Locus of Solubilization of Benzene in Surfactant Micelles

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The nature of the microenvironment of benzene in micelles is examined experimentally and interpreted theoretically. For slightly polar solubilizates such as benzene, a compensation effect is identified in the free energy of solubilization, involving the compensation of changes in the interfacial free energy by those in the transfer free energy, when the molecules are located on various sites. On this basis, values of the same order could be obtained for the micelle–water partition coefficients, for different locations of the solubilizate. Consequently, the benzene molecules could be located both in the interior as well as at the interface of the micelle. New experimental data on the solubilization of binary mixtures of hexane + benzene are presented, which reveal a synergistic effect on the solubilization of hexane in the presence of small amounts of benzene. This synergism provides evidence that at least a part of benzene is solubilized in the surface region of the micelles. One concludes that benzene is distributed both in the interfacial and in the interior sites of micelles, the fractional distribution being affected by the polar head group of the surfactant and by the amount of benzene present in the micelle.

Introduction

The solubility of predominantly hydrophobic molecules in aqueous solutions is enhanced by the addition of surfactants to the solution. The added surfactant molecules self-assemble to form micelles or vesicles which by providing a more compatible environment for the sparingly soluble molecules increase their solubilization. This tendency to solubilize constitutes the basis on which surfactants find useful applications in many biological, pharmaceutical, and industrial systems. In view of its importance, the solubilization of various chemicals in different surfactant solutions has been investigated over the years.[1–6] There are two major questions that need to be answered in order to achieve a better understanding of the phenomenon of solubilization. Firstly, one would like to know what is the extent to which a particular compound can be solubilized in a given surfactant solution. The other aspect of interest is to know the regions of location of the solubilizate molecules within the micelle. The latter aspect is of particular interest in understanding the nature of catalytic activity of micellar systems.

In earlier papers,[7,8] we have presented a thermodynamic approach for the estimation of the extent of solubilization, i.e., the ratio of the solubilizate molecules to the surfactant molecules in a micelle (hereafter designated as the molar solubilization ratio). In this paper, we use the framework of that thermodynamic approach in conjunction with experimental solubilization data to explore the nature of the microenvironment of the solubilizate molecules in micelles.

Surfactant micelles can be pictured as having a highly nonpolar interior and a relatively polar interfacial region. The interior of the micelle is generally considered to be the locus of solubilization for very nonpolar solubilizates such as *n*-alkanes. Solubilizate molecules of relatively high polarity such as alcohols are believed to be solubilized in the interfacial region of the micelle so that their polar functional groups (OH for example) could retain their contact with water. However, for molecules such as aromatic hydrocarbons, which are only slightly polar, conflicting suggestions have been presented in the literature[6,9–16] concerning their location in the micelle.

Eriksson and Gillberg[9] carried out ¹H NMR chemical shift measurements in cetyltrimethylammonium bromide (CTAB) micellar solutions containing benzene as solubilizate. It was observed that small amounts of benzene had a clear effect on the shift of protons near the polar group of the surfactant. This was interpreted to imply that, at low molar solubilization ratios, benzene is located close to the micelle–water interface. This

interpretation was also supported by the observation that the chemical shift of solubilized benzene was close to that of benzene dissolved in water. When the molar solubilization ratio of benzene was increased beyond unity, a change in the slope of the chemical shift curve was observed. This was interpreted as being due to the saturation of the interfacial region of the micelle with benzene and a transition to solubilization of benzene in the micellar interior.

Fendler and Patterson[10,11] investigated the rates of hydrated electron attachment to benzene in micellar solutions using pulse radiolysis. The reactivity of the hydrated electron with benzene was estimated by monitoring the electron decay rate in solution since the decay occurs principally by virtue of electron attachment to benzene. The half-lives of hydrated electrons were measured in the presence of benzene dissolved in water as well as benzene solubilized in CTAB and sodium dodecyl sulfate (SDS) micelles. They found that the reactivity of the hydrated electron with benzene is enhanced when benzene is solubilized in CTAB micelles and diminished when benzene is solubilized in SDS micelles compared to when benzene is molecularly dissolved in water. They attributed the observed difference in reactivities to differences in solubilization sites of benzene in these two systems; namely, benzene is located in the interfacial region in CTAB micelles, whereas in SDS micelles it is located in the interior.

Investigations of Rehfeld[12,13] based on UV spectra of benzene in micelles led to quite different conclusions. In UV studies, a measurable quantity such as a chemical shift or the energy of a band maximum characteristic of the microenvironment of the solubilizate is chosen as the spectroscopic sensor and its values are measured in a number of reference solvents. A calibration curve is thus prepared between the measured value of the spectral

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sensor and the dielectric constant of the reference solvents. One can then measure the value of the sensor in micelles and obtain an estimate for the polarity of the microenvironment in micelles from the calibration curve.[14] Rehfeld compared the UV spectra of benzene in various polar and nonpolar solvents[12,13] with its spectra in CTAB and SDS micelles. He concluded that the environment of benzene in both CTAB and SDS micelles are similar and also that in both the systems benzene is predominantly located in the interior of the micelles.

Rehfeld's conclusions were contradicted by Mukerjee and Cardinal,[14,15] who observed that different UV spectral sensors have different degrees of sensitivity to the polarity of the reference solvents. A desirable requirement of a good sensor is that it should be continuously and fairly uniformly sensitive to variations in the polarities of the reference solvents. Mukerjee and Cardinal showed that, if the polarity sensitivity of the sensor is not reasonably uniform, as was the case with the sensor chosen by Rehfeld, then the estimates of the polarity of the microenvironment based on the measurements of this sensor are not reliable. From their comprehensive UV measurements using better spectral sensors, Mukerjee and Cardinal concluded that the microenvironment of solubilized benzene in both SDS and cetyltrimethylammonium chloride (CTAC) micelles are quite polar at low concentrations of benzene. For alkyl-substituted benzenes, they observed that the microenvironment becomes gradually less polar as the size of the alkyl group is increased. To account for these results qualitatively, Mukerjee proposed a two-state description of solubilization, with one state representing the location of the solubilizate in the nonpolar micelle interior and the other state denoting its location in the polar interfacial region of the micelle.

Recently, Simon et al.[17] have questioned the use of UV spectroscopy to study the microenvironment of benzene in micelles. This is because of their finding that benzene spectra vary widely even among solvents of similar dielectric constant. Consequently, the effective dielectric constants obtained on the basis of spectral sensors are not single valued. Therefore, they have argued that extrapolations regarding benzene's microenvironment using the UV technique are arbitrary.

Hirose and Sepulveda[16] measured the transfer free energies of benzene from water to CTAB and SDS micelles and found them to be equal to the transfer free energy of benzene from water to heptane. On this basis, they concluded that benzene must be located in the interior rather than in the interfacial region of both SDS and CTAB micelles. Along similar lines, by comparing the transfer free energies of benzene from water to benzene, hexane, SDS micelles, CTAB micelles, and lipid bilayer systems, Simon et al.[17] have concluded that, on the average, benzene is situated in the nonpolar interior of the micelles.

The main goal of this paper is to explore the possibility of identifying the location of benzene in micelles by using the thermodynamic approach to solubilization developed earlier in conjunction with experimental solubilization data. It will be shown that, because of a compensation effect, the partition equilibrium constant between water and micelles could be independent of the location (at the interface or in the micellar interior) of the benzene molecules. This suggests that both locations are possible. More interestingly, experimental data on solubilization of binary mixtures of hexane + benzene reveal a synergistic effect for the amount of hexane solubilized in the presence of small amounts of benzene. The occurrence of such a synergism is shown to indicate that benzene molecules should be located at least in part in the interfacial region of micelles. The observed synergistic effect is prominent in cetylpyridinium chloride (CPC) micelles but weak in SDS micelles. One concludes that, in general, benzene can be solubilized in both the interfacial region and in the interior of the micelles, consistent with a two-state description. The fractional distribution between the two states is, however, affected by the

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nature of the polar head group of the surfactant as well as by the amount of benzene solubilized in the micelle.

Thermodynamics of Solubilization

The thermodynamic treatment of solubilization presented here is for the case of a surfactant solution containing a binary mixture of solubilizate molecules of type S' and S''. The solution is considered to include singly dispersed surfactant and solubilizate molecules as well as micelles of various sizes in which S' and S'' are solubilized. All the species in the solution are also assumed to mix ideally. From the condition that the total free energy of the solution be a minimum, one can obtain the following expression for the size distribution of micelles:[7,8]

$$X_{gj'j''} = X_1^g X_{1S'}^{j'} X_{1S''}^{j''} \exp\left[-\left(\frac{\mu^\circ_{gj'j''} - g\mu^\circ_1 - j'\mu^\circ_{1S'} - j''\mu^\circ_{1S''}}{kT}\right)\right] \quad (1)$$

In the above equation, $X_{gj'j''}$ is the mole fraction of micelles made up of g surfactant molecules, j' solubilizate molecules of type S' and j'' solubilizate molecules of type S''; X refers to the mole fractions of different species in solution; subscripts 1, 1S', and 1S'' denote the singly dispersed surfactant, solubilizate S', and solubilizate S'', respectively; μ° is the standard chemical potential of the species referred to an infinitely dilute solution; k is the Boltzmann constant, T is the absolute temperature. When there is only one solubilizate, $j'' = 0$, and for a surfactant solution in the absence of any solubilizates, $j' = j'' = 0$. Using the above size distribution function, one can compute all other quantities of interest, like for example the average size of the micelle, the molar solubilization ratio of the solubilizates, and the partition equilibrium constant of the solubilizate between micelle and water.

The size of the micelle, in terms of the weight average aggregation number, is given by

$$\langle g_w \rangle = \frac{\sum_{g>1}\sum_{j'}\sum_{j''} g^2 X_{gj'j''}}{\sum_{g>1}\sum_{j'}\sum_{j''} g X_{gj'j''}} \quad (2)$$

while micelle size in terms of the number average aggregation number results from

$$\langle g_n \rangle = \frac{\sum_{g>1}\sum_{j'}\sum_{j''} g X_{gj'j''}}{\sum_{g>1}\sum_{j'}\sum_{j''} X_{gj'j''}} \quad (3)$$

The molar solubilization ratio of the solubilizates S' is computed from

$$\left\langle \frac{j'}{g} \right\rangle = \frac{\sum_{g>1}\sum_{j'}\sum_{j''} j' X_{gj'j''}}{\sum_{g>1}\sum_{j'}\sum_{j''} g X_{gj'j''}} \quad (4)$$

The numerator in the above expression gives the total number of solubilizate molecules S' contained in the micelles, while the denominator gives the total number of surfactant molecules present in the form of micellar aggregates. A similar expression is used to calculate the molar solubilization ratio of S''.

The average mole fraction of solubilizate S' in micelles is given by

$$X_{mic,S'} = \left\langle \frac{j'}{g} \right\rangle \bigg/ \left(1 + \left\langle \frac{j'}{g} \right\rangle + \left\langle \frac{j''}{g} \right\rangle\right) \quad (5)$$

The equilibrium constant for the partitioning of the solubilizate molecule S' between the micelle and water is calculated from

$$K_{mic/w} = X_{mic,S'}/X_{1S'} \quad (6)$$

where $X_{1S'}$ is the mole fraction of the singly dispersed solubilizate S' in the aqueous solution.

The commonly reported free energy of transfer of the solubilizate molecule from water to the micelle is evaluated from

$$\Delta G_{mic/w} = -RT \ln K_{mic/w} \qquad (7)$$

In the expression for the size distribution of micelles (eq 1), the factor $g\Delta\mu^\circ = (\mu^\circ_{g'j'j''} - g\mu^\circ_1 - j'\mu^\circ_{1S'} - j''\mu^\circ_{1S''})$ represents the difference in the standard chemical potentials of the g surfactant and j' and j'' solubilizate molecules of type S' and S'' in their micellized and singly dispersed states. Given an explicit expression for $g\Delta\mu^\circ$, one can compute the size distribution $X_{g'j'j''}$ from which other quantities such as the molar solubilization ratio and the partition coefficient of the solubilizate between micelle and water can be obtained.

An explicit expression for the free energy difference $g\Delta\mu^\circ$ can be developed along the lines of our earlier treatment for simple micellization.[18,19] When only surfactant molecules are present ($j' = j'' = 0$), the process of micellization is accompanied by the following changes. The hydrocarbon tail of the surfactant is removed from contact with water and transferred into an essentially hydrocarbon liquidlike micellar interior. A hydrocarbon core–water interface is thus generated. The polar head groups of the surfactant molecules which are brought into close proximity of one another interact sterically as well as electrostatically (in ionic surfactant systems). The free energy changes accompanying micellization can be quantitatively estimated from the following expression:

$$\Delta\mu^\circ = \Delta\mu^\circ_{hc/w,1} + \Delta\mu^\circ_{ex,1} - kT \ln\left(\frac{\Omega_{mic}}{\Omega_{hc}}\right)_1 + \sigma(a - a_0) -$$
$$kT \ln\left(1 - \frac{a_p}{a}\right) + \frac{ge^2\beta^2}{2\epsilon r}\left[\frac{1 + \kappa a_i}{1 + \kappa a_i + \kappa r}\right] \qquad (8)$$

The first term is the transfer free energy of the surfactant tail from water to a bulk liquid hydrocarbon phase. From experimental data, $\Delta\mu^\circ_{hc/w,1}$ has been estimated by using $-1.47kT$ per CH_2 group and $-3.25kT$ per CH_3 group in n-alkanes and $-1.28kT$ per CH group in benzene.[20,21] The configurational freedom of the surfactant tail in a micelle is different from that of an equivalent hydrocarbon molecule in a bulk liquid phase. This is because the polar groups of the surfactant molecules are constrained to remain at the micellar interface. For a hydrocarbon molecule in a bulk liquid phase, no such constraint exists. This ordering of the surfactant chains inside the micelle has two opposite effects. One of them is enthalpic and is due to a small enhancement of the van der Waals interactions between the tails, compared to their interactions in a bulk hydrocarbon liquid. This excess contribution is denoted by $\Delta\mu^\circ_{ex,1}$ and, for a reason mentioned later in the paper, its value is taken $-1kT$. The second effect is entropic and is due to the decrease in the conformational freedom of the molecule. The lower conformational probability of the surfactant tail in the micelle, Ω_{mic}, compared to an equivalent hydrocarbon molecule in bulk liquid phase, Ω_{hc}, is accounted for by the third term. One can obtain an estimate of $kT \ln (\Omega_{mic}/\Omega_{hc})$ either from the calculation of the internal ordering of the hydrocarbon tails in a micelle[22,23] or by considering that some degrees of rotation are frozen by micellization.[18,19] An alternate empirical way is based on the use of experimental critical micelle concentration (cmc) data for a homologous series of surfactants.[4] An estimate of $0.25kT$ per CH_2 group and $0.42kT$ per CH_3 group in n-alkyl surfactant tails is used here to account for this contribution. The fourth term represents the interfacial free energy associated with the formation of the hydrocarbon core–water interface. σ is the micellar core–water interfacial tension, a is

the surface area of the micellar core per surfactant molecule, and a_0 is the surface area per molecule shielded from contact with water because of the terminal polar group of the surfactant. The fifth term accounts for the steric or excluded volume interactions between the polar head groups at the micelle–water interface. An expression of the form appearing in the van der Waals equation of state is used to estimate this contribution to $\Delta\mu^\circ$. In this expression, a_p is the hard-core cross-sectional area of the polar head group of the surfactant and $(1 - a_p/a)$ is the fractional surface area not excluded by the presence of the head groups. The last term takes into account the electrostatic interactions between the ionic head groups at the micellar interface. The expression has been obtained in the framework of the Debye–Hückel approximation and has been written here for spherical micelles. A similar expression can be written for cylindrical micelles (see Appendix).

The free energy difference $\Delta\mu^\circ$ in the presence of solubilizates S' and S'' retains essentially the same form as that for micellization. The only additional changes that occur on solubilization are the transfer of the solubilizate molecule from the water to the hydrocarbon liquidlike environment of the micelle and the resulting mixing of surfactant tails and solubilizate molecules inside the micelle. Taking these additional effects into account, one can extend eq 8 to solubilization as follows:

$$\Delta\mu^\circ = \Delta\mu^\circ_{hc/w,1} + \Delta\mu^\circ_{ex,1} - kT \ln\left(\frac{\Omega_{mic}}{\Omega_{hc}}\right)_1 + \sigma(a - a_0) -$$
$$kT \ln\left(1 - \frac{a_p}{a}\right) + \frac{ge^2\beta^2}{2\epsilon r}\left[\frac{1 + \kappa a_i}{1 + \kappa a_i + \kappa r}\right] +$$
$$\left\{\frac{j'}{g}\Delta\mu^\circ_{hc/w,1S'} + \frac{j'}{g}\Delta\mu^\circ_{ex,1S'} - \frac{j'}{g} \ln\left(\frac{\Omega_{mic}}{\Omega_{hc}}\right)_{1S'} + \frac{j''}{g}\Delta\mu^\circ_{hc/w,1S''}\right.$$
$$+ \frac{j''}{g}\Delta\mu^\circ_{ex,1S''} - \frac{j''}{g} \ln\left(\frac{\Omega_{mic}}{\Omega_{hc}}\right)_{1S''} + kT\left[\ln\frac{g}{g + j' + j''} +\right.$$
$$\left.\left.\frac{j'}{g} \ln\frac{j'}{g + j' + j''} + \frac{j''}{g} \ln\frac{j''}{g + j' + j''}\right]\right\} \qquad (9)$$

The first six terms of eq 9 are identical with those in eq 8 for the pure surfactant system. The last seven terms within {} have been added to account for the presence of the two solubilizates S' and S''. Of these, the first and the fourth terms denote the transfer free energy from water to the bulk liquid hydrocarbon phase of the solubilizate molecules S' and S''. The second and the fifth terms account of the small enhancements in the van der Waals interactions of the solubilizates S' and S'', caused by the ordering produced by the surfactant molecules. Any difference in the entropic freedom of the solubilizate molecules inside the micelle compared to that of their bulk liquid state is accounted for by the third and the sixth terms. The last term represents the entropy of internal mixing of surfactant tails and solubilizate molecules inside a micelle.

Estimates for $\Delta\mu^\circ_{hc/w}$ have already been presented for n-alkanes and for benzene. These estimates are used for the solubilizates S' and S'' as well, in addition to the surfactant tails. Further, we set

$$(\Omega_{mic}/\Omega_{hc})_{1S'} = (\Omega_{mic}/\Omega_{hc})_{1S''} = 1 \qquad (10)$$

The above equations imply that the solubilizate molecules have the same conformational freedom in the micelle as in the bulk liquid hydrocarbon phases. This is likely to be so because, in contrast to the hydrocarbon tail of the surfactant which has one end anchored to the micellar interface, the solubilizate molecules are not tied to any specific position within the micelle. Probably, this approximation can no longer be used when long-chain solubilizates such as n-hexadecane are considered. The values of $\Delta\mu^\circ_{ex,1}$, $\Delta\mu^\circ_{ex,S'}$ and $\Delta\mu^\circ_{ex,S''}$ are taken to be $-1kT$, since good results are thus obtained for the molar solubilization ratios. It should, however, be pointed out that the presence of the solubilizates decreases the extent of ordering produced by the surfactant

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molecules in the micelles. When the amount of solubilizate is large enough, the interior of the micelle might be nearly liquid like ($\Delta\mu°_{ex,l} \approx \Delta\mu°_{ex,S'} \approx \Delta\mu°_{ex,S''} \approx 0$).

On the above basis, one can compute X_{gff}, $\langle j'/g \rangle$, $\langle j''/g \rangle$, and the partition coefficient for the solubilizate between micelle and water, $K_{mic/w}$.

Experimental Method

The molar solubilization ratios of benzene and hexane have been experimentally determined in micellar solutions of cetylpyridinium chloride (CPC), sodium dodecyl sulfate (SDS), dodecylammonium chloride (DAC), and sodium diamyl sulfosuccinate (Aerosol AY). All the surfactants obtained from commercial sources have been used as received. The solubilization measurements have been made in 0.1 M solutions of CPC, SDS, and DAC and 0.3 M solution of Aerosol AY. All the measurements have been carried out at 25 °C.

A direct gas chromatographic technique was used to determine the amount of hydrocarbon solubilized. The experiment was performed as follows: Equal volumes of aqueous surfactant solution and solubilizate phase were contacted over a period of 24 h to reach equilibration. The amounts of hydrocarbons in the aqueous phase were then determined by a gas chromatograph using a flame ionization detector. The use of the flame ionization detector eliminates the water peaks which otherwise would have overshadowed the hydrocarbon peaks, thereby preventing their detection and quantitative estimation. A guard column is used to permit the deposition of the (less volatile) surfactant molecules and thus prevent them from contaminating the main column used for separating the hydrocarbon solubilizates.

The molar solubilization ratios were calculated from the experimental data by using the definition

molar solubilization ratio =
(moles of total solubilizate in surfactant solution −
moles of singly dispersed solubilizate in solution)/
(moles of total surfactant in solution −
moles of singly dispersed surfactant in solution) (11)

The moles of singly dispersed surfactant in solution is assumed to be equal to its cmc. The cmc values are 1.44 mM for CPC, 8.2 mM for SDS, 12 mM for DAC, and 28 mM for Aerosol AY. It is known that the cmc decreases slightly due to solubilization. This is also predicted by the present calculations. However, the total concentration of the surfactant in solution is so large that the amount of surfactant molecules present in the form of micelles is hardly affected by the slight depression in the cmc. The concentration of the singly dispersed solubilizate is assumed to be equal to its solubility in pure water. This solubility limit may be somewhat affected in the surfactant solution because of the presence of the singly dispersed surfactant and premicellar aggregates.[24] However, in the absence of any experimental data, it is assumed here that it remains unaffected in the surfactant solution. Of course, compared to the amount of hydrocarbon solubilized, any change in the concentration of the singly dispersed solubilizate is negligibly small, and hence, it has no effect on the molar solubilization data. At 25 °C, the solubilities of hexane and benzene are taken to be 4.24 × 10⁻⁶ and 4.6 × 10⁻⁴, respectively, in mole fraction units.[20,21] When binary mixtures of benzene and hexane are solubilized, the mole fractions of the singly dispersed solubilizates are taken to be the products of the pure component solubility in water and the mole fractions of the components in the binary solubilizate phase which is in equilibrium with the aqueous micellar solution. This implies the assumption of ideality of the binary hydrocarbon mixture, which is satisfactory at least for the benzene + hexane system.

Results and Discussion

Experimental Results. The molar solubilization ratios of hexane and benzene in 0.1 M CPC, 0.1 M SDS, 0.1 M DAC, and

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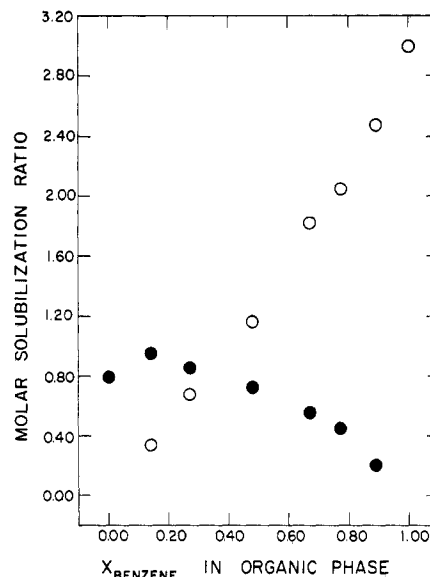
Figure 1. Molar solubilization ratio of benzene and hexane in 0.1 M CPC solution as a function of the composition of the bulk solubilizate phase of benzene + hexane. Open symbols represent benzene, and the filled symbols represent hexane.

TABLE I: Transfer Free Energies of Hexane from Water to Other Solvents at 25 °C

solvent	$10^{-5}K_{solvent/w}$	$-\Delta G_{solvent/W}$, kcal/mol	ref
0.1 M CPC	1.04	6.89	this work
0.1 M SDS	0.65	6.61	this work
0.1 M CPC[a]	1.16	6.95	this work
0.1 M SDS[a]	0.67	6.62	this work
0.1 M CPC[b]	1.14	6.94	this work
0.1 M SDS[b]	0.81	6.74	this work
SDS	0.603	6.56	24
n-hexane	4.37	7.74	4
n-hexane	2.38	7.37	20

[a] From solubilization data on binary mixture of benzene + hexane at $X_{benzene}$ = 0.14. [b] From solubilization data on binary mixture of benzene + hexane at $X_{benzene}$ = 0.48.

TABLE II: Transfer Free Energies of Benzene from Water to Other Solvents at 25 °C

| solvent	$10^{-3}K_{solvent/w}$	$-\Delta G_{solvent/w}$, kcal/mol	ref
0.1 M CPC	1.62	4.40	this work
0.1 M SDS	1.16	4.21	this work
0.1 M CPA[a]	2.29	4.61	this work
0.1 M SDS[a]	2.0	4.53	this work
0.1 M CPC[b]	1.82	4.48	this work
0.1 M SDS[b]	1.54	4.38	this work
CTAB	1.36	4.3	16
SDS	1.15	4.2	16
n-heptane	1.36	4.3	16
SDS	1.1	4.15	17
n-hexadecane	1.5	4.33	17
n-hexane	1.46	4.31	25

[a] From solubilization data on binary mixture of benzene + hexane at $X_{benzene}$ = 0.14. [b] From solubilization data on binary mixture of benzene + hexane at $X_{benzene}$ = 0.48.

0.3 M Aerosol AY solutions are shown in Figures 1–4 as a function of the composition of the solubilizate phase in equilibrium with the aqueous solution. From these experimental data, the partition coefficient of the solubilizates between the micelle and water is calculated from eq 6. The corresponding transfer free energy from water to micelles is calculated from eq 7. The calculated results are presented in Table I for hexane and in Table II for benzene.
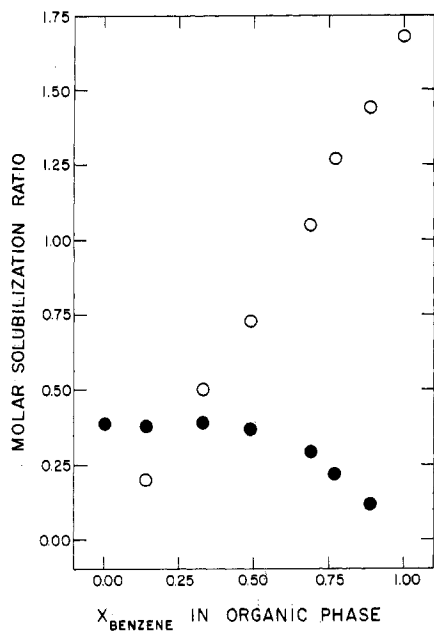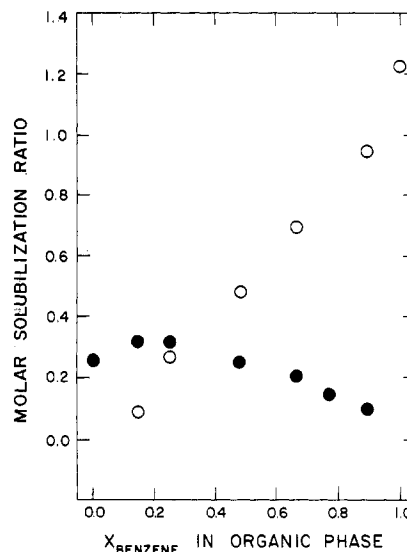
Figure 2. Molar solubilization ratio of benzene and hexane in 0.1 M SDS solution as a function of the composition of the bulk solubilizate phase of benzene + hexane. Open symbols represent benzene, and the filled symbols represent hexane.
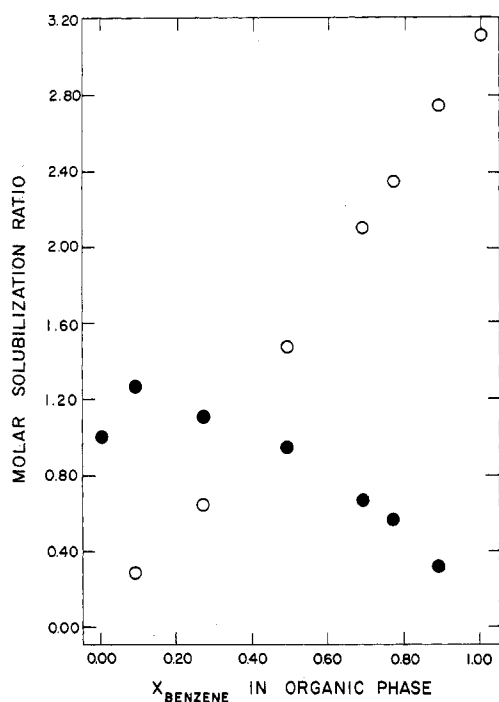
Figure 3. Molar solubilization ratio of benzene and hexane in 0.1 M DAC solution as a function of the composition of the bulk solubilizate phase of benzene + hexane. Open symbols represent benzene, and the filled symbols represent hexane.

Available data from literature[16,17,25-27] are also shown, which indicate satisfactory agreement with the present experimental results.

Interpretation of Partition Coefficient for Hexane. It is generally believed that the nonpolar hexane molecules are solubilized in the nonpolar interior of the micelle. However, experiment shows

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Figure 4. Molar solubilization ratio of benzene and hexane in 0.3 M Aerosol AY solution as a function of the composition of the bulk solubilizate phase of benzene + hexane. Open symbols represent benzene, and the filled symbols represent hexane.

that the transfer free energy of hexane from water to the micelles is somewhat smaller than that from water to the bulk liquid hexane phase. This difference has been attributed to possible conformational constraints experienced by the hexane molecule inside the micelle, compared to its conformational state in bulk liquid hydrocarbon.[17,25] In the present treatment, hexane molecules are assumed to have the same conformational freedom inside the micelle as in the bulk hexane. Nonetheless, the theory still predicts (in agreement with experiment) a distribution between micelles and water different from that between bulk hexane and water. This happens because in the former case the partition coefficient is also affected by the contributions in eq 9 associated with the interactions at the micellar interface; the latter contributions do not play any role for the partition coefficient between bulk hexane and water.

Compensation Effect and Partition Coefficient of Benzene. The partition coefficients of the slightly polar benzene between micelles and water, listed in Table II, are very close to those between bulk hydrocarbon liquid and water. On this basis, some authors[16,17] concluded that benzene is located in the nonpolar micellar interior. However, in what follows, it is shown that there is a "compensation effect" which makes the partition coefficient insensitive to the location of the benzene molecules in the micelles.

In eq 9, the interfacial free energy term and the transfer free energy term for the solubilizate are both affected by the location of benzene inside the micelle. For example, if benzene is located in the micellar interior, the interfacial tension σ is that of the surfactant tail–water interface, which is taken as 50 dyn/cm because of the aliphatic hydrocarbon tail of the surfactant. The transfer free energy $\Delta\mu^\circ_{hc/w,1S}$ corresponds in this case to the complete transfer of benzene from water into the bulk hydrocarbon liquid. Therefore, $\Delta\mu^\circ_{hc/w,1S}$ is −7.68 kT. On the other hand, if the benzene molecules are located in the interfacial region of the micelles, then σ will be less than 50 dyn/cm. Of course, the smallest value of σ is 34 dyn/cm, corresponding to the interfacial tension between benzene and water. This probably would be the case when the entire micellar–water interface is saturated with benzene. However, when the benzene molecules are located in the interfacial region, the magnitude of $\Delta\mu^\circ_{hc/w,1S}$ should be decreased from −7.68 kT, reflecting the fact that the benzene molecules are incompletely removed from contact with water. The greater the reduction in σ, implying increasing preponderance of benzene at the micellar interface, the greater will be the reduction in the magnitude of $\Delta\mu^\circ_{hc/w,1S}$. For illustrative purposes, the molar solubilization ratios of benzene in CPC micelles have been calculated from eq 9, for different assumed values of σ and $\Delta\mu^\circ_{hc/w,1S}$.

TABLE III: Predicted Equilibrium Constant for the Partitioning of Benzene between CPC Micelles and Water for Different Assumed Values of σ and $\Delta\mu^{\circ}_{hc/w,1S}$

| σ, dyn/cm	$\Delta\mu^{\circ}_{hc/w,1S}$, kT	$\langle j/g \rangle$	$10^{-3}K_{mic/w}$	$-\Delta G_{mic/w}$, kcal/mol
A. Benzene Located at Micelle Interior				
50	−7.68	2.93	1.62	4.4
B. Benzene Located near Micelle–Water Interface				
45	−7.53	2.93	1.62	4.4
40	−7.40	2.93	1.62	4.4
35	−7.28	2.92	1.62	4.4

The different combinations of values for these two parameters qualitatively reflect different fractional distributions of benzene between the micellar interface and micelle interior. The results are presented in Table III. These calculations show that, for a number of combinations of values of σ and $\Delta\mu^{\circ}_{hc/w,1S}$, the molar solubilization ratios of benzene in micelles are the same. This is a consequence of the compensation effect in which the decrease in interfacial tension, and consequently in the micellar core–water interfacial free energy, is compensated by the simultaneous decrease in the magnitude of $\Delta\mu^{\circ}_{hc/w,1S}$ (free energy of transfer of benzene from water to bulk liquid hydrocarbon). Therefore, one may conclude that the mere equivalence of the partition coefficients $K_{mic/w}$ and $K_{hc/w}$ does not permit the identification of the hydrocarbon core as the site of solubilization of benzene in micelles. Further, since the values obtained for $K_{mic/w}$ by assuming that benzene is located in the interior of the micelle or at the interfacial region of the micelle are comparable, both locations could be sites of solubilization.

Synergistic Effect and Locus of Solubilization. A new indicator of the locus of solubilization is revealed by the observation that there are synergistic effects in the solubilization of mixtures of hydrocarbons. One notes from Figure 1 that, at low concentrations of benzene in the binary solubilizate phase, the molar solubilization ratio of hexane in micelle increases initially, even though the concentration of hexane in the bulk hydrocarbon phase in equilibrium with the aqueous micellar solution decreases. This synergism is not uniquely observed in CPC micelles alone but also occurs in different degrees in SDS, DAC, and Aerosol AY micelles (Figures 2–4). The synergism has also been observed in a number of other anionic and cationic surfactant systems.[28]

This synergism can be explained as follows. When molecules are solubilized, the micellar core–water interfacial area increases. If the interfacial tension remains constant, the corresponding positive free energy of formation of the interface increases. However, the other contributions to the total free energy (namely, the steric repulsions and electrostatic repulsions among surfactant head groups) compensate for this effect. If both benzene and hexane are located in the micelle interior, the interfacial tension is not altered by solubilization. In this case, the competition between benzene and hexane for the micelle interior results in a monotonic decrease of the molar solubilization ratio of hexane as its mole fraction in the bulk hydrocarbon phase is decreased.

On the other hand, if at least some surface solubilization of benzene occurs, then the micellar core–water interfacial tension decreases. This allows a larger increase in the core–water area and hence in the amount of solubilization. However, the molar solubilization ratio of benzene is not much affected because of the compensation effect discussed earlier. Consequently, the allowed increase in solubilization represents an increase in the molar solubilization ratio of hexane. Thus, the nonmonotonic variation of the molar solubilization ratio of hexane is incompatible with the complete interior location of benzene and suggests at least partial surface location of benzene.

Illustrative calculations have also been carried out for CPC micelles to quantitatively simulate the synergistic effect. The results are shown in Figure 5 and compared against the measured

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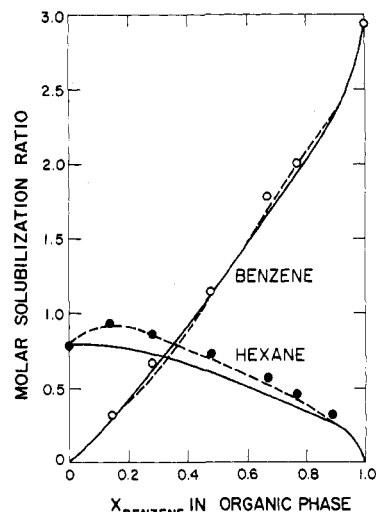
Figure 5. Comparison of the calculated molar solubilization ratios of benzene and hexane in 0.1 M CPC solution against the experimentally determined values. Open points refer to benzene, and the filled points refer to hexane, both experimentally obtained. The continuous lines are the calculated results if one assumes that the benzene molecules are located entirely in the micellar interior ($\sigma = 50$ dyn/cm). The dotted lines are the calculated results if one assumes that at least some of the benzene molecules are located at the micellar interface ($\sigma = 45$ dyn/cm).

experimental data. The calculations based on $\sigma = 50$ dyn/cm and $\Delta\mu^{\circ}_{hc/w,1S} = -7.68$ kT for benzene assume that all the benzene molecules are located in the micellar interior and do not sample the surface. The calculated results indeed predict a monotonically decreasing molar solubilization ratio for hexane. On the other hand, if some of the benzene molecules are assumed to be present at the micellar interface such that $\sigma = 45$ dyn/cm and $\Delta\mu^{\circ}_{hc/w,1S} = -7.53$ kT for benzene, then the calculated molar solubilization ratios for hexane and benzene agree remarkably well with the measured data. If calculations are made assuming $\sigma = 35$ dyn/cm and $\Delta\mu^{\circ}_{hc/w,1S} = -7.28$ kT for benzene, then a more pronounced synergism is predicted, exceeding that indicated by the experimental data. Therefore, one may conclude that the micellar interface is probably not saturated with benzene but it definitely contains an appreciable amount of benzene molecules. A quantitative prediction of the extent of partitioning of benzene between the micelle interface and the micelle interior is not possible without a meaningful estimate of the value of σ as a function of the surface concentration of benzene.

The synergistic effect on the solubilization of hexane is very pronounced in CPC micelles, but is not as prominent in the SDS micelles. This indicates that the fractional distribution of benzene between the surface and interior is different for these two surfactant micelles. Indeed, since solubilization is affected by the interactions at the micellar interface, it is natural to expect that surfactants with different polar head groups would influence the partitioning of benzene between the two sites differently.

Conclusions

The nature of the microenvironment of benzene in micelles is explored experimentally as well as on the basis of thermodynamic considerations. It is shown that the partition coefficient of benzene between micelle and water could have comparable values if the molecules of benzene are located in the interior or at the interface of the micelle. This happens because, for the solubilization of benzene or other slightly polar solubilizates, the decrease in the interfacial tension at the micellar core–water interface when benzene is located at the interface could be compensated by a corresponding decrease in the free energy gain due to the transfer of benzene from water to the micelle. As a consequence, both the interface and the interior of the micelle could be sites for the location of benzene.

New experimental data are presented on the solubilization of binary mixtures of hexane + benzene in four different surfactant

solutions. These data reveal a synergistic effect for the molar solubilization ratio of hexane in the presence of small amounts of benzene. This synergistic effect is shown to indicate that at least a part of the benzene molecules are located at the micellar interface. These binary solubilization data thus support the two-state description of solubilization proposed by Mukerjee, according to which solubilization molecules can be distributed in both the interfacial and interior sites of the micelle.

The observed synergistic effect is prominent in some surfactants such as CPC but is weak in others such as SDS. This is interpreted to imply a difference in the fractional distribution of benzene among the two loci of solubilization in the CPC and SDS micelles, confirming the earlier speculations of Fendler and Patterson. In general, it is concluded that the fractional distribution of benzene between the interfacial and the interior sites is influenced by the polar head group of the surfactant as well as the extent of benzene molecules solubilized in the micelle.

Acknowledgment. This work was supported by the National Science Foundation.

Appendix

Notations and Definitions

a_p cross-sectional area of the polar head group of the surfactant (= 30 Å^2 for CPC).

a_0 area per surfactant molecule shielded from contact with water (= 21 Å^2).

a_i radius of the counterion (= 1.9 Å for chloride).

C_1 molar concentration of singly dispersed surfactant molecules.

C_{add} molar concentration of added salt.

e electronic charge (= 4.8×10^{-10} esu).

k Boltzmann constant (1.38×10^{-16} erg/K).

K equilibrium constant for counterion binding (= 0.5 M^{-1} for CPC).

l_0 length of the hydrocarbon tail of surfactant (= 1.50 + $1.269N_c$ Å).

N_c number of CH_2 and CH_3 groups in the hydrocarbon chain (= 16 for CPC).

T absolute temperature (= 298 K in the present calculations).

v molecular volume (= 27 Å^3 for CH_2, 54 Å^3 for CH_3 in *n*-alkanes, and 27 Å^3 for CH in benzene).

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 (= 0.8 for CPC).

δ distance of separation between the hydrophobic surface of the micelle and the location of charge on the polar head group of the surfactant (= 1.5 Å for CPC).

ϵ dielectric constant of water (= 80).

κ reciprocal Debye length (= $(C_1 + C_{add})^{1/2}/(3.08 \times 10^{-8})$ cm^{-1} at 25 °C).

Geometrical Properties of Micelles. For spherical micelles

$$r = r_0 + \delta = [3(gv_1 + j'v_{1s'} + j''v_{1s''})/4\pi]^{1/3} + \delta$$

$$r_0 \leq l_0$$

$$a = 4\pi r_0^2/g$$

For cylindrical micelles

$$r = l_0 + \delta$$

$$L = [(gv_1 + j'v_{1s'} + j''v_{1s''}) - \tfrac{4}{3}\pi l_0^3]/(\pi l_0^2)$$

$$a = (4\pi l_0^2 + 2\pi L l_0)/g$$

Electrostatic Interactions at Micellar Surface. For spherical micelles

$$\Delta\mu° = \frac{ge^2\beta^2}{2\epsilon r}\left[\frac{1 + \kappa a_i}{1 + \kappa a_i + \kappa r}\right]$$

For cylindrical micelles

$$\Delta\mu° = \frac{ge^2\beta^2}{\epsilon L}\left[\frac{K_0(\kappa r)}{\kappa r K_1(\kappa r)} + \ln\left(\frac{r + a_i}{r}\right)\right]$$

K_0 and K_1 are modified Bessel functions of orders 0 and 1.

Registry No. Benzene, 71-43-2; hexane, 110-54-3; sodium dodecyl sulfate, 151-21-3; cetylpyridinium chloride, 123-03-5; dodecylammonium chloride, 929-73-7; Aerosol AY, 922-80-5.

COMMENTS

Comments on "Laser-Excited Fluorescence of the Hydroxyl Radical: Relaxation Coefficients at Atmospheric Pressure" by C. Y. Chan, R. J. O'Brien, T. M. Hard, and T. B. Cook

Sir: The lifetime of the excited state of an atom or molecule can often be determined from the rate of fluorescence decay orginating from the excited state. By measuring this fluorescence lifetime as a function of buffer gas pressure, an accurate determination can be made of the rates of collision-induced transitions away from the excited state. In the case of the hydroxyl radical (OH), direct lifetime measurements have been made over a range of low system pressures up to about 25 torr.[1-5] However, attempts to extend

this type of measurements to atmospheric pressure have been met with increasing difficulty since excitation and detection with *subnanosecond* resolution are required. Recently, Chan et al.[6] reported measurements near atmospheric pressure by using a 7-ns laser for excitation, concluding that a strong pressure dependence existed for the electronic quenching cross section of OH due to oxygen. They also stated that this pressure dependence would mean a factor of ten error in the OH concentrations deduced from fluorescence measurements in ambient air, a topic of considerable interest to us. The purpose of this Comment is to point out that their reported results do not support their conclusion, and that the results themselves do not appear to be internally consistent. On the other hand, various observations published in the past ten years by a number of other independent workers[1-4,7] all tend to support the supposition that pressure dependence at atmospheric

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