INFORMATION TO USERS

This reproduction was made from a copy of a manuscript sent to us for publication and microfilming. While the most advanced technology has been used to photograph and reproduce this manuscript, the quality of the reproduction is heavily dependent upon the quality of the material submitted. Pages in any manuscript may have indistinct print. In all cases the best available copy has been filmed.

The following explanation of techniques is provided to help clarify notations which may appear on this reproduction.

- 1. Manuscripts may not always be complete. When it is not possible to obtain missing pages, a note appears to indicate this.
- 2. When copyrighted materials are removed from the manuscript, a note appears to indicate this.
- 3. Oversize materials (maps, drawings, and charts) are photographed by sectioning the original, beginning at the upper left hand corner and continuing from left to right in equal sections with small overlaps. Each oversize page is also filmed as one exposure and is available, for an additional charge, as a standard 35mm slide or in black and white paper format.*
- 4. Most photographs reproduce acceptably on positive microfilm or microfiche but lack clarity on xeregraphic copies made from the microfilm. For an additional charge, all photographs are available in black and white standard 35mm slide format.*

*For more information about black and white slides or enlarged paper reproductions, please contact the Dissertations Customer Services Department.



8604582

Bushong, Donna Smith

OSMOMETRY STUDIES OF SURFACTANT AGGREGATION AND SOLUBILIZATION BY MICELLAR SYSTEMS

The University of Oklahoma

Рн. . 1985

University Microfilms International 300 N. Zeeb Road, Ann Arbor, MI 48106

PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark $\underline{\checkmark}$.

- 1. Glossy photographs or pages _____
- 2. Colored illustrations, paper or print _____
- 3. Photographs with dark background _____
- 4. Illustrations are poor copy
- 5. Pages with black marks, not original copy
- 6. Print shows through as there is text on both sides of page_____
- 7. Indistinct, broken or small print on several pages
- 8. Print exceeds margin requirements
- 9. Tightly bound copy with print lost in spine _____
- 10. Computer printout pages with indistinct print _____
- 11. Page(s) ______ lacking when material received, and not available from school or author.
- 12. Page(s) ______ seem to be missing in numbering only as text follows.
- 13. Two pages numbered _____. Text follows.
- 14. Curling and wrinkled pages _____
- 15. Dissertation contains pages with print at a slant, filmed as received
- 16. Other_____

University Microfilms International

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

OSMOMETRY STUDIES OF SURFACTANT AGGREGATION AND SOLUBILIZATION BY MICELLAR SYSTEMS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

DONNA SMITH BUSHONG

Norman, Oklahoma

OSMOMETRY STUDIES OF SURFACTANT AGGREGATION AND SOLUBILIZATION BY MICELLAR SYSTEMS

APPROVED BY

91 \mathcal{B} 3.1.1

DISSERTATION COMMITTEE

ACKNOWLE DGMENT

I wish to thank the National Science Foundation and the Department of Energy, Basic Energy Sciences and the Bartlesville Energy Technology Center, for funding grants which provided research assistantships for me during my graduate studies.

I wish to thank the members of my advisory committee. Their guidance throughout my graduate studies, and time spent on and in consideration of this dissertation are greatly appreciated.

Several undergraduate students helped collect data for two of the systems studied in the dissertation research. I wish to express my sincere gratitude to them. They are Mr. Craig Cott, Mrs. Mercedes Gonzales, Mr. Doug Klumpp, and Miss Kathryn Terrell.

Results for several systems discussed in the dissertation were generously provided by members of the research group. I wish to thank them for their results and our many discussions of the systems. They are Mr. George Smith, Dr. Pedro Bernal, and Dr. Subray Bhat.

Much of the effort in the dissertation research was spent on data modelling. This included, fortunately, using a computer to do innumerable tedious calculations for me. However, this can be quite frustrating at times. Therefore, I wish to thank Dr. Ed Tucker for his endless assistance and sharing his knowledge of compute: programming.

My family has been a continuous source of support during my graduate studies. I really have appreciated that support. In particular, my sister, Dr. Linda Smith, has been extremely helpful, both professionally and as a very dear friend. Thank you.

I especially wish to thank my sons, Jason and Kyle, for their patience and love, particularly during such a difficult time in our lives. They have always brought a smile to my face, even when I felt I was turning their world up-side-down. They have provided my ultimate source of encouragement, and I love them dearly.

The contributions of my research advisor to my success as a graduate student cannot be overstated. Prof. Sherril Christian has been both an encouraging mentor and an understanding friend. His approach to chemical problems and the professionalism in his work are exemplary. He is a wonderful man to work with, and I feel priviledged to have had the opportunity to work with him. The completion of

this dissertation is dedicated to

my sons,

Jason and Kyle,

with all my love.

TABLE OF CONTENTS

		Page
LIST OF T	ABLES	vii
LIST OF F	IGURES	viii
I. INTR	CODUCTION	1
II. OBJE	CTIVES AND APPROACH	9
III. EXPE	CRIMENTAL	
i.	Vapor Pressue Osmometry	10
ii.	Vapor Pressure Measurements	14
iii.	Counterion Activity Measurements	16
iv.	Surface Tension	17
v.	Semi-equilibrium Dialysis	21
vi.	Other Sources of Data	23
vii.	Chemicals	24

TABLE OF CONTENTS cont.

Page

V. RESULTS

i.	Sodium Octylsulfate in Water	45
ii.	Cetylpyridinium Chloride in Water	61
iii.	Self-association of 2-Phenylacetic Acid	72
iv.	Solubilization	75

VI. DISCUSSION

i.	Surfactants in Water	96
ii.	Self-association of 2-Phenylacetic Acid	106
iii.	Solubilization	111

VII. CONCLUSIONS 118

REFERENCES		120
------------	--	-----

LIST OF TABLES

V-1.	Experimental and Calculated Data for Sodium Octylsulfate in Water at 25°C	47
V-2.	Least-squares Parameters from the Mass-action Model for Sodium Octylsulfate in Water at 25°C	56
V-3.	Experimental and Calculated Data for Cetylpyridinium Chloride in Water at 25°C	62
V-4.	Least-squares Parameters from the Mass-action Model for Cetylpyridinium Chloride in Water at 25°C	69
V-5.	Experimental and Calculated Data for 2-Phenylacetic Acid in Water at 25°C	73
V-5.	Experimental and Calculated Data using Kesults from Osmometry, and Chloride and Proton Activities of 2-Phenylacetic Acid Solubilized in Cetylpyridinium Chloride in Water at 25°C	76
V-7.	Experimental and Calculated Data using Results from Semi-equilibrium Dialysis of 2-Phenylacetic Acid Solubilized in Cetylpyridinium Chloride in Water at 25°C	92
VI-1.	Least-squares Parameters from the Mass-action Model for Individual Fits of Sodium Octylsulfate	97
VI-2.	Least-squares Parameters from the Mass-actionModel for Individual Fits of Cetylpyridinium Chloride	100
VI-3.	Self-association and 1:1 Complex Formation Constants for Organics in Water at 25°C	107
VI-4.	Apparent Solubilization Constants for Various Organic Molecules in Cetylpyridinium Chloride	115

Page

LIST OF FIGURES

Page

I-1.	A Pictorial Description of the Micelle, and Solubilization Sites in the Micelle	3
I-2.	Physical Properties of Surfactants	4
III-1.	Diagram of the Vapor Pressure Osmometer	11
III-2.	Calibration Curve for Vapor Pressure Osmometer	13
III-3.	Osmotic Coefficients of Sodium Octylsulfate in Water at 25°C	15
III-4.	Diagram of the Maximum Double-Bubble Pressure Apparatus	18
111-5.	Diagram of the Rosano Surface Tensiometer	20
III-6.	Semi-Equilibrium Dialysis Cell	22
V-1.	Osmotic Coefficients of Sodium Octylsulfate in Water at 25 °C	52
V-2.	Activity Coefficients of Sodium Octylsulfate in Water at 25°C	53
V-3.	Surface Tensions of Sodium Octylsulfate in Water at 25°C	54
V-4.	Monomer Concentration of Sodium Octylsulfate in Water at 25°C Calculated from the Mass-Action Model	58
V-5.	Osmotic Coefficients of Cetylpyridinium Chloride in Water at 25°C	66
V-6.	Activity Coefficients of Cetylpyridinium Chloride in Water at 25°C	67
V-7.	Surface Tensions of Cetylpyridinium Chloride in Water at 25°C	68

LIST OF FIGURES cont.

Page

Mean Ionic Molality and Monomer Molality of Cetylpyridinium Chloride in Water at 25°C Calculated from the Mass-Action Model	70
Osmometry of 2-Phenylacetic Acid in Water at 25° C .	74
Fraction of Counterions Bound for Phenylacetic Acid Solubilized in Cetylpyridinium Chloride in Water at 25°C	84
Apparent Solubilization Constants of Phenylacetate Solubilized in Cetylpyridinium Chloride in Water at 25°C	85
Apparent Solubilization Constants for Phenylacetic Acid Sclubilized in Cetylpyridinium Chloride in Water at 25°C (in 0.1, 0.2, 0.4 m CPC)	86
Apparent Solubilization Constants for Phenylacetic Acid Solubilized in Cetylpyridinium Chloride in Water at 25°C (in 0.1, 0.2 m CPC)	87
Activity Coefficiencs for Intramicellar Components for Phenylactic Acid Solubilized in Cetylpyridinium Chloride in Water at 25°C	91
Comparison of Different Techniques Used to Determine Apparent Solubilization Constants for Phenylacetic Acid Solubilized in Cetylpyridinium Chloride in Water at 25°C	94
	Mean Ionic Molality and Monomer Molality of Cetylpyridinium Chloride in Water at 25°C Calculated from the Mass-Action Model Osmometry of 2-Phenylacetic Acid in Water at 25°C . Fraction of Counterions Bound for Phenylacetic Acid Solubilized in Cetylpyridinium Chloride in Water at 25°C Apparent Solubilization Constants of Phenylacetate Solubilized in Cetylpyridinium Chloride in Water at 25°C Apparent Solubilization Constants for Phenylacetic Acid Solubilized in Cetylpyridinium Chloride in Water at 25°C (in 0.1, 0.2, 0.4 m CPC) Apparent Solubilization Constants for Phenylacetic Acid Solubilized in Cetylpyridinium Chloride in Water at 25°C (in 0.1, 0.2 m CPC) Apparent Solubilization Constants for Phenylacetic Acid Solubilized in Cetylpyridinium Chloride in Water at 25°C (in 0.1, 0.2 m CPC) Activity Coefficiences for Intramicellar Components for Phenylacetic Acid Solubilized in Cetylpyridinium Chloride in Water at 25°C

OSMOMETRY STUDIES OF SURFACTANT AGGREGATION

AND

SOLUBILIZATION BY MICELLAR SYSTEMS

CHAPTER I

INTRODUCTION

Surfactants can be used in a variety of fields; for example, detergency, enhanced oil recovery, micellar catalysis, drug delivery, and separation. All these functions are based on the solubilizing power of the micelle. It is necessary to understand the energetics involved in the aggregation and solubilization processes in order to be able to predict appropriate systems for a particular application.

Micelles are aggregates of amphiphilic molecules. These compounds can be ionic (e.g., sodium octylsulfate, anionic; and n-hexadecylpyridinium chloride, cationic); nonionic (e.g., monoglyceride of long-chain fatty acid, and polyoxyethylenated alkyl phenol); or zwitterionic (e.g., long-chain amino acid, and N-alkyl betaine) (1). In aqueous solution, the hydrophobic portions or tails of the surfactant monomers are associated in a random fashion in the interior of the micelle. The hydrophilic portions or head groups are oriented away from the micelle interior and directed toward, and in intimate contact with, the bulk aqueous phase. (See Figure I-1.)

By their very nature, micelles are able greatly to enhance the solubility of slightly water-soluble organic compounds in aqueous micellar solutions. The solubilization site of the organic in the micelle depends on the nature of both the organic and the surfactant. This site can be in the interior or core of the micelle; between the head group region and the core, (sometimes called the palisade layer); in the surface region, among the head groups; or, in the interfacial region between the micellar "phase" and the bulk aqueous solution. Organics solubilized in the core generally are less polar, while those solubilized closer to the surface region are more polar. Surfactant monomers aggregate to form micelles when the total concentration reaches a critical micelle concentration, or cmc. Above this concentration, monomers and micelles are in dynamic equilibrium, and the solubilization of organic compounds increases dramatically.

The association of surfactants, and solubilization by micellar systems have been the subjects of several excellent reviews in the literature (1-14).

Surfactant solutions have been studied by many different physical techniques. A plot of the data vs the total concentration of surfactant exhibits a "break" in the appropriate function. (See Figure I-2.) The parameters and types of information sought, which describe properties of the aggregation process, include the cmc; aggregation



or Cetylpyridinium Chloride (CPC)



PHYSICAL PROPERTIES OF SURFACTANTS

FIGURE I-2

Figure from reference 8

size; degree of counterions bound; degree of water penetration; enthalpy and entropy of micelle formation; enthalpy and entropy of transfer for various groups from the bulk phase into the micelle; specific volume; compressibility; and more recently, size distribution, Variable temperature studies have been used to determine and shape. heat capacity and expansibility from enthalpy and volume information, The aggregation size can be determined using results respectively. from light scattering, fluorescent probe techniques, or colligative Ion-selective electrodes are often used to measure measurements. counterion binding. To study how deep into the micelle water of hydration penetrates, one can use fluorescent probe techniques, and Heats of formation and transfer are best determined using NMR _ Density provides a direct measure of volume changes. calorimetry. Sound velocity can be used to study compressibility. Several studies of size distribution have been performed using light scattering and ion-selective electrodes. The aggregate shape might be determined using light scattering and rheological measurements, for example, density, viscosity, and centrifugation. All the techniques mentioned above and in Figure I-2 can be used to predict the cmc. Investigations of these types of information are attempts to contribute to a better understanding of the forces involved in the micellization process. Thermodynamic models which treat the data can be categorized into mass-action models (15), and phase or pseudo-phase separation models It is generally agreed that the two models become nearly (16).equivalent for micelles with aggregation sizes above about 50 to 100 monomers.

Although in the literature there are many reports of aqueous surfactant aggregation, and models which predict very well the data from a reported technique, there tends to be a large range of values for a particular parameter depending on the technique used. In addition, in most models, the parameters included in the description are highly correlated; that is, the choice of the value for one parameter is likely to have a very large influence on the resulting calculated value for another parameter.

Therefore, it would be very useful if a single set of parameters could be determined which would adequately predict the data from several techniques. This universal set of parameters, unique for a given surfactant and temperature, would provide a more realistic and wore complete description of the aqueous aggregation behavior.

Solubilization by micellar systems has been studied using techniques such as solubility and turbidity, light scattering, ion-selective electrodes, dialysis, semi-equilibrium dialysis, and vapor pressure measurements. Most reports in the literature study the solubilization system only at concentrations where the micellar solution is saturated with respect to the organic. However, several investigators have studied the effect of the composition of, or mole fraction of organic solubilized in the micelle (17-36).

It is well known that the cmc of the pure surfactant will be decreased in the presence of a slightly water-soluble organic solute. However, there are reports where the cmc can increase with the addition of, for example, an alcohol (37). Contradictory results have been reported of the effect of solubilizate on counterion binding to ionic

micelles (18,38). The aggregation size of the micelle usually is observed to increase as the mole fraction of solubilized organic increases. This is due in part to the incorporation of more organic molecules, but also the increase in the average number of surfactant molecules in the micelle.

However, the effects the solubilized species can have on parameters describing the micelle, and in general on the forces involved in micellization and solubilization are not well characterized. These effects are dependent on properties of both the organic and surfactant; the solubilization site; and, the composition of the aggregate species; as well as, for example, the temperature and pressure of the system.

A systematic study of the solubilization of a series of various types of organic molecules into a particular surfactant should be valuable in gaining insight into the factors which contribute to the solubilization process. In order to study these systems, information is needed which describes the behavior of the surfactant, and the organic molecule in aqueous solutions.

Christian, Smith, Tucker, and Scamehorn (24) have recently developed a technique, semi-equilibrium dialysis, which appears to be very useful for studying the solubilization of a wide variety of materials by surfactant solutions. It is desirable always to confirm, whenever possible, that experimental results are reasonable; that is, that the results from one technique can be reproduced using a different technique and data treatment. However, use of any technique for solubilization studies requires knowledge of the aqueous surfactant

behavior in the absence of an organic molecule. This is essential in interpreting the solubilization results.

CHAPTER II

OBJECTIVES and APPROACH

The purpose of this research is to

i) provide precise solute and solvent activity data for sodium octylsulfate, and n-hexadecylpyridinium chloride in water; 2-phenyl-acetic acid in water; and, 2-phenylacetic acid solubilized in n-hexa-decylpyridinium chloride and water;

ii) retrieve interaction parameters describing the complexes formed; and,

iii) gain insight into the micellization and micelle-solubilization
processes.

The method of approach to achieve these objectives will be to use vapor pressure osmometry and equilibrium vapor pressure measurements to obtain solvent activity information; surface tensiometry and semi-equilibrium dialysis data to obtain solute activity data; and ion-selective electrode studies to measure ion activities. Data from these techniques for a given system will be modelled simultaneously using a mass-action theory of micellization and solubilization.

CHAPTER III

EXPERIMENTAL

i. VAPOR PRESSURE OSMOMETRY

Solvent activity data are collected using a vapor pressure osmometer (Corona Wescan Model 232A Molecular Weight Apparatus). The cell, thermostated at 25.00±.01°C, consists of two thermistors in a solvent vapor-saturated environment. (See Figure III-1.) Syringes are used to introduce a drop of reference solution onto one thermistor and a drop of test solution onto the other thermistor. The approach to equilibrium involves vapor condensation onto the test solution drop (and reference drop if different from the cell solution) thereby warming the drop and increasing its vapor pressure, so that it approaches that of the reference (or cell) solution. The heat of condensation causes the solution and thermistor temperatures to increase. The temperature difference between the two thermistors is detected as a voltage difference across a bridge connecting the two Although equilibrium is not reached in the experiment, thermistors. the difference in temperature between the two thermistors is very







nearly proportional to the difference that would be attained at equilibrium.

Spaium chloride is used to calibrate the osmometer. Voltages of known molalities of solutions of NaCl versus water activity of those solutions (39,40) are empirically fitted either to the equation for a straight line or to a quadratic equation, depending on what the data (See Figure III-2.) Assuming that a given activity of water require. will generate the same voltage response regardless of the nature of the solute, water activites are then calculated from voltage measurements for a solution of interest. Molecular weight determinations of sucrose, inositol, and sodium octylsulfate were very good, indicating the validity of the above assumption. NaCl is used as a standard because reliable values of activity have been determined for water at known molalities (39,40). Once water activities are obtained, the data can be processed to obtain other functions of the activity, including: 1) the osmotic coefficient, $\phi = -1000 \ln(a_{\mu})/(vM_{1}m)$, where a_{μ} is the water activity, v is the number of ions per mole of solute, M_1 is the solvent molecular weight, and the molality of the solute is m; and 2) the colligative mole fraction, $1-a_{\mu}$ which, in the case of nonelectrolyte species, is assumed to be equal to the total mole fraction of solute species (moles of monomers + moles of dimers + ... + moles of n-mers).



ii. VAPOR PRESSURE MEASUREMENTS

Although osmometry gives a steady state measurement of the water activity, the data have been shown to agree quite well with data from a manual static vapor pressure measurement, using a high precision bourdon-type pressure gauge. Here a solution is introduced into a thermostated ($25.00\pm.01^{\circ}$ C) flask and degassed. The vapors are collected and weighed to determine the solution concentration, and the pressure over the solution, P/P°, is recorded (41). A direct measure of the water activity (42,43) is thus provided, which can be converted to an osmotic coefficient, ϕ =-1000 ln(a_{tr})/(vM₁m).

This technique yields highly reproducible and precise data for a solution in equilibrium with its vapor. The agreement between the two techniques (see Figure III-3) justifies the assumption that a given activity of water will produce the same voltage response regardless of the nature of the solute present; and, more importantly, confirms that the steady state measurement of the osmometer is sufficient to infer equilibrium water activities in these systems. The advantage of the osmometer is that a steady state output is reached within about five to fifteen minutes, where the manual static vapor pressure apparatus requires approximately an hour and a half or two hours to reach equilibrium.



iii. COUNTERION ACTIVITY MEASUREMENTS

Counterion activities are measured with a Fisher glass Nat ion-selective electrode or Corning solid state Cl ion-selective electrode. The reference electrode is a Corning Ag/AgCl glass double junction electrode with an internal solution of 4 \underline{M} KCl saturated with AgC1 and an external solution of 1 \underline{M} KNC2. An Orion Research Inc. Digital pH millivolt Meter model 701A (for sodium octylsulfate in water systems), and a Fisher Accumet pH Meter model 620 (all other systems) provide millivolt readings of ±0.1 millivolt. Solutions are thermostated at 25.00±.01°C. Voltages of standard solutions of NaCl are measured concurrently with those of surfactant solutions. It is assumed that a given activity of Na⁺ or Cl⁻ will generate the same voltage response regardless of the anion or cation, respectively, present in solution (that is, the surfactant ion does not interfere with the electrode response). This assumption is partially justified if the voltage vs the log of the ion activity is Nernstian (that is, if this function is linear with a slope of approximately 0.059 volts) in the presence of the surfactant in the pre-cmc region. This is the case for the systems reported here. The mean ionic activity is assumed to be equal to the individual ion activities.

iv. SURFACE TENSION

Surface tension measurements for sodium octylsulfate with no added electrolyte are obtained using a differential maximum double bubble pressure method as described by Razouk and Walmsley (44). The apparatus consists of a thermostated cell, two capillary tubes of different diameters, a Validyne heater and pressure transducer, and a Hagen Elite 801 air pump in series with a drying tube and filter. (See Figure III-4.) A stopcock is used to regulate the rate at which bubbles form. Care must be taken to insure that the previous bubbles are not near the capillary wall when the next reading is taken, and to insure that the capillaries are submerged the same distance beneath the surface during the successive pressure measurements. For these experiments, the tubes were 1.0 mm beneath the solution surface. То determine surface tension, $\gamma = A\Delta P(1+0.69rg\rho/\Delta P).(44)$ The correction term $(0.69rg_{P}/\Delta P)$ is smaller than the detectable limits of this technique and was therefore eliminated to give γ =A Δ P. A is a cell constant, r is the diameter of the large tube, g is the gravitational acceleration, and ρ is the density of the liquid. A is determined by measuring the pressure difference, ΔP , for deionized water and setting $\gamma(H_2 0) = 72.44 \text{ dyne/cm at } 25.00^{\circ}C (45).$





FIGURE

III-4

The bubble pressure apparatus is easier to use and produces data faster than one based on a Wilhelmy plate method. However, the former is insensitive at low concentrations and is very difficult to use with surfactants which foam easily. Therefore, a Wilhelmy plate method is used to study the surface tension of n-hexadecylpyridinium chloride in water, and in NaCl and water (46). A Biolar Rosano Surface Tensiometer Model LG is designed so that the entire balance can be moved up and down manually. The Pt plate is suspended below the balance into a solution which is immersed in a bath thermostated at 25.00±.01°C. (See Figure III-5.) The balance is lowered until the plate is just pulled into the solution by capillarity. Then the dial is turned until the null indicator is rezeroed and the additional pull on the plate is recorded as Δw_{*} . Then $\gamma \cos = g \Delta W/P$; where the contact angle θ is assumed to be zero; P=4.92 cm is the perimeter of the plate in contact with the solution (47); and, g, the gravitational constant, is 979.65 cm/sec² corrected for the altitude of Oklahoma City (45).



FIGURE III-5

DIAGRAM OF THE ROSANO SURFACE TENSIOMETER

.

• .•

.
v. SEMI-EQUILIBRIUM DIALYSIS

Solubilization data are obtained using a semi-equilibrium dialysis technique (SED) developed in this laboratory by Christian, Smith, Tucker and Scamehorn (24). The cell consists of two chambers separated by a regenerated cellulose membrane having a 6000 dalton molecular weight cutoff. (See Figure III-6.) In one side is placed the surfactant solution and the organic compound at known concentrations in 0.1 M HCl, and the other compartment contains 0.1 M HCl only. Surfactant monomers and unsolubilized organic molecules are allowed to pass freely through the membrane. Surfactant micelles and therefore solubilized organics are retained on the solution or Concentrations of organic and surfactant are retentate side. determined by analyzing the permeate solution, using a Varian Cary model 118 UV-visible spectrophotometer. Ordinary 5 ml equilibrium dialysis cells and transparent regenerated cellulose membranes were obtained from Fisher Scientific and used without modification (48).

Studies have been made to determine whether adsorption to the membrane occurs, or if materials from the membrane are dissolved into the solution. Results indicate that neither of these phenomena occur to an extent large enough to effect the results of the solubilization studies using the techniques described here (24,21).







INITIAL SETUP AT TIME = 0



SYSTEM AT SEMI-EQUILIBRIUM

vi. OTHER SOURCES OF DATA

pH measurements are collected using a Sensorex combination pH electrode model S200C. A Fisher Accumet pH Meter model 620 provides pH readings of \pm .001 pH units. Solutions are thermostated at 25.00 \pm .01°C. The electrode is standardized by using a two-point standardization technique, with buffers at pH=7.00 and pH=4.00 (48).

Kalé and Evans provided Na^+ activity data and octylsulfate activity data for sodium octylsulfate using a Na^+ ion-selective electrode and an octylsulfate ion-selective electrode developed in their lab (49).

vii. CHEMICALS

Sodium chloride (Baker) is ground to a powder, oven dried, and stored in a desiccator.

Sodium octylsulfate (Kodak) (abbreviated SOS) is purified (8) by dissolving in boiling 2-propanol (Fisher certified A.C.S. grade) and recrystallizing. This is repeated, and the precipitant is washed twice with diethyl ether and allowed to air dry overnight. The product is oven-dried for about ten minutes, then placed under vacuum for 48 hours and stored in a desiccator. An aqueous solution of the resulting white flakes has less than approximately 0.05% (67) surface-active impurities, as none are detected with surface tension measurements.

n-Hexadecylpyridinium chloride.monohydrate (Hexcel Corp.) is used as received. (This compound is also called cetylpyridinium chloride, and will be abbreviated CPC.) Surface tension measurements indicate that no detectable surface-active impurities are present (that is, less than 0.05% (67) are present). A Mohr method (50) determination of volumetric Cl^- indicates that the molecular weight calculated (47) is consistent with the mono-hydrate of CPC.

Phenylacetic acid (Aldrich, 99%) (abbreviated PAA) is used as received.

The buffers for the pH standardization are Fisher Certified Buffers: Buffer Solution Concentrate for a solution of pH=7.00 \pm .02 (potassium phosphate monobasic-sodium hydroxide); and Buffer Solution pH=4.00 \pm .01 (potassium biphthalate). Both solutions are used as received and as directed.

CHAPTER IV

DATA TREATMENT

i. THERMODYNAMIC MODEL FOR SURFACTANTS IN WATER

The aggregation behavior of surfactants in solution has been modelled using a mass-action approach. This has been used widely in the literature (51,52) in an attempt to understand micellization. The description outlined below follows very closely that presented by Burchfield and Woolley (51), except for the treatment of surface tension data. For the equilibrium

$$[1] nA^{-} + nBM^{+} = A_{n nB}^{\{-n(1-B)\}}$$

where n is the aggregation number, β is the fraction of counterions bound to the micelle, A⁻ is the surfactant monomer, M⁺ is the counterion, and the subscript B denotes the micellar species, the equilibrium constant can be written

 $[2] K = [m_B / (m_A^n m_M^{n\beta})][\gamma_B / (\gamma_A^n \gamma_M^{n\beta})].$

If the fraction of surfactant in the micelle is denoted as $\alpha = nm_B/m$, then the mass balance relations are $m=m_A+nm_B$ and $m=m_M+ngm_B$. Rearranging gives the following expression for the equilibrium constant,

$$[3] K = [\gamma_{B}/(\gamma_{A}^{n}\gamma_{M}^{n\beta})]\alpha/[n(1-\alpha)^{n}(1-\beta\alpha)^{n\beta}m^{\{n(1+\beta)-1\}}].$$

The activity coefficients are expressed using the extended Debye-Hückel equation,

[4]
$$\log(\gamma_{M}) = -A_{V}/(1+b_{M}/I)$$
,

[5]
$$\log(\gamma_A) = -A_{\gamma}\sqrt{I}/(1+b_A\sqrt{I})$$
, and

$$[6] \log(\gamma_B) = -n^2 (1-\beta)^2 \delta^2 A_{\gamma} \sqrt{I} / (1+b_B \sqrt{I}).$$

I is the ionic strength of the solution. A is the Debye-Hückel limiting slope. A limitation on the values of the ion size parameter is that $b_M = b_A = b_B$ must hold for thermodynamic consistency. δ is a micellar charge shielding factor introduced by Hill (8). (The activity coefficients can be expressed in terms of Guggenheim's description of mixed electrolyte solutions (51,53), where metal-monomer and metal-micelle interaction terms which are linear in concentration can be included to account for deviations from the extended Debye-Hückel expressions. However, these terms were tried and found to be unnecessary for a satisfactory fit of the data.) Combining equations

[4] and [5] yields an expression for the mean ionic activity coefficient,

$$[7] \log(\gamma_{\pm}) = -A_{\gamma} \sqrt{I/(1+b/I)} + .5\log(1-\alpha) + .5\log(1-\beta\alpha),$$

where the second and third terms are added to account for the association of solute particles in solution. The mean ionic activity coefficient on the basis of a measurement of a_{+} and a_{-} vs the total solute molality (that is, equation [7] without the second and third terms) is integrated using the Gibbs-Duhem equation to give an expression for the stoichiometric osmotic coefficient. Including terms which again account for association of solute particles yields finally,

$$[8] (1-\Phi) = \alpha (1+\beta-1/n)/2 + \ln(10) A_{\gamma} \sqrt{I_{G}(b/I)}/3m,$$

where $\sigma(b\sqrt{I}) = 3[1+b\sqrt{I}-1/(1+b\sqrt{I})-2\ln(1+b\sqrt{I})]/b^3/I^{3/2}$. The ionic strength, I, which appears in these equations is defined in the manor first suggested by Lewis and Randall (53),

$$[9] I = \sum_{i=1}^{\infty} \frac{z_{i}^{2}}{2} = [2(1-\alpha)+n \delta^{2}(1-\beta)^{2}\alpha+(1-\beta)\alpha]m/2.$$

The micellar term has in it an additional parameter, δ , which was introduced by Hill (3) to decrease the effective charge on the micelle.

Surface tension measurements are modelled using the Szyszkowski equation (7),

$$[10] \gamma = \gamma^{\circ} - \Gamma_{m} RTln(c/[a_{2}+c]).$$

The Gibbs surface excess quantity r_2 in the Gibbs adsorption equation is approximated by a Langmuir adsorption model so that r_m is the monolayer excess quantity. c is the concentration at which the surface is half-saturated with solute molecules. a_2 is the activity of the solute calculated from the ln_{r_+} and ln_{r_-} equations.

Although equations [4], [5], [8], and [10] look rather complex, they are simple in the sense that they are expressed in terms of a measured quantity, m; several parameters, n, β , K, b, Γ_m , and c; and only a single unknown, α , which can be calculated iteratively using a Newton method. Then the parameters are calculated using a weighted non-linear least-squares program, NLLSQ (54), which provides least-squares values for the parameters and values calculated by the model corresponding to each data point. These "Ycalc" values can then be compared directly with experimental data.

In modelling these systems, the data were actually fitted as ϕm vs m, a_M vs m, and a_A vs m; rather than as ϕ vs m, γ_M vs m, and γ_A vs m. The equations for a_M and a_A , the activities of the metal and surfactant ions, respectively, are as follows:

[11] $a_{M} = m(1-\beta\alpha)\gamma_{M}$, and

[12] $a_A = m(1-\alpha)_{Y_A}$,

where $\boldsymbol{\gamma}_{M}$ and $\boldsymbol{\gamma}_{A}$ are inferred from equations [4] and [5], respectively.

Fitting the data both as the product of the osmotic coefficient and molality, and activity coefficient and molality vs molality, and as the osmotic coefficient vs molality and activity coefficient vs molality were tried for the SOS system. (Surface tension results were fitted unaltered, as described by equation [10], in both cases.) While the iteration procedure was much slower for the latter case, results from both fits were quite similar. The CPC data could not be fitted as the coefficients vs molality, but could be modelled using the product of the coefficients and molality vs molality.

In using a weighted NLLSQ (54) program, the error in each data point is assumed to be associated entirely with the ordinate. Errors are determined graphically by plotting results from repeated runs of the same technique superimposed on each other. Then the average discrepancy between observed values and the mean value gives the approximate percent error for each point. Generally, this is about 3-4% in the low [SOS] region, about 2-3% through the cmc region, and 1-2% at higher [SOS]. Errors in the low [CPC] region, that is, at molalities below the cmc, the errors may be as high as 5%. A root-mean square deviation of 1.00 then means that the sum of the squares of the estimated errors is the same as that predicted from the difference between the calculated and experimental Y values.

ii. SELF-ASSOCIATION DATA TREATMENT

The behavior of a slightly water-soluble organic molecule in aqueous solution is interesting to study for at least two reasons: i) a study of self-association in water of the organic can yield information about hydrophobic associations; and, ii) it is necessary to understand how the organic behaves in bulk water, or at least how it is partitioned into its various aqueous forms (e.g., monomer, dimer, ion, etc.), in order to be able to study properly the solubilization of an organic molecule by a micellar solution. The aggregation behavior of cetylpyridinium chloride in water has been presented in the previous section. What follows is a description of the behavior of phenylacetic acid, PAA, in water.

In the case of dilute solutions of nonelectrolyte species, the vapor pressure osmometer can be used to "count" the number of particles in solution. Vapor pressure osmometry is, therefore, nicely suited to studying the aggregation behavior or self-association of non-ionics. PAA is a weak acid; the fraction of ionized particles is very small and the degree of ionization decreases with increasing concentration of solute. The self-association behavior of PAA is studied using this technique.

The mass balance of the total acid can be written

[1] [PAA] = [A⁻] + [HA] + 2[HA.HA] + 2[HA.A⁻].

A⁻ represents the anion formed by dissociation, HA is the neutral form of the acid, and [PAA] is the total concentration of PAA in the solution. Additional terms could be included to represent trimers, tetramers, ..., and n-mers. However, including more terms than those shown does not improve the goodness of fit of the data. Equation [1] can be re-written in terms of [HA],

$$[2] [PAA] = K_{1}[HA]/[H^{+}] + [HA] + 2K_{2}[HA]^{2} + 2K_{2}K_{2}[HA]^{2}/[H^{+}].$$

 K_i is the ionization constant and is held constant at 5.56×10^{-5} <u>M</u> (55). Notice that the association constant, K_2 , has been taken to be the same for both the HA.HA dimer and the HA.A⁻ species or the hetero-dimer. Association is likely to occur primarily through stacking of the phenyl rings, with the side chains oriented on opposite sides of the stacked pair (14). So whether the carboxylate group is charged or neutral may have only a small effect, undetectable by the limits of the vapor pressure osmometer. The formation of the dimer and hetero-dimer cannot be separated with these data, primarily because the fraction of acid anion in solution is so very small (only a few percent as large as the concentration of neutral acid).

Equation [2] is written in terms of two unknowns, $[H^+]$ and [HA]. Therefore, another equation is needed to solve for these two

concentrations. An expression is chosen which describes the charge balance of the solution. Neglecting any effects from the ionization of water, the charge balance is written as

$$[3] [H^+] = [A^-] + [HA.A^-] = K_2[HA]/[H^+] + K_2K_1[HA]^2/[H^+].$$

Equations [2] and [3] can be solved simultaneously for $[H^+]$ and [HA], for a known value of K_i and using an assumed or tentative value of K₂. The colligative mole fraction or osmotic effect, x"osm", represents the solute activity as $1-a_w$. $a_2 = \Sigma x_i$ where x_i represents the mole fraction of each species in solution, and the mole fraction is calculated from the molality, m, using the expression x = 18.015m/1000/(1+18.015m/1000). The activity coefficient is 1 (or very nearly, because for PAA the fraction of ions is very small, decreasing with increasing [PAA]) (*). Then

[4]
$$1-a_w = x''osm'' = x_A - + x_H + x_{HA} + x_{HA+HA} + x_{HA+A}$$

is the osmotic effect of the solution. Using the NLLSQ (54) program, values of $1-a_w$ are predicted as described above, for provisional values of K_2 , and the optimum or least-squares value of this parameter is determined.

^(*) At saturation, 0.13 <u>M</u> PAA, the mean ionic molality of ions, $([H^+]+[A^-]+[HA.A^-])$, is only about 0.0025 m. At 0.0025 m NaCl, the difference between the sum of the mole fractions of ions, $x_{u} + x_{cl}$, and 1-a, is only about 0.2%. (Values for NaCl are calculated from ref. 38.)

iii. SOLUBILIZATION DATA TREATMENT

Surfactants are useful in many fields, as described in the introduction. The usefulness of these amphiphiles is in many cases related to their ability to solubilize slightly water-soluble organic molecules. One approach to study how these systems work is to investigate the thermodynamics of micellar solubilization.

The aqueous solution behavior of the pure surfactant, cetylpridinium chloride, CPC, and of 2-phenylacetic acid, PAA, has been described in the previous two sections. Results from PAA in water illustrate the ability of the vapor pressure osmometer to "count" the particles in solution. In this system, the ionic strength is not large enough to cause 1-a, to deviate significantly from Σx_1 . However for CPC in water, 1-a, does not equal the sum of the mole fractions of the chemical species present $(x_{C1}^{-+x} + x_{mic}^{-+x} = \Sigma x_i)$ because of the high ionic strength of the solution. Σx_i for aqueous CPC can be calculated from the mass action-model of the osmometry results. It has been found that Σx_{i} is considerably smaller than 1-a, (in the concentrated CPC solutions), but the two quantities may be related by the following equation:

 $[1] 1-a_{w} = \Sigma x_{i} + Z1(\Sigma x_{i})^{3/2} + Z2(\Sigma x_{i})^{5/2} = Z(\Sigma x_{i}).$

Although this function is purely empirical, the lead term is taken to be Σx_i because in the limit as x approaches 0, $1-a_w$ must equal the total mole fraction of solute species. The discrepancy between Σx_i and $1-a_w$ arises from activity coefficient effects.

In the solubilization experiments, the addition of PAA causes the concentration of ionic species to vary by as much as 5 to 15%. Therefore, in interpreting the osmometry data, it is necessary to account for the changes in $1-a_w$ caused by this variation in ionic concentrations. In these fairly concentrated electrolyte solutions, it seems reasonable to assume that the change in $1-a_w$, owing to the change in concentration of monovalent ions, can be expressed by equation [1]. On the other hand, a neutral molecule, such as HA, should have an activity coefficient that is nearly constant, so that its contribution to $1-a_w$ will be practically equal to its mole fraction.

In the solubilization studies, data are collected for a series of solutions with constant surfactant concentration and increasing [PAA]. The osmotic effect that will be modelled is the effect of the added PAA. In other words, $1-a_w$ of the CPC solution with no added PAA is subtracted from $1-a_w$ of the solutions with added PAA.

The total osmotic effect for the solubilization system can be written, without including any activity coefficient-based correction, as

 $\begin{bmatrix} 2 \end{bmatrix} 1-a = x_{+} + x_{-} + x_{+} + x_{+} + x_{+} + x_{+} + x_{-} + x_{-} + x_{+} +$

But this can be simplified. First of all, the concentration of the CPC

monomer can be neglected. A plot (see Figure V-8) of the total surfactant molality as the abscissa and the monomer molality (calculated from the mass-action model) as the ordinate for CPC in water shows how small the monomer concentration is at the concentrations of CPC used (.11 m, $.c\bar{c}$ m, and .44 m).

Secondly, the concentration of the micellar surfactant is assumed to be constant, and therefore can be omitted from equation [2]. At 0.44 m CPC, the [micelle] will be approximately 0.004 m. This represents only 4% of the total osmotic effect of 0.44 m CPC. Even so, the osmotic effect of interest is the difference of the micellar contribution in the presence and absence of PAA, and this is below the detectable limits of the osmometer.

The mole fraction of Cl⁻ in equation [2] is calculated from Cl⁻-selective electrode data by simultaneously solving the following equations. The fraction of counterions bound is the ratio of bound Cl⁻ to micellar surfactant,

 $[3] B = ([CPC]-[CL^{-}])/([CPC]-[CP^{+}]).$

The ionic strength is expressed in the usual manner,

$$\begin{bmatrix} 4 \end{bmatrix} I = .5([CL^{-}] + [H^{+}] + [A^{-}] + [HA.A^{-}] + n\delta^{2} (1-\beta)^{2} ([CPC]-[CP^{+}])).$$

Here the micelle term accounts for all different types of micellar aggregates: pure surfactant, micelle with ionized acid solubilized,

micelle with neutral acid solubilized, and any combination thereof, where the charge and size of all are assumed to be the same. From the extended Debye-Hückel expression of the activity coefficient,

$$[5] \log(\gamma_{\pm}) = -A_{\gamma} \sqrt{I/(1+b/I)}$$

(b is the same as for the pure surfactant determined with the mass-action model) the Ci^- molality can be calculated, $m_{Cl}^{-=a}=a_{Cl}^{-}/\gamma_+$.

The ionic strength of the solution determines γ_{\pm} . This γ_{\pm} from Cl⁻ data will be the same for all singly charged ions. Therefore the same value is used to obtain proton molalities from pH measurements.

In order to describe the organic dimer terms, x_{HA+HA} and x_{HA+A}^{-} , information from the behavior of PAA in water is needed. It is assumed that the unsolubilized PAA in the bulk water of the surfactant solution behaves the same as PAA in pure water. That is, the solubility limit of unsolubilized PAA in the bulk water of the surfactant solution is 0.131 <u>M</u> (55), the same as the solubility of PAA in pure water; and the ionization constant and association constant are the same for the unsolubilized PAA in the bulk water of the surfactant solution as for PAA in pure water.

Three types of information, vapor pressure osmometry, Cl^{-} activities, and pH, are used to investigate the solubilization of PAA by aqueous CPC solutions. First, the expression for 1-a_w (equation [2]) is rewritten, based on the assumptions described above, to obtain:

[6] $1-a_w = x"osm" = Z(\Sigma x_i) + x_{HA} + x_{HA \cdot HA}$.

 $\Sigma x_i = x_{Cl} + x_H + x_A + x_{HA*A}$, and $Z(\Sigma x_i)$ is the function described in equation [1]. This is rewritten in terms of the mole fractions of the neutral acid and measured quantities as

$$[7] 1-a_{w} = x''osm'' = Z(\Sigma x_{i}) + x_{HA} + K_{2} x_{HA}^{2},$$

where $x_A^- = K_2 x_{HA}^{\prime} / x_H^+$ and $x_{HA+A}^- = K_2 K_1 x_{HA}^{\prime} / x_H^+$ are substituted into the $Z(\Sigma x_1)$ function. Since the only unknown is x_{HA}^{\prime} , equation [7] can be solved for a value of x_{HA}^{\prime} by an iterative method.

The total mass balance of the acid can be expressed using a titratable acid basis. Only H^+ and species containing the neutral acid need be considered, because the unprotonated anion (whether in the micelle, or in the extremicellar solution) is not titratable.

[8]
$$x_{PAA} = x_{H}^{+} + x_{HA}^{+} + 2x_{HA+HA}^{+} + x_{HA+A}^{-} + X_{HA+CPC}^{+}$$
, or

$$[9] x_{PAA} = x_{H} + x_{HA} + 2K_{2}x_{HA}^{2} + K_{2}x_{HA}x_{A} - K_{s1}x_{HA}x_{CPC,mic}$$

 $X_{CPC,mic}$ is the mole fraction of surfactant in the micelle. The next to last term has a coefficient of 1, because only one HA unit contributes to the titratable acid. The only unknown in equation [9] is K_{s1} , which is calculated then for each data point. Now, the acid mass balance can be expressed in terms of the total concentration of phenylacetate. On this basis, one may write:

$$[10] x_{PAA} = x_{A} + x_{HA} + 2x_{HA + HA} + 2x_{HA + A} - + X_{HA + CPC} + X_{A} - CPC$$
, or

[11]
$$x_{PAA} = x_{A}^{-} + x_{HA}^{+} + 2K_{2}x_{HA}^{2} + 2K_{2}x_{HA}x_{A}^{-} + K_{s1}x_{HA}x_{CPC,mic}^{+}$$

+ $K_{s2}x_{A}^{-}x_{CPC,mic}^{+}$

The fourth term on the r.h.s. of these two equations has a coefficient of 2, reflecting the fact that it includes both the anion and the neutral acid. But more importantly, the final term has been introduced to represent the micelle-solubilized acid anion. With the value of K_{s1} determined from equation [9], K_{s2} is calculated from equation [11] for each data point, and the contribution to the solubilization process can be separated into that of the neutral acid and that of the acid anion.

The mole fraction of organic in the micelle, X_p , is expressed as

[12]
$$(X_{HA}+X_{A}-)_{mic} = X_{PAA} - X_{HA} - X_{A} - X_{HA+HA} - X_{HA+A}$$
, and

[13]
$$X_{P} = (X_{HA} + X_{A} -)_{mic} / [(X_{HA} + X_{A} -)_{mic} + X_{CPC, mic}].$$

From the information given above, the activity coefficient <u>in</u> <u>the</u> <u>micelle</u> for the organic solute and for the surfactant can be calculated. This is defined by the equation

$$[14] \gamma'_{P} = a_{HA} / X_{P},$$

where γ'_{p} and X_{p} are the activity coefficient and mole fraction, respectively, of the organic in the micelle. The activity of the organic is $a_{HA} = f_{HA}/f_{HA}^{\circ}$, where f_{HA} is the fugacity of the organic in solution, f_{HA}° equals the vapor pressure of the organic in the saturated solution in equilibrium with the pure solid; f_{HA}° is also equal to the vapor pressure of the pure solid. For the intramicellar solution, a more reasonable standard state is super-cooled liquid PAA at 25°C. The ratio of the pure liquid vapor pressure, P_L , and pure solid vapor pressure, P_S , (87) may be used to convert γ'_P into an activity coefficient based on pure super-cooled liquid PAA as the standard state. Thus,

$$[15] \gamma_{\rm P} = \gamma'_{\rm P} ({\rm P}_{\rm S} / {\rm P}_{\rm L})$$

defines the activity coefficient for the more appropriate liquid-based standard state.

Organic activity coefficients are numerically integrated through the Gibbs-Duhem equation to calculate surfactant activity coefficients in the micelle, $\gamma_{\rm CPC}$, from the expression

[16]
$$d \ln_{\gamma_{CPC}} = -X_P d \ln_{\gamma_P} / X_{CPC}$$
,

where $X_{CPC} = 1-X_{P}$ is the mole fraction of the surfactant in the micelle. For additional discussion of activity coefficients, see the next section.

iv. SED DATA TREATMENT

Solubilization parameters are determined using semi-equilibrium dialysis, SED, where the surfactant and organic are placed in one side of the cell, and 0.1 M HCl is present in both sides. The ionization of PAA will be practically negligible in this medium and is treated as such here. The cell is allowed to equilibrate at 25°C until the organic activity has reached the same value on both sides of the membrane. The surfactant activity will not be at equilibrium, but after 18 to 36 hours (24) the concentration on the low side (permeate) will be just at or a little above the cmc of the pure surfactant (24) in 0.1 M HCl (taken to be the same as that in 0.1 m NaCl). Results are about the same if analyzed at 1, 2 and 3 days (48).

solution is U٧ The permeate analyzed usina absorbance measurements. Extinction coefficients at 10 nm intervals, throughout the major CPC and PAA absorbance peaks, are determined from Beer's Law plots of data for the pure components. A non-linear least squares analysis is used to calculate the concentration of organic and CPC in the permeate. Although the concentration of surfactant is slightly above the cmc, in other words, even though micelles with solubilized organic molecules are present, no correction is needed for an effect on the extinction coefficients due to the solublized organic. This is

because the solutions must be diluted to micromolar levels in order to obtain reasonable absorbance measurements. At this concentration of surfactant, the fraction of micelles present, and therefore the contribution of solubilized organic, can be neglected.

Following the data treatment previously described (26), the total concentration of each component on either side of the dialysis cell can be written as the sum of the species present; that is, the sum of the monomer and micelle concentrations, and, for the organic mass balance, the dimer concentration:

$$[1] [PAA] = c_{p} + [X_{p}/(1-X_{p})][CPC]_{mic} + 2K_{2}c_{p}^{2}, \text{ and}$$

where [PAA] and [CPC] are total stoichiometric concentrations, the subscript "mic" denotes a micellar concentration, and the subscripts "P" and "CPC" signify the organic and surfactant, respectively. The monomer concentrations, c_p and c_{CPC} , are expressed in terms of the activity coefficients of the component in the micelle, γ_p and γ_{CPC} , as

[3]
$$c_p = \gamma_p X_p c_p^{\circ}$$
, and $c_{CPC} = \gamma_{CPC} (1-X_p) c_{CPC}^{\circ}$.

These equations are combined to give

$$\begin{bmatrix} 4 \end{bmatrix} \begin{bmatrix} (1 - X_p / X_p] \begin{bmatrix} PAA \end{bmatrix} - (1 - X_p) \gamma_p c_p^{\circ} - 2K_2 (1 - X_p) \gamma_p^2 c_p^{\circ} {}^2 X_p \\ = \tilde{L} CPC \end{bmatrix} - \gamma_{CPC} (1 - X_p) c_{CPC}^{\circ}.$$

Then X_p is solved for iteratively, where the activity coefficients are described by Hansen-Miller (24) expressions,

[5]
$$\ln \gamma_{p} = (1-X_{p})^{2} (A+BX_{p}+CX_{p}^{2})$$
, and

[6]
$$\ln \gamma_{CPC} = X_{P}^{2} (A - B/2 + [B - 2C/3] X_{P} + C \lambda_{P}^{2}).$$

Equation [6] is obtained by a Gibbs-Duhem integration of equation [5]. The Gibbs-Duhem relation between the two activity coefficients has been justified experimentally for the intramicellar components (25). A, B and C are constants determined using NLLSQ (54). Once $X_{\!_{\rm D}}$ in the permeate is calculated, then the total organic in the permeate is predicted as Ycalc using equation [1]. The standard state of PAA is the super-cooled liquid at 25°C. A value of the cmc=0.022 mm is inferred from surface tension data for CPC in 0.1 m NaCl (88), and is as c° CPC.per, the surfactant monomer concentration in the used permeate. This value is neglected on the retentate side; although the magnitude is similar, the ratio of monomer to total surfactant is very small on the high concentration side. Knowledge of X_p on both sides allows the calculation of [CPC] from equation [2] and the apparent solubilization, K_{c} , (24) from

where the subscripts "per" and "ret" refer to the species concentration in the permeate and retentate solutions, respectively. CHAPTER V

RESULTS

i. SODIUM OCTYL SULFATE IN WATER

The study of surfactant behavior in water has been a very active field of research. Many reports are available in the literature which present results of determining parameters using mass-action descriptions of micellization. And these models have been used to correlate data from many individual techniques. However, the values of a given parameter can vary widely depending on the technique used. several techniques have Therefore. data from been modelled simultaneously to provide a single set of parameters which will predict the data from each technique.

For sodium octylsulfate (SOS), solvent activity data are measured using vapor pressure osmometry and the static vapor pressure technique. Solute activity data are determined from surface tensiometry. Counterion acitivities have been measured with sodium ion-selective electrodes by this investigator and provided by Kalé and Evans (49). Octylsulfate activity data were provided by Kalé and Evans (49). These data are all modelled simultaneously using a weighted NLLSQ (54) program.

Data are presented in Table V-1. the experimental values of water activities and ion activities are calculated from the raw data of voltages using a fitted equation of the appropriate NaCl calibration. These calibrations are reported in the footnotes of Table V-1. The RMSD value is the root-mean square deviation, or the error in the fit of the NaCl calibration data. This RMSD is in units of the y value (that is, this is not a weighted fit, as in the case of the combined fits of the SOS data and CPC data). Although more digits are indicated than are significant in the parameters of the NaCl calibration fits, all the digits are kept and used. This is because changing these parameters (in other words, truncating them) decreases the goodness of fit of the data. The experimental data for the surfactant solutions reported in the table include more digits than are significant. However, errors in these values are reported in the last column of the table.

The calculated values from the mass-action model agree well with the experimental results (see Table V-1), as can be seen from plots of the data: the osmotic coefficient vs [SOS] results in Figure V-1, the Na^+ and OS^- activity coefficients vs [SOS] results in Figure V-2, and surface tension vs [SOS] data in Figure V-3. All the curves exhibit the expected break at concentrations near the cmc. The solid line in each figure represents the fitted results of the mass-action model. Each fitted curve is influenced not only by the experimental points, but also by the data from the other types of measurements, since these

TABLE V-1

EXPERIMENTAL AND CALCULATED DATA FOR SODIUM OCTYLSULFATE IN WATER AT 25°C

Vapor pressure osmometer

mene	Φ	Φm	Φm calc	I	α	^m os ⁻	Φm error
9.1379E-03	1.0227E+00 ^a	9.3453E-03	9.0671E-03	9.1379E-03	2.0290E-20	9.1379E-03	1.8691E-04
1.7866E-02	1.0151E+00	1.8135E-02	1.7733E-02	1.7866E-02	1.9835E-20	1.7866E-02	3.6270E-()4
3.6412E-02	1.0186E+00	3.7090E-02	3.6164E-02	3.6412E-02	2.1705E-19	3.6412E-02	7.4181E-04
5.5854E-02	1.0097E+00	5.6398E-02	5.5502E-02	5.5854E-02	1.6309E-13	5.5854E-02	1.1280E-03
7.6975E-02	1.0302E+00	7.9296E-02	7.6522E-02	7.6975E-02	4.1358E-09	7.6975E-02	1.5859E-0.3
9.6469E-02	9.9807E-01	9.6283E-02	9.5931E-02	9.6469E-02	5.1992E-06	9.6468E-02	1.9257E-03
1.1580E-01	9.8996E-01	1.1463E-01	1.1505E-01	1.1583E-01	1.5999E-03	1.1561E-01	2.2927E-03
1.2589E-01	9.8335E-01	1.2380E-01	1.2389E-01	1.2628E-01	1.5433E-02	1.2395E-01	2.4759E-03
1.3626E-01	9.7870E-01	1.3336E-01	1.3009E-01	1.3781E-01	5.7759E-02	1.2839E-01	2.6672E-03
1.5616E-01	8.9701E-01	1.4008E-01	1.3739E-01	1.6127E-01	1.6587E-01	1.3026E-01	2.8016E-03
1.7638E-01	8.2813E-01	1.4607E-01	1.4293E-01	1.8563E-01	2.6597E-01	1.2947E-01	2.9214E-03
1.9267E-01	7.7660E-01	1.4963E-01	1.4698E-01	2.0537E-01	3.3448E-01	1.2823E-01	2.9926E-03
2.1621E-01	7.2386E-01	1.5650E-01	1.5259E-01	2.3396E-01	4.1683E-01	1.2609E-01	3.1301E-03
2.3748E-01	6.8078E-01	1.6168E-01	1.5759E-01	2.5983E-01	4.7775E-01	1.2403E-01	3.2335E-03
2,6813E-01	6.2015E-01	1.6628E-01	1.6478E-01	2.9710E-01	5.4852E-01	1.2106E-01	1.6628E-03
3.0077E-01	5.7971E-01	1.7436E-01	1.7253E-01	3.3677E-01	6.0765E-01	1.1801E-01	1.7436E-03
3.2511E-01	5.5268E-01	1.7968E-01	1.7838E-01	3.6634E-01	6.4370E-01	1.1584E-01	1.7968E-03
3.6355E-01	5.2397E-01	1.9049E-01	1.8777E-01	4.1298E-01	6.9025E-01	1.1261E-01	1.9049E-03
4.0699E-01	4.8646E-01	1.9798E-01	1.9858E-01	4.6564E-01	7.3156E-01	1.0925E-01	1.9798E-03
4.3962E-01	4.7252E-01	2.0773E-01	2.0604E-01	5.0516E-01	7.5680E-01	1.0692E-01	2.0773E-03
4.8266E-01	4.5539E-01	2.1980E-01	2.1789E-01	5.5723E-01	7.8440E-01	1.0406E-01	2.1980E-03
5.1942E-01	4.3879E-01	2.2792E-01	2.2746E-01	6.0168E-01	8.0400E-01	1.0180E-01	2.2792E-03
9.1379E-03	1.1194E+00 ^a	1.0229E-02	9.0671E-03	9.1379E-03	2.0290E-20	9.1379E-03	2.0459E-04
1.7866E-02	1.0178E+00	1.8184E-02	1.7733E-02	1.7866E-02	1.9835E-20	1.7866E-02	3.6368E-04
3.6412E-02	1.0200E+00	3.7139E-02	3.6164E-02	3.6412E-02	2.1705E-19	3.6412E-02	7.4279E-04
5.5854E-02	1.0067E+00	5.6227E-02	5.5502E-02	5.5854E-02	1.6309E-13	5.5854E-02	1.1245E-03

				TABLE V-1	(CONTINUED)		
7.6975E-02	1.0128E+00	7.7961E-02	7.6522E-02	7.6975E-02	4.1358E-09	7.6975E-02	1.5592E-03
9.6469E-02	9.7701E-01	9.42516-02	9.5931E-02	9.6469E-02	5.1992E-06	9.6468E-02	1.8850E-03
1.1580E-01	9.8926E-01	1.1455E-01	1.1505E-01	1.1583E-01	1.5999E-03	1.1561E-01	2.2910E-03
1.2589E-01	9.6017E-01	1.2088E-01	1.2389E-01	1.2628E-01	1.5433E-02	1.2395E-01	2.4176E-03
1.3626E-01	9.4541E-01	1.2882E-01	1.3009E-01	1.3781E-01	5.7759E-02	1.2839E-01	2.5764E-03
1.5616E-01	8.7368E-01	1.3644E-01	1.3739E-01	1.6127E-01	1.6587E-0'	1.3026E-01	2.7287E-03
1.7638E-01	8.0795E-01	1.4251E-01	1.4293E-01	1.8563E-01	2.6597E-01	1.2947E-01	2.8502E-03
2.1621E-01	7.0404E-01	1.5222E-01	1.5259E-01	2.3396E-01	4.1683E-01	1.2609E-01	3.0444E-03
2.6813E-01	6.1443E-01	1.6475E-01	1.6478E-01	2.9710E-01	5.4852E-01	1.2106E-01	1.6475E-03
3.6355E-01	5.1777E-01	1.8823E-01	1.8777E-01	4,1298E-01	6.9025E-01	1.1261E-01	1.8823E-03
4.8266E-01	4.5322E-01	2.1875E-01	2.1789E-01	5.5723E-01	7.8440E-01	1.0406E-01	2.1875E-03
	h .						
1.8156E-02	1.0355E+00 ^D	1.8801E-02	1.8021E-02	1.8156E-02	2.0157E-20	1.8156E-02	3.7602E-04
3.6293E-02	1.0244E+00	3.7180E-02	3.6046E-02	3.6293E-02	1.9572E-19	3.6293E-02	7.4360E-04
5.4443E-02	1.0133E+00	5.5168E-02	5.4098E-02	5.4443E-02	7.2635E-14	5.4443E-02	1.1034E-03
7.2689E-02	1.0169E+00	7.3917E-02	7.2256E-02	7.2689E-02	6.7606E-10	7.2689E-02	1.4783E-03
9.2112E-02	9.9504E-01	9.1655E-02	9.1592E-02	9.2112E-02	1.2063E-06	9.2112E-02	1.8331E-03
1.0992E-01	9.9133E-01	1.0896E-01	1.0930E-01	1.0992E-01	3.1904E-04	1.0988E-01	2.1793E-03
1.2885E-01	9.6678E-01	1.2457E-01	1.2596E-01	1.2949E-01	2.4846E-02	1.2565E-01	2.4915E-03
1.4586E-01	9.2490E-01	1.3490E-01	1.3403E-01	1.4900E-01	1.0947E-01	1.2989E-01	2.6981E-03
1.6729E-01	8.3888E-01	1.4033E-01	1.4055E-01	1.7464E-01	2.2301E-01	1.2998E-01	2.8067E-03
1.8806E-01	7.7076E-01	1.4495E-01	1.4586E-01	1.9977E-01	3.1612E-01	1.2861E-01	2.8990E-03
2.2773E-01	6.7657E-01	1.5408E-01	1.5530E-01	2.4797E-01	4.5122E-01	1.2497E-01	3.0815E-03
2.6776E-01	6.0915E-01	1.6311E-01	1.6469E-01	2.9665E-01	5.4776E-01	1.2109E-01	1.6311E-03
3.0901E-01	5.6605E-01	1.7492E-01	1.7450E-01	3.4678E-01	6.2053E-01	1.1726E-01	1.7492E-03
3.7302E-01	5.0102E-01	1.8689E-01	1.9011E-01	4.2446E-01	7.0014E-01	1.1185E-01	1.8689E-03
4.3726E-01	4.6523E-01	2.0343E-01	2.0624E-01	5.0230E-01	7.5511E-01	1.0708E-01	2.0343E-03
5.0237E-01	4.4473E-01	2.2342E-01	2.2301E-01	5.8107E-01	7.9531E-01	1.0283E-01	2.2342E-03

Static vapor pressure apparatus (41)

5.8075E-02	1.0274E+00	5.9665E-02	5.7712E-02	5.8075E-02	5.5959E-13	5.8075E-02	1.1933E-03
6.4993E-02	1.0353E+00	6.7289E-02	6.4596E-02	6.4993E-02	1.9648E-11	6.4993E-02	1.3458E-03
7.3513E-02	1.0271E+00	7.5503E-02	7.3076E-02	7.3513E-02	9.6570E-10	7.3513E-02	1.5101E-03
9.2685E-02	9.9827E-01	9.2524E-02	9.2163E-02	9.2685E-02	1.4674E-06	9.2685E-02	1.8505E-03

TABLE V-1 (CONTINUED)

1.1533E-01 9.6518E-01 1.1517E-01 1.1132E-01 1.1461E-01 1.1537E-01 1.4171E-0.5 2.2264E-03 1.5704E-01 8.9226E-01 1.4012E-01 1.3765E-01 1.6232E-01 1.7055E-01 1,3026E-01 2.8024E-03 7.4459E-01 1.4836E-01 1.4857E-01 2.1335E-01 3.5930E-01 1.2766E-01 1.9925E-01 2.9671E-03 2.9549E-01 5.7377E-01 1.6954E-01 1.7127E-01 3.3035E-01 1.1849E-01 1.6954E-03 5.9901E-01 Na⁺-selective electrode (49)

msos	Υ_	a	a_ calc	I	α	mos ⁻	a, ercor
8.3200E-03	1.0373E+00	8.6303E-03	7.9889E-03	8.3200E-03	1.8474E-20	8.3200E-03	4,3152E-04
1.2430E-02	1.0531E+00	1.3090E-02	1.1900E-02	1.2430E-02	2.7599E-20	1.2430E-02	6.5450E-04
1.6510E-02	1.0436E+00	1.7230E-02	1.5774E-02	1.6510E-02	1.8329E-20	1,6510E-02	8.6149E-04
2.0550E-02	1.0263E+00	2.1090E-02	1.9605E-02	2.0550E-02	2.2815E-20	2.0550E-02	1.0545E-03
2.4570E-02	1.0175E+00	2.5000E-02	2.3413E-02	2.4570E-02	8.5734E-2%	2.4570E-02	1.2500E-03
2.8550E-02	1.0126E+00	2.8910E-02	2.71808-02	2.8550E-02	9.8965E-23	2.8550E-02	1.4455E-03
3.2500E-02	9.8430E-01	3.1990E-02	3.0917E-02	3.2500E-02	5.9627E-21	3.2500E-02	1.5995E-03
3.6420E-02	9.7170E-01	3.5389E-02	3.4623E-02	3.6420E-02	2.1857E-19	3,6420E-02	1.7695E-03
4.0310E-02	9.5190E-01	3.8371E-02	3.8299E-02	4.0310E-02	5.4126E-18	4.0310E-02	1.9186E-03
4.8010E-02	9.3940E-01	4.5101E-02	4.5572E-02	4.8010E-02	1.3621E-15	4.8010E-02	2.2550E-03
5.5580E-02	9.4620E-01	5.2590E-02	5.2717E-02	5.5580E-02	1.3960E-13	5,5580E-02	2.6295E-03
6.3040E-02	9.3050E-01	5.8659E-02	5.9756E-02	6.3040E-02	7.4883E-12	6.3040E-02	2.9329E-03
7.0400E-02	9.2170E-01	6.4888E-02	6.6697E-02	7.0400E-02	2.4584E-10	7.0400E-02	3,2444E-03
1.1230E-01	8.5880E-01	9.6443E-02	1.0615E-01	1.1231E-01	6.2345E-04	1.1223E-01	3.8577E-03
1.4457E-01	8.2980E-01	1.1996E-01	1.3050E-01	1.4748E-01	1.0235E-01	1.2977E-01	4.7986E-03
1.7469E-01	8.1050E-01	1.4159E-01	1.4643E-01	1.8358E-01	2.5823E-01	1,2958E-01	4.2476E-03
2.0286E-01	7.8170E-01	1.5858E-01	1.6050E-01	2.1774E-01	3.7232E-01	1.2733E-01	4.7573E-03
2.5409E-01	7.3360E-01	1.8640E-01	1.8575E-01	2.8003E-01	5.1825E-01	1,2241E-01	5,5920E-03
2.9946E-01	7.0550E-01	2.11278-01	2.0815E-01	3.3518E-01	6.0554E-01	1.1813E-01	6.3381E-03
3.4937E-01	6.7720E-01	2.3659E-01	2.3293E-01	3.9578E-01	6.7435E-01	1.1377E-01	7.0978E-03
3.9305E-01	6.6060E-01	2.5965E-01	2.5476E-01	4.4875E-01	7.1938E-01	1.1030E-01	7.7895E-03
4.6583E-01	6.5260E-01	3.0400E-01	2.9139E-01	5.3688E-01	7.7427E-01	1.0515E-01	9.1200E-03
5.2406E-01	6.3660E-01	3.3362E-01	3.2090E-01	6.0729E-01	8.0626E-01	1.0153E-01	1.0008E-02
OS ⁻ selec	tive elect	rode (49)					
mor-	γ	а	a calc	I	α	mor-	a error

^m os ⁻	Υ	a_	a_ calc	I	α	^m os ⁻	a_error
8.3200E-03	1.0349E+00	8.6104E-03	7.9889E-03	8.3200E-03	1.8474E-20	8,3200E-03	4.3052E-04
1.2430E-02	1.0491E+00	1.3040E-02	1.1900E-02	1.2430E-02	2.7599E-20	1.2430E-02	6.5202E-04

				TABLE V-1	(CONTINUED)		
1.6510E-02	1.0351E+00	1.7090E-02	1.5774E-02	1,6510E-02	1.8329E-20	1.6510E-02	8,5448E-04
2.0550E-02	1.0511E+00	2.1600E-02	1.9605E-02	2.0550E-02	2.2815E-20	2.0550E-02	1.0800E-03
2.45708-02	1.0085E+00	2.4779E-02	2,3413E-02	2.4570E-02	8.5734E-25	2.4570E-02	1.2389E-03
2.8550E-02	1.0035E+00	2.8650E-02	2.7180E-02	2.8550E-02	9.8965E-23	2.8550E-02	1.4325E-03
3.2500E-02	9.6340E-01	3.1311E-02	3.0917E-02	3.2500E-02	5.9627E-21	3.2500E-02	1,5655E-03
3,6420E-02	9.5880E-01	3.4919E-02	3.4623E-02	3.6420E-02	2.1857E-19	3.6420E-02	1.7460E-03
4.0310E-02	9.5830E-01	3.8629E-02	3.8299E-02	4.0310E-02	5.4126E-18	4.0310E-02	1.9315E-03
4.8010E-02	9.4170E-01	4.5211E-02	4.5572E-02	4.8010E-02	1.3621E-1'	4.8010E-02	2.2606E-03
5.5580E-02	9.5590E-01	5.3129E-02	5.2717E-02	5.5580E-02	1.3960E-15	5.5580E-02	2.6564E-03
6.3040E-02	9.3990E-01	5.9251E-02	5.9756E-02	6.3040E-02	7.4883E-12	6.3040E-02	2.9626E-03
7.0400E-02	9.3100E-01	6.5542E-02	6.6697E-02	7.0400E-02	2.4584E-10	7.0400E-02	3.2771E-03
1.1230E-01	8.6330E-01	9.6949E-02	1.0611E-01	1.1231E-01	6.2345E-0 !	1.1223E-01	3.8779E-03
1.4457E-01	8.4750E-01	1.2252E-01	1.2257E-01	1.4748E-01	1.0235E-01	1.2977E-01	4.9009E-03
1.7469E-01	7.5420E-01	1.3175E-01	1.2230E-01	1.8358E-01	2.5823E-01	1.2958E-01	3.9525E-03
2.0286E-01	6.2380E-01	1.2654E-01	1.2011E-01	2.1774E-01	3.7232E-01	1.2733E-01	3.7963E-03
2.5409E-01	4.5760E-01	1.1627E-01	1.1538E-01	2.8003E-01	5.1825E-01	1.2241E-01	3.4881E-03
2.5946E-01	3.5520E-01	1.0637E-01	1.1129E-01	3.3518E-01	6.0554E-01	1.1813E-01	3.1910E-03
3.4937E-01	3.0450E-01	1.0638E-01	1.0714E-01	3.9578E-01	6.7435E-01	1.1377E-01	3.19!5E-03
3.9305E-01	2.5990E-01	1.0215E-01	1.0384E-01	4.4875E-01	7.1938E-01	1.1030E-01	3.0646E-03
4.6583E-01	2.0480E-01	9.5402E-02	9.8953E-02	5.3688E-01	7.7427E-01	1.0515E-01	2.8621E-03
5.2406E-01	1.8130E-01	9.5012E-02	9.5523E-02	6.0729E-01	8.0626E-01	1.0153E-01	2.8504E-03
Na ⁺ -selec	tive electi	ode					
Mene	Υ.	a_	a_ calc	I	α	mos-	a_ error
9.3941E-03	1.0017E+00	9.4100E-03 ^C	9.0119E-03	9.3941E-03	2.0859E-20	9.3941E-03	4.7050E-04
1.6750E-02	9.7069E-01	1.8200E-02	1.7898E-02	1.8750E-02	2.0816E-20	1.8750E-02	9.1000E-04
3.9400E-02	9.5177E-01	3.7500E-02	3.7439E-02	3.9400E-02	2.6293E-18	3.9400E-02	1.8750E-03
5.6597E-02	9.4528E-01	5,3500E-02	5.3677E-02	5.6597E-02	2.4768E-13	5.6597E-02	2.6750E-03
7.86.50E-02	9.4111E-01	7.4000E-02	7.4457E-02	7.8630E-02	8.1052E-09	7.8630E-02	3.7000E-03
9.4518E-02	9.2469E-01	8.7400E-02	8.9429E-02	9.4518E-02	2.7255E-06	9.4518E-02	4.3700E-03
1.1911E-01	9.1593E-01	1.0910E-01	1.1241E-01	1.1920E-01	3.6936E-03	1.1867E-01	4.3640E-03
1.2383E-01	9.1338E-01	1.1310E-01	1.1650E-01	1.2408E-01	1.0472E-02	1.2253E-01	4.5240E-03
1.4058E-01	8.9911E-01	1.2640E-01	1.2817E-01	1.4281E-01	8.0498E-02	1.2927E-01	5.0560E-03
1.4583E-01	8.8596E-01	1.2920E-01	1.3121E-01	1.4897E-01	1.0932E-01	1.2989E-01	5.1680E-03
1.7270E-01	8.2455E-01	1.4240E-01	1.4543E-01	1.8117E-01	2.4899E-01	1.2970E-01	4.2720E-03

TABLE V-1 (CONTINUED)

1.8648E-01	8.0008E-01	1.4920E-01	1.5236E-01	1.9786E-01	3.0965E-01	1.2874E-01	4.4760E-03
2.1848E-01	7.4332E-01	1.6240E-01	1.6821E-01	2.3672E-01	4.2389E-01	1.2587E-01	4.8720E-03
2.3009E-01	7.2449E-01	1.6670E-01	1.7394E-01	2.5085E-01	4.5785E-01	1.2475E-01	5.0010E-03
2.6286E-01	6.8400E-01	1.7980E-01	1.9007E-01	2.9070E-01	5.3755E-01	1.2156E-01	5,3940F-0.3
2.8013E-01	6.7218E-01	1.3830E-01	1.9859E-01	3.1169E-01	5.7193E-01	1.1992E-01	5.6490F-03
3.1650E-01	6.5055E-01	2.0590E-01	2.1659E-01	3.5588E-01	6.3162E-01	1.1659E-01	6.1770E-03

Surface tension - maximum double-bubble pressure apparatus

^m sos	γ	Υm	γ calc	I	α	mos-	γ error
1.8156E-02	6.4812E+01	1.1767E+00	6.4258E+01	1.8156E-02	2.0157E-20	1.81563-02	1.2962E+00
3.6293E-02	5.8096E+01	2.1085E+00	5.7637E+01	3.6293E-0?	1.9572E-19	3.6293E-02	1.1619E+00
5.4443E-02	5.3328E+01	2.9034E+00	5.3360E+01	5.4443E-02	7.2635E-14	5.4443E-02	1.0666E+00
7.2689E-02	5.0790E+01	3.6919E+00	5.0232E+01	7.2689E-02	6.7606E-10	7.2689E-02	5.0790E-01
9.2112E-02	4,6472E+01	4.2806E+00	4.7642E+01	9.2112E-02	1.2063E-06	9.2112E-02	4.6472E-01
1.0992E-01	4.4722E+01	4.9157E+00	4.5701E+01	1.0992E-01	3.1904E-04	1.0988E-01	4.4722E-01
1.2885E-01	4.3618E+01	5.6204E+00	4.4145E+01	1.2949E-01	2.4846E-02	1.2565E-01	4.3618E-01
1.4586E-01	4.3254E+01	6.3088E+00	4.3489E+01	1.4900E-01	1.0947E-01	1.2989E-01	4.3254E-01
1.6729E-01	4.3012E+01	7.1954E+00	4.3025E+01	1.7464E-01	2.2301E-01	1.2998E-01	4.3012E-01
1.8806E-01	4.2935E+01	8.0743E+00	4.2693E+01	1.9977E-01	3.1612E-01	1.2861E-01	4.2935F-01
2.2773E-01	4.2591E+01	9.6994E+00	4.2186E+01	2.4797E-01	4.5122E-01	1.2497E-01	4.2591(-01
2.6776E-01	4.2300E+01	1.1326E+01	4.1765E+01	2.9665E-01	5.4776E-01	1.2109E-01	4.2300E-01
3.0901E-01	4.2027E+01	1.2987E+01	4.1386E+01	3.4678E-01	6.2053E-01	1.1726E-01	4.2027E-01
8.7396E-03	6.9821E+01	6.1021E-01	6.9220E+01	8.7396E-03	1.9405E-20	8.7396E-03	1.3964E+00
1.8156E-02	6.5924E+01	1.1969E+00	6.4258E+01	1.8156E-02	2.0157E-20	1.8156E-02	1.3185E+00
3.6293E-02	5.8896E+01	2.1375E+00	5.7637E+01	3.6293E-02	1.9572E-19	3.6293E-02	1.1779E+00
5.4443E-02	5.3938E+01	2.9366E+00	5.3360E+01	5.4443E-02	7.2635E-14	5.4443E-02	1.0788E+00
7.2689E-02	5.0055E+01	3.6384E+00	5.0232E+01	7.2689E-02	6.7606E-10	7.2689E-02	5.0055E-01

Calibration curves for data sets:

a	$\Delta \mu volts = 337834.073(1-a_w) + 1156281.96(1-a_w)^2$	RMSD = $12.4 \mu volts$
b	$\Delta \mu volts = 301223.22(1-a_w) + 699056.61(1-a_w)^2$	RMSD = $10.4 \mu volts$
с	mvolts = 245.764857 + 59.6598252(log a _{Na} +)	RMSD = 0.50 mvolts





წკ



data from several techniques have all been modelled simultaneously. It is of course possible to obtain a better fit of each type of data by fitting only that type of data alone. However, it is not possible to determine all the parameters with reasonable uncertainties using the data from only a single technique. This is possible when the data from several techniques are modelled simultaneously. (vide infra)

Values for the least-squares parameters of the mass-action fit of these data are shown in Table V-2. The effect of the magnitude of the ion-size parameter, b, is shown for the osmotic coefficient and activity coefficients. Guggenheim has suggested that b=1 for simple 1:1 electrolytes (51,53). From calorimetry studies of solutions of SOS in the pre-micellar range, this parameter has been determined by Birch and Hall (56) to be approximately 1. However, the results indicate this is too smal! to give a satisfactory fit of osmometry and activity data. This is probably due to the rather high values of activity and osmotic coefficients in the pre-micellar region. The data used by Burchfield and Woolley (51) also show rather large values for these coefficients at concentrations below the cmc. At present, no explanation of this behavior is available. At larger values of b, the fit is not greatly different, particularly when it is considered that the error in the data is largest in the low concentration region, where a change in b has the most noticeable effect. The data in these studies converged on a value of b=18. This value gives a satisfactory fit of the data over the entire range of SOS concentrations, approximately 3.5 to 4 times the cmc.

LEAST-SQUARES PARAMETERS FROM THE MASS-ACTION MODEL FOR SODIUM OCTYLSULFATE IN WATER AT 25°C K = 2.507 ± .007 + cmc = .1591 m β = .43 ± .01 n = 23 ± 3 b = 18 \hat{o} = .5 $\Gamma_{\rm m}$ = (2.25 ± .09)x10⁻¹⁰ + 74Å²/molecule c = (9 ± 2)x10⁻⁵ + .009 m ½ saturation

•
Since the micelle charge attenuation factor, δ , is highly coupled with the aggregation size, and since the goodness of fit of the data is not significantly improved by varying δ from 0.2 to 0.8, this parameter is held constant at 0.5 in this model. It was shown by Hill (8), and Burchfield and Woolley (51) that δ needs to be less than 1 to give a proper fit of the data, but it is difficult to converge on a value of this parameter, while all the other parameters are allowed to float in the NLLSQ routine, without greatly escalating errors in the least-squares parameters. The literature cited (8,52) also discusses difficulty in pinpointing this parameter.

By manipulating the equilibrium constant, one can approximate the cmc of the surfactant as $1/K^2 = 0.16$ m. The literature value for SOS is 0.131 m (57). A decreasing monomer concentration beyond the cmc is shown graphically by plotting [monomer] vs [total surfactant] where the curve exhibits a broad maximum around the cmc. (See Figure V-4.) This tendency of the monomer concentration to decrease beyond the cmc is consistent with the mass-action theory.

The value of the fraction of counterions bound to the micelle, β =0.43, agrees reasonably well with literature values. From pNa measurements Satake and coworkers (58) report β =0.56. Nishikido (59)reports β =0.45 at 25°C from pNa and conductivity data. Conductivity at 40°C by Evans (60) yields β =0.685. For benzene in SOS using vapor pressure measurements, Tucker and Christian (22) report a value of β =0.4.

Comparison of the aggregation size determined from the model, n=23, with literature values shows very nice agreement. Light



scattering results by Hutchinson and Melrose (61) yield n=20. Adair and co-workers (62) determined n=24 from viscosity studies. From ultrasonic relaxation studies by Gettins and co-workers (63), n=25. A value of n=27 is determined from fluorescent probe measurements by Aniansson and co-workers (64). Nishikido's (59) pNa and conductivity studies show n=30.

The monolayer surface excess quantity, introduced to incorporate surface tension into the mass-action model, is manipulated to calculate a molecular area for SOS in water of 74\AA^2 . This compares with a value of 75\AA^2 calculated from Tsutsui and coworkers' (65) data at 30°C, and 62\AA^2 at 25° C by Lone (66). For comparison, the molecular area is 46\AA^2 at the cmc for sodium dodecylsulfate (SDS) from Elworthy and Mysels' data (67).

Another parameter introduced by the surface tension model is c, the concentration at which the surface is half-saturated. The data reported here are best fit with a value of c=0.009 m. Using Tsutsui and coworkers' (65) data for SOS, c is calculated from the Szyszkowski equation (equation IV.i.[10]) to be 0.009 m.

In using the Langmuir adsorption mode! to approximate the Gibbs surface excess quantity, both a_{\pm} and a_2 were substituted, $\Gamma_2 = \Gamma_m a_{\pm}/(a_{\pm}+c)$ and $\Gamma_2 = \Gamma_m a_2/(a_2+c)$. The fits of the data indicated that the dependence of surface tension on molality is not linear in the limit as m approaches 0, as is predicted when a_{\pm} is used. Rather the data approach the limiting value of the surface tension of water parabolically as surfactant molality decreases. This relationship of and m is predicted when a_2 is used in the Langmuir approximation. This

shape is apparent from Elworthy and Mysels' (67) SDS data as well. Using \ddot{a} seems physically more feasible than using a_{\pm} since the latter suggests only OS⁻ ions, with no associated counterions, adsorb at the surface creating a huge charge imbalance.

ii. CETYLPYRIDINIUM CHLORIDE IN WATER

For cetylpyridinium chloride, CPC, experimental data and values predicted using the mass-action model are shown in Table V-3. The experimental data reported in the table are calculated from the appropriate calibration curves included in the footnotes of Table V-3. The same comments apply to these data and calibration fits as to those in Table V-1. Figure V-5 shows the osmotic coefficient vs [CPC]; Figure V-6 shows the activity coefficient vs [CPC] (only Cl⁻ activity data are available, but the predicted activity of CP⁺ is also shown); Figure V-7 shows surface tension vs [CPC]; and the least-squares parameters from the mass-action model are shown in Table V-4.

Although the equilibrium constant is consistent with a value for the cmc of 0.00135 m, about 50% higher than the literature value of 0.0009 m (1), this is not surprising. It is very difficult to infer quantities for solutions of such low concentration. This pre-micellar range is below the sensitivity of the osmometer and ion-selective electrode. The decreasing [monomer] vs [total surfactant] for CPC as calculated from the model is shown in Figure V-8, and shows a similar dependence of the monomer concentration on the total surfactant concentration as is seen for the SOS system. (See Figure V-4.) The function of [monomer] vs [total surfactant] appears to be much broader

TABLE V-3

EXPERIMENTAL AND CALCULATED DATA FOR CETYLPYRIDINIUM CHLORIDE IN WATER AT 25°C

Vapor pressure osmometer

•

^m ono	Φ	Φm	Φm calc	I	α	^m CP ⁺	^m +	Φm error
1.1176E-03	8.8761E-01 ^a	9.9202E-04	1.1050E-03	1.1176E-03	1.7869E-12	1.1176E-03	1.1176E-03	1.9840E-05
5.5376E-03	2.6701E-01	1.4786E-03	1.4225E-03	6.4254E-03	8.3820E-01	8.9596E-04	1.4022E-03	1.4786E-05
1.1141E-02	1.6380E-01	1.8248E-03	1.7814E-03	1.3150E-02	9.4297E-01	6.3534E-04	1.5069E-03	1.8248E-05
1.6713E-02	1.3494E-01	2.2552E-03	2.2126E-03	1.9814E-02	9.7018E-01	4.9844E-04	1.5840E-03	2,2552E-05
4.5168E-02	1.0419E-01	4.7062E-03	4.6252E-03	5.3757E-02	9.9432E-01	2.5664E-04	1.8138E-03	4.7062E-05
1.1176E-03	9.1505E-01 ^b	1.0227E-03	1.1050E-03	1.1176E-03	1.7869E-12	1.1176E-03	1.1176E-03	2.0454E-05
5.5376E-03	2.6287E-01	1,4557E-03	1.4225E-03	6.4254E-03	8.3820E-01	8.9596E-04	1.4022E-03	1.4557E-05
1.1141E-02	1.5051E-01	1.6768E-03	1.7814E-03	1.3150E-02	9.42976-01	6.3534E-04	1.5069E-03	1.6768E-05
1.6713E-02	1.2734E-01	2.1281E-03	2.2126E-03	1.9814E-02	9.7018E-01	4.9844E-04	1.5840E-03	2.1281E-05
4.5168E-02	1.0747E-01	4.8542E-03	4.6252E-03	5.3757E-02	9.9432E-01	2.5664E-04	1.8138E-03	4.8542E-05
6.6125E-02	9.8752E-02	6.5299E-03	6.4341E-03	7.8733E-02	9.9703E-01	1.9670E-04	1.9147E-03	6.5299E-05
9.1017E-02	9.2780E-02	8.4445E-03	8.5926E-03	1.0839E-01	9.9827E-01	1.5709E-04	2.0043E-03	8.4445E-05
1.3583E-01	9.2589E-02	1.2576E-02	1.2515E-02	1.6178E-01	9.9913E-01	1.1837E-04	2.1?30E-03	1.2576E-04
1.8356E-01	9.1808E-02	1.6852E-02	1.6758E-02	2.1864E-01	9.9948E-01	9.5614E-05	2.21728-03	1.6052E-04
7.9383E-04	9.0531E-01 ^b	7.1866E-04	7.8610E-04	7.9383E-04	9.8452E-33	7.9383E-04	7.9383E-04	3.5933E-05
1.1176E-03	9.0682E-01	1.0135E-03	1.1050E-03	1.1176E-03	1.7869E-12	1.1176E-03	1.1176E-03	2.0270E-05
5.5376E-03	2.5954E-01	1.4373E-03	1.4225E-03	6.4254E-03	8.3820E-01	8.9596E-04	1.4022E-03	1.4373E-05
1.1141E-02	1.5878E-01	1.7689E-03	1.7814E-03	1.3150E-02	9,4297E-01	6.3534E-04	1.5069E-03	1.7689E-05
1.6713E-02	1.2954E-01	2.1650E-03	2.2126E-03	1.9814E-02	9.7018E-01	4.9844E-04	1.5840E-03	2.1650E-05
2.6157E-02	1.1658E-01	3.0492E-03	2.9972E-03	3.1088E-02	9.8576E-01	3.7260E-04	1.6811E-03	3.0492E-05
4.5168E-02	1.0462E-01	4.7253E-03	4.6252E-03	5.3757E-02	9.9432E-01	2.5664E-04	1.8138E-03	4.7253E-05
6.6125E-02	1.0000E-01	6.6128E-03	6.4341E-03	7.8733E-02	9.9703E-01	1.9670E-04	1.9147E-03	6.6128E-05
9.1017E-02	9.1061E-02	8.2881E-03	8.5926E-03	1.0839E-01	9.9827E-01	1.5709E-04	2.0043E-03	8.2881E-05
1.3583E-01	9.1099E-02	1.2374E-02	1.2515E-02	1.6178E-01	9.9913E-01	1.18378-04	2.1230E-03	1.2374E-04
1.8356E-01	9.0456E-02	1.6604E-02	1.6758E-02	2.1864E-01	9.9948E-01	9.5614L-05	2.2172E-03	1.6604E-04

TABLE V-3 (CONTINUED)

3.5561E-01	1.1609E-03	1.3239E-03	3.6834E-03	6.7070E-01	1.0750E-03	1.3469E-03	5.8044E-05
2.6299E-01	1.2806E-03	1.3896E-03	5.6208E-03	8.0646E-01	9.4249E-04	1.3869E-03	6.4032E-05
1.7552E-01	1.5202E-03	1.6083E-03	1.0178E-02	9.1593E-01	7.2812E-04	1.4648E-03	7.6008E-05
1.5739E-01	1.5386E-03	1.6841E-03	1.1515E-02	9.3013E-01	6.8300E-04	1.4845E-03	4.6158E-05
1.2800E-01	2.0637E-03	2.1652E-03	1.9108E-02	9.6838E-01	5.0976E-04	1.5767E-03	6.1910E-05
1.1505E-01	2,2295E-03	2.4299E-03	2.2998E-02	9.7659E-01	4.5370E-04	1.6148E-03	6.6884E-05
1.0315E-01	3.3532E-03	3.5378E-03	3.8661E-02	9.9010E-01	3.2177E-04	1.7321E-03	6.7063E-05
1.0174E-01	3.9518E-03	4.0808E-03	4.6214E-02	9.9267E-01	2.8485E-04	1.7757E-03	7.9036E-05
9.7869E-02	6.3642E-03	6.3392E-03	7.7425E-02	9.9694E-01	1.9902E-04	1.9101E-03	1.2728E-04
9.4166E-02	7.5978E-03	7.6951E-03	9.6082E-02	9.9788E-01	1.7102E-04	1.9700E-03	1.5196E-04
9.1631E-02	9.9078E-03	1.0084E-02	1.2878E-01	9.9871E-01	1.3910E-04	2.0545E-03	1.9816E-04
9.1138E-02	1.2208E-02	1.2350E-02	1.5954E-01	9.9911E-01	1.1954E-04	2.1188E-03	2.4416E-04
9.3810E-02	1.5399E-02	1.5025E-02	1.9553E-01	9.9937E-01	1.0350E-04	2.1817E-03	3.0799E04
9.4051E-02	1.7937E-02	1.7399E-02	2.2717E-01	9.9951E-01	9.3055E-05	2.2294E-03	3.5874E-04
9.3988E-02	2.1016E-02	2.0369E-02	2.6634E-01	9.9963E-01	8.3121E-05	2.2812E-03	4.2032E-04
	3.5561E-01 2.6299E-01 1.7552E-01 1.5739E-01 1.2800E-01 1.1505E-01 1.0315E-01 1.0174E-01 9.7869E-02 9.4166E-02 9.1631E-02 9.1138E-02 9.3810E-02 9.4051E-02 9.3988E-02	3.5561E-01 1.1609E-03 2.6299E-01 1.2806E-03 1.7552E-01 1.5202E-03 1.5739E-01 1.5386E-03 1.2800E-01 2.0637E-03 1.1505E-01 2.2295E-03 1.0315E-01 3.3532E-03 1.0174E-01 3.9518E-03 9.7869E-02 6.3642E-03 9.4166E-02 7.5978E-03 9.1631E-02 9.9078E-03 9.1138E-02 1.2208E-02 9.3810E-02 1.5399E-02 9.4051E-02 1.7937E-02 9.3988E-02 2.1016E-02	3.5561E-01 1.1609E-03 1.3239E-03 2.6299E-01 1.2806E-03 1.3896E-03 1.7552E-01 1.5202E-03 1.6083E-03 1.5739E-01 1.5386E-03 1.60841E-03 1.2800E-01 2.0637E-03 2.1652E-03 1.1505E-01 2.2295E-03 2.4299E-03 1.0315E-01 3.5532E-03 3.5378E-03 1.0174E-01 3.9518E-03 4.0808E-03 9.7869E-02 6.3642E-03 6.3392E-03 9.1631E-02 9.9078E-03 1.0084E-02 9.1138E-02 1.2208E-02 1.2350E-02 9.3810E-02 1.5399E-02 1.5025E-02 9.4051E-02 1.7937E-02 1.7399E-02 9.3988E-02 2.1016E-02 2.0369E-02	3.5561E-011.1609E-031.3239E-033.6834E-032.6299E-011.2806E-031.3896E-035.6208E-031.7552E-011.5202E-031.6083E-031.0178E-021.5739E-011.5386E-031.6841E-031.1515E-021.2800E-012.0637E-032.1652E-031.9108E-021.1505E-012.2295E-032.4299E-032.2998E-021.0315E-013.3532E-033.5378E-033.8661E-021.0174E-013.9518E-034.0808E-034.6214E-029.7869E-026.3642E-036.3392E-037.7425E-029.4166E-027.5978E-031.0084E-021.2878E-019.1138E-021.2208E-021.2350E-021.5954E-019.3810E-021.7937E-021.7399E-022.2717E-019.3988E-022.1016E-022.0369E-022.6634E-01	3.5561E-011.1609E-031.3239E-033.6834E-036.7070E-012.6299E-011.2806E-031.3896E-035.6208E-038.0646E-011.7552E-011.5202E-031.6083E-031.0178E-029.1593E-011.5739E-011.5386E-031.6841E-031.1515E-029.3013E-011.2800E-012.0637E-032.1652E-031.9108E-029.6838E-011.1505E-012.2295E-032.4299E-032.2998E-029.7659E-011.0315E-013.3532E-033.5378E-033.8661E-029.9010E-011.0174E-013.9518E-034.0808E-034.6214E-029.9267E-019.7869E-026.3642E-036.3392E-037.7425E-029.9694E-019.4166E-027.5978E-031.0084E-021.2878E-019.9871E-019.1138E-021.2208E-021.2350E-021.5954E-019.9937E-019.3810E-021.5399E-021.7399E-022.2717E-019.9951E-019.3988E-022.1016E-022.0369E-022.6634E-019.9951E-01	3.5561E-011.1609E-031.3239E-033.6834E-036.7070E-011.0750E-032.6299E-011.2806E-031.3896E-035.6208E-038.0646E-019.4249E-041.7552E-011.5202E-031.6083E-031.0178E-029.1593E-017.2812E-041.5739E-011.5386E-031.60841E-031.1515E-029.3013E-016.8300E-041.2800E-012.0637E-032.1652E-031.9108E-029.6838E-015.0976E-041.1505E-012.2295E-032.4299E-032.2998E-029.7659E-014.5370E-041.0174E-013.9518E-033.5378E-033.8661E-029.9010E-013.2177E-041.0174E-013.9518E-034.0808E-034.6214E-029.9267E-012.8485E-049.7869E-026.3642E-036.3392E-037.7425E-029.9694E-011.9902E-049.4166E-027.5978E-031.0084E-021.2878E-019.9911E-011.3910E-049.1138E-021.2208E-021.2550E-021.5954E-019.9937E-011.0350E-049.4051E-021.7337E-021.7399E-022.2717E-019.9937E-011.0350E-049.4051E-021.7937E-021.7399E-022.2717E-019.9951E-019.3055E-059.3988E-022.1016E-022.0369E-022.6634E-019.9951E-018.3121E-05	3.5561E-011.1609E-031.3239E-033.6834E-036.7070E-011.0750E-031.3469E-032.6299E-011.2806E-031.3896E-035.6208E-038.0646E-019.4249E-041.3869E-031.7552E-011.5202E-031.6083E-031.0178E-029.1593E-017.2812E-041.4648E-031.5739E-011.5386E-031.66841E-031.1515E-029.3013E-016.8300E-041.4845E-031.2800E-012.0637E-032.1652E-031.9108E-029.6838E-015.0976E-041.5767E-031.1505E-012.2295E-032.4299E-032.2998E-029.7659E-014.5370E-041.6148E-031.0174E-013.9518E-033.5578E-033.8661E-029.9010E-013.2177E-041.7521E-031.0174E-013.9518E-034.0808E-034.6214E-029.9267E-012.8485E-041.7757E-039.7869E-026.3642E-036.3392E-037.7425E-029.9694E-011.9902E-041.9101E-039.4166E-027.5978E-037.6951E-039.6082E-029.9788E-011.7102E-041.9700E-039.1138E-021.2208E-021.2550E-021.5954E-019.9911E-011.1954E-042.1188E-039.3810E-021.5399E-021.5025E-021.9553E-019.9937E-011.0350E-042.1817E-039.4051E-021.7937E-021.7399E-022.2717E-019.9951E-019.3055E-052.2294E-039.3988E-022.1016E-022.0369E-022.6634E-019.9963E-018.3121E-052.2812E-03

Cl⁻-selective electrode

Mana	γ	а	a calc	I	α	^m cn ⁺	m_	a error
3.26456-03	4.7236E-01	1.5420E-03 ^C	1,5891E-03	3.6834E-03	6,7070E-01	1.0750E-03	1.3469E-03	7.7102E-05
4.8696E-03	4.1469E-01	2.0194E-03	1.9001E-03	5.6208E-03	8.0646E-01	9.4249E-04	1.3869E-03	1.0097E-04
8.6607E-03	3.5148E-01	3.0441E-03	2.6923E-03	1.0178E-02	9.1593E-01	7.2812E-04	1.4648E-03	1.2176E-04
9.7758E-03	3.4202E-01	3,3435E-03	2.9349E-03	1.1515E-02	9.3013E-01	6.8300E-04	1.4845E-03	1.3374E-04
1.6122E-02	3.0537E-01	4,9233E-03	4.3522E-03	1.9108E-02	9.6838E-01	5.0976E-04	1.5767E-03	1.9693E-04
1.9379E-02	2.9938E-01	5.8016E-03	5.09078-03	2.2998E-02	9.7659E-01	4.5370E-04	1.6148E-03	1.7405E-04
3.2506E-02	2.7435E-01	8,9182E-03	8.0764E-03	3.8661E-02	9.9010E-01	3.2177E-04	1.7321E-03	2.6755E-04
3.8840E-02	2.6847E-01	1.0427E-02	9.5111E-03	4.6214E-02	9.9267E-01	2.8485E-04	1.7757E-03	3.1282E-04
6.5028E-02	2.4843E-01	1.6155E-02	1.5379E-02	7.7425E-02	9.9694E-01	1.9902E-04	1.9101E-03	4.8464E-04
8.0685E-02	2.4439E-01	1.9718E-02	1.8842E-02	9.6082E-02	9.9788E-01	1.7102E-04	1.9700E-03	5.9155E-04
1.0813E-01	2.3056E-01	2.4930E-02	2.4850E-02	1.2878E-01	9.9871E-01	1.3910E-04	2.0545E-03	7.4790E-04
1.3395E-01	2.2628E-01	3.0311E-02	3.0444E-02	1.5954E-01	9.9911E-01	1.1954E-04	2.1188E-03	9.0932E-04
1.6416E-01	2.2102E-01	3.6281E-02	3.6932E-02	1.9553E-01	9.9937E-01	1.0350E-04	2.1817E-03	1.0884E-03
1.9071E-01	2.1391E-01	4.0795E-02	4.2597E-02	2.2717E-01	9.9951E-01	9.3055E-05	2.2294E-03	1.2238E-03
2.2360E-01	2.1416E-01	4.7885E-02	4.9569E-02	2.6634E-01	9.9963E-01	8.3121E-05	2.2812E-03	1.4366E-03
4.5978E-03	3.9369E-01	1.8101E-0ቻ []]	1.8461E-03	5.2931E-03	7.9060E-01	9.6277E-04	1.3805E-03	7.2405E-05

				TABLE	V-3 (CONTINU	ED)			
9.4070E-03	3,2268E-01	3.0355E-03	2.8543E-03	1.1073E-02	9.2588E-01	6.9724E-04	1.4781E-03	1.2142E-04	
3.8712E-02	2.5461E-01	9.8565E-03	9.4822E-03	4.6061E-02	9.9263E-01	2.8549E-04	1.7749E-03	3.9426E-04	
7.7749E-02	2.3796E-01	1.8501E-02	1.8195E-02	9.2584E-02	9.9774E-01	1.7554E-04	1.9595E-03	5.5503E-04	
1.1951E-01	2.2658E-01	2.7079E-02	2.7323E-02	1.4234E-01	9.9892E-01	1.2959E-04	2.0843E-03	8.1237E-04	
1.5044E-01	2.2290E-01	3.3533E-02	3.3994E-02	1.7919E-01	9.9927E-01	1.1010E-04	2.1545E-03	1.0060E-03	
1.7700E-01	2.1791E-01	3.8570E-02	3.9677E-02	2.1083E-01	9.9945E-01	9.8113E-05	2.2056E-03	1.1571E-03	
2.0973E-01	2.1317E-01	4.4709E-02	4.6635E-02	2.4983E-01	9.9959E-01	8.6985E-05	2.2602E-03	1.5413E-03	
2.6714E-01	2.0887E-01	5.5798E-02	5.8740E-02	3.1821E-01	9,9973E-01	7.3258E-05	2.3405E-03	1.6739E-03	
3.2457E-01	2.0319E-01	6.5949E-02	7.0756E-02	3.8663E-01	9.9980E-01	6.3795E-05	2.4072E-03	1.9785E-03	
3.9881E-01	1.9851E-01	7.9168E-02	8.6178E-02	4.7506E-01	9.9986E-01	5.5111E-05	2.4799E-03	2.3750E-03	
4.6995E-01	1.9452E-01	9.1413E-02	1.0087E-01	5.5982E-01	9.9990E-01	4.9043E-05	2.5394E-03	2.7424E-03	
Surface t	ension - R	osano surfa	ice tension	eter (46)					
^m cpc	γ	γm	γ calc	I	α	^m CP ⁺	m_+	γ error	
4.6509E-04	5.2298E+01	2.4323E-02	5.4362E+01	4.6509E-04	3.7035E-29	4.6509E-04	4.6509E-04	1.5689E+00	
9.2177E-04	4.4034E+01	4.0589E-02	4.6412E+01	9.2177E-04	7.2662E-28	9.2177E-04	9.2177E-04	1.3210E+00	
1.7657E-03	4.3487E+01	7.6784E-02	4.2427E+01	1.8686E-03	3.0470E-01	1.2277E-03	1.3007E-03	8.6974E-01	
4.6003E-03	4.2676E+01	1.9632E-01	4.2011E+0!	5.2961E-03	7.9075E-01	9.6258E-04	1.3806E-03	8.5352E-01	
8.1618E-03	4.2033E+01	3.4306E-01	4.1596E+01	9.5792E-03	9.0805E-01	7.5044E-04	1.4556E-03	4,2033E-01	
9.1359E-03	4.2090E+01	3.8453E-01	4.1498E+01	1.0748E-02	9.2249E-01	7.0813E-04	1.4734E-03	4.2090E-01	
1.7024E-02	4.1153E+01	7.0059E-01	4.0883E+01	2.0186E-02	9.7106E-01	4.9269E-04	1.5878E-03	4.1153E-01	
1.9034E-02	4.1110E+01	7.8248E-01	4.0763E+01	2.2586E-02	9.7589E-01	4.5897E-04	1.6110E-03	4.1110E-01	
2.7915E-02	4.0516E+01	1.1310E+00	4.0340E+01	3.3186E-02	9.8722E-01	1.5669E-04	1.6961E-03	4.0516E-01	
3.8030E-02	4.0032E+01	1.5224E+00	3.9989E+01	4.5247E-02	9.9240E-01	2.8901E-04	1.7705E-03	4.0032E-01	
4.6923E-02	3.9980E+01	1.8760E+00	3.9749E+01	5.5849E-02	9.9467E-01	2.4994E-04	1.8236E-03	3.9980E-01	
5.7421E-02	3.9256E+01	2.2541E+00	3.9517E+01	6.8361E-02	9.9622E-01	2.1713E-04	1.8766E-03	3.9256E-01	
7.8630E-02	3.8887E+01	3.0577E+00	3.9155E+01	9.3633E-02	9,9779E-01	1.7415E-04	1.9627E-03	3.8887E-01	
3.7477E-02	3.8957E+01	3.4078E+00	3.9032E+01	1.0418E-01	9.9815E-01	1.6155E-04	1.9929E-03	3.8957E-01	
9.6662E-02	3.8980E+01	3.7679E+00	3.8916E+01	1.1512E-01	9.9844E-01	1.5056E-04	2.0217E-03	3.8980E-01	
1.3484E-01	3.8141E+01	5.1428E+00	3.8528E+01	1.6060E-01	9.9912E-01	1.1898E-04	2.1208E-03	3.8141E-01	
2.0042E-01	3.7852E+01	7.5862E+00	3.8060E+01	2.3873E-01	9.9955E-01	8.9835E-05	2.2454E-03	3.7852E-01	
1.6661E-03	4.3702E+01	7.2813E-02	4.2449E+01	1.7480E-03	2.5684E-01	1.2382E-03	1.2967E-03	1.3111E+00	
4.0413E-03	4.2959E+01	1.7361E-01	4.2085E+01	4.6218E-03	7.5084E-01	1.0069E-03	1.3670E-03	8.5918E-01	
8.2776E-03	4.1994E+01	3.4761E-01	4.1584E+01	9.7183E-03	9.0998E-01	7.4513E-04	1.4578E-03	4.1994E-01	

						- /		
1.7326E-02	4.1137E+01	7.1274E-01	4.0864E+01	2.0546E-02	9.7188E-01	4.8727E-04	1.5914E-03	4.1137E-01
3.8337E-02	4.0231E+01	1.5424E+00	3.9980E+01	4.5614E-02	9.9250E-01	2.8741E-04	1.7725E-03	4.0231E-01
5.5862E-02	3.9624E+01	2.2135E+00	3.9549E+01	6.6502E-02	9.9604E-01	2.2135E-04	1.8692E-03	3.9624E-01
7.6162E-02	3.9166E+01	2.9829E+00	3.9192E+01	9.0693E-02	9.9766E-01	1.7810E-04	1.9538E-03	3.9166E-01
9.2948E-02	3.8828E+01	3.6089E+00	3.8962E+01	1.1069E-01	9.9833E-01	1.5478E-04	2.0103E-03	3.8828E-01
1.4191E-01	3.8230E+01	5.4252E+00	3.8468E+01	1.6902E-01	9.9919E-01	1.1475E-04	2.1364E-03	3.8230E-01
2.0042E-01	3.7822E+01	7.5802E+00	3.8060E+01	2.3873E-01	9.9955E-01	₿ .9835E-05	2.2454E-03	3.7822E-01
4.6439E-06	7.1284E+01	3.3103E-04	7.2428E+01	4.6439E-06	1.5597E-14	4.6439E-06	4.6439E-06	3.5642E+00
1.3218E-05	7.0487E+01	9.3172E-04	7.2345E+01	1.3218E-05	4.3098E-20	1.3218E-05	1.3218E-05	3.5244E+00
4.4988E-05	6.8814E+01	3.0958E-03	7.1430E+01	4.4988E-05	2.8959E-27	4.4988E-05	4.4988E-05	3.4407E+00
1.3315E-04	6.2801E+01	8.3617E-03	6.6718E+01	1.3315E-04	7.6207E-22	1.3315E-04	1.3315E-04	2.5120E+00
4.4528E-04	5.1571E+01	2.2963E-02	5.4856E+01	4.4528E-04	1.3869E-25	4.4528E-04	4.4528E-04	2.0628E+00
8.1479E-04	4.4184E+01	3.6000E-02	4.7862E+01	8.1479E-04	1.2566E-31	8.1479E-04	8.1479E-04	1.3255E+00
2.0276E-03	4.3567E+01	8.8336E-02	4.2378E+01	2,1861E-03	4.0839E-01	1.1995E-03	1.3103E-03	8.7133E-01
6.6967E-03	4.1655E+01	2.7895E-01	4.1756E+01	7.8197E-03	8.7678E-01	8.2515E-04	1.4269E-03	8.3310E-01
9.2456E-03	4.1536E+01	3.8402E-01	4.1488E+01	1.0879E-02	9.2389E-01	7.0368E-04	1.4753E-03	8.3071E-01
1.8830E-02	4.1018E+01	7.7236E-01	4.0775E+01	2.2342E-02	9.7546E-01	4.6215E-04	1.6087E-03	4.1018E-01
4.6177E-02	3.9425E+01	1.8205E+00	3.9767E+01	5.4960E-02	9.9453E-01	2.5273E-04	1.8195E-03	3.9425E-01
9.5380E-02	3.8828E+01	3.7034E+00	3.8932E+01	1.1359E-01	9.9841E-01	1.5198E-04	2.0178E-03	3.8828E-01
1.0614E-01	3.8629E+01	4.1001E+00	3.8807E+01	1.2641E-01	9.9867E-01	1.4093E-04	2.0490E-03	3.8629E-01
1.3565E-01	3.8469E+01	5.2182E+00	3.8521E+01	1.6156E-01	9.9913E-01	1.1848E-04	2.1226E-03	3.8469E-01
1.8257E-01	3.7672E+01	6.8778E+00	3.8171E+01	2.1747E-01	9.9947E-01	9.5980E-05	2.2154E-03	3.7672E-01

Calibration curves for data sets:

a	$\Delta \mu volts = 297262.094(1-a_{W}) + 573259.194(1-a_{W})^{2}$	RMSD	Ξ	10.6	µvolts
b	$\Delta \mu volts = 301223.22(1-a_w) + 699056.61(1-a_w)^2$	RMSD	=	10.4	µvolts
с	mvolts = 44.2509032 - 58.9099276(log a _{Cl} -)	RMSD	=	0.47	mvolts
d	$mvolts = 13.0522548 - 59.2380028(log a_{Cl}^{-})$	RMSD	=	0.71	mvolts







```
TABLE V-4
```

LEAST-SQUARES PARAMETERS FROM THE MASS-ACTION MODEL FOR CETYLPYRIDINIUM CHLORIDE IN WATER AT 25°C

 $K = 27.4 \pm .2 \rightarrow cmc \approx .00133 m$ $\beta = .720 \pm .004$ $n = 108 \pm 2$ b = 3.1 $\delta = .5$ $\Gamma_{m} = (2.4 \pm .2) \times 10^{-10} \rightarrow 69 \text{Å}^{2}/\text{molecule}$ $c = (1.1 \pm .6) \times 10^{-8} \rightarrow .00011 \text{ m}^{\frac{1}{2}} \text{ saturation}$



70

in the case of SOS than in the case of CPC. However, it should be noted that the studies of aqueous CPC cover a concentration range approximately 400 times the cmc, whereas the studies of aqueous SOS cover a concentration range only 3.5 to 4 times the cmc.

No reports in the literature have been found which make it possible to determine the aggregation size and counterion binding fraction for CPC in water. Various studies have been performed with CPC in the presence of added electrolyte. However, it is apparent that cetyltrimethylammonium chloride, CTAC, behaves similarly to CPC. Mathews and coworkers (68) report a β of 0.75 for CTAC in water. Roelants and coworkers (69) and Lianos and coworkers (70) report aggregation sizes of 80 to 115, with a mean aggregation size of 115 for CTAC in water, using fluorescent probe techniques. These values agree reasonably well with the present results for CPC, β =0.720, and n=108.

Information is not available on the ion-size parameter for CPC. b is related to the distance of closest approach of hydrated ions of opposite charge. The sphere of hydration around the two groups will be different due to their water structure "making" or "breaking" ability. So the "real" value of b for CPC could conceivably be quite different than that for the corresponding alkylsulfate of the same chain length.

Hauser and Niles (71) measured the surface tension of CPC in water at 25°C using the pendant drop technique. Their study covers a range of only 0.001 m. A molecular area of 76\AA^2 is calculated from their data.

iii- SELF-ASSOCIATION OF 2-PHENYLACETIC ACID

The osmometry results for 2-phenylacetic acid, PAA, in water (see Table V-5) are shown in Figure V-9 where the ordinate is $1-a_w$ and the abscissa is the mole fraction of PAA. The solid line is the calculated curve where K_i is held constant at 5.56×10^{-5} <u>M</u> (55), and the least-squares parameter for the self-association constant, K_2 , is allowed to vary in an unrestricted way. The least squares fit provides a value of $K_2=2.34\pm0.07$ <u>M</u>⁻¹ (3% error). In Figure V-9, one can see that the mole fraction of ions increases with mole fraction of total acid, and levels off quickly. On the other hand, the mole fraction of dimer increases very slowly at low mole fractions of total acid, then increases faster as the mole fraction of total acid increases. These features are consistent with the expected behavior of a weak acid, and with a compound which self-associates.

TABLE V-5

EXPERIMENTAL AND CALCULATED DATA FOR 2-PHENYLACETIC ACID IN WATER AT 25°C

x	1-a	1-a calc	x	x -	x +	× _{нд•на} +
PAA	- W	w	HA	A	Н	× _{HA•A} -
1.4232E-04	1.5126E-04 ^a	1.5140E-04	1.2661E-04	1.1170E-05	1.1354E-05	2.2733E-06
3.9222E-04	3.9178E-04	3.9509E-04	3.4201E-04	1.8110E-05	1.8917E-05	1.6051E-05
6.7493E-04	6.5723E-04	6.5625E-04	5.6529E-04	2.2965E-05	2.4657E-05	4.3338E-05
8.4736E-04	8.0456E-04	8.1008E-04	6.9257E-04	2.5225E-05	2.7502E-05	6.4787E-05
1.1136E-03	1.0469E-03	1.0412E-03	8.7807E-04	2.8093E-05	3.1308E-05	1.0370E-04
1.3544E-03	1.2544E-03	1.24475-03	1.0361E-03	3.0239E-05	3.4323E-05	1.4400E-04
1.6457E-03	1.49282-03	1.4852E-03	1.2170E-03	3.2437E-05	3.7582E-05	1.9816E-04
2.5479E-03	2.0815E-03	2.0443E-03	1.6156E-03	3.6563E-05	4.4262E-05	3.4787E-04
7.2040E-05	8.1357E-05 ^a	7.9433E-05	6.2967E-05	7.9095E-06	7.9745E-06	5.8163E-07
1.4232E-04	1.4949E-04	1.5140E-04	1.2661E-04	1.1170E-05	1.1354E-05	2.2733E-06
3.9222E-04	3.8420E-04	3.9509E-04	3.4201E-04	1.8110E-05	1.8917E-05	1.6051E-05
6.7493E-04	6.5068E-04	6.5625E-04	5.6529E-04	2.2965E-05	2.4657E-05	4.3338E-05
1.1402E-03	1.0590E-03	1.0639E-03	8.9599E-04	2.8349E-05	3,1659E-05	1.0794E-04
1.3544E-03	1.2416E-03	1.2447E-03	1.0361E-03	3.0239E-05	3.4323E-05	1.4400E-04
1.8945E-03	1.6760E-03	1.6862E-03	1.3636E-03	3.4056E-05	4.0108E-05	2.4839E-04
2.3479E-03	2.0613E-03	2.0443E-03	1.6156E-03	3.6563E-05	4.4262E-05	3.4787E-04
3.6143E-05	4.1573E-05 ^a	4.1526E-05	3.0356E-05	5.5034E-06	5.5252E-06	1.4186E-07
9.1992E-05	1.0162E-04	1.0010E-04	8.11205-05	8.9671E-06	9.0619E-06	9.5241E-07
1.7934E-04	1.8366E-04	1.8853E-04	1.5966E-04	1.2517E-05	1.2777E-05	3.5825E-06
3.9569E-04	3.8319E-04	3.9931E-04	3.4569E-04	1.8203E-05	1.9023E-05	1.6395E-05
6.5788E-04	6.2194E-04	6.4084E-04	5.5237E-04	2.2719E-05	2.4354E-05	4.1399E-05
8.6129E-04	8.0280E-04	8.2235E-04	7.0258E-04	2.5392E-05	2.7717E-05	6.6656E-05
1.0878E-03	1.0022E-03	1.0192E-03	8.6068E-04	2.7842E-05	3.0965E-05	9.9664E-05
1.3421E-03	1.2156E-03	1.2345E-03	1.0283E-03	3.0138E-05	3.4177E-05	1.4185E-04
1.7147E-03	1.5223E-03	1.5413E-03	1.2583E-03	3.2907E-05	3.8304E-05	2.1175E-04
2.0987E-03	1.8332E-03	1.8487E-03	1.4794E-03	3.5247E-05	4.2043E-05	2.9203E-04
$K_{i} = 5.56$	×10 ⁻⁵ M					
$K_2 = 2.33$	\pm .05 m ⁻¹					
RMSD = 1.	34x10 ⁻⁵ in	units of 1	-a.,			
Calibrati	on curve f	or data set	 S:			
- Auvolte	= 394417 \$	(1-a) +	1807997-5(*	$(-a)^2$ R	MSD = 6.3	volts
a up or co		w''	200,227,02(.	ิ ซี เ		1.0103



×_{PAA}, Total

FIGURE V-9

iv. SOLUBILIZATION

Results from the Cl⁻ electrode and osmometry data for PAA solubilized into aqueous CPC are tabulated in Table V-6. (A discussion of the calibration curves at the bottom of the table can be found in section i. of this chapter.) The dependence of bound Cl⁻ on micellar composition is shown graphically in Figure V-10. The fraction of counterions bound to the micelle, β , is decreasing as the mole fraction of solubilized organic increases. Vikingstad (72) also observed a decrease in β with increasing mole fraction of solubilized alkandiol. The results presented in Figure V-10 show that the decrease in β is dependent also on the total surfactant concentration, where the rate of decreasae is less for higher [surfactant]. Additionally, the limiting values of β are increasing slightly as the concentration of CPC increases.

Apparent solubilization constants for the anion and neutral acid in CPC are plotted against the micellar composition in Figures V-11.a, V-11.b, and V-11.c. The solubilization parameters start high, decrease and level off with increasing mole fraction of organic in the micelle. This apparent solubilization "constant" or parameter is not constant with mole fraction. Some investigators will define K_c as

TABLE V-6

EXPERIMENTAL AND CALCULATED DATA USING RESULTS FROM OSMOMETRY AND CHLORIDE AND PROTON ACTIVITIES OF 2-PHENYLACETIC ACID SOLUBILIZED IN CETYLPYRIDINIUM CHLORIDE IN WATER AT 25°C

PAA in 0.10788 m CPC

X _{DAA}	∆(1-a_)	Δ× _{C1} -	× _H +	×HA	×^-	β	K _{e1}	K _{e2}
3.7539E-04	1.0704E-04 a	4.6414E-05 ³	5.1523E-05 h	2.3154E-05	4.5015E-07	7.9429E-01	1.2076E+02	1.0556E+03
7.5482E-04	2.0278E-04	7.1655E-05	7.8573E-05	7.7735E-05	9.9101E-07	7.8117E-01	7.1451E+01	7.2852E+02
1.1392E-03	2.9034E-04	9.7638E-05	9.8910E-05	1.3235E-04	1.3404E-06	7.6972E-01	6.3529E+01	6.7760E+02
1.5212E-03	4.0568E-04	1.1170E-04	1.1445E-04	2.1904E-04	1.9170E-06	7.6029E-01	4.9945E+01	5.4649E+02
1.9143E-03	5.5416E-04	1.2875E-04	1.2666E-04	3.3744E-04	2,6688E-06	7.5138E-01	3.9191E+01	4.3248E+02
2.3703E-03	7.4513E-04	1.5370E-04	1.3668E-04	4.8683E-04	3.5679E-06	7.3836E-01	3,2221E+01	3.4719E+02
2.7949E-03	9.0343E-04	1.7040E-04	1.4285E-04	6.1061E-04	4.2818E-06	7.2960E-01	2.9645E+01	3.0104E+02
3.2288E-03	1.0490E-03	1.8766E-04	1.4623E-04	7.2168E-04	4.9435E-06	7.2054E-01	2.8712E+01	2.6577E+02
3.6659E-03	1.1789E-03	2.0549E-04	1.4696E-04	8.1847E-04	5,5789E-06	7.1118E-01	2.8744E+01	2.3552E+02
4.1645E-03	1.3622E-03	2.2600E-04	1.4479E-04	9.5581E-04	6.6124E-06	7.0040E-01	2.7540E+01	1.9396E+02
4.7334E-03	1.5554E-03	2.4942E-04	1.3877E-04	1.0973E-03	7.9208E-06	6.8808E-01	2.7031E+01	1.5300E+02
5.5071E-03	1.8155E-03	2.8753E-04	1.2496E-04	1.2807E-03	1.0266E-05	6.6805E-01	2.6738E+01	1.0288E+02
3.7539E-04	1.1169E-04 ^{.C}	4.6414E-05 ^b	5.1523E-05 h	2.7704E-05	5.3862E-07	7.9429E-01	9.9373E+01	8.8063E+02
7.5482E-04	2.0066E-04	7.1655E-05	7.8573E-05	7.5673E-05	9.6473E-07	7.8117E-01	7.3662E+01	7.4863E+02
1.1392E-03	3.0059E-04	9.3638E-05	9.8910E-05	1.4216E-04	1.4397E-06	7.6972E-01	5.8452E+01	6.3016E+02
1.5212E-03	4.1862E-04	1.1170E-04	1.1445E-04	2.3116E-04	2.0232E-06	7.6029E-01	4.6777E+01	5.1730E+02
1.9143E-03	5.6789E-04	1.2875E-04	1.2666E-04	3.4995E-04	2.7677E-06	7.5138E-01	3,7395E+01	4.1666E+02
2.3703E-03	7.4403E-04	1.5370E-04	1.3668E-04	4.8587E-04	3.5608E-06	7.3836E-01	3.2309E+01	3.4790E+02
2.7949E-03	9.3418E-04	1.7040E-04	1.4285E-04	6.3686E-04	4.4660E-06	7.2960E-01	2.7909E+01	2.8818E+02
3.2288E-03	1.0764E-03	1.8766E-04	1.4623E-04	7.4450E-04	5.0998E-06	7.2054E-01	2.7433E+01	2.5728E+02
3.6659E-03	1.2409E-03	2.0549E-04	1.4696E-04	8.6886E-04	5.9224E-06	7.1118E-01	2.6291E+01	2.2120E+02
4.1645E-03	1.4287E-03	2.2600E-04	1.4479E-04	1.0083E-03	6.9754E-06	7.0040E-01	2.5366E+01	1.8325E+02
4.7334E-03	1.6307E-03	2.4942E-04	1.3877E-04	1.1550E-03	8.3370E-06	6.8808E-01	2.4934E+01	1.4475E+02
5.5071E-03	1.8521E-03	2.8753E-04	1.2496E-04	1.3078E-03	1.0483E-05	6.6805E-01	2.5857E+01	1.0049E+02

4.8933E-04	1.1031E-04 ^d	6.2869E-05 ^e	6.0666E-05 ^h	6,9125E-06	1.1414E-07	7.9116E-01	5.6768E+02	4.9365E+03
8.2869E-04	1.8925E-04	7.7525E-05	8.3079E-05	5.7077E-05	6.8819E-07	7.8352E-01	1.1212E+02	1.1143E+03
1.2685E-03	3.6695E-04	1.0055E-04	1.0483E-04	1.9646E-04	1.8774E-06	7.7152E-01	4.5339E+01	5.1040E+02
1.7062E-03	4.3674E-04	1.2319E-04	1.2079E-04	2.3634E-04	1.9600E-06	7.5972E-01	5.2573E+01	5.6449E+02
2.14295-03	6.1060E-04	1.4351E-04	1.3237E-04	3.7574E-04	2.8434E-06	7.4910E-01	3.9600E+01	4.2410E+02
2.60382-03	7.7759E-04	1.6834E-04	1.4056E-04	5.0411E-04	3.5926E-06	7.3613E-01	3.4967E+01	3.5486E+02
3.0728E-03	9.5605E-04	1.8496E-04	1.4550E-04	6.4537E-04	4.4430E-06	7.2740E-01	3.1364E+01	2.9536E+02
3.5557E-03	1.1356E-03	2.0994E-04	1.4705E-04	7.8033E-04	5.3156E-06	7.1432E-01	2.9478E+01	2.4788E+02
4.0402E-03	1.2831E-03	2.2996E-04	1.4565E-04	8.9000E-04	6.1211E-06	7.0381E-01	2.9292E+01	2.1173E+02
4.5172E-03	1.4629E-03	2.4230E-04	1.4167E-04	1.0279E-03	7.2682E-06	6.9727E-01	2.7848E+01	1.7146E+02
5.0763E-03	1.6639E-03	2.7000E-04	1.3353E-04	1.1720E-03	8.7920E-06	6.8272E-01	2.7138E+01	1.3115E+02
5.6053E-03	1.8159E-03	2.8322E-04	1.2312E-04	1.2840E-03	1.0447E-05	6.7569E-01	2.7358E+01	9.9257E+01
PAA in 0.2	20007 m CPC	~	1					
4.1610E-04	8.8841E-05 ¹	4,2168E-05 ^g	2.2437E-051	3.0874E-05	1.3784E-06	8.2225E-01	5.8936E+01	9.5217E-01
8.3703E-04	1.4629E-04	7.2395E-05	3.3572E-05	5.4863E-05	1.6370E-06	8.1375E-01	6.8443E+01	8.6340E-01
1.2710E-03	2.0502E-04	9.1685E-05	4.3744E-05	9.0006E-05	2.0610E-06	8.0829E-01	6.3353E+01	7.8817E-01
1.7055E-03	2.7876E-04	1.0903E-04	5.3318E-05	1.4157E-04	2.6597E-06	8.0337E-01	5.3434E+01	7.2604E-01
2.2645E-03	3.8865E-04	1.2422E-04	6.5093E-05	2.2687E-04	3.4912E-06	7.9901E-01	4.3411E+01	6.6905E-01
2.9889E-03	5.4145E-04	1.5839E-04	7.9412E-05	3.3614E-04	4.2401E-06	7.8932E-01	3.8065E+01	6.0870E-01
3.5847E-03	6.8077E-04	1.8857E-04	9.0476E-05	4.3574E-04	4.8243E-06	7.8076E-01	3.4748E+01	5.5653E-01
4.1594E-03	8.2695E-04	1.9981E-04	1.0072E-04	5.5126E-04	5.4827E-06	7.7749E-01	3.1305E+01	5.1892E-01
4.9259E-03	1.0086E-03	2.2576E-04	1.1328E-04	6.8397E-04	6.0479E-06	7.7005E-01	2.9505E+01	4.8238E-01
5.6986E-03	1.1588E-03	2.4051E-04	1.2488E-04	7.9400E-04	6.3689E-06	7.6574E-01	2.9297E+01	4.4475E-01
6.7143E-03	1.4241E-03	2.8653E-04	1.3780E-04	9.7540E-04	7.0906E-06	7.5259E-01	2,7682E+01	4.0849E-01
7.8118E-03	1.6839E-03	3.3842E-04	1.4899E-04	1.1434E-03	7.6875E-06	7.3775E-01	2.7279E+01	3.7277E-01
PAA in 0.2	21568 m CPC	1	1					
4.1343E-04	7.0700E-05 ^K	4.7353E-05 ¹	2.2331E-05	9.4816E-06	4.2531E-07	8.2705E-01	1.8745E+02	9.5304E-01
8.1468E-04	9.6163E-05	7.0589E-05	3.3015E-05	8.0681E-06	2.4479E-07	8.2097E-01	4.4680E+02	8.6698E-01
1.2657E-03	1.5964E-04	9.4657E-05	4.3597E-05	4.4113E-05	1.0136E-06	8.1466E-01	1.2442E+02	7.9436E-01
1.7092E-03	2.3396E-04	1.0697E-04	5.3402E-05	1.0016E-04	1.8788E-06	8.1139E-01	7.2296E+01	7.3412E-01
2.2841E-03	3.7171E-04	1.2460E-04	6.5491E-05	2.1053E-04	3.2201E-06	8.0671E-01	4.4234E+01	6.8012E-01
3.0788E-03	5.4473E-04	1.5055E-04	8.1238E-05	3.4306E-04	4.2300E-06	7.9983E-01	3,5695E+01	6,2050E-01
3.6760E-03	7.0396E-04	1.7199E-04	9.2337E-05	4.6550E-04	5.0498E-06	7.9415E-01	3.0706E+01	5.6889E-01

				IABLE V	-6 (CONTINUE	:0)		
4.3097E-03	8.6194E-04	1.8844E-04	1.0347E-04	5.8672E-04	5-6799E-06	7.8975E-()1	2.8099E+01	5.3151E-01
5.1013E-03	1.0962E-03	2.0807E-04	1.1631E-04	7.6556E-04	6.5933E-06	7.8448E-()1	2.4821E+01	4.9499E-01
5.6936E-03	1.2443E-03	2.2528E-04	1.2504E-04	8.7214E-04	6.9866E-06	7.7988E-()1	2.4110E+01	4.6367E-01
6.8592E-03	1.5260E-03	2.6690E-04	1.3986E-04	1.0647E-03	7.6257E-06	7.6879E-01	2.3551E+01	4.2870E-01
7.9725E-03	1.8098E-03	2.9471E-04	1.5117E-04	1.2603E-03	8.3511E-06	7.6128E-01	2.2840E+01	3.8968E-01
8.1468E-04	1.3112E-04 ^m	7.0589E-05 ¹	3.3015E-05 ¹	4.1994E-05	1.2742E-06	8.2097E-01	8,2011E+01	9.1732E-01
1.2657E-03	2.0521E-04	9.4657E-05	4.3597E-05	8.8139E-05	2.0251E-06	8,1466E-01	5.9852E+01	8.0134E-01
1.7092E-03	2.8441E-04	1.0697E-04	5.3402E-05	1.4833E-04	2.7823E-06	8.1139E-01	4.7199E+01	7.4113E-01
2.2841E-03	3.7280E-04	1.2460E-04	6.5491E-05	2.1155E-04	3.2356E-06	8.0671E-01	4.3996E+01	6.8358E-01
3.0788E-03	5.3663E-04	1.5055E-04	8.1238E-05	3.3569E-04	4.1392E-06	7.9983E-01	3.6599E+01	6.2019E-01
3.6760E-03	7.1223E-04	1.7199E-04	9.2337E-05	4.7280E-04	5.1291E-06	7.9415E-01	3.0141E+01	5.6885E-01
4.3097E-03	8.7078E-04	1.8844E-04	1.0347E-04	5.9431E-04	5.7533E-06	7.8975E-01	2.7662E+01	5.3215E-01
5.1013E-03	1.1002E-03	2.0807E-04	1.1631E-04	7.6885E-04	6.6217E-06	7.8448E-01	2.4687E+01	4.9542E-01
5.6936E-03	1.2731E-03	2.2528E-04	1.2504E-04	8.9530E-04	7.1722E-06	7.7988E-01	2.3308E+01	4.6456E-01
6.8592E-03	1.5315E-03	2.6690E-04	1.3986E-04	1.0690E-03	7.6564E-06	7.6879E-01	2.3427E+01	4.2959E-01
7.9725E-03	1.7547E-03	2.9471E-04	1.5117E-04	1.2191E-03	8.0776E-06	7.6128E-01	2.3878E+01	3.8880E-01
DAA in)	44574 m CD(n						
PAA III JA	44J/4 III CP(i					
1.4634E-03	1.3223E-04"	1.1220E-04°	3.3874E-05 J	1.1572E-05	3.4221E-07	8.4715E-01	2.7752E+02	9.2297E-01
1.8133E-03	1.7558E-04	1.1894E-04	3.9431E-05	4.4886E-05	1.1403E-06	8,4625E-01	8.7232E+01	8.3229E-01
2.7529E-03	2.51718-04	1.3253E-04	5.4169E-05	9.8652E-05	1.8243E-06	8.4439E-01	5.9696E+01	7.8449E-01
3.7558E-03	3.9634E-04	1.3932E-04	6.9803E-05	2.2086E-04	3.1694E-06	8.4338E-01	3.5466E+01	7.2174E-01
4.7893E-03	5.0993E-04	1.7089E-04	8,5625E-05	2.9540E-04	3.4558E-06	8,3923E-01	3.3717E+01	6.6643E-01
6.1916E-03	5.5469E-04	1.2863E-04	1.0714E-04	3.5024E-04	3.2745E-06	8.4434E-01	3.7030E+01	6.0831E-01
7.7345E-03	7.6141E-04	1.4935E-04	1.2945E-04	5.0811E-04	3.9317E-06	8.4148E-01	3.1510E+01	5.5065E-01
9.1551E-03	1.0166E-03	1.7762E-04	1.4869E-04	6.9895E-04	4.7087E-06	8.3767E-01	2.6687E+01	5.0497E-01
1.0404E-02	1.2353E-03	2.1391E-04	1.6432E-04	8.5025E-04	5.1831E-06	8.3286E-01	2.4705E+01	4.7048E-01
	n	0	i					
8.8848E-04	1.0267E-04 P	8.8770E-05	2.4465E-05 J	7.0607E-06	2.8910E-07	8.5018E-01	2.7473E+02	9.5028E-01
1.4634E-03	1.2210E-04	1.1220E-04	3.3874E-05	1.6800E-06	4.9679E-08	8.4715E-01	1.9251E+03	8.7271E-01
1.8133E-03	1.5551E-04	1.1894E-04	3.9431E-05	2.5373E-05	6.4457E-07	8,4625E-01	1.5611E+02	8.3085E-01
2.7529E-03	2.6645E-04	1.3253E-04	5.4169E-05	1.1280E-04	2.0859E-06	8.4439E-01	5.1905E+01	7.8414E-01
3.7558E-03	3.7292E-04	1.3932E-04	6.9803E-05	1.9889E-04	2.8542E-06	8,4338E-01	3.9663E+01	7.2156E-01
4.7893E-03	4.3687E-04	1.7089E-04	8.5625E-05	2.2765E-04	2.6632E-06	8.3923E-01	4.4528E+01	6.6378E-01

				TABLE	V-6 (CONTINUI	ED)		
6.1916E-03	5.3395E-04	1,2863E-04	1.0714E-04	3.3135E-04	3.0979E-06	8.4434E-01	3.9295E+01	6.0595E-01
7.7345E-03	7.1745E-04	1.4935E-04	1.2945E-04	4.6941E-04	3.6323E-06	8.4148E-01	3.4346E+01	5.4943E-01
1.0404E-02	1.3090E-03	2.1391E-04	1.6432E-04	9.0977E-04	5.5459E-06	8.3286E-01	2.2867E+01	7.2870E-01
1.2847E-02	1.8093E-03	2,7027E-04	1.9131E-04	1.2529E-03	6.5599E-06	8.2528E-01	2.0071E+01	4.3338E-01
1.5585E-02	2.2738E-03	3,3310E-04	2.1492E-04	1.5467E-03	7.2089E-06	8.1678E-01	1.9570E+01	3.8691E-01
1.4157E-03	1.6441E-04 ^d	1,0982E-04 ^q	3.3118E-05 ³	4.5079E-05	1,3635E-06	8,4777E-01	6,7153E+01	9.2683E-01
1.7724E-03	1.9339E-04	1.1333E-04	3.8805E-05	6.6588E-05	1.7189E-06	8.4727E-01	5.6663E+01	8.3888E-01
2.6926E-03	3.0127E-04	1,3125E-04	5.3238E-05	1.4751E-04	2.7754E-06	8.4488E-01	3.8203E+01	7.9129E-01
3.5982E-03	4.1606E-04	1.3112E-04	6.7398E-05	2.4627E-04	3.6602E-06	8.4475E-01	3.0106E+01	7.3152E-01
4.5415E-03	4.5845E-04	1.4566E-04	8.1963E-05	2.6667E-04	3.2591E-06	8.4277E-01	3.5543E+01	6.7785E-01
5.9128E-03	5.1193E-04	1.4920E-04	1.0284E-04	3.0054E-04	2.9273E-06	8.421!E-01	4.1508E+01	6.1882E-01
7.4637E-03	6.3771E-04	1.4904E-04	1.2562E-04	4.0084E-04	3.1963E-06	8.4188E-01	3.9176E+01	5.5808E-01
8.9423E-03	9.3027E-04	2.3304E-04	1.4538E-04	5.9503E-04	4.1000E-06	8.3100E-01	3.1077E+01	5.0895E-01
1.0088E-02	1.1938E-03	2,3295E-04	1.6022E-04	8.0793E-04	5.0512E-06	8.3082E-01	2.5280E+01	4.7540E-01
1.2645E-02	1.6996E-03	2.7286E-04	1.8922E-04	1.1699E-03	6.1930E-06	8.2531E-01	2.1366E+01	4.3696E-01
1.5249E-02	2.1741E-03	3.3512E-04	2.1234E-04	1.4761E-03	6.9632E-06	8.1691E-01	2.0179E+01	3.8997E-01

Calibration curves for data sets:

a
$$\Delta\mu\nu$$
olts = 359360.80(1-a_w) + 3116760.51(1-a_w)² RHSD = 8.7 $\mu\nu$ olts
b mvolts = 17.5214041 - 58.7579484(log a_{C1}-) RHSD = 0.78 mvolts
c $\Delta\mu\nu$ olts = 358693.39(1-a_w) + 3110972(1-a_w)² RHSD = 8.7 $\mu\nu$ olts
d $\Delta\mu\nu$ olts = 366073.68(1-a_w) + 978576.87(1-a_w)² RHSD = 13.0 $\mu\nu$ olts
e mvolts = 16.9124076 - 59.5368124(log a_{C1}-) RHSD = 0.45 mvolts
f $\Delta\mu\nu$ olts = 370039.68(1-a_w) + 3209379.1(1-a_w)² RHSD = 8.7 $\mu\nu$ olts
g mvolts = 16.4707438 - 59.4024639(log a_{C1}-) RHSD = 0.54 mvolts
h a_{H} + 0.0146058245/m_{PAA} + 0.0832779643m_{PAA} - 0.14750008m_{PAA} , ² RHSD = 7.1x10⁻⁵ in a_{H} +
i a_{H} + 0.0100060221/m_{PAA} -9.74463988x10⁻⁵ m_{PAA} + 0.0690801413m_{PAA} - 0.0625136881m²_{PAA} RHSD = 1.8x10⁻⁴
j a_{H} + 7.33540374x10⁻⁵/m_{PAA} - 7.59132577x10⁻⁵ m_{PAA} + 0.0451029944m³/₂ - 0.0287976306m²_{PAA} RHSD = 4.0x10⁻⁴
K $\Delta\mu\nu\nu$ olts = 364700.24(1-a_w) + 3151492.5(1-a_w)² RHSD = 8.7 $\mu\nu$ olts
m $\mu\nu\nu$ olts = 352019.08(1-a_w) + 3063085.3(1-a_w)² RHSD = 8.7 $\mu\nu$ olts
o mvolts = -2.16795842 - 75.9660811(log a_{C1}-) RHSD = 1.15 mvolts
m $\Delta\mu\nu\nu$ olts = 349349.36(1-a_w) + 3029930.6(1-a_w)² RHSD = 8.7 $\mu\nu$ olts
q mvolts = -2.16795842 - 75.9660811(log a_{C1}-) RHSD = 8.7 $\mu\nu$ olts
q mvolts = 325019.08(1-a_w) + 3029930.6(1-a_w)² RHSD = 8.7 $\mu\nu$ olts
q mvolts = -2.16795842 - 75.9660811(log a_{C1}-) RHSD = 1.11 mvolts
p $\Delta\mu\nu\nu$ olts = 349349.36(1-a_w) + 3029930.6(1-a_w)² RHSD = 8.7 $\mu\nu$ olts
q mvolts = -2.16795842 - 75.9660811(log a_{C1}-) RHSD = 1.11 mvolts
q mvolts = 2.56274807 - 71.8561263(log a_{C1}-) RHSD = 1.77 mvolts

× _{PAA}	×CPC	x _P	۳ _P	Υ _{CPC}
PAA in O.	10788 m CPC	;		
3.75395-04	1.9389E-03	1.5210E-01	3.9837E-02	7.4471E-01
7.5482E-04	1.9382E-03	2.5639E-01	7.9341E-02	6.2819E-01
1.1392E-03	1.9374E-03	3.3912E-01	1.0213E-01	5.6473E-01
1.5212E-03	1.9367E-03	3.9835E-01	1.4389E-01	4.6314E-01
1.9143E-03	1.9359E-03	4.4379E-01	1.9898E-01	3.6662E-01
2.3703E-03	1.9350E-03	4.8618E-01	2.6205E-01	2.8904E-01
2.7949E-03	1.9342E-03	5.2183E-01	3.0621E-01	2.4681E-01
3.2288E-03	1.9334E-03	5.5505E-01	3.4025E-01	2.1827E-01
3.6659E-03	1.9325E-03	5.8555E-01	3.6578E-01	1.9829E-01
4.16455-03	1.9316E-03	6.1277E-01	4.0819E-01	1.6834E-01
4.7334E-03	1.9304E-03	6.4073E-01	4.4817E-01	1.4390E-01
5.5071E-03	1.9289E-03	6.7312E-01	4-9791E-01	1.1766E-01
3.7539E-04	1.9389E-03	1.5022E-01	4.8261E-02	9.1995E-01
7.5482E-04	1.9382E-03	2.5703E-01	7.7046E-02	8.1799E-01
1.1392E-03	1.9374E-03	3.3672E-01	1.1049E-01	7.0364E-01
1.5212E-03	1.9367E-03	3.9585E-01	1.5282E-01	5.8431E-01
1.9143E-03	1.9359E-03	4.4154E-01	2.0741E-01	4.6971E-01
2.3703E-03	1.9350E-03	4.8633E-01	2.6144E-01	3.8477E-01
2.7949E-03	1.9342E-03	5.1810E-01	3.2168E-01	3.1238E-01
3.2288E-03	1.9334E-03	5.5218E-01	3.5283E-01	2.8086E-01
3.6659E-03	1.9325E-03	5.7988E-01	3.9210E-01	2.4478E-01
4.1645E-03	1.9316E-03	6.0747E-01	4.3435E-01	2.1081E-01
4.7334E-03	1.9304E-03	6.3556E-01	4.7557E-01	1.8167E-01
5.5071E-03	1.9289E-03	6.7105E-01	5.0999E-01	1.5927E-01
4.8933E-04	1.9387E-03	1.9860E-01	9.1087E-03	1.1205E+00
8.2869E-04	1.9380E-03	2.8291E-01	5.2797E-02	7.1618E-01
1.2685E-03	1.9372E-03	3.5236E-01	1.4591E-01	4.6298E-01
1.7062E-03	1.9363E-03	4.2794E-01	1.4453E-01	4.6581E-01
2.1429E-03	1.9355E-03	4.7203E-01	2.0831E-01	3.4654E-01
2.6038E-03	1.9346E-03	5.1384E-01	2.5674E-01	2.8302E-01
3.0728E-03	1.9337E-03	5.4836E-01	3.0799E-01	2.3043E-01
3.5557E-03	1.9327E-03	5.7984E-01	3.5218E-01	1.9377E-01
4.0402E-03	1.9318E-03	6.0954E-01	3.8210E-01	1.7194E-01
4.5172E-03	1.9309E-03	6.3206E-01	4.2559E-01	1.4415E-01
5.0763E-03	1.9298E-03	6.5644E-01	4.6721E-01	1.2175E-01
5.6053E-03	1.9288E-03	6.7825E-01	4.9543E-01	1.0824E-01
PAA in 0.	20007 m CPC			
4-1610E-04	3.5898F-03	9,5651F-02	8-4468E-02	1-0021E+00
8-37035-04	3.58835-03	1.7755E-01	8-0861F-02	1.00905+00
1.27105-03	3.5867F-03	2.4610F-01	9.5708#-02	9.6445F-01
1.70555-03	3-5851F-03	3.0182F=01	1.22755-01	8.7844F-01
2.2645E-03	3-58315-03	3-6008F-01	1.6488F-01	7.5993F-01
2.98895-03	3.58055-03	4-2252F-01	2-0819F-01	6-5456E-01
L. 70071-0J	20 20 2C-02	HELLIC'UI	2000192 01	

3.5847E-03	3.5784E-03	4.6443E-01	2.4553E-01	5.7411E-01
4.1594E-03	3.5763E-03	4.9774E-01	2.8983E-01	4.9244E-01
4.9259E-03	3.5736E-03	5.3750E-01	3.3300E-01	4.2437E-01
5.6986E-03	3.5708E-03	5.7301E-01	3.6262E-01	3.8157E-01
6.7143E-03	3.5C72E-03	6.1001E-01	4.1844E-01	3.1024E-01
7.8118E-03	3.5632E-03	6.4445E-01	4.6431E-01	2.6046E-01
PAA in 0.3	21568 m CPC	:		
4.1343E-04	3.8689E-03	9.3915E-02	2.6420E-02	1.0202E+00
8.1468E-04	3.8673E-03	1.7213E-01	1.2266E-02	1.1414E+00
1.2657E-03	3.8656E-03	2.3916E-01	4.8269E-02	8.3888E-01
1.7092E-03	3.8639E-03	2.9260E-01	8.9584E-02	6.7518E-01
2.2841E-03	3.8616E-03	3.4717E-01	1.5869E-01	5.1964E-01
3.0788E-03	3.8586E-03	4.1184E-01	2.1799E-01	4.2863E-01
3.5760E-03	3.8563E-03	4.5038E-01	2.7047E-01	3.6421E-01
4.3097E-03	3.8538E-03	4.8660E-01	3.1554E-01	3.1804E-01
5.1013E-03	3.8507E-03	5.2341E-01	3.8276E-01	2.6132E-01
5.6936E-03	3.8484E-03	5.4925E-01	4.1554E-01	2.3764E-01
6.8592E-03	3.8439E-03	5.9335E-01	4.6958E-01	2.0195E-01
7.9725E-03	3.8396E-03	6.2729E-01	5.2578E-01	1.6921E-01
8.1468E-04	3.8673E-03	1.6537E-01	6.6456E-02	8.3504E-01
1.2657E-03	3.8656E-03	2.3196E-01	9.9438E-02	7.5665E-01
1.7092E-03	3.8639E-03	2.8579E-01	1.3582E-01	6.7916E-01
2.28415-03	3.8616E-03	3.4705E-01	1.5952E-01	6.3055E-01
3.0788E-03	3.8586E-03	4.1258E-01	2.1293E-01	5.2898E-01
3.6760E-03	3.8563E-03	4.4972E-01	2.7512E-01	4.3606E-01
4.3097E-03	3.8538E-03	4.8598E-01	3.2002E-01	3.8188E-01
5.1013E-03	3.8507E-03	5.2317E-01	3.8458E-01	3.1687E-01
5.6936E-03	3.8484E-03	5.4770E-01	4.2778E-01	2.8031E-01
6.8592E-03	3.8439E-03	5.9311E-01	4.7166E-01	2.4625E-01
7.9725E-03	3.8396E-03	6.2930E-01	5.0694E-01	2.1986E-01
PAA in 0.4	44574 m CPC			
1.4634E-03	7.9544E-03	1.5406E-01	1.9657E-02	8.4627E-01
1.8133E-03	7.9516E-03	1.8136E-01	6.4768E-02	6.8232E-01
2.7529E-03	7.9442E-03	2.4965E-01	1.0341E-01	6.0141E-01
3.7558E-03	7.9362E-03	3.0687E-01	1.8834E-01	4.8048E-01
4.7893E-03	7.9279E-03	3.6028E-01	2.1456E-01	4.5018E-01
6.1916E-03	7.9168E-03	4.2310E-01	2.1663E-01	4.4742E-01
7.73455-03	7.9045E-03	4.7560E-01	2.7958E-01	3.6374E-01
9.1551E-03	7.8932E-03	5.1446E-01	3.5554E-01	2.8771E-01
1.0404E-02	7.88325-03	5.4459E-01	4.0857E-01	2.4609E-01
8.8848E-04	7.9590E-03	9.9442E-02	1.8581E-02	9.0064E-01
1.4634E-03	7.9544E-03	1.5514E-01	2.8339E-03	1.1161E+00
1.8133E-03	7.9516E-03	1.8316E-01	3.6252E-02	7.8799E-01
2.7529E-03	7.9442E-03	2.4857E-01	1.1876E-01	5.8783E-01
3.7558E-03	7.9362E-03	3.0832E-01	1.6882E-01	5.1393E-01
4.7893E-03	7.9279E-03	3.6412E-01	1.6361E-01	5.2216E-01
6.1916E-03	7.91682-03	4.2399E-01	2.0451E-01	4.5189E-01
7.7345E-03	7.90458-03	4.7715E-01	2.5745E-01	3.74475-01

TABLE V-6 (CONTINUED)							
1.0404E-02	7.8832E-03	5.4261E-01	4.3877E-01	1.7784E-01			
1.2847E-02	7.8637E-03	5.9064E-01	5.5510E-01	1.3095E-01			
1.5585E-02	7.8419E-03	6.3554E-01	6.3688E-01	1.0536E-01			
1.4157E-03	7.9548E-03	1.4634E-01	8.0610E-02	9.5908E-01			
1.7724E-03	7.9520E-03	1.7589E-01	9.9072E-02	9.2196E-01			
2.6926E-03	7,9446E-03	2.4154E-01	1.5981E-01	8.1463E-01			
3.5982E-03	7.9374E-03	2.9542E-01	2.1815E-01	7.2737E-01			
4.5415E-03	7.9299E-03	3.4888E-01	2.0003E-01	7.5795E-01			
5.9128E-03	7.9190E-03	4.1349E-01	1.9020E-01	7.8183E-01			
7.4637E-03	7.90665-03	4.7034E-01	2.2302E-01	6.8944E-01			
8.9423E-03	7.8948E-03	5.1175E-01	3.0428E-01	5.1210E-01			
1.00885-02	7.8857E-03	5.3745E-01	3.93398-01	3.8630E-01			
1.2645E-02	7.8654E-03	5.8864E-01	5.2009E-01	2.7020E-01			
1.5249E-02	7.8446E-03	6.3143E-01	6.1176E-01	2.0972E-01			

•









where X_p is the mole fraction of organic in the micelle, and c_{org} is the concentration of organic in the aqueous region. The activity coefficient of PAA is then

$$\gamma = 1/(c_{\text{org }S}^{\circ}K'),$$

where c_{org}° is the concentration of free organic in the surfactant solution saturated with organic. So if K_{S} ' is constant, γ will be constant and vice-versa. This K_{S} ' and, therefore γ are not dependent on the micellar composition. The solubilization "constants" reported in this work are defined,

[1]
$$K_{S} = [bound organic]/([free organic][surfactant]_{mic})$$

= $X_{p}/[c_{org}^{\circ}(1-X_{p})]$, and

$$[2] \gamma = 1/[c_{org}^{\circ}(1-X_{p})K_{s}].$$

Here γ depends not only on K_S but also on the fraction of organic in the micelle. And K_S is inversely proportional to the composition in the micelle, and the activity coefficient. $K_S'/K_S = 1/(1-X_p)$, so in the limit as X_p approaches 0, $K_S = K_S'$.

The apparent solubilization constants for the solubilized acid anion are shown in Figure V-11.a. One can see a difference in the

dependence of the solubilization constant on the mole fraction of acid in the micelle for different surfactant concentrations. One possible explanation for this difference is that, in the absence of PAA, the CPC aggregate shape becomes more elongated. This will increase headgroup repulsion in the micelle, but this effect will be offset in part by the increased counterion binding that must result. It is possible that the specific interaction of phenylacetate with the more-spherical micelle is much stronger than that with the less-spherical micelle. As the mole fraction of solubilized organic increases, the shape of the micelie changes enough to significantly decrease the affinity of the acid anion with the surface region. At a certain point, the micelle attains a shape or asphericity such that the fractional change in the shape no longer has a strong influence on the affinity of phenylacetate for the micellar surface. In the low mole fraction range, the large error in solubilization constants is due in large part to the very small concentration of anion present, and therefore the large percent error in the anion concentration.

Apparent solubilization constants for the acid are shown in Figure V-11.b. The data are fairly reproducible, and are dependent on the mole fraction of solubilized organic. In the low region of mole fraction of solubilized organic, the large error is due likely to the large error in the anion solubilization constants. A rather peculiar sudden change in measured quantity appears at approximately 0.3 mole fraction of solubilized acid in 0.4 m CPC. This same peculiarity was seen in both the osmometry data and the Cl⁻ activity data. However, at higher mole fractions of solubilized organic, the data agree well

with those in 0.1 m and 0.2 m CPC. In view of the peculiar behavior seen in 0.4 m CPC, the data are shown in Figure V-11.c for only PAA solubilized in 0.1 m and 0.2 m CPC. The dependence only on micelle composition is evident. I think it is worthwhile to emphasize that these data are the results of combining 4 measured quantities: total concentrations of solutes, $1-a_w$, Cl^- activity, and H^+ activity. In view of this, the data presented are relatively fairly reproducible.

Activity coefficients for the micellar components plotted as a function of composition are shown in Figure V-12. Again the activity coefficient changes considerably with variation in the mole fraction of solubilized organic and is not dependent on the total surfactant present in solution. This is evidenced by the superimposed curves of different total surfactant concentrations. The activity coefficient of CPC starts at 1 in the limit as X_p approaches 0, as expected for a pure liquid. For the organic, the activity coefficient vs X_p curve has been shown to turn over and approach nearer to 1 in the limit as X_p approaches 1 for n-pentanol and n-butanol (25). Using super-cooled liquid phenylacetic acid as the standard state, it is resonable to assume this curve will also approach 1 in the limit.

Data from SED measurements of the solubilization of PAA in CPC are shown in Table V-7. The results are plotted in Figure V-13. Since the SED data are for solutions in the presence of 0.1 M HCl, ionization of the acid is assumed negligible and the K_S pertains only to the neutral acid interacting with the micelle. Both the magnitude and trend of these numbers are nearly the same using entirely different techniques



TABLE V-7

EXPERIMENTAL AND CALCULATED DATA USING RESULTS FROM SEMI-EQUILIBRIUM DIALYSIS OF 2-PHENYLACETIC ACID SOLUBILIZED IN CETYLPYRIDINIUM CHLORIDE IN WATER AT 25°C

PAA in O.	1 m CPC							
S ^{ret} tot	p ^{ret} tot	S ^{per} tot	p ^{per} tot	P ^{per} calc	xper	x ^{ret}	Кs	cret,per cp
9.9924E-02	1.7688E-02	7.7484E-05	2.3193E-03	2.6706E-03	1.1207E-01	1.3045E-01	6.6607E+01	2.6633E-03
9.9907E-02	3.5092E-02	9.4476E-05	4.9517E-03	5.3843E-03	2.1281E-01	2.2851E-01	6.1263E+01	5.3634E-03
9.9889E-02	5.2132E-02	1.1186E-04	7.8895E-03	8.7902E-03	2.7963E-01	3.0100E-01	5.6503E+01	8.7525E-03
9.9814E-02	6.7306E-02	1.8692E-04	1.2724E-02	1.2438E-02	3.4719E-01	3.5205E-01	4.3381E+01	1.2345E-02
9.9595E-02	8.2136E-02	4.0644E-04	1.8019E-02	1.6537E-02	3.9511E-01	3.9340E-01	3.6389E+01	1.6278E-02
9,9896E-02	1.7439E-02	1.0482E-04	2.5683E-03	2.6418E-03	1.2387E-01	1.2886E-01	5.8298E+01	2.6297E-03
9.9884E-02	3.4640E-02	1.1749E-04	5.4043E-03	5.3142E-03	2.2518E-01	2.2634E-01	5.4513E+01	5.2849E-03
9.9878E-02	5.1186E-02	1.2314E-04	8.8363E-03	8.5922E-03	2.9577E-01	2.9747E-01	4.8291E+01	8.5464E-03
9.9850E-02	6.7510E-02	1.5147E-04	1.2519E-02	1.2465E-02	3,4511E-01	3.5261E-01	4.4326E+01	1.2391E-02
9.9826E-02	8.3608E-02	1.7513E-04	1.6546E-02	1.6743E-02	3.8430E-01	3.9671E-01	4.0943E+01	1.6641E-02
9.9903E-02	1.7498E-02	9.8314E-05	2.5090E-03	2.6486E-03	1.2110E-01	1.2924E-01	6.0130E+0;	2.6377E-03
9.9897E-02	1.7219E-02	1.0373E-04	2.7887E-03	2.6125E-03	1.3404E-01	1.2741E-01	5.2068E+01	2.5995E-03
9.9876E-02	3.4072E-02	1.2530E-04	5.9725E-03	5.2204E-03	2.3951E-01	2.2356E-01	4.7402E+01	5.1860E-03
9.9889E-02	3.4737E-02	1.1234E-04	5.3074E-03	5.3290E-03	2.2262E-01	2.2680E-01	5.5862E+01	5.3017E-03
9.9885E-02	5.1628E-02	1.1565E-04	8.3943E-03	8.6832E-03	2.8848E-01	2.9912E-01	5.1886E+01	8.6422E-03
9.9886E-02	5.1879E-02	1.1538E-04	8.1426E-03	8.7373E-03	2.8413E-01	3.0006E-01	5.4123E+01	8.6973E-03
9.9864E-02	6.8264E-02	1.3719E-04	1.1765E-02	1,2643E-02	3.3641E-01	3.5485E-01	4.8439E+01	1.2579E-02
9.9853E-02	8.4353E-02	1.4824E-04	1.5802E-02	1.6924E-02	3.7797E-01	3.9851E-01	4.3768E+01	1.6840E-02
9,9823E-02	8.2925E-02	1.7837E-04	1.7229E-02	1.6561E-02	3.8998E-01	3.9501E-01	3.8510E+01	1.6454E-02
PAA in O.	2 m CPC							
1.9989E-01	1.8615E-02	1.1438E-04	1.4510E-03	1.6439E-03	6.7488E-02	7.8233E-02	5.9535E+01	1.6371E-03
1.9987E-01	3.7181E-02	1.3180E-04	2.9516E-03	3.0188E-03	1.4108E-01	1.4588E-01	5.8436E+01	3.0003E-03
1.9986E-01	5.5543E-02	1.4225E-04	4.6549E-03	4.5415E-03	2.0360E-01	2.0310E-01	5.5110E+01	4.5095E-03
1.9985E-01	7.3697E-02	1.4876E-04	6.4503E-03	6.3207E-03	2.5041E-01	2.5172E-01	5.2565E+01	6.2763E-03

:
		TABLE V-7 (CONTINUED)							
1.9984E-01	9.1806E-02	1.6270E-04	8.3187E-03	8.3969E-03	2.8686E-01	2.9379E-01	5.0636E+01	8.3373E-03	
1.9989E-01	1.8745E-02	1.1288E-04	1.3214E-03	1.6527E-03	6.0797E-02	7.8742E-02	6.6395E+01	1.6467E-03	
1.9986E-01	3.7191E-02	1.3840E-04	2.9408E-03	3.0207E-03	1.4056E-01	1.4592E-01	5.8716E+01	3.0012E-03	
1.9986E-01	5.5637E-02	1.4186E-04	4.5611E-03	4.5491E-03	2.0070E-01	2.0337E-01	5.6459E+01	4.5179E-03	
1.9985E-01	7.3763E-02	1.5444E-04	6.3835E-03	6.3295E-03	2.4887E-01	2.5190E-01	5.3243E+01	6.2836E-03	
1.9984E-01	9.1818E-02	1.6317E-04	8.3065E-03	8.3986E-03	2.8665E-01	2.9382E-01	5.0727E+01	8.3388E-03	
PAA in O.	4 m CPC								
4.0005E-01	1.9174E-02	2.0884E-04	8.6292E-04	9.7847E-04	3.7601E-02	4.3510E-02	5.3601E+01	9.7114E-04	
4.0003E-01	3.8440E-02	2.2879E-04	1.6628E-03	1.7634E-03	7.7985E-02	8.3991E-02	5.5963E+01	1.7458E-03	
3.9988E-01	5.7557E-02	3.8140E-04	2.5238E-03	2.5169E-03	1.1997E-01	1.2103E-01	5.5680E+01	2.4675E-03	
3.9999E-01	7.6648E-02	2.7006E-04	3.3811E-03	3.2587E-03	1.5801E-01	1.5503E-01	5.4959E+01	3.2116E-03	
3.9992E-01	9.5437E-02	3.3414E-04	4.5704E-03	4.0839E-03	1.99498-01	1.8595E-01	5.0549E+01	4.0050E-03	
4.0003E-01	1.4343E-01	2.3327E-04	6.6741E-03	6.4849E-03	2.5470E-01	2.5486E-01	5.1828E+01	6.4105E-03	
4.0005E-01	1.9199E-02	2.0887E-04	8.3723E-04	9.7934E-04	3.6366E-02	4.3567E-02	5.5419E+01	9.7226E-04	
4.0002E-01	3.8142E-02	2.3418E-04	1.9607E-03	1.7564E-03	9.3229E-02	8.3391E-02	4.6616E+01	1.7344E-03	
3.99998-01	5.7518E-02	2.6536E-04	2.5626E-03	2.4998E-03	1.2254E-01	1.2093E-01	5.4363E+01	2.4655E-03	
4.0003E-01	7.6780E-02	2.3220E-04	3.2495E-03	3.25516-03	1.5297E-01	1.5524E-01	5.7289E+01	3.2166E-03	
4.0002E-01	9.5670E-02	2.3658E-04	4.3373E-03	4.0666E-03	1.9282E-01	1.8629E-01	5.3284E+01	4.0143E-03	
4.0001E-01	1.4322E-01	2.4442E-04	6.8760E-03	6.4793E-03	2.5891E-01	2.5460E-01	5.0170E+01	6.3994E-03	

data from reference 48

Values of least-squares parameters from equations IV.iv.5 and 6 $A = -2.1 \pm .2$ $B = -8 \pm 2$ $C = 6 \pm 3$ RMSD = 4.55×10^{-4} in units of concentration of P^{per}_{tot}



(results from SED, and results from osmometry and ion-selective electrodes) and numerical methods to calculate these parameters.

CHAPTER VI

DISCUSSION

i. SURFACTANTS IN WATER

For a particular surfactant at a given temperature, a rather large range of values can be found in the literature for a single parameter depending on the technique used. It is believed that a combined fit of all the data for aqueous surfactant solutions gives results more likely to be correct than if data from a single technique are modelled.

Table VI-1 shows the least-squares parameters from the model fitting each type of data individually for SOS in water. Surface tension measurements give a value of K which best predicts the literature value of the cmc for SOS. This technique by itself does not yield a reasonable value for the aggregation size. The fraction of counterions bound agrees with the literature using pNa (59) data but the error is rather large, 33 to 83%. The error in the value of the ion-size parameter determined from surface tension results is quite ridiculous. The additional parameters which arise from including the surface tension in the model are presumably best determined by surface

	Osmometry	Cl Activity	Surface Tension	Combined Fit	Parameter	
	2.50±.01 .160 m	2.52±.02 .157 m	2.76±.05 .131 m	2.507±.007 .1591 m	K cmc	
	.44±.03	.44±.01	.6±.2	.43±.01	β	
Fits of dat	21±6	27±9	40±60	23±3	n	
holding b constant	18	18	18 (2.70±.09)×10 ⁻¹⁰ 61Ų	18 (2.25±.09)x10 ⁻¹⁰ 74Ų	b 18 Γ (2.25±.09)x10 [°] area 74 ^R ²	
			(1.7±.2)×10 ⁻⁴ .013 m	(9±2)x10 ⁻⁵ .009 m	c ½ sat'n	
	1.231	1.145	0.582	1.190	RMSD	
_	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	2.47±.06 .164 m	2.8±.4 .13 m	2.51±.01 .159 m	K cmc	
		.43±.02	.6±.5	.43±.01	β	
	No	30±10	40±60	23±3	n	
~	convergence;	15±3	7±90	18±3	b	
~ Fits of data allowing b	v approaches		(3±1)×10 ⁻¹⁰ 55Ų	(2.25±.09)×10 ⁻¹⁰ 74 ²	ľ m area	
to vary			(1.6±.7)x10 ⁻⁴ .013 m	(9±2)x10 ⁻⁵ .009 m	c ½ sat'n	
		1 1/0	0 (01	4 404	DNOD	

LEAST-SQUARES PARAMETERS FROM THE MASS-ACTION MODEL FOR INDIVIDUAL FITS OF SODIUM OCTYLSULFATE

TABLE VI-1

tension data. However, these parameters are influenced by the activity data in the combined fit, because $a_2 = (\gamma_+ m_+)(\gamma_- m_-)$ appears in the equation describing the surface tension results. (See equation IV.i.[10]) γ_+ and γ_- are calculated using the same eqns as for the individual ion activity measurements. Additionally, the values of the two parameters, Γ_m and c in the individual surface tension fit, are likely to be less reliable because of the large error in β and n in calculating I, γ_+ , and γ_- .

The analysis of data from the ion-selective electrodes yields the best estimate of the fraction of counterions bound. The aggregation size is reasonable but the error is still large, 33 to 39%. Of the techniques used in the present study, only the results from the ion-selective electrodes are able reasonably to predict the ion-size parameter.

The vapor pressure osmometer provides data which best predict an aggregation size, although this is better illustrated by the CPC in water system (vide infra). However, for ionic surfactants, it is an advantage to have the value of the counterion binding fraction precisely determined using the ion activity data before the osmometer results are employed in calculating the aggregation size. For SOS the ratio of the concentration of free Na⁺ to the sum of the concentrations of the monomer and micelle is not so large. In other words the monomer is contributing a sizeable portion of the osmotic effect, as is the counterion. So it is not so difficult, using only osmometry results, to converge on a reasonable aggregation size for this system.

 β is determined well from the osmometry data, too. Again this is because the free Na⁺ contributes the largest single portion to the osmotic effect. However, for SOS b cannot be determined from osmometry data alone.

Data from the various techniques used to study CPC in water were also fit individually. Results are shown in Table VI-2. Similar patterns to those for SOS are inferred from these fits. The value of K determined from surface tension data can infer a value for the cmc which agrees very well with the literature value. The value of β is a little low compared to literature values of this parameter, but the parameter determined from surface tension data has a small estimated error. The calculated value of the aggregation number has a large probable error.

Chloride electrode data determine the closest-approach parameter, b, rather well. The calculated results shown for b=3.1 indicate that the fit of the data is very sensitive to the value of b chosen. The RMSD is four times higher for the fit where b is held constant at 3.1 than the RMSD for the fit where b is allowed to float. The aggregation number chosen does not affect the fit of the data, and this is reflected in the huge errors in both Cl⁻ data fits.

The osmometer results may be used to determine reasonable values of the aggregation number and β , with relatively small probable errors, once a value of b is determined and held constant. Errors in K are also quite acceptable. The results from this technique should be able to determine a reasonable value for β since the Cl⁻ ions contribute a huge portion of the osmotic effect for CPC. Considering the very small

LEAST-SQUARES	PARAMETERS FROM	THE MASS-ACTION MOI	OF CETYLPYRIDINIUM CHLORID		
Parameter	Combined Fit	Surface Tension	Cl Activity	Osmometry	
K cmc	27.4±.2 .00133 m	32.8±.7 .00093 m	26±3 .0015 m	27.2±.3 .00135 m	
β	.710±.004	.67±.01	.7±.1	.76±.03	
n	108±2 3 .1	90±50 3.1 (2.3±.1)x10 ⁻¹⁰ 72Å ²	70±700 3.1	90±20 3.1	Fits of data holding b constant
Ь					
ľ area	(2.4±.2)x10 ⁻¹⁰ 69 ^{8²}				
c १ sat'n	(1.1±.6)x10 ⁻⁸ .000105 m	(5±1)×10 ⁻⁹ .00007 m			
RMSD	2.012	0.402	2.016	2.681	
K cmc	27.5±.2 .00132 m	32.4±.8 .00095 m	31±1 .00104 m	27.3±.3 .0013 m	-
β	.720±.004	.72±.06	.57±.04	.77±.06	
Ե	3.1±.2	5±6	1.12±.05	3±1	Fits of data allowing b to vary
n	107±4	40±40	700±300	80±60	
Г area	(2.5±.2)x10 ⁻¹⁰ 66Ų	(2.28±.05)×10 ⁻¹⁰ 73 ⁸ ²			
c ½ sat'n	(1.1±.6)x10 ⁻⁸ .000105 m	(4.8±.4)x10 ⁻⁹ .000069 m			
RMSD	2.022	0.406	0.509	2.711	

mole fraction of monomers and micelles, a reasonable value of the aggregation number (compared to literature values of n for comparable compounds) is found for the case where b is held constant at 3.1. This parameter also has a small probable error.

Although values of fitting parameters for surfactant systems have been reported in the literature, no reports have been found where a single parameter is determined which best fits data from several techniques. The osmotic coefficient and activity coefficient can be related by the following equation, (53,40)

 $\ln(\gamma_{+}) = (1-\phi) + \int_{0}^{m} ((1-\phi)/m) dm.$

However, in the limit of infinite dilution, the integrand is indeterminant. Therefore one must assume linear behavior, in ϕ vs \sqrt{m} or in $_{\gamma_+}$ vs $\surd\text{m}$ from m=0 to some arbitrary concentration, in order to use this relation. The results presented emphasize the rationale of fitting osmotic coefficients as osmotic coefficients, activity coefficients as activity coefficients, and so on, rather than attempting to calculate one from the other. The same parameters (excluding ${\bf r}_{\rm m}$ and c) are present in the different functions which model osmotic coefficients, activity coefficients, or surface tension. Yet. a single technique has not been found from which the results can reasonably predict all the parameters in the mass-action model. Usually results from a single technique will only determine one or two parameters well. The technique whose results best determine a particular parameter will have the largest influence (in the combined fit) on the optimum value of that parameter, because the larger error in the same parameter determined from the other techniques indicates that the goodness of fit of data from the latter is not <u>as</u> much affected by the parameter value. In this way then, each technique pins down the parameter(s) it best determines, which in turn affects all the other parameters to give the best fit of the combined data. By simultaneously modelling different types of data from several techniques, a comprehensive description of the aggregation behavior of these surfactants is presented.

When modelling surfactant aggregation behavior to a particular theory, often a mass-action description will be used to describe systems where the micelle size does not exceed 50 to 100 monomers; and a pseudo-phase separation model will be fitting to data for systems where the aggregation size is larger than 50 to 100 monomers. The major difference between the two models is that: 1) the mass-action model predicts the mean ionic activity of the surfactant must increase above the cmc; while 2) the phase-separation model assumes the monomer and micelle activities remain constant with increasing surfactant concentration beyond the cmc. However, osmotic coefficients from colligative measurements continue to decrease above the cmc. This suggests the activity of the solutes is increasing. And the surface tension also continually decreases, albeit very slowly, with increasing surfactant concentration beyond the cmc, even for the CPC system. It seems quite logical to use the mass-action model for the SOS system. But the results here show that even for an aggregation size of, or in excess of, 100 monomers, the mass-action model better predicts the observed trends in these experimental data as well.

The relative shape of the micellar aggregate, whether it is spherical or spheroidal, can be predicted from ceometrical considerations based on arguments by Tanford (72) and others (73,74). If the micelle is assumed to consist entirely of the hydrophobic portions of the surfactant molecules (that is, no holes are present in the core of the micelle); and one or more dimensions of the aggregate are limited by the maximum possible extension of the hydrocarbon chain; then the maximum aggregation number of a spherical micelle is dependent on the number of carbons in the chain, and on the extent to which solvent water penetrates the hydrocarbon "core". For a surfactant with 6, 7, and 8 carbons in the hydrocarbon chain embedded in the core, the maximum aggregation number is 17, 22, and 27, respectively (72). For SOS, the implication can be either that 1) the solvent water penetrates only as deeply as one carbon, and the aggregate shape is spherical; or, 2) the solvent water penetrates to the second carbon (or deeper), and the aggregate shape is spheroidal. The ratio of the major to minor semiaxis for a prolate ellipsoid is 1.38 for an aggregate with 6 carbons embedded in the core and an aggregation size of 23 (72). The SDS micelle has an aggregation size of about 65 (17,64). If it assumed that solvent water penetrates as deep as two carbons (72), then the maximum spherical aggregation size is 40. The experimental n is approximately 1.6 times larger than this spherical aggregation number. The counterion binding fraction for SDS is 0.75 (58). The fraction of counterions bound to the SOS micelle is only about 60% of the value for that of SDS. As the aggregation size increases, the shape must become more elongated. This is because of the restriction that the maximum

length of one dimension of the micelle is the maximum length of the extended hydrocarbon chain. Therefore, for a more elongated aggregate, or for one with a larger major to minor semi-axis ratio. the packing of the surfactant head groups becomes more dense. That is, the head group repulsion and surface charge density increase. То counter this effect, more counterions bind to the surface region of the micelle. When one considers two surfactants with the same head group which differ primarily in their hydrocarbon chain length, and the significant difference in the value of β , it seems reasonable to suggest that this can be explained by a difference in the shape of the micelle; or that the SOS micelle is less elongated than that of SDS.

Using Tanford's (72) arguments for CPC, the maximum aggregation number for a spherical micelle containing a hydrocarbon with 14, 15, or 16 carbons is 74, 83, and 94, respectively. It is impossible to predict just how far solvent water goes into the micelle. However, assuming water only penetrates as deeply as one carbon, it is still evident that the CPC micelle is not spherical, but spheroidal in shape. Several references in the literature (74-77) mention that CPC does not exhibit a sphere-to-rod transition in the aggregate shape as the surfactant concentration increases. where this is seen for cetylpyridinium bromide and cetyltrimethylammonium bromide. This may appear at first to be in contradiction to the present conclusion. However, these reports (74,77) suggest that the shape of the CPC micelle does not significantly change or become elongated further with increasing concentration. The results of the calculated aggregation size for CPC discussed (vide supra) show that the average aggregation number for CPC over the concentration range studied suggests that the shape of the micelle is spheroidal throughout this concentration range.

ii. SELF-ASSOCIATION OF 2-PHENYLACETIC ACID IN WATER

Surfactants aggregate in water, in large part, due to the hydrophobic association of the hydrocarbon chains. The forces involved in this micellization process can be studied on a less complex level by investigating the aqueous self-association of molecules which have exposed organic groups. The forces which control the self-association of these compounds (that is, those due to hydrophobic association) are believed to be the same forces which control the aggregation and solubilization processes, as well as association in more complex systems (such as protein folding and transport through membranes) (14,42,43,78,79).

The self-association and 1:1 complex of 2-phenylacetic acid in water has been measured at 25°C. The results can be compared to those of similar compounds studied in this laboratory, listed in Table VI-3 (42,43,47,80). All the complex formation constants have been determined from vapor pressure measurements (vapor of volatile solute, or vapor of water for PAA) except for the benzoic acid:benzoate system, for which the solubility of the acid was determined by titration, at known added concentrations of sodium benzoate. The concentration ranges throughout which these data were collected were 0 to 0.017 m for benzene or fluorbenzene, 0.022 to 0.033 m for benzoic acid, and 0 to

TABLE VI-3

SELF-ASSOCIATION AND 1:1 COMPLEX FORMATION CONSTANTS FOR ORGANICS IN WATER AT 25°C

Complex	Formula	K ₂ or K ₁₁	
Benzene:Benzene	φH – φH	0.46	
Benzene:Phenol	¢Ή – φOH	0.624	
Benzene:Benzyl alcohol	¢н – ¢Сн ₂ Он	0.545	
Benzene:Phenethyl alcohol	¢н – ¢Сн ₂ Сн ₂ Он	0.605	
Fluorobenzene: Benzyl alcohol	φF – φCH ₂ OH	0.643 dimer only (0.575 dimer + 8.6 trimer)	
Benzene:Benzene	φH – ¢H	0.46	
Fluorobenzene:Fluorobenzene	$\phi F - \phi F$	0.7	
Benzene:Phenylacetic acid	фн – фСн ₂ СООН	0.65	
Fluorobenzene: Phenylacetic acid	¢F − ¢CH ₂ COOH	0.7	
Phenylacetic acid: Phenylacetic acid	¢СН ₂ СООН – ¢СН ₂ СООН	2.35	
Benzoic acid:Benzoate	¢COOH - ¢COO	1	
ϕ H - ϕ H ϕ H - ϕ OH ϕ CH ₂ COOH - ϕ CH ₂ COOH ϕ COOH - ϕ COO ⁻ all others	see reference 42 see reference 43 this work see reference 47 see reference 80		

0.131 m for PAA. Fitting the PAA data to a model with terms of higher order than the dimer did not significantly improve the fit of the data. If a trimer constant is included in the fit of the data, the error in this parameter is unreasonable $(K_3 = 5 \pm 70 \text{ M}^{-1})$, but the value of the dimer constant in this fit, 1.8, is lower than if only a dimer term is This same result occurs whether $[H^{\dagger}]$ is used to fit the data. calculated from osmometry data alone, or is determined from pH measurements. The $[H^+]$ is so low that using an additional technique such as pH does not improve the goodness of fit of the data. However it does verify the numerical method used to treat the results from the In any case, it is likely that higher order complexes are osmometer. This is apparent in all the fluorobenzene present. systems. particularly in the fluorobenzene:benzylalcohol system, and is not ruled out by the fit of the PAA data with only a dimer term. If it is the case that higher order complexes are present, this would account in part for the fact that the inferred value of the dimer constant is quite large, because this compound is studied over a range almost 8 times that of the benzene and fluorobenzene systems. Contributions from higher order terms will undoubtedly be more significant with increasing concentration. (See Figure V-9.) These contributions (if present) are incorporated into the dimer constant.

It has been noted in the literature (81,82) that PAA has an anomalous solubility dependence on temperature, in that the solubility increase with temperature is larger than expected. The magnitude of the PAA dimer constant may be rather large due to a related anomalous behavior. But this can only be clarified by studying the self-association process over a range of temperatures to determine the enthalpy, entropy, and heat capacity of formation of the associated complex.

For several of the systems listed in Table VI-3, there may be a contribution from a hydrogen-bonded dimer or complex. However, it is believed that the major difference in the tendency of these systems to self-associate or form 1:1 complexes is due to a difference in the extent of hydrophobic association (14,78-80). The side chains of the aromatics are small compared to the phenyl group, and association of these complexes might well be expected to be controlled by the planar portion of the molecule (14,78). But the data suggest that even small polar groups can have a specific effect on the complex, owing in part to their ability to disrupt the ordered water structure around the phenyl group as compared with the unsubstituted benzene (42,43,78,79). The length of, or number of methylene groups in the side chain has an additional effect (14,78,79), which will, in part, increase the ordered water around the monomer, contributing to the stability of the complex. Inductive effects of the side chain will also be important. This "very simple" association is quite complex and is controlled by several contributing forces. The balance of these forces will determine the tendency of complex formation.

This is not an attempt to clarify the hydrophobic interaction or to determine the relative hydrophobicities of the compounds discussed. Information of this kind cannot be determined from complex formation constants alone, and <u>must</u> include a very careful study of the heats, entropies, and heat capacities of formation of the complexes

(42,43,79). The self-association of PAA has only been studied at 25°C with the vapor pressure osmometer, and therefore temperature-dependent parameters are not available at this time.

However a study of this type is beyond the scope of this dissertation. The purpose in studying phenylacetic acid in water in the present context, is to provide precise solute and solvent activity data for this system. This information is essential in studying the solubilization of PAA by a micellar system.

iii. SOLUBILIZATION

Now reliable results are available which describe the aqueous aggregation of cetylpyridinium chloride. These results are independent of the technique chosen to study this system. The present study also provides information which describes the behavior of 2-phenylacetic acid in water. These two pieces of information can be used to study the perhaps more interesting, but much more complex system of PAA solubilized by aqueous CPC.

Results from Cl⁻ electrode and osmometry data show that the limiting values of β are increasing slightly as the concentration of CPC increases. Following the logic of Tanford (72), Leibner and Jacobus (73), Porte and coworkers (74), and others, it may be argued that as the surfactant concentration increases, the shape of the micelle becomes less-nearly spherical. Surfactant monomers are more crowded in the interfacial region so that the surface charge density of the micelle increases. To compensate for this, more counterions are bound, or β increases. Another possible contribution to an increase in β is due to the increase in concentration of free Cl⁻. This increase in counterion concentration may compress the electrical double-layer of the micelle, thereby increasing β .

At a constant surfactant concentration, increasing the fraction of solubilized organic lowers β . There are at least three possible contributions to this change in β :

i) solubilized acid anion may exchange with bound Cl⁻, thereby decreasing β ;

ii) the solubilization of organic compounds into the head group region will increase the size of the micelle and the asphericity of the aggregate. This effect by itself should increase ß by increasing the crowding of the surfactants and therefore the surface charge density; on the other hand,

iii) the solubilized organic will physically separate the like-charged pyridinium rings, decreasing the repulsion and the surface charge density. This will act to decrease g.

At the larger concentrations of surfactant, β will change less with increasing organic concentration than at lower surfactant concentrations. This is consistent with the ideas presented. The larger micelle has a higher surface charge density in the absence of any solubilized acid. Therefore, the less-nearly spherical micelles will require a larger fraction of acid to lower the surface charge density to the same extent as in the case of a smaller or more-nearly spherical micelle.

The solubilization constant of the acid anion is greater than that of the neutral acid. This is reasonable, because the solubilization constant reflects not only the dipole-dipole interaction of the aromatic groups present in both anion and neutral acid, but also the electrostatic attraction of opposite charge in the case of the anion.

As the activity coefficient of phenylacetic acid in the micelle increases with increasing mole fraction, the region of primary solubilization (the head group region of the micelle) becomes saturated, and a larger fraction of the organic molecule is solubilizing deeper into the micelle. The bulk environment in the micellar phase or "solution" is less favorable than that of the head group region or potential-determining layer, but is more favorable than the bulk water of the ternary solution.

The behavior of PAA in aqueous CPC appears to be very similar to that of phenol in aqueous CPC (25). The limiting apparent solubilization constant is approximately the same, and both the solubilization constant and the intramicellar organic activity coefficient have a similar dependence on the micellar composition. The rather small value of the limiting activity coefficient indicates that there is a specific interaction between the organic molecule and the micelle.

The straight chain alcohols, n-butanol and n-pentanol, solubilized in aqueous CPC (25) also have a very low activity coefficient at low mole fractions of alcohol in the micelle. It seems quite reasonable to suggest that there are specific interactions between the hydroxyl groups of the alcohol and the head groups of the surfactants in the micelle. The dependence of the activity coefficient on micellar composition for these two molecules is also similar to that for PAA in aqueous CPC.

The specific interaction between the organic molecule and the pyridinium ring of CPC is also evidenced by comparing the activity

coefficient of benzene in different surfactants. The activity coefficient increases for benzene solubilized into the micelle in the order CPC (25) < SDS (90) < SOS (22). The limiting values of the activity coefficients are approximately 1.1, 2.5, and 4.3, respectively. The indication is that there are specific interactions between the benzene and aromatic head group of CPC, which are not present (at least not nearly to the same extent) in the alkysulfates.

As the mole fraction of PAA or phenol in the CPC micelle increases, the activity coefficient approaches nearer to 1. That is, the escaping tendency of the solubilizate is increasing until it approaches that of the solubilizate in the pure component standard The specific interaction between the organic molecule and the state. micellar surface becomes weaker as the "sites" are filled and increasing amounts of the organic molecule solubilize in less energetically favorable regions of the micelle. At high enough mole fractions, of course, the micelle would be much like the pure component standard state (if this region could be investigated without encountering a phase separation of the solution, or if PAA were liquid at 25°C under normal conditions).

Studies have been made for series of related compounds solubilizing into CPC. It is very interesting to compare the types of compounds solubilized. The limiting solubilization constants of several compounds studied at the University of Oklahoma are presented in Table VI-4. Preliminary results show that introducing a hydroxide onto the phenyl ring does not have much effect on the K_S ; nor does introducing a hydroxide onto toluene. Additionally, introducing a

TABLE VI-4

APPARENT SOLUBILIZATION CONSTANTS FOR VARIOUS ORGANIC MOLECULES IN CETYLPYRIDINIUM CHI.ORIDE

Solubilizate		K _{S,app} (M ⁻¹) Technique
Benzene	Ф-Н	40	v.p.ª
Fluorobenzene	Φ- F	51	v.p. ^b
Phenol	Ф-ОН	60	v.p. ^c
Toluene	Ф-СН ₃	125	v.p. ^d
Cresol	Φ CH	180	SED ^{d,e}
Phenylacetic acid	Ф-СН ₂ СООН	60	osm, SED ^f
n-Butanol	с ₄ -он	5	v.p. ^a
n-Pentanol	СОН	15	v.p., SED ^a
n-Hexanol	сон	57	meuf ^g , sed ^g
n-Heptanol	с ₇ -он	200	MEUF ^g
n-Octanol	с_8-он	700	meuf ^g , sed ^g
K S,app v.p. → vapor press	in the lim sure appara	it as X _p app tus	proaches 0.
SED → Semi-equili	orium dialy	rsis	
MEUF - Micelle-enl	nanced ultr	a-filtration	,E
osm → vapor press	ire osmomet	er	
a see reference 2			

a see reference 25 b see reference 39 c see reference 26 d see reference 90 e see reference 91 f see reference 48 g see reference 92

methylene onto the phenyl ring or phenol shows an increase of about two to three times the K of the molecule without the added methylene. A comparison of PAA with toluene suggests that adding carboxylate into the side chain decreases the effect the methylene had on the original phenyl group, since the K_c of PAA in CPC is about one half that of Results for a series of alcohols show that the K_c toluene in CPC. increases by a factor of three or four with each successive addition of methylene into the hydrocarbon chain. However, the change in K_c with increasing mole fraction of solubilized organic is minimal for the alcohols (25,92). It is also important to emphasize that the K_{s} is, in part, dependent on the aqueous solubility of the organic molecule. aqueous solubility decreases, the apparent That is, as the solubilization constant will increase (see equation V.iv.[1]).

The activity coefficient of a solution can be influenced by various factors (25), for example: solute-solvent and solute-solute interactions described by "regular" solution theory and those of the Flory-Huggins type (79,83,84); the possible presence of any Laplace pressure effects which arise due to the curvature of the aggregate "surface" (85) (this would have the effect of decreasing the intramicellar concentration of the organic); and, interactions between the solubilized organic and the electrical potential of the micellar surface (86).

Many solubilization systems are being studied using various techniques. Vapor pressure osmometry can be used to study only those systems with solutes having a low or negligible vapor pressure compared to the solvent. The equilibrium vapor pressure measurements require one component to be sufficiently volatile compared to the receiving solution. SED can be used to study both these types of systems and those with organic molecules of intermediate volatility, provided an appropriate analytical method is available to analyze the permeate solution. These techniques are being used to collect data for many organic molecules solubilizing into a surfactant micelle, so that one can predict the contribution to the energetics of solubilization by the functional groups which comprise the organic molecule. However, in order to study these systems, reliable information is needed to describe the aqueous surfactant aggregation behavior in the absence of an organic molecule. This has been accomplished for SOS and CPC, by simultaneously fitting the data from several techniques.

CHAPTER VII

CONCLUSIONS

Several types of data for pure surfactant in water have been modelled simultaneously using a mass-action theory. The least-squares parameters provide a comprehensive description of the aggregation behavior of the surfactant, and can be used to infer the molecular relationships of the surfactant monomer, micelle, and counterion. Precise activities as a function of surfactant concentration have been determined. These results provide a significant contribution to the study of aqueous surfactant behavior, because they are independent of the technique chosen to study the aggregation process.

The self-association of 2-phenylacetic acid in water has been investigated using the vapor pressure osmometer. Precise activities of the various complexes present, consistent with a mass-action model, have been determined as a function of organic concentration. This system has not been studied previously in the literature. The results will be useful in studying the association of hydrophobic moieties in water. Additionally, these results are necessary to determine the

solubilization properties of this molecule in any surfactant solution, or other mixed system.

Information obtained from these two studies is essential in treating data for the combined system in order to understand the equilibrium between the bulk solution and the micelle. The studies of aqueous solutions of CPC are crucial to the entire series of studies of solubilization of organics in CPC, because it is this information which allows separation of the various components in solution in all the techniques being used to study micellar solubilization.

For each system it is neceeary to understand the aqueous behavior of the organic solute, as well. The vapor pressure osmometer will be very well suited for obtaining this information for low volatility organic molecules.

Plans for further research include determining the effect on the solubilization process of:

i) the series of organic acids with varying side chain length (benzoic and hydrocinnamic acids are being studied);

ii) branching in the side chain on the phenyl ring;

iii) more than one substitution on the phenyl ring;

iv) various aliphatic homologous series;

v) the surfactant; and

vi) temperature.

These types of studies will aid in further understanding the association of hydrophobic moieties; and the role of the functional groups of the organic molecule in their contributions to the energetics of solubilization by micellar systems.

REFERENCES

- Rosen, M. J., "Surfacatants and Interfacial Phenomena", Mittal, K. L., ed., Vol. 1, Plenum Press, New York, 1979.
- 2. Mittal, K. L., "Solution Chemistry of Surfactants", Vol. 2, Plenum Press, New York, 1979.
- 3. McBain, M. E. L.; Hutchinson, E.; "Solubilization and Related Phenomena", Academic Press, New York, 1955.
- 4. Mukerjee, P., in "Solution Chemistry of Surfactants", Mittal, K. L., ed., Vol. 1, Plenum Press, New York, 1979.
- Desnoyers, J. E.; DeLisi, R.; Ostiguy, C,; Perron, G.; in "Solution Chemistry of Surfactants", Mittal, K. L., ed., Vol. 1, Plenum Press, New York, 1979.
- Nagarajan, R.; Ruckenstein, E.; in "Surfactants in Solution: Theoretical and Applied Aspects", Mittal, K. L., ed., Vol. 2, Plenum Press, New York, 1983.
- Adamson, A. W., "Physical Chemistry of Surfaces", 4th ed., Wiley, New York, 1982.
- 8. Hill, R. M., Ph. D. Dissertation, The University of Oklahoma, Norman, 1982.
- 9. Kresheck, G. C., in "Water: A Comprehensive Treatise", Franks, F., ed., Vol. 4, Chap. 2, Plenum Press, New York, 1978.
- 10. Nagarajan, R.; Ruckenstein. E.; Sep. Sci Tech. 16 (1981) 1429.
- 11. Mukerjee, P., Pure Appl. Chem. 52 (1980) 1317.
- Lindman, B.; Wennerstrom, H.; in, "Solution Behavior of Surfactants", Mittal, K. L.; Fendler, E. T.; eds., Plenum, New York, 1982.
- 13. Wennerstrom, H.; Lindman, B.; Phys. Rep. <u>52</u> (1979) 1.
- 14. Mukerjee, P., J. Pharm. Sci. 63 (1974) 972.

- For example, see references 1-14, and, Shinoda, K., in "Colloidal Surfactants", Shinoda, K.; Tamamushi, B.; Nakagawa, T.; Isemura, T.; eds., Academic Press, New York, 1963.
- For example, see references 1-14; and, Abu-Hamdiyyah, M.; Mysels, K. J.; J. Phys. Chem. <u>71</u> (1967) 418.
- 17. Lianos, P.; Zana, R.; J. Colloid Interface Sci. 84 (1981) 100.
- Lindblom, G.; Lindman, B.; Mandell, L.; J. Colloid Interface Sci. 42 (1973) 400.
- Nagarajan, R.; Chaiko, M. A.; Ruckenstein, E.; J. Phys. Chem. <u>88</u> (1984) 2916.
- Chaiko, M. A.; Nagarajan, R.; Ruckenstein, E.; J. Colloid Interface Sci. <u>99</u> (1984) 168.
- Christian, S. D.; Smith, L. S.; Bushong, D. S.; Tucker, E. E.; J. Colloid Interface Sci. <u>89</u> (1982) 514.
- 22. Tucker, E. E.; Christian, S. D.; Faraday Symp. Chem. Soc. <u>17</u> (1982) 11.
- 23. Tucker, E. E., Christian, S. D.; J. Colloid Interface Sci. <u>104</u> (1985) 562.
- 24. Christian, S. D.; Smith, G. A.; Tucker, E. E.; Scamehorn, J. F.;Langmuir <u>1</u> (1985) 564.
- 25. Christian, S. D.; Tucker, E. E.; Smith, G. A.; Bushong, D. S.; submitted to J. Colloid Interface Sci.
- 26. Smith, G. A.; Christian, S. D.; Tucker, E. E.; Scamehorn, J. F.; submitted to J. Solution Chem.
- Dunn, Jr., R. O.; Scamehorn, J. F.; Christian, S. D.; Sep. Sci. Tech. <u>20</u> (1985) 257.
- 28. Aboutaleb, A. E.; Sakr, A. M.; Elsabbagh, H. M.; Abdelrahman, S. I.; J. Arch. Pharm. Sci. Ed. <u>5</u> (1977) 105.
- Patel, N. K.; Kostenbauder, H. B.; J. Amer. Pharm. Assoc., Sci. Ed. <u>47</u> (1958) 289.
- 30. Kazmi, S. J. A.; Mitchell, A. G.; J. Pharm. Pharmac. <u>23</u> (1971) 482.
- 31. Mitchell. A. G.; Brown, K. F.; J. Pharm. Pharmac. <u>18</u> (1966) 115.
- 32. Potel, N. K., Foss, N. E.; J. Pharm. Sci. <u>54</u> (1965) 1495; and, J. Pharm. Sci. <u>53</u> (1964) 94.

- 33. Ashworth, R. W.; Heard, D. D.; J. Pharm. Pharmac. 18 (1966) 985.
- 34. Matsumoto, H.; Matsumura, H.; Iguchi, S., Chem. Pharm. Bull. <u>14</u> (1966) 385.
- 35. Donbrow, M.; Azaz, E.; Hamburger, R.; J. Pharm. Sci. <u>59</u> (1970) 1427.
- 36. Dougherty, S. J.; Berg, J. C.; J. Colloid Interface Sci. <u>48</u> (1974) 110.
- 37. Birdi, K. S.; Backlund, S.; Sorensen, K.; Krag, T.; Dalsager, S.; J. Colloid Interface Sci. <u>66</u> (1978) 118.
- 38. Mathews, W. K.; Larsen, J. W.; Pikal, M. J.; Tetrahedron Lett. <u>6</u> (1972) 513.
- 39. Silvester. L. F.; Pitzer, K. S.; J. Phys. Chem. 81 (1977) 1822.
- 40. Hamer, W. J.; Wu, Y-C.; J. Phys. Chem. Ref. Data 1 (1972) 1047.
- 41. Nord, Leif, unpublished research.
- 42. Tucker, E. E.; Lane, E. H.; Christian, S. D.; J. Soln. Chem. <u>10</u> (1981) 1.
- 43. Stellner, K. L; Tucker, E. E.; Christian, S. D.; J. Soln. Chem. <u>12</u> (1983) 307.
- 44. Razouk, R.; Walmsley, D.; J. Colloid Interface Sci.47 (1974) 515.
- 45. Thomas, D. C., Ph.D. Dissertation, The University of Oklahoma, 1978.
- 46. Cott, Craig; Klumpp, Doug; Terrell, Kathryn; unpublished research, surface tension data using Rosano Tensiometer.
- 47. Terrell, Kathryn, unpublished research.
- 48. Gonzales, Mercedes, unpublished research.
- 49. Kalé, K. M.; Evans, D. F.; personal communication; and Kalé, K. M.; Cussler, E. L.; Evans, D. F.; J. Soln. Chem. <u>11</u> (1982) 581.
- 50. Hamilton, L. F.; Simpson, S. G.; "Quantitative Chemical Analysis", Macmillan, New York, 1958.
- 51. Burchfield, T. E.; Woolley, E. M.; J. Phys. Chem. 88 (1984) 2149.
- 52. Desnoyers, J. E.; Caron, G.; DeLisi, R.; Roberts, D.; Roux, A.; Perron, G.; J. Phys. Chem. <u>87</u> (1983) 1397.

- Pitzer, K. S.; Brewer, L.; "Thermodynamics", 2nd ed., McGraw-Hill, New York, 1961.
- 54. Christian, S. D.; Tucker, E. E.; Am. Lab. <u>14</u> (1982) 31.
- 55. "The Merck Index of Chemicals and Drugs", 6th ed., Merck, Rahway, NJ, 1952.
- 56. Birch, B. J.; Hall, D. G.; J. Chem. Soc., Farad. Trans. I <u>68</u> (1972) 2350.
- 57. Mukerjee, P.; Mysels, K. J.; "Critical Micelle Concentrations of Aqueous Surfactant Systems", NSRDS-NBS-36, Superintendent of Documents, US Government Printing Office, Wash. D.C. 20402, 1971.
- 58. Satake, I.; Tahara, T.; Matuura, R.; Bull. Chem. Soc. Jap. <u>42</u> (1969) 319.
- 59. Nishikido, N., J. Colloid Interface Sci. <u>92</u> (1983) 588.
- 60. Evans, H. C., J. Chem. Soc. 159 (1956) 579.
- 61. Hutchinson, E.; Melrose, J. C.; Z. Phys. Chem. 2 (1954) 363.
- Adair, D. A. W., Hicks, J. R.; Jobe, D. J.; Reinsborough, V. C.; Aust. J. Chem. <u>36</u> (1983) 1021.
- 63. Gettins, J.; Jobling, P. L.; Walsh, M. F.; Wyn-Jones, E.; J. Chem. Soc., Farad. Trans. 2 <u>76</u> (1980) 794.
- 64. Aniansson, E. A. G.; Wall, S. N.; Almgren, M.; Hoffmann, H.; Kielmann, I.; Ulbricht, W.; Zana, R.; Lang, J.; Tondre, C.; J. Phys. Chem. 80 (1976) 905.
- 65. Tsutsui, T.; Murata, H,; Tajima, K,; Colloid and Polym. Sci. <u>258</u> (1980) 968.
- 66. Lane, E. E., unpublished research.
- 67. Elworthy, P. H.; Mysels, K. J.; J. Colloid Interface Sci. <u>21</u> (1966) 331.
- 68. Mathews, W. K.; Larsen, J. W.; Pikal, M. J.; Tetrahedron Lett. <u>6</u> (1972) 513.
- Roelants, E.; Gelade, E.; van der Auweraer, M.; Croonen, Y.; de Schryver, F. C.; J. Colloid Interface Sci. <u>96</u> (1983) 288.
- 70. Lianos, P.; Viriot, M-L.; Zana, R.; J. Phys. Chem. <u>88</u> (1984) 1098.
- 71. Hauser, E. A.; Niles, G. E.; J. Phys. Chem. 45 (1941) 954.

- 124
- 72. Tanford, C.; J. Phys. Chem. 76 (1972) 3020.
- 73. Leibner, J. E.; Jacobus, J.; J. Phys. Chem. 81 (1977) 130.
- 74. Porte, G.; Poggi, Y.; Appell, J.; Maret, G., J. Phys. Chem. <u>88</u> (1984) 5713.
- 75. Porte, G.; Appell, J.; J. Phys. Chem. 85 (1981) 2511.
- 76. Dorshow, R. B.; Bunton, C. A.; Nicoll, D. F.; J. Phys. Chem. <u>87</u> (1983) 1409.
- 77. Anacker, E. W.; Ghose, H. M.; J. Am. Chem. Soc. 90 (1968) 3161.
- 78. Kauzmann, W., Adv. Prot. Chem. <u>14</u> (1959) 1.
- Franks, F., in "Water: A Comprehensive Treatise", Franks, F., ed., Vol. 4, Plenum Press, New York, 1973.
- 80. Bernal, P.; Christian, S. D.; Tucker, E. E.; manuscript in preparation.
- 81. Morrison, T. J., Trans. Farad. Soc. 40 (1944) 43.
- 82. Paul, M. A., J. Am Chem. Soc. 75 (1953) 2513.
- 83. Robinson, R. A.; Stokes, R. H.; J. Phys. Chem. 65 (1961) 1954.
- 84. Hildebrand, J. H., Prausnitz, J. M.; Scott, R. L.; "Regular and Related Solutions", Van Nostrand Reinhold, New York, 1970.
- 85. Mittal, K. L., "Solution Chemistry of Surfactants", Vol. 1, Plenum Press, New York, 1978.
- 86. Frech, R. E., unpublished research.
- 87. "Handbook of Chemistry and Physics", 66th ed., Chemical Rubber Company, Cleveland, OH, 1985.
- 88. Klumpp, Doug, unpublished research.
- 89. Bernal, P., unpublished research.
- 90. Smith, G., unpublished research.
- 91. Bhat, S., unpublished research.
- 92. Gibbs, L., MS Thesis, The University of Oklahoma, 1985.