Solubilization in Aqueous Mixed Micellar Solutions: Water-Potassium Oleate-1-Pentanol-Benzene

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ABSTRACT

Spectral parameters of the UV absorption and emission spectrum of benzene dissolved in aqueous solutions of potassium oleate and 1-pentanol were measured. By comparing these parameters with those for solutions of benzene in hydrocarbon solvents, it was concluded that the major portion of the benzene solubilized in the mixed micelles was in a relatively nonpolar environment. These results agree with previous studies of benzene dissolved in sodium lauryl sulfate solutions. Estimations of the energy of transfer of benzene from water to the mixed micelle also support this conclusion.

INTRODUCTION

Solubilization of lipophilic components in aqueous surfactant solutions has been studied for many years (1-10). Spectroscopic studies of solubilized species have been useful in determining the environment of solubilization in many systems. Rehfeld (7) studied the 2600 A bands in the UV spectrum of benzene to determine the environment of the oil solubilized in aqueous solutions of sodium dodecyl sulfate. He concluded that the environment was similar to a solution of benzene in a hydrocarbon. The environment was not seen to be completely uniform, however.

Waggoner and coworkers (2-4) had come to a similar conclusion on the basis of electron spin resonance studies of solubilized long chain nitroxides. Riegelman and coworkers (5) postulated several different sites for solubilization in micellar solutions, depending on the type of solute. They studied the solubilization of ethylbenzene, naphthalene, anthracene, and several other solutes in micellar solutions of potassium laurate, dodecylamine hydrochloride, and polyoxyethylene ether using differential UV absorption spectroscopy. Fluorescence and differential UV spectra of aqueous micellar solutions of 10-phenylundecanoic acid reported by Rehfeld (6) revealed that the phenyl ring of the acid was in a "liquid" state inside the micelle similar to that in the pure acid.

These studies were concerned with solubility in the presence of a single amphiphilic species. It is possible to increase the amount of oil solubilized in some surfactant solutions by adding an appropriate amphiphilic agent of lower hydrophile-lipophile balance, a cosurfactant, to the surfactant solution. Schulman studied systems of this type (11-14). He used the term "microemulsion" to describe these transparent fluids, which generally have low viscosities. Two reviews of the literature of this subject have recently been published (15,16).

This investigation was undertaken to determine the region of solubilization in these mixed micellar systems. These systems differ from surfactant solutions in several aspects because of the presence of the cosurfactant (13). It is possible for the cosurfactant to destroy the micelle structure and solubilize the lipophilic species into a molecular solution. Benzene was used as the oil phase here, and this would have been apparent in the UV absorption and fluorescence spectra of the benzene (solute). The effort was primarily aimed at trying to determine the region of solubilization of the solute and the effect of the particular cosurfactant on that environment.

Shinoda and Kunieda have taken issue with the term "microemulsion" (17); Gerbacia and Rosano have also commented on this matter (18). It was felt that the term "micellar" should be used for a thermodynamically stable system of swollen micelles and "microemulsion" should be used for those transparent dispersions which are not thermodynamically stable. The term "micellar solution" will be used here because it is believed that the particular system studied is thermodynamically stable.

EXPERIMENTAL PROCEDURES

Materials

Benzene, n-hexane, 1-pentanol (Fisher Scientific Co., Fairlawn, NJ), and the potassium hydroxide (J.T. Baker Co., Phillipsburg, NJ) were reagent grade. The oleic acid was a highly purified grade purchased from The Hormel Institute (Austin, MN, lot F-1A). All chemicals were used without further purification, and freshly distilled water was used in all experiments.

Procedures

The surfactant solution of 0.28 M potassium oleate was prepared by adding an excess of KOH to oleic acid and adding water to make the final solution. The final pH was 10.5. Benzene (1 ml) was then added to 25.0 ml of the K-oleate solution in a thermostated flask (30±0.5 C). This mixture resulted in a coarse emulsion, lactescent in appearance, which would separate rapidly on standing. The coarse emulsion was then titrated to a clearing point with 1-pentanol. Other systems were prepared with 0.5, 0.3, and 0.1 ml benzene and are listed in Table I with the molar concentration of benzene ($M\phi$); λ_{max}, the wavelength of the maximum absorption for the second peak in the 2600 A band of benzene (the solution spectrum exhibits four peaks when it is well resolved [7]); $\Delta\nu_{1/2}$, the half band width of the second peak; and $n\phi/n_a$, the mol ratio of benzene to 1-pentanol In the case of the micellar solutions, the term "solvent" refers to the continuous phase, water. $\Delta\nu_I$ represents the average frequency interval between the four peaks observed in the benzene spectrum (7).

The first micellar system listed contains 0.5 ml of benzene, the second and third contain 0.3 ml, and the last contains 0.1 ml. The second and fourth contain an excess of 1-pentanol over that which was required to produce a transparent system.

Absorption spectra: Differential UV spectra were measured on a Cary 14 automatic spectrometer using matched cells in the usual way (7) at a scan rate of 2.5 A/sec. Micellar solutions were run against a solution of potassium oleate with the appropriate amount of 1-pentanol added. The benzene solutions were measured against the hydrocarbon solvents.

Fluorescence spectra: A Perkin-Elmer 203 fluorescence spectrometer was used to measure fluorescence emission spectra. The solvent or potassium oleate solution with 1-pentanol was used to zero the spectrometer. Uncorrected spectra are reported as they were considered adequate for

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TABLE I

UV Absorption Data[a]

Solvent	M_ϕ	n_ϕ/n_a	λ_{max} (A)	$\Delta\nu_I$ (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})
Micellar solutions					
Water	0.21	1.06	2546	931 ± 10	415 ± 10
Water	0.13	0.64	2545	915 ± 10	453 ± 10
Water	0.13	0.93	2545	926 ± 10	462 ± 20
Water	0.044	0.21	2546	933 ± 10	400 ± 10
Solutions					
1-Pentanol	4.44	0.80	2545	885 ± 15	410 ± 20
1-Pentanol	0.82	0.096	2542	938 ± 15	378 ± 10
1-Pentanol	0.072	0.0079	2541	934 ± 15	365 ± 10
n-Hexane	0.0094	--	2539	938 ± 25	320 ± 15

[a] M_ϕ = molar concentration of benzene (mol/liter); λ_{max} = wavelength of the maximum absorption for the second peak in the 2600 A band; n_ϕ/n_a = molar ratio of benzene to 1-pentanol; $\Delta\nu_I$ = frequency interval for the progression (7); and $\Delta\nu_{1/2}$ = half-band width for the second peak (7).

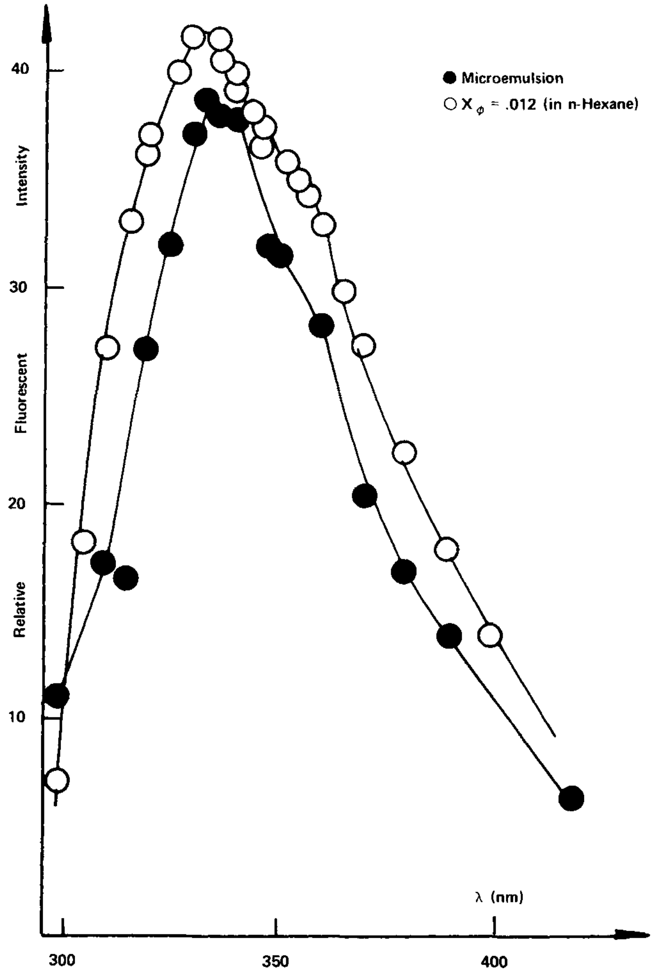

FIG. 1. Uncorrected emission spectra of benzene.

comparative purposes and support of the absorption spectra.

Nuclear magnetic resonance (NMR) spectra: NMR spectra were recorded using a Jeolco C-60 high resolution spectrometer (Japan Electron Optics Lab., Tokyo, Japan) at 60 Mhz. The methyl resonance was used as an internal standard, as its position was observed to be invariant with concentration when tetramethylsilane was used as a reference. This had also been noted previously (19-20). The micellar solutions of benzene, potassium oleate, 1-pentanol, and water showed five peaks: those due to methyl, chain methylene, α-methylene, hydroxyl, and aromatic protons. All spectroscopic measurements were performed at 25±1 C.

RESULTS

The values of λ_{max}, $\Delta\nu_{1/2}$, and $\Delta\nu_I$ reported in Table I are seen to be in the same range as those reported by Rehfeld (7). The absorption frequency remained constant in the benzene micellar systems over the concentration range studied. The solution spectra of benzene in 1-pentanol or hexane (7) showed a slight red shift with increasing benzene concentration. The fluorescent emission spectra (Fig. 1) showed a broad emission band around 350 nm (28,000 cm^{-1}) which shifted to longer wavelengths in more concentrated solutions (Table II). This is in the range of the emission bands reported by Gilmore et. al. (21) for benzene dissolved in EPA (5 parts ether, 5 parts isopentane, and 2 parts ethanol by vol) at 77 K (24,000-29,000, 34,000-37,000 cm^{-1}). However, it is red shifted with respect to the fluorescent emission at 275.6 nm (36270 cm^{-1}) reported by Kistiakowsky and Nelles (22) for benzene vapor at 0.01 nm pressure. This effect has been observed before (23).

No significant difference was observed in the NMR chemical shift for the aromatic protons in any of the systems studied here. The benzene resonance appeared at 374±1 Hz downfield of the methyl resonance. This is in reasonable agreement with the chemical shifts reported for the aromatic protons of benzene in water-hexanol-potassium oleate-benzene systems by Gillberg et. al. (24). They reported chemical shifts between 380-375 Hz at 20 C. The half band width for the benzene resonance was ca. 2 Hz in all cases, indicating that the aromatic protons were in a state of high mobility, with a relaxation time of ca. 0.5 sec.

By gas chromatography, the solubility of benzene and 1-pentanol was found to be the same in water and potassium oleate solution just below the critical micelle concentration (cmc) of 14±1 mmol/liter (25).

DISCUSSION

The data reported in Table I show that the peak position for the second maxima of the 2600 A band in the UV absorption spectrum of benzene did not change with the concentration of benzene or the ratio of 1-pentanol in the micellar system. This would occur if the absorption spectrum were completely insensitive to the properties of the media or if the environment were invariant for the four sets of conditions for which spectra were recorded. The latter seems unlikely inasmuch as the overall benzene alcohol ratio is different; this would be expected to produce a change in the ratio in the droplet interior. It is important, then, to determine the magnitude of the differences that can be expected in the absorption parameters when the environment of the benzene molecules is changed.

The solution spectra of benzene in 1-pentanol showed that a two order of magnitude change in the ratio of benzene to 1-pentanol resulted in only a 4 A shift in the absorption maxima. The results previously reported by Rehfeld (7) for benzene in various solvents also showed low sensitivity. His results demonstrate that the peak position was essentially unchanged for benzene in hexane ($\epsilon = 1.9$) and in methanol ($\epsilon = 32.6$) at a molar concentration of 0.014. However, on changing the solvent from hexane at 0.021 M to water ($\epsilon = 81$) at 0.024 M, a 6 A blue shift was observed (7). Rehfeld referred to an 8 A shift on going from a hydrocarbon to an aqueous environment. His comparison, however, was made at two different concentrations, 4.78 M for benzene in hexane and 0.024 M for benzene in water. It must be concluded that the absorption frequency is not very sensitive to changes in dielectric constant of the solvent medium. Therefore, only gross differences in solvent environment can be discerned using this parameter alone. Fendler and Patterson (26) have also stated this in their criticism of Rehfeld's work.

The concentration dependence for the peak position can be seen in the data reported in Table I and by Rehfeld (7). In 1-pentanol, a two order of magnitude change in benzene concentration resulted in no more than a 4 A shift in wavelength. A larger shift was observed in the fluorescent emission spectra. For solutions of benzene in hexane (7) between 11.06 M-0.014 M, λ_{max} varied between 2552-2544 A, respectively. This represents a variation as large as that observed for a change in media from oleic to aqueous. However, a large part of the observed variation occurred in the more concentrated solutions. In the range 0.021 M-0.1725 M benzene, the peak position was 2546±1 A. It is clear, then, that comparisons of spectral parameters must be made in the same range of concentrations to obtain any useful information about the molecular environment.

The peak position observed in all of the dispersed systems was 2545 or 2546 A. The most dilute system was 0.044 M in benzene. Benzene in water at 0.024 M has a λ_{max} of 2539. Although these concentrations are not identical, they are close enough for comparison because in this concentration range the peak position is fairly insensitive to concentration. The peak position apparently indicates a hydrocarbon-like environment for the region of solubilization for benzene in these systems. This is also supported by the NMR spectra in which the chemical shift was the same in all hydrocarbon and micellar solutions. Molecular solubilization of large amounts of benzene in the aqueous phase can be excluded on this basis.

Further information regarding the nature of the solubilization region can be obtained from the behavior of $\Delta\nu_{1/2}$ in the various environments. Table I shows that $\Delta\nu_{1/2}$ increases with benzene concentration in 1-pentanol. The same behavior was seen in solutions of benzene in n-hexane (7). However, even at high benzene concentrations, $\Delta\nu_{1/2}$ did not exceed 410 cm^{-1} in these solvents. In water, however, $\Delta\nu_{1/2}$ was 530 cm^{-1} at a concentration of 0.024 M. It should be noted that in hexane at $M_\phi = 0.0094$, where $\lambda_{max} = 2539$ A, the same for water, $\Delta\nu_{1/2}$ equals 320 cm^{-1}. The dispersed systems all had values of $\Delta\nu_{1/2}$ between 400-462 cm^{-1} at relatively low concentrations of benzene. At these concentrations, values of 340-350 cm^{-1} would be expected if a comparison with hexane solutions were made, and values of 360-380 cm^{-1} would be expected if 1-pentanol solutions were used for comparison. On this basis, it must be concluded that there is some degree of polar character to the region of solubilization for benzene in these systems.

Two explanations are possible for this observation. If some benzene penetrated into the mixed film of 1-pentanol and potassium oleate, or adsorbed on the surface of the mixed micelle, it would experience a more polar environment. The strongly polar nature of the environment could affect the polarizability of the π electrons, causing a shift in absorption frequency. If only a small fraction of the benzene molecules experienced this environment at any one time, a shift in λ_{max} would not be apparent, but a broadening of the resonance peak would be observed. Broadening would also occur if some fraction of benzene were dissolved in the aqueous phase. No assumption was made regarding the concentration of benzene in aqueous solution, and no benzene was in the reference cell when the spectra were recorded. Therefore, any benzene in the continuous aqueous fluid was not compensated for and would broaden the adsorption band. Rehfeld (7) chose to assume that the intermicellar fluid was saturated with benzene when measuring the spectra of the micellar solutions and used a saturated aqueous phase for a reference.

TABLE II

Fluorescent Emission Data

Solvent	M_ϕ	n_ϕ/n_a	Fluorescent maximum (nm)
Micellar solutions			
Water	0.21	1.06	337 ± 5
Solutions			
n-Hexane	0.092	--	332 ± 5
1-Pentanol	0.093	0.016	328 ± 5
1-Pentanol	7.5	4.2	355 ± 5

$^aM_\phi$ = molar concentration of benzene (mol/liter); n_ϕ/n_a = molar ratio of benzene to 1-pentanol.

The shape of the spectral resonance also indicates a hydrocarbon-like environment for the dispersed benzene. The absorption bands were well resolved, approaching the appearance of the spectra of the vapor state. The spectra are well represented by the one shown by Rehfeld (7). Spectra for benzene in a polar environment would not be so well resolved (5).

When the spectroscopic evidence is taken as a whole, it represents strong evidence indicating that the major proportion of benzene in the potassium oleate-1-pentanol micellar system is in a relatively nonpolar environment in the droplet interior, with a smaller fraction in a more polar environment.

A further insight into the nature of the droplet environment can be achieved by using the thermodynamic treatment described by Tanford (27) in his discussion of the solubilization of hydrocarbons in surfactant micelles. Tanford assumed that any solute dissolved in the micelle formed an ideal solution with the hydrocarbon chains of the surfactant. He further assumed that the solute (hydrocarbon) dissolved in the aqueous continuous phase formed an ideal solution, inasmuch as it was present only in low concentrations. The standard free energy of transfer from the aqueous environment to the micelle interior would then be given by

$$\mu_m^o - \mu_w^o = RT \ln(X_w/X_m) \qquad (I)$$

where μ_m^o and μ_w^o are the standard chemical potentials in the micelle and water, respectively, R is the gas constant, T is temperature, and X_m and X_w are the mole fractions of solute in the micelle and water. The X_w's used were those for the solubilities of the hydrocarbons in water (28). He did not take into account changes in solubility in the aqueous part resulting from the presence of the surfactant micelles or monomers.

He then went on to compare values calculated from equation I with those for the free energy of transfer from pure hydrocarbons to water. These were calculated from the solubility of the hydrocarbons in water:

$$\mu_h^o - \mu_w^o = RT \ln X_w \qquad \text{(II)}$$

Comparisons of values calculated in this way showed that the free energies of transfer to the micelle were only slightly less negative (ca. 15%) than that for transfer to the hydrocarbon. He attributed this difference to a smaller entropy of transfer to the micelle due to restricted motion in the micelle. The enthalpies were ca. the same within experimental error. Tanford considered the similarities in the energies of transfer as an indication of the hydrocarbon nature of the micelle interior.

If the mixed micellar systems investigated here are considered to be saturated with solute (benzene) at the point at which they become transparent on the addition of 1-pentanol, similar calculations can be made. An equation similar to equation I can be used:

$$\mu_d^o - \mu_w^o = RT \ln (X_w/X_d) \qquad \text{(III)}$$

where X_d and μ_d^o are the mole fraction and standard chemical potential of the solute in the droplet. The droplet is composed of surfactant, 1-pentanol, and benzene. It was assumed that the aqueous part contained potassium oleate at a level equivalent to the cmc and benzene equivalent to the concentration in saturated water (23). On this basis and using equation III, the calculated transfer energies are -3.7 and -3.9 kcal for the systems, with n_ϕ/n_a equal to 0.93 and 1.07, respectively. These values are somewhat higher than the values for transfer to pure hydrocarbons but lower than those for transfer to pure alcohols (29,30). To the extent that these equations are valid, the results are not inconsistent with the spectroscopic data.

It is obvious that these equations are not strictly applicable, however. The free energy of transfer to pure benzene is calculated as -4.6 kcal (29,30), whereas in the system reported here $\mu_d^o - \mu_w^o \approx -3.8$ kcal. Using the data reported by Rehfeld (7) for the solubility of benzene in sodium dodecyl sulfate micelles, $\mu_m^o - \mu_w^o = -4.2$ kcal. Tanford's data show the same behavior (30,31), i.e., the energy of transfer to the micelle is higher yet no bulk hydrocarbon phase separates out. This inconsistency can be explained away by the high uncertainty in the numbers. The value for X_w in the presence of the surfactant is not known and, because solutes in micelles can lower the cmc of a surfactant (32), there should be a change in the chemical potential of the surfactant. This implies that the activity coefficient of the solute is not 1, as assumed, and the micellar part cannot be ideal. Although this type of calculation can only be considered approximate, it does serve to illustrate the similarity in the nature of the solubilization process in the mixed micellar and some single surfactant micellar systems (33).

Considering the evidence presented here, it would not be unreasonable to assume, for the purposes of model calculations, a representation in which the lipophilic core of solute and cosurfactant was surrounded by a mixed film of surfactant and cosurfactant. Naturally, this view may not apply to other systems. However, it can be assumed that more hydrophobic oils such as aliphatic hydrocarbons would also fit this picture.

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