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SELECTIVE SOLUBILIZATION IN AQUEOUS SURFACTANT SOLUTIONS

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Experimental results as well as a thermodynamic treatment of solubilization of mixtures of hydrocarbons in aqueous surfactant solutions are presented. Binary mixtures of benzene-hexane, benzene-cyclohexane and hexane-cyclohexane have been solubilized in aqueous solutions of some common anionic and cationic surfactants and of sodium deoxycholate. It is shown that molecules can be selectively solubilized from binary hydrocarbon mixtures. Large selectivity ratios of up to about seven have been obtained for benzene compared to hexane especially when the binary solubilize phase is hexane-rich. In general, the selectivity ratio of one component over another depends on the difference in the molar solubilization ratios of the single components.

A thermodynamic treatment is developed to examine the origin of the selective solubilization and to predict the molar solubilization ratios of various compounds both singly and in mixtures. The treatment takes into account (i) the change in the surface area per amphiphile of the micelle due to the incorporation of the solubilizates (this causes a change in the steric and electrostatic interactions between the head groups and in the micellar core-water interactions), (ii) the hydrophobic effect associated with the transfer of the solubilize from water to the micelle, and (iii) the entropy of mixing of the surfactant and solubilizates in the micelle. It is found that the relative balance between the changes in the head group

interactions on the one hand and that in the micellar core-water interactions on the other principally determine the nature and magnitude of solubilization. In general, the more polar solubilizates, those with smaller molecular volumes and those possessing low stereochemical flexibility, are preferentially solubilized.

The observed absence of any selectivity for benzene over hexane or cyclohexane in solutions of sodium deoxycholate is shown to be consistent with the comparable molar solubilization ratios of the two pure hydrocarbons. This markedly different solubilization behavior is interpreted in terms of the peculiar molecular structure of sodium deoxycholate and its ability to generate only very small primary aggregates.

Experimental solubilization data involving benzene + hexane mixtures are observed to display a synergistic effect. In the framework of the thermodynamic treatment, this synergism is shown to imply that at least some of the benzene molecules are located close to the micelle-water interface.

INTRODUCTION

Surface active molecules self-assemble as micelles or vesicles in dilute aqueous solutions so as to minimize the contact between their hydrophobic tails and water. As a result, the interior of micelles and the spherical shells of vesicles are highly non-polar, capable of accommodating other non-polar molecules. Consequently, hydrocarbon molecules which are only sparingly soluble in water can be solubilized in significant amounts in aqueous surfactant solutions¹⁻³. Here, by solubilization we understand both (i) the molecular dispersion of the solubilizates between the hydrocarbon tails of the surfactant molecules forming the micelles or vesicles (Type I) as well as (ii) the formation of a core of solubilizates surrounded by a layer of surfactant molecules (Type II) (Figure 1). The extent of solubilization depends on the chemical characteristics of surfactant and solubilizate as well as on the concentration of the solution and temperature. Experimental data regarding single component solubilizates show that the solubilization capacity of surfactants differs significantly for different solubilizates. Figure 2 shows the molar solubilization ratios (i.e., moles of solubilizate per mole of surfactant in micelles) for various solubilizates in 0.1M cetyl pyridinium chloride solution as a function of the molecular volume of the solubilizate. The same data are also represented against a combined function of both

molecular volume and polarity of the solubilize, using the interfacial tension of the solubilize against water σ_s as a measure of the polarity. In general, the molar solubilization ratio is found to decrease with increasing molecular volume of the solubilize. Also, the more polar molecules are solubilized in relatively larger

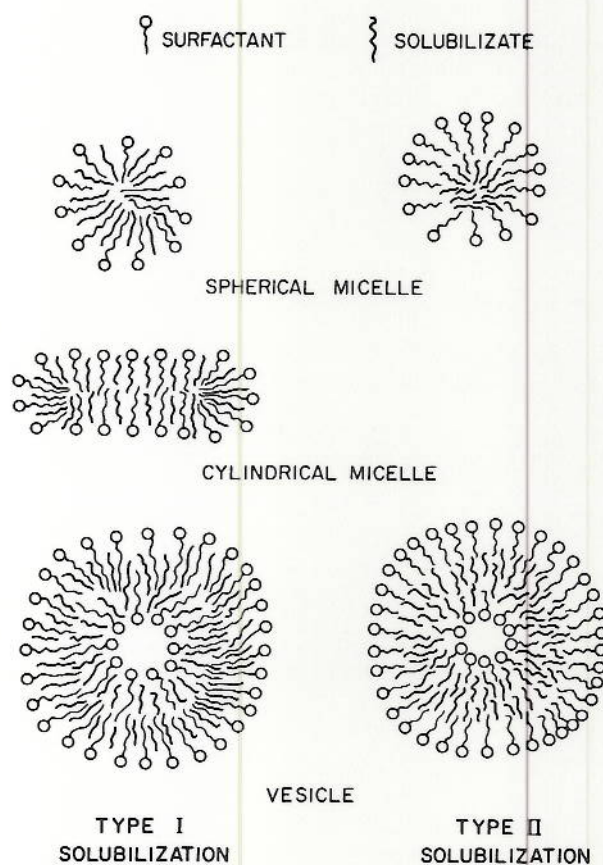


Figure 1. Schematic representation of micelles and vesicles containing solubilizates. For Type I solubilization, the solubilize molecules are located between the surfactant tails in the aggregates. For Type II solubilization, the solubilize molecules do not mix with the surfactant tails in the aggregates and form a core of their own in micelles or a shell in vesicles.

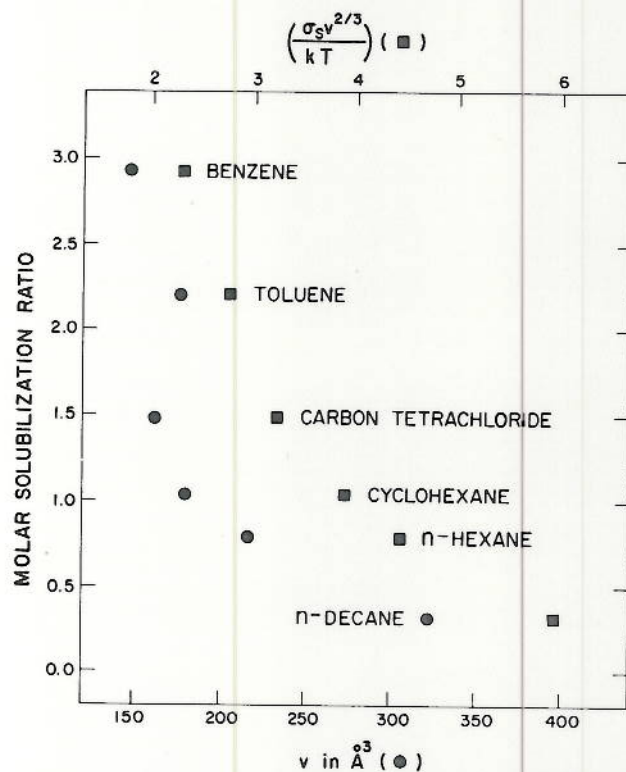


Figure 2. Molar solubilization ratio of hydrophobic solubilizes in 0.1M Cetyl Pyridinium Chloride solution against the molecular volume of the solubilize. The same data are also plotted against the product of σ_s/kT (representing the polarity of the solubilize) and $v^{2/3}$ (representing the molecular size of the solubilize).

amounts compared to the less polar ones. Similar results have been reported in the literature for other surfactants⁴⁻⁷. A natural question is whether this significant variation in the molar solubilization ratios can lead to highly selective solubilization of one of the components when the surfactant solution is contacted with a binary or a multicomponent mixture of solubilizes. The only experimental study that has been reported in literature⁸ involves the binary mixture of benzene + cyclohexane solubilized by sodium deoxycholate micelles. In this case, the composition of benzene + cyclohexane solubilized inside the micelles is found to be identical to that of the bulk organic phase in contact with the aqueous surfactant solution. This implies that there is no preference for one or the other of the compounds. It should be noted, however, that in this case, even for single

components, the molar solubilization ratios do not differ appreciably. Consequently, there is no a priori reason to anticipate any selectivity when binary mixtures of benzene + cyclohexane are solubilized in sodium deoxycholate solutions.

One goal of this paper is to investigate and explain why the surfactant solutions exhibit high solubilization capacity for some molecules and low capacity for others. In particular, one would like to identify the role of the molecular volume of solubilize, its polarity, the nature of surfactant tail and of the polar head group, in determining the molar solubilization ratios. For this purpose, a thermodynamic treatment of solubilization is developed linking measurable solubilization characteristics to the molecular characteristics of the surfactant and solubilize. Further, one is especially interested in knowing whether the molecules with high molar solubilization ratios as single components would also be selectively solubilized when present in binary or multicomponent mixtures. Consequently, the second goal of this paper is to determine, both experimentally and on the basis of a thermodynamic treatment, the molar solubilization ratios and the selectivity when binary hydrocarbon mixtures are solubilized.

In the next section, the experimental results obtained in this laboratory are presented. In Section III, a thermodynamic treatment for the solubilization of single components and binary mixtures is developed. In Section IV, the experimental results are interpreted on the basis of the thermodynamic model and the origin of high or low solubilization capacities for various solubilizes is explained.

II. EXPERIMENTAL STUDY

The solubilization capacities for benzene, hexane and cyclohexane as single components and as binary mixtures in a number of surfactant solutions have been measured. The surfactants used include cetyl pyridinium chloride (CPC), sodium dodecyl sulfate (SDS), sodium deoxycholate (SDC), dodecyl trimethylammonium chloride (DTAC), Aerosol AY, and some of their binary mixtures. The effect of added electrolytes has also been examined. Only representative results are presented in this paper; more complete experimental data will be published elsewhere⁹.

The solubilization measurements have been carried out as follows: equal volumes of aqueous surfactant solution and solubilize phase have been contacted over a period of 24 hours to insure equilibration. The resulting system was centrifuged to break any emulsion formed and to separate the aqueous and organic phases. The composition of the solubilizes in both phases have

been determined by gas chromatography using a flame ionization detector. In a few cases, a third emulsion phase has been observed. The solubilize composition in this emulsion phase was always found to be identical to that of the organic phase. From the gas chromatographic analysis the total amount of solubilize in the aqueous phase was determined. Assuming that the entire surfactant is retained in the aqueous phase and accounting for the critical micelle concentration (CMC) of the surfactant and for the solubility of the hydrocarbon in water, the molar solubilization ratio (i.e., the moles of solubilize per mole of surfactant in the micelle) has been calculated.

Figure 2 presents the molar solubilization ratios in 0.1M cetyl pyridinium chloride solutions for a number of organic compounds. As mentioned before, the molar solubilization ratio is found to bear a relation to the molecular volume v of the solubilize. This correlation improves further if in addition to the molecular volume, one takes into account the polarity of the solubilize as well. It should be noted that while cyclohexane and toluene have comparable molecular volumes, they give rise to significantly different molar solubilization ratios. However, if the polarity of toluene via σ_s is taken into account, then the figure shows that the correlation is improved.

Figure 3 contains results for the solubilization of benzene + cyclohexane mixtures in sodium deoxycholate solutions. The only other experimental data available in literature⁸ for this binary system are also included for comparison. The present results, obtained using a direct gas chromatographic analysis method, are in reasonable agreement with those from literature; the somewhat lower values reported in literature⁸ are probably due to the limitations of the method of extraction into carbon tetrachloride of the solubilized micelles, prior to analysis. Both sets of experimental data show that, in sodium deoxycholate solutions, the molar solubilization ratios for single component benzene and cyclohexane phases do not differ appreciably. These results can be contrasted to those shown in Figure 2 for cetyl pyridinium chloride solutions.

Figure 4 shows the molar solubilization ratios of benzene and hexane in cetyl pyridinium chloride (CPC) and sodium dodecyl sulfate (SDS) solutions as functions of the bulk phase composition. The selectivity ratio for benzene over hexane in CPC, SDS and DTAC are shown in Figure 5. The selectivity ratio for component A in a binary mixture of A and B is defined as:

$$\text{Selectivity Ratio for A} = \frac{(X_A/X_B) \text{ in micelles}}{(X_A/X_B) \text{ in bulk solubilize phase}}, \quad (1)$$

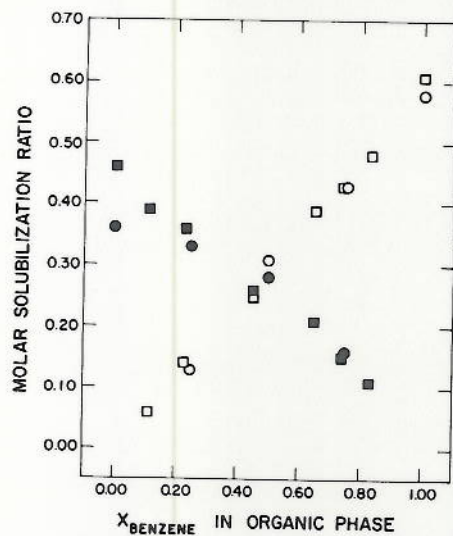


Figure 3. Molar solubilization ratio of benzene and cyclohexane in 0.1M sodium deoxycholate solutions as a function of the composition of the bulk solubilize phase of benzene + cyclohexane. Open symbols are benzene and filled symbols are cyclohexane. Squares represent present experimental data and circles are from literature⁸ both at 0.01M NaOH and 0.15M NaCl.

where X is the mole fraction. The experimental data show that there is no selectivity for benzene or cyclohexane when sodium deoxycholate is used as surfactant. In marked contrast, DTAC, CPC and SDS solutions show significant selectivity for benzene when the organic phase is hexane-rich. The selectivity ratio is as large as seven when solutions of DTAC are contacted with hexane-rich phases. The selectivity for benzene is exhibited over the entire range of composition, the selectivity ratio decreasing as the mole fraction of benzene increases in the solubilize phase. These results are interpreted later on the basis of a thermodynamic treatment of solubilization which is developed in the paper.

III. THERMODYNAMICS OF SOLUBILIZATION

At equilibrium, the aqueous solution consists of singly dispersed surfactant and solubilize molecules, as well as surfactant aggregates containing solubilizates. The size distribution of the

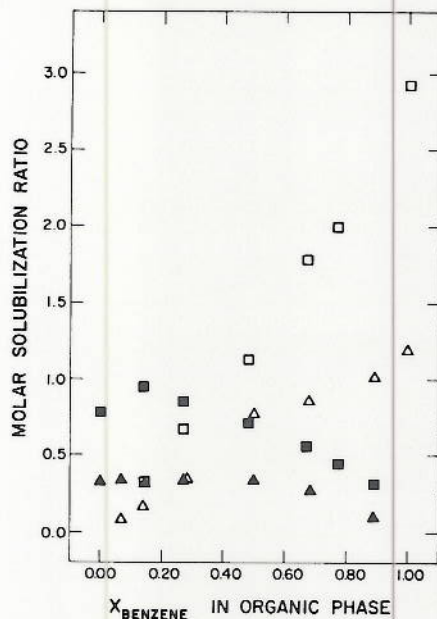


Figure 4. Molar solubilization ratio of benzene and hexane in 0.1M cetyl pyridinium chloride (squares) and in 0.1M sodium dodecyl sulfate (triangles) solutions as a function of the composition of the bulk solubilize phase of benzene + hexane. Open symbols represent benzene and filled symbols represent hexane.

aggregates containing g surfactant molecules and j' and j'' solubilize molecules of kind s' and s'' respectively, is given¹⁰ by

$$X_{gj'j''} = X_{1s'}^{gX_{1s'}^{j'}} X_{1s''}^{j''} \exp\left(-\frac{\mu_{gj'j''}^0 - g\mu_{1s'}^0 - j'\mu_{1s''}^0 - j''\mu_{1s''}^0}{kT}\right). \quad (2)$$

In the above equation, X is the mole fraction, μ^0 is the standard chemical potential in dilute solutions, k is the Boltzmann constant and T is the temperature. The subscripts 1 , $1s'$ and $1s''$ refer to the singly dispersed surfactant and solubilizates s' and s'' , respectively. When there is only one solubilize $j''=0$ and for surfactant solutions containing no solubilize $j'=j''=0$. The molar solubilization ratio of solubilize j' can be calculated as the ratio

$$\left(\frac{\sum_{g>1} \sum_{j'} \sum_{j''} j' X_{gj'j''}}{\sum_{g>1} \sum_{j'} \sum_{j''} g X_{gj'j''}} \right)$$

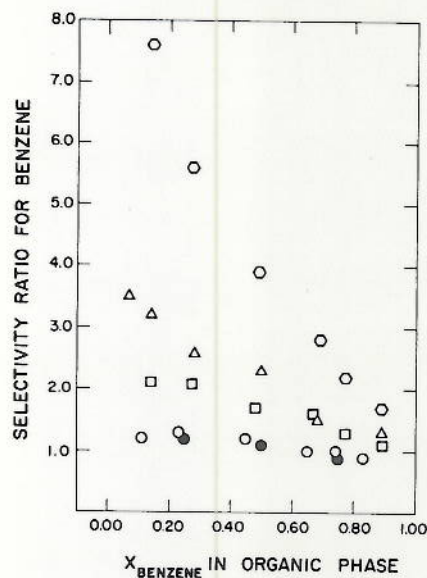


Figure 5. Selectivity ratio for benzene against the mole fraction of benzene in the bulk phase. Open circles: benzene + cyclohexane solubilized in 0.1M sodium deoxycholate; Filled circles: benzene + cyclohexane solubilized in 0.1M sodium deoxycholate from literature⁸; Squares: benzene + hexane solubilized in 0.1M sodium dodecyl sulfate; Triangles: benzene + hexane solubilized in 0.1M cetyl pyridinium chloride; Hexagons: benzene + hexane solubilized in 0.1M dodecyl trimethyl ammonium chloride.

Since the surfactants used here form only micelles and not vesicles, the thermodynamic treatment is developed only for micelles.

The calculations are carried out, in case of Type I solubilization, assuming the micelles to be spherical at small aggregation numbers and cylindrical with hemispherical ends at large aggregation numbers. The transition from spheres to cylinders is considered to occur when the radius of the micelle becomes equal to the extended length of the surfactant molecule. For micelles of intermediate sizes in the transition region between spheres and cylinders, various shapes such as ellipsoids, discs, etc., have been suggested¹¹. Here, the intermediate sized micelles are also treated as cylinders with hemispherical ends. For Type II solubilization, the micelles are assumed to be spherical and to contain a core of solubilize molecules.

The difference in the standard chemical potential, $\Delta\mu^{\circ} = (\mu_{g,j,i}^{\circ} - g\mu_1^{\circ} - j'\mu_{1s}^{\circ} - j''\mu_{1s}^{\circ})$, contains the following contributions: (i) the free energy change due to the transfer of the surfactant tail and solubilizates from water to the micelle, $\Delta\mu_{Tr}^{\circ}$, (ii) the interfacial free energy at the micellar core-water interface, $\Delta\mu_{interface}^{\circ}$, (iii) the free energy due to steric interactions between the surfactant head groups at the micellar surface, $\Delta\mu_{steric}^{\circ}$, (iv) electrostatic interactions between the head groups (for ionic surfactants) at the micellar surface, $\Delta\mu_{electrostatic}^{\circ}$, and, (v) the free energy change due to the mixing of surfactant and solubilizate molecules inside the micelles, $\Delta\mu_{mixing}^{\circ}$ (in the case of Type I solubilization). Expressions for these contributions have been obtained in an earlier paper¹⁰ by using a statistical thermodynamic approach, but are presented here in a simplified form so as to facilitate their use in calculations. A thermodynamic treatment of single component solubilization has been independently developed by Dadyburjor¹² along somewhat similar lines.

Transfer free energy. When singly dispersed surfactant and solubilizate molecules are incorporated into micelles, the hydrocarbon tail of the surfactant and the hydrocarbon solubilizate molecule are transferred from water to an almost liquid hydrocarbon-like environment. This change in environment produces a negative free energy contribution to $\Delta\mu^{\circ}$.

$$\Delta\mu_{Tr}^{\circ} = g\Delta\mu_{Tr,1}^{\circ} + j'\Delta\mu_{Tr,1s}^{\circ} + j''\Delta\mu_{Tr,1s}^{\circ} \quad (3)$$

For the transfer of a hydrocarbon molecule from water to a bulk hydrocarbon liquid, the transfer free energy $\Delta\mu_{Tr}^{\circ}$ has been experimentally estimated^{3,13} to be about $-1.47kT$ per CH_2 group and $-3.25kT$ per CH_3 group for aliphatic hydrocarbons, $-1.83kT$ per CH_2 group for cyclohexane, and $-1.28kT$ per CH group for benzene. However, compared to a hydrocarbon molecule in a bulk hydrocarbon liquid, the hydrocarbon tails of the surfactant constituting the micelle are somewhat constrained, since their polar heads are anchored at the micellar surface^{3,14-19}. To estimate the correction to the free energy change $\Delta\mu_{Tr,1}^{\circ}$ associated with these conformational constraints, a model was used in which the surfactant molecules in the micelle were free to rotate about their long axis while rotation about their two short axes were forbidden^{14,15}. On the basis of such a physical model, the correction to $\Delta\mu_{Tr,1}^{\circ}$ due to the conformational constraints has been estimated to be $0.25kT/CH_2$ group and $0.42kT/CH_3$ group of an aliphatic hydrocarbon tail. Taking into account these corrections, $\Delta\mu_{Tr,1}^{\circ}$ for the surfactant tail is estimated for aliphatic hydrocarbons by using the following modified group contributions: $-1.22kT/CH_2$ group and $-2.83kT/CH_3$ group. Values of $\Delta\mu_{Tr,1}^{\circ}$ can also be estimated using the experimental values of CMC as a function of surfactant tail length for a homologous series of surfactants. On this basis, Tanford³ has

In the above equation, a is the surface area of the hydrophobic core of the micelle per surfactant molecule and a_0 is the area per surfactant molecule shielded by the polar head from contact with water. σ is taken equal to the interfacial tension between the surfactant tail and water for Type II solubilization and also for those cases of Type I solubilization in which the solubilize is assumed to be located farther away from the interface. However, when in Type I solubilization the solubilize is assumed to be located near the interface, σ has to account for the presence of the solubilize.

Steric Interactions. The micellar surface is crowded with polar head groups of the surfactants. Therefore, the steric repulsions between the head groups at the micellar surface has a positive free energy contribution to $\Delta\mu^0$. An expression for the free energy due to steric repulsions can be written by analogy with those used for excluded volume interactions. One of the simplest forms appears in the van der Waals equation where the volume occupied by the molecules themselves is unavailable for their translation. This excluded volume thus constitutes a measure of steric repulsion between the molecules. Using a two dimensional analog of the above physical picture, one can write the following expression for the free energy due to steric repulsions:

$$\Delta\mu_{\text{steric}}^0 = -g kT \ln(1-a_p/a) \quad (5)$$

Here, a_p is the effective cross-sectional area of the polar head group.

Electrostatic Interactions. In ionic surfactant solutions one has to consider also the electrostatic interactions between the head groups at the micellar surface. In the framework of the Debye-Hückel approximation, this repulsive contribution to $\Delta\mu^0$ can be written^{3,27} as

$$\Delta\mu_{\text{Electrostatic}}^0 = \left(\frac{e^2 \beta^2 g^2}{2\epsilon r}\right) \left(\frac{1+\kappa a_i}{1+\kappa a_i + \kappa r}\right) \quad (6)$$

for spherical micelles and

$$\Delta\mu_{\text{Electrostatic}}^0 = \left(\frac{e^2 \beta^2 g^2}{\epsilon L}\right) \left(\frac{K_0(\kappa r)}{\kappa r K_1(\kappa r)} + \ln\left(\frac{r+a_i}{r}\right)\right) \quad (7)$$

for cylindrical micelles. In the above expressions, e is the electronic charge, β is the degree of dissociation of the ionic head groups at the micellar surface, ϵ is the dielectric constant of water, κ is the reciprocal Debye length, a_i is the radius of the counterion, r is the radius of the spherical (or cylindrical) micelle measured at the location of the charged head group, L is the length of the cylindrical micelle and K_0 and K_1 are the modified Bessel functions of order 0 and 1, respectively.

Internal Mixing in Micelles. For Type I solubilization, the surfactant tails mix with the solubilize molecules, whereas for Type II solubilization, the solubilizes form a core and do not mix with the surfactant tail. Therefore, the internal mixing of surfactant tails and solubilizes provides, for Type I solubilization, another negative free energy contribution to $\Delta\mu^0$. This entropic contribution can be estimated from

$$\Delta\mu_{\text{mixing}}^0 = kT \left(g \ln \frac{g v_1}{g v_1 + j' v_{1s}' + j'' v_{1s}''} + j' \ln \frac{j' v_{1s}'}{g v_1 + j' v_{1s}' + j'' v_{1s}''} + j'' \ln \frac{j'' v_{1s}''}{g v_1 + j' v_{1s}' + j'' v_{1s}''} \right) \quad (8)$$

In the above expression, the entropy of mixing inside the micelles is calculated by taking into account the differences in the molecular volumes of the surfactant tail (v_1) and of solubilizes (v_{1s}' and v_{1s}'').

Introducing the various contributions to $\Delta\mu^0$ in Equation (2), one can calculate the micellar size distribution and, consequently, the various solution properties of the system.

IV. RESULTS AND DISCUSSION

Some illustrative calculated results on solubilization in anionic sodium dodecyl sulfate (SDS) and cationic cetyl pyridinium chloride (CPC) solutions are now presented. In these calculations, it is assumed that the degree of dissociation of the ionic head groups at the micellar surface is unaffected by the extent of solubilization.

The concentration of the singly dispersed solubilize molecules has an upper bound given by its solubility limit. It has been suggested that this solubility limit may be modified somewhat by the presence of the singly dispersed surfactant and its pre-micellar aggregates²⁸. However, in the absence of quantitative solubility data, the solubility limit in the presence of the surfactant is assumed to be the same as that in water. The limiting solubilization capacity in the surfactant solution is calculated for this upper bound of the concentration of singly dispersed solubilize molecule. For binary systems, the limiting concentrations in water of the singly dispersed solubilize molecules are taken to be proportional to their mole fractions in the bulk solubilize phase.

This simplification is satisfactory because of the ideal behavior of the mixtures considered here.

The values of the molecular parameters appearing in the expressions for the various contributions to $\Delta\mu^0$ are listed in Table I and in the Appendix.

For the surfactants and solubilizates used in the present calculations, only Type I solubilization, i.e., solubilization between the surfactant tails, appears to occur.

Table I. Properties of Surfactant and Solubilizate Molecules

	CPC	SDS	Hexane	Cyclo- hexane	Benzene
a_p (\AA^2)	30	17			
a_i (\AA)	1.9	1.0			
K (litre/mole)	0.5	1.0			
β^*	0.8	0.7			
v (\AA^3)	460	352	216	180	162
$\Delta\mu_{Tr}^0$ (in units of kT)	-21.13	-16.26	-12.17	-10.6	-7.68
Solubility in water (mole fraction)	--	--	4.24×10^{-6}	1.7×10^{-5}	4.6×10^{-4}

Single Component Saturated Hydrocarbon Solubilizates. The solubilization capacity of saturated hydrocarbons hexane and cyclohexane in solutions of SDS and CPC have been calculated. Since the solubilizates are highly non-polar, they are assumed to be located farther away from the micellar interface. As mentioned earlier, $\Delta\mu_{Tr,1s}^0$ for these solubilizates is calculated for two extreme cases. If the solubilizates are considered to have in the micelles an environment similar to that of a bulk hydrocarbon liquid, then $\Delta\mu_{Tr,1s}^0$ is -12.38kT per molecule of hexane and -10.98kT per molecule of cyclohexane. On the other hand, if the solubilizates are assumed to be as constrained as the surfactant tails are, then $\Delta\mu_{Tr,1s}^0$ is -10.54kT for hexane and -9.48kT for cyclohexane (assuming a correction due to conformational constraints of $0.25\text{kT}/\text{CH}_2$ group which has been estimated for aliphatic hydrocarbon molecule). As anticipated before on intuitive grounds, the calculations based on the latter assumption predict very low solubilization capacities

compared to the available experimental data. The former assumption, namely, that the solubilizates are in a hydrocarbon liquid like environment, predicts solubilization capacities which are only 10 to 20 percent larger than those experimentally observed. The modification of the transfer free energy to hydrocarbon liquid by $0.2kT$ and $0.4kT$ for hexane and cyclohexane, respectively (the resulting values are listed in Table I), leads to excellent agreement between the experimentally observed (Fig. 2) and calculated molar solubilization ratios. These corrections are a measure of the slight conformational constraints experienced by the solubilizates in the micelles. The calculations thus suggest a predominantly hydrocarbon liquid like environment for these solubilizates. Calculations of molecular conformations such as those of Dill²⁹ and Gruen³⁰, but incorporating solubilizates inside micelles, may be used to examine theoretically the above observations.

The calculations further show that the average number of surfactant molecules per micelle slightly increases in the presence of solubilizates. The molar solubilization ratio increases from a low value near the CMC, to reach its maximum asymptotic value at sufficiently high concentration of surfactant. This ratio becomes practically constant when the surfactant concentration is appreciably higher than the CMC. The calculated values of CMC and the molar solubilization ratio are presented in Table II for both SDS and CPC solutions. The calculated molar solubilization ratios in CPC compare well with the experimental data shown in Figure 2. The calculated decrease in the CMC due to the presence of the solubilizates is about 30 to 40 percent, comparable to available experimental data in literature³¹.

Table II. Solubilization Characteristics of CPC and SDS at 25°C.

(The molar solubilization ratio and the CMC are calculated for a surfactant solution saturated with the solubilizates)

Solubilizate	CPC		SDS	
	Molar Solubilization Ratio	CMC (mole fraction)	Molar Solubilization Ratio	CMC (mole fraction)
None	--	2.6×10^{-5}	--	1.55×10^{-4}
Hexane	0.79	1.8×10^{-5}	0.36	1.10×10^{-4}
Cyclohexane	1.03	1.47×10^{-5}	0.50	0.96×10^{-4}
Benzene	2.93	0.71×10^{-5}	1.10	0.68×10^{-4}

Single Component Aromatic Solubilizates. Calculations of the molar solubilization ratio of benzene in solutions of SDS and CPC have been carried out. Because they have some polarity (due to the aromatic ring) in addition to their hydrophobicity, the aromatic solubilizate may be located farther away from the polar interface of the micelle or close to this interface. When they are assumed located away from the interface, the calculations have been carried out using values for $\Delta\mu_{Tr,1s}^0$ given in Table I (which correspond to $\Delta\mu_{Tr}^0$ for the transfer to liquid hydrocarbon) and a value of 50 dyne/cm for the interfacial tension σ at the micellar core-water interface. The calculated molar solubilization ratios listed in Table II compare well with our experimental data plotted in Figure 2. The calculated CMC, for CPC and SDS with and without the solubilizate are also listed in Table II. Again, the depression in CMC in the presence of solubilizates is about 50 percent, comparable to typical experimental values available in literature.

The possibility that the solubilized benzene molecules are located near the micellar interface was also considered. In this case a part of the solubilizate molecules remains exposed to water instead of being in a highly hydrophobic environment. Consequently, the magnitude of $\Delta\mu_{Tr,1s}^0$ has to be decreased with respect to that indicated in Table I. Further, because of the location near the interface of the aromatic solubilizates, the value of the interfacial tension σ has also to be reduced somewhat from the value of 50 dyne/cm. The larger the reduction in the magnitude of $\Delta\mu_{Tr,1s}^0$, the lower should be the corresponding value of σ . Of course, the smallest value which can be taken for σ is 34 dyne/cm, i.e., the benzene-water interfacial tension. Since $\Delta\mu_{Tr,1s}^0$ becomes less negative and σ less positive, the two effects at least in part compensate one another.

Model calculations have been carried out here to examine the solubilization of benzene in solutions of CPC for arbitrary values of $\Delta\mu_{Tr,1s}^0$ and σ . The calculated molar solubilization ratio and the CMC of CPC in the presence of solubilized benzene are presented in Table III. It can be seen that for interfacial tensions less than 50 dyne/cm and values of $\Delta\mu_{Tr,1s}^0$ smaller in magnitude than those listed in Table I, one can obtain reasonable results for the molar solubilization ratio and for the depression in CMC caused by the solubilizates. These calculations show that the experimentally measured molar solubilization ratio can be satisfactorily explained by either of the assumptions regarding the location of benzene inside the micelles. Some calculations discussed later in the paper indicate that it is likely that benzene does occupy both locations. Such a model involving a part of the solubilized benzene near the interface and the remaining located away from the interface can predict satisfactorily both the observed molar solubilization ratio and the depression in the CMC. It is worthwhile to note that many experiments²⁰⁻²⁴ indicate that aromatic molecules are solubilized

near the interface while some observations²⁶ suggest that aromatic molecules are solubilized in the micellar interior.

Table III. Solubilization of Benzene in CPC for Various Assumed Values of $\Delta\mu_{Tr,1s}^{\circ}$ and σ at 25°C

σ (dyne/cm)	$\Delta\mu_{Tr,1s}^{\circ}$ (in units of kT)	Molar Solubilization Ratio	CMC (in mole fraction)
<u>Benzene is assumed located farther away from the interface</u>			
50	-7.68	2.93	0.71×10^{-5}
<u>Benzene is assumed located near the interface</u>			
45	-7.53	2.92	0.40×10^{-5}
45	-7.48	2.57	0.45×10^{-5}
40	-7.48	3.5	0.16×10^{-5}
40	-7.28	2.1	0.26×10^{-5}
35	-7.48	5.1	0.50×10^{-6}
35	-7.28	2.9	0.90×10^{-6}

Binary Solubilizate Mixtures. The experimental results as well as the calculated ones for single solubilizates show that the molar solubilization ratio decreases in the order benzene > cyclohexane > hexane. In order to examine whether these differences in solubilization capacities are retained in binary systems, calculations have been carried out for benzene + hexane, benzene + cyclohexane, and hexane + cyclohexane mixtures in CPC and SDS solutions. While hexane and cyclohexane are assumed to be located in a highly non-polar environment, for benzene, two extreme locations inside the micelles as described earlier are considered. When benzene is assumed located farther away from the interface, the calculations have been carried out using $\Delta\mu_{Tr,1s}^{\circ} = -7.68$ kT and $\sigma = 50$ dyne/cm.

When benzene is assumed located near the interface, the calculations have been performed with $\Delta\mu_{Tr,1s}^{\circ} = -7.53$ kT and $\sigma = 45$ dyne/cm. One may note again that both of the above assumptions predict satisfactory values of the molar solubilization ratio for pure benzene (see Table III).

The calculated molar solubilization ratios in CPC micelles are plotted against composition, for the benzene + hexane mixture, in

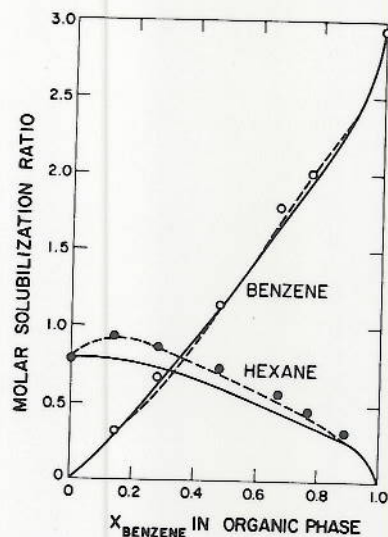


Figure 6. Calculated molar solubilization ratio of benzene and hexane in 0.1M cetyl pyridinium chloride. The continuous line is based on the assumption that benzene is located farther away from the interface and the dotted line is based on the assumption that some benzene molecules are located near the micellar interface. Open circles are experimental molar solubilization ratio of benzene and the filled circles are the experimental data for hexane.

Figure 6. For comparison, the experimental values presented in Figure 4 are also replotted in Figure 6. One may observe that the experimental data show a synergistic effect for the solubilization of hexane in the presence of benzene, namely, the molar solubilization ratio of hexane does not decrease with decreasing mole fraction of hexane in the bulk solubilize phase. While the molar solubilization ratio of hexane in CPC micelles is 0.79 when the organic phase is 100% hexane, the ratio increases to about 0.89 when the organic phase is 90% hexane and 10% benzene. If one assumes that benzene is farther away from the interface, it is difficult to explain this synergistic effect. For, in this case, there are deviations between the calculated results and the experimental data. However, if one assumes that the solubilized benzene is located near the interface, the calculations predict well the observed synergistic effect. This supports the assumption that benzene is at least partly located near the micellar interface.

A significant prediction of the present calculations is the selective solubilization of benzene compared to hexane or cyclohexane and of cyclohexane over hexane. The calculated results are plotted in Figure 7 for the three binary mixtures solubilized in 0.1M CPC and 0.1M SDS solutions. The data are represented as selectivity ratio for one component over another (defined by Equation (1)) against the composition of the organic phase. The selectivity ratio for benzene over hexane is comparable to the experimentally measured values presented in Figure 5. The selectivity ratio for benzene is greater than unity over the entire range of composition and particularly for hexane-rich conditions. If the three binary mixtures are compared, then the maximum selectivity ratio is shown by benzene + hexane and the smallest selectivity is shown by cyclohexane + hexane. Thus, the selectivity ratio parallels the molar solubilization ratios of single component solubilizates, the selectivity ratio being the largest when the two components have the widest difference in their molar solubilization ratios.

Origin of Selectivity in Solubilization. The experimental results on the solubilization of single component solubilizates shown in Figure 2 suggest that the ratio of solubilizate to surfactant in a micelle increases with decreasing molecular volume and increasing polarity of the solubilizate. In the framework of the thermodynamic treatment, the incorporation of a solubilizate in the micelle alters the area per surfactant molecule of the micelle giving rise to two opposing effects: the positive interfacial free energy contribution to $\Delta\mu^0$ increases (when σ does not change) whereas the steric and the electrostatic repulsions between the head groups at the micellar surface decrease. The same increase in the area per surfactant molecule of micelle can be caused either by a larger number of solubilizates with a low molecular volume or by solubilizing fewer solubilizates with larger molecular volumes. The former possibility also gives rise to a larger negative contribution to $\Delta\mu^0$ arising from the entropy of internal mixing in micelles. These explain why the smaller solubilizate molecules are preferentially solubilized. This would also explain the experimental observation⁴ that the molar solubilization ratios of various isomers of a hydrocarbon molecule are comparable. When the solubilizations of two aliphatic straight chain hydrocarbons are compared, then the longer chain experiences a greater restriction on its conformational flexibility inside the micelles than the shorter chain does. This effect (in addition to the molecular volume effect mentioned above) modifies the magnitude of the transfer free energy $\Delta\mu_{Tr,1s}^0$ and significantly reduces the solubilization ratio for longer chain hydrocarbons. The experimental molar solubilization ratios for n-alkanes reflect the above trend.

Aromatic compounds are solubilized in larger amounts than the corresponding saturated hydrocarbon. The larger solubilization

capacity for benzene as compared to hexane is partly due to the smaller molecular volume of the former. The molecular restrictions inside the micelle compared to liquid hydrocarbon state reduces further the capacity of hexane to be solubilized. An additional contributing factor is the polarity of benzene which reduces somewhat

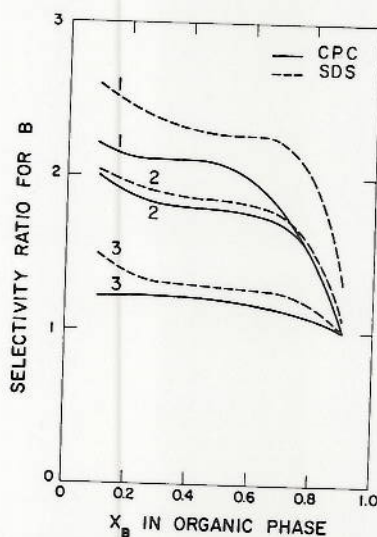


Figure 7. Calculated selectivity ratio of component B as a function of the mole fraction of B in the bulk phase for cetyl pyridinium chloride (—) and sodium dodecyl sulfate (----) solutions. (1) Component A is hexane, B is benzene; (2) Component A is cyclohexane and B is benzene; (3) Component A is hexane and B is cyclohexane.

the micellar core-water interaction energy thus permitting larger solubilization of benzene. The latter two factors can be invoked to explain the higher molar solubilization ratio for toluene compared to cyclohexane which has about the same molecular volume.

Naturally, the factors affecting the molar solubilization ratios of single components are operative when binary mixtures are considered. The experimental results shown in Figure 4 and Figure 5 for the solubilization of benzene + hexane mixtures in CPC and SDS solutions clearly show the selective solubilization of benzene, especially for organic phase compositions that are hexane-rich. The calculated selectivity ratios plotted in Figure 7 indicate that benzene is preferred to hexane. In general, the selectivity for a component in binary systems closely parallels the trend observed in molar solubilization ratios of single components.

In solutions of sodium deoxycholate the molar solubilization ratios for cyclohexane and benzene are not too different from one another. Consequently, no selectivity is observed when their binary mixtures are solubilized. The solubilization behavior can be explained in this case in terms of the markedly different structure and micellization characteristics of sodium deoxycholate, compared to those of SDS and CPC. Sodium deoxycholate forms very small primary aggregates³²⁻³⁵ with an aggregation number in the range of 4 to 10. These primary aggregates can further associate to form secondary aggregates of large aggregation numbers. Solubilization occurs inside the primary aggregates and not in the more polar region between the primary aggregates. Therefore, the factors governing the formation of primary aggregates rather than that of the secondary aggregates are relevant here. The primary aggregates are generated when the hydrophobic steroid surfaces of sodium deoxycholate are packed close to each other such that the polyhydroxylated surfaces are in contact with water. The forces responsible for such an association are relatively weak compared to those involved in the micellization of typical surfactants such as SDS and CPC. This is reflected in the very small aggregation numbers of the primary micelles of sodium deoxycholate. The incorporation of the solubilizates inside the primary aggregates hinders the close packing of the deoxycholate molecules thus exposing very large hydrocarbonaceous areas to water. As a result, the total number of molecules solubilized per micelle is rather small, irrespective of the nature of the solubilizate. Indeed, the experimentally observed molar solubilization ratio is 0.44 for cyclohexane and 0.56 for benzene which implies that each primary aggregate can incorporate only 2 to 4 molecules of benzene or cyclohexane.

V. CONCLUSIONS

Using a direct gas chromatographic analysis method, the molar solubilization ratios for a number of solubilizates as single components and in binary mixtures have been determined experimentally. It is shown for the first time, that molecules can be selectively solubilized from binary hydrocarbon mixtures. Large selectivity ratios of up to about seven have been obtained for benzene compared

to hexane especially when the binary mixture is hexane-rich. In general, the selectivity ratio of a binary mixture depends on the difference in the molar solubilization ratios of the single components, the selectivity is the largest when the two solubilizates have the widest difference in their molar solubilization ratios.

A thermodynamic treatment is developed and used to predict the molar solubilization ratio of various compounds singly and in mixtures. The treatment reveals the importance of the molecular volume and polarity of the solubilizate as well as the role of molecular constraints experienced by the molecules inside the micelles in determining the observed molar solubilization ratios.

Further, the absence of any selectivity for benzene or cyclohexane in solutions of sodium deoxycholate is shown to be consistent with the comparable molar solubilization ratios of the two pure components. This markedly different solubilization behavior is interpreted in terms of the peculiar molecular structure of sodium deoxycholate and its ability to generate only very small primary aggregates.

Finally the solubilization data involving benzene + hexane mixtures are used to explore the location of benzene inside the micelles. The synergistic effect observed experimentally is shown to imply, in the framework of the thermodynamic treatment, that at least some of the benzene molecules are located close to the interface.

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APPENDIX

Notations and Definitions

- a_p = cross-sectional area of the polar head group of the surfactant.
 a_o = area per surfactant molecule shielded from contact with water = 21 \AA^2 .
 C_1 = molar concentration of singly dispersed surfactant molecules, moles/litre.
 C_{add} = molar concentration of added salt, moles/litre.
 e = electronic charge = 4.8×10^{-10} esu.
 g = number of surfactant molecules in a micelle.
 k = Boltzmann constant = 1.38×10^{-16} erg/°K.
 K = equilibrium constant for counterion binding.
 l_o = length of the hydrocarbon tail of surfactant = $(1.50 + 1.269 N_c)$ in Å.
 N_c = number of CH_2 and CH_3 groups in the hydrocarbon chain.
 T = absolute temperature, = 298°K in the present calculations.
 β = degree of dissociation of the ionic head groups at the micellar surface, = $\beta^*/\{1 + K(C_1 + C_{add})\}$.
 β^* = the value of β at zero ionic strength.
 δ = distance of separation between the hydrophobic surface of the micelle and the location of charge on the polar head group of the surfactant.
 ϵ = dielectric constant of water, = 80.
 κ = reciprocal Debye length, = $(C_1 + C_{add})^{1/2}/(3.08 \times 10^{-8}) \text{ cm}^{-1}$ at 25°C .

Geometrical Properties of Micelles

For spherical micelles (Type I solubilization):

$$r = r_o + \delta = [3 (gv_1 + j'v_{1s'} + j''v_{1s''})/4\pi]^{1/3} + \delta$$

$$r_o \leq l_o$$

$$a = 4\pi r_o^2/g$$

For spherical micelles (Type II solubilization):

$$r = r_o + \delta = [3(gv_1 + j'v_{1s'} + j''v_{1s''})/4\pi]^{1/3} + \delta$$

$$a = 4\pi r_o^2/g$$

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For cylindrical micelles (Type I solubilization):

$$r = r_0 + \delta$$

$$L = [(gv_1 + j'v_{1s}' + j''v_{1s}'') - \frac{4}{3} \pi r_0^3] / \pi r_0^2$$

$$a = (4\pi r_0^2 + 2\pi L r_0) / g$$