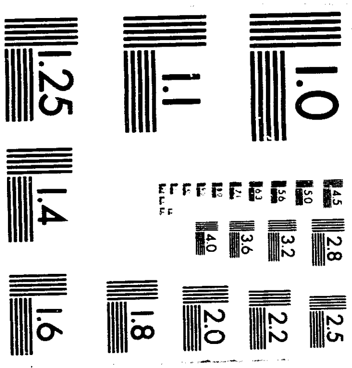

1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3

1 of 2

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

SOLUBILIZATION OF PENTANOL BY CATIONIC SURFACTANTS AND BINARY MIXTURES OF CATIONIC SURFACTANTS

A THESIS
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
MASTER OF SCIENCE

BY
MATTHEW EARLE MORGAN
Norman, Oklahoma
1993

SOLUBILIZATION OF PENTANOL BY CATIONIC SURFACTANTS AND BINARY MIXTURES OF SURFACTANTS

A THESIS

APPROVED FOR THE DEPARTMENT OF CHEMISTRY

APPROVED BY

THESIS COMMITTEE

Special thanks go to Dr. Sherril Christian, Dr. Hirotaka Uchiyama, and Dr. Edwin Tucker. Without their constant advice, direction, and professional aid, this thesis would never have been completed. I also wish to thank the United States Air Force for allowing me to pursue my academic aspirations while still being a member of the Armed Forces. This past eighteen months I have enjoyed the best of both worlds.

This thesis is dedicated to my wife, Patsy, for her unending personal support during many long nights and short weekends. I hope she keeps her good humor while I get my PhD. I also owe special thanks to my parents, Jim and Norma Morgan, for without their lifetime of hard work and love, none of this would have been possible.

"Once more unto the breach, dear friends, once more..."

"On, on, on, on, on! to the breach, to the breach!"

-Henry V

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Chapter 1

Introduction

Surfactants are a classification of molecule that have captivated surface chemists for decades. The word "surfactant" comes from an abbreviation of "surface-active agent." As the name implies, surfactants operate at liquid-solid, liquid-liquid, or liquid-vapor solution interfaces. A surfactant molecule is typically made up of two parts: one hydrophobic and one hydrophilic. The hydrophilic moiety, called the head group, can be a polar or charged species, such as a ethoxy, sulfate, or substituted ammonium group. The hydrophobic portion, or tail group, is usually a hydrocarbon or fluorocarbon chain comprised of eight to sixteen carbons. The head and the tail groups together form a surfactant, and the resulting molecule exhibits many properties useful to both science and industry. (See Figure 1)

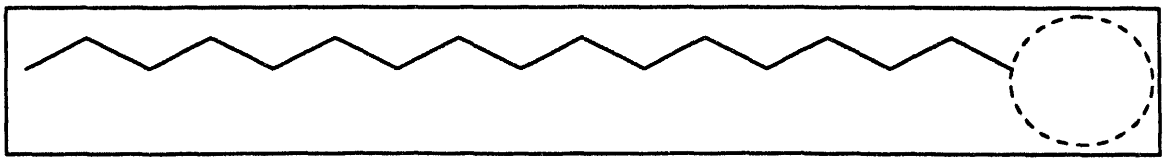


Figure 1 Surfactant Molecule.

Surfactants are usually classified into four major categories according to the charge of the hydrophilic group on the molecule[1]. These classifications are cationic, anionic, nonionic, and zwitterionic. Cationic surfactants have a head group that is positively charged, while anionics have a negatively charged head group. A surfactant is classified as nonionic if the head group is polar but has no positive or negative charge. Finally, zwitterionic surfactants have both a positive and negative charge on the head group, and depending on the pH of the solution, can have either a net positive or negative charge[2].

The head groups of cationic surfactants are usually quaternary amines or pyridines with a chloride, bromide, or iodide counterion. The charged head groups of anionic surfactants normally consist of a sulfate or sulfonate group, offset with a sodium or other positively charged counterion[3].

The emphasis of this research is on cationic surfactants. Cationic surfactants are relatively easy to synthesize and purify, and are highly resistant to bacteria, fungus, and algae[4]. They are also the major ingredients used in many industrial detergents[5].

One of the most important properties of surfactants is in a polar solvent at a high enough concentration, the surfactant molecules associate to form large clusters called micelles. Water molecules do not mix freely with the tail group of a surfactant, but when surfactant molecules are present in aqueous solution, water molecules are forced into contact with the hydrophobic half of the surfactant. (See Figure 2) Frank[6] suggested that water molecules form a highly ordered region similar to an "iceberg" around hydrophobic molecules or hydrophobic regions of molecules. The formation of these ordered regions results in a lower entropy than a system of pure water molecules.

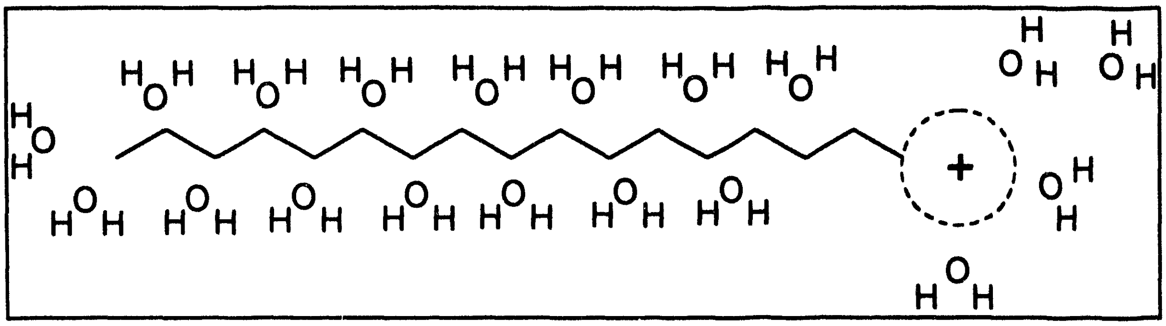


Figure 2 Cationic surfactant molecule in water.

It is this entropic effect that helps drive the surfactant tail groups together to form a micelle. A micelle formed from cationic surfactants is often a sphere made up of approximately 50 surfactant molecules[7]. The shell of the sphere is made up of the surfactant head groups, while the interior is comprised of the tails[8]. (See Figure 3)

If an organic solute is present in an aqueous solution containing surfactant micelles, the organic will usually be more thermodynamically stable in the interior of a micelle than in the surrounding aqueous solution. The process by which solute molecules move from the bulk solution to the interior of a micelle is called solubilization. A micellar surfactant solution can often solubilize as many as three or four organic solute molecules per molecule of surfactant. Thus, an organic solute that is normally sparingly soluble in pure aqueous solution can show a dramatic increase in solubility when micelles are present[9].

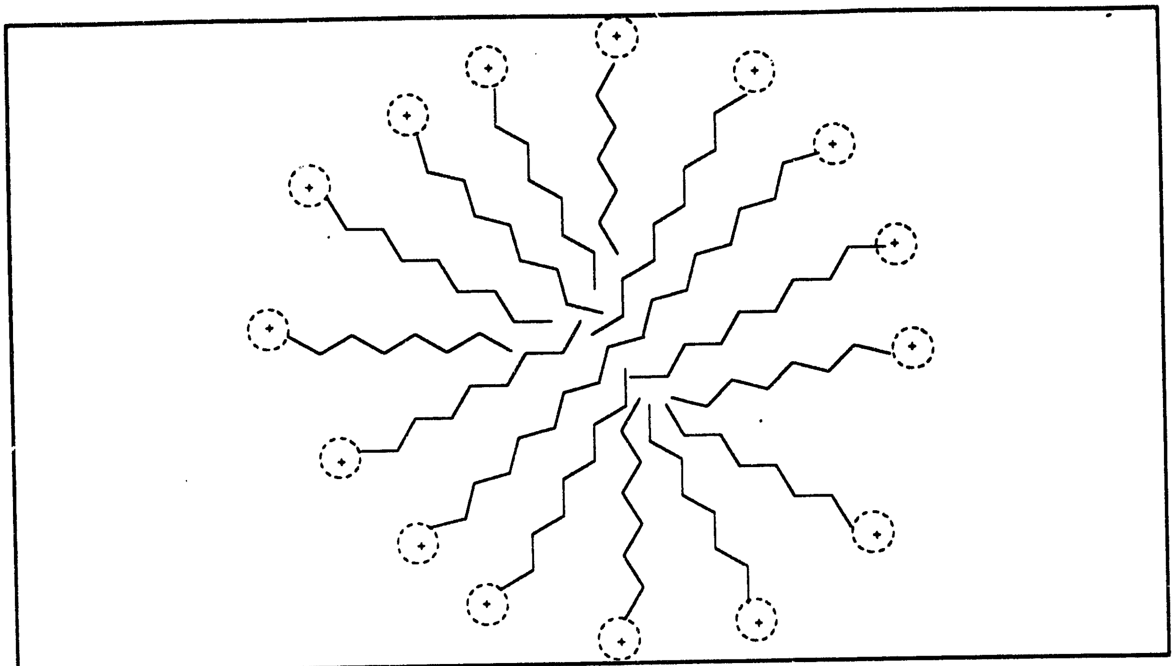


Figure 3 Surfactant tail groups join to form micelle.

Micellar solutions differ from emulsions in that when organic solutes are solubilized in micelles, the solution is isotropic, or in a single phase[10]. This isotropic solution is thermodynamically stable and will not separate into two phases. An oil in water emulsion, on the other hand, consists of droplets of an organic solute surrounded by surfactant molecules. The dispersed oil is actually a separate phase from the solvent. The emulsion is not thermodynamically stable, and it will eventually break apart into separate bulk oil and water phases.

Just as monomeric surfactant molecules have hydrophobic and hydrophilic regions, so do micelles. The degree of hydrophobicity of the solute will determine the location of the solute within the micelle[11]. Strongly hydrophobic molecules, such as hexane, will solubilize in the interior of the micelle. Charged species, such as chromate ions, are strongly attracted to the cationic head groups in the Stern Layer, which is the electrostatic region around the charged surface of the micelle[12]. The region of the micelle that starts at the polar head group and extends to the first two or three carbons in the tail group is usually called the palisade layer. Polar molecules that are slightly hydrophobic, such as long chain alcohols will solubilize at least partly in the palisade layer[3]. (See Figure 4)

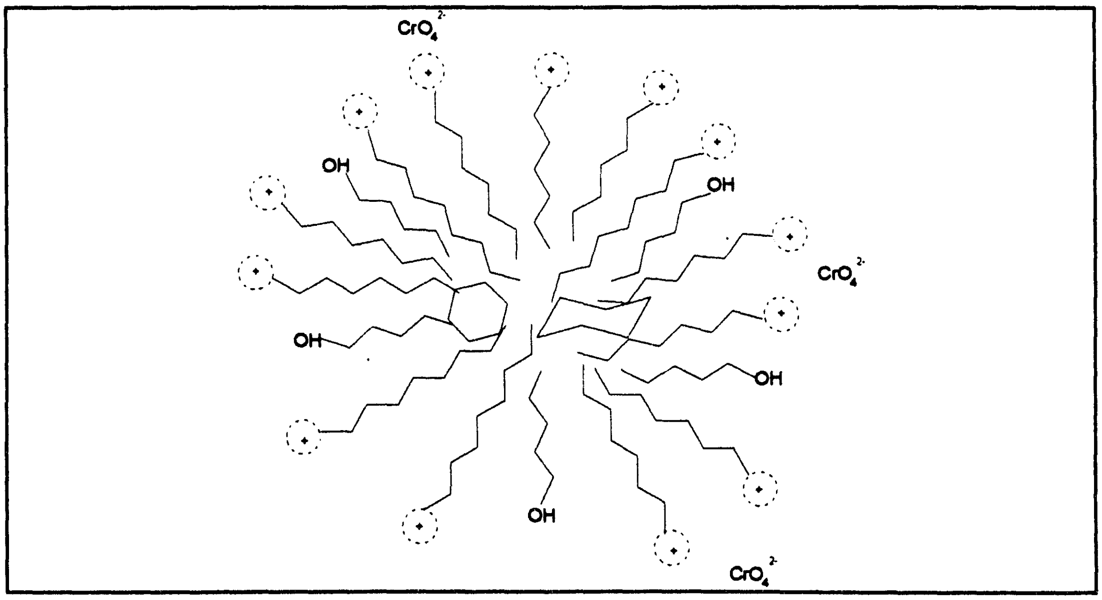


Figure 4 Hydrophobicity determines locus of solubilization.

Micellar solubilization of organic solutes is quantitatively measured by methods such as vapor pressure[13], semi-equilibrium dialysis[14], headspace chromatography[15], and calorimetric methods[16]. Each method has its advantages and disadvantages. The last two methods will be specifically discussed later.

The concentration at which a surfactant forms micelles is called the critical micelle concentration, or CMC. At surfactant concentrations above the CMC, adding more surfactant to the solution makes more micelles, which enhances the solubility of the organic solute. A surfactant with a lower CMC will therefore often solubilize more organic at a given concentration than will a similar surfactant with a high CMC. Surfactant molecules and organic solutes that exist in the bulk solution and have not formed a micelle are called monomers. The concentration of an ionic surfactant monomer in a solution is approximately equal to or less than the critical micelle concentration.

Properties of a surfactant molecule influence the CMC of the particular surfactant. The critical micelle concentration is lower for nonionic surfactants than for cationic, anionic, or zwitterionic surfactants having similar hydrophobic groups[17]. This effect is due to repulsion of the ionic head groups, making micelle formation more difficult for the charged surfactants. Many external factors can also change the CMC of a surfactant. The head group repulsion found in ionic surfactants can be minimized by the addition of an electrolyte such as sodium chloride to a surfactant solution. The presence of the extra electrolyte tends to screen the repulsion that the head groups exert on each other[18].

Another external factor that lowers the CMC of a surfactant is the addition of a cosurfactant to the solution. A cosurfactant is a molecule that will not form micelles on its own, but greatly reduces the critical micelle concentration when mixed with a surfactant. This effect is especially noticeable in ionic surfactants. Straight chain alcohols containing four or more carbons are good examples of cosurfactants. As previously noted, the alcohol will orient itself with the hydroxy group directed toward the charged shell of the micelle, and the carbon chain will be directed toward the interior of the micelle. The alcohol molecule occupies space between the surfactant molecules, resting in the palisade layer and shielding the electrical repulsion of the head groups[3].

The research reported here has included studies of the solubilization of pentanol in hexadecylpyridinium chloride (CPC), trimethyltetradecylammonium chloride ($C_{14}Cl$), benzyldimethyltetradecylammonium chloride ($C_{14}BzCl$), benzyldimethylhexadecylpyridinium chloride ($C_{16}BzCl$), hexadecyltrimethylammonium bromide (CTAB), and binary mixtures of CPC + $C_{16}BzCl$ and $C_{14}Cl$ + $C_{14}BzCl$. (See figure 5) There have been a number of studies involving solubilization properties of mixtures of cationic + anionic surfactants and cationic + nonionic surfactants[15,16,19], but there is comparatively little information about mixtures of cationic + cationic surfactants. Some reported work on these mixtures has described presumably strong synergistic effects on the solubilization of normal alcohols such as pentanol and hexanol[20,21]. Most of the

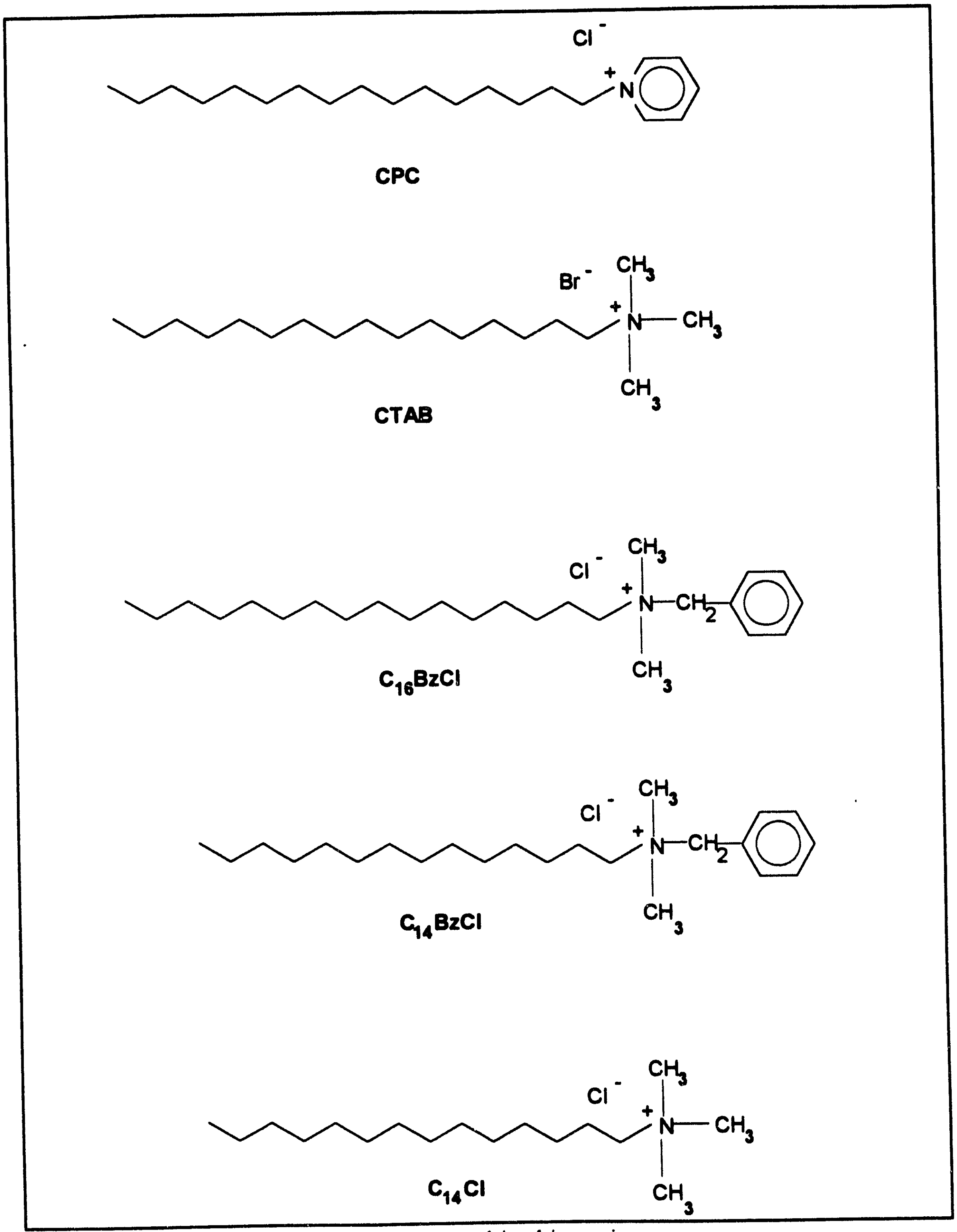


Figure 5 Structures of surfactants used in this project.

solubilization data in these studies were obtained by a calorimetric method. The calorimetric method infers solubilization partition coefficient from heat measurements, along with Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS)[22].

If the strong synergistic solubilization suggested by these studies exists, it could be of great benefit in industrial applications. From experimental data, it would be possible to formulate optimum surfactant mixtures to solubilize large amounts of organic contaminants, and perhaps even to find surfactant ratios that are solute specific.

Rather than using calorimetric methods, this project will employ headspace chromatography to measure solubilization of pentanol over a wide range of solute concentrations. While not yielding as much thermodynamic data as calorimetry, headspace chromatography is a more direct measure of the extent of solubilization. Using headspace chromatography, this study will seek to determine whether strongly synergistic mixture ratios exist in the case of binary cationic surfactant systems.

The principle behind headspace chromatography is very simple. A known amount of pentanol is added to a solution containing a known amount of surfactant. The pentanol-water-surfactant solution is sealed in an airtight vial and allowed to come to equilibrium. A sample of pentanol vapor above the solution is withdrawn from the vial and injected into a gas chromatograph. The gas chromatograph measures the pentanol peak and an integrator calculates the area of that peak.

There are two equilibria in the pentanol-water-surfactant system: 1) The pentanol solubilized in micelles is in equilibrium with the monomeric pentanol in solution, and 2) the monomeric pentanol is in equilibrium with the pentanol in the vapor above the solution. The constants for these equilibria are K_S and K_{d0}, respectively. (See figure 6)

To establish the link between the two equilibria, a sample of the vapor above pure liquid pentanol must be collected, in order to find the activity of pentanol in solution. Also, a calibration curve for various concentrations of pentanol in water must be calculated to relate activity of pentanol to concentration of pentanol in solution[23]. When comparing activity versus pentanol concentration curves for solutions with and without surfactants, it can be noted that the surfactant-containing solutions show a much lower pentanol activity for a given concentration. (See figure 7)

From this type of data is is possible to infer both the concentration of pentanol solubilized in micelles and the concentrations of pentanol in the "bulk" solution outside the micelles. The method is equally applicable to systems containing a single surfactant as well as mixtures of surfactants.

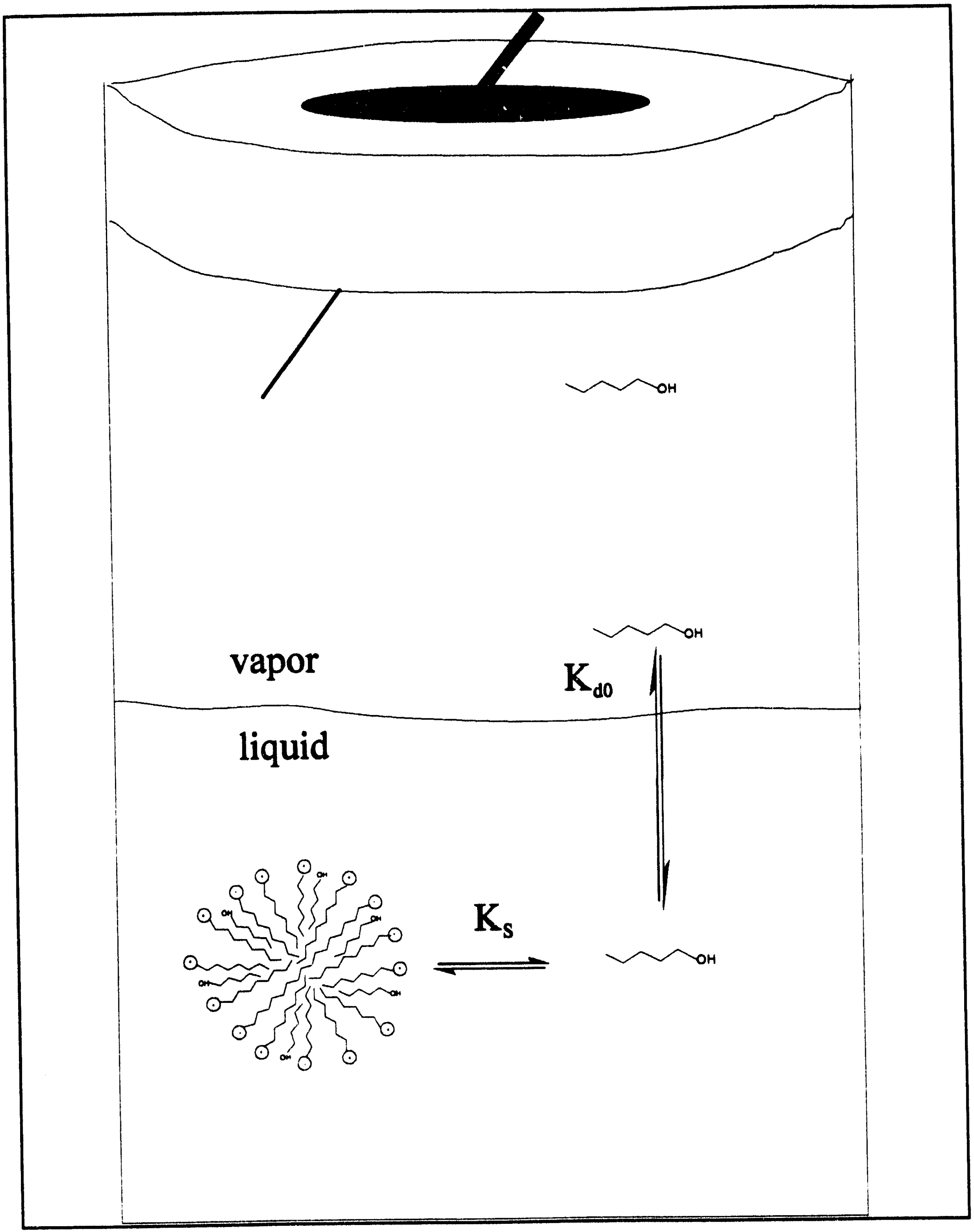


Figure 6 Sample vial.

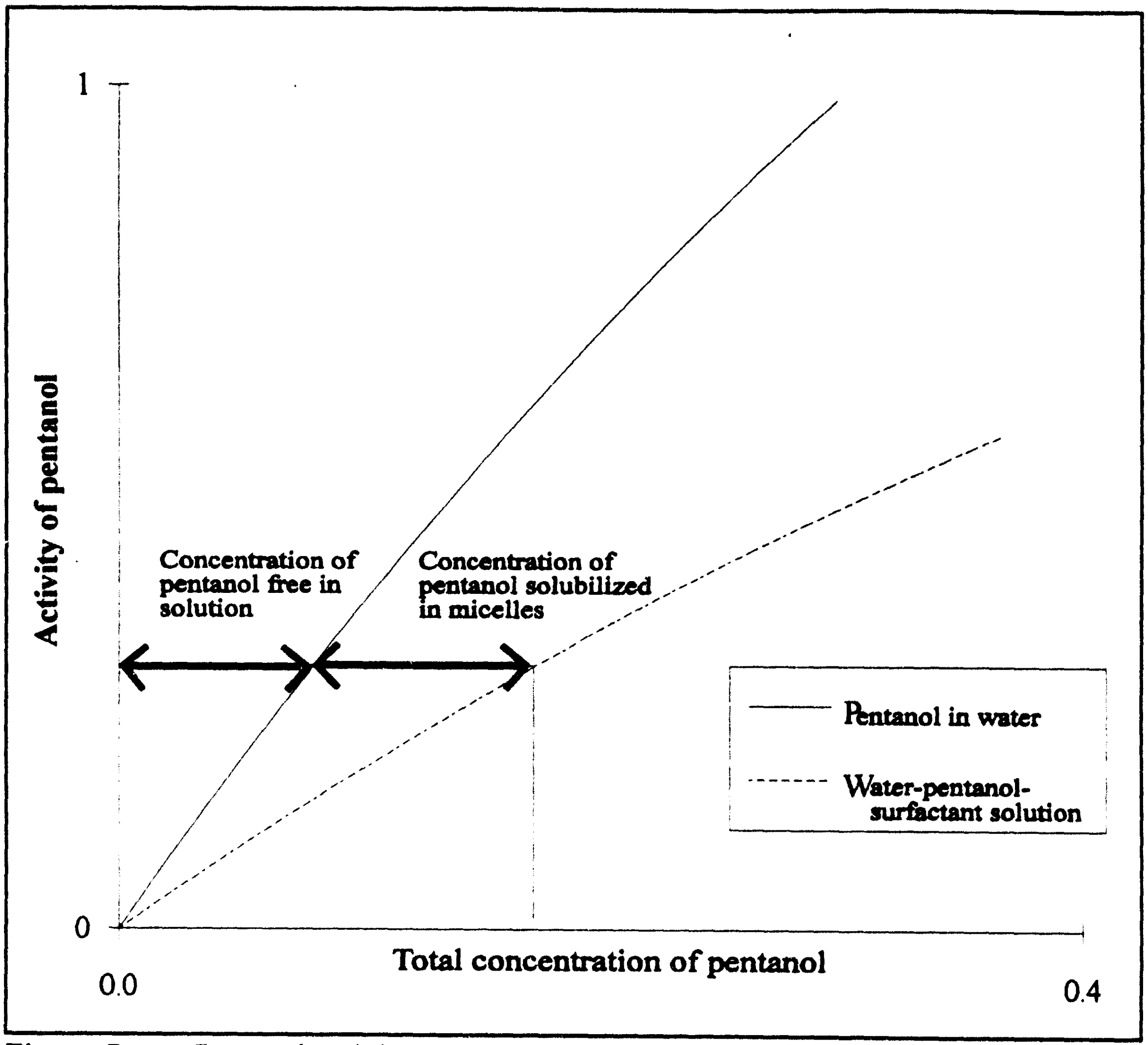


Figure 7 Pentanol activity versus concentration with and without surfactants.

REFERENCES

1. Rosen, M. "Surfactants and Interfacial Phenomena"; John Wiley & Sons: New York, 1989; p 100.
2. Reference 1, p 29.
3. Lee, B. Ph.D. Dissertation, University of Oklahoma, Norman, OK, 1990.
4. Zana, R. In "Cationic Surfactants: Physical Chemistry"; Rubingh, D.; Holland, P., Ed.; Marcel Dekker: New York, 1991; Chapter 2.
5. Adamson, A. "Physical Chemistry of Surfaces", 5th ed.; John Wiley & Sons: New York, 1990; p 516.
6. Frank, H.; Evans, M. *J. Chem. Phys.* **1945,** *13* (11), 507-532.
7. Tanford, C. *J. Phys. Chem.* **1972,** *76*, 3020-3024.
8. Anacker, E. In "Cationic Surfactants"; Jungermann, E. Ed.; Marcel Dekker: New York, 1970, Chapter 7.
9. Reference 1, p 170.
10. Reference 1, p 171.
11. Reference 1, p 172.
12. Reference 1, p 36.
13. Christian, S. D.; Tucker, E. E.; Smith, G. E.; Bushong, D. S. *J. Colloid Interface Sci.* **1986,** *113*, 439-448.
14. Christian, S.; Smith, G.; Tucker, E.; Scamehorn, J. *Langmuir* **1985,** *1*, 564-567.
15. Nguyen, C.; Scamehorn, J.; Christian, S. *Colloids Surf.* **1988,** *30*, 335-344.
16. Bury, R.; Treiner, C. *J Solution Chem.* **1989,** *18* (6), 499-513.
17. Reference 1, p 100.
18. Reference 1, p 136.

19. Scamehorn, J. In "Phenomena in Mixed Surfactant Systems"; Scamehorn, J. Ed.; American Chemical Society: Washington DC, 1986. The articles in this book cover a wide variety of subjects involving various surfactant mixtures.

20. Treiner, C.; Bocquet, J.; Pommier, C. *J. Phys. Chem.* **1986**, *90*, 3052-3054.

21. Bury, R.; Treiner, C. *J. Phys. Chem.* **1991**, *95*, 3824-3829.

22. Bury, R.; Treiner, C.; Chevalet, J.; Makaysi, A. *Anal. Chim. Acta* **1991**, *251*, 69-77.

23. Ioffe, B.; Vitenberg, A. "Head-Space Analysis and Related Methods in Gas Chromatography"; John Wiley & Sons: New York, 1982; p 13.

Chapter 2

Experimental

Trimethyltetradecylammonium chloride, $C_{14}Cl$, was obtained from TCI Japan. Its purity was ascertained using a fast atom bombardment mass spectrometer. Benzyldimethyltetradecylammonium chloride, $C_{14}BzCl$, and benzyldimethylhexadecylpyridinium chloride, $C_{16}BzCl$, were obtained from Sigma, and were 99% pure and 97% pure, respectively. Hexadecylpyridinium chloride, CPC, was obtained from Hexcel Corporation. Its purity was deduced from the lack of a surface tension minimum in plots of surface tension versus concentration. Hexadecyltrimethylammonium bromide, CTAB, was purified by dissolving in ethanol, recrystallizing, and vacuum drying. 1-pentanol, obtained from Sigma, was greater than 99% pure. All solutions were prepared by weight, and all water used was doubly distilled and deionized.

Gas chromatographic measurements were performed on a Perkin-Elmer model Sigma 300 Gas Chromatograph with a Flame Ionization Detector. The column used was a Tenax GC, with a packing material made of a porous polymer based on 2,6-

diphenyl-p-phenylene oxide. Peak areas were recorded on a Varian 4270 integrator. Surfactant/pentanol solutions were prepared and 20 mL of solution were placed in 40 mL sample vials, sealed airtight with silicon septa, and allowed to equilibrate in a water bath at 20° C for twenty-four hours before injection.

Conditions of the headspace gas chromatograph:

Oven Temperature	200° C
Injector Temperature	200° C
Detector Temperature	200° C
Column Temperature	200° C
Column Length, Width	3 ft, OD ⅛"
Mesh Range	80/100
Carrier Gas	Helium (20 psi)
Air Pressure	30 psi
Hydrogen Pressure	20 psi
Running Time	1 minute
Stabilization Time	24 hours

All samples were injected manually. The syringe was flushed with air several times before and between injections. Approximately one mL of sample was drawn out of the sample vial, the sample volume adjusted to 0.5 mL, and then the sample was injected into the gas chromatograph. This procedure is very similar to that used for other headspace measurements[1].

Data Treatment for Single Surfactant Systems

The peak areas from the gas chromatograph were used to determine the amount of pentanol vapor in the headspace above the solution. In calculating the activity of pentanol in solution, it was only necessary to divide the peak area of pentanol above the solution by the peak area given by an equal volume of vapor equilibrated with pure pentanol. Definitions of all symbols used are in Appendix 1.

$$a_P = \frac{Pk_P}{Pk_P^o} \tag{1}$$

The partial vapor pressure of pentanol is then found by multiplying the activity calculated in equation (1) by the vapor pressure of pure pentanol at 20 °C, found to be 1.69 torr[2].

$$P_P = P_P^o \cdot a_P \tag{2}$$

From the ideal gas equation and the partial vapor pressure of pentanol calculated in equation (2), the number of moles of pentanol in the vapor can be calculated. Common sense suggests that the amount of pentanol in vapor above a 20 mL solution will be extremely small. The experimental data verify this assertion.

$$n_{P,vap} = \left(\frac{P_P}{760\,torr}\right) \cdot \left(\frac{\left(\frac{20\,mL}{1000\,mL/L}\right)}{(.08206\,L\cdot atm/K\cdot mol) \cdot 293.15\,K}\right) \tag{3}$$

The total amount of pentanol added to the vial is a known quantity. From this value and the amount of pentanol in the vapor phase from equation (3), the amount of pentanol in solution can be determined.

$$n_{P,sol} = n_{P,tot} - n_{P,vap} \tag{4}$$

The concentration of pentanol in solution is easily obtained from the volume of liquid in the sample vial.

$$C_{P,sol} = \frac{n_{P,sol}}{20\,mL} \cdot \frac{1000\,mL}{1\,L} \tag{5}$$

With the amount of pentanol in solution known, the distribution between pentanol solubilized in micelles and unsolubilized pentanol in bulk solution can be calculated. The activity of pentanol is a function of the concentration of pentanol in bulk. To find the relationship between these values, a calibration curve was generated by measuring the peak areas for known concentrations of pentanol in water, with no surfactants added. A second order equation was fit to this curve, and this function was used to calculate the concentration of unsolubilized pentanol in solution from a given activity. This equation could be modified to include third or fourth degree terms, but the slight improvement in approximation would be offset by the increase in complexity of solving the equation for bulk concentration of pentanol.

$$a_P = 3.270C_{P,bulk} - 1.368C_{P,bulk}^2 \tag{6}$$

The partial pressure of pentanol above a pentanol/water solution indicates that the activity of pentanol does not exactly vary linearly with pentanol concentration. The deviation from linear Henry's law behavior can be attributed to the self-association of pentanol into dimers and trimers. The actual activity change can be quantified by the Hansen-Miller equations, which calculate activity coefficients for a solute from mole fraction of solute and empirical constants[3]. Smith determined Hansen-Miller coefficients for pentanol in water at 25°C using the vapor pressure method[4]. The values determined using headspace chromatography at 20°C during this project are in quite good agreement with the results reported by Smith. (See figure 8)

The self-association of pentanol in the bulk solution into dimers and trimers must be taken into account. Only the monomeric pentanol is measured by the gas chromatograph, and equation (6) can be modified to find the amount of monomeric pentanol in solution. As the concentration of pentanol in bulk solution goes to 0, the second term in equation (6) becomes negligible. Therefore in this limit, the concentration of monomeric pentanol in solution equals $a_P/3.270$. Even at concentrations of pentanol in water outside of this limit, the expression $a_P/3.270$ will provide a measure of the monomeric pentanol concentration.

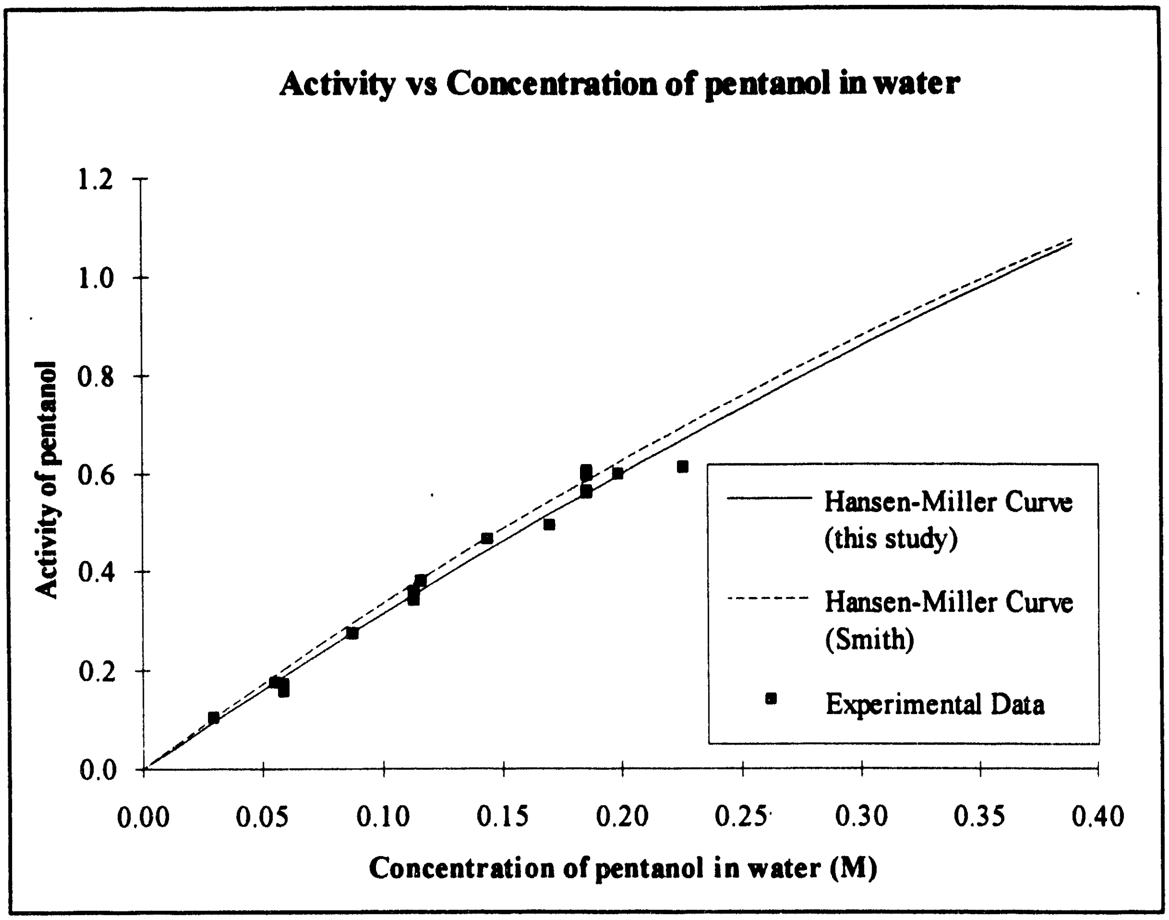


Figure 8 Hansen-Miller curves for pentanol in water.

The concentration of pentanol in the micelle must be the difference between the concentration of pentanol in solution, a known quantity, and the concentration of pentanol in the bulk solution, which is inferred from headspace measurements.

$$C_{P,mic} = C_{P,sol} - C_{P,bulk} \tag{7}$$

The mole fraction of pentanol in the micelle can be calculated from the concentration of pentanol in the micelle and the concentration of surfactant in the micelle. The concentration of surfactant in the micelle is the difference between the total surfactant concentration and the concentration of monomeric surfactant.

The effective monomeric concentration, or activity, of an ionic surfactant is lowered by the addition of organic solutes and by an increase in concentration of counterion in solution. This dependence of counterion concentration on surfactant activity is given by the Corrin/Harkins equation[5]:

$$\log C_{mon} = -\beta \log C_{Clfree} - \alpha \tag{8}$$

where α and β are empirical constants that are found by meausuring the CMC of a surfactant in the presence of different concentrations of electrolyte. Tipton measured α and β values for CPC[6]. β is related to the size of the surfactant head group and the nature of its hydrophobic group. Equation (8) can be used to calculate the concentration of counterions that are bound to the micelle. Because there are more variables than equations, two more expressions are needed before the C_{mon} can be calculated.

$$C_{surf,tot} = C_{mon} + C_{surf,mic} \tag{9}$$

$$C_{surf,tot} = C_{Cl,free} + \beta C_{surf,mic} \tag{10}$$

The Corrin-Harkins parameters used in the study are:

Surfactant	CMC	β	α
CPC	9.0E-4[7]	-0.73	-5.286
$C_{16}BzCl$	4.0E-4[8]	-0.73	-5.878
CTAB	9.2E-4[8]	-0.73	-5.253
$C_{14}Cl$	5.4E-3[9]	-0.70	-3.862
$C_{14}BzCl$	2.2E-3[9]	-0.70	-4.535

Equation (8) demonstrates that $C_{surf,mon}$ is considerably smaller than the uncorrected surfactant CMC.

Once the monomeric concentration of surfactant is found, the mole fraction of pentanol in the micelle can be calculated.

$$X_P = \frac{C_{P,mic}}{C_{P,mic} + (C_{surf,tot} - C_{mon})} \tag{11}$$

The solubilization constant, K_S, can now be calculated from the ratio of the mole fraction of pentanol in the micelle to the concentration of monomeric pentanol in the bulk solution. Note that K_S is not dimensionless, and as the results section will show, the value of K_S varies with a change in X_P.

$$K_S = \frac{X_P}{C_{P,mon}} \tag{12}$$

An important variable that can be inferred from X_P and the measured activity of pentanol is the activity coefficient of pentanol in the micelle.

$$\gamma_P = \frac{a_P}{X_P} \tag{13}$$

The activity coefficient measures the deviation of a solution component from the ideal behavior predicted if Raoult's law is obeyed. After finding the amount of pentanol in bulk solution and converting this number to units of molarity, one can calculate the distribution between the concentration of pentanol in bulk solution and the concentration of pentanol in vapor.

It should be noted that the partition coefficient of pentanol between the vapor and pentanol in bulk solution is defined here by:

$$K_{d0} = \frac{C_{P,mon}}{C_{P,vap}} \tag{14}$$

where the concentrations of pentanol in the two phases are monomer concentrations, rather than total concentrations. Figure 6 in Chapter 1 indicates that the equations defining both K_{d0} and K_S involve the monomeric form of pentanol. Only the knowledge of the self-association of pentanol in water is needed to correct the total aqueous concentration of pentanol for the presence of pentanol dimers and trimers. It is also worthwhile to note that both the numerator and denominator of equation (14) are directly related to a_P. Therefore, K_{d0} is independent of pentanol concentration and surfactant effects. The value of K_{d0} found in this experiment is 3308.

The dependence of K_S on X_P, the mole fraction of pentanol in the micelle, is an important phenomenon. It is from this relationship that the solubilizing effectiveness of a surfactant is expressed as a function of micellar composition. Simple algebraic equations are often used to fit data throughout a wide range of mole fractions. Previous studies[9,10] have shown that the following equation gives an excellent fit of solubilization data for polar solutes such as phenols and other aromatic solutes in ionic surfactant micelles. Although pentanol is not aromatic, the polar nature of the compound apparently leads to a similar dependence of K_S on X_P, so that the equation is valid for modelling the solubilization.

$$K_S = K_0(1 - BX_P)^2 \tag{15}$$

K_0 is the value of the solubilization constant at $X_P = 0$, and B is an constant found from the plot of $(K_S)^{1/2}$ versus X_P.

The effect of the presence of pentanol on the activity of surfactant can be inferred from the known value of B from equation (15)[11].

$$\ln \gamma_{surf} = \left(\frac{2}{1 - B}\right) \cdot [B \ln(1 - X_p) - \ln(1 - BX_p)] \tag{16}$$

Thus, the corrected monomeric surfactant concentration can be calculated from:

$$C'_{mon} = \gamma_{surf}(1 - X_p)C_{mon} \tag{17}$$

and used in equation (12) to recalculate K_S.

Appendix 2 contains a summary of factors that reduce the CMC of a single surfactant system.

Data Treatment for Binary Mixtures of Cationic Surfactants

The calculations required for determining solubilization constants for single surfactant systems are much simpler than the analogous calculations for a binary mixed surfactant system. In the mixture studies, an aqueous surfactant solution at a concentration above the CMC comprises both micelles and monomeric surfactant molecules. In a binary surfactant system, the micelles will be made up of both types of surfactants. A problem arises because the composition of the micelle does not depend solely on the ratio of surfactants added to the solution. For example, if equal molar amounts of two surfactants are present in solution, the ratio of surfactant molecules in micelles may not be 1:1, because the monomer concentrations of the two surfactants may differ[11]. Finding the values of the mole fractions of individual surfactants in the micelle and solubilization equilibrium constants for organic solutes in mixed micelles requires solving a system of many equations and many unknowns. The computer software programs SEQS[12] and MathCad[13] were employed to set up and solve these systems.

Before calculating the extent of solubilization of an organic solute in a binary surfactant mixture, one should consider the properties of the surfactant mixture itself. To begin, the concentration of each surfactant in the mixture is equal to the sum of the concentrations of the surfactant in micelle and monomeric form.

$$C_{surf1} = C_{mon1} + C_{mic1} \tag{18}$$

$$C_{surf2} = C_{mon2} + C_{mic2} \tag{19}$$

If it is possible to infer the individual monomer and micellar concentration terms in equations (18) and (19), then the mole fraction of each surfactant in the mixed micelle can be calculated from

$$X_{mic1} = \frac{C_{mic1}}{C_{mic1} + C_{mic2} + C_{P,mic}} \tag{20}$$

$$X_{mic2} = \frac{C_{mic2}}{C_{mic1} + C_{mic2} + C_{P,mic}} \tag{21}$$

The concentrations of pentanol and surfactants in the micelle are therefore simply related to the mole fraction of each surfactant in the micelle.

The CMC of an individual surfactant in a binary mixed surfactant system at a given mole fraction is related to both the CMC of that surfactant by itself, and to the concentration of counterions in solution[14]. This equation applies to surfactant mixtures with the same counterion, and is another application of the Corrin-Harkins equation. For all surfactants used in this project the counterion was chloride.

$$CMC_{surf1x} = \frac{(CMC_{surf1})^{\beta+1}}{(C_{Clfree})^{\beta}} \tag{22}$$

$$CMC_{surf2x} = \frac{(CMC_{surf2})^{\beta+1}}{(C_{Clfree})^{\beta}} \tag{23}$$

β is assumed to be the same counterion binding parameter used to calculate monomer concentrations for a single surfactant. Equations (22) and (23) are applied with the assumption that 70% to 73% of the surfactant counterions are bound to the Stern layer of the micelle, and the rest are "free" in solution[15].

Two additional equations must be included in the model. The first relates the total concentration of counterions in solution to the sum of the total concentrations of the surfactants. This reflects the one-to-one surfactant/counterion stoichiometric ratio. The second equation correlates the total concentration of counterions in solution to the sum of the concentration of free counterions and the portion of counterions bound to the micelles.

$$C_{Cltot} = C_{surf1} + C_{surf2} \tag{24}$$

$$C_{Cltot} = C_{Clfree} + \beta C_{mictot} \tag{25}$$

Additional equations are introduced to calculate the activity coefficient of the individual surfactants in the mixed micelle. As explained earlier in this section, the activity of a surfactant in solution changes in the presence of organic solutes. The activities of surfactants in a binary mixture also change due to interactions of surfactants with each other[16].

A common formula used to relate surfactant activity coefficients to the mole fraction of that surfactant in micelles is part of a surfactant mixing model introduced by Rubingh[17]. The activity coefficient for each surfactant in the micelle is calculated using the mole fraction found from equations (20) and (21), and an empirical parameter β_m, which is a measurement of the nonideality of the surfactant mixture. The β_m values for the two surfactant systems measured in the project are -0.50 for $C_{14}Cl + C_{14}BzCl$, and -0.8 for CPC + $C_{16}BzCl$[9].

$$\gamma_{surf1} = e^{\beta_m X^2_{mic2}} \tag{26}$$

$$\gamma_{surf2} = e^{\beta_m X^2_{mic1}} \tag{27}$$

The concentration of each monomeric surfactant in equilibrium with the mixed micelle can be inferred by multiplying the CMC calculated for the individual surfactants from equations (22) and (23) by the mole fraction of each surfactant in the micelle and the activity coefficients calculated by equations (26) and (27). As in the case of single surfactant systems, the presence of pentanol will cause an additional lowering of the monomer concentration of surfactant in solution. In binary surfactant mixtures, this correction is taken into account by calculating the mole fraction of each surfactant in the micelle. All of the mole fraction calculations require knowledge of the concentrations of surfactant 1, surfactant 2, and pentanol in the micelle. Thus:

$$C_{mon1} = CMC_{surf1x} \cdot X_{mic1} \cdot \gamma_{surf1} \tag{29}$$

$$C_{mon2} = CMC_{surf2x} \cdot X_{mic2} \cdot \gamma_{surf2} \tag{28}$$

Finally, the monomer concentration of each surfactant is subtracted from the total concentration of surfactant in solution to yield the concentration of each surfactant in micellar form. Adding these values together gives the total concentration of surfactant in micelles. This value is used to calculate the mole fraction of pentanol in the micelle.

$$X_P = \frac{C_{P,mic}}{C_{P,mic} + C_{mic1} + C_{mic2}} \tag{30}$$

Note the similarity between equation (30) and equations (20) and (21). After X_P is calculated, the same equations for the single surfactant systems are used to calculate values of γ_P, K_S, and the rest of the required values. A summary of factors that act to lower the monomer concentration of a surfactant in solution is located in Appendix 2. A sample printout of a MathCad calculation for a binary surfactant system is included in Appendix 3.

REFERENCES

1. Hewitt, A.; Mlyares, P.; Leggett, D.; Jenkins, T. *Environs. Sci. Technol.* **1992**, *26*, 1932-1938.
2. Butler, J.; Ramchandani, C.; Thomson, D. *J. Chem. Soc.* **1935**, *138*, 280-285.
3. Rehfeld, D. *J. Phys. Chem.* **1971**, *75*, 3905-3907.
4. Smith, G. Ph.D. Dissertation, University of Oklahoma, Norman, OK, 1989.
5. Corrin, M.; Harkins, W. *J. Am. Chem. Soc.* **1947**, *69*, 683-688.
6. Tipton, R. M. S. Thesis, University of Oklahoma, Norman, OK, 1989.
7. Rosen, M. "Surfactants and Interfacial Phenomena"; John Wiley and Sons: New York, 1989; p 122.
8. Treiner, C.; Makayssi, A. *Langmiur* **1992**, *8*, 794-800.
9. Uchiyama, H.; Christian, S.; Scamehorn, J.; Abe, M.; Ogino, K. *Langmuir* **1991**, *7*, 95-100.
10. Lee, B.; Christian, S.; Tucker, E.; Scamehorn, J. *Langmuir* **1990**, *6*, 230-235.
11. Scamehorn, J. In "Phenomena in Mixed Surfactant Systems"; Scamehorn, J. Ed.; American Chemical Society: Washington DC, 1986; Chapter 1.
12. *SEQS*, computer software, CET Research Group Ltd., 1991.
13. *MathCad 3.1*, computer software, MathSoft Inc., 1992.
14. Barry, B.; Morrison, J.; Russell, J. *J. Coll. Interface Sci.* **1970**, *33*, 554-561.
15. Rathman, J.; Scamehorn, J. *J. Phys. Chem.* **1984**, *88*, 5807-5816.
16. Shinoda, K. *J. Phys. Chem.* **1954**, *58*, 541-544.
17. Rubingh, D. In "Solution Chemistry of Surfactants"; Mittal, K., Ed.; Plenum Press: New York, 1979; Vol. I, p 37.

Chapter 3

Results

The tables on the following pages show the results of headspace chromatography analysis for CPC, CTAB, $C_{16}BzCl$, $C_{14}BzCl$, and $C_{14}Cl$, and for the mixtures CPC + $C_{16}BzCl$ and $C_{14}Cl$ + $C_{14}BzCl$.

A table of uncertainties associated with pentanol concentration follows each surfactant data set. The largest source of error in this experiment stems from the signal sensitivity of the gas chromatograph. The relative uncertainty in a measurement of pentanol vapor is larger when measuring solutions with low pentanol concentrations than when measuring higher concentrations. Errors are listed according to concentration of pentanol in solution for single surfactant systems. Pentanol concentration is constant for the binary surfactant systems, and errors are listed at the bottom of each column.

Further discussion of the causes and implications of these errors are addressed in chapter 4.

Table 1

Solubilization data for pentanol in hexadecylpyridinium chloride (CPC).

Surfactant concentration 0.05M

Surfactant CMC 9.0E-04M

Note: All concentration units are molar, all vapor pressures are torr, all amounts are moles. See Appendix 1 for symbol definitions.

$C_{P,tot}$	a_P	P_P	$n_{P,vap}$	$n_{P,sol}$	$C_{P,sol}$	$C_{P,bulk}$
9.405E-03	1.454E-02	2.457E-02	2.687E-08	1.881E-04	9.403E-03	4.454E-03
9.405E-03	1.669E-02	2.820E-02	3.085E-08	1.881E-04	9.403E-03	5.114E-03
9.405E-03	1.502E-02	2.539E-02	2.777E-08	1.881E-04	9.403E-03	4.603E-03
1.618E-02	2.641E-02	4.462E-02	4.881E-08	3.235E-04	1.617E-02	8.103E-03
1.618E-02	2.821E-02	4.768E-02	5.216E-08	3.235E-04	1.617E-02	8.659E-03
1.618E-02	2.775E-02	4.690E-02	5.130E-08	3.235E-04	1.617E-02	8.517E-03
2.246E-02	3.951E-02	6.677E-02	7.304E-08	4.491E-04	2.246E-02	1.214E-02
2.246E-02	4.064E-02	6.867E-02	7.513E-08	4.491E-04	2.246E-02	1.249E-02
2.246E-02	3.929E-02	6.640E-02	7.264E-08	4.491E-04	2.246E-02	1.208E-02
3.501E-02	6.916E-02	1.169E-01	1.278E-07	7.000E-04	3.500E-02	2.134E-02
3.501E-02	6.655E-02	1.125E-01	1.230E-07	7.000E-04	3.500E-02	2.053E-02
3.501E-02	5.855E-02	9.894E-02	1.082E-07	7.000E-04	3.500E-02	1.804E-02
5.439E-02	9.538E-02	1.612E-01	1.763E-07	1.088E-03	5.439E-02	2.953E-02
5.439E-02	1.041E-01	1.759E-01	1.924E-07	1.088E-03	5.439E-02	3.227E-02
5.439E-02	1.107E-01	1.871E-01	2.047E-07	1.088E-03	5.438E-02	3.435E-02
8.031E-02	1.522E-01	2.572E-01	2.814E-07	1.606E-03	8.030E-02	4.750E-02
8.031E-02	1.648E-01	2.785E-01	3.047E-07	1.606E-03	8.030E-02	5.151E-02
8.031E-02	1.501E-01	2.536E-01	2.774E-07	1.606E-03	8.030E-02	4.681E-02
1.228E-01	2.416E-01	4.083E-01	4.466E-07	2.456E-03	1.228E-01	7.632E-02
1.228E-01	2.460E-01	4.157E-01	4.548E-07	2.456E-03	1.228E-01	7.776E-02
1.228E-01	2.564E-01	4.333E-01	4.740E-07	2.456E-03	1.228E-01	8.117E-02
1.861E-01	3.783E-01	6.393E-01	6.994E-07	3.721E-03	1.861E-01	1.219E-01
1.861E-01	3.841E-01	6.490E-01	7.100E-07	3.721E-03	1.861E-01	1.239E-01
1.861E-01	4.193E-01	7.085E-01	7.751E-07	3.721E-03	1.861E-01	1.360E-01
2.506E-01	5.177E-01	8.749E-01	9.571E-07	5.010E-03	2.505E-01	1.705E-01
2.506E-01	5.053E-01	8.539E-01	9.342E-07	5.010E-03	2.505E-01	1.661E-01
2.506E-01	5.335E-01	9.015E-01	9.862E-07	5.010E-03	2.505E-01	1.761E-01

Table 1 con't.

Solubilization data for 0.05M CPC.

$C_{P,tot}$	$C_{P,mic}$	X_P	K_S (M^{-1})	γ_P	$n_{P,bulk}$	$C_{P,mon}$
9.405E-03	4.949E-03	9.026E-02	2.030E+01	1.611E-01	8.908E-05	4.446E-03
9.405E-03	4.290E-03	7.919E-02	1.552E+01	2.107E-01	1.023E-04	5.103E-03
9.405E-03	4.800E-03	8.778E-02	1.910E+01	1.711E-01	9.206E-05	4.594E-03
1.618E-02	8.072E-03	1.393E-01	1.724E+01	1.896E-01	1.621E-04	8.075E-03
1.618E-02	7.515E-03	1.309E-01	1.517E+01	2.155E-01	1.732E-04	8.628E-03
1.618E-02	7.657E-03	1.331E-01	1.568E+01	2.085E-01	1.703E-04	8.487E-03
2.246E-02	1.031E-02	1.713E-01	1.417E+01	2.306E-01	2.429E-04	1.208E-02
2.246E-02	9.963E-03	1.665E-01	1.339E+01	2.441E-01	2.499E-04	1.243E-02
2.246E-02	1.038E-02	1.722E-01	1.433E+01	2.281E-01	2.415E-04	1.202E-02
3.501E-02	1.366E-02	2.150E-01	1.016E+01	3.217E-01	4.268E-04	2.115E-02
3.501E-02	1.447E-02	2.249E-01	1.105E+01	2.959E-01	4.105E-04	2.035E-02
3.501E-02	1.696E-02	2.537E-01	1.416E+01	2.308E-01	3.608E-04	1.791E-02
5.439E-02	2.485E-02	3.326E-01	1.140E+01	2.868E-01	5.907E-04	2.917E-02
5.439E-02	2.212E-02	3.072E-01	9.645E+00	3.389E-01	6.454E-04	3.183E-02
5.439E-02	2.003E-02	2.865E-01	8.458E+00	3.864E-01	6.870E-04	3.386E-02
8.031E-02	3.280E-02	3.967E-01	8.517E+00	3.837E-01	9.500E-04	4.655E-02
8.031E-02	2.879E-02	3.659E-01	7.257E+00	4.504E-01	1.030E-03	5.040E-02
8.031E-02	3.349E-02	4.017E-01	8.517E+00	3.736E-01	9.362E-04	4.589E-02
1.228E-01	4.647E-02	4.823E-01	6.524E+00	5.009E-01	1.526E-03	7.389E-02
1.228E-01	4.504E-02	4.745E-01	6.303E+00	5.185E-01	1.555E-03	7.523E-02
1.228E-01	4.162E-02	4.549E-01	5.797E+00	5.637E-01	1.623E-03	7.842E-02
1.861E-01	6.415E-02	5.626E-01	4.860E+00	6.725E-01	2.438E-03	1.157E-02
1.861E-01	6.218E-02	5.549E-01	4.721E+00	6.922E-01	2.477E-03	1.175E-02
1.861E-01	5.010E-02	5.011E-01	3.905E+00	8.368E-01	2.719E-03	1.282E-02
2.506E-01	8.004E-02	6.161E-01	3.889E+00	8.404E-01	3.410E-03	1.583E-02
2.506E-01	8.445E-02	6.287E-01	4.066.E+00	8.038E-01	3.321E-03	1.545E-02
2.506E-01	7.441E-02	5.987E-01	3.667E+00	8.911E-01	3.522E-03	1.631E-02

Table 1 con't.

Uncertainties in data for pentanol in 0.05M CPC listed according to total pentanol concentration in solution.

$C_{P,tot}$	$\delta\ a_P$	$\delta\ P_P$	$\delta\ n_{P,vap}$	$\delta\ n_{P,sol}$	$\delta\ C_{P,sol}$	$\delta\ C_{P,bulk}$
9.4E-03	1.4E-03	2.3E-03	2.6E-09	2.6E-09	1.3E-07	4.2E-04
1.6E-02	2.2E-03	3.8E-03	4.2E-09	4.2E-09	2.1E-07	6.9E-04
2.2E-02	2.6E-03	4.3E-03	4.7E-09	4.7E-09	2.4E-07	7.9E-04
3.5E-02	4.6E-03	7.8E-03	8.5E-09	8.5E-09	4.3E-07	1.4E-03
5.4E-02	8.8E-03	1.5E-02	1.6E-08	1.6E-08	8.2E-07	2.8E-03
8.0E-02	1.2E-02	2.0E-02	2.2E-08	2.2E-08	1.1E-06	3.8E-03
1.2E-01	1.6E-02	2.7E-02	3.0E-08	3.0E-08	1.5E-06	5.3E-03
1.9E-01	2.3E-02	4.0E-02	4.3E-08	4.3E-08	2.2E-06	8.0E-03
2.5E-01	2.4E-02	4.0E-02	4.4E-08	4.4E-08	2.2E-06	8.4E-03

$C_{P,tot}$	$\delta\ C_{P,mic}$	$\delta\ X_P$	$\delta\ K_S\ (M^{-1})$	$\delta\ \gamma_P$	$\delta\ n_{P,bulk}$	$\delta\ C_{P,mon}$
9.4E-03	3.0E-02	7.1E-03	3.3E+00	7.1E-03	8.5E-06	4.2E-04
1.6E-02	3.3E-02	1.0E-02	2.6E+00	1.0E-02	1.4E-05	6.9E-04
2.2E-02	3.0E-02	1.1E-02	1.8E+00	1.1E-02	1.6E-05	7.8E-04
3.5E-02	3.9E-02	1.7E-02	1.8E+00	1.7E-02	2.9E-05	1.4E-03
5.4E-02	5.5E-02	2.6E-02	1.8E+00	2.6E-02	5.5E-05	2.7E-03
8.0E-02	7.0E-02	3.1E-02	1.2E+00	3.1E-02	7.7E-05	3.7E-03
1.2E-01	6.9E-02	3.0E-02	7.9E-01	3.0E-02	1.1E-04	4.9E-03
1.9E-01	9.1E-02	3.4E-02	5.5E-01	3.4E-02	1.6E-04	7.2E-03
2.5E-01	7.0E-02	2.4E-02	3.4E-01	2.4E-02	1.7E-04	7.2E-03

Experimental data and non-linear least squares analysis of the function

$K = K_0(1 - BX_P)^2$ for 0.05M CPC.

$B = 0.969 \pm .051$ $K_0 = 20.4 \pm 0.8\ M^{-1}$

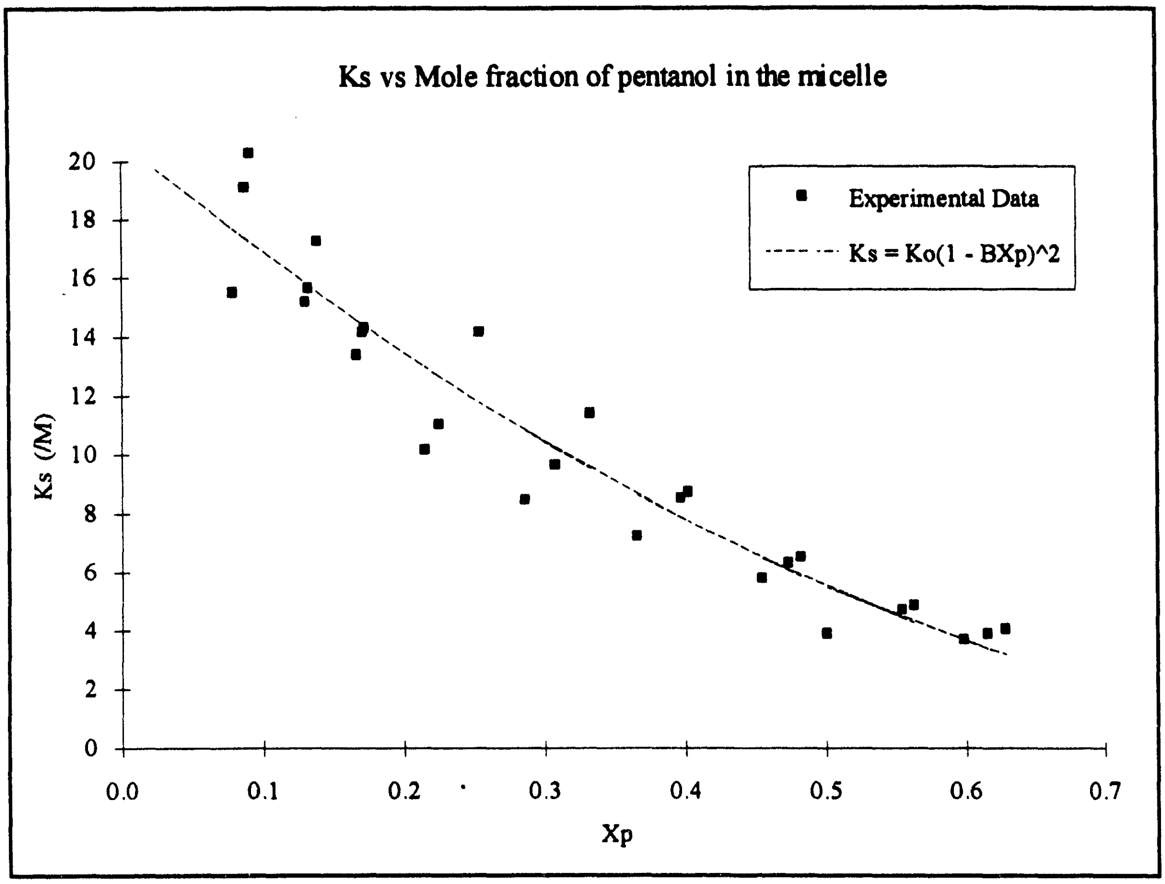


Figure 9 K_S versus X_P data for 0.05M CPC.

Table 2

Solubilization data for pentanol in hexadecyltrimethylammonium bromide (CTAB).

Surfactant concentration 0 .05M

Surfactant CMC 9.2E-04M

Note: All concentration units are molar, all vapor pressures are torr, all amounts are moles. See Appendix 1 for symbol definitions.

$C_{P,tot}$	a_P	P_P	$n_{P,vap}$	$n_{P,sol}$	$C_{P,sol}$	$C_{P,bulk}$
2.223E-02	3.872E-02	6.544E-02	7.159E-08	4.446E-04	2.223E-02	1.190E-02
2.223E-02	4.374E-02	7.391E-02	8.085E-08	4.446E-04	2.223E-02	1.345E-02
4.408E-02	8.115E-02	1.371E-01	1.500E-07	8.815E-04	4.408E-02	2.508E-02
4.408E-02	8.048E-02	1.360E-01	1.488E-07	8.815E-04	4.408E-02	2.487E-02
5.631E-02	1.123E-01	1.897E-01	2.075E-07	1.126E-03	5.630E-02	3.484E-02
5.631E-02	1.065E-01	1.800E-01	1.970E-07	1.126E-03	5.630E-02	3.304E-02
8.936E-02	1.694E-01	2.862E-01	3.131E-07	1.787E-03	8.934E-02	5.297E-02
8.936E-02	1.658E-01	2.802E-01	3.065E-07	1.787E-03	8.934E-02	5.182E-02
1.133E-01	2.029E-01	3.429E-01	3.751E-07	2.266E-03	1.133E-01	6.376E-02
1.133E-01	2.097E-01	3.544E-01	3.877E-07	2.266E-03	1.133E-01	6.595E-02
1.363E-01	2.619E-01	4.425E-01	4.841E-07	2.726E-03	1.363E-01	8.296E-02
1.363E-01	2.651E-01	4.480E-01	4.901E-07	2.726E-03	1.363E-01	8.402E-02
1.704E-01	3.157E-01	5.335E-01	5.837E-07	3.408E-03	1.704E-01	1.008E-01
1.704E-01	3.338E-01	5.640E-01	6.170E-07	3.408E-03	1.704E-01	1.068E-01
1.812E-01	3.532E-01	5.969E-01	6.530E-07	3.624E-03	1.812E-01	1.134E-01
1.812E-01	3.596E-01	6.077E-01	6.648E-07	3.624E-03	1.812E-01	1.156E-01
2.274E-01	4.333E-01	7.322E-01	8.011E-07	4.548E-03	2.274E-01	1.408E-01
2.274E-01	4.565E-01	7.713E-01	8.438E-07	4.548E-03	2.274E-01	1.489E-01
2.277E-01	4.393E-01	7.423E-01	8.121E-07	4.554E-03	2.277E-01	1.429E-01
2.277E-01	4.396E-01	7.428E-01	8.126E-07	4.554E-03	2.277E-01	1.430E-01
2.832E-01	5.478E-01	9.257E-01	1.013E-06	5.662E-03	2.831E-01	1.813E-01
2.832E-01	5.928E-01	1.002E+00	1.096E-06	5.662E-03	2.831E-01	1.976E-01
3.397E-01	6.407E-01	1.083E+00	1.184E-06	6.792E-03	3.396E-01	2.153E-01
3.397E-01	6.815E-01	1.152E+00	1.260E-06	6.792E-03	3.396E-01	2.306E-01
3.870E-01	6.817E-01	1.152E+00	1.260E-06	7.738E-03	3.869E-01	2.307E-01
3.870E-01	7.083E-01	1.197E+00	1.309E-06	7.738E-03	3.869E-01	2.409E-01
4.538E-01	7.689E-01	1.299E+00	1.421E-06	9.075E-03	4.537E-01	2.644E-01
4.538E-01	7.596E-01	1.284E+00	1.404E-06	9.075E-03	4.537E-01	2.607E-01
5.092E-01	8.257E-01	1.395E+00	1.526E-06	1.018E-02	5.091E-01	2.869E-01
5.092E-01	8.114E-01	1.371E+00	1.500E-06	1.018E-02	5.091E-01	2.812E-01

Table 2 con't.

Solubilization data for 0.05M CTAB.

$C_{P,tot}$	$C_{P,mic}$	X_P	K_S (M^{-1})	γ_P	$n_{P,bulk}$	$C_{P,mon}$
2.223E-02	1.033E-02	1.715E-01	1.448E+01	2.258E-01	2.380E-04	1.184E-02
2.223E-02	8.779E-03	1.496E-01	1.119E+01	2.923E-01	2.690E-04	1.337E-02
4.408E-02	1.900E-02	2.757E-01	1.111E+01	2.943E-01	5.016E-04	2.482E-02
4.408E-02	1.921E-02	2.779E-01	1.129E+01	2.896E-01	4.974E-04	2.461E-02
5.631E-02	2.145E-02	3.006E-01	8.755E+00	3.735E-01	6.968E-04	3.433E-02
5.631E-02	2.326E-02	3.178E-01	9.754E+00	3.353E-01	6.608E-04	3.258E-02
8.936E-02	3.637E-02	4.214E-01	8.135E+00	4.020E-01	1.059E-03	5.180E-02
8.936E-02	3.752E-02	4.290E-01	8.461E+00	3.865E-01	1.036E-03	5.070E-02
1.133E-01	4.952E-02	4.978E-01	8.022E+00	4.076E-01	1.275E-03	6.206E-02
1.133E-01	4.733E-02	4.865E-01	7.586E+00	4.310E-01	1.319E-03	6.413E-02
1.363E-01	5.337E-02	5.165E-01	6.450E+00	5.070E-01	1.659E-03	8.008E-02
1.363E-01	5.230E-02	5.115E-01	6.309E+00	5.183E-01	1.680E-03	8.107E-02
1.704E-01	6.960E-02	5.821E-01	6.029E+00	5.424E-01	2.016E-03	9.655E-02
1.704E-01	6.355E-02	5.598E-01	5.485E+00	5.962E-01	2.137E-03	1.021E-01
1.812E-01	6.780E-02	5.757E-01	5.329E+00	6.136E-01	2.268E-03	1.080E-01
1.812E-01	6.565E-02	5.678E-01	5.163E+00	6.333E-01	2.311E-03	1.100E-01
2.274E-01	8.658E-02	6.340E-01	4.784E+00	6.835E-01	2.816E-03	1.325E-01
2.274E-01	7.852E-02	6.111E-01	4.378E+00	7.470E-01	2.977E-03	1.396E-01
2.277E-01	8.483E-02	6.292E-01	4.684E+00	6.981E-01	2.857E-03	1.343E-01
2.277E-01	8.473E-02	6.290E-01	4.679E+00	6.989E-01	2.860E-03	1.344E-01
2.832E-01	1.018E-01	6.708E-01	4.004E+00	8.167E-01	3.625E-03	1.675E-01
2.832E-01	8.549E-02	6.311E-01	3.481E+00	9.393E-01	3.952E-03	1.813E-01
3.397E-01	1.243E-01	7.132E-01	3.640E+00	8.984E-01	4.306E-03	1.959E-01
3.397E-01	1.090E-01	6.855E-01	3.290E+00	9.941E-01	4.613E-03	2.084E-01
3.870E-01	1.562E-01	7.575E-01	3.634E+00	8.999E-01	4.615E-03	2.085E-01
3.870E-01	1.460E-01	7.449E-01	3.439E+00	9.508E-01	4.817E-03	2.166E-01
4.538E-01	1.894E-01	7.911E-01	3.365E+00	9.719E-01	5.287E-03	2.351E-01
4.538E-01	1.930E-01	7.942E-01	3.419E+00	9.564E-01	5.215E-03	2.323E-01
5.092E-01	2.222E-01	8.163E-01	3.233E+00	1.011E+00	5.739E-03	2.525E-01
5.092E-01	2.279E-01	8.201E-01	3.305E+00	9.894E-01	5.624E-03	2.481E-01

Table 2 con't.

Uncertainties in data for pentanol in 0.05M CTAB listed according to total pentanol concentration in solution.

$C_{P,tot}$	$\delta\ a_P$	$\delta\ P_P$	$\delta\ n_{P,vap}$	$\delta\ n_{P,sol}$	$\delta\ C_{P,sol}$	$\delta\ C_{P,bulk}$
2.2E-02	3.4E-03	5.7E-03	6.3E-09	6.3E-09	3.1E-07	1.0E-03
5.6E-02	6.6E-03	1.1E-02	1.2E-08	1.2E-08	6.1E-07	2.1E-03
1.1E-01	1.1E-02	1.9E-02	2.0E-08	2.0E-08	1.0E-06	3.5E-03
1.7E-01	2.1E-02	3.5E-02	3.9E-08	3.9E-08	1.9E-06	6.8E-03
2.3E-01	2.6E-02	4.4E-02	4.8E-08	4.8E-08	2.4E-06	8.8E-03
2.8E-01	3.1E-02	5.2E-02	5.7E-08	5.7E-08	2.9E-06	1.1E-02
3.4E-01	3.3E-02	5.5E-02	6.1E-08	6.1E-08	3.0E-06	1.2E-02
3.9E-01	3.1E-02	5.3E-02	5.8E-08	5.8E-08	2.9E-06	1.1E-02
4.5E-01	2.0E-02	3.4E-02	3.7E-08	3.7E-08	2.2E-06	7.4E-03
5.1E-01	1.6E-02	2.7E-02	2.9E-08	3.4E-08	1.5E-06	5.9E-03

$C_{P,tot}$	$\delta\ C_{P,mic}$	$\delta\ X_P$	$\delta\ K_S\ (M^{-1})$	$\delta\ \gamma_P$	$\delta\ n_{P,bulk}$	$\delta\ C_{P,mon}$
2.2E-02	2.9E-02	1.4E-02	3.4E+00	1.4E-02	2.1E-05	1.0E-03
5.6E-02	2.7E-02	1.6E-02	1.8E+00	1.6E-02	4.1E-05	2.0E-03
1.1E-01	2.6E-02	1.3E-02	1.1E+00	1.3E-02	7.0E-05	3.3E-03
1.7E-01	4.3E-02	1.8E-02	9.1E-01	1.8E-02	1.4E-04	6.4E-03
2.3E-01	5.0E-02	1.7E-02	6.1E-01	1.7E-02	1.8E-04	7.9E-03
2.8E-01	5.7E-02	1.6E-02	4.7E-01	1.6E-02	2.2E-04	9.5E-03
3.4E-01	5.3E-02	1.2E-02	3.8E-01	1.2E-02	2.3E-04	1.0E-02
3.9E-01	4.6E-02	8.6E-03	3.3E-01	8.6E-03	2.3E-04	9.6E-03
4.5E-01	2.8E-02	4.1E-03	1.7E-01	4.1E-03	1.5E-04	6.2E-03
5.1E-01	2.1E-02	2.6E-03	1.2E-01	2.5E-03	1.2E-04	4.8E-03

Experimental data and non-linear least squares analysis of the function

$K = K_0(1 - BX_P)^2$ for 0.05M CTAB.

$B = 0.728 \pm 0.025$ $K_0 = 16.6 \pm 0.6$ M-1

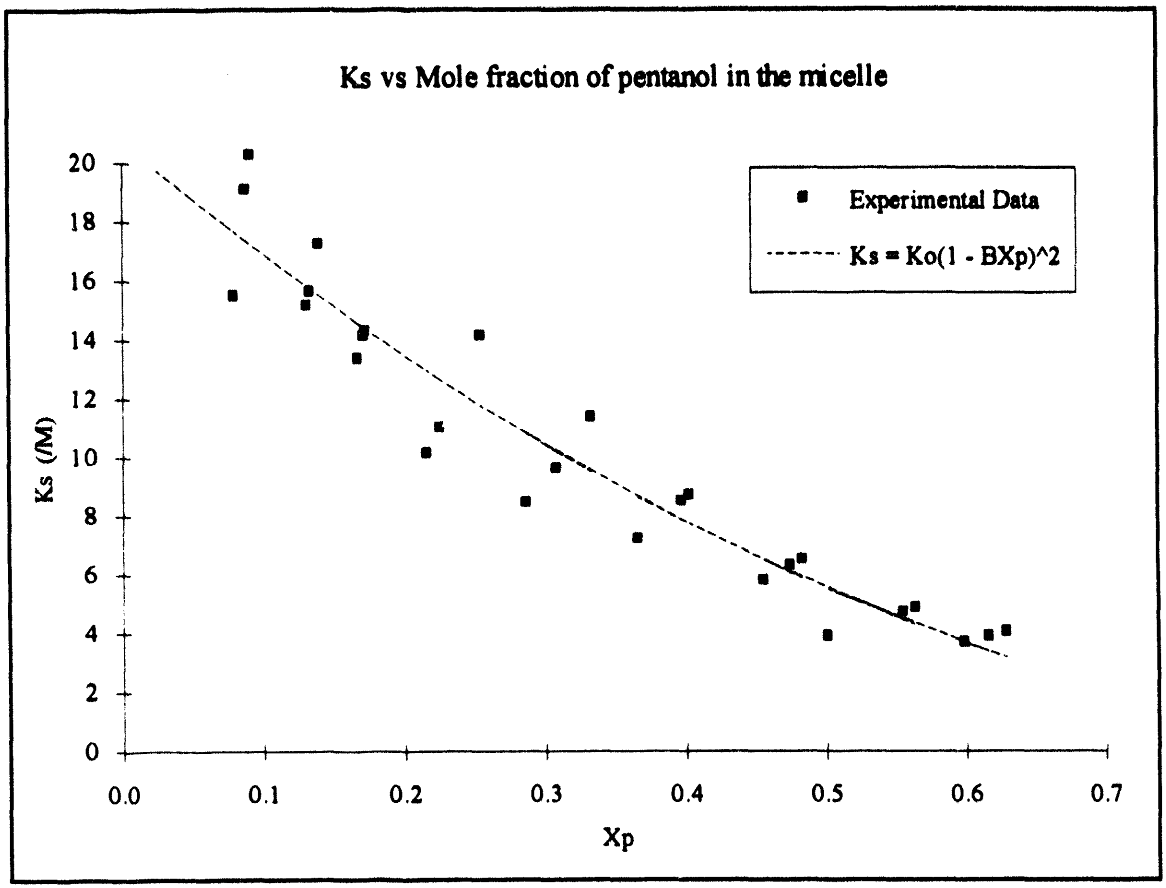


Figure 10 K_S versus X_P data for 0.05M CTAB.

Table 3

Solubilization data for pentanol in $C_{16}BzCl$.

Surfactant concentration 0.01M

Surfactant CMC 4.0E-04M

Note: All concentration units are molar, all vapor pressures are torr, all amounts are moles. See Appendix 1 for symbol definitions.

$C_{P,tot}$	a_P	P_P	$n_{P,vap}$	$n_{P,sol}$	$C_{P,sol}$	$C_{P,bulk}$
6.432E-03	1.893E-02	3.200E-02	3.500E-08	1.286E-04	6.430E-03	5.805E-03
6.432E-03	1.771E-02	2.993E-02	3.274E-08	1.286E-04	6.430E-03	5.428E-03
1.165E-02	3.398E-02	5.743E-02	6.282E-08	2.329E-04	1.165E-02	1.044E-02
1.165E-02	3.400E-02	5.745E-02	6.285E-08	2.329E-04	1.165E-02	1.044E-02
1.716E-02	4.846E-02	8.189E-02	8.959E-08	3.432E-04	1.716E-02	1.491E-02
1.716E-02	4.718E-02	7.973E-02	8.722E-08	3.432E-04	1.716E-02	1.452E-02
2.305E-02	6.183E-02	1.045E-01	1.143E-07	4.609E-04	2.305E-02	1.906E-02
3.499E-02	9.721E-02	1.643E-01	1.797E-07	6.995E-04	3.498E-02	3.011E-02
3.499E-02	9.741E-02	1.646E-01	1.801E-07	6.995E-04	3.498E-02	3.017E-02
5.872E-02	1.636E-01	2.764E-01	3.024E-07	1.174E-03	5.870E-02	5.112E-02
1.142E-01	3.066E-01	5.181E-01	5.667E-07	2.284E-03	1.142E-01	9.775E-02
1.142E-01	3.200E-01	5.408E-01	5.916E-07	2.284E-03	1.142E-01	1.022E-01
1.142E-01	3.094E-01	5.229E-01	5.720E-07	2.284E-03	1.142E-01	9.870E-02
1.995E-01	4.949E-01	8.364E-01	9.150E-07	3.990E-03	1.995E-01	1.624E-01
1.995E-01	4.859E-01	8.211E-01	8.982E-07	3.990E-03	1.995E-01	1.592E-01
1.995E-01	4.930E-01	8.331E-01	9.114E-07	3.990E-03	1.995E-01	1.617E-01
2.891E-01	7.294E-01	1.233E+00	1.348E-06	5.780E-03	2.890E-01	2.490E-01
2.891E-01	6.526E-01	1.103E+00	1.206E-06	5.780E-03	2.890E-01	2.198E-01
2.891E-01	7.370E-01	1.245E+00	1.363E-06	5.780E-03	2.890E-01	2.519E-01

Table 3 con't.

Solubilization data for 0.01M $C_{16}BzCl$.

$C_{P,tot}$	$C_{P,mic}$	X_P	K_s (M^{-1})	γ_P	$n_{P,bulk}$	$C_{P,mon}$
6.432E-03	6.254E-04	5.941E-02	1.023E+01	3.187E-01	1.161E-04	5.790E-03
6.432E-03	1.002E-03	9.187E-02	1.692E+01	1.928E-01	1.086E-04	5.416E-03
1.165E-02	1.209E-03	1.088E-01	1.043E+01	3.122E-01	2.088E-04	1.039E-02
1.165E-02	1.205E-03	1.085E-01	1.039E+01	3.134E-01	2.088E-04	1.040E-02
1.716E-02	2.245E-03	1.848E-01	1.239E+01	2.622E-01	2.983E-04	1.482E-02
1.716E-02	2.642E-03	2.106E-01	1.451E+01	2.240E-01	2.903E-04	1.443E-02
2.305E-02	3.986E-03	2.870E-01	1.506E+01	2.155E-01	3.812E-04	1.891E-02
3.499E-02	4.870E-03	3.297E-01	1.095E+01	2.949E-01	6.021E-04	2.973E-02
3.499E-02	4.808E-03	3.268E-01	1.083E+01	2.980E-01	6.034E-04	2.979E-02
5.872E-02	7.587E-03	4.338E-01	8.486E+00	3.771E-01	1.022E-03	5.002E-02
1.142E-01	1.645E-02	6.243E-01	6.387E+00	4.911E-01	1.955E-03	9.375E-02
1.142E-01	1.196E-02	5.470E-01	5.350E+00	5.851E-01	2.045E-03	9.787E-02
1.142E-01	1.551E-02	6.103E-01	6.183E+00	5.070E-01	1.974E-03	9.462E-02
1.995E-01	3.709E-02	7.893E-01	4.861E+00	6.271E-01	3.248E-03	1.514E-02
1.995E-01	4.029E-02	8.027E-01	5.043E+00	6.053E-01	3.194E-03	1.486E-02
1.995E-01	3.777E-02	7.923E-01	4.899E+00	6.223E-01	3.234E-03	1.508E-02
2.891E-01	4.000E-02	8.016E-01	3.219E+00	9.100E-01	4.980E-03	2.231E-02
2.891E-01	6.925E-02	8.749E-01	3.981E+00	7.459E-01	4.395E-03	1.996E-02
2.891E-01	3.706E-02	7.892E-01	3.132E+00	9.340E-01	5.039E-03	2.254E-02

Table 3 con't.

Uncertainties in data for pentanol in 0.01M C_{16}BzCl listed according to total pentanol concentration in solution.

$C_{P,tot}$	δ a_P	δ P_P	δ $n_{P,vap}$	δ $n_{P,sol}$	δ $C_{P,sol}$	δ $C_{P,bulk}$
6.4E-03	1.1E-03	1.8E-03	2.0E-09	2.0E-09	1.0E-07	3.3E-04
1.2E-02	1.8E-03	3.0E-03	3.3E-09	3.3E-09	1.6E-07	5.5E-04
1.7E-02	2.1E-03	3.5E-03	3.8E-09	3.8E-09	1.9E-07	6.4E-04
2.3E-02	3.2E-03	5.4E-03	5.9E-09	5.9E-09	2.9E-07	9.9E-04
3.5E-02	3.7E-03	6.3E-03	6.8E-09	6.8E-09	3.4E-07	1.2E-03
5.9E-02	1.1E-02	1.8E-02	2.0E-08	2.0E-08	9.9E-07	3.4E-03
1.1E-01	1.1E-02	1.8E-02	2.0E-08	2.0E-08	9.8E-07	3.5E-03
2.0E-01	1.8E-02	3.0E-02	3.2E-08	3.2E-08	1.6E-06	6.0E-03
2.9E-01	3.9E-02	6.6E-02	7.3E-08	7.3E-08	3.6E-06	1.4E-02

$C_{P,tot}$	δ $C_{P,mic}$	δ X_P	δ K_S (M^{-1})	δ γ_P	δ $n_{P,bulk}$	δ $C_{P,mon}$
6.4E-03	1.5E-01	6.3E-03	1.7E+00	6.3E-03	6.6E-06	3.3E-04
1.2E-02	1.0E-01	9.6E-03	1.6E+00	9.6E-03	1.1E-05	5.4E-04
1.7E-02	7.9E-02	1.1E-02	1.3E+00	1.1E-02	1.3E-05	6.3E-04
2.3E-02	8.0E-02	1.5E-02	1.4E+00	1.5E-02	2.0E-05	9.7E-04
3.5E-02	6.8E-02	1.6E-02	9.7E-01	1.6E-02	2.3E-05	1.1E-03
5.9E-02	1.0E-01	3.6E-02	1.5E+00	3.6E-02	6.8E-05	3.3E-03
1.1E-01	8.3E-02	2.8E-02	5.2E-01	2.8E-02	7.0E-05	3.2E-03
2.0E-01	6.1E-02	2.3E-02	3.7E-01	2.3E-02	1.2E-04	5.4E-03
2.9E-01	1.1E-01	3.6E-02	4.4E-01	3.6E-02	2.9E-04	1.2E-02

Experimental data and non-linear least squares analysis of the function
$K = K_0(1 - BX_P)^2$ for 0.01M $C_{16}BzCl$.
B = 0.534 ± 0.068 **K_0** = 14.9 ± 1.1 M^{-1}

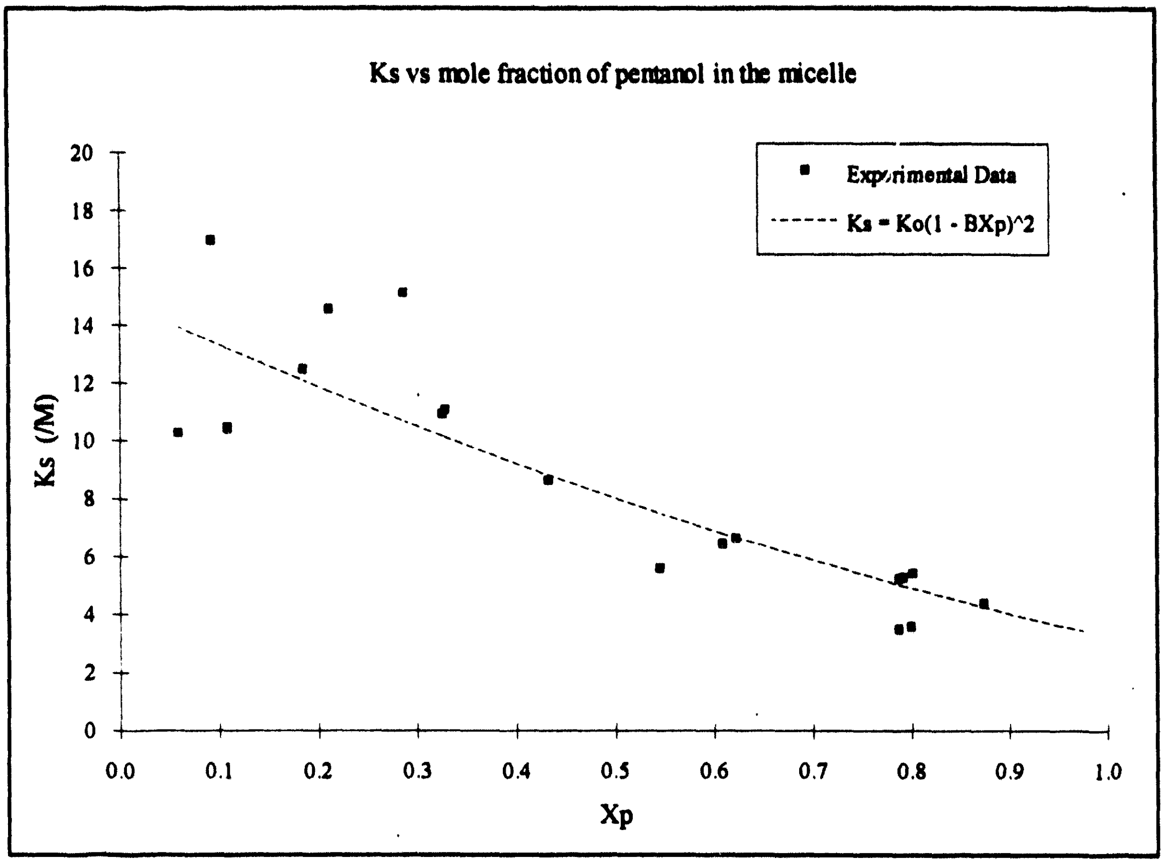


Figure 11 K_S versus X_P data for 0.01M $C_{16}BzCl$.

Table 4

Solubilization data for pentanol in $C_{16}BzCl$.

Surfactant concentration 0.05M

Surfactant CMC 4.0E-04M

Note: All concentration units are molar, all vapor pressures are torr, all amounts are moles. See Appendix 1 for symbol definitions.

$C_{P,tot}$	a_P	P_P	$n_{P,vap}$	$n_{P,sol}$	$C_{P,sol}$	$C_{P,bulk}$
1.194E-02	2.187E-02	3.695E-02	4.043E-08	2.387E-04	1.193E-02	6.706E-03
1.194E-02	2.005E-02	3.387E-02	3.706E-08	2.387E-04	1.193E-02	6.146E-03
2.369E-02	4.524E-02	7.645E-02	8.363E-08	4.737E-04	2.369E-02	1.392E-02
2.369E-02	4.960E-02	8.381E-02	9.169E-08	4.737E-04	2.369E-02	1.526E-02
3.383E-02	6.610E-02	1.117E-01	1.222E-07	6.764E-04	3.382E-02	2.039E-02
3.383E-02	7.368E-02	1.245E-01	1.362E-07	6.764E-04	3.382E-02	2.275E-02
5.726E-02	1.185E-01	2.002E-01	2.190E-07	1.145E-03	5.725E-02	3.680E-02
5.726E-02	1.133E-01	1.914E-01	2.094E-07	1.145E-03	5.725E-02	3.516E-02
6.740E-02	1.417E-01	2.395E-01	2.620E-07	1.348E-03	6.738E-02	4.415E-02
6.740E-02	1.432E-01	2.420E-01	2.648E-07	1.348E-03	6.738E-02	4.464E-02
8.036E-02	1.642E-01	2.775E-01	3.036E-07	1.607E-03	8.035E-02	5.132E-02
8.036E-02	1.544E-01	2.608E-01	2.853E-07	1.607E-03	8.035E-02	4.817E-02
9.148E-02	2.085E-01	3.524E-01	3.855E-07	1.829E-03	9.146E-02	6.557E-02
9.148E-02	1.872E-01	3.164E-01	3.461E-07	1.829E-03	9.146E-02	5.870E-02
1.026E-01	2.125E-01	3.591E-01	3.928E-07	2.052E-03	1.026E-01	6.685E-02
1.026E-01	2.108E-01	3.562E-01	3.896E-07	2.052E-03	1.026E-01	6.629E-02
1.135E-01	2.482E-01	4.194E-01	4.589E-07	2.269E-03	1.135E-01	7.848E-02
1.135E-01	2.217E-01	3.746E-01	4.098E-07	2.269E-03	1.135E-01	6.983E-02
1.698E-01	3.238E-01	5.472E-01	5.987E-07	3.395E-03	1.697E-01	1.035E-01
1.698E-01	3.248E-01	5.489E-01	6.004E-07	3.395E-03	1.697E-01	1.038E-01

Table 4 con't.

Solubilization data for 0.05M $C_{16}BzCl$.

$C_{P,tot}$	$C_{P,mic}$	X_P	K_S (M^{-1})	γ_P	$n_{P,bulk}$	$C_{P,mon}$
1.194E-02	5.228E-03	9.470E-02	1.416E+01	2.309E-01	1.341E-04	6.687E-03
1.194E-02	5.788E-03	1.038E-01	1.693E+01	1.931E-01	1.229E-04	6.130E-03
2.369E-02	9.771E-03	1.635E-01	1.182E+01	2.766E-01	2.783E-04	1.383E-02
2.369E-02	8.422E-03	1.442E-01	9.508E+00	3.439E-01	3.053E-04	1.517E-02
3.383E-02	1.343E-02	2.118E-01	1.048E+01	3.121E-01	4.078E-04	2.022E-02
3.383E-02	1.107E-02	1.813E-01	8.047E+00	4.064E-01	4.550E-04	2.253E-02
5.726E-02	2.045E-02	2.903E-01	8.013E+00	4.081E-01	7.360E-04	3.623E-02
5.726E-02	2.209E-02	3.065E-01	8.849E+00	3.696E-01	7.031E-04	3.464E-02
6.740E-02	2.323E-02	3.173E-01	7.323E+00	4.465E-01	8.830E-04	4.333E-02
6.740E-02	2.275E-02	3.128E-01	7.140E+00	4.580E-01	8.927E-04	4.380E-02
8.036E-02	2.903E-02	3.674E-01	7.317E+00	4.469E-01	1.026E-03	5.022E-02
8.036E-02	3.218E-02	3.916E-01	8.297E+00	3.941E-01	9.635E-04	4.720E-02
9.148E-02	2.589E-02	3.412E-01	5.351E+00	6.111E-01	1.311E-03	6.377E-02
9.148E-02	3.277E-02	3.960E-01	6.916E+00	4.728E-01	1.174E-03	5.726E-02
1.026E-01	3.577E-02	4.171E-01	6.419E+00	5.094E-01	1.337E-03	6.498E-02
1.026E-01	3.632E-02	4.209E-01	6.530E+00	5.008E-01	1.326E-03	6.445E-02
1.135E-01	3.499E-02	4.118E-01	5.424E+00	6.028E-01	1.570E-03	7.591E-02
1.135E-01	4.365E-02	4.661E-01	6.876E+00	4.756E-01	1.397E-03	6.779E-02
1.698E-01	6.621E-02	5.698E-01	5.753E+00	5.684E-01	2.070E-03	9.903E-02
1.698E-01	6.589E-02	5.686E-01	5.725E+00	5.712E-01	2.077E-03	9.933E-02

Table 4 con't.

Uncertainties in data for pentanol in 0.05M $C_{16}BzCl$ listed according to total pentanol concentration in solution.

$C_{P,tot}$	$\delta\ a_P$	$\delta\ P_P$	$\delta\ n_{P,vap}$	$\delta\ n_{P,sol}$	$\delta\ C_{P,sol}$	$\delta\ C_{P,bulk}$
1.2E-02	1.6E-03	2.7E-03	3.0E-09	3.0E-09	1.5E-07	5.0E-04
2.4E-02	4.7E-03	8.0E-03	8.7E-09	8.7E-09	4.4E-07	1.5E-03
3.4E-02	6.0E-03	1.0E-02	1.1E-08	1.1E-08	5.5E-07	1.9E-03
4.3E-02	9.4E-03	1.6E-02	1.7E-08	1.7E-08	8.7E-07	2.9E-03
5.7E-02	5.3E-03	9.0E-03	9.8E-09	9.8E-09	4.9E-07	1.7E-03
6.7E-02	7.5E-03	1.3E-02	1.4E-08	1.4E-08	6.9E-07	2.4E-03
8.0E-02	1.1E-02	1.9E-02	2.0E-08	2.0E-08	1.0E-06	3.5E-03
9.1E-02	1.2E-02	2.0E-02	2.2E-08	2.2E-08	1.1E-06	3.9E-03
1.0E-01	9.9E-03	1.7E-02	1.8E-08	1.8E-08	9.2E-07	3.2E-03
1.1E-01	1.7E-02	2.9E-02	3.2E-08	3.2E-08	1.6E-06	5.5E-03
1.7E-01	1.0E-02	1.7E-02	1.9E-08	1.3E-08	9.4E-07	3.4E-03

$C_{P,tot}$	$\delta\ C_{P,mic}$	$\delta\ X_P$	$\delta\ K_S\ (M^{-1})$	$\delta\ \gamma_P$	$\delta\ n_{P,bulk}$	$\delta\ C_{P,mon}$
1.2E-02	2.2E-02	7.7E-03	4.0E+00	7.7E-03	9.9E-06	4.9E-04
2.4E-02	4.2E-02	1.9E-02	4.0E+00	1.9E-02	2.9E-05	1.4E-03
3.4E-02	4.2E-02	2.1E-02	2.9E+00	2.1E-02	3.7E-05	1.8E-03
4.3E-02	4.9E-02	2.7E-02	3.6E+00	2.8E-02	5.8E-05	2.9E-03
5.7E-02	2.3E-02	1.3E-02	1.3E+00	1.3E-02	3.3E-05	1.6E-03
6.7E-02	3.3E-02	1.8E-02	1.2E+00	1.8E-02	4.7E-05	2.3E-03
8.0E-02	3.5E-02	2.0E-02	1.7E+00	2.0E-02	6.9E-05	3.4E-03
9.1E-02	4.4E-02	2.3E-02	1.2E+00	2.3E-02	7.7E-05	3.7E-03
1.0E-01	3.1E-02	1.6E-02	8.7E-01	1.6E-02	6.4E-05	3.0E-03
1.1E-01	5.1E-02	2.5E-02	1.3E+00	2.5E-02	1.1E-04	5.3E-03
1.7E-01	2.1E-02	8.6E-03	4.4E-01	8.6E-03	6.7E-05	3.1E-03

Experimental data and non-linear least squares analysis of the function

$K = K_0(1 - BX_P)^2$ for 0.05M $C_{16}BzCl$.

$B = 0.815 \pm 0.1$ $K_0 = 14.8 \pm 1.2\ M^{-1}$

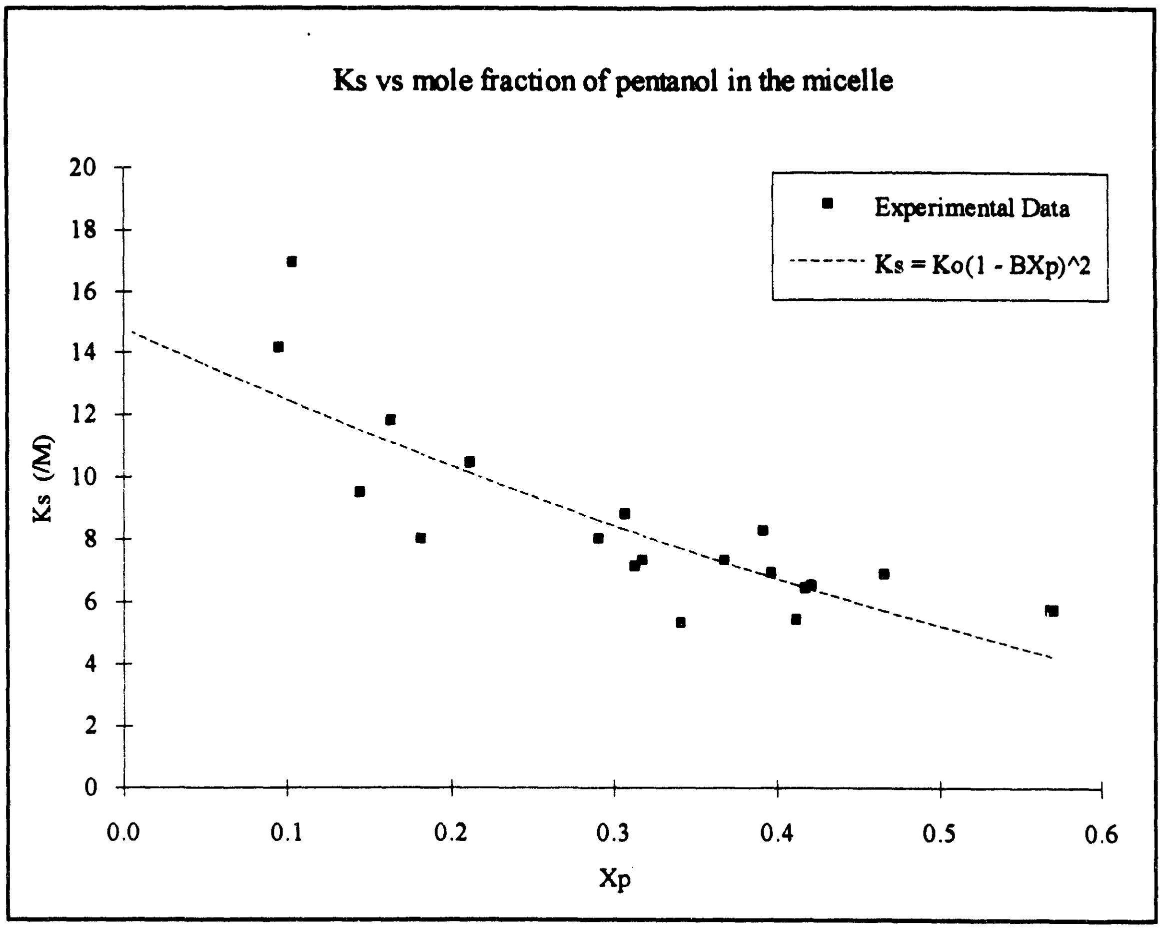


Figure 12 K_S versus X_P for 0.05M $C_{16}BzCl$.

Table 5

Solubilization data for pentanol in $C_{14}Cl$.

Surfactant concentration 0.05M

Surfactant CMC 5.4E-03M

Note: All concentration units are molar, all vapor pressures are torr, all amounts are moles. See Appendix 1 for symbol definitions.

$C_{P,tot}$	a_P	P_P	$n_{P,vap}$	$n_{P,sol}$	$C_{P,sol}$	$C_{P,bulk}$
2.427E-02	4.491E-02	7.589E-02	8.303E-08	4.854E-04	2.427E-02	1.381E-02
2.427E-02	4.786E-02	8.088E-02	8.848E-08	4.854E-04	2.427E-02	1.473E-02
4.447E-02	8.796E-02	1.486E-01	1.626E-07	8.893E-04	4.446E-02	2.721E-02
4.447E-02	8.958E-02	1.514E-01	1.656E-07	8.893E-04	4.446E-02	2.772E-02
7.550E-02	1.377E-01	2.328E-01	2.546E-07	1.510E-03	7.549E-02	4.289E-02
7.550E-02	1.438E-01	2.430E-01	2.658E-07	1.510E-03	7.549E-02	4.481E-02
1.003E-01	1.906E-01	3.220E-01	3.523E-07	2.006E-03	1.003E-01	5.977E-02
1.003E-01	2.015E-01	3.406E-01	3.726E-07	2.006E-03	1.003E-01	6.331E-02
1.278E-01	2.279E-01	3.852E-01	4.214E-07	2.555E-03	1.278E-01	7.186E-02
1.278E-01	2.698E-01	4.559E-01	4.988E-07	2.555E-03	1.278E-01	8.557E-02
1.395E-01	2.670E-01	4.511E-01	4.935E-07	2.789E-03	1.395E-01	8.463E-02
1.395E-01	2.600E-01	4.394E-01	4.807E-07	2.789E-03	1.395E-01	8.236E-02
2.813E-01	5.045E-01	8.525E-01	9.326E-07	5.626E-03	2.813E-01	1.658E-01
2.813E-01	5.440E-01	9.193E-01	1.006E-06	5.626E-03	2.813E-01	1.799E-01
4.245E-01	7.490E-01	1.266E+00	1.385E-06	8.488E-03	4.244E-01	2.566E-01
4.245E-01	7.884E-01	1.332E+00	1.457E-06	8.488E-03	4.244E-01	2.720E-01
5.661E-01	7.668E-01	1.296E+00	1.418E-06	1.132E-02	5.660E-01	2.636E-01
5.661E-01	7.959E-01	1.345E+00	1.471E-06	1.132E-02	5.660E-01	2.750E-01

<u>Table 5 con't.</u>

Solubilization Data for 0.05M $C_{14}Cl$.

$C_{P,tot}$	$C_{P,mic}$	X_P	K_S (M^{-1})	γ_P	$n_{P,bulk}$	$C_{P,mon}$
2.427E-02	1.046E-02	1.786E-01	1.301E+01	2.514E-01	2.763E-04	1.373E-02
2.427E-02	9.542E-03	1.657E-01	1.132E+01	2.888E-01	2.946E-04	1.464E-02
4.447E-02	1.726E-02	2.631E-01	9.780E+00	3.344E-01	5.442E-04	2.690E-02
4.447E-02	1.675E-02	2.574E-01	9.395E+00	3.481E-01	5.543E-04	2.740E-02
7.550E-02	3.260E-02	4.004E-01	9.505E+00	3.440E-01	8.579E-04	4.212E-02
7.550E-02	3.068E-02	3.862E-01	8.783E+00	3.723E-01	8.962E-04	4.397E-02
1.003E-01	4.055E-02	4.528E-01	7.770E+00	4.209E-01	1.195E-03	5.828E-02
1.003E-01	3.701E-02	4.307E-01	6.988E+00	4.679E-01	1.266E-03	6.163E-02
1.278E-01	5.589E-02	5.314E-01	7.624E+00	4.289E-01	1.437E-03	6.970E-02
1.278E-01	4.218E-02	4.624E-01	5.604E+00	5.835E-01	1.711E-03	8.251E-02
1.395E-01	5.483E-02	5.267E-01	6.452E+00	5.068E-01	1.693E-03	8.164E-02
1.395E-01	5.710E-02	5.367E-01	6.749E+00	4.845E-01	1.647E-03	7.952E-02
2.813E-01	1.155E-01	6.989E-01	4.530E+00	7.218E-01	3.315E-03	1.543E-01
2.813E-01	1.014E-01	6.711E-01	4.034E+00	8.107E-01	3.598E-03	1.664E-01
4.245E-01	1.678E-01	7.708E-01	3.365E+00	9.716E-01	5.131E-03	2.290E-01
4.245E-01	1.524E-01	7.534E-01	3.125E+00	1.046E+00	5.441E-03	2.411E-01
5.661E-01	3.024E-01	8.582E-01	3.660E+00	8.936E-01	5.271E-03	2.345E-01
5.661E-01	2.910E-01	8.534E-01	3.506E+00	9.326E-01	5.500E-03	2.434E-01

Table 5 con't.

Uncertainties in data for pentanol in 0.05M $C_{14}Cl$ listed according to total pentanol concentration in solution.

$C_{P,tot}$	$\delta\ a_P$	$\delta\ P_P$	$\delta\ n_{P,vap}$	$\delta\ n_{P,sol}$	$\delta\ C_{P,sol}$	$\delta\ C_{P,bulk}$
2.4E-02	3.6E-03	6.1E-03	6.7E-09	6.7E-09	3.3E-07	1.1E-03
4.4E-02	6.0E-03	1.0E-02	1.1E-08	1.1E-08	5.5E-07	1.9E-03
7.6E-02	1.0E-02	1.7E-02	1.9E-08	1.9E-08	9.4E-07	3.2E-03
1.0E-01	1.5E-02	2.6E-02	2.9E-08	2.9E-08	1.4E-06	4.9E-03
1.3E-01	2.0E-02	3.4E-02	3.8E-08	3.8E-08	1.9E-06	6.6E-03
1.4E-01	2.0E-02	3.4E-02	3.7E-08	3.7E-08	1.8E-06	6.5E-03
2.8E-01	3.7E-02	6.3E-02	6.9E-08	6.9E-08	3.5E-06	1.3E-02
4.2E-01	4.2E-02	7.1E-02	7.8E-08	7.8E-08	3.9E-06	1.6E-02
5.7E-01	4.1E-02	6.9E-02	7.6E-08	7.6E-08	3.8E-06	1.5E-02

$C_{P,tot}$	$\delta\ C_{P,mic}$	$\delta\ X_P$	$\delta\ K_S$ (M^{-1})	$\delta\ \gamma_P$	$\delta\ n_{P,bulk}$	$\delta\ C_{P,mon}$
2.4E-02	3.4E-02	1.4E-02	2.7E+00	1.4E-02	2.2E-05	1.1E-03
4.4E-02	3.6E-02	1.8E-02	1.8E+00	1.8E-02	3.7E-05	1.8E-03
7.6E-02	3.6E-02	2.0E-02	1.6E+00	2.0E-02	6.4E-05	3.1E-03
1.0E-01	4.8E-02	2.5E-02	1.5E+00	2.5E-02	9.9E-05	4.7E-03
1.3E-01	5.4E-02	2.6E-02	1.3E+00	2.6E-02	1.3E-04	6.2E-03
1.4E-01	5.0E-02	2.3E-02	1.1E+00	2.3E-02	1.3E-04	6.1E-03
2.8E-01	6.7E-02	1.9E-02	6.0E-01	1.9E-02	2.6E-04	1.1E-02
4.2E-01	6.5E-02	1.2E-02	3.2E-01	1.2E-02	3.1E-04	1.3E-02
5.7E-01	5.1E-02	5.1E-03	2.9E-01	5.1E-03	3.1E-04	1.3E-02

Experimental data and non-linear least squares analysis of the function

K = $K_0(1 - BX_P)^2$ for 0.05M $C_{14}Cl$.

B = 0.648 ± 0.038 $K_0 = 14.9 \pm 0.7\ M^{-1}$

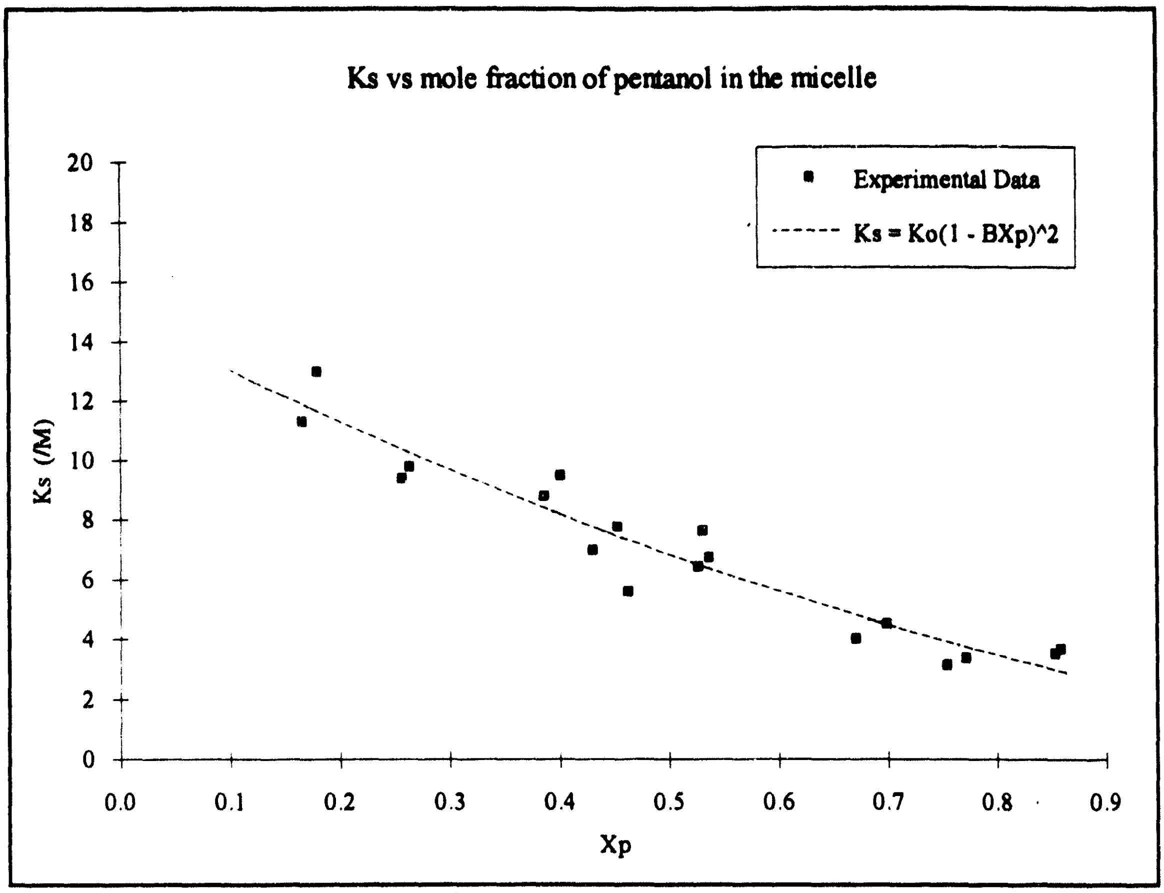


Figure 13 K_S versus X_P data for 0.05M $C_{14}Cl$.

Table 6

Solubilization data for pentanol in C_{14}BzCl.

Surfactant concentration 0.05M

Surfactant CMC 2.2E-03M

Note: All concentration units are molar, all vapor pressures are torr, all amounts are moles. See Appendix 1 for symbol definitions.

$C_{P,tot}$	a_P	P_P	$n_{P,vap}$	$n_{P,sol}$	$C_{P,sol}$	$C_{P,bulk}$
3.738E-02	8.518E-02	1.439E-01	1.575E-07	7.475E-04	3.738E-02	2.634E-02
6.214E-02	1.404E-01	2.372E-01	2.595E-07	1.242E-03	6.212E-02	4.373E-02
6.214E-02	1.315E-01	2.222E-01	2.431E-07	1.242E-03	6.212E-02	4.092E-02
7.496E-02	1.655E-01	2.796E-01	3.059E-07	1.499E-03	7.494E-02	5.172E-02
7.496E-02	1.735E-01	2.931E-01	3.207E-07	1.499E-03	7.494E-02	5.428E-02
1.126E-01	2.472E-01	4.178E-01	4.570E-07	2.252E-03	1.126E-01	7.816E-02
1.126E-01	2.678E-01	4.525E-01	4.950E-07	2.252E-03	1.126E-01	8.490E-02
1.270E-01	2.814E-01	4.756E-01	5.203E-07	2.539E-03	1.270E-01	8.941E-02
1.270E-01	2.967E-01	5.014E-01	5.485E-07	2.539E-03	1.270E-01	9.446E-02
1.502E-01	3.071E-01	5.190E-01	5.677E-07	3.004E-03	1.502E-01	9.793E-02
1.502E-01	3.388E-01	5.725E-01	6.264E-07	3.004E-03	1.502E-01	1.085E-01
1.893E-01	3.802E-01	6.425E-01	7.029E-07	3.784E-03	1.892E-01	1.226E-01
1.893E-01	4.318E-01	7.296E-01	7.982E-07	3.784E-03	1.892E-01	1.403E-01
2.278E-01	4.931E-01	8.333E-01	9.116E-07	4.556E-03	2.278E-01	1.617E-01
2.278E-01	4.652E-01	7.860E-01	8.599E-07	4.556E-03	2.278E-01	1.519E-01
2.647E-01	5.599E-01	9.461E-01	1.035E-06	5.292E-03	2.646E-01	1.856E-01
2.647E-01	5.142E-01	8.689E-01	9.506E-07	5.292E-03	2.646E-01	1.692E-01
3.032E-01	5.495E-01	9.285E-01	1.016E-06	6.063E-03	3.031E-01	1.819E-01
3.032E-01	5.997E-01	1.013E+00	1.109E-06	6.062E-03	3.031E-01	2.001E-01
3.420E-01	6.063E-01	1.024E+00	1.121E-06	6.839E-03	3.419E-01	2.026E-01
3.420E-01	7.184E-01	1.214E+00	1.328E-06	6.839E-03	3.419E-01	2.448E-01

Table 6 con't.

Solubilization data for C_{14}BzCl.

$C_{P,tot}$	$C_{P,mic}$	X_P	K_s (M^{-1})	γ_P	$n_{P,bulk}$	$C_{P,mon}$
3.738E-02	1.104E-02	1.821E-01	6.993E+00	4.676E-01	5.268E-04	2.605E-02
6.214E-02	1.839E-02	2.704E-01	6.299E+00	5.191E-01	8.746E-04	4.293E-02
6.214E-02	2.121E-02	2.993E-01	7.442E+00	4.394E-01	8.184E-04	4.022E-02
7.496E-02	2.322E-02	3.186E-01	6.297E+00	5.193E-01	1.034E-03	5.060E-02
7.496E-02	2.067E-02	2.940E-01	5.542E+00	5.901E-01	1.086E-03	5.304E-02
1.126E-01	3.442E-02	4.091E-01	5.411E+00	6.043E-01	1.563E-03	7.560E-02
1.126E-01	2.768E-02	3.578E-01	4.369E+00	7.485E-01	1.698E-03	8.189E-02
1.270E-01	3.755E-02	4.302E-01	4.998E+00	6.542E-01	1.788E-03	8.606E-02
1.270E-01	3.249E-02	3.952E-01	4.356E+00	7.506E-01	1.889E-03	9.073E-02
1.502E-01	5.227E-02	5.121E-01	5.453E+00	5.997E-01	1.959E-03	9.392E-02
1.502E-01	4.166E-02	4.557E-01	4.398E+00	7.435E-01	2.171E-03	1.036E-01
1.893E-01	6.667E-02	5.722E-01	4.921E+00	6.645E-01	2.451E-03	1.163E-01
1.893E-01	4.894E-02	4.957E-01	3.754E+00	8.710E-01	2.805E-03	1.320E-01
2.278E-01	6.605E-02	5.700E-01	3.780E+00	8.652E-01	3.235E-03	1.508E-01
2.278E-01	7.589E-02	6.035E-01	4.243E+00	7.707E-01	3.038E-03	1.422E-01
2.647E-01	7.898E-02	6.130E-01	3.580E+00	9.133E-01	3.712E-03	1.712E-01
2.647E-01	9.539E-02	6.566E-01	4.175E+00	7.832E-01	3.384E-03	1.572E-01
3.032E-01	1.213E-01	7.084E-01	4.216E+00	7.757E-01	3.637E-03	1.680E-01
3.032E-01	1.030E-01	6.736E-01	3.673E+00	8.903E-01	4.003E-03	1.834E-01
3.420E-01	1.394E-01	7.362E-01	3.971E+00	8.235E-01	4.051E-03	1.854E-01
3.420E-01	9.717E-02	6.607E-01	3.007E+00	1.087E+00	4.895E-03	2.197E-01

Table 6 con't.

Uncertainties in data for pentanol in 0.05M $C_{14}BzCl$ listed according to total pentanol concentration in solution.

$C_{P,tot}$	$\delta\ a_P$	$\delta\ P_P$	$\delta\ n_{P,vap}$	$\delta\ n_{P,sol}$	$\delta\ C_{P,sol}$	$\delta\ C_{P,bulk}$
3.7E-02	6.1E-03	1.0E-02	1.1E-08	1.1E-08	5.6E-07	1.9E-03
6.2E-02	8.0E-03	1.3E-02	1.5E-08	1.5E-08	7.3E-07	2.5E-03
7.5E-02	1.0E-02	1.7E-02	1.9E-08	1.9E-08	9.5E-07	3.3E-03
1.1E-01	1.4E-02	2.4E-02	2.6E-08	2.6E-08	1.3E-06	4.6E-03
1.3E-01	1.6E-02	2.6E-02	2.9E-08	2.9E-08	1.4E-06	5.1E-03
1.5E-01	2.2E-02	3.8E-02	4.1E-08	4.1E-08	2.1E-06	7.3E-03
1.9E-01	2.4E-02	4.0E-02	4.4E-08	4.4E-08	2.2E-06	8.0E-03
2.3E-01	2.2E-02	3.8E-02	4.1E-08	4.1E-08	2.1E-06	7.6E-03
2.6E-01	3.3E-02	5.6E-02	6.2E-08	6.2E-08	3.1E-06	1.2E-02
3.0E-01	3.4E-02	5.7E-02	6.2E-08	6.2E-08	3.1E-06	1.2E-02
3.4E-01	3.9E-02	6.6E-02	7.3E-08	7.3E-08	3.6E-06	1.4E-02

$C_{P,tot}$	$\delta\ C_{P,mic}$	$\delta\ X_P$	$\delta\ K_s\ (M^{-1})$	$\delta\ \gamma_P$	$\delta\ n_{P,bulk}$	$\delta\ C_{P,mon}$
3.7E-02	4.0E-02	2.0E-02	2.6E+00	2.0E-02	3.8E-05	1.9E-03
6.2E-02	3.7E-02	2.0E-02	1.5E+00	2.0E-02	5.0E-05	2.4E-03
7.5E-02	4.6E-02	2.3E-02	1.3E+00	2.4E-02	6.5E-05	3.1E-03
1.1E-01	4.6E-02	2.3E-02	9.7E-01	2.3E-02	9.1E-05	4.3E-03
1.3E-01	4.8E-02	2.3E-02	8.7E-01	2.3E-02	1.0E-04	4.8E-03
1.5E-01	5.8E-02	2.6E-02	9.9E-01	2.6E-02	1.5E-04	6.8E-03
1.9E-01	5.2E-02	2.0E-02	7.5E-01	2.0E-02	1.6E-04	7.3E-03
2.3E-01	4.4E-02	1.5E-02	5.1E-01	1.5E-02	1.5E-04	6.8E-03
2.6E-01	6.2E-02	1.9E-02	5.8E-01	1.8E-02	2.3E-04	1.0E-02
3.0E-01	5.5E-02	1.4E-02	5.2E-01	1.4E-02	2.4E-04	1.0E-02
3.4E-01	6.3E-02	1.4E-02	4.7E-01	1.4E-02	2.8E-04	1.2E-02

Experimental data and non-linear least squares analysis of the function

$K = K_0(1 - BX_P)^2$ for 0.05M $C_{14}BzCl$.

$B = 0.480 \pm 0.062$ $K_0 = 8.1 \pm 0.6\ M^{-1}$

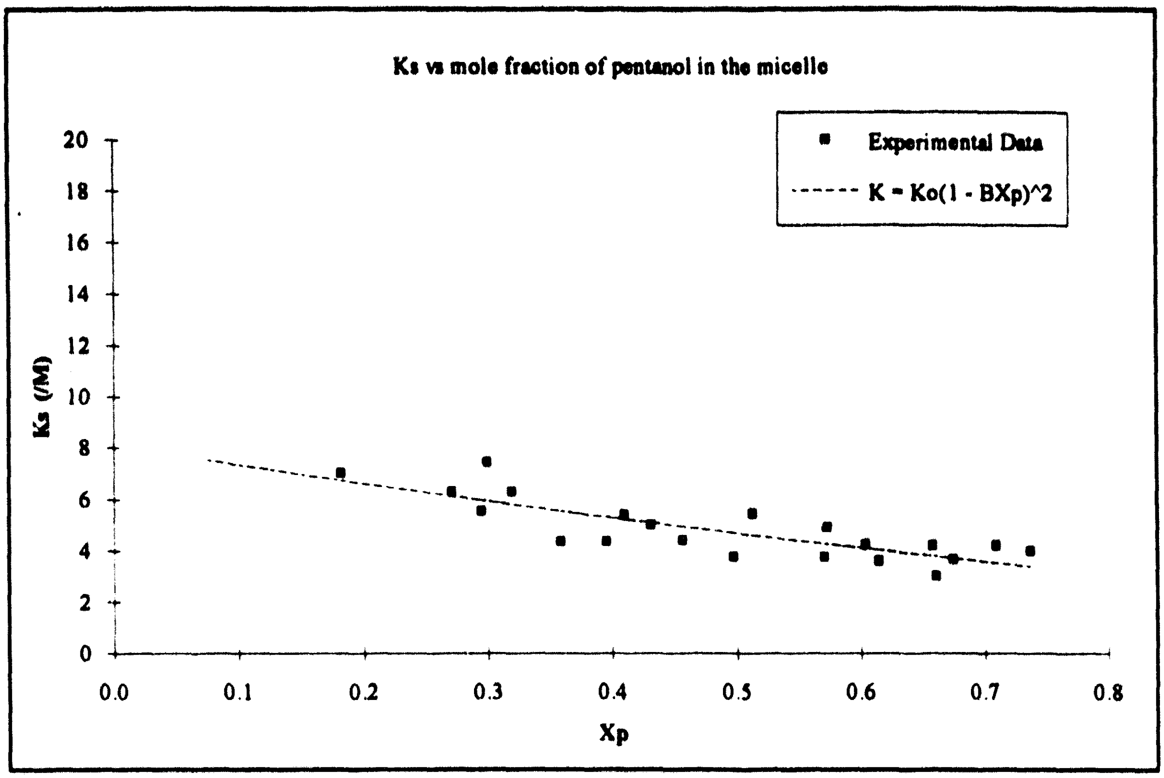


Figure 14 K_S versus X_P data for 0.05M $C_{14}BzCl$.

Table 7

Solubilization data for the surfactant mixture CPC + C_{16}BzCl.

Total surfactant concentration remained constant at 0.05M.

Total pentanol concentration remained approximately 0.05M. (See $C_{P,tot}$)

See Appendix 1 for symbol definitions.

Surfactant 1 = CPC

Surfactant 2 = C_{16}BzCl

X_{S2}	a_P	P_P	$n_{P,vap}$	$n_{P,sol}$	$C_{P,tot}$	$C_{P,sol}$
0.0	9.876E-02	1.669E-01	1.826E-07	1.030E-03	5.015E-02	5.149E-02
0.0	1.005E-01	1.698E-01	1.860E-07	1.030E-03	5.015E-02	5.149E-02
0.1	9.907E-02	1.674E-01	1.831E-07	1.030E-03	5.015E-02	5.149E-02
0.1	9.464E-02	1.599E-01	1.750E-07	1.030E-03	5.015E-02	5.149E-02
0.2	1.006E-01	1.700E-01	1.859E-07	1.040E-03	5.200E-02	5.199E-02
0.2	1.045E-01	1.767E-01	1.933E-07	1.040E-03	5.200E-02	5.199E-02
0.3	1.072E-01	1.811E-01	1.981E-07	9.998E-04	5.000E-02	4.999E-02
0.3	1.050E-01	1.774E-01	1.940E-07	9.998E-04	5.000E-02	4.999E-02
0.4	1.038E-01	1.754E-01	1.919E-07	1.026E-03	5.130E-02	5.129E-02
0.4	1.085E-01	1.833E-01	2.006E-07	1.026E-03	5.130E-02	5.129E-02
0.5	1.109E-01	1.873E-01	2.050E-07	1.012E-03	5.060E-02	5.059E-02
0.5	1.062E-01	1.795E-01	1.964E-07	1.012E-03	5.060E-02	5.059E-02
0.6	1.147E-01	1.938E-01	2.120E-07	1.012E-03	5.060E-02	5.059E-02
0.6	1.117E-01	1.888E-01	2.066E-07	1.012E-03	5.060E-02	5.059E-02
0.7	1.053E-01	1.780E-01	1.947E-07	1.008E-03	5.040E-02	5.039E-02
0.7	1.085E-01	1.833E-01	2.006E-07	1.008E-03	5.040E-02	5.039E-02
0.8	1.178E-01	1.990E-01	2.177E-07	1.034E-03	5.170E-02	5.169E-02
0.8	1.094E-01	1.848E-01	2.022E-07	1.034E-03	5.170E-02	5.169E-02
0.9	1.057E-01	1.786E-01	1.953E-07	1.014E-03	5.070E-02	5.069E-02
0.9	1.095E-01	1.851E-01	2.025E-07	1.014E-03	5.070E-02	5.069E-02
0.98	1.078E-01	1.822E-01	1.993E-07	1.004E-03	5.020E-02	5.019E-02
1.0	1.100E-01	1.859E-01	2.034E-07	1.014E-03	5.070E-02	5.069E-02
1.0	1.108E-01	1.873E-01	2.049E-07	1.014E-03	5.070E-02	5.069E-02
Error	5.2E-03	8.7E-03	9.6E-09	1.4E-05	6.3E-04	6.3E-04

Table 7 con't.

Surfactant 1 = CPC.

Surfactant 2 = $C_{16}BzCl$.

X_{S2}	CMC_{surf1x}	CMC_{surf2x}	γ_{surf1}	γ_{surf2}	C_{mon1}	C_{mon2}
0.0					1.193E-04	
0.0					1.193E-04	
0.1	1.243E-04	3.055E-05	9.960E-01	7.241E-01	7.861E-05	1.564E-06
0.1	1.243E-04	3.055E-05	9.962E-01	7.331E-01	7.712E-05	1.553E-06
0.2	1.243E-04	3.056E-05	9.842E-01	7.751E-01	6.904E-05	3.347E-06
0.2	1.243E-04	3.056E-05	9.836E-01	7.680E-01	7.023E-05	3.375E-06
0.3	1.243E-04	3.057E-05	9.604E-01	8.028E-01	6.255E-05	5.518E-06
0.3	1.243E-04	3.057E-05	9.612E-01	8.065E-01	6.195E-05	5.486E-06
0.4	1.244E-04	3.058E-05	9.352E-01	8.603E-01	5.044E-05	7.616E-06
0.4	1.244E-04	3.058E-05	9.324E-01	8.546E-01	5.138E-05	7.731E-06
0.5	1.244E-04	3.059E-05	8.921E-01	8.923E-01	4.188E-05	1.031E-05
0.5	1.244E-04	3.059E-05	8.964E-01	8.967E-01	4.117E-05	1.014E-05
0.6	1.244E-04	3.059E-05	8.432E-01	9.272E-01	3.226E-05	1.310E-05
0.6	1.244E-04	3.060E-05	8.472E-01	9.291E-01	3.196E-05	1.294E-05
0.7	1.245E-04	3.060E-05	8.076E-01	9.616E-01	2.224E-05	1.521E-05
0.7	1.245E-04	3.060E-05	8.024E-01	9.605E-01	2.243E-05	1.542E-05
0.8	1.245E-04	3.061E-05	7.394E-01	9.813E-01	1.412E-05	1.845E-05
0.8	1.245E-04	3.061E-05	7.567E-01	9.828E-01	1.389E-05	1.776E-05
0.9	1.245E-04	3.062E-05	7.039E-01	9.957E-01	6.446E-06	2.019E-05
0.9	1.245E-04	3.062E-05	6.949E-01	9.955E-01	6.480E-06	2.056E-05
0.98	1.245E-04	3.062E-05	6.499E-01	9.998E-01	1.211E-06	2.247E-05
1.0						3.061E-05
1.0						3.061E-05
Error	9.2E-08	2.3E-08				

Table 7 con't.

Surfactant 1 = CPC.

Surfactant 2 = $C_{16}BzCl$.

X_{S2}	$C_{P,bulk}$	$C_{P,mic}$	γ_P	$n_{P,bulk}$	$C_{Cl,free}$
0.0	3.059E-02	2.090E-02	3.345E-01	6.119E-04	1.359E-02
0.0	3.114E-02	2.035E-02	3.469E-01	6.228E-04	1.359E-02
0.1	3.069E-02	2.080E-02	3.368E-01	6.138E-04	1.356E-02
0.1	2.930E-02	2.219E-02	3.076E-01	5.860E-04	1.356E-02
0.2	3.117E-02	2.082E-02	3.417E-01	6.233E-04	1.355E-02
0.2	3.241E-02	1.958E-02	3.711E-01	6.482E-04	1.355E-02
0.3	3.324E-02	1.675E-02	4.267E-01	6.648E-04	1.355E-02
0.3	3.254E-02	1.745E-02	4.052E-01	6.508E-04	1.355E-02
0.4	3.217E-02	1.912E-02	3.749E-01	6.434E-04	1.354E-02
0.4	3.365E-02	1.764E-02	4.156E-01	6.730E-04	1.354E-02
0.5	3.440E-02	1.619E-02	4.529E-01	6.880E-04	1.354E-02
0.5	3.294E-02	1.765E-02	4.068E-01	6.588E-04	1.354E-02
0.6	3.560E-02	1.499E-02	4.970E-01	7.121E-04	1.353E-02
0.6	3.468E-02	1.591E-02	4.625E-01	6.935E-04	1.353E-02
0.7	3.266E-02	1.773E-02	4.022E-01	6.532E-04	1.353E-02
0.7	3.365E-02	1.674E-02	4.324E-01	6.731E-04	1.353E-02
0.8	3.658E-02	1.511E-02	5.072E-01	7.316E-04	1.352E-02
0.8	3.393E-02	1.776E-02	4.170E-01	6.785E-04	1.352E-02
0.9	3.276E-02	1.793E-02	4.002E-01	6.552E-04	1.352E-02
0.9	3.398E-02	1.671E-02	4.371E-01	6.796E-04	1.352E-02
0.98	3.344E-02	1.675E-02	4.295E-01	6.688E-04	1.352E-02
1.0	3.414E-02	1.655E-02	2.488E-01	6.827E-04	1.352E-02
1.0	3.439E-02	1.630E-02	2.460E-01	6.878E-04	1.352E-02
Error	1.6E-03	1.9E-03	6.9E-02	3.3E-05	1.4E-05

Table 7 con't.

Surfactant 1 = CPC.

Surfactant 2 = C_{16}BzCl.

X_{S2}	X_{mic1}	X_{mic2}	C_{mic1}	C_{mic2}	C_{mictot}
0.0	7.048E-01		4.988E-02		4.988E-02
0.0	7.048E-01		4.988E-02		4.988E-02
0.1	6.352E-01	7.068E-02	4.492E-02	4.998E-03	4.992E-02
0.1	6.230E-01	6.932E-02	4.492E-02	4.998E-03	4.992E-02
0.2	5.644E-01	1.413E-01	3.993E-02	9.997E-03	4.993E-02
0.2	5.745E-01	1.438E-01	3.993E-02	9.997E-03	4.993E-02
0.3	5.239E-01	2.249E-01	3.494E-02	1.499E-02	4.993E-02
0.3	5.185E-01	2.225E-01	3.494E-02	1.499E-02	4.993E-02
0.4	4.337E-01	2.895E-01	2.995E-02	1.999E-02	4.994E-02
0.4	4.431E-01	2.958E-01	2.995E-02	1.999E-02	4.994E-02
0.5	3.774E-01	3.778E-01	2.496E-02	2.499E-02	4.995E-02
0.5	3.692E-01	3.697E-01	2.496E-02	2.499E-02	4.995E-02
0.6	3.075E-01	4.618E-01	1.997E-02	2.999E-02	4.995E-02
0.6	3.031E-01	4.553E-01	1.997E-02	2.999E-02	4.996E-02
0.7	2.213E-01	5.168E-01	1.498E-02	3.498E-02	4.996E-02
0.7	2.246E-01	5.245E-01	1.498E-02	3.498E-02	4.996E-02
0.8	1.534E-01	6.144E-01	9.986E-03	3.998E-02	4.997E-02
0.8	1.474E-01	5.903E-01	9.986E-03	3.998E-02	4.997E-02
0.9	7.354E-02	6.624E-01	4.994E-03	4.498E-02	4.997E-02
0.9	7.488E-02	6.745E-01	4.994E-03	4.498E-02	4.997E-02
0.98	1.497E-02	7.340E-01	9.988E-04	4.898E-02	4.998E-02
1.0		7.512E-01		4.997E-02	4.997E-02
1.0		7.540E-01		4.997E-02	4.997E-02
Error					1.9E-05

Table 7 con't.

Surfactant 1 = CPC.

Surfactant 2 = C_{16}BzCl.

X_{S2}	C_{Pmon}	X_P	K_s (M^{-1})
0.0	3.020E-02	2.952E-01	9.775E+00
0.0	3.074E-02	2.897E-01	9.427E+00
0.1	3.030E-02	2.941E-01	9.708E+00
0.1	2.894E-02	3.077E-01	1.063E+01
0.2	3.076E-02	2.943E-01	9.569E+00
0.2	3.197E-02	2.817E-01	8.812E+00
0.3	3.278E-02	2.512E-01	7.664E+00
0.3	3.210E-02	2.590E-01	8.069E+00
0.4	3.174E-02	2.768E-01	8.723E+00
0.4	3.318E-02	2.610E-01	7.868E+00
0.5	3.390E-02	2.448E-01	7.220E+00
0.5	3.248E-02	2.611E-01	8.038E+00
0.6	3.507E-02	2.308E-01	6.580E+00
0.6	3.417E-02	2.416E-01	7.070E+00
0.7	3.222E-02	2.619E-01	8.130E+00
0.7	3.318E-02	2.509E-01	7.562E+00
0.8	3.602E-02	2.322E-01	6.447E+00
0.8	3.344E-02	2.623E-01	7.842E+00
0.9	3.231E-02	2.640E-01	8.171E+00
0.9	3.350E-02	2.506E-01	7.482E+00
0.98	3.297E-02	2.510E-01	7.614E+00
1.0	3.365E-02	2.488E-01	7.395E+00
1.0	3.389E-02	2.460E-01	7.257E+00
Error	1.6E-03	2.1E-02	1.1E+00

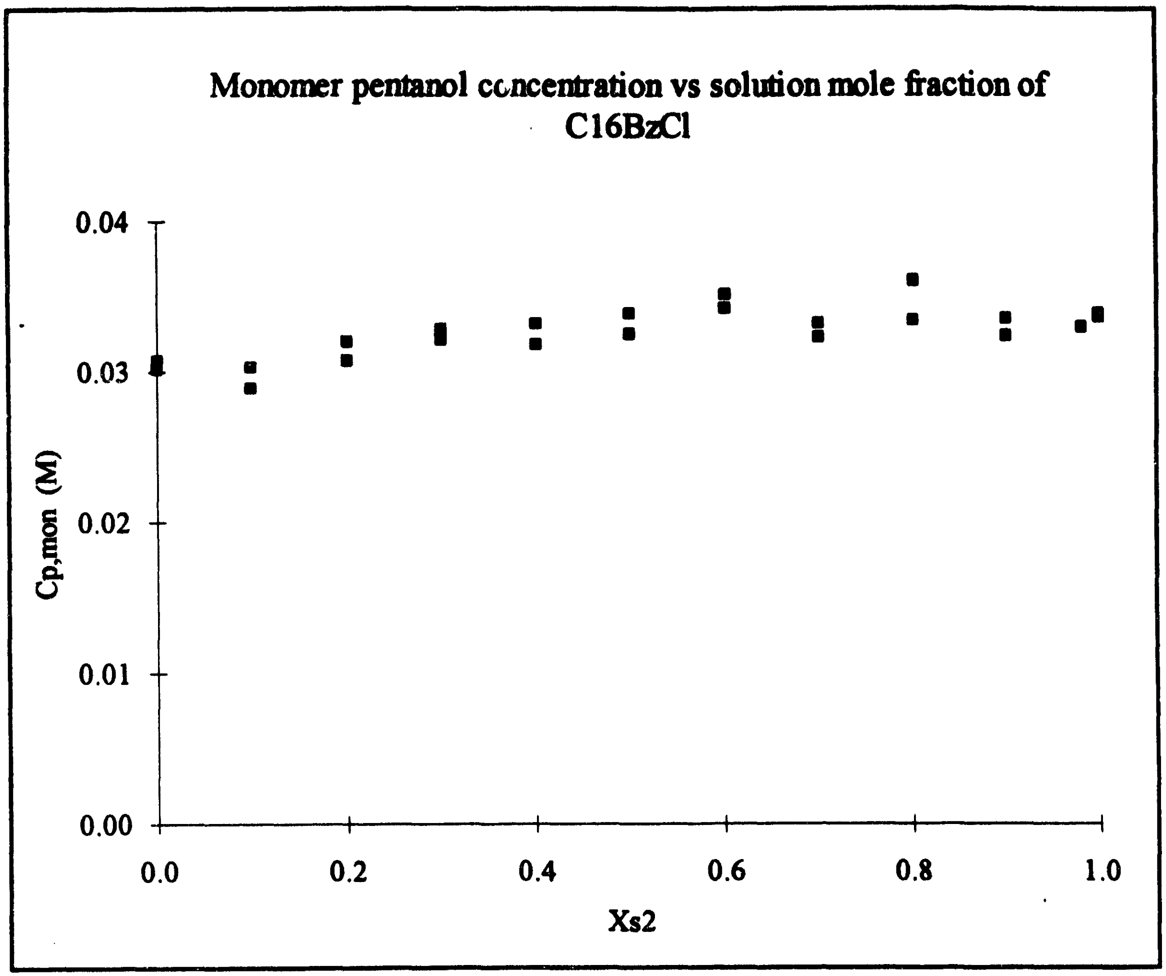


Figure 15 $C_{P,mon}$ versus X_{S2} for pentanol in CPC $+C_{16}BzCl$.

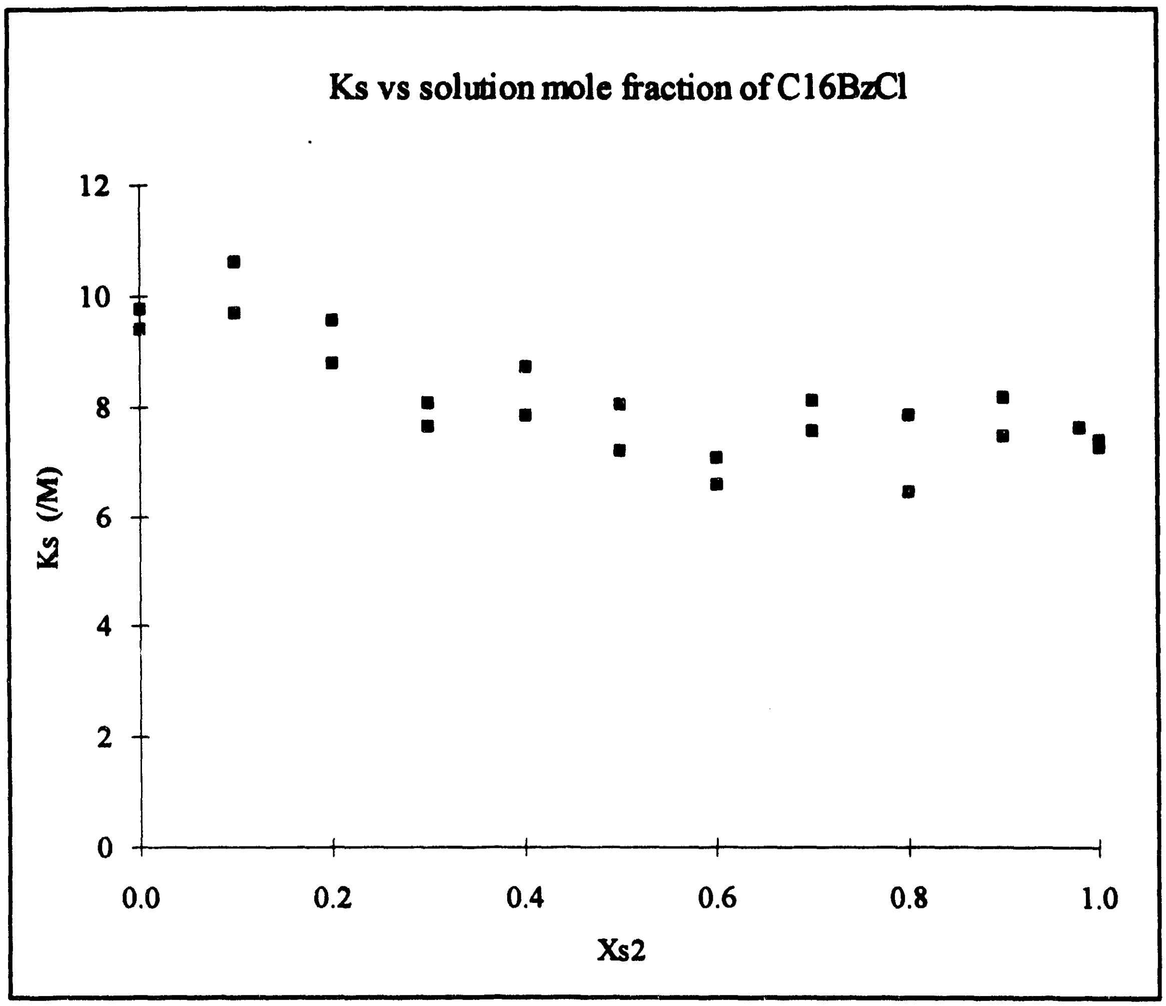


Figure 16 K_S versus X_{S2} for pentanol in CPC + C_{16}BzCl.

Table 8

Solubilization data for the surfactant mixture $C_{14}Cl$ + $C_{14}BzCl$.

Total surfactant concentration remained constant at 0.05M.

Total pentanol concentration remained approximately 0.05M. (See $C_{P,tot}$)

See Appendix 1 for symbol definitions.

Surfactant 1 = $C_{14}Cl$.

Surfactant 2 = $C_{14}BzCl$.

X_{S2}	a_P	P_P	$n_{P,vap}$	$n_{P,sol}$	$C_{P,tot}$	$C_{P,sol}$
0.00	9.076E-02	1.534E-01	1.678E-07	1.011E-03	5.056E-02	5.055E-02
0.00	9.263E-02	1.565E-01	1.712E-07	1.011E-03	5.056E-02	5.055E-02
0.02	9.515E-02	1.608E-01	1.759E-07	1.011E-03	4.989E-02	5.055E-02
0.02	9.432E-02	1.594E-01	1.744E-07	1.011E-03	4.989E-02	5.055E-02
0.04	1.013E-01	1.712E-01	1.870E-07	1.011E-03	5.057E-02	5.056E-02
0.04	1.022E-01	1.727E-01	1.890E-07	1.011E-03	5.057E-02	5.056E-02
0.08	1.016E-01	1.716E-01	1.880E-07	9.960E-04	4.981E-02	4.980E-02
0.08	1.025E-01	1.732E-01	1.890E-07	9.960E-04	4.981E-02	4.980E-02
0.10	1.019E-01	1.722E-01	1.880E-07	9.960E-04	4.982E-02	4.981E-02
0.12	1.037E-01	1.752E-01	1.920E-07	1.000E-03	5.003E-02	5.002E-02
0.12	1.023E-01	1.729E-01	1.890E-07	1.000E-03	6.003E-02	5.002E-02
0.17	1.005E-01	1.699E-01	1.860E-07	9.910E-04	4.955E-02	4.954E-02
0.17	1.014E-01	1.713E-01	1.870E-07	9.910E-04	4.955E-02	4.954E-02
0.21	1.018E-01	1.720E-01	1.880E-07	9.980E-04	4.990E-02	4.989E-02
0.21	1.053E-01	1.779E-01	1.950E-07	9.980E-04	4.990E-02	4.989E-02
0.44	1.106E-01	1.869E-01	2.050E-07	1.029E-03	5.147E-02	5.146E-02
0.44	1.143E-01	1.932E-01	2.110E-07	1.029E-03	5.147E-02	5.146E-02
0.70	1.116E-01	1.886E-01	2.060E-07	1.002E-03	5.013E-02	5.012E-02
0.70	1.064E-01	1.797E-01	1.970E-07	1.002E-03	5.013E-02	5.012E-02
1.00	1.051E-01	1.775E-01	1.942E-07	1.008E-03	5.041E-02	5.040E-02
1.00	1.118E-01	1.890E-01	2.068E-07	1.008E-03	5.041E-02	5.040E-02
Error	6.2E-03	1.0E-02	1.1E-08	1.3E-05	2.2E-03	5.3E-04

Table 8 con't.

Surfactant 1 = $C_{14}Cl$.

Surfactant 2 = $C_{14}BzCl$.

X_{S2}	CMC_{surf1x}	CMC_{surf2x}	γ_{surf1}	γ_{surf2}	C_{mon1}	C_{mon2}
0.00					2.413E-03	
0.00					2.413E-03	
0.02	2.465E-03	5.234E-04	9.999E-01	7.926E-01	1.681E-03	5.942E-06
0.02	2.466E-03	5.235E-04	9.999E-01	7.940E-01	1.675E-03	5.931E-06
0.04	2.464E-03	5.230E-04	9.996E-01	7.902E-01	1.690E-03	1.220E-05
0.04	2.464E-03	5.230E-04	9.996E-01	7.886E-01	1.697E-03	1.230E-05
0.08	2.467E-03	5.240E-04	9.982E-01	8.018E-01	1.637E-03	2.540E-05
0.08	2.467E-03	5.240E-04	9.982E-01	8.003E-01	1.644E-03	2.540E-05
0.10	2.469E-03	5.240E-04	9.971E-01	8.094E-01	1.601E-03	3.220E-05
0.12	2.471E-03	5.250E-04	9.958E-01	8.158E-01	1.570E-03	3.940E-05
0.12	2.472E-03	5.250E-04	9.958E-01	8.179E-01	1.561E-03	3.920E-05
0.17	2.477E-03	5.260E-04	9.925E-01	8.343E-01	1.480E-03	5.390E-05
0.17	2.477E-03	5.260E-04	9.924E-01	8.331E-01	1.485E-03	5.410E-05
0.21	2.482E-03	5.270E-04	9.880E-01	8.499E-01	1.399E-03	6.950E-05
0.21	2.480E-03	5.270E-04	9.876E-01	8.453E-01	1.420E-03	7.030E-05
0.44	2.508E-03	5.320E-04	9.462E-01	9.202E-01	9.680E-04	1.630E-04
0.44	2.507E-03	5.321E-04	9.443E-01	9.175E-01	9.825E-04	1.653E-04
0.70	2.536E-03	5.385E-04	8.645E-01	9.759E-01	4.847E-04	2.836E-04
0.70	2.538E-03	5.387E-04	8.707E-01	9.770E-01	4.764E-04	2.770E-04
1.00						5.424E-04
1.00						5.424E-04

Table 8 con't.

Surfactant 1 = $C_{14}Cl$.

Surfactant 2 = $C_{14}BzCl$.

X_{S2}	$C_{P,bulk}$	$C_{P,mic}$	γ_P	$n_{P,bulk}$	C_{Clfree}
0.00	2.809E-02	2.247E-02	2.830E-01	5.617E-04	1.669E-02
0.00	2.867E-02	2.188E-02	2.941E-01	5.734E-04	1.669E-02
0.02	2.946E-02	2.109E-02	3.131E-01	5.892E-04	1.618E-02
0.02	2.920E-02	2.135E-02	3.078E-01	5.840E-04	1.618E-02
0.04	3.139E-02	1.917E-02	3.566E-01	6.280E-04	1.619E-02
0.04	3.168E-02	1.888E-02	3.637E-01	6.340E-04	1.620E-02
0.08	3.147E-02	1.833E-02	3.694E-01	6.290E-04	1.616E-02
0.08	3.177E-02	1.804E-02	3.772E-01	6.350E-04	1.617E-02
0.10	3.158E-02	1.824E-02	3.721E-01	6.310E-04	1.614E-02
0.12	3.213E-02	1.789E-02	3.841E-01	6.430E-04	1.613E-02
0.12	3.171E-02	1.831E-02	3.727E-01	6.340E-04	1.612E-02
0.17	3.115E-02	1.839E-02	3.654E-01	6.230E-04	1.607E-02
0.17	3.142E-02	1.813E-02	3.724E-01	6.280E-04	1.608E-02
0.21	3.154E-02	1.835E-02	3.709E-01	6.310E-04	1.603E-02
0.21	3.263E-02	1.726E-02	4.012E-01	6.530E-04	1.604E-02
0.44	3.432E-02	1.714E-02	4.261E-01	6.860E-04	1.579E-02
0.44	3.548E-02	1.597E-02	4.639E-01	7.097E-04	1.580E-02
0.70	3.463E-02	1.549E-02	4.662E-01	6.926E-04	1.554E-02
0.70	3.298E-02	1.714E-02	4.121E-01	6.597E-04	1.553E-02
1.00	3.257E-02	1.783E-02	3.966E-01	6.515E-04	1.538E-02
1.00	3.471E-02	1.569E-02	4.643E-01	6.941E-04	1.538E-02
Error	1.9E-03	1.9E-03	5.2E-02	3.9E-05	3.5E-04

Table 8 con't.

Surfactant 1 = $C_{14}Cl$.

Surfactant 2 = $C_{14}BzCl$.

X_{S2}	X_{mic1}	X_{mic2}	C_{mic1}	C_{mic2}	C_{mictot}
0.00	6.835E-01		4.759E-02		4.759E-02
0.00	6.891E-01		4.759E-02		4.759E-02
0.02	6.818E-01	1.432E-02	4.732E-02	9.941E-04	4.831E-02
0.02	6.793E-01	1.427E-02	4.733E-02	9.941E-04	4.832E-02
0.04	6.863E-01	2.961E-02	4.630E-02	1.998E-03	4.830E-02
0.04	6.892E-01	2.974E-02	4.629E-02	1.998E-03	4.829E-02
0.08	6.646E-01	6.044E-02	4.431E-02	4.030E-03	4.834E-02
0.08	6.675E-01	6.072E-02	4.430E-02	4.030E-03	4.833E-02
0.10	6.503E-01	7.594E-02	4.331E-02	5.058E-03	4.837E-02
0.12	6.382E-01	9.197E-02	4.230E-02	6.096E-03	4.839E-02
0.12	6.341E-01	9.137E-02	4.230E-02	6.096E-03	4.840E-02
0.17	6.019E-01	1.230E-01	4.025E-02	8.221E-03	4.847E-02
0.17	6.043E-01	1.235E-01	4.024E-02	8.221E-03	4.846E-02
0.21	5.703E-01	1.553E-01	3.815E-02	1.039E-02	4.853E-02
0.21	5.797E-01	1.579E-01	3.813E-02	1.039E-02	4.851E-02
0.44	4.079E-01	3.325E-01	2.692E-02	2.195E-02	4.887E-02
0.44	4.151E-01	3.385E-01	2.691E-02	2.194E-02	4.885E-02
0.70	2.210E-01	5.396E-01	1.431E-02	3.493E-02	4.923E-02
0.70	2.156E-01	5.262E-01	1.431E-02	3.493E-02	4.925E-02
1.00		7.357E-01		4.946E-02	4.946E-02
1.00		7.597E-01		4.946E-02	4.946E-02
Error					5.0E-04

Table 8 con't.

Surfactant 1 = $C_{14}Cl$.

Surfactant 2 = $C_{14}BzCl$.

X_{S2}	C_{Pmon}	X_P	K_S (M^{-1})
0.00	2.776E-02	3.165E-01	1.140E+01
0.00	2.833E-02	3.109E-01	1.097E+01
0.02	2.910E-02	3.039E-01	1.044E+01
0.02	2.884E-02	3.065E-01	1.062E+01
0.04	3.098E-02	2.841E-01	9.171E+00
0.04	3.126E-02	2.811E-01	8.992E+00
0.08	3.106E-02	2.749E-01	8.853E+00
0.08	3.134E-02	2.717E-01	8.670E+00
0.10	3.116E-02	2.738E-01	8.788E+00
0.12	3.170E-02	2.699E-01	8.513E+00
0.12	3.129E-02	2.745E-01	8.774E+00
0.17	3.074E-02	2.751E-01	8.949E+00
0.17	3.100E-02	2.722E-01	8.780E+00
0.21	3.112E-02	2.744E-01	8.816E+00
0.21	3.219E-02	2.624E-01	8.152E+00
0.44	3.383E-02	2.596E-01	7.675E+00
0.44	3.496E-02	2.464E-01	7.049E+00
0.70	3.413E-02	2.394E-01	7.014E+00
0.70	3.253E-02	2.581E-01	7.936E+00
1.00	3.213E-02	2.643E-01	8.225E+00
1.00	3.420E-02	2.403E-01	7.027E+00
Error	1.8E-03	2.0E-02	1.2E+00

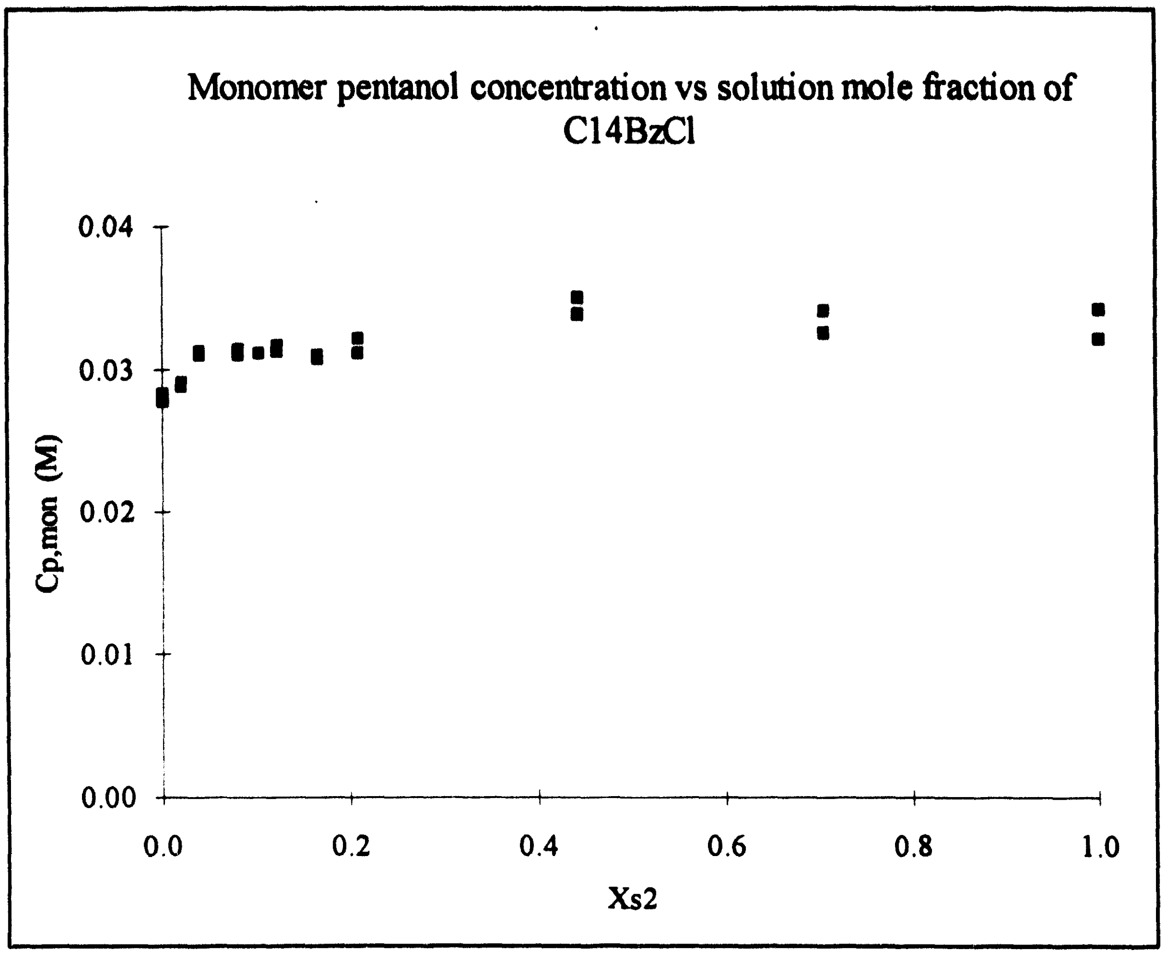


Figure 17 $C_{P,mon}$ versus X_{S2} for pentanol in $C_{14}Cl$ + $C_{14}BzCl$.

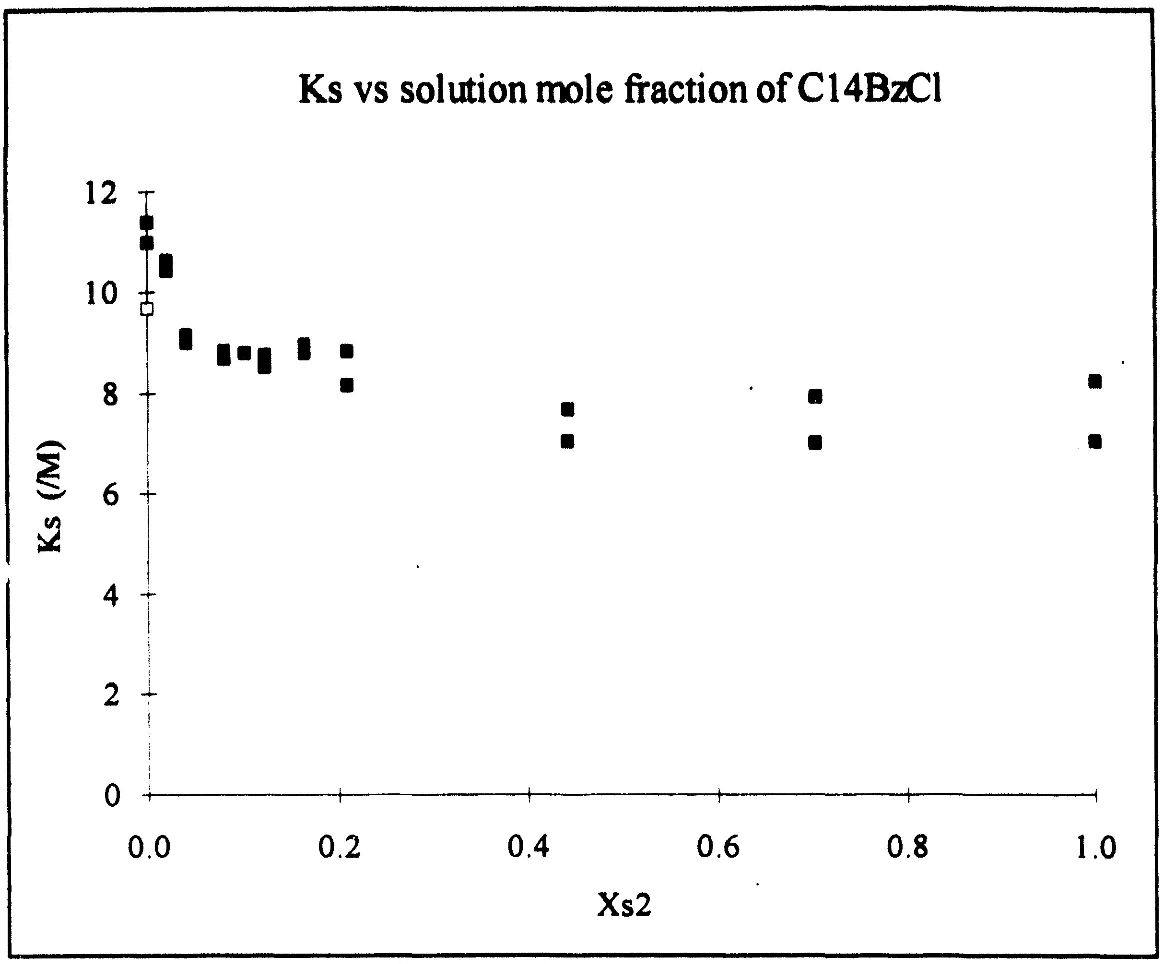


Figure 18 K_S versus X_{S2} for pentanol in $C_{14}Cl$ + $C_{14}BzCl$.

- ■ Points found experimentally.
- ☐ Calculated from X_P and $K = K_0(1 - X_PB)^2$, using K_0 and B values from figure 13 (pentanol in 0.05M $C_{14}Cl$).

Chapter 4

Discussion

For the single surfactant systems, the solubilization constant, K_S, decreases with increasing mole fraction of pentanol in the micelle. This can be explained by considering the probable location of pentanol in the micelle. The pentanol molecule is believed to solubilize in the palisade layer, with the OH group oriented toward the surface of the micelle and the five-carbon chain directed toward the interior of the micelle. As more pentanol solubilizes, the number of solubilization sites should decrease and the micelle should become less prone to solubilize any additional pentanol[1].

CPC, CTAB, and C_{16}BzCl all have the same hydrophobic tail group and show similar pentanol solubilization characteristics. While CPC is more effective at solubilizing pentanol at low values of X_P, the K_S values of all three surfactants converge in the region of X_P = 0.4-0.5. (See Figure 19) The moderate differences in solubilization at low mole fractions can be attributed to the different head groups on

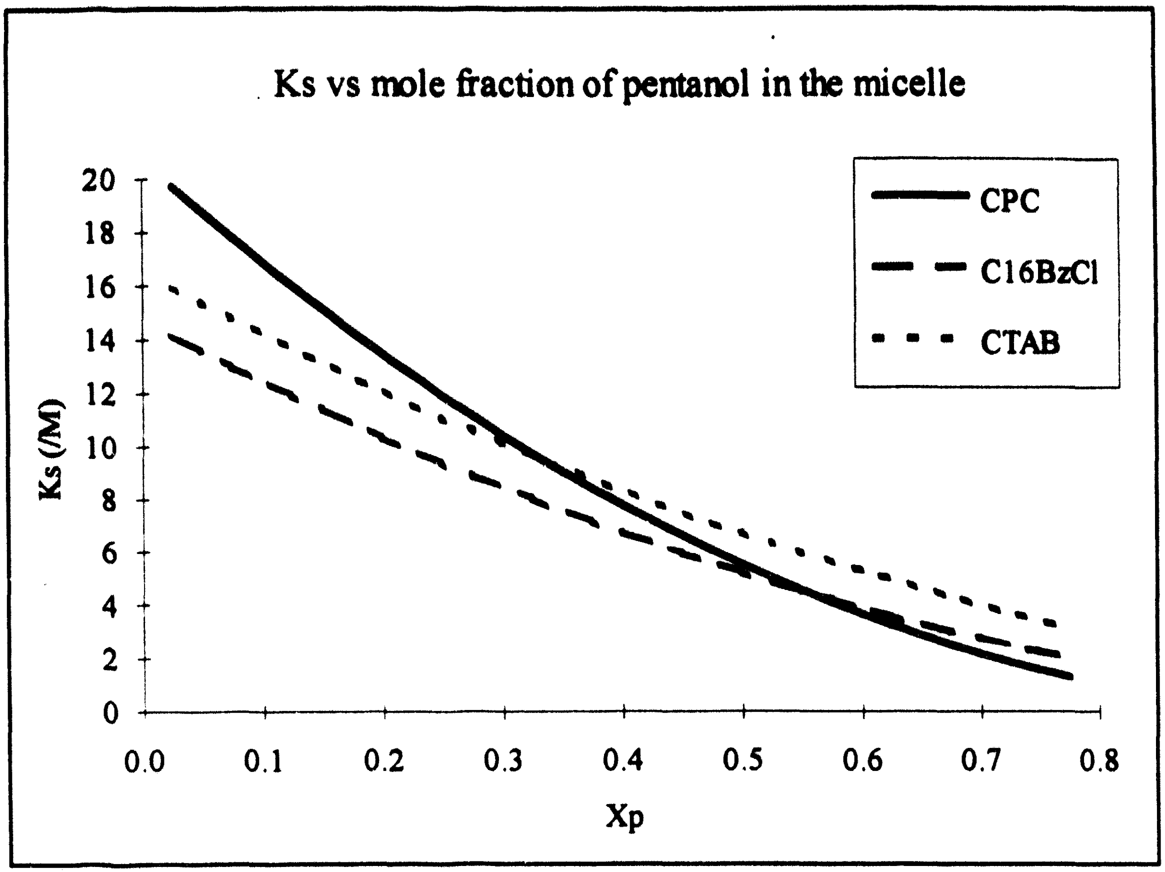


Figure 19 K_S versus X_P comparison of 16-carbon surfactants.

Note: The smooth lines above were obtained by fitting experimental data to the equation $K = K_0(1 - BX_P)^2$ using non-linear least squares analysis. Experimental points and least squares parameters for these surfactants are in Figures 9, 10, and 12.

each surfactant. The pyridinium cation in the CPC head group is apparently more favorable toward solubilizing pentanol at low mole fractions, while the benzyl group is less favorable. CTAB, having no aromatic groups in its hydrophilic moiety, is intermediate between CPC and $C_{16}BzCl$ at low mole fractions of pentanol.

The two surfactants with a fourteen-carbon hydrophilic group, $C_{14}Cl$ and $C_{14}BzCl$, exhibit similar results. (See figure 20) At low mole fractions the $C_{14}Cl$ has larger solubilization constants, but as more pentanol fills the micelle, the K_S values converge. These data imply that head group effects dominate at low solute mole fractions and decrease as more solute fills the micelle. At high solute mole fractions, the solute molecules compete with each other for sites in the micelle, as would be expected for a Langmuir-type adsorption[1,2]. Note also that surfactants with longer hydrophobic groups consistently solubilize more pentanol than the shorter-tailed surfactants.

When the K_S versus X_P graphs for 0.01M $C_{16}BzCl$ and 0.05M $C_{16}BzCl$ are compared (See Figure 21) it could be inferred that the less concentrated $C_{16}BzCl$ solutions have larger K_S values than the more concentrated $C_{16}BzCl$ solution. This apparent result may be due to the errors inherent in the gas chromatograph. As long as the surfactant is present in solution at concentrations greater than the CMC, the solubilization will not ordinarily change significantly over a wide range of surfactant concentrations. It should be noted that in the absence of added pentanol, $C_{16}BzCl$ will not dissolve in water to a concentration of 0.05M.

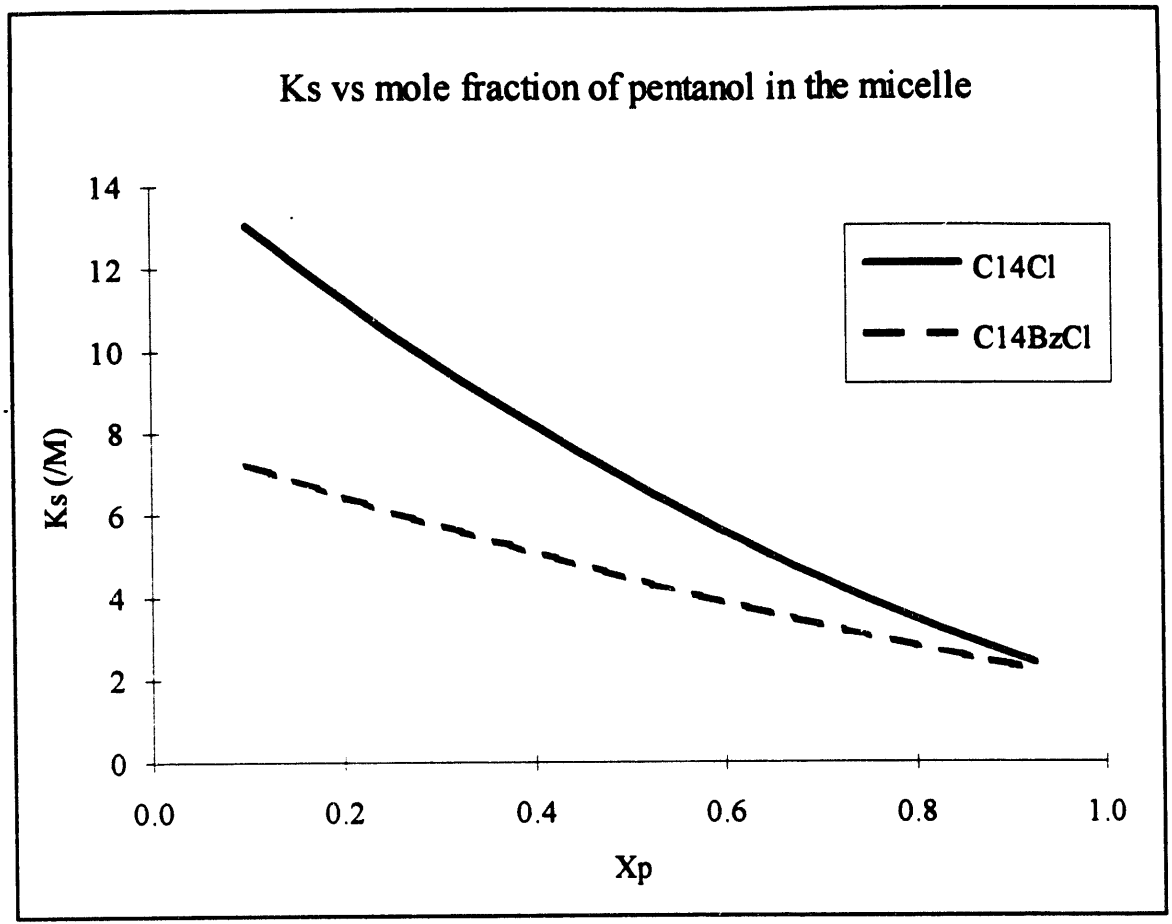


Figure 20 K_S versus X_P comparison of 14-carbon surfactants.

Note: The smooth lines above were obtained by fitting experimental data to the equation $K = K_0(1 - BX_P)^2$ using non-linear least squares analysis. Experimental points and least squares parameters for these surfactants are in Figures 13 and 14.

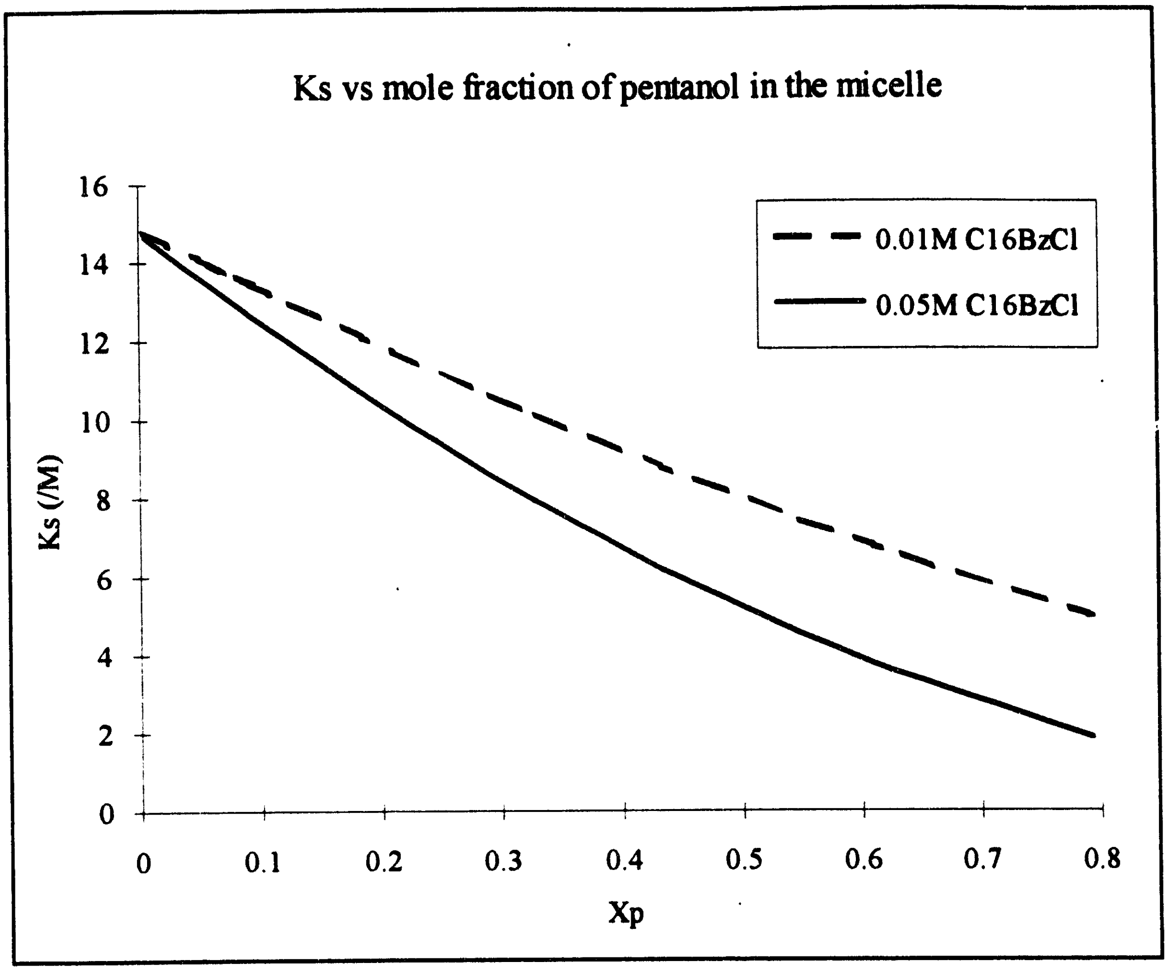


Figure 21 K_S versus X_P comparison of 0.01M $C_{16}BzCl$ and 0.05M $C_{16}BzCl$.

Note: The smooth lines above were obtained by fitting experimental data to the equation $K = K_0(1 - BX_P)^2$ using non-linear least squares analysis. Experimental points and least squares parameters for these surfactants are in Figures 11 and 12.

One of the goals of this project was to determine whether the large synergistic effect reported when pentanol is solubilized by mixtures of $C_{14}Cl$ and $C_{14}BzCl$ is real. More than a twofold increase in solubilization of pentanol was reported for mole fractions in the vicinity of 0.1 mole fraction $C_{14}BzCl^3$. In the present study, a large number of samples was prepared in this mole fraction region in order not to overlook any indication of synergistic solubilization. A side by side comparison of both results indicates that the reported synergism is not reproduced by this project; there is no sharp increase in solubilization at 0.1 mole fraction, or at any mole fraction.

(See figure 22)

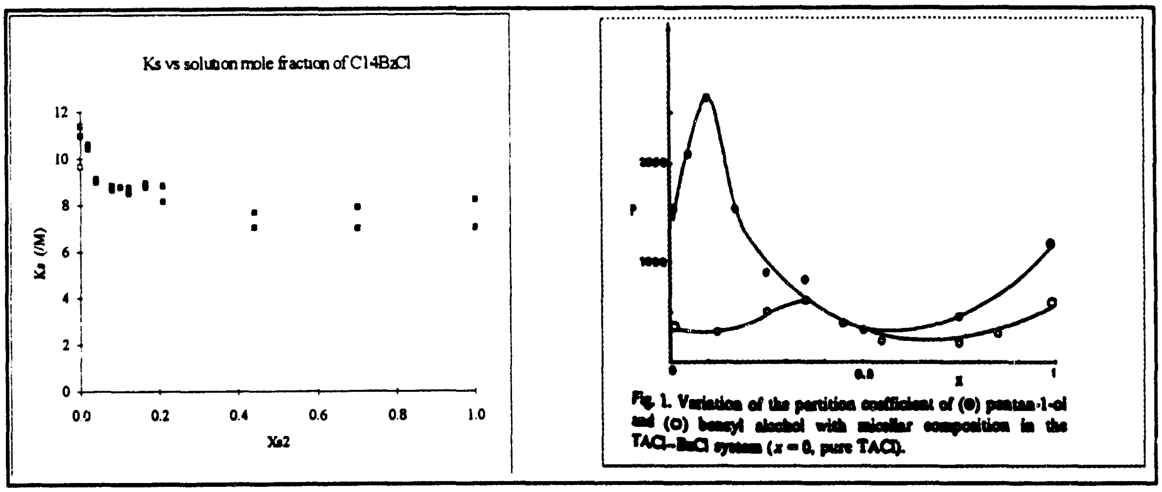


Fig. 1. Variation of the partition coefficient of (●) pentan-1-ol and (○) benzyl alcohol with micellar composition in the TACl–BzCl system ($x = 0$, pure TACl).

Figure 22 Comparison of $C_{14}Cl$ + $C_{14}BzCl$ systems.

The comparison figure on the right was adapted from reference 3. TACl refers to $C_{14}Cl$, and BzCl is $C_{14}BzCl$. Note that $K_S \approx P/55.5$, so that P = 2700 (the maximum in the second figure) corresponds to a $K_S \approx 48\ M^{-1}$. It is not clear whether the difference in the results originates in the analytical method used to obtain the data, or in the mathematical model used to interpret the data.

The solubilization results obtained in the present study for $C_{14}Cl$ + $C_{14}BzCl$ are very similar to data reported for hexanol solubilized in mixed micelles[4]. The value of K_S starts at about 11.5 M^{-1} with pure $C_{14}Cl$, and decreases with the addition of $C_{14}BzCl$ to a value of 8.5 at a solution mole fraction of 0.1 $C_{14}BzCl$. (See Figure 18) This initial sharp decrease in solubilization is probably real, although the uncertainty of ± 1.5 M^{-1} in K_S may make it difficult to determine the magnitude of the slope of a plot of K_S versus X_{S2} in the 0.1 mole fraction region. From the single surfactant analysis of $C_{14}Cl$, K_S was calculated to be closer to 10 than 11.5, which implies that the initial decrease of K_S is more gradual. The value of K_S remains nearly constant at X_{S2} values from 0.2 to 1.0 (pure $C_{14}BzCl$). The initial decrease in K_S might be explained by a competition between pentanol and $C_{14}BzCl$ for solubilization sites in the palisade layer of the predominantly $C_{14}Cl$ micelle[5,6]. As the mole fraction of $C_{14}BzCl$ increases, the micelle takes on the solubilization characteristics of a micelle composed of pure $C_{14}BzCl$. The new solubilization data are inherently interesting, although they do not verify the report of a synergistic solubilization effect.

A strong anti-synergistic solubilization effect was reported for the mixture of CPC + $C_{16}BzCl$[7]. The solubilization of pentanol in this mixture allegedly decreases dramatically in the solution mole fraction range of 0.1 to 0.9 $C_{16}BzCl$. Figure 18 from the present study shows a much more gradual change in K_S with variation in solution mole fraction, with the values of K_S being intermediate between the K_S values for each individual surfactant. As in the case of $C_{14}Cl$ + $C_{14}BzCl$, there was no observed evidence for pronounced synergistic or anti-synergistic effects.

Headspace chromatography is capable of measuring solubilization data for single and binary surfactant systems over a wide range of solute concentrations. Every method has limitations however, and headspace chromatography is no exception.

The first limitation is that the organic solute being solubilized should have a pure component vapor pressure of at least 1 torr. Solubilization studies of 2-naphthol (vapor pressure $\approx 10^{-3}$ torr at 20° C) were attempted using headspace chromatography, and the results were inconsistent.

The second limitation is that relative errors of measurements can be large, especially at low solute mole fractions. The measurements in this study were taken in duplicate or triplicate, but a variation in K_S values of plus or minus 3 M^{-1} is possible in this low solute mole fraction region. One reason for this scattering of data is limitations in the detection ability of the gas chromatograph. The amount of pentanol vapor removed from the space above the sample vial is only on the order of 10^{-8} moles at low mole fractions of pentanol in the micelle. At this level, the signal to noise ratio is low enough to cause large fluctuations in the measured peak areas. Since the samples were manually injected during this project, injection technique is always a possible source of error. Taking multiple measurements using an automated apparatus, and the use of solutes with higher vapor pressures would increase the precision of the measurements. Figure 23 is an example of K_S versus X_P for pentanol in 0.05M CPC with the associated error bars included. Note that the uncertainty decreases as more pentanol is detected by the gas chromatograph.

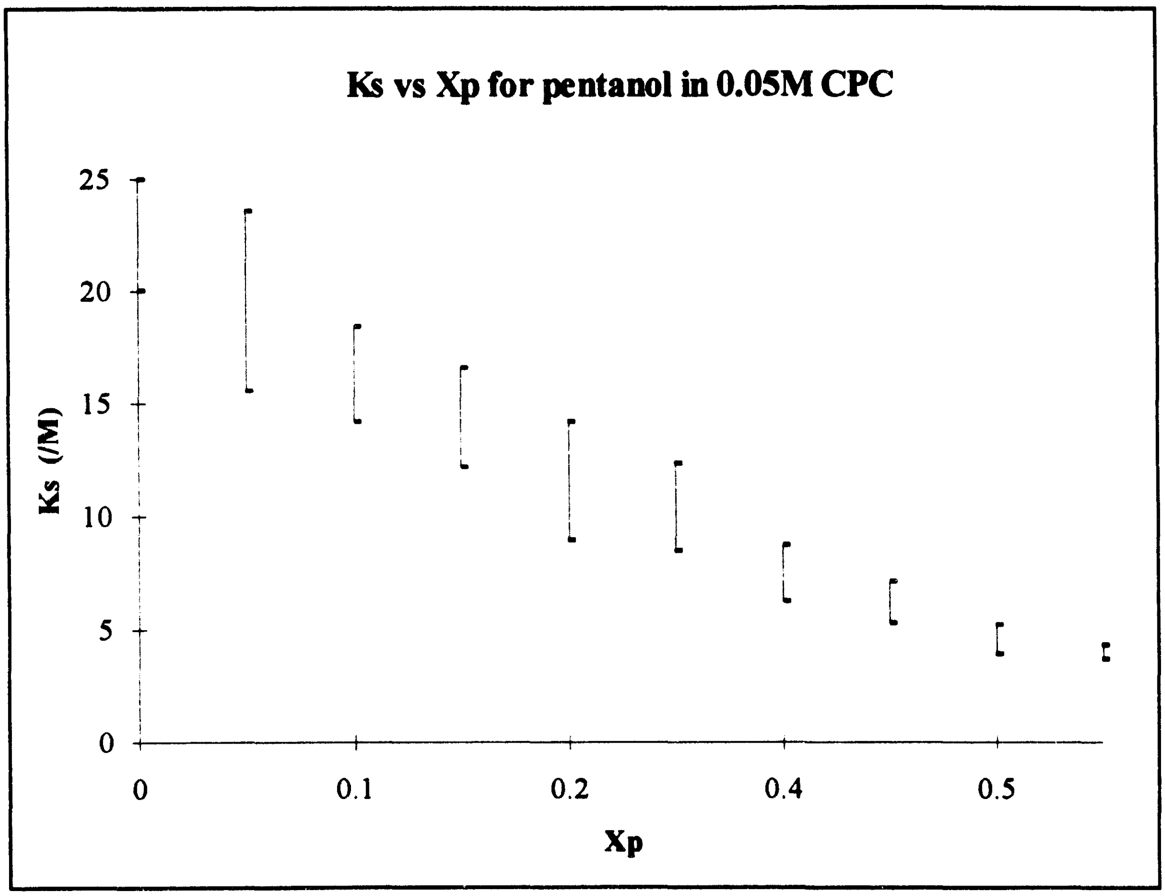


Figure 23 K_S versus X_P for pentanol in 0.05M CPC with error bars.

An accurate mathematical model is almost as important to solubilization studies as a reliable detection apparatus. All significant factors that affect the experimental results need to be included in the model. Changes in surfactant monomer micellar concentrations, counterion effects, and pentanol self-association cannot be ignored in processing experimental data to derive meaningful information. Our knowledge has progressed beyond the point where we need only subtract the CMC from total surfactant concentration to get the concentration of surfactant in micelles. Such a simplistic treatment of data may produce erroneous results and equally erroneous conclusions.

It is worth noting that each subsequent correction applied to a surfactant's monomer concentration, C_{mon}, (for counterion concentration, surfactant concentration, and presence of the organic solubilizate) *decreases* C_{mon}. C_{mon} becomes so small in some cases, for example in 0.05M C_{16} surfactant solutions, that it is a reasonably good approximation to ignore the presence of C_{mon} in the solubilization calculations. Table 9 lists values of K_S calculated for the pentanol/0.05M CPC system using: 1) values of C_{mon} calculated using equations 8-17, and 2) assuming that $C_{mon} = 0$.

Table 9 Comparison of K_S values for CPC.

K_S (M^{-1}) eqn. (8-17)	K_S (M^{-1}) with C_{mon}= 0
20.30	20.26
15.52	15.48
19.10	19.07
17.24	17.21
15.17	15.14
15.68	15.65
14.17	14.15
13.39	13.37
14.33	14.31
10.16	10.15
11.05	11.03
14.16	14.14
11.40	11.38
9.65	9.63
8.46	8.45
8.52	8.51
7.26	7.25
8.75	8.74
6.52	6.52
6.30	6.30
5.80	5.79
4.86	4.86
4.72	4.72
3.91	3.90
3.89	3.89
4.07	4.06
3.67	3.67

Table 9 demonstrates that any difference between the two sets of values is well within experimental error. On the other hand, for the 14-carbon surfactants this difference would start to become appreciable, particularly at low molarities of the surfactant.

REFERENCES

1. Dougherty, S.; Berg, J. *J.Coll. Interface Sci.* **1974,** *48,* 110-121.

2. Lee, B.; Christian, S.; Tucker, E.; Scamehorn, J. *Langmuir* **1990,** *6,* 230-235.

3. Bury, R.; Treiner, C.; Chevalet, J.; Makaysi, A. *Anal. Chim. Acta* **1991,** *251,* 69-77.

4. Nguyen, C.; Scamehorn, J.; Christian, S. *Colloid Surf.* **1988,** *30,* 335-344.

5. Uchiyama, H.; Christian, S.; Scamehorn, J.; Abe, M.; Ogino, K. *Langmuir* **1991,** *7,* 95-100.

6. Treiner, C.; Nortz, M.; Vaution, C. *Langmuir* **1990,** *6,* 1211-1216.

7. Treiner, C. 204th National Meeting of the American Chemical Society, Washington, D.C., August 1992; American Chemical Society: Washington, D. C.; Abstr. COLL 128.

Chapter 5

Conclusions and Future Work

The results of the present study confirm that headspace chromatography is a viable method for directly measuring solubilization of organic solutes in micelles throughout a wide range of solute mole fractions. This method is equally effective for single surfactant systems and for mixtures of surfactants.

The apparent synergism of the $C_{14}Cl$ + $C_{14}BzCl$ binary surfactant system in solubilizing pentanol[1] is not confirmed by this study. On the contrary, from headspace chromatography measurements, the behavior of the $C_{14}Cl$ + $C_{14}BzCl$ system has been shown to be much closer to ideality than has been previously claimed. Calorimetric determination of solubilization results, while potentially capable of producing reliable thermodynamic data, may not be the method of choice for measuring K_S values for single or binary surfactant systems.

Future Work

Headspace chromatography is not limited to measuring solubilities of organic solutes in cationic + cationic surfactant systems. Holland and Rubingh[2] have published numerous β_m values for other types of surfactant mixtures, opening the door to measuring K_S for many other binary surfactant systems. To calculate solubilization of binary mixed surfactant systems, the information needed is the CMCs for each surfactant, and the β_m value for the surfactant mixture. The surfactants should also be chosen to have the same counterion if the mathematical model developed here is to apply.

Another interesting project would be to measure the solubilization of 2- and 3-pentanol, and compare these data with those obtained for n-pentanol. Also, the effect of temperature on solubilization could be measured. Additionally, the extent of solubilization could be determined as a function of different surfactant concentrations, to show how possible changes in micelle size and shape influence solubilization.

Much more work needs to be accomplished in the area of mixed surfactant solubilization. Scamehorn[3] wrote, "The need for a simple, universal method of measuring individual monomer activities in mixed micelle systems is the most pressing problem in this field of research and deserves substantial attention." While headspace chromatography is not quite a universal method, it is a significant analytical tool for quantifying solubilization phenomena.

REFERENCES

1. Bury, R.; Treiner, C.; Makayssi, A. *Anal. Chim. Acta* **1991,** *251*, 69-77.

2. Holland, P.; Rubingh, D. In "Cationic Surfactants, Physical Chemistry"; Rubingh, D.; Holland, P., Ed; Marcel Dekker, Inc.: New York, 1991; Chapter 4.

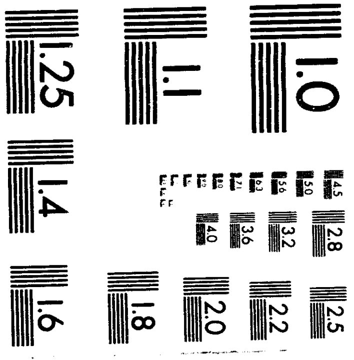
3. Scamehorn, J. In "Phenomena in Mixed Surfactant Systems"; Scamehorn, J., Ed.; American Chemical Society: Washington DC, 1986; Chapter 24.

APPENDIX 1

Nomenclature

α	Corrin-Harkins parameter (surfactant head size)
a_P	Activity of pentanol
β	Corrin-Harkins parameter (counter ion binding)
β_m	Nonideality coefficient of surfactant mixture
C_{Clfree}	Concentration of Cl^- ions not bound to micelles
C_{Cltot}	Total conc of Cl^- ions in solution
CMC_{surf}	CMC of surfactant (for 1-surfactant system)
CMC_{surf1}	CMC of surfactant 1
CMC_{surf1x}	CMC of surfactant 1 corrected for counterions
CMC_{surf2}	CMC of surfactant 2
CMC_{surf2x}	CMC of surfactant 2 corrected for counterions
C_{mic1}	Concentration of surfactant 1 in micelles
C_{mic2}	Concentration of surfactant 2 in micelles
C_{mictot}	Concentration of total surfactant in micelles
C_{mon}	Monomer concentration of surfactant (for 1-surfactant system)
C_{mon1}	Monomer concentration of surfactant 1
C_{mon2}	Monomer concentration of surfactant 2
$C_{P,bulk}$	Concentration of pentanol in bulk phase (unsolubilized pentanol in solution)
$C_{P,mic}$	Concentration of pentanol in the micelle
$C_{P,mon}$	Concentration of monomeric pentanol in bulk solution
$C_{P,sol}$	Concentration of pentanol in solution
$C_{P,tot}$	Total concentration of pentanol added to system
C_{surf1}	Concentration of surfactant 1 in solution
C_{surf2}	Concentration of surfactant 2 in solution
$C_{surf,tot}$	Concentration total surfactant in solution
$C_{surf,mic}$	Concentration of surfactant in micelles (for 1-surfactant system)
γ_P	Activity coefficient of pentanol in the micelle
γ_{surf1}	Activity coefficient for surfactant 1
γ_{surf2}	Activity coefficient for surfactant 2

K_0	Solubilization constant at $X_P = 0$
K_{d0}	Ratio of $C_{P,mon}$ to $C_{P,vap}$
K_S	Ratio of X_P to $C_{P,mon}$
$n_{P,bulk}$	Amount of pentanol in bulk phase
$n_{P,sol}$	Amount of pentanol in solution
$n_{P,tot}$	Total amount of pentanol in the system
$n_{P,vap}$	Amount of pentanol in vapor
Pk°_P	Peak height of pure pentanol
Pk_P	Peak height of pentanol in vapor
P_P	Partial vapor pressure of pentanol
P°_P	Vapor pressure of pure pentanol
X_{mic1}	Mole fraction of surfactant 1 in the micelle
X_{mic2}	Mole fraction of surfactant 2 in the micell
X_P	Mole fraction of pentanol in the micelle
X_{S2}	Solution mole fraction of surfactant 2


1.25
1.1
1.0
1.4
4.5
5.0
5.6
6.3
7.1
4.0
3.6
3.2
2.8
1.6
1.8
2.0
2.2
2.5

2 of 2

APPENDIX 2

Causes of Lower CMC for Single Surfactant Systems

At concentrations above the CMC, unbound surfactant counterions act on the surfactant monomers, forming more micelles. This makes C_{mon} less than the CMC. (Equations 8-10)

1

The presence of organic solute in solution lowers the activity coefficient of the surfactant. (Equation 16)

2

Organics solubilized in micelles reduce the mole fraction of surfactant in the micelle. (Equation 11)

3

$$C'_{mon} = \underset{(box\ 1)}{C_{mon}} \cdot \underset{(box\ 2)}{\gamma_{surf}} \cdot \underset{(box\ 3)}{(1 - X_p)} \qquad (Equation\ 17)$$

Causes of Lower CMC for Binary Surfactant Mixtures

At concentrations above the CMC, unbound surfactant counterions from both surfactants in the mixture act on the surfactant monomers, forming more micelles. This makes C_{mon1} and C_{mon2} less than the CMCs for each surfactant individually. (Equations 22-23)

4

Organics solubilized in micelles reduce the mole fraction of each surfactant in the micelle. (Equations 20-21)

5

Mixing two surfactants according to Rubingh solution theory lowers the activity coefficient, γ_{surf} of each surfactant, if β is negative. Organic in solution also acts to lower γ_{surf}. (Equations 26-27)

6

$$C_{mon,1,2} = \underset{(box\ 4)}{CMC_{surf1x,2x}} \cdot \underset{(box\ 5)}{\gamma_{surf,1,2}} \cdot \underset{(box\ 6)}{X_{mic,1,2}} \qquad \textit{(Equations 28-29)}$$

APPENDIX 3

SAMPLE MATHCAD PRINTOUT

In order to calculate the required solubilization data for binary cationic surfactant systems, it was necessary to set up a system of twenty-one unknowns and twenty-four equations and constraints. With forty-four total data points measured from both binary surfactant systems, it is obvious that the task of calculating the required values would be nearly impossible without the help of a digital computer. The software package MathCad 3.1 was used to calculate the data for this project. Equations were set up and values were also obtained using the SEQS software. In many cases SEQS delivered more accurate results, which were used as initial guesses in MathCad. MathCad was primarily used because of the readability of its input and output parameters. The sample MathCad printout shows the different steps and equations used to take the raw input data and produce the results shown in Chapter 3.

Section 1 is the section into which known values, such as CMCs of each surfactant and gas chromatograph peak areas, are entered.

Section 2 includes a series of equations that contain only one unknown. These values are calculated separately from the simultaneous equations in order to keep the simultaneous section as simple as possible.

Section 3 contains estimated values for all the variables to be solved. The computer starts with these "guesses" and performs multiple iterative calculations, changing values in order to minimize differences on both sides of the equal sign for each equation in the solve block. The actual method employed by MathCad to solve systems of simultaneous equations is called the Levenberg-Marquardt method.

Section 4 contains the "solve block," the actual set of simultaneous equations that will be solved. In addition to the actual equations, constraints such as $C_{mon2} > 0$ are inserted to keep the values positive. An equation system this large may have a large number of false solutions, and these constraints keep the solutions meaningful.

The solution vector is in section 5. When solving a system for more than one unknown value, MathCad lists the solutions in vector format. Each element of the vector represents one unknown value. After the solution vector are two more single-unknown equations that require values from the solution vector.

The final section displays the solutions to the system of equations. Each element from the solution vector is listed individually with its variable name. In addition to the solutions to the equations, the ERR value is shown. ERR is the size of the error vector for the solutions approximated in the solve block.

Headspace calculation for CPC-C16BzCl mixture

Section 1 Given information

$CMC\_surf1 := 9.0 \cdot 10^{-4}$

$CMC\_surf2 := 4 \cdot 10^{-4}$

$\beta := -0.8$

$P\_p0 := 1.68983$

$C\_surftot := .05$

$Pk\_p0 := 65944.5$

$C\_ptot := .0515$

$Pk\_p := 6241$

$X\_s2 := .1$

Section 2 Single unknown calculations

$$a\_p := \frac{Pk\_p}{Pk\_p0}$$

$$P\_p := P\_p0 \cdot a\_p$$

$$n\_pvap := \left(\frac{P\_p}{760}\right) \cdot \left[\frac{\frac{20}{1000}}{(.082057 \cdot 293.15)}\right]$$

$$n\_psol := \left(C\_ptot \cdot \frac{20}{1000}\right) - n\_pvap$$

$$Kd := \frac{n\_psol}{n\_pvap}$$

$$C\_pvap := \frac{n\_pvap}{\left(\frac{20}{1000}\right)}$$

$$C\_psol := \left(\frac{n\_psol}{20}\right) \cdot 1000$$

Section 3 Estimated values for unknowns in simultaneous equations

$CMC\_surf1x := 1 \cdot 10^{-4}$

$CMC\_surf2x := 1$

$\gamma\_surf1 := 1$

$\gamma\_surf2 := .8$

$C\_mon1 := 1 \cdot 10^{-6}$

$C\_mon2 := 1 \cdot 10^{-4}$

$X\_mic1 := .6$

$X\_mic2 := .05$

$C\_clfree := .00177$

$C\_mic1 := .04$

$C\_mic2 := .004$

$X\_s1 := .9$

$C\_mictot := .05$

$Ks := 11$

$X\_p := .3$

$C\_pbulk := .03$

$C\_pmic := .02$

$\gamma\_p := .3$

$C\_surf1 := .045$

$C\_surf2 := .005$

$C\_pmon := .03$

Section 4 Simultaneous equations

Given

$$\mathrm{CMC\_surf1x} = \frac{(\mathrm{CMC\_surf1})^{1.73}}{\mathrm{C\_clfree}^{.73}} \qquad \mathrm{CMC\_surf2x} = \frac{(\mathrm{CMC\_surf2})^{1.73}}{\mathrm{C\_clfree}^{.73}}$$

$$\mathrm{C\_surf1} = \mathrm{C\_mon1} + \mathrm{C\_mic1} \qquad \mathrm{C\_surf2} = \mathrm{C\_mon2} + \mathrm{C\_mic2}$$

$$\mathrm{C\_mon1} = \mathrm{CMC\_surf1x} \cdot (\mathrm{X\_mic1}) \cdot \gamma\mathrm{\_surf1} \qquad \mathrm{C\_mon2} = \mathrm{CMC\_surf2x} \cdot \mathrm{X\_mic2} \cdot \gamma\mathrm{\_surf2}$$

$$\gamma\mathrm{\_surf1} = e^{\beta \cdot \mathrm{X\_mic2}^2} \qquad \gamma\mathrm{\_surf2} = e^{\beta \cdot \mathrm{X\_mic1}^2}$$

$$\mathrm{X\_mic1} = \frac{\mathrm{C\_mic1}}{(\mathrm{C\_mic1} + \mathrm{C\_mic2} + \mathrm{C\_pmic})} \qquad \mathrm{X\_mic2} = \frac{\mathrm{C\_mic2}}{(\mathrm{C\_mic1} + \mathrm{C\_mic2} + \mathrm{C\_pmic})}$$

$$\mathrm{X\_p} = \frac{\mathrm{C\_pmic}}{(\mathrm{C\_pmic} + \mathrm{C\_mictot})} \qquad \mathrm{C\_pmon} = \frac{\mathrm{a\_p}}{3.2700052623}$$

$$\mathrm{C\_mictot} = \mathrm{C\_mic1} + \mathrm{C\_mic2}$$

$$\mathrm{X\_p} + \mathrm{X\_mic2} + \mathrm{X\_mic1} = 1$$

$$\mathrm{C\_pmic} = \mathrm{C\_psol} - \mathrm{C\_pbulk} \qquad \mathrm{C\_surftot} = \mathrm{C\_surf1} + \mathrm{C\_surf2}$$

$$\mathrm{C\_clfree} + \mathrm{C\_mictot} \cdot .73 = \mathrm{C\_surf1} + \mathrm{C\_surf2}$$

$$\mathrm{Ks} = \frac{\mathrm{X\_p}}{\mathrm{C\_pmon}}$$

$$\mathrm{a\_p} = 3.2700052623 \cdot \mathrm{C\_pbulk} - 1.3676195658 \cdot \mathrm{C\_pbulk}^2$$

$$\mathrm{X\_s1} = \frac{\mathrm{C\_surf1}}{\mathrm{C\_surftot}} \qquad \gamma\mathrm{\_p} = \frac{\mathrm{a\_p}}{\mathrm{X\_p}}$$

$$\mathrm{C\_mon2} > 0$$

$$\mathrm{X\_s1} = 1 - \mathrm{X\_s2}$$

$$\mathrm{C\_mon1} > 0$$

Section 5 Solution vector

$$\begin{bmatrix} \text{C\_pmon} \\ \text{C\_surf1} \\ \text{C\_surf2} \\ \text{X\_s1} \\ \gamma\text{\_p} \\ \text{C\_pmic} \\ \text{C\_pbulk} \\ \text{Ks} \\ \text{X\_p} \\ \text{X\_mic1} \\ \text{CMC\_surf1x} \\ \text{CMC\_surf2x} \\ \gamma\text{\_surf1} \\ \gamma\text{\_surf2} \\ \text{C\_mon1} \\ \text{C\_mon2} \\ \text{X\_mic2} \\ \text{C\_clfree} \\ \text{C\_mic1} \\ \text{C\_mic2} \\ \text{C\_mictot} \end{bmatrix} := \text{minerr}(\text{C\_pmon}, \text{C\_surf1}, \text{C\_surf2}, \text{X\_s1}, \gamma\text{\_p}, \text{C\_pmic}, \text{C\_pbulk}, \text{Ks}, \text{X\_p}, \text{X\_mic1}, \text{CMC\_}$$

More single equation calculations requiring values found in solution vector

$$\text{n\_pbulk} := \text{C\_pbulk} \cdot \frac{20}{1000} \qquad \text{Kd0} := \frac{\text{C\_pmon}}{\text{C\_pvap}}$$

Section 6 Solutions and residuals displayed

$\mathrm{a\_p} = 9.46401899 \cdot 10^{-2}$

$\mathrm{P\_p} = 1.59925832 \cdot 10^{-1}$

$\mathrm{n\_pvap} = 1.74956261 \cdot 10^{-7}$

$\mathrm{n\_psol} = 1.02982504 \cdot 10^{-3}$

$\mathrm{n\_pbulk} = 5.86019583 \cdot 10^{-4}$

$\mathrm{CMC\_surf1x} = 1.24265368 \cdot 10^{-4}$

$\mathrm{CMC\_surf2x} = 3.05544417 \cdot 10^{-5}$

$\gamma\mathrm{\_surf1} = 9.96163674 \cdot 10^{-1}$

$\gamma\mathrm{\_surf2} = 7.33104786 \cdot 10^{-1}$

$\mathrm{C\_mon1} = 7.71157846 \cdot 10^{-5}$

$\mathrm{C\_mon2} = 1.55263857 \cdot 10^{-6}$

$\mathrm{C\_psol} = 5.14912522 \cdot 10^{-2}$

$\mathrm{C\_pbulk} = 2.93009792 \cdot 10^{-2}$

$\mathrm{C\_pmic} = 2.2190273 \cdot 10^{-2}$

$\gamma\mathrm{\_p} = 3.07551689 \cdot 10^{-1}$

$\mathrm{Kd0} = 3.30847348 \cdot 10^{3}$

$\mathrm{C\_clfree} = 1.35574279 \cdot 10^{-2}$

$\mathrm{X\_mic1} = 6.22963314 \cdot 10^{-1}$

$\mathrm{X\_mic2} = 6.93154367 \cdot 10^{-2}$

$\mathrm{C\_mic1} = 4.49228842 \cdot 10^{-2}$

$\mathrm{C\_mic2} = 4.99844736 \cdot 10^{-3}$

$\mathrm{C\_mictot} = 4.99213316 \cdot 10^{-2}$

$\mathrm{X\_s1} = 9 \cdot 10^{-1}$

$\mathrm{X\_s2} = 1 \cdot 10^{-1}$

$\mathrm{Ks} = 1.06323762 \cdot 10^{1}$

$\mathrm{Pk\_p} = 6.241 \cdot 10^{3}$

$\mathrm{X\_p} = 3.07721249 \cdot 10^{-1}$

$\mathrm{C\_pmon} = 2.89419075 \cdot 10^{-2}$

$\mathrm{C\_surf1} = 4.5 \cdot 10^{-2}$

$\mathrm{C\_surf2} = 5 \cdot 10^{-3}$

$\mathrm{ERR} = 4.37411961 \cdot 10^{-15}$

DATE
FILMED
6/6/94

END