

essentially constant over the complete sorption range. $\Delta\bar{S}_m$ changes very little once most of the pore space is filled, as the environment of the sorbed molecules remains nearly constant. Consequently, $\Delta\bar{G}_m$ is almost invariant from about 5 to 6.5 molecules sorbed per unit cell (Figure 4). This could clearly lead to sorption hysteresis being observed in isotherm experiments.⁴

The reason this hysteresis is only found with low Al content materials is linked with the fact that the number of strong sorption sites is determined by the number of Al atoms present. The effect has little to do with anything unusual about *p*-xylene/*p*-xylene interactions in the sorbed state, which are weak, and nothing to do with the rate of transport of *p*-xylene within the crystal environment becoming slow at a critical sorbed molecular concentration, as the kinetic experiment described in the Results section shows.

$\Delta\bar{G}_m$ for benzene sorption on silicalite also changes rather slowly as saturation is approached, and this too is manifest in a somewhat unusual isotherm shape, although no hysteresis has been reported.

However, the $\Delta\bar{H}_m$ and $\Delta\bar{S}_m$ curves show that the effect arises in a quite different way, as both these functions change appreciably with amount sorbed. The molecular reasons for this have been discussed earlier in the paper.

This work therefore helps to confirm the view that the properties of ZSM-5 zeolites do vary in a systematic and regular way with aluminum content,⁷ and that the apparently very strange behavior observed in the sorption isotherms does not have an obscure origin.

Acknowledgment. I acknowledge the help of Dr. D. M. Bibby and his co-workers in providing the samples of the adsorbents, and of Dr. D. V. Fenby for his willing assistance in making equipment available for this work.

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A Fluorescence Probe Investigation of the Effect of Alkali Metal Ions on the Micellar Properties of a Crown Ether Surfactant

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Fluorescence parameters of pyrene were employed to investigate the effect of added alkali metal ions, M⁺, on aqueous solutions of a crown ether surfactant C₁₀O18C. It is concluded that M⁺ ions complex with the nonionic crown ether surfactant to produce an ionic surfactant C₁₀O18CM⁺ and that the latter forms comicelles with C₁₀O18C. The variation of the ratio of the intensity of the first and third vibrational bands (*I*₁/*I*₃) of pyrene was employed to examine the microscopic polarity of the comicelles (ϵ_M), and time-resolved pyrene excimer/monomer fluorescence emission was employed to evaluate the aggregation number, *N*, of the comicelles. A correlation was found between the binding efficiency of M⁺ and the fluorescence parameters. The critical micelle concentration, cloud point, micropolarity, and aggregation number were all found to depend in a systematic manner on the fraction of complexed surfactant in the comicelles.

Introduction

Crown ethers are cyclic oligoethers with an outstanding ability to complex cations selectively and to behave as ionophores capable of transporting cations across lipophilic barriers.¹ The attachment of a lipophilic long-chain alkyl group to a crown ether can convert the latter into a crown ether surfactant, capable of forming micelles in a manner analogous to classical nonionic surfactants.^{2,3} The nature and behavior of such micellar systems upon addition of a metal cation capable of complexing with the crown ether moiety of the surfactant are of interest because of the possibility of producing comicelles containing both nonionic crown surfactant molecules and ionic complexed surfactant molecules. As a result, the solution properties of aqueous solutions of crown ether surfactants are expected to respond very differently to the addition of alkali metal salts than conventional nonionic polyoxyethylenated long-chain alcohol types. Classical measurements of surface tension, critical micelle concentrations (CMC), cloud points, and foaming properties have been employed to investigate the influence of added alkali metal ions on the surfactant properties of crown ether surfactants.^{4,5} We report an investigation of the influence

of added alkali metal salts to aqueous solutions of decyl 18-crown-6 (C₁₀O18C), a crown ether surfactant, by a fluorescence probe technique. Pyrene has been previously employed to interrogate micellar properties of ionic and nonionic surfactants.^{6,7} In this work pyrene fluorescence is employed to probe micellar micropolarity and to determine micellar aggregation numbers. These and other micellar parameters in the presence of alkali metal salts will be shown to correlate well with the complexing ability of the alkali metal cation to the crown ether.

Experimental Section

Decyl 18-crown-6 (C₁₀O18C) was a generous gift of Professor M. Okahara, Osaka University.⁸ Pyrene (Aldrich) was recrystallized three times from ethanol. The alkali metal salts (Alfa, ultrapure grade) were used as supplied.

Fluorescence spectra were recorded on either a Perkin-Elmer MPF-3L spectrometer or a SLM Model 8000 spectrometer. The ratio of pyrene emission intensity at the vibrational maxima at 373 nm to that at 383 nm is defined as *I*₁/*I*₃. The latter fluorescence parameter has been shown to be a faithful reporter of the microscopic polarity of pyrene.⁶ Micropolarity (ϵ_M) was

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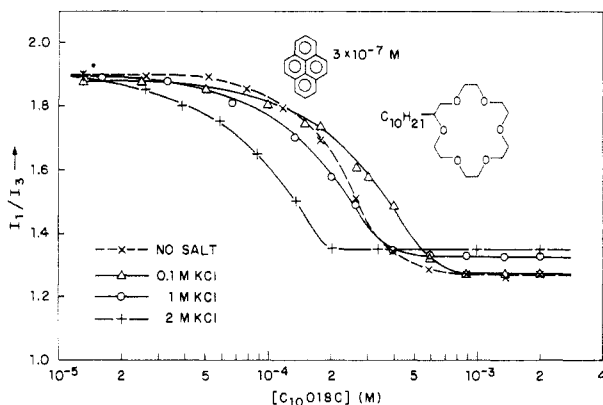


Figure 1. I_1/I_3 of pyrene in $C_{10}O18C$ (2 mM) with or without salt as a function of surfactant concentration.

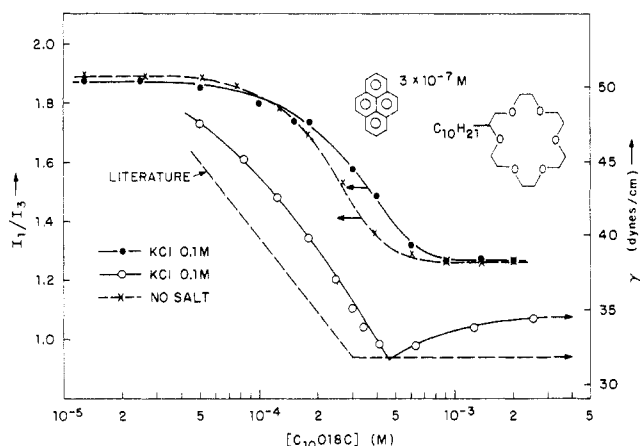


Figure 2. Relationship between I_1/I_3 and γ as a function of surfactant concentration with KCl (0.1 M) or without salt.

estimated from the I_1/I_3 value by eq 1 (vide infra). Fluorescence decays were determined on a PRA single-photon-counting spectrometer which has been described previously.⁹

A stirred 1% aqueous solution of surfactant in a test tube equipped with a thermometer was heated in a water bath. The temperature of the reversible critical (cloud) point at which the solution suddenly turned turbid or turned clear on cooling was determined by visual inspection and found to be reproducible within ± 0.5 °C.

In the presence of salt, the comicelles are mixtures of $C_{10}O18C/C_{10}O18CM^+$, but the composition of the comicelle is fixed (vide infra) at a given concentration of surfactant and salt. The turbidity changes occurred over a very narrow temperature range compared to the range observed with (typical polydisperse) commercial nonionic surfactants, presumably due to the monodisperse character of the hydrophobic and hydrophilic groups of $C_{10}O18C$.

Results

Figure 1 shows the I_1/I_3 of aqueous solutions of pyrene as a function of $C_{10}O18C$ concentration. The sharp decrease in I_1/I_3 from ca. 1.9 to ca. 1.3 is typical of transfer of pyrene from a highly polar aqueous environment to a less polar, more hydrophobic environment.⁶ The shape of the curves is typical of cmc plots, and we may assume from Figure 1 that the cmc of $C_{10}O18C$ is ca. 3×10^{-3} M. This value is in agreement with that (ca. 3×10^{-3} M, see Figure 2) obtained by conventional surface tension measurements (γ data are cited from ref 5). The addition of 0.1 M KCl causes an increase in the cmc to ca. 4.0×10^{-3} M, whereas the addition of 2 M KCl causes a decrease in the cmc to ca. 1.3×10^{-3} M. Thus, the cmc for $C_{10}O18C$ micelle formation is increased at low (0.1 M KCl) salt concentrations but decreased

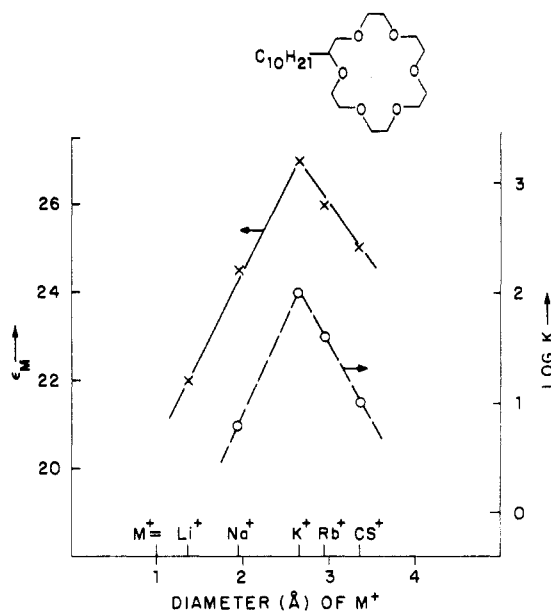


Figure 3. Correlation between ϵ_M (calculated from eq 1) and $\log K$ in $C_{10}O18C$ (2 mM) as a function of the diameter of added salts (1 M).

at high (2 M KCl) salt concentrations.

Figure 2 compares the variation of I_1/I_3 and the surface tension,⁵ γ , as a function of $C_{10}O18C$ concentration. Although the pairs of curves have similar shapes in the presence and absence of 0.1 M KCl, I_1/I_3 remains constant above the cmc in the presence and absence of 0.1 M KCl, whereas γ remains constant above the cmc only in the absence of 0.1 M KCl. In the presence of salt γ increases slightly above the cmc. Thus, there is a difference in the response of the pyrene probe and γ to detergent concentration in the presence of 0.1 M KCl.

A linear relation has been shown to exist between the value of I_1/I_3 and the polarity of a homogeneous solvent.¹⁰ We assume that the value of I_1/I_3 for pyrene dissolved in micelles represents the micropolarity ϵ_M of the pyrene environment. A quantitative linear relationship between ϵ_M and I_1/I_3 is given by eq 1 (based on measurements of I_1/I_3 in homogeneous solvents of known dielectric constant).¹⁰

$$\epsilon_M = 86.2(I_1/I_3) - 87.8 \quad (1)$$

The values of I_1/I_3 were measured for aqueous solutions of pyrene containing 1 M added alkali metal chloride and 2×10^{-3} M $C_{10}O18C$. The calculated ϵ_M values are plotted in Figure 3 as a function of the alkali metal cation. Also shown for comparison is the log of the equilibrium constants (K) for binding of the cation with 18-crown-6.¹¹ It is apparent that the shapes of the two curves are qualitatively similar, implying that the factors controlling ion complexing and micropolarity experienced by pyrene are related.

The aggregation numbers of ionic and nonionic micelles have been determined for a large number of systems by the measurement of time-resolved pyrene monomer/excimer emission. This method appears to be reliable and of broad generality. Under appropriate conditions the decay of pyrene monomer emission is given by use of eq 2,^{11,12} where \bar{n} is the average number of fluorophors per micelle. Extrapolation of a plot of $\ln(I_m/I_m^0)$ vs.

$$\ln(I_m/I_m^0) \approx -(\bar{n} + k_1 t) \quad (2)$$

$$N = \frac{\bar{n}(c - \text{cmc})}{C_p} \quad (3)$$

t to $t = 0$ yields \bar{n} . The aggregation number, N , is obtained from

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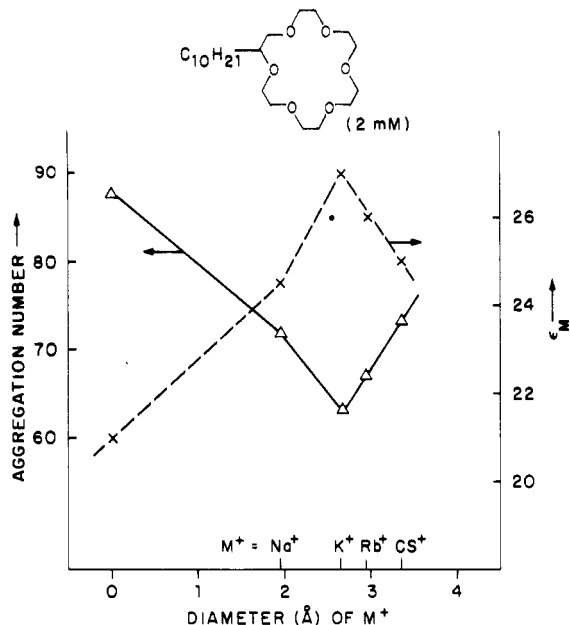


Figure 4. Correlation between aggregation number and ϵ_M in $C_{10}O_{18}C$ (2 mM) as a function of the diameter of added salts (1 M).

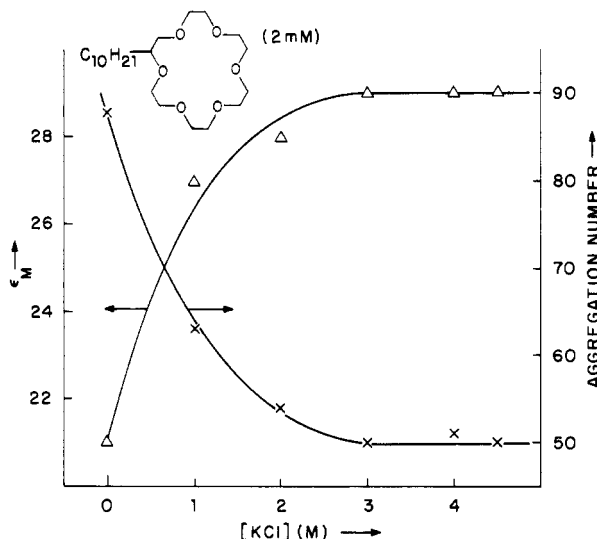


Figure 5. Correlation between ϵ_M (calculated from eq 1) of pyrene and aggregation number in the micelle of $C_{10}O_{18}C$ (2 mM) as a function of salt concentration.

eq 3 where C_p is the concentration of pyrene and C and cmc are the surfactant concentration and critical micelle concentration, respectively.

As a test of the method, the values of N for an anionic (sodium dodecyl sulfate, SDS), a cationic (hexadecyltrimethylammonium chloride, HDTCl), and a nonionic (Brij 35) surfactant were determined. From eq 2 and 3 and experimental data, the estimated values (with an error of $\pm 10\%$) were found to be 60 (SDS), 50 [HDTCl], and 44 (Brij 35), in reasonable agreement with literature values from light-scattering measurements: 62 (SDS), 59 (HDTCl), and 40 (Brij 35).¹³

Employing the pyrene method, we found the $C_{10}O_{18}C$ micelles to have a value of $N = 88$ at 2×10^{-3} M. Figure 4 shows a plot of the measured value of N for $C_{10}O_{18}C$ at 1 M alkali metal chloride as a function of alkali metal cation. For comparison, the value of ϵ_M for pyrene (from I_1/I_3 measurements) as a function of alkali metal cation is given. It is clear from Figures 3 and 4 that $\log K$, ϵ , and N all correlate qualitatively with common factors.

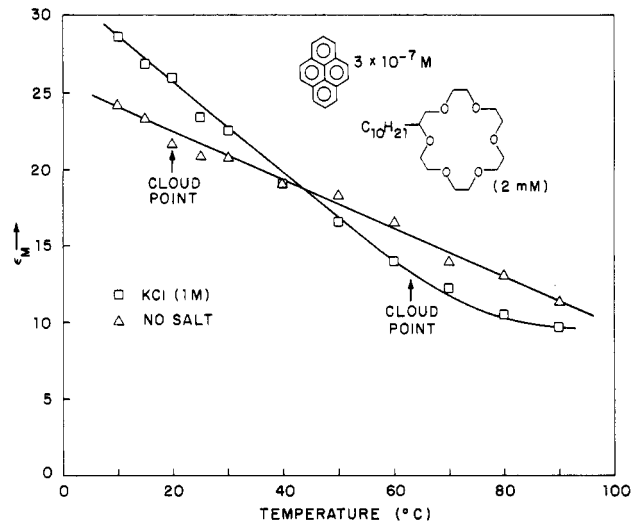


Figure 6. ϵ_M (calculated from eq 1) of pyrene in $C_{10}O_{18}C$ (2 mM) with or without KCl (1 M) as a function of temperature.

TABLE I: Summary of the Micellar Properties of $C_{10}O_{18}C$ under Different Kinds of Salts and Salt Concentrations

| salt | concn, M | I_1/I_3 | ϵ_M | aggregation no. | cloud point ^b |
|------|----------|-----------|--------------|-----------------|--------------------------|
| | 1 | 1.26 | 21 | 88 | 20 |
| LiCl | 1 | 1.27 | 22 | 62 ^a | 18 |
| NaCl | 1 | 1.30 | 24 | 72 | 33 |
| KCl | 1 | 1.33 | 27 | 63 | 63 |
| RbCl | 1 | 1.32 | 26 | 67 | 46 |
| CsCl | 1 | 1.31 | 25 | 74 | 32 |
| KCl | 2 | 1.34 | 28 | 54 | 65 |
| KCl | 3 | 1.35 | 29 | 50 | 56 |
| KCl | 4 | 1.35 | 29 | 51 | 46 |
| KCl | 4.5 | 1.35 | 29 | 50 | 44 |

^a Measured at 10 °C. ^b In °C.

The influence of KCl concentration on ϵ_M and N is shown in Figure 5. Initially an increase in the concentrations of KCl causes an increase in ϵ_M , but at ca. 3 M the value of ϵ_M reaches a plateau. The value of N undergoes an initial decrease as the concentration of KCl is increased and then reaches a limiting value at ca. 3 M KCl. Again there appears to be a correspondence between aggregation number and micropolarity experienced by pyrene.

Figure 6 shows the temperature dependence of ϵ_M for pyrene dissolved in $C_{10}O_{18}C$ micelles. In the presence and absence of KCl, ϵ_M decreases monotonically with increasing temperature. Interestingly, in the absence of salt the plot of ϵ_M vs. T is nearly linear.

In the presence of 1 M alkali metal halide, the cmc of $C_{10}O_{18}C$ should be less than 2×10^{-4} M (the cmc in the presence of 1 M KCl). The concentration of $C_{10}O_{18}C$ was selected (2×10^{-3} M) for the experiments shown in Figures 3–6 to be 10 times higher than the cmc with 1 M KCl in order to ensure the existence of micelles in the presence of high concentration of salt.

Some of the micellar properties of $C_{10}O_{18}C$ under various conditions are summarized in Table I.

Discussion

We seek to explain the interrelationships between K , ϵ_M , and N for various cations and $C_{10}O_{18}C$ that is suggested by that data in Figures 1–6. Furthermore, we seek explanations based on conventional concepts for ionic and nonionic micelles.

As a general rule in aqueous solution, the greater the "disimilarity" between surfactant and solvent, the greater the aggregation number and the lower the cmc .¹⁴ For example, longer hydrophobic groups for ionic micelles and shorter oxyethylene units in nonionic micelles cause aggregation numbers to increase. The

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addition of neutral electrolyte to solutions of ionic surfactants generally causes an increase in aggregation number¹⁵ because of a reduction in the neutral repulsion of the ionic head groups. The effect of neutral electrolyte on the aggregation number of nonionic surfactants is generally small,¹⁵ because the addition of electrolyte does little to modify the existing interactions of the hydrophilic outer core. On the other hand, an increase in temperature usually causes only small changes in the aggregation number of ionic surfactants but often causes a large increase in the aggregation number of polyoxyethylenated nonionics.¹⁶ The mechanism of the salt effect on the properties of ionic surfactants differs from that for nonionic surfactants. Added neutral electrolytes mainly interact with the ionic atmosphere of the hydrophilic surface¹⁷ for ionic micelles, but may interact to salt in or salt out the hydrophobic group of nonionic micelles.¹⁸

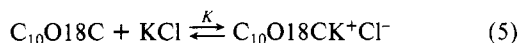
Salt effects on the properties of aqueous solutions of nonionic surfactants have been extensively studied by measuring the change in cloud point as a function of salt concentration.^{16b,19,20} The decrease or increase in cloud point is defined as "salting-out" and "salting-in" effects,¹⁹ respectively. Inorganic electrolytes may salt in or salt out aqueous solutions of polyoxyethylenated nonionics depending on the properties of the anion: water structuring anions tend to salt out and water structure breaking anions tend to salt in.^{19,20} For example, halide ions tend to salt out as a result of their water structuring ability. However, in the case of nonionic crown ether surfactants, alkali metal halides increase the cloud point, a salting-in effect. The salting-in effect in these cases is due to the special contribution of alkali metal ion complexing to the hydrophilic head group of the crown ether surfactant. This salting-in effect of complexing is compensated by a concurrent salting-out effect of the anion on the water structure.

As a cationic surfactant, $C_{10}O18CM^+$ is unusual since it possesses a positive charge that is dispersed over the oxygen atoms of the crown ring and thus possesses a hydrophilic moiety that is much larger than that of a typical cationic surfactant. In certain respects this factor modifies the behavior of micelles containing $C_{10}O18CM^+$ so that the properties of these micelles are intermediate between those of typical cationic micelles and nonionic micelles, i.e., $C_{10}O18CM^+$ is a "pseudocationic" surfactant. As a result, suitable relations between cmc values and aggregation numbers and experimental observables must be devised for $C_{10}O18CM^+$.

If we assume that comicelles of $C_{10}O18C$ and $C_{10}O18CM^+$ are formed when an alkali metal, M^+ , is added to an aqueous solution of $C_{10}O18C$ above its cmc, quantitative relations among the cmc of the mixed surfactant system (C^*), the mole fraction of surfactant 1 ($C_{10}O18C$) in a comicelle (x), and the cmc's of the individual surfactants (C_1 for $C_{10}O18C$ and C_2 for $C_{10}O18CK^+$) can be expressed from a formulation proposed by Rubingh²¹ (eq 4), where α is the mole fraction of surfactant 1 in the total mixed surfactant solution.

$$1 = \frac{x^2 \ln (C^* \alpha / C_1 x)}{(1 - x^2) \ln [C^*(1 - \alpha) / C_2(1 - x)]} \quad (4)$$

The equilibrium constant for $C_{10}O18C$ (eq 5) is not to be



substantially different from that for the parent crown ether (e.g., $\log K = 1.7$ for octyl 18-crown-6⁴ and 2.0 for 18-crown-6¹). Thus, $[C_{10}O18CK^+]$ as well as the ratio of $[C_{10}O18K^+]$ to the total surfactant concentration ($C_t = [C_{10}O18C] + [C_{10}O18CK^+]$) can

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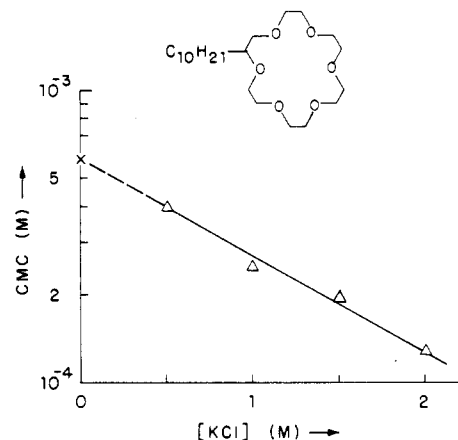


Figure 7. The cmc values of $C_{10}O18CK^+$ in the presence of KCl (0.5, 1, and 2 M).

TABLE II: Parameters Calculated for the $C_{10}O18C$ - $C_{10}O18CK^+$ Comicellar System

| parameters | C_t , M | | |
|------------|----------------------|----------------------|----------------------|
| | 4.3×10^{-4} | 1×10^{-3} | 2×10^{-3} |
| x | 0.27 | 0.27 | 0.27 |
| f_1 | 0.49 | 0.49 | 0.49 |
| f_2 | 0.91 | 0.91 | 0.91 |
| CM_1 , M | 4.3×10^{-5} | 2.4×10^{-5} | 1.9×10^{-5} |
| CM_2 , M | 3.9×10^{-4} | 4.5×10^{-4} | 4.7×10^{-4} |
| β | -1.3 | -1.3 | -1.3 |

^a cmc of $C_{10}O18C$ (C_1) is 3.3×10^{-4} M; cmc of $C_{10}O18CK^+$ (C_2) is 5.8×10^{-4} M; cmc of mixed surfactant systems (C^*) is 4.3×10^{-4} M. The mole fraction of surfactant 1 in total surfactant (α) is 0.09; $[KCl] = 0.1$ M.

be calculated assuming $\log K = 2.0$.

The calculated values of $[C_{10}O18CK^+]/C_t$ at 0.5, 1, and 2 M KCl are 0.98, 0.99, and 0.995, respectively, approaching a value of 1.0; it is reasonable to assume that the mechanism of the salt on the micelle remains constant under these concentrations. In this region, a linear plot can be obtained from $\log \text{cmc}$ vs. $[KCl]$ (Figure 7). Then, the cmc of $C_{10}O18CK^+$ (C_2) can be estimated by extrapolating the line of $\log \text{cmc}$ vs. $[KCl]$ to $[KCl] = 0$, i.e., 6×10^{-4} M.

In the plot of γ vs. $[C_{10}O18C]$ shown in Figure 2 ($[KCl] = 0.1$ M), $[C_{10}O18CK^+]/C_t$ above the cmc is nearly constant (e.g., the calculated value from eq 3 is 0.910 at $C_t = 4 \times 10^{-4}$ M and 0.0908 at $C_t = 2 \times 10^{-3}$ M). Therefore, the cmc value of this plot is assumed to be its C^* so that $\alpha = 0.09$. From the knowledge of C_1 , C_2 , C^* , and α , the x value can be calculated by eq 4. An interaction parameter, β , calculated by eq 6 on the basis of the calculated x value, allows evaluation of the activity coefficients f_1 and f_2 of surfactants 1 and 2 from eq 7 and 8, respectively.

$$\beta = \ln (C^* \alpha / C_1 x) / (1 - x)^2 \quad (6)$$

$$f_1 = \exp[\beta(1 - x)^2] \quad (7)$$

$$f_2 = \exp(\beta x^2) \quad (8)$$

The concentration of monomeric surfactant 1 and surfactant 2 (CM_1 and CM_2 , respectively) at a given C_t can be calculated from eq 9 and 10, respectively.

$$CM_1 = \frac{-(C_t - \Delta) + [(C_t - \Delta)^2 + 4\alpha C_t \Delta]^{1/2}}{2(f_1 C_2 / f_1 C_1) - 1} \quad (9)$$

$$CM_2 = (1 - CM_1 / f_1 C_1) f_2 C_2 \quad (10)$$

where

$$\Delta = f_2 C_2 - f_1 C_1$$

The values of x , f_1 , f_2 , CM_1 , and CM_2 calculated from the above equations are given in Table II for three points above the cmc in Figure 2. The following conclusions are derived from the

calculations: (1) The mole fraction of $C_{10}O18C$ in the mixed micelles remains constant above the cmc. (2) The monomer concentration of $C_{10}O18C$ decreases as the total concentration of surfactant is increased above the cmc. (Since, above the cmc, $[C_{10}O18CK^+]$ is the sum of monomeric $C_{10}O18CK^+$ in the aqueous phase and $C_{10}O18CK^+$ in the micellar phase, $[C_{10}O18CK^+]/C_1$ is approximately constant, but CM_2/C_1 is not a constant.) (3) The interaction parameter remains constant above the cmc. (4) The activity coefficients of $C_{10}O18C$ and $C_{10}O18CK^+$ in the mixed micelle remain constant at 0.49 and 0.91, respectively, above the cmc. We now employ these conclusions to assist in a mechanistic interpretation of the data in Figure 2.

The constant composition of the mixed micelles in the presence of KCl above the cmc (conclusion 1, above) is responsible for the constant value of I_1/I_2 shown in Figure 2. The decrease in the monomer concentration of $C_{10}O18C$ in the presence of KCl above the cmc (conclusion 2, above) is responsible for the increase of γ , since less surfactant monomer is available to operate on the water/air surface.

As $[KCl]$ is increased from 0.1 to 1 M, the x value as calculated by the above method decreases from 0.27 to 0.18, consistent with our interpretations. This result confirms the suitability of the model for analyzing the solution composition for the $C_{10}O18C/C_{10}O18CK^+$ system.

Figures 3 and 4 demonstrate a clear correlation between the parameters ϵ_M , aggregation number, and the binding constant for the various alkali metals, M^+ , to $C_{10}O18C$. The complexing efficiency of M^+ to a crown ether depends on the "fit" of M^+ in the crown; i.e., the binding depends on both the size of the crown ring and the ionic diameter of the cation.²² For $C_{10}O18C$, the ionic diameter of K^+ is optimal for the "best fit". The increase of ϵ_M with increasing K (Figure 3) is attributed to an increase in the micropolarity experienced by solubilized pyrene. As the metal binding efficiency increases, the fraction of cationic surfactants in the mixed micelles increases. Thus, for a given concentration of $C_{10}O18C$ and salt, pyrene, which tends to be located in the inner layer of micelles, experiences a greater number of contacts with cationic surfactants and water as K increases.

The aggregation number of ionic surfactants is typically smaller than that of nonionic surfactants of comparable structure. This difference in behavior is usually attributed to the smaller repulsions between the hydrophilic moieties of nonionic detergents relative to ionic detergents. An alternate accepted description emphasizes the greater water solubility of ionic surfactants relative to comparable nonionics.¹⁴ The decrease in aggregation number (Figure 4) with increasing metal binding is attributed to the same factor which causes an increase in ϵ_M with increasing metal binding, i.e., an increasing content of $C_{10}O18CM^+$ in the comicelles. The latter factor causes the comicelles to become "more ionic" in character than the pure nonionic micelles. Greater head-group repulsions and enhanced water solubility cause the aggregation number to decrease. Thus, the addition of K^+ results in the strongest binding to the crown, the largest concentration of $C_{10}O18CM^+$ in the comicelles, and the smallest aggregation number. Similarly, addition of K^+ increases the cmc (Figure 1) to the greatest extent of any added alkali metal.

These results and their interpretation are consonant with reports that added alkali metal salts selectively increase the cloud point, the cmc, and the foaming properties of surfactant crown ethers.⁵

For example, the cloud point of $C_{10}O18C$ is significantly increased by added KCl. Thus, the same working hypotheses of comicelle formation, the compositional variation of comicelles with added alkali metal, and the variation of binding efficiency of metals to the crown can rationalize the variation of cmc, ϵ_M , cloud point, foaming properties, and aggregation numbers of $C_{10}O18C$ with variation in concentration and structure of added alkali metal salts.

We now consider the influence of variation of salt concentration on the parameters ϵ_M and N (Figure 5). Salt effects or neutral electrolyte effects on the properties of nonionic surfactants are usually small but tend to "salt out" nonionic micelles.¹⁴ In the case of $C_{10}O18CK^+$ a "salting-in" effect occurs in competition with a "salting-out" effect of the neutral $C_{10}O18C$. From Figure 5, we deduce that the "salting-in" effect dominates in the region $[K^+] = 0-1$ M. In this region, ϵ and N increase with increasing $[K^+]$. Above 1 M the "salting-out" effect becomes noticeable and the result is a slower increase in ϵ and decrease in N with increasing $[K^+]$. Above 3 M, changes in both the micellar composition and the water structure upon increasing salt concentration continue to influence micellar properties. The opposing salting-in and salting-out effects tend to compensate one another. As a result, above 3 M further increase in $[KCl]$ does not appreciably change N or ϵ_M . The cloud point of $C_{10}O18C$ increases sharply in the range $[K^+] = 0-1$ M and then experience a slight decrease in the range $[K^+] > 3$ M (Table I).

It is interesting to note (Figure 6) that, with and without salt, ϵ_M continues to decrease with increasing temperature above the cloud point (63 and 20 °C, respectively). Since the pyrene solubility in water (ca. 3×10^{-7} M) is much smaller than that in micelles or in dodecane, probe molecules are assumed to be nearly completely solubilized in the micellar phase above the cloud point. Increasing temperature is known to increase the aggregation number of nonionic micelles.¹⁶ An increase in aggregation number and a concomitant increase in micelle size produce a larger hydrophobic core for the pyrene probe to explore. As a result, the average polarity experienced by the pyrene probe decreases. These results suggest that comicelles continue to exist above the cloud point.

Conclusion

The behavior of the crown ether surfactant $C_{10}O18C$ above the cmc in the presence of alkali metal salts is consistent with the formation of comicelles of a nonionic surfactant $C_{10}O18C$ and a ionic surfactant $C_{10}O18CM^+$. The polarity, ϵ_M , experienced by a pyrene probe, the aggregation number of the comicelles, N , the magnitude of the cmc, and the cloud point are all dependent on the fraction of cationic surfactant in the comicelles. The higher the fraction of $C_{10}O18CM^+$, the more the comicelles behave like ionic micelles. Thus, for a given concentration of added salt the largest effects are found for K^+ since this ion possesses the largest binding constant with $C_{10}O18C$. The increase in ϵ_M with added salt is attributed to an increase in the polarity of comicelles which contain $C_{10}O18CM^+$ components. The increase in cloud point, decrease in N , and the increase in cmc with added salt are attributed to the same factor.

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Registry No. $C_{10}O18C$, 60742-60-1; SDS, 151-21-3; HDTCl, 112-02-7; Brij 35, 9002-92-0; LiCl, 7447-41-8; NaCl, 7647-14-5; KCl, 7447-40-7; RbCl, 7791-11-9; CsCl, 7647-17-8; pyrene, 129-00-0.

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