Effects of Various Hydrocarbons on Micellar Growth

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ABSTRACT: The effect of aliphatic and aromatic hydrocarbons on surfactant micellar growth has been investigated by viscosity measurements at 40°C. Aqueous and aqueous KBr (0.1 M) solutions of 0.1 M cetylpyridinium bromide (CPB) showed that the viscosity behavior changed substantially in the presence of KBr. This is attributed to favorable conditions produced by KBr that assist micellar growth by addition of hydrocarbons. Reasons for the effectiveness of the solubilized hydrocarbons are suggested and supported by theoretical arguments. The causes of viscosity decrease at higher aromatic hydrocarbon concentrations are also explained. Micellar growth with soluble aromatic/aliphatic hydrocarbons could also be initiated if a moderate salt concentration is present in CPB micellar solutions. The chainlength, solubilization site, and molar volume of the soluble hydrocarbons all affect the bulk viscosity of the solution. Such surfactant and hydrocarbon combinations may find use in micellar-enhanced ultrafiltration of benzene and its derivatives, but it should be kept in mind that micellar shape may change and be more curved at higher benzene derivative concentrations.
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KEY WORDS: Cetylpyridinium bromide, hydrocarbons, micelle, molar volume, palisade layer, solubilization, surfactant, ultrafiltration, viscosity.

Considerable progress has been made during the last fifteen years regarding our knowledge of the properties and behavior of surfactant solutions. Many studies have been devoted to the elucidation of micellar structure under different conditions. Cooperative self-association of surfactant molecules into spherical micelles is the result of a delicate balance of competing forces of hydrophobic interaction, repulsive interaction of head groups, hydration, and the energy spent in the deformation of hydrocarbon chains (1). Initially, hydrophobic interaction was thought to be the driving force for micellization (2); later, considerable importance was given to London-dispersion interactions (3).

In several surfactant systems in which solutions possess viscoelasticity, there is a transformation of spherical micelles to globular and rod-shaped micelles at higher surfactant concentrations (4). Both phenomena are governed by several factors, such as electric affinity and size of the counter-ion, size of the headgroup, and length of the hydrocarbon chain.

Since Stigter (5) reported the phenomenon of micellar shape transition, the possibilities of changes of shape or size have continually been proposed experimentally (6,7), mathematically (8), and theoretically (9). Examination of packing conditions of the micelles shows that the critical conditions for formation of different micellar structures are the following (8,10): (i) spherical micelles, $v/al \leq 1/3$; (ii) globular or cylindrical micelles, $1/3 \leq v/al \leq 1/2$; (iii) vesicles or bilayers, $1/2 \leq v/al \leq 1$; and (iv) inverted structures, $v/al \geq 1$, where v is the volume of the surfactant's hydrocarbon tail, a is the cross-sectional area per head group, and l is the length of the fully extended hydrocarbon tail, obtainable from Tanford's formula (11).

Fang (12) used the packing ratio to explain a series of phase transitions in three- and four-component systems. For surfactants to form spherical shapes, a should be large. Surfactants with smaller a tend to form larger, less curved, or even inverted aggregates. For ionic surfactants, the area shrinking effect may be obtained by salt (with common counter-ion) addition (13,14) or organic compound solubilization (6,7,15–17).

Apart from a few reports (18–21) on viscosity enhancement in the presence of hydrocarbons, no attempt has been made to study the role of aromatic and aliphatic hydrocarbons in micellar growth processes. Only recently (6) has study of this class of compounds attracted attention because they are important constituents of microemulsions (21). They are unique due to the large size of micelles, allowing the possibility of filtration with an ultrafiltration membrane having pores large enough to reject aggregates that contain organic pollutants. The performance of a filtration method is directly related to the micellar size. A few surfactant and hydrocarbon studies are available but not in the context of micellar growth (22).

More studies are needed to increase understanding of the effect of hydrocarbons on the properties of micellar systems and micellar growth. In the last few years, the authors have reported micellar growth processes in the presence of various alcohols and amines (7,15–17). These reports have shown how these compounds can be used to vary the area per ionic group (a), a parameter of overriding importance for such growth processes.

During these studies, a few systems have been found that showed peaked behavior in viscosity curves plotted against additive concentrations when a salt and organic compound

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(e.g., alcohol or amine) were both present in the system. The viscosity decrease was explained in light of micellar core solubilization of organic compounds in the presence of salt. The authors have measured the viscosities of micellar solutions of CPB in the presence of different hydrocarbons with and without added 0.1 M KBr to improve understanding of the effect of soluble hydrocarbons, singly or concurrently with a salt, on the growth process. The effect of alkyl chainlength and aromaticity have also been investigated, and the authors show how such combinations affect the variation of a in a mixed surfactant system in which the mixed surfactant is a combination of surfactant (7), and soluble hydrocarbon.

EXPERIMENTAL PROCEDURES

n-Cetylpyridinium bromide (CPB, Merck-Schuchardt, Munchen, Germany; purity >99%) was used as received. All aromatic hydrocarbons (>99%) were from E. Merck (Bombay, India) except that toluene was a Glaxo (Bombay, India) Ltd. product. The aliphatic hydrocarbons (>99%), *n*-octane and *n*-decane, were from Merck-Schuchardt, and from BDH (Poole, England), respectively. Cyclohexane was from Glaxo (India) Ltd. KBr (purity > 99%) was an E. Merck product. All chemicals were used as supplied. The water used to prepare the solutions was demineralized and double-distilled in an all-glass distillation apparatus. The specific conductivity of this water was in the range of $1–2 \times 10^{-6}$ ohm^{-1} cm^{-1}.

Stock solutions of CPB (in water or in 0.1 M KBr) were prepared volumetrically. Sample solutions were made by measuring the required volumes of the hydrocarbons with micropipettes into volumetric flasks and making up the volumes with the CPB stock solution. After proper mixing, the sample solutions were kept overnight for equilibration. Prior to the measurements, these solutions were kept at 40°C for at least 1 h to attain thermal equilibrium.

Viscosities of the solutions were measured by an Ubbelohde viscometer, thermostated at 40 ± 0.1°C. The flow time for solvent water was 103 s. At least four flow-time measurements were made for each sample, and mean deviations from the mean of all measurements were required not to exceed 0.1 s. Density corrections were not required because they were negligible (23). The method of viscosity measurement under Newtonian flow conditions was followed as described elsewhere (17). The effective specific volume, V, of CPB micelles that contained varying amounts of hydrocarbons were computed from:

$$V = \frac{\phi}{C} \qquad [1]$$

where C is the concentration of the solution in g/cm^3.

Einstein's equation, modified for higher concentration ranges of micelles in aqueous solutions (24), was used to obtain the volume fraction, ϕ:

$$\eta_r = 1 + 2.5\,\phi + 14.1\,\phi^2 \qquad [2]$$

RESULTS AND DISCUSSION

Table 1 records the viscosity data of 0.1 M CPB solutions with added aliphatic/aromatic hydrocarbons in the absence (S_a) and presence (S_p) of 0.1 M KBr. The aliphatic hydrocarbons have almost no effect (except cyclohexane in the presence of 0.1 M KBr). Furthermore, solubilities of *n*-octane and *n*-decane in 0.1 M CPB micellar solutions are small; this precludes studies of these hydrocarbons at higher concentrations. It has been suggested that the size of the hydrocarbon molecule (i.e., its molar volume), its polarity, its location in the aggregates, and its concentration influence the solubilization capacity of micelles (25); thus, all previously mentioned factors, in turn, would determine the additive's capacity to change the micellar shape and/or size. The slight increase of viscosity with cyclohexane, a solute of low molar volume, can be attributed to swelling of the micelle because cyclohexane solubilization in the interior of the micelle is preceded by palisade layer solubilization (26).

Except for a slight increase in viscosity of 0.1 M CPB micellar solution (without KBr) with aromatic oils, no marked change is observed relative to aliphatic hydrocarbon additions. However, the aromatic hydrocarbons behave differently when added to 0.1 M CPB solutions that contain 0.1 M KBr (Table 1).

The ability of benzene ring compounds to enhance micellar growth may stem from interaction of the π-electron cloud with the head group of the CPB, a behavior similar to that of the surface area shrinking effect by addition of a salt or cosurfactant. The resulting reduction of the head group charge (and also a) favors micellar growth and allows the viscosity value to increase (only in the presence of salt). In the absence of salt (S_a), these additives behave much like the aliphatic hydrocarbons (Table 1, Fig. 1).

A change in the viscosity behavior of the micellar solution in the presence of KBr is possible due to increased counterion association and dehydration of the micellar palisade layer. It has been argued that the curvature of the micellar shape is strongly influenced by the ratio a/a_c, where a_c is the effective cross-sectional area of the hydrocarbon chain (27). In this context, the addition of 0.1 M KBr would reduce a of the surfactant head group. The counter-ion association and subsequent reduction in a weakens the electrostatic interactions with aromatic hydrocarbons. The dehydration effect will predominantly increase the micellar solubilization in the palisade layer, which will cause an increase in the mutual interaction. For lower hydrocarbon/amphiphile ratios, aromatic compounds will become solubilized close to the polar surface of the micelle, while at higher ratios solubilization also occurs inside the micelle (28). Thus, micellar growth as well as an increase in interparticle interactions occurs and causes a substantial viscosity change in the initial concentration range (before maximum) of the additive. Because turbidity appears at higher concentration, further addition of aromatic hydrocarbons, whenever possible, may change the structure from grown to swollen micelle due to an increased size of the hy-

TABLE 1

Relative Viscosities ($\eta_r = \eta/\eta_o$) and Effective Specific Volumes (*V*) of 0.1 M CPB Micellar Solutions in Absence (S_a) and Presence (S_p) of 0.1 M KBr with Added Aliphatic and Aromatic Hydrocarbons at 40°C[a]

Concentration of hydrocarbon (mM)	S_a		S_p	
	η_r	V^b	η_r	V
0	1.37	2.39	1.58	3.30
Cyclohexane				
14	1.38	2.43	3.00	7.41
27	1.39	2.47	3.50	8.49
40	1.42	2.62	4.74	10.78
54	1.42	2.62	4.53	10.42
65	1.48	2.88	3.85	9.18
81	1.48	2.88	3.70	8.89
94	Turbid		1.60	3.38
100				
n-Octane				
5	—	—	1.77	4.00
8	—	—	1.82	4.18
10	—	—	Turbid	
14	1.42	2.62		
23	1.44	2.71		
25	Turbid			
n-Decane				
4	1.38	2.43	1.51	3.01
7	1.22	1.60	—	
8			1.34	2.24
9			Turbid	
Benzene				
15	—	—	3.22	7.90
32	—	—	4.54	10.44
43	1.30	2.04	—	—
48	—	—	16.69	24.10
64	—	—	28.91	32.82
79	—	—	51.74	44.98
86	1.46	2.80	—	—
96	—	—	98.23	63.08
112	—	—	92.48	61.12
120	—	—	Turbid	
129	1.53	3.09		
172	1.56	3.22		
215	1.63	3.49		
239	1.63	3.49		
250	Turbid			

Concentration of hydrocarbon (mM)	S_a		S_p	
	η_r	V	η_r	V
Toluene				
7	—	—	5.03	11.26
14	—	—	44.13	41.31
41	—	—	52.36	45.27
55	—	—	133.09	73.88
68	1.49	2.93	220.44	95.85
83	—	—	291.08	110.52
96	—	—	265.57	105.46
116	—	—	209.88	93.46
126	—	—	Turbid	
136	1.79	4.08		
205	1.79	4.08		
273	1.97	4.68		
296	2.04	4.89		
300	Turbid			
o-Xylene				
12	1.40	2.53	1.75	3.94
25	1.43	2.66	6.47	13.43
35	1.46	2.80	34.14	35.95
46	1.49	2.93	80.07	56.68
57	1.50	2.97	198.77	90.88
65	1.54	3.14	143.40	76.79
70	Turbid		—	—
81			142.18	76.45
93			137.00	75.00
100			Turbid	

Concentration of hydrocarbon (mM)	S_a		S_p	
	η_r	V	η_r	V
Ethylbenzene				
6	—	—	2.63	6.53
12	—	—	4.65	10.62
25	—	—	14.85	22.52
31	1.44	2.71	—	—
37	—	—	42.27	40.36
49	—	—	114.25	68.25
62	1.56	3.22	156.60	80.37
70	—	—	151.57	79.02
80	—	—	Turbid	
93	1.62	3.45		
124	1.65	3.57		
155	1.77	4.00		
160	Turbid			
Nitrobenzene				
15	—	—	3.93	9.34
30	—	—	11.74	19.59
37	1.39	2.48	—	—
45	—	—	30.98	34.10
60			48.86	43.63
74	1.43	2.66	57.70	47.67
89	—	—	39.02	38.66
95	—	—	Turbid	
112	1.51	3.01		
149	1.52	3.05		
186	1.68	3.68		
223	1.78	4.04		
	2.30	Turbid		

[a] CPB, cetylpyridinium bromide; KBr, potassium bromide.

[b] In cm^3/g.

drophobic center (6). The latter effect is observed due to the fact that the association structure can maintain spherical shape because there is no conformational stress on the surfactant tail to reach the center of the micelle.

If solubilization will only change the radius of the particle present at the viscosity maximum, the ratio of length/radius will decrease, even if the length of the micelle remains constant. In such a situation, the particle structure tends slightly towards the ellipsoidal side with a more curved surface than the structure present at the viscosity maximum. This increased sphericity of the particles will promote easier flow of such solutions. This explains the slight decrease in the viscosities of micellar solutions at higher aromatic hydrocarbon concentrations (Fig. 2).

The data on effective specific volume, *V*, also confirm these explanations regarding micellar shape and size (Table 1). Table 1 also shows that the magnitude of viscosity at the maximum (η_r^{max}) is different for different aromatic hydrocarbons. From the preceding discussion, it is clear that, for micellar growth, the compound should be solubilized in the palisade layer. There are two factors responsible for solubilization of aromatic hydrocarbons in the palisade layer. The first is the electrostatic interaction between the π-electron cloud and the head groups of the micelle. The second is the molar volume of the additive, which restricts the solubilization of the additive as a whole and in the palisade layer in particular (29).

If equal micellar palisade layer volume is available for solubilization of aromatic hydrocarbons, then large numbers of

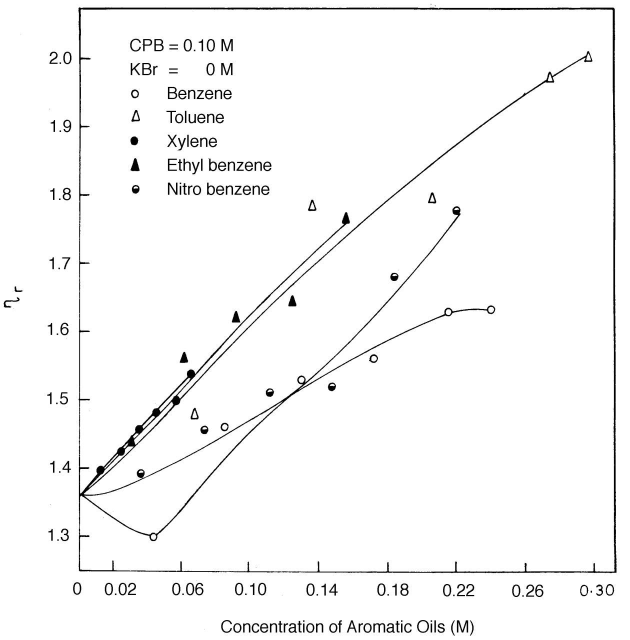

FIG. 1. Variation of η_r for 0.1 M CPB micellar solutions with concentration of the added aromatic hydrocarbons (in absence of KBr) at 40°C.

benzene molecules, due to its low molar volume, get solubilized, and hence the viscosity of this system should become higher. But reality is different. The strength of the π-electron cloud, and hence the interaction with surfactant head groups, will increase with the alkyl group in the benzene ring. Thus,

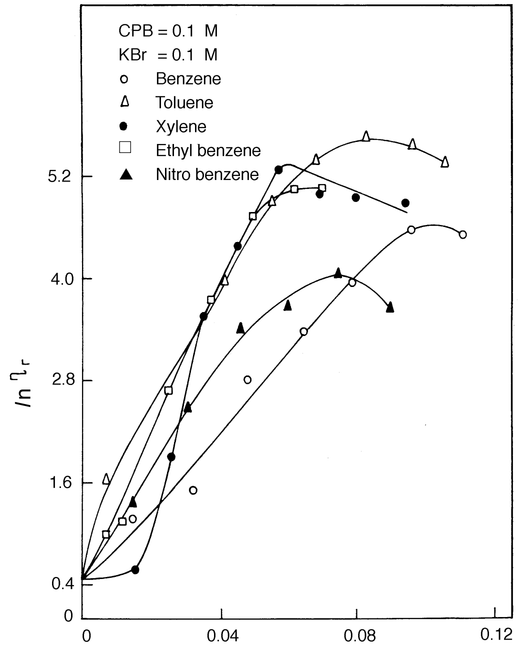

FIG. 2. Variation of *ln* η_r for 0.1 M CPB micellar solutions with concentration of the added aromatic hydrocarbons (in presence of 0.1 M KBr) at 40°C.

3. Evans, D.F., and B.W. Ninham, Ion Binding and the Hydrophobic Effect, *J. Phys. Chem. 87*:5025–5032 (1983).
4. Rao, U.R.K., C. Manohar, B.S. Valaulikar, and R.M. Iyer, On the Origin of Viscoelasticity in Micellar Solutions of Cetyltrimethylammonium Bromide and Sodium Salicylate, *Ibid. 91*:3286–3292 (1987).
5. Stigter, D., On Density, Hydration, Shape, and Charge of Micelles of Sodium Dodecyl Sulfate and Dodecylammonium Chloride, *J. Colloid Interface Sci. 23*:379–388 (1967).
6. Lindemuth, P.M., and G.L. Bertrand, Calorimetric Observations of the Transition of Spherical to Rodlike Micelles with Solubilized Organic Additives, *J. Phys. Chem. 97*:7769–7773 (1993).
7. Kumar, S., V.K. Aswal, H.N. Singh, P.S. Goyal, and Kabir-ud-Din, Growth of Sodium Dodecyl Sulfate Micelles in the Presence of *n*-Octylamine, *Langmuir 10*:4069–4072 (1994).
8. Israelachvili, J.N., D.J. Mitchell, and B.W. Ninham, Theory of Self-Assembly of Hydrocarbon Amphiphiles into Micelles and Bilayers, *J. Chem. Soc., Faraday Trans. 2. 72*:1525–1568 (1976).
9. Bohmer, M.R., L.K. Koopal, and J. Lyklema, Micellization of Ionic Surfactants. Calculations Based on a Self-Consistent Field Lattice Model, *J. Phys. Chem. 95*:9569–9578 (1991).
10. Mitchell, D.J., and B.W. Ninham, Micelles, Vesicles and Microemulsions, *J. Chem. Soc., Faraday Trans. 2. 77*:601–629 (1980).
11. Tanford, C., Micelle Shape and Size, *J. Phys. Chem. 76*: 3020–3024 (1972).
12. Fang, J., Article II: Ph.D. Dissertation, University of Missouri-Rolla, 1987.
13. Ozeki, S., and S. Ikeda, The Sphere-Rod Transition of Micelles and the Two Step Micellization of Dodecyltrimethylammonium Bromide in Aqueous NaBr Solutions. *J. Colloid Interface Sci. 87*:424–435 (1982).
14. Khatory, A., F. Kern, F. Lequeux, J. Appell, G. Porte, N. Morie, A. Ott, and W. Urbach, Entangled Versus Multiconnected Network of Wormlike Micelles, *Langmuir 9*:933–939 (1993).
15. Kumar, S., Kirti, K. Kumari, and Kabir-ud-Din, Role of Alkanols in Micellar Growth: A Viscometric Study, *J. Am. Oil Chem. Soc. 72*:817–821 (1995).
16. Kabir-ud-Din, S. Kumar, Kirti, and P.S. Goyal, Micellar Growth in Presence of Alcohols and Amines: A Viscometric Study, *Langmuir 12*:1490–1494 (1996).
17. David, S.L., S. Kumar, and Kabir-ud-Din, Viscosities of Cetylpyridinium Bromide Solutions (Aqueous and Aqueous KBr) in the Presence of Alcohols and Amines, *J. Chem. Eng. Data 42*:198–201 (1997).
18. Winsor, P.A., Hydrotropy, Solubilization and Related Emulsification Processes, *Trans. Faraday Soc. 2. 44*:376–398 (1948).
19. Eriksson J.C., and G. Gillberg, NMR Studies of the Solubilization of Aromatic Compounds in Cetyltrimethylammonium Bromide Solution II, *Acta Chem. Scand. 20*:2019–2027 (1966).
20. Venable, R.L., K.L. Elders, and J. Fang, Microemulsions with High Water Solubilizing Capacity at High Hydrocarbon Levels and Very Low Surfactant Concentrations, *J. Colloid Interface Sci. 109*:330–335 (1986).
21. Abe, M., D. Schechter, R.S. Schechter, W.H. Wade, U. Weersdooriya, and S. Xiv, Microemulsion Formation with Branched Tail Polyoxyethlene Sulfonate Surfactants, *Ibid. 114*:342–356 (1986).
22. Almgren, M., and S. Swarup, Size of Sodium Dodecyl Sulfate Micelles in the Presence of Additives. 2. Aromatic and Saturated Hydrocarbons, *J. Phys. Chem. 86*:4212–4216 (1982).
23. Ozeki, S., and S. Ikeda, The Viscosity Behavior of Aqueous NaCl Solutions of Dodecyl Dimethyl Ammonium Chloride and the Flexibility of its Rod-like Micelle, *J. Colloid Interface Sci. 77*:219–231 (1980).
24. Ogino, K., and N. Takeshita, Electrophoresis and Diffusion Studies of the Solubilization of Polar and Nonpolar Oily Com-

pounds with Sodium Dodecyl Sulfate. II, *Bull. Chem. Soc. Jpn .* *53*:611–615 (1980).

25. Rosen, M.J., *Surfactants and Interfacial Phenomena*, Wiley, New York, 1989.
26. Lindblom, G., B. Lindman, and L. Mandell, Effect of Micellar Shape and Solubilization on Counterion Binding Studied by ^{81}Br NMR, *J. Colloid Interface Sci. 42*:400–409 (1973).
27. Hoffmann, H., Fascinating Phenomena in Surfactant Chemistry, *Adv. Colloid Interface Sci. 32*:123–150 (1990).
28. Mukerjee, P., Formation and Some Properties of Micelles, *Ber Bunsenges. Phys. Chem. 82*:931–936 (1978).
29. Gadelle, F., W.J. Koros, and R.S. Schechter, Solubilization Isotherms of Aromatic Solutes in Surfactant Aggregates, *J. Colloid Interface Sci. 170*:57–64 (1995).

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