Water Solubilization in Microemulsions Containing Amines as Cosurfactant

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Water-in-oil microemulsions were produced by mixing different combinations of the cationic surfactants cetyltrimethylammonium bromide and cetylpyridinium chloride, *n*-alkanes (C_5–C_7) and benzene as oils, *n*-alkylamines (C_6 and C_8) and cyclohexylamine as cosurfactants with water. The influence of chainlength of the alkanes and amines on water solubilization behavior of these systems has been investigated. The solubilization of water in a particular microemulsion is governed by the partitioning of amines among oil, water and interfacial phases, depending on the chainlength and nature of oil and amine, and their interaction with the surfactant. The molar ratio of amine to surfactant at the droplet interface increased with the length of the oil chain. The free energy changes accompanying cosurfactant adsorption at the interface have also been computed.

KEY WORDS: Cosurfactant, interface, microemulsion, solubilization, surfactant.

Microemulsions are isotropic, clear or translucent, thermodynamically stable dispersions of oil, water, emulsifiers, usually salt, and often a small amphiphilic molecule called a cosurfactant (1,2). The droplet diameters in microemulsions range from 100–1000 Å. The droplets are stabilized by a mixed interfacial film of surfactant and cosurfactant. A number of studies have been carried out on microemulsions with alcohols as cosurfactant (2–9). Recently, monohexyl (10) and monobutyl (11) ethers of ethylene or diethylene glycol have been used as cosurfactants. The alkyl chainlengths of oil and cosurfactant strongly influence the interfacial composition and distribution of cosurfactant in the oil and water phases (5–9). The formation and various physicochemical properties of the microemulsions are influenced by the alkyl chainlength of alcohol and hydrocarbons (3,5–8).

Recently, some linear medium-chain aliphatic amines and salts of some amines have been getting more recognition as cosurfactants in microemulsion preparations (12–15). The use of amines as cosurfactant was first referred to in Winsor's work (16). Ahmad *et al.* (17) mapped the phase behavior of C_8NH_3Cl and C_8NH_2 in xylene and water. Amines exhibit higher amphiphilicity than all other similar amphiphiles with simple polar head groups (12,18). A comparison of some of the major properties of alcohols and amines shows that amines are weak bases and K_b is approximately 10^{-4} for most short-chain amines, whereas alcohols are weak acids and are slightly deprotonated. Amines are more surface-active than alcohols at the air/water interface (19). Longer-chain amines ($C_{10}NH_2$) form micelles, and some form liquid crystals (20,21), whereas long-chain alcohols are surface-active but do not form micelles or mesophases (18). These properties should manifest themselves in the formation of microemulsion systems.

Visualizing the importance of amines as suitable cosurfactants in microemulsion formation and solubilization of water, coupled with their characteristic favorable properties as compared to alcohols, the present paper has been devoted to the study of formation and characterization of water-in-oil (W/O) microemulsions composed of cationic surfactants [cetyltrimethylammonium bromide (CTAB) and CPC], water, *n*-alkanes (C_5–C_7)/benzene and hexyl-, octyl- and cyclohexylamine.

EXPERIMENTAL PROCEDURES

Materials. CTAB, pro analysis grade obtained from Merck (Darnstadt, Germany), was used as supplied. CPC obtained from Sigma Chemical Company (St. Louis, MO) was recrystallized twice from ethanol-ethylacetate mixture and dried at 60°C under moderate vacuum. The purity of surfactants was ensured from the absence of minima in plots of the surface tension *vs.* the logarithm of concentration. *n*-Hexane and *n*-heptane (99%) were obtained from BDH (Poole, U.K.), while *n*-pentane and benzene (99%) were E. Merck (Bombay, India) products. *n*-Hexylamine and *n*-octylamine, Purum-grade were obtained from Fluka (Buchs, Switzerland), while cyclohexylamine was a BDH product (99.5%). All the solvents were used as supplied. Demineralized water redistilled from alkaline potassium permanganate was used.

Methods. W/O microemulsions were produced by titrating a coarse emulsion of oil-water-surfactant with cosurfactant until the mixture became clear. Addition of oil in small amounts turned the mixture turbid. The entire contents were mixed thoroughly with a magnetic stirrer and titrated with cosurfactant until the mixture was transparent again. For water solubilization studies, maximum water solubilization in the microemulsion was obtained from the titration of initially formed W/O microemulsion with water until turbidity commenced. At the endpoint, the systems were initially turbid, but after a few minutes standing, two clear phases were formed which, on further shaking, resulted in a turbid solution. All titration experiments were carried out at 25 ± 0.1°C.

RESULTS AND DISCUSSION

Table 1 summarizes the results of the water solubilization capacities of W/O microemulsion systems. Water solubilization of a microemulsion increases linearly with the chainlength of the oil. The rate of increase of water solubilization with alkyl chainlength is large in CTAB-containing microemulsions as compared to CPC microemulsions. The water solubilization limit for both CTAB and CPC microemulsions remains the same for all *n*-alkanes used when cyclohexylamine was used as a cosurfactant. The continuous increase of water solubilization with the alkyl chain of the oil may be due to preferential partitioning of amines at the interface for higher-chainlength oil. Table 1 also shows clearly that the water solubility in

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TABLE 1

Water Solubilization Capacities of *n*-Hexylamine, *n*-Octylamine and Cyclohexylamine Microemulsion Systems Composed of 1 g Surfactant (fixed), 10 mL *n*-Alkane or Benzene (fixed), 5 mL Amine (fixed) and Water at 25°C[a]

	Water solubilized (mL)					
	CTAB			CPC		
Oil	*n*-Hexylamine	*n*-Octylamine	Cyclohexylamine	*n*-Hexylamine	*n*-Octylamine	Cyclohexylamine
Pentane	9.65	11.30	1.30	11.25	10.90	1.30
Hexane	10.60	11.90	1.50	12.20	11.69	1.50
Heptane	11.70	12.52	1.75	12.60	12.08	1.93
Benzene	7.35	6.76	8.75	8.60	7.90	3.48

[a]Abbreviations: CTAB, cetyltrimethylammonium bromide; CPC, cetylpyridinium chloride.

benzene microemulsions is much lower than in *n*-akane-containing systems. This is possibly due to a difference in the interaction based on the structural difference of oils, such as chainlength and polarity, with the head-group of the surfactant, which influences the partitioning of amine in the continuous and interfacial phases. Similar interaction effects have been reported for sodium dodecyl sulfate (SDS) microemulsions, and it was found that the cosurfactant preferentially partitioned at the interface for alkanes than for benzene (22).

Table 1 also shows that water solubilization is higher in case of a *n*-octylamine/CTAB microemulsion, while it is lower in a CPC microemulsion. The opposite behavior was observed with *n*-hexylamine systems. Because the head-group size of the surfactant is one of the factors that decides the packing of molecules at the droplet interface, we would expect a difference of packing in the case of CTAB and CPC. Of course, with aromatic pyridinium salts there would be delocalization of charge as well as less charge-shielding in comparison to trimethyl ammonium salts. This is the reason for the opposite behavior of these two surfactants. The interrelated factors undoubtedly affect interactions between amines and water and, therefore, the water-solubilizing capacity.

The partitioning of amine at the interface was determined by the titration method proposed by Bowcott and Schulman (23). The present microemulsion system may be considered to be made up of three phases, namely continuous oil phase, dispersed water phase and the interfacial phase. Assuming that the amine is distributed in these phases, the total concentration of amine, n_a, can be written as (22)

$$n_a = n_a^o + n_a^d + n_a^i \qquad [1]$$

where n_a^o, n_a^d and n_a^i are the number of moles of amine in the oil, dispersed (water) and interfacial phases, respectively. Further, because the solubility of amine is constant in the continuous (oil) phase, the distribution constant for amine can be written as

$$K = \frac{n_a^o}{n_o} \qquad [2]$$

where n_o is the number of moles of oil. By combining Equations 1 and 2 and dividing by moles of surfactant, n_s, we get

$$\frac{n_a}{n_s} = K\frac{n_o}{n_s} + \frac{n_a^d + n_a^i}{n_s} \qquad [3]$$

Equation 3 suggests that a plot of n_a/n_s *vs.* n_o/n_s would give a straight line with slope K and intercept I, where $I = (n_a^d + n_a^i)/n_s$. Assuming that the solubility of these amines in water is negligible ($n_a^d = 0$), then I simply gives the number of moles of amine per mole of surfactant at the interface (n_a^i/n_s). Plots of n_a/n_s *vs.* n_o/n_s for different oil, *n*-hexylamine and surfactant combinations are shown in Figure 1. Similar plots were obtained for *n*-octylamine and cyclohexylamine microemulsions but are not shown here. From the slope, K and intercept I of these straight-line plots, the mole fraction of amine at the interface, X_a^i, and in the continuous oil phase, X_a^o, were calculated (22),

$$X_a^i = I/(I + 1) \qquad [4]$$

$$X_a^o = K/(K + 1) \qquad [5]$$

Values of I, K, mole fraction of amine at the interface (X_a^i) and mole fraction of amine in the continuous phase (X_a^o) for CTAB and CPC microemulsion systems are given in Tables 2 and 3, respectively.

The experimental results presented in Tables 2 and 3 show many interesting features of microemulsion formation. It is clear that the mole fraction of amine, X_a^i, and number of moles of amine per mole of surfactant, I, at the interface increase with an increase in the oil chainlength. It may be concluded that the partitioning of amines at the interface is favored for higher-chainlength oils. A similar type of behavior was reported for sodium stearate and CTAB microemulsions with medium-chainlength alcohols as cosurfactants (6,8,24).

I (n_a^i/n_s) values for medium-chainlength alcohols (24) and amines for similar microemulsions are compared in Table 4. It is clear that I values are much higher for amine microemulsions than for corresponding alcohol microemulsions. These results clearly indicate that, in comparison to medium-chainlength alcohols, amines are preferentially partitioned at the droplet interface for a particular oil phase. These differences in interfacial parameters are responsible for higher water solubilizations in amine microemulsions.

Water solubilization limits in *n*-pentanol-containing microemulsion systems prepared with the same quantity of CTAB and *n*-alkanes (as used for amine microemulsion) were reported to be 4.45, 4.55 and 5.10 mL for *n*-pentane, *n*-hexane and *n*-heptane systems, respectively (6). From Table 1, water solubilization in amine microemulsion systems seems to be very high in comparison with alcohol systems (6,24). This behavior may be understood

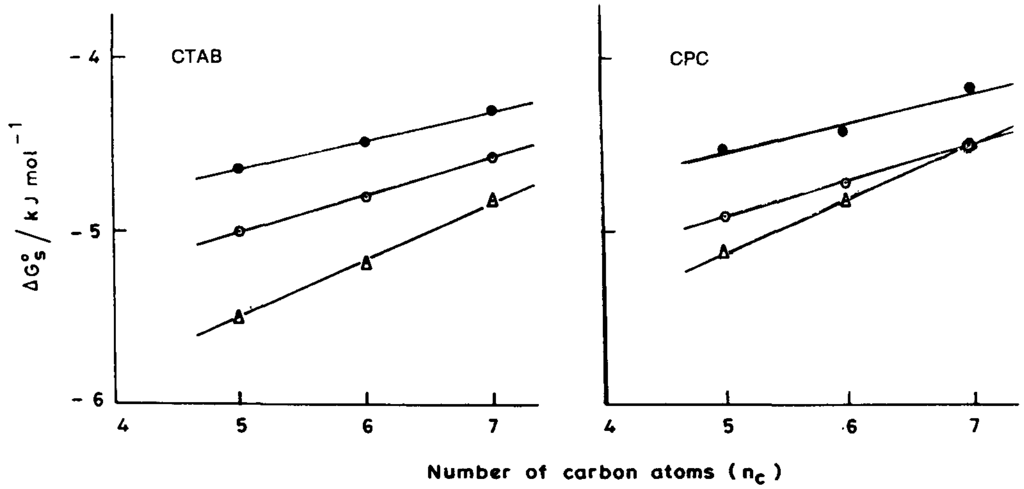

FIG. 1. Plots of n_a/n_s *vs.* n_o/n_s for microemulsion systems composed of 1 g surfactant (fixed), 1 g water (fixed), oil and *n*-hexylamine at 25°C. ▲, Benzene; X, *n*-pentane; ■, *n*-hexane; and ⊡, *n*-heptane.

TABLE 2

Intercept (I = n_a^i/n_s) and Slope (K = n_a^o/n_o) of Plots of n_a/n_s *vs.* n_o/n_s and Mole Fraction of Amine at the Interface (X_a^i) and in Continuous Oil Phase ($X^o{}_a$) for the Microemulsion System Composed of 1 g CTAB (fixed), 1 g Water (fixed), Oil and Amine at 25°C[a]

	n-Hexylamine				*n*-Octylamine				Cyclohexylamine			
Oil	I	K	X_a^i	X_a^o	I	K	X_a^i	X_a^o	I	K	X_a^i	X_a^o
Pentane	3.15	0.112	0.759	0.101	3.85	0.095	0.794	0.087	7.96	0.158	0.888	0.136
Hexane	3.60	0.126	0.783	0.112	4.15	0.110	0.806	0.099	8.51	0.172	0.895	0.146
Heptane	4.05	0.146	0.802	0.127	4.40	0.132	0.815	0.117	9.15	0.189	0.902	0.159
Benzene	1.55	0.097	0.608	0.088	1.38	0.10	0.580	0.089	2.66	0.08	0.727	0.089

[a]CTAB, cetyltrimethylammonium bromide.

TABLE 3

Intercept (I = n_a^i/n_s) and Slope (K = n_a^o/n_o) of Plots of n_a/n_s *vs.* n_o/n_s and Mole Fraction of Amine at the Interface (X_a^i) and in Continuous Oil Phase ($X^o{}_a$) for the Microemulsion System Composed of 1 g CPC (fixed), 1 g Water (fixed), Oil and Amine at 25°C[a]

	n-Hexylamine				*n*-Octylamine				Cyclohexylamine			
Oil	I	K	X_a^i	X_a^o	I	K	X_a^i	X_a^o	I	K	X_a^i	X_a^o
Pentane	3.75	0.122	0.789	0.109	3.55	0.111	0.780	0.100	6.74	0.165	0.871	0.142
Hexane	4.20	0.136	0.808	0.120	4.05	0.131	0.802	0.116	7.80	0.175	0.886	0.149
Heptane	4.70	0.156	0.825	0.135	4.25	0.153	0.810	0.133	8.10	0.200	0.890	0.167
Benzene	2.29	0.125	0.696	0.111	1.63	0.130	0.620	0.115	0.62	0.140	0.382	0.123

[a]CPC, cetylpyridinium chloride.

TABLE 4

Comparison of the Values for Moles of Cosurfactant Per Mole of Surfactant, n^i_{cos}/n_s, for Different Medium-Chainlength Alcohols and Amines in the Microemulsion System Composed of 1 g CTAB, 1 g Water, Oil and Cosurfactant[a]

Oil	*n*-Hexylamine	*n*-Octylamine	*n*-Octanol[b]	*n*-Heptanol[b]	*n*-Hexanol[b]	*n*-Pentanol[b]
Pentane	3.15	3.85	1.35	1.38	1.45	1.64
Hexane	3.60	4.15	1.85	2.21	2.42	1.97
Heptane	4.05	4.40	2.23	2.47	2.44	2.11
Benzene	1.65	1.45	—	0.50	1.00	1.52

[a]CTAB, cetyltrimethylammonium bromide. [b]Reference 24.

in view of greater partitioning of amines at the interface in comparison to the corresponding alcohols (Table 4).

Tables 1–3 show that X_a^i values and water solubilization increase with an increase in chainlength of the amine in CTAB microemulsions, whereas reverse behavior is observed in CPC microemulsions. However, in the case of cyclohexylamine, the mole fraction of amine at the interface, X_a^i, seems to be high, but the water solubilization is less compared to linear chain alkylamine systems. This is due to the high solubility of cyclohexylamine in water (25), and the term n_a^d/n_s in Equation 3 could not be neglected for the calculation of I values as generally done for the water-insoluble amines (C_6NH_2, C_8NH_2). Thus, the actual value of I for cyclohexylamine systems should be $(n_a^i + n_a^d)/n_s$. The I values reported in Tables 2 and 3 for cyclohexylamine systems included the term n_a^d/n_s, which has a fairly high value. From this, one could easily guess the actual value for the mole fraction of amine at the interface, X_a^i, for the cyclohexylamine system, which must be less than for *n*-hexylamine and *n*-octylamine systems. Another factor that influences water solubilization in cyclohexylamine microemulsion systems is the solubility of surfactant molecules in the water plus the cyclohexylamine pool, which removes it gradually from the interface. This will decrease the total interfacial area and hence a concomitant decrease in the water solubilization capacity. Such type of behavior was also reported for *n*-butanol (water-soluble cosurfactant) microemulsions (8).

The standard free energy change, ΔG_s^o, for transfer of amine from the continuous oil phase to the interfacial region was calculated from the relation (22)

$$\Delta G_s^o = -RT \ln (X_a^i/X_a^o) \qquad [6]$$

where T is the experimental temperature. The calculated values of ΔG_s^o from Equation 6 are tabulated in Table 5. The negative value of ΔG_s^o suggests that microemulsions form spontaneously. Table 5 shows that the free energy change for transfer of amine becomes less negative as the chainlength of oil increases. This indicates that the transfer of amine from the continuous oil phase to the interfacial region is an entropy-driven process. This further suggests that the association between emulsifier and amine at the interface becomes more favored in higher-chainlength oils. Microemulsion structures are not completely described in the literature at the molecular level. Therefore, no satisfactory theory is available to explain the ΔG_s^o values. However, in all surface chemical systems where amphiphilic molecules are used, it has always been the practice to measure the effect of alkyl chainlength on the free energy of the system (26).

TABLE 5

The Standard Free Energy of Transfer, ΔG_s^o, for the Microemulsion System Composed of 1g Surfactant (fixed), 1 g Water (fixed), Oil and Amine at 25°C[a]

	$-\Delta G_s^o$/kJ mol^{-1}					
	CTAB			CPC		
Oil	*n*-Hexylamine	*n*-Octylamine	Cyclohexylamine	*n*-Hexylamine	*n*-Octylamine	Cyclohexylamine
Pentane	5.01	5.49	4.65	4.91	5.10	4.50
Hexane	4.82	5.20	4.49	4.73	4.80	4.42
Heptane	4.57	4.82	4.30	4.49	4.48	4.15
Benzene	4.71	4.57	5.21	4.47	4.10	2.81

[a]Abbreviations: See footnote in Table 1.

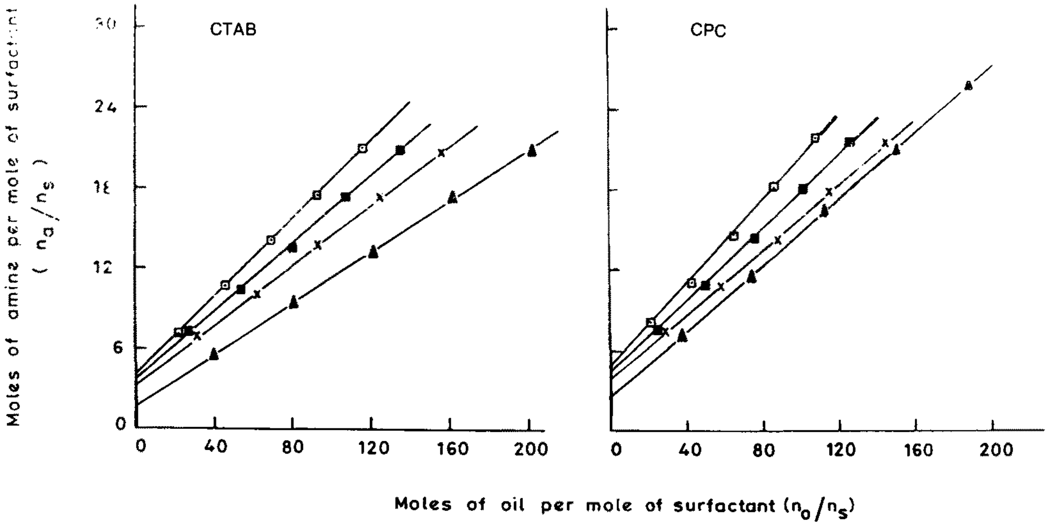

FIG. 2. Variation of ΔG_s^o with the number of carbon atoms, n_c, in the alkyl chain of the *n*-alkane. ●, Cyclohexylamine; ⊙, *n*-hexylamine; and ▲, *n*-octylamine.

The standard free energy change, ΔG_s^o, for transfer of amine is found to increase linearly with the number of carbon atoms, n_c, in the alkyl chain of the oil phase (Fig. 2). The free energy change per methylene group, $\Delta G_s^o/CH_2$ of the oil phase (for *n*-alkanes), has been estimated to be −220 and −335 J/mole for *n*-hexylamine and *n*-octylamine, respectively, in CTAB microemulsions. In CPC microemulsions, these values are −210 and −310 J/mole for hexylamine and octylamines, respectively. However, for cyclohexylamine systems, $\Delta G_s^o/CH_2$ of *n*-alkanes was found to be −175 J/mole for both of the surfactants CTAB and CPC. These results clearly indicate that $\Delta G_s^o/CH_2$ values depend much more on the chainlength of amine than on the surfactant head-group. Table 5 also shows that ΔG_s^o values are less negative for CPC systems than for CTAB systems, indicating that the amines are preferentially associated with CPC than with CTAB surfactants.

The partitioning of cosurfactant at the microemulsion droplet interface is responsible for higher water solubilization. This greater partitioning of amine explains why *n*-alcohol microemulsions solubilize less water than amine microemulsions.

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