Pressure Effects on the Fluorescence Decay of Pyrene in Micellar Solutions

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The monomer fluorescence decay of pyrene was measured in sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium chloride (HDTCl) micellar solutions as a function of pressure from 0.1 to 203 MPa at 25 °C by a single-photon-counting technique. The decay curves were analyzed successfully by a conventional fluorescence decay analysis for micellar solution over the pressure ranges examined. From the analysis, it was found that the rate constant (k_E) for intramicellar excimer formation decreased significantly with increasing pressure in both micellar solutions, while the cmc and the aggregation number (N) for SDS and HDTCl micelles were found to be almost independent of pressure. The activation volumes for excimer formation were 19 and 16 cm^3/mol for SDS and HDTCl micellar solutions, respectively. An attempt to obtain an activation volume for a nonionic detergent was unsuccessful because of the failure of the decay profile to fit the theoretical model. However, activation volumes for microviscosity were obtained by studying the pressure dependence of intramolecular excimer formation of a dinaphthylpropane probe. The diffusion processes in micelles and microviscosities are discussed by comparing the activation volume for excimer formation with those for microviscosities determined by the pressure effect on intramolecular excimer formation, and by comparing the results with those reported in the literature for a dipyrenylpropane probe.

Introduction

Surfactant micelles solubilize various types of hydrophobic molecules in aqueous solutions.[1a] Fluorescence probe techniques have provided invaluable information about the microenvironment of micelles (i.e., their viscosity, polarity, aggregation number, etc.), which allow conclusions to be made concerning the structure, location, and dynamics of molecules solubilized in micelles.[2] In particular, the application of time-resolved fluorescence techniques to the excimer systems[3] has led to a direct estimation of kinetic and other characteristic parameters associated with the micellar environment such as the rate constant for intramicellar excimer formation, the micelle aggregation number, and the dynamic behavior of various types of micelles.

The present work focuses on the pressure dependence of the micelle aggregation number and of the rate of intramicellar excimer formation from the analysis of the transient decay kinetics of pyrene. The excimer formation process in micelles is expected to be sensitive to pressure, because microviscosity inside the micelles and possibly the size of micelles might be strongly affected by compression. In fact, previous relevant research has involved the pressure dependence of the ratio of excimer to monomer fluorescence intensities by using pyrene,[4] 1,3-di-α-naphthylpropane (DNP),[4] and 1,3-di-α-pyrenylpropane (DPyP)[5] as probes, and also of the degree of fluorescence depolarization of pyrene.[6] However, these high-pressure studies have focused on microviscosity. Intramicellar excimer formation process is possibly related not only to microviscosity, but also to the micelle size, the location of the probe in the micelle, and any specific interactions of the probe with the head groups or the surfactant hydrophobic core. In this study, we have investigated the diffusion processes in micelles by comparing the pressure dependence of the rate constant for the intramicellar excimer formation with that for the microviscosity measured by intramolecular excimer formation.[5]

Experimental Section

Materials. Pyrene (Aldrich) was chromatographed on silica gel, eluted with hexane, and then recrystallized from ethanol twice. DNP and pyrene-3-carboxaldehyde (PA) were available from previous work and were purified according to the literature.[4,7] Hexadecyltrimethylammonium chloride (HDTCl) and sodium dodecyl sulfate (SDS) were available from previous studies.[8] n-Dodecyl hexaethylene glycol monomer ($C_{12}E_6$) was used as received from Nikko Chemical Co.

Fluorescence Decay Measurements. Surfactant/probe solutions were prepared by evaporating a desired volume of pyrene/acetone stock solution in a given volumetric flask and then filling to volume with a stock solution of surfactant. The solutions were stirred for 1 day with a magnetic stirrer. The solubilized solutions were checked for probe concentration by UV measurements and by measurement of fluorescence spectra and lifetimes at 0.1 MPa.

The high-pressure apparatus and the associated experimental techniques have been described elsewhere.[4] The sample solution was deoxygenated by blowing argon gas saturated with water vapor on the liquid surface while stirring with a magnetic stirrer for 1 h. The concentration change of pyrene with deoxygenation was checked by UV spectroscopy. The deoxygenated solution was charged into the high-pressure cell via a syringe under an argon atmosphere.

Fluorescence decay curves were measured by a time-correlated single-photon-counting technique described previously.[9] A flash lamp was operated at a high voltage of 5 kV and a repetition rate of 20 kHz. Nitrogen gas was used as the discharge gas. An interference filter (337 nm) was used to isolate the exciting light. The pyrene monomer fluorescence at 385 nm was observed through a monochromator and a filter. The decay data were analyzed with a Hewlett-Packard 87 XM microcomputer.

Fluorescence Spectra Measurements. All fluorescence spectra were taken with SPEX FLUOROLOG at 25 °C. The microviscosity of $C_{12}E_6$ micelles (22 mM) at 0.1 MPa and at high pressures was estimated from the ratio of monomer to excimer fluorescence intensities of DNP as described before.[4] The cmc of HDTCl at 0.1 MPa and at high pressures was determined from the plots of the maximum wavelength of PA (443–476 nm) against HDTCl concentrations as described previously.[7]

Results

In the present work, monomer fluorescence was used to determine the individual parameters associated with the fluorescence decay of pyrene in micellar solutions. Figure 1 shows the fluorescence decay in SDS micellar solution at 0.1 and at 203 MPa at 25 °C. Similar decay curves were observed in HDTCl micellar

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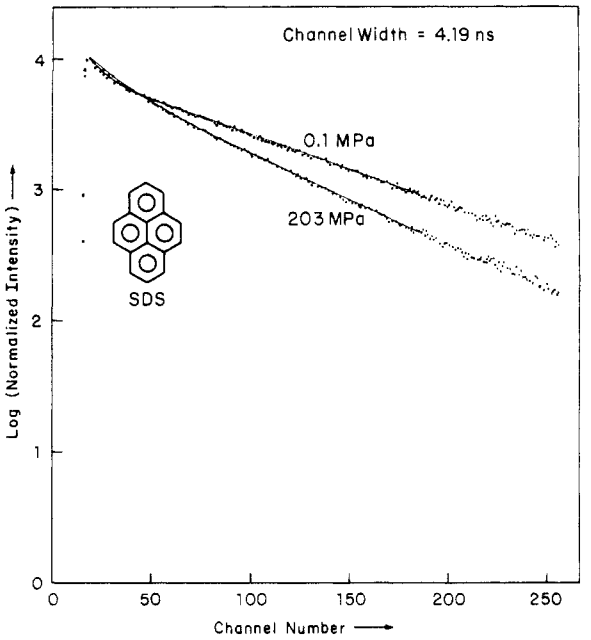

Figure 1. A typical example of the decay curves for SDS micelles at two pressures. The solid lines show the curve fitting to eq 1. [SDS] = 50.3 mM and [pyrene] = 0.267 mM at 0.1 MPa.

TABLE I: Values of k_1, k_E, and n in SDS Micellar Solutions at Various Pressures and 25 °C[a] ([SDS] = 50.3 mM)

press./MPa	$k_1/10^6$ s^{-1}	$k_E/10^7$ s^{-1}	n
	[Pyrene] = 0.102 mM		
0.1	2.72	2.66	0.147
44	2.78	1.66	0.146
97	2.85	1.27	0.141
151	2.88	0.84	0.154
203	2.94	0.67	0.170
	[Pyrene] = 0.179 mM		
0.1	2.78	2.54	0.292
44	2.94	1.63	0.303
97	2.97	1.33	0.280
151	3.01	1.03	0.298
203	3.04	0.77	0.299
	[Pyrene] = 0.267 mM		
0.1	2.87	2.60	0.383
44	3.26	2.04	0.369
97	3.59	1.45	0.382
151	3.64	1.17	0.385
203	3.62	0.86	0.410

[a] Uncertainty of the parameters was within 10%.

solutions as a function of pressure. As seen in Figure 1, the decay curves are nonexponential and are characterized by a transient fast decay in earlier time regions at 0.1 MPa, while a longer decay is observed at 203 MPa. However, at both pressures a single exponential decay is observed for longer times. For micellar solutions with excimer forming probes, it has been demonstrated that the decay curve is expressed for δ-pulse excitation by[3]

$$I(t) = I(0) \exp[-k_1 t - n\{1 - \exp(-k_E t)\}] \quad (1)$$

$$n = [\text{pyrene}]/[\text{micelle}] \quad (2)$$

In eq 1, k_1 and k_E represent the rate constants for the fluorescence decay and excimer formation processes of pyrene in micellar solutions, respectively.

The data obtained from the decay measurements were analyzed by curve fitting to eq 1 by a nonlinear least-squares method.[10] In the analysis, it is necessary to have a zero-time channel: The channel corresponding to one-half of maximum intensity during the rise in the decay curve was selected (Figure 1). The shift of zero-time channel to the channel in maximum intensity led to a difference in the parameters of only a few percent, which is expected because of the short excitation light pulse duration (ca. 4 ns) in comparison to the long fluorescence lifetimes. The short pulse duration also required no deconvolution with the apparatus function. A typical example of the curve fitting is shown with the solid line in Figure 1. The parameters in eq 1 obtained are listed in Tables I and II for SDS and HDTCl micellar solutions, respectively.

As indicated in Tables I and II, k_E decreases significantly with increasing pressure and is almost independent of pyrene concentration at each pressure as predicted in eq 1. Hence, the values of k_E were averaged and are listed in Tables III and IV. The

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TABLE II: Values of k_1, k_E, and n in HDTCl Micellar Solution at Various Pressures and 25 °C[a] ([HDTCl] = 18.9 mM)

press./MPa	$k_1/10^6$ s^{-1}	$k_E/10^6$ s^{-1}	n
	[Pyrene] = 0.0511 mM		
0.1	2.70	6.32	0.341
44	2.71	4.33	0.369
97	2.75	3.34	0.397
151	2.85	2.83	0.357
203	2.85	2.20	0.391
	[Pyrene] = 0.0764 mM		
0.1	2.76	7.05	0.434
44	2.77	4.94	0.478
97	2.91	3.95	0.429
151	2.96	2.77	0.431
203	2.96	2.26	0.458
	[Pyrene] = 0.130 mM		
0.1	2.82	7.48	0.822
44	3.50	5.24	0.838
97	3.37	3.92	0.752
151	3.36	3.09	0.693
203	3.27	2.16	0.740
	[Pyrene] = 0.216 mM		
0.1	2.73	7.02	1.22
44	2.99	4.91	1.26
97	2.92	4.11	1.18
151	3.11	3.20	1.09
203			

[a] Uncertainty of the parameters was within 10%.

TABLE III: Values of k_E, [micelle], and Aggregation Number N for SDS Micellar Solution ([SDS] = 50.3 mM)

press./MPa	$k_E/10^7$ s^{-1}	[micelle]/mM	N[a]
0.1	2.60 ± 0.03	0.67 ± 0.05	63 ± 4
			60[b]
44	1.80 ± 0.13	0.68 ± 0.06	63 ± 5
97	1.35 ± 0.05	0.71 ± 0.03	61 ± 2
151	1.01 ± 0.10	0.70 ± 0.05	63 ± 4
203	0.77 ± 0.06	0.68 ± 0.03	67 ± 3

[a] N was determined by eq 3. In eq 3, [SDS] was corrected with the compressibility of water,[14] and the cmc at high pressures was taken from ref 15. [b] Turro, N. J.; Yekta, A. *J. Am. Chem. Soc.* **1978**, *100*, 5951.

TABLE IV: Values of k_E, [micelle], and Aggregation Number N for HDTCl Micellar Solution ([HDTCl] = 18.9 mM)

press./MPa	$k_E/10^6$ s^{-1}	[micelle]/mM	N[a]
0.1	7.0 ± 0.2	0.17 ± 0.01	104 ± 6
			113,[b] 112[c]
44	4.9 ± 0.2	0.17 ± 0.01	106 ± 5
97	3.8 ± 0.2	0.18 ± 0.01	102 ± 5
151	3.0 ± 0.1	0.20 ± 0.01	94 ± 9
203	2.2 ± 0.03	0.18 ± 0.02	106 ± 10

[a] N was determined by eq 3. In eq 3, [HDTCl] was corrected with the compressibility of water,[14] and the cmc at high pressures was measured in this work (1.2 mM). [b] Reference 13. [c] Roelants, E.; Gelade, E.; Smid, J.; Schryver, F. C. *J. Colloid Interface Sci.* **1985**, *107*, 337.

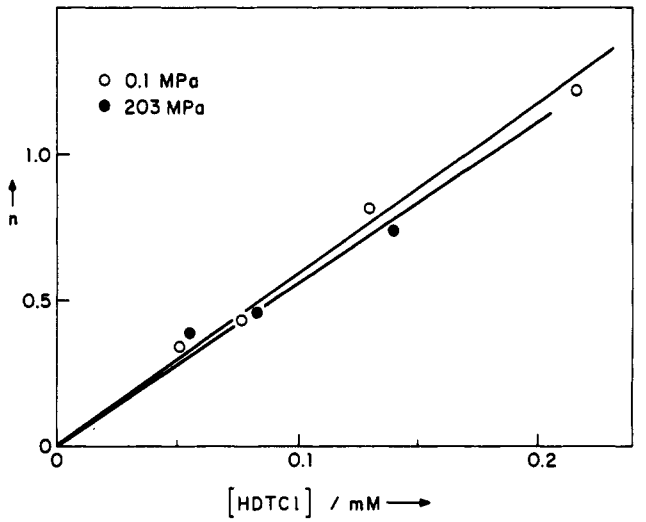

Figure 2. Typical plots of n against the concentration of HDTCl at two pressures.

pressure effect on k_1 is slightly different at various pyrene concentrations, but the pressure dependence is small. Turley and Offen[11] have measured the fluorescence lifetime of pyrene (0.01 mM) in HDTCl micellar solution at high pressures and obtained a pressure coefficient (k_1) of −11 ns/100 MPa. The present results at lower pyrene concentration (for 0.0511 and 0.0764 mM) in Table II are consistent with their value. For both the micellar solutions, the values of k_1 and k_E at 0.1 MPa are in good agreement with those of other workers.[12,13]

The average number of pyrene molecules per micelle n defined by eq 2 shows a distinct pyrene concentration dependence at 0.1 MPa and at high pressures (Tables I and III). The plots (Figure 2) of n against [pyrene] were linear through the origin. The slopes correspond to [micelle]$^{-1}$. In the plots, the pyrene concentration at high pressures was corrected for the compressibility of water.[14] The numerical values of [micelle] obtained thus are listed in Tables III and IV for SDS and HDTCl micelles, respectively.

The micelle aggregation number N is given by

$$N = ([\text{sur}] - \text{cmc})/[\text{micelle}] \quad (3)$$

where [sur] and the cmc are the surfactant and the critical micelle concentrations, respectively. The values of N for SDS calculated by eq 3 from the known cmc[15] are listed in Table III. The cmc for HDTCl micelles measured in this study was independent of pressure (Figure 3). The value of the cmc at 0.1 MPa (1.2 mM) is in good agreement with that reported by other workers (1.4 mM).[12a] The values of N for HDTCl micelles are listed in Table IV. A minimum N value around 97 MPa for SDS and 151 MPa for HDTCl can be observed. But the size of the minima is small compared to that obtained by the light scattering method.[16]

The following points from our results are worthy of note: (1) the agreement between the experimental data and the theoretical curves predicted from eq 1 is very good, (2) the values of k_1 and k_E are almost independent (within 10%) of the pyrene concentration at each pressure, and (3) n is linearly related to [pyrene] over the pressure and concentration ranges examined. The evidence suggests that the excimer fluorescence decay kinetics which have been established at 0.1 MPa are still maintained at high pressures. The pressure dependence on N and k_E in micelles will be discussed below.

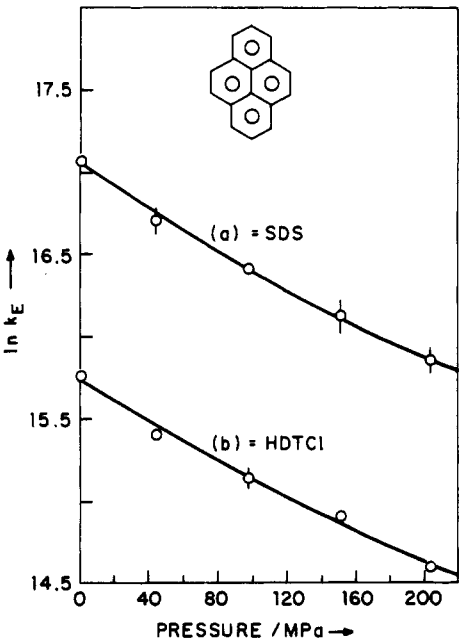

Figure 3. Pressure dependence on k_E for the pyrene–SDS (a) and pyrene–HDTCl (b) systems at 25 °C. The solid lines show the quadratic analysis.

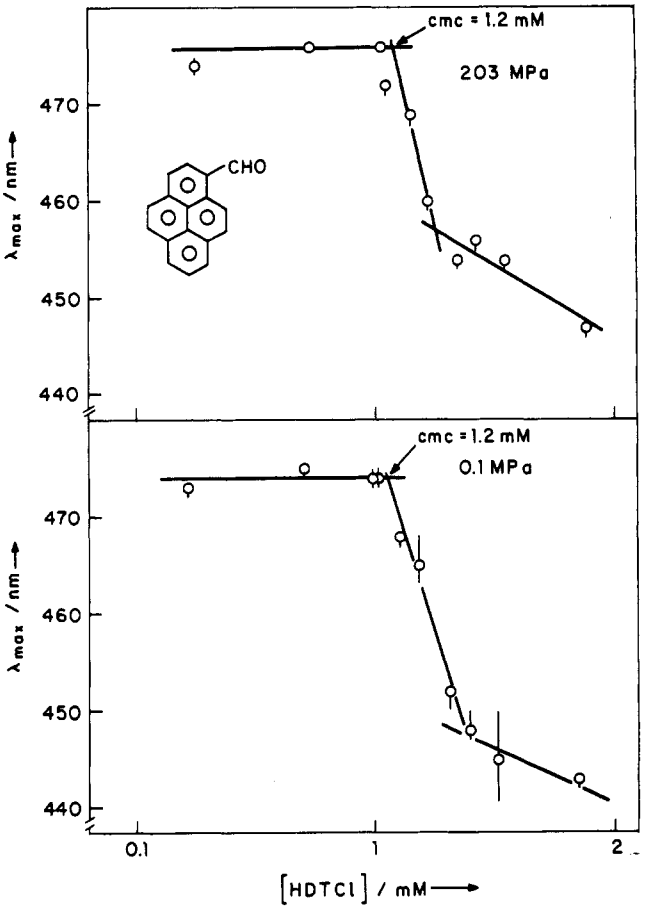

Figure 4. Typical plots of the peak wavelength of PA, λ_{max}, against the concentration of HDTCl at two pressures.

Discussion

The volume of activation ΔV_E^* for excimer formation in micellar solutions was determined from

$$(\partial \ln k_E/\partial P)_T = -\Delta V_E^*/RT \quad (4)$$

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TABLE V: Activation Volumes for the Probe–Micelle Systems at 25 °C and 0.1 MPa

surfactant	ΔV_E^*/cm^3 mol^{-1} pyrene	ΔV_η^*/cm^3 mol^{-1} DNP	ΔV_η^*/cm^3 mol^{-1} DPyP[c]
SDS	19 ± 2	22 ± 3[b]	13
HDTCl	16 ± 3	19 ± 2[b]	24
$C_{12}E_6$		28 ± 2[d]	25

[a] The plots of ln η and ln k_E against pressure were assumed to be quadratic. [b] Reference 4. [c] Reference 5. [d] The microviscosity at high pressures was measured in this work.

TABLE VI: Microviscosity (η) of $C_{12}E_6$ Estimated by the DNP Probe at Various Pressures

press./MPa	η/cP
0.1	57 ± 7
44	90 ± 6
97	147 ± 15
151	198 ± 20
203	252 ± 10

Figure 3 shows the plot of ln k_E against pressure for SDS and HDTCl micellar solutions. Values of ΔV_E^* were determined by a quadratic analysis[1b] of the data in Tables III and IV and are listed in Table V. The volume of activation for microviscosity η (i.e., ΔV_η^*) was determined from

$$(\partial \ln \eta/\partial P)_T = \Delta V_\eta^*/RT \quad (5)$$

where η was taken from the literature values[4] for SDS and HDTCl and was measured and calibrated in a corresponding fashion for the nonionic surfactant $C_{12}E_6$. ΔV_η^* was determined by a quadratic analysis and is also listed in Table V together with the literature results for the dipyrenylpropane (DPyP) probe.[5] The magnitude for diffusion-controlled intermolecular excimer formation of pyrene in toluene is 11 cm^3/mol[17] and that for exciplex formation of the pyrene-acceptor systems in organic solvents is 6–9 cm^3/mol.[18] The activation volumes for viscosity of organic solvents, however, tend to be larger than activation volumes for diffusion; e.g., ΔV_η^* = 21 cm^3/mol for isobutyl alcohol.[5] The major contributions to the activation volumes for excimer and exciplex formations have been attributed to those for solvent viscosities.[17,18]

For SDS micelles, ΔV_E^* is close to the activation volume for the viscosity of dodecane (22 cm^3/mol)[19] and also to that for the microviscosity estimated from the intramolecular excimer formation of DNP, which suggests that the intramicellar excimer formation of pyrene is diffusion controlled. However, there is a large difference in the activation volume (13 cm^3/mol) for viscosity derived from the DPyP probe by comparison.[5] This difference may be due to a number of causes such as the large geometrical size of DPyP compared to the pyrene and DNP probes since the microviscosity estimated by intramolecular excimer type probes shows the probe size dependence.[20] In fact, for $C_{12}E_6$ nonionic micelles with large micelle size (N = 318,[21] 330[16]) the microviscosity for DNP probe at 0.1 MPa (57 ± 7 cP) is in good agreement with that for DPyP probe (57 cP),[5] and the activation volumes for microviscosity estimated by the DNP and DPyP probes are nearly equal (Tables V and VI). Other reasons for the discrepancy may reside in the method of deriving the activation volumes, since for the DPyP probe the excimer lifetime, and not just intensities, is included in the analysis. In addition, a different solvent system for calibration was employed for DNP and DPyP. A more intriguing, but speculative, cause of the differences might be ascribed to a distinction between the microdiffusion and microviscosity concepts.

The intermolecular excimer formation within a micelle is affected not only by the diffusion-controlled rate constant k_{diff} (= $8RT/3000\eta$ M^{-1} s^{-1}), but also by the micelle volume v because the concentration of pyrene in micelles depends on v. We can express the pseudo-first-order rate constant k_E in eq 1 by

$$k_E = 10^3 k_{diff}/(vN_A)\ \text{s}^{-1} \quad (6)$$

where N_A is Avogadro's number. Since v is expected to be proportional to the aggregation number of the micelle N, the slope of the plot of ln (Nk_E) against pressure should give ΔV_{diff}^*. As listed in Table III, N is almost independent of pressure, so that ΔV_E^* is equal to ΔV_{diff}^*. Further, k_E at 0.1 MPa can be estimated to be 2.9 × 10^7 s^{-1} from eq 6 by using the microviscosity (11.5 cP)[4] and the micelle radius (20 Å)[22] for SDS. The estimated value is in good agreement with our results (Table III). Therefore, we conclude that the intramicellar excimer formation of pyrene in SDS is diffusion controlled. This conclusion is consistent with those for the temperature dependence of pyrene excimer formation in micelles.[13]

For the HDTCl–probe system, N is almost independent of pressure, which means that ΔV_E^* for HDTCl (Table V) contains no significant contribution from the micelle size, but the activation volumes do depend on the nature of the probes.

Malliaris, Zana et al.[13] have studied the temperature dependence of micelle aggregation numbers and rate constants of intramicellar excimer formation for various micelles using pyrene as a probe at 0.1 MPa. They concluded that the large differences in k_E between SDS and HDTCl micelles is attributable not only to their different microviscosities, but also to interactions between pyrene and head groups of HDTCl. On the other hand, the large difference in ΔV_η^* for DPyP between SDS and HDTCl micelles has been explained[5] as being due to stronger hydration of SDS head groups compared to the HDTCl ones, which leads to a smaller ΔV_η^* for SDS, although the interaction of the pyrene moieties with the cationic surfactant head groups was also considered as an explanation.

The rate of diffusional encounter between probes is expected to depend on the location of the probes in the micelles.[23] For the HDTCl–pyrene and for other similar probe systems, probe molecules reside near the surface of the micelles.[12a] Further, I_1/I_3 for the pyrene–micelles system (the fluorescence intensity ratio of the 0–0 band to the third peak of pyrene, a measure of the micropolarity experienced by the pyrene probe) is almost independent of pressure, which means that the location of pyrene in micelles is essentially unaltered by compression.[12b] The hydration hypothesis could lead to large differences in the activation volumes for SDS and HDTCl micelles for pyrene and DNP probes. As seen in Table V, however, the activation volumes for the SDS–pyrene and SDS–DNP systems are comparable to those of the corresponding HDTCl systems, which suggest that an explanation by the hydration hypothesis alone is not sufficient.

On the other hand, the probe dependence on the activation volume could be reasonably explained as the differences in the interactions between the probes and the head groups of HDTCl, since the association constants of arene probes with hexadecyltrimethylammonium bromide have been shown to increase with increasing hydrophobicity (size of arene).[24] In addition, ΔV_η^* for HDTCl micelles may involve the reduced geometrical size effect of the probes compared to SDS micelles since N for HDTCl is larger than that for SDS. Consequently, the probe dependence on the activation volumes for HDTCl micelles may be mainly attributed to the pressure effects on the interactions between the head groups of HDTCl and the probes.

Conclusion

The activation volumes for pyrene excimer formation have been determined for SDS and HDTCl micelles and compared to the

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activation volumes determined for intramolecular excimer formation via the concept of microviscosity. The activation volumes appear to depend somewhat on the probe. The aggregation numbers for SDS and HDTCl micelles were found to be independent of pressure; thus the size of the micelle is not an important factor in analyzing activation volume data. However, in addition to microviscosity considerations, specific interactions between the probe and the micellar head groups must be considered in analyzing activation volume data.

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Registry No. SDS, 151-21-3; HDTCl, 112-02-7; DNP, 14564-86-4; PA, 3029-19-4; $C_{12}E_6$, 3055-96-7; pyrene, 129-00-0.

Counterion and Co-Ion Specificity in Ionic Microemulsions

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Partial phase diagrams and conductances are reported for three-component microemulsions employing didodecyldimethylammonium chloride, bromide, iodide, or halide mixtures as the surfactant. The physical properties and structures of these inverted microemulsions exhibit a very large dependence upon counterion and added salt. These effects illustrate how microemulsion structure can be controlled from the aqueous side of the oil–water interface.

Introduction

The role of counterion specificity in determining the properties of surfactant aggregates remains a central problem. In the past decade there has been significant progress in quantifying counterion effects for micelles, vesicles, and bilayer systems. These include the role of hydration forces,[1,2] the effects of ion–ion correlations upon double-layer forces,[3] the nature of counterion binding in micelle, vesicles, and bilayers,[4] and the transformation of bilayers to spontaneous vesicles and anomalous micelles.[5] Some old questions have been answered and numerous other raised.[6] For example, the competition and interplay between specific counterion effects, hydration forces and new bilayer fluctuation[7] forces is completely open. No completely general theory yet exists. Nevertheless, real progress has been made in understanding specific ion effects for surfactant aggregates like micelles and vesicles which possess positive curvature.

Considerably less attention has been given to specific ion effects in inverted surfactant structures. Theory is more difficult and suitable experimental systems are less readily accessible. Inverted structures are important in microemulsions and porous media and may be useful models for capillary blood flow and transport through membrane channels. In this paper we describe the effect of counterions on the properties of a microemulsion containing both bicontinuous and inverted micellar structures.

Before proceeding we briefly summarize relevant features of a reference three-component microemulsion. This employs didodecyldimethylammonium bromide (DDAB) as the surfactant. The key observations[8–11] are as follows:

1. DDAB is only sparingly soluble in water and oil and therefore the oil–water interfacial area is directly related to the surfactant concentration.

2. Both the minimum water line for formation of a microemulsion (for example, the A–B line in Figure 1 for decane) and the extent of the microemulsion region depend upon the chain length of the oil. The role of oil penetration in the surfactant chains which sets interfacial curvature can be readily determined.

3. Along the minimum water lines (A–B, Figure 1) the system is bicontinuous as evidenced by conductance and NMR diffusion measurements, but upon addition of water the microemulsions (except for tetradecane as oil) becomes discontinuous in water as indicated by the dotted line B–D.

These observations are consistent with a bicontinuous structure comprised of water-filled interconnected conduits whose curvature is set up by a balance between head group repulsion which favors

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