITY IN 0.10M NaDC, 0.01M NaOH, AND 0.15M NaCl WITH CYCLOHEXANE ADDED (60% OF SATURATION)

| Vol. Benzene Added | Gauge Units | |
|---|---|---|
| 0.00 | | (23.487 mm Hg) |
| 0.615 ml Cyclohexane | 83.954 | (86.078 mm Hg) |
| 0.00 ml $C_6H_6$ | 83.954 | 62.591 mm Hg Cyclohexane |
| 0.02978 | 85.088 | |
| 0.05958 | 87.416 | |
| 0.08999 | 89.945 | |
| 0.12037 | 92.642 | |
| 0.15163 | 95.214 | |
| 0.18232 | 97.714 | |
| 0.21290 | 101.029 | |
| 0.24434 | 102.951 | |
| 0.27541 | 105.438 | |
| 0.35591 | 112.745 | |

Temp.: 25.001 ± 0.001°C
Liq. Vol.: 98.40 ml

TABLE IV-8

VAPOR PRESSURE MEASUREMENT OF BENZENE SOLUBILITY
IN 0.10M NaDC, 0.01M NaOH, AND 0.50M NaCl

| Vol. Benzene Added | Gauge Units | |
|---|---|---|
| 0.00 | 22.433 | (22.959 mm Hg) |
| 0.03007 | 25.938 | |
| 0.06050 | 29.340 | |
| 0.091885 | 32.737 | |
| 0.123105 | 36.051 | |
| 0.15318 | 39.181 | |
| 0.18446 | 42.341 | |
| 0.21447 | 45.321 | |
| 0.24447 | 48.271 | |
| 0.27561 | 51.271 | |
| 0.307005 | 54.243 | |
| 0.33701 | 57.061 | |
| 0.36720 | 59.815 | |
| 0.39721 | 62.469 | |
| 0.42871 | 65.243 | |
| 0.44002 | 66.246 | |
| 0.45327 | 67.403 | |
| 0.48409 | 70.070 | |
| 0.53629 | 74.488 | |
| 0.58786 | 78.716 | |
| 0.64007 | 82.947 | |
| 0.69136 | 86.978 | |
| 0.79229 | 94.484 | |
| 0.89389 | 101.528 | |
| 0.99574 | 106.935 | |
| 1.09732 | 111.756 | |

Temp.: 24.997 $\pm$ 0.0059°C
Liq. Vol.: 100.445 ml

TABLE IV-9

VAPOR PRESSURE MEASUREMENT OF BENZENE SOLUBILITY IN 0.10M NaDC, 0.01M NaOH, AND 0.50M NaCl WITH CYCLOHEXANE ADDED (20% OF SATURATION)

| Vol. Benzene Added | Gauge Units | |
|---|---|---|
| 0.00 | | (23.122 mm Hg) |
| 0.2327 ml Cyclohexane | 46.299 | (47.506 mm Hg) |
| 0.00 ml $C_6H_6$ | 46.299 | 24.384 mm Hg Cyclohexane |
| 0.03174 | 49.637 | |
| 0.06319 | 52.795 | |
| 0.09343 | 55.719 | |
| 0.12444 | 58.727 | |
| 0.15547 | 61.668 | |
| 0.23731 | 69.298 | |
| 0.28964 | 74.082 | |
| 0.34126 | 78.625 | |
| 0.39135 | 83.087 | |
| 0.44312 | 87.605 | |
| 0.49509 | 92.098 | |
| 0.59588 | 100.114 | |

Temp.: 24.999 $\pm$ 0.003°C
Liq. Vol.: 95.23 ml

TABLE IV-10

VAPOR PRESSURE MEASUREMENT OF BENZENE SOLUBILITY IN 0.10M NaDC, 0.01M NaOH, AND 0.50M NaCl WITH CYCLOHEXANE ADDED (40% OF SATURATION)

| Vol. Benzene Added | Gauge Units | |
|---|---|---|
| 0.00 | 22.665 | (23.197 mm Hg) |
| 0.4005 ml Cyclohexane | 62.804 | (64.357 mm Hg) |
| 0.00 ml $C_6H_6$ | 62.804 | 41.160 mm Hg Cyclohexane |
| 0.03077 | 65.614 | |
| 0.06120 | 68.453 | |
| 0.08229 | 70.495 | |
| 0.11302 | 73.471 | |
| 0.14335 | 76.339 | |
| 0.17439 | 79.261 | |
| 0.20517 | 82.126 | |
| 0.23609 | 85.010 | |
| 0.26668 | 87.771 | |
| 0.29686 | 90.482 | |
| 0.34744 | 95.140 | |
| 0.39772 | 99.226 | |
| 0.43777 | 102.607 | |
| 0.53895 | 110.629 | |

Temp.: 24.999 ± 0.001°C
Liq. Vol.: 100.50 ml

TABLE IV-11

EMPIRICAL CONSTANTS USED IN THE REDLICH-KISTER EQUATIONS
TO CALCULATE ACTIVITY COEFFICIENTS FOR
BENZENE AND CYCLOHEXANE

| Temperature | B | C | D |
|---|---|---|---|
| 25°C | 0.209 | 0.0046 | 0.0165 |
| 40°C | 0.194 | 0.0040 | -0.0009 |
| 70°C | 0.169 | 0.0030 | -0.0324 |

TABLE IV-12

SUMMARY OF ANALYZED VAPOR PRESSURE DATA FOR MICELLAR SOLUTIONS

| Sample Description | Vapor Volume ml | Liquid Volume ml | Aqueous Vapor Pressure mm Hg | Initial Volume, ml | Cyclohexane Pressure mm Hg | $M_B = A + BP + CP^2$ A | B | C |
|---|---|---|---|---|---|---|---|---|
| Benzene only into 0.10M NaDC 0.01M NaOH, 0.15M NaCl | 998.41 | 98.30 | 23.292 | 0 | 0 | $9.061\times10^{-5}$ | $8.848\times10^{-5}$ | $4.214\times10^{-7}$ |
| Benzene into ~20% Cyclohexane 0.1M NaDC, 0.01M NaOH, 0.15M NaCl | 999.06 | 97.45 | 23.276 | 0.2023 | 22.359 | $-2.743\times10^{-3}$ | $1.179\times10^{-4}$ | $1.226\times10^{-7}$ |
| Benzene into ~40% Cyclohexane 0.1M NaDC, 0.01M NaOH, 0.15M NaCl | 998.81 | 97.54 | 23.456 | 0.3610 | 36.944 | $-3.445\times10^{-3}$ | $8.635\times10^{-5}$ | $2.878\times10^{-7}$ |
| Benzene into ~60% Cyclohexane 0.1M NaDC, 0.01M NaOH, 0.15M NaCl | 997.65 | 98.40 | 23.487 | 0.615 | 62.591 | $-8.150\times10^{-3}$ | $1.364\times10^{-4}$ | $-4.62\times10^{-8}$ |
| Benzene only into 0.10M NaDC 0.01M NaOH, 0.50M NaCl | 996.27 | 100.45 | 22.959 | 0 | 0 | $5.783\times10^{-5}$ | $8.938\times10^{-5}$ | $4.303\times10^{-7}$ |
| Benzene into ~20% Cyclohexane 0.10M NaDC, 0.01M NaOH, 0.50M NaCl | 1001.13 | 95.23 | 23.122 | 0.2327 | 23.951 | $-2.479\times10^{-3}$ | $9.550\times10^{-5}$ | $2.495\times10^{-7}$ |
| Benzene into ~40% Cyclohexane 0.10M NaDC, 0.01M NaOH, 0.50M NaCl | 995.81 | 100.50 | 23.197 | 0.4005 | 41.160 | $-3.801\times10^{-3}$ | $8.091\times10^{-5}$ | $3.130\times10^{-7}$ |

TABLE IV-13

SOLUBILITY OF BENZENE AND CYCLOHEXANE IN AQUEOUS SOLUTIONS

| | Benzene | Cyclohexane |
|---|---|---|
| Solubility in Water | 0.0226M | 0.0011M |
| 0.01M NaOH, 0.15M NaCl | | |
| Salting-Out Coeff. | 1.0771 | 1.0771 |
| Solubility | 0.02098 | 0.00103 |
| Henry Law Const. | 4511.63 mm Hg/M | 94766.99 mm Hg/M |
| 0.01M NaOH, 0.50M NaCl | | |
| Salting-Out Coeff. | 1.263 | 1.263 |
| Solubility | 0.01789 | 0.00088 |
| Henry Law Const. | 5290.89 mm Hg/M | 110920.4 mm Hg/M |

TABLE IV-14

COMPARISON OF CALCULATED AND OBSERVED MICELLAR SOLUTION COMPOSITIONS: BENZENE

| Benzene Mole Fraction* | Calculated** | | | Observed*** | | |
|---|---|---|---|---|---|---|
| | $[BZ]_T$ | $[BZ]_E$ | $[BZ]_M$ | $[BZ]_T$ | $[BZ]_E$ | $[BZ]_M$ |
| | 0.1M NaDC, 0.01M NaOH, 0.15M NaCl | | | | | |
| 1.00 | 0.0728 | 0.0210 | 0.0518 | 0.080 | 0.022 | 0.058 |
| 0.854 | 0.0635 | 0.0182 | 0.0453 | 0.070 | 0.020 | 0.050 |
| 0.717 | 0.0526 | 0.0160 | 0.0366 | 0.060 | 0.0178 | 0.042 |
| 0.468 | 0.0340 | 0.0114 | 0.0226 | 0.040 | 0.0128 | 0.027 |
| | 0.1M NaDC, 0.01M NaOH, 0.50M NaCl | | | | | |
| 1.00 | 0.0727 | 0.0179 | 0.0548 | 0.073 | 0.023 | 0.050 |
| 0.829 | 0.0599 | 0.0151 | 0.0448 | 0.062 | 0.0195 | 0.042 |
| 0.682 | 0.0471 | 0.0129 | 0.0342 | 0.051 | 0.0168 | 0.034 |

$[BZ]_T$ = Total Benzene Concentration in Aqueous Phase, M

$[BZ]_E$ = Benzene Concentration in the Electrolyte, M

$[BZ]_M = [BZ]_T - [BZ]_E$ = Intramicellar Solution Concentration, M

*Benzene mole fraction predicted by extrapolation of vapor pressure data to saturation with increasing amounts of cyclohexane.

**Composition of solutions calculated using the iterative procedure described in the text.

***Composition of solutions observed, determined by picking points off of plotted curves made from experimental data.

TABLE IV-15

COMPARISON OF CALCULATED AND OBSERVED MICELLAR SOLUTION COMPOSITIONS: CYCLOHEXANE

| Benzene Mole Fraction* | Calculated** | | | Observed*** | | |
|---|---|---|---|---|---|---|
| | $[CH]_T$ | $[CH]_E$ | $[CH]_M$ | $[CH]_T$ | $[CH]_E$ | $[CH]_M$ |
| | 0.10M NaDC, 0.01M NaOH, 0.15M NaCl | | | | | |
| 1.00 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.854 | 0.008 | 0.0002 | 0.0078 | 0.0098 | 0.00024 | 0.0096 |
| 0.717 | 0.0148 | 0.0003 | 0.0145 | 0.0176 | 0.0003 | 0.0173 |
| 0.468 | 0.0263 | 0.0006 | 0.0257 | 0.0281 | 0.0005 | 0.0276 |
| | 0.10M NaDC, 0.01M NaOH, 0.50M NaCl | | | | | |
| 1.00 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.829 | 0.0094 | 0.00025 | 0.0092 | 0.010 | 0.00026 | 0.0097 |
| 0.682 | 0.0163 | 0.0004 | 0.0159 | 0.0175 | 0.0004 | 0.0153 |

$[CH]_T$ = Total Cyclohexane Concentration in Aqueous Phase, M

$[CH]_E$ = Cyclohexane Concentration in the Electrolyte, M

$[CH]_M = [CH]_T - [CH]_E$ = Intramicellar Solution Concentration, M

*Benzene mole fraction predicted by extrapolation of vapor pressure data to saturation with increasing amounts of cyclohexane.

**Composition of solutions calculated using the iterative procedure described in the text.

***Composition of solutions observed, determined by picking points off of plotted curves made from experimental data.

TABLE IV-16

FREE ENERGY OF SOLUBILIZATION PER MOLE
OF SODIUM DEOXYCHOLATE

| Mole Fraction Benzene | $[BZ]_M$ | $[BZ]_E$ | $\Delta G_S$ Kcal/$M_{BZ}$ $M_{NaDC}$ | $[CH]_M$ | $[CH]_E$ | $\Delta G_S$ Kcal/$M_{CH}$ $M_{NaDC}$ |
|---|---|---|---|---|---|---|
| | Electrolyte: 0.01M NaOH, 0.15M NaCl | | | | | |
| 0.00 | 0 | 0 | ------ | 0.0364 | 0.00121 | -3.380 |
| 0.25 | 0.0133 | 0.0077 | -1.688 | 0.033 | 0.00076 | -3.598 |
| 0.50 | 0.0313 | 0.0116 | -1.952 | 0.0227 | 0.00045 | -3.687 |
| 0.75 | 0.0431 | 0.0191 | -1.846 | 0.0161 | 0.0003 | -3.724 |
| 1.00 | 0.0583 | 0.022 | -1.941 | 0 | 0 | ------ |
| | Electrolyte: 0.01M NaOH, 0.50M NCl | | | | | |
| 0.00 | 0 | 0 | ------ | 0.0380 | 0.00088 | -3.595 |
| 0.25 | 0.0133 | 0.00623 | -1.813 | 0.0312 | 0.00066 | -3.648 |
| 0.50 | 0.0260 | 0.0114 | -1.852 | 0.0255 | 0.00044 | -3.769 |
| 0.75 | 0.0392 | 0.0174 | -1.845 | 0.0134 | 0.00022 | -3.799 |
| 1.00 | 0.0502 | 0.0235 | -1.814 | 0 | 0 | ------ |

TABLE IV-17

CALCULATION OF THE SALTING OUT RATIO OF
BENZENE AND CYCLOHEXANE IN SODIUM DEOXYCHOLATE MICELLES

| Benzene Mole Fraction | $[BZ]_{MIC}$ | | Ratio Low/High | $[CH]_{MIC}$ | | Ratio Low/High |
|---|---|---|---|---|---|---|
| | Low $\mu$ | High $\mu$ | | Low $\mu$ | High $\mu$ | |
| 0.00 | 0 | 0 | ---- | 0.0364 | 0.0380 | 0.96 |
| 0.25 | 0.0133 | 0.0133 | 1.00 | 0.0330 | 0.0312 | 1.06 |
| 0.50 | 0.0313 | 0.0260 | 1.20 | 0.0277 | 0.0255 | 1.09 |
| 0.75 | 0.0431 | 0.0392 | 1.10 | 0.0161 | 0.0134 | 1.20 |
| 1.00 | 0.0583 | 0.0502 | 1.16 | 0 | 0 | ---- |

Average Ratio: $1.10 \pm 0.09$

$\mu$ = Ionic strength

Low $\mu$ = 0.26, 0.1M NaDC, 0.01M NaOH, 0.15M NaCl

High $\mu$ = 0.61, 0.1M NaDC, 0.01M NaOH, 0.50M NaCl

FIGURE IV-1

COMPARISON OF THE CONCENTRATION OF BENZENE IN THE INTRAMICELLAR SOLUTION WITH THE BENZENE CONCENTRATION OF THE CONTACTING SOLUTION

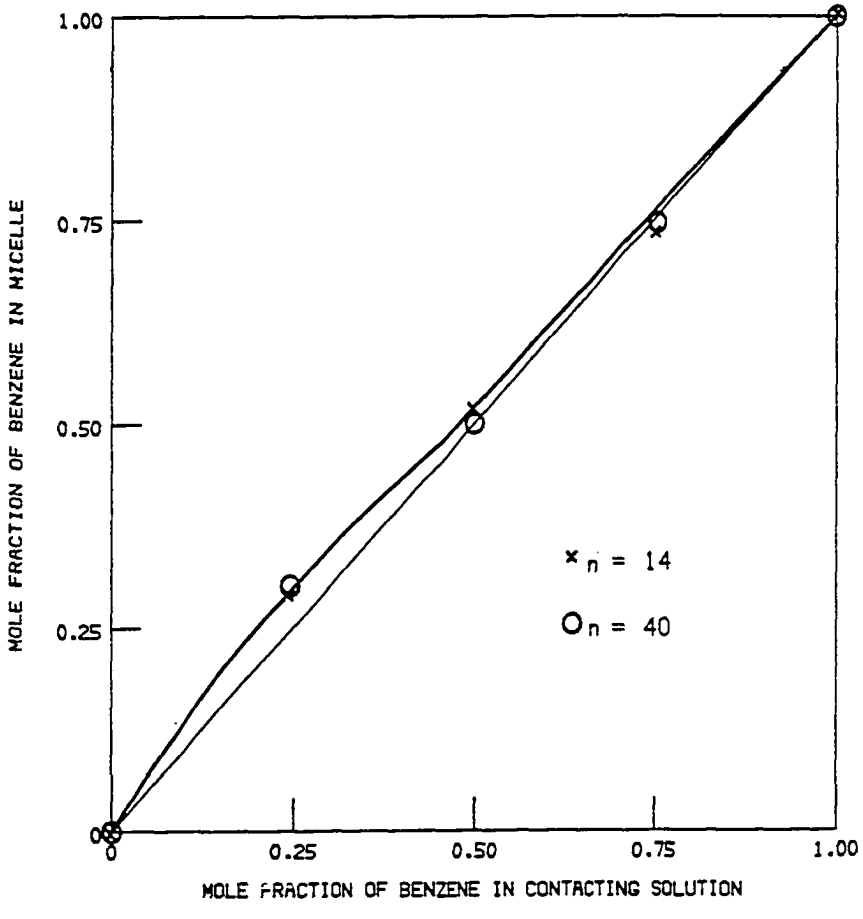


FIGURE IV-2

VAPOR PRESSURE OF BENZENE-CYCLOHEXANE MIXTURES AT 25°C

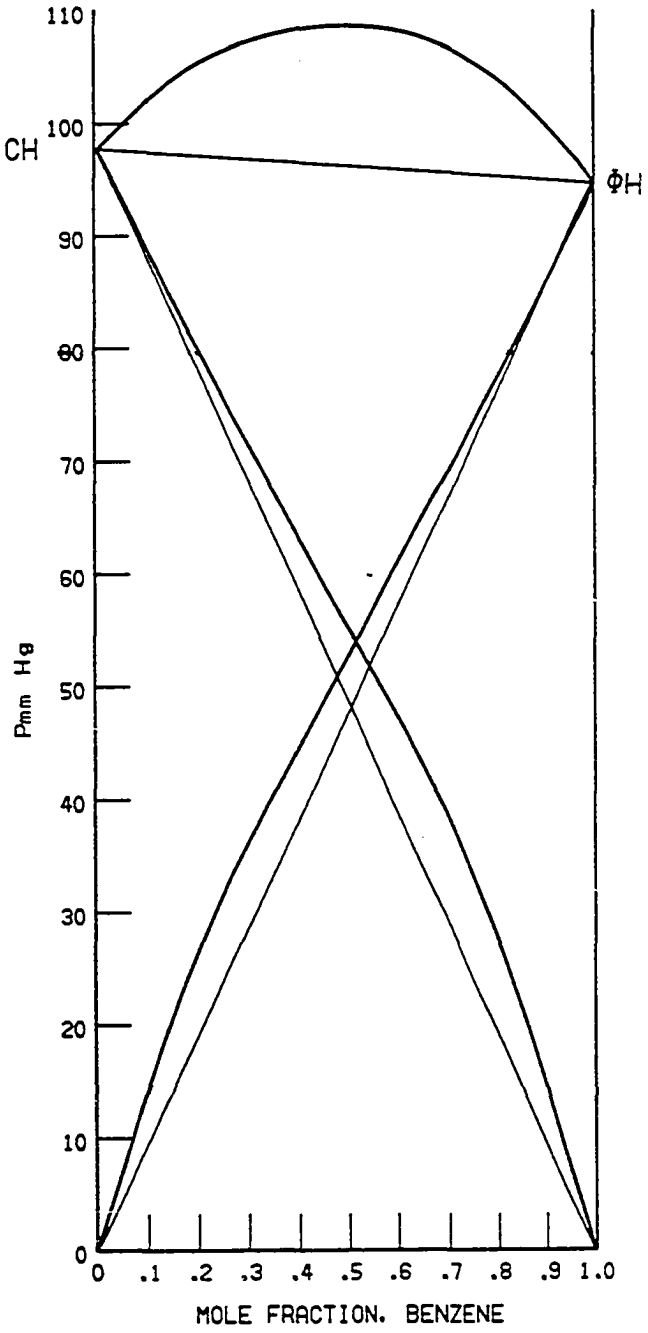


FIGURE IV-3
SOLUBILITY OF BENZENE AND
CYCLOHEXANE IN 0.01M NaOH, 0.15M NaCl

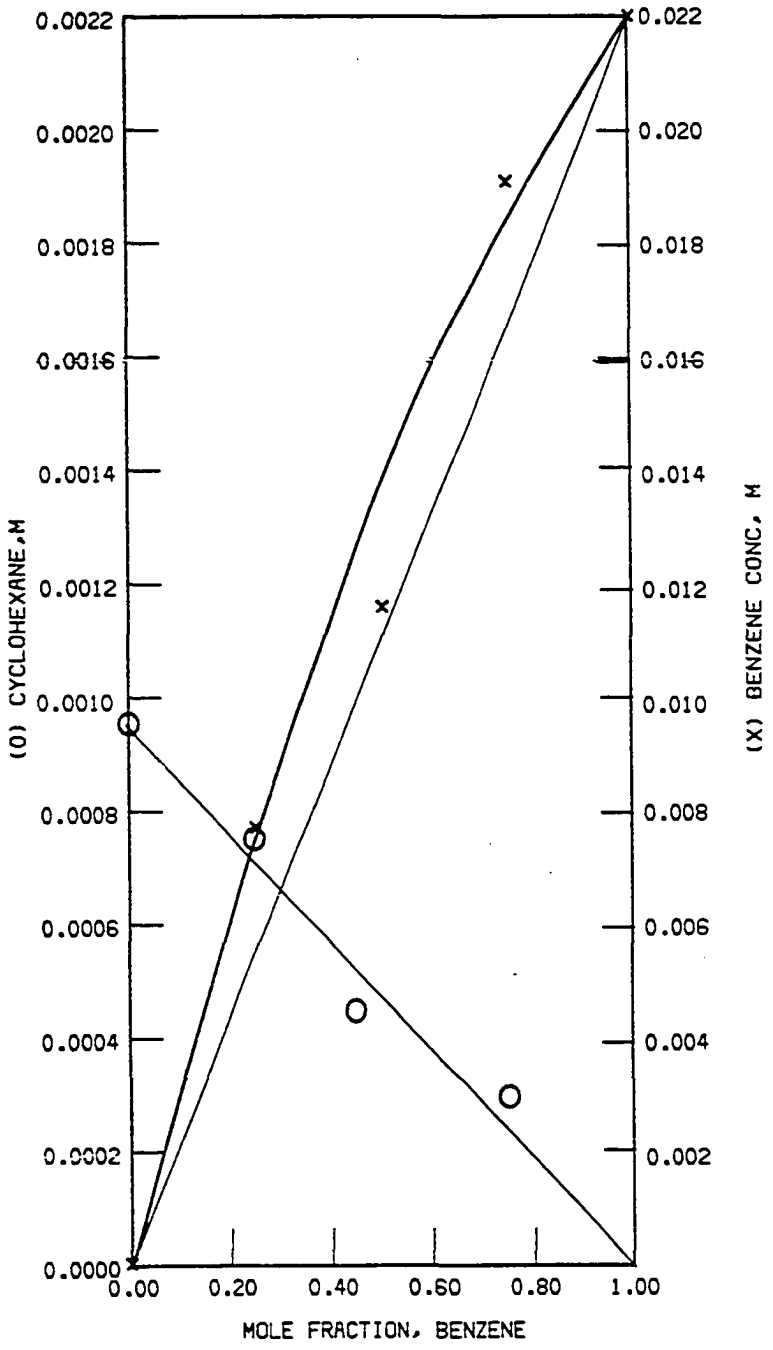


FIGURE IV-4

SOLUBILITY OF BENZENE AND CYCLOHEXANE
IN 0.10M NaDC, 0.01M NaOH 0.15M NaCl

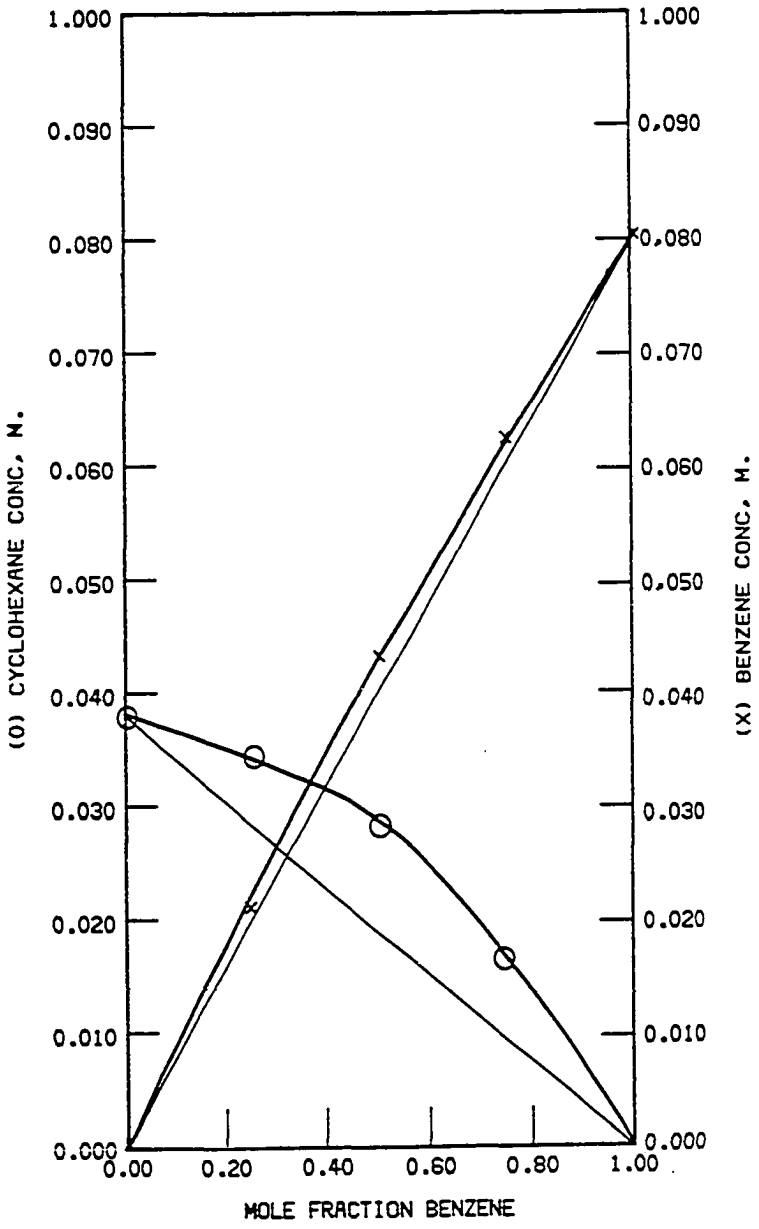


FIGURE IV-5

SOLUBILITY OF BENZENE AND CYCLOHEXANE
IN 0.01M NaOH, 0.50M NaCl

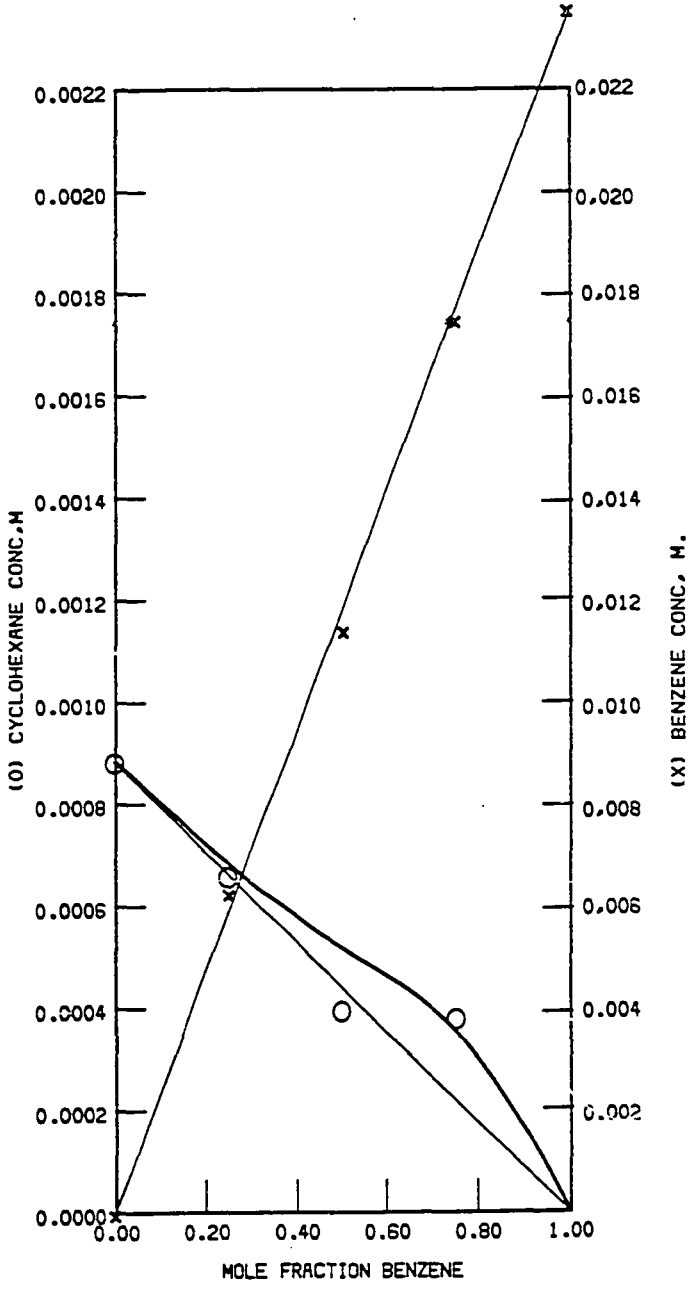


FIGURE IV-6

SOLUBILITY OF BENZENE AND CYCLOHEXANE IN 0.10M NaDC, 0.01M NaOH, 0.50M NaCl

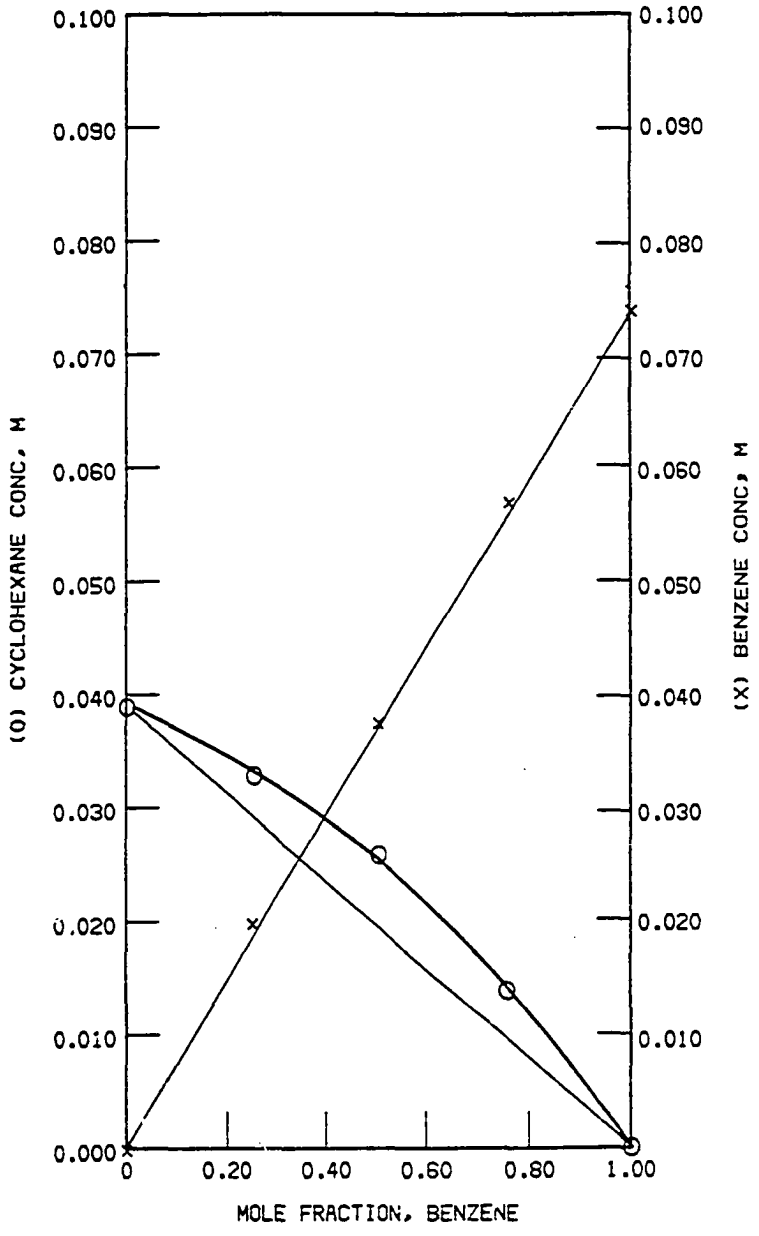


FIGURE IV-7

RATIO OF HYDROCARBON MOLECULES TO SODIUM DEOXYCHOLATE MOLECULES IN THE MICELLE

