Viscosities of Cetylpyridinium Bromide Solutions (Aqueous and Aqueous KBr) in the Presence of Alcohols and Amines

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The effect of organic additives (aliphatic/aromatic amines or alcohols) on the viscosities of aqueous and 0.1 M KBr solutions of 0.05 or 0.1 M cetylpyridinium bromide have been measured under Newtonian flow conditions. The viscosity changed dramatically in the presence of KBr. This is explained by the favorable conditions produced by the salt which assists the micellar growth by organic additives with a concomitant enhancement in viscosity. Reasons for the effectiveness of these additives are suggested. The causes of the viscosity decrease at higher concentrations of the additive are also explained.

Introduction

Surfactants are generally used in the presence of additives in order to improve their properties. Among the large number of additives, alcohols hold a special place, being by far the most common cosurfactants which are added to surfactant−oil combinations to generate microemulsions. Though the studies using amines as cosurfactant in microemulsions are few, it has been proved that they are also potential candidates for such formulations (Fang and Venable, 1987; Wormuth and Kaler, 1987; Singh *et al.*, 1993).

In several surfactant systems there is a transformation of spherical micelles to globular/rod-shaped micelles at a higher surfactant concentration where the solution possesses higher viscosity. For ionic surfactants, the same effect may be achieved by addition of a suitable cosurfactant (Lindemuth and Bertrand, 1993; Kumar *et al.*, 1994). A sharp increase in the viscosity can be related to an increase in micellar size (or change in shape) (Kabir-ud-Din *et al.*, 1996b). Viscosity can be used to get an approximation about micellar size in surfactant solutions, and such results are in qualitative agreement with the scattering techniques (Forland *et al.*, 1994; Kabir-ud-Din *et al.*, 1996a,b). Further, micelles can be filtered with an ultrafiltration membrane having pores small enough to reject the aggregates containing organic compounds (may be pollutants). Obviously, the performance of these methods is directly related to the micellar size and hence to the viscosity of the solution. These facts explain why the understanding of the effect of amines/alcohols on the properties of surfactant systems is so important.

In the present article, we report the measured viscosities of micellar solutions of cetylpyridinium bromide (a cationic surfactant) in the presence of different amines/alcohols with and without 0.1 M KBr.

Experimental Section

Cetylpyridinium bromide (Merck-Schuchardt; purity >99%) was used as received. KBr (purity >99%) was an E. Merck product which was further purified by ignition. All alcohols (1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol) were BDH "high purity" chemicals (>99%) and were used as supplied. Heptyl- and octylamines were from Fluka (puriss grade, >99%), while hexylamine (∼99%) and aniline (GR grade) were from Merck-Schuchardt and E. Merck, respectively. All amines were used as supplied. The water used to prepare the solutions was demineralized and double-distilled in an all-glass (Pyrex) distillation setup. The specific conductivity of this water was in the range $(1-2) \times 10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

Special care was observed for cleaning the glassware (by immersing successively in 1 M NaOH−ethanol and 1 M nitric acid baths, then by rinsing with the demineralized double-distilled water). Stock solutions of cetylpyridinium bromide (in water or in 0.1 M KBr) were prepared volumetrically. The sample solutions were made by taking the required volumes of the additives with the help of disposable micropipets (Drummond) in standard volumetric flasks and making up the volumes with the cetylpyridinium bromide stock solution. The error chances in composition of the samples were not more than ±0.02%. After proper mixing, the sample solutions were kept overnight for equilibration. Prior to measurements, these solutions were kept at 40 °C for at least 1 h to attain thermal equilibrium. To avoid evaporation, the flasks/viscometer were kept properly stoppered and sealed during equilibration.

Viscosities of the solutions were measured by an Ubbelohde viscometer thermostated at 40 ± 0.1 °C. At higher additive concentrations (especially in presence of 0.1 M KBr), viscosities were dependent on the rate of flow. To obtain viscosities under Newtonian flow conditions, a wide U-shaped tube containing water was connected to the limb of the viscometer (Gamboa and Sepulveda, 1986). This arrangement allowed us to vary the pressure (P) under which the solution flows and thus to determine viscosity values at various rates of flow (at least four flow time measurements were made at each concentration/rate of flow, and mean deviation from the mean of all measurements not exceeding 0.1 s was required) from the slope of the straight line obtained by variation of P *vs* $1/t$ (according to the Poiseuille equation $P = \eta A/t$, where t is the time of flow of the solution in a given viscometer, A is the characteristic constant of the viscometer obtained by calibration with liquids of known viscosities, and η is the viscosity of the solution). The relative viscosity of the solution, $\eta_r = \eta/\eta_o$ (where η_o is the viscosity of the solvent water), is given by $\eta/\eta_o = \rho t/\rho_o t_o$, where ρ and ρ_o are the densities of the solution and water and t_o is the flow time of water. At a surfactant concentration C, ρ is given by

$$\rho = \rho_o + (1 - \bar{V}\rho_o)C$$

($\bar{V}$ is the partial specific volume of the surfactant). It has

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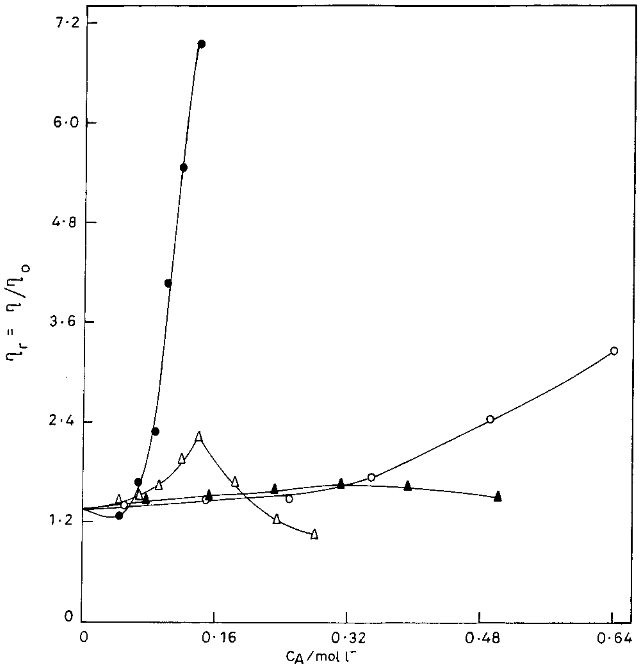

Figure 1. Variation of relative viscosities, η_r, of 0.1 M cetylpyridinium bromide micellar solutions with the concentration of the added amines, C_A (in the absence of KBr), at 40 °C: (○) hexylamine; (△) heptylamine; (●) octylamine; (▲) aniline.

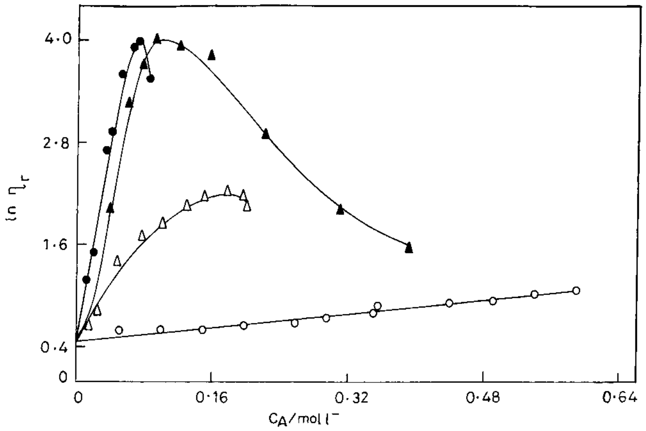

Figure 2. Variation of ln η_r of 0.1 M cetylpyridinium bromide micellar solutions with concentration of the added amines, C_A (in presence of 0.1 M KBr), at 40 °C: (○) hexylamine; (△) heptylamine; (●) octylamine; (▲) aniline.

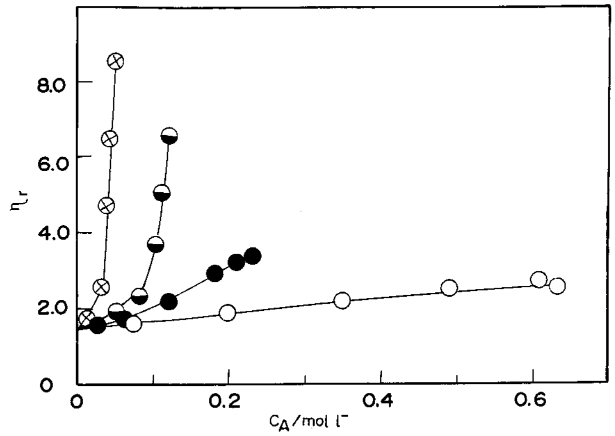

Figure 3. Variation of η_r of 0.1 M cetylpyridinium bromide micellar solutions with concentration of the added alcohols, C_A (in absence of KBr), at 40 °C: (○) 1-pentanol; (●), 1-hexanol; (◒) 1-heptanol; (⊗) 1-octanol.

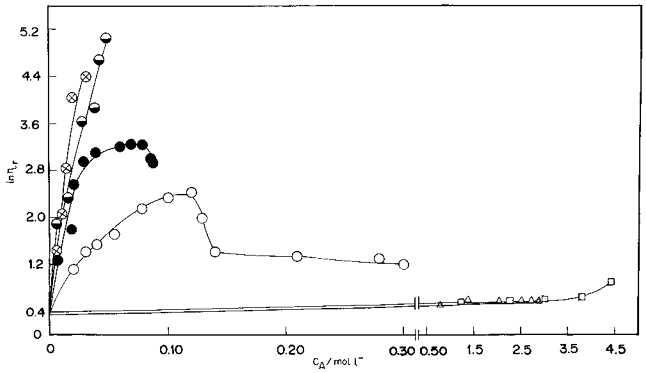

Figure 4. Variation of ln η_r of 0.1 M cetylpyridinium bromide micellar solutions with concentration of the added alcohols, C_A (in presence of 0.1 M KBr), at 40 °C: (□) 1-propanol; (△) 1-butanol; (○) 1-pentanol; (●) 1-hexanol; (◒) 1-heptanol; (⊗) 1-octanol.

been reported that variation in ρ was insignificant when either the surfactant or additive concentrations were varied (Ozeki and Ikeda, 1980). Therefore, density corrections in calculating η_r were not made, *i.e.* $\eta_r = t/t_o$.

Results and Discussion

The measured η_r values of 0.05 M and 0.1 M cetylpyridinium bromide micellar solutions, as a function of the concentration of added amines and alcohols (C_A), are given in Tables 1 and 2, in both the presence (S_p) and absence (S_a) of 0.1 M KBr, and representative plots are shown in Figures 1−4. The results are explained separately under the following two categories of the additives.

(i) Amines. From Table 1 and Figures 1 and 2 it can be seen that hexylamine shows a regular increase in the viscosity. For 0.1 M KBr the behavior is similar. An increase in the concentration of cetylpyridinium bromide causes a marginal effect on viscosity, even in the presence of KBr. These observations can be explained in light of the distribution of hexylamine between the aqueous and micellar phases. Even if the distribution coefficient increases as a result of added KBr, a significant part of the hexylamine will still be dissolved in the aqueous phase. However, as the hexylamine concentration increases, the number of hexylamine molecules per micelle increases regularly, which brings about micellar growth and a regular increase in viscosity.

With the increase in chain length of the amine (*e.g.*, heptylamine), the viscosity of 0.05 M cetylpyridinium bromide, in the presence or absence of the salt, remains more or less the same; but the presence of salt causes a significant viscosity increase of 0.1 M cetylpyridinium bromide (and, later on, a decrease at higher concentrations of heptylamine, in both the presence and absence of 0.1 M KBr). The effect was more pronounced with octylamine and with higher cetylpyridinium bromide concentrations (the viscosity decrease at higher concentrations of octylamine occurred only in the presence of 0.1 M KBr, Figures 1 and 2). The initial increase of viscosity, especially in the presence of 0.1 M KBr, is due to the combined effect of two factors. Firstly, the increase in the ionic strength of the solution lowers the aqueous solubility of the amines. Secondly, solubilization (or intercalation) of the amine increases the hydrophobic interaction between and/or among the micelles. These two effects produce favorable conditions for micellar growth which impart higher viscosities to the solutions.

At higher concentrations of heptyl- or octylamines, the viscosity decrease may be due to the fact that once the

Table 1. Relative Viscosities, η_r, of Cetylpyridinium Bromide (B) Micellar Solutions in the Presence (S_p) and Absence (S_a) of 0.1 M KBr with Added Amines (A)

	η_r at 40 °C					η_r at 40 °C			
	$C_B = 0.05$ mol L^{-1}		$C_B = 0.1$ mol L^{-1}			$C_B = 0.05$ mol L^{-1}		$C_B = 0.1$ mol L^{-1}	
C_A/mol L^{-1}	S_a	S_p	S_a	S_p	C_A/mol L^{-1}	S_a	S_p	S_a	S_p
0	1.18	1.08	1.37	1.58					
Hexylamine									
0.025		1.15			0.600				turbid
0.050	1.15	1.15	1.38	1.78	0.640			3.26	
0.980	1.21	1.16		1.80	0.740	2.95			
0.148	1.27	1.21	1.45	1.81	0.790			3.46	
0.197	1.31	1.41		1.93	0.890	5.22			
0.250	1.32	1.49	1.47	1.95	0.940			3.88	
0.295		1.81		2.08	1.130			3.90	
0.350	1.71	1.78	1.73	2.22	1.200	5.63			
0.360		turbid			1.300	5.53			
0.395				2.36	1.480	5.38		4.62	
0.440				2.52	1.500	turbid			
0.490	2.08		2.42	2.56	2.960			4.89	
0.540				2.74	3.000			turbid	
0.590				2.91					
Heptylamine									
0.013				1.90	0.130	1.56	turbid		7.99
0.015		1.29			0.141			2.24	
0.025	1.05	1.50		2.30	0.150	1.86			8.79
0.040		2.01			0.180	1.92			9.16
0.047			1.44		0.185	turbid		1.69	
0.051	1.24	2.55		4.06	0.192				8.68
0.066		2.89			0.200				7.53
0.070			1.50		0.205				turbid
0.075	1.29	2.95		5.49	0.235			1.21	
0.094			1.62		0.282			1.04	
0.100	1.35	3.69		6.46	0.285			turbid	
0.120		4.27	1.96						
Octylamine									
0.013		2.09		3.30	0.072				53.06
0.021	1.26	6.49		4.45	0.082	1.72			
0.034		9.84		15.11	0.085				34.17
0.038		13.29			0.091	2.07		2.27	turbid
0.042	1.28	17.54		18.23	0.095	turbid			
0.046			1.28		0.114			4.04	
0.051		18.72		36.56	0.127			5.43	
0.064				51.19	0.128			6.94	
0.068	1.47		1.68		0.130			turbid	
0.070		turbid							
Aniline									
0.038		3.47			0.210		4.76		
0.039				7.45	0.230			1.58	17.99
0.042	1.21	4.25			0.250	1.40	3.42		
0.062				26.11	0.260		2.84		
0.070		3.88			0.270		turbid		
0.080			1.44	41.41	0.290	1.32			
0.085	1.26	10.96			0.310			1.66	7.54
0.090				56.81	0.390	1.30		1.64	4.86
0.100		8.01			0.400				turbid
0.120				50.37	0.460	1.29		1.52	
0.130		7.03			0.470	turbid		turbid	
0.170	1.27	5.67	1.51	43.77					

Table 2. Relative Viscosities, η_r, of 0.1 M Cetylpyridinium Bromide Solutions in the Presence (S_p) and Absence (S_a) of 0.1 M KBr with added Alcohols (A)

	η_r at 40 °C			η_r at 40 °C	
C_A/mol L^{-1}	S_a	S_p	C_A/mol L^{-1}	S_a	S_p
0	1.41	1.46			
1-Propanol					
1.02	1.43	1.70	3.81	1.68	1.88
2.27	1.55	1.75	4.45	2.17	2.43
3.08		1.86			
1-Butanol					
0.80	1.10	1.33	2.10	1.76	1.79
1.38	1.54	1.83	2.12	1.81	1.68
2.08		1.80			
1-Pentanol					
0.02		3.00	0.13		12.46
0.03		4.04	0.14		4.05
0.04		4.49	0.15		turbid
0.05		4.58	0.21	1.80	
0.06		4.81	0.35	2.12	
0.07	1.52	5.00	0.49	2.47	
0.10		8.61	0.63	2.54	
0.12		10.42	0.61	2.68	
1-Hexanol					
0.01		3.54	0.079		28.33
0.018		6.01	0.080		28.34
0.02		12.52	0.10		turbid
0.03	1.57	18.95	0.12	2.19	
0.04		21.62	0.18	2.90	
0.05	1.70	24.34	0.21	3.11	
0.07		25.33	0.23	3.30	
0.075		27.10	0.24	turbid	
1-Heptanol					
0.005		6.97	0.048		turbid
0.016		10.43	0.05	1.92	
0.027		36.46	0.08	2.29	
0.03		47.65	0.10	3.51	
0.038		104.13	0.11	4.99	
0.042		152.69	0.12	6.47	
0.047			0.13	turbid	
1-Octanol					
0.005		4.07	0.032		80.00
0.01	1.72	7.56	0.033		turbid
0.014		16.98	0.035	4.65	
0.02	1.96	56.82	0.04	6.45	
0.028		65.15	0.05	8.50	
0.03	2.50		0.06	turbid	

solubilization sites become saturated in the micellar palisade layer, these amines start going deep inside the core (rather than remaining in the vicinity of the interfacial region), thus relaxing the requirement of surfactant chains to reach the center of the micelle (Lindemuth and Bertrand, 1993). Therefore, at higher concentrations of the amine, micelles distintegrate to smaller ones, resulting in a decrease in viscosity. Further, solubilized molecules have available a range of sites of decreasing hydration as they approach the interior and, once inside the core, they may increase the size of the hydrophobic center and give a swollen micelle instead of a grown micelle.

Comparison of the viscosity behavior of cetylpyridinium bromide with amines and aniline shows that aniline is more effective in the presence of 0.1 M KBr. Most likely, the π-electron cloud of the benzene ring interacts with the positive charge of the head group, thereby allowing the micelle to grow more. With aniline also, the viscosity decrease after the maximum is due to reasons similar to those discussed above for amines.

(ii) Alcohols. The results (Table 2, Figures 3 and 4) clearly show that lower chain length alcohols (*e.g.*, 1-propanol or 1-butanol) have a marginal effect on the η_r values of cetylpyridinium bromide micellar solutions which remain nearly the same when 0.1 M KBr is present. The higher chain length alcohols are more effective in increasing the η_r, and the magnitude depends upon the number of carbon atoms in the alkyl part of the particular alcohol; the reason being the same as invoked in the case of amines. The lower homologues affect the water structure while the penetration of higher ones outweighs the effect, resulting in an increase of both the micellar size and viscosity.

Tables 1 and 2 show that for equal chain lengths the viscosity rise is more with alcohols than with amines. It was reported earlier that C_4-C_{10} alkylamines are solubilized in ionic micelles with the amine group left on the surface of the micelle (Yamashita *et al.*, 1983). Their partial dissociation into $-NH_3^+$ and OH^- (though feebly) may affect the electrostatic interactions with the cationic pyridinium head group, which will hinder the micellar growth (size). Hence, alcohols will be more effective in increasing the viscosity of cetylpyridinium bromide micellar solutions. This indeed is observed in our present investigations.

Here we can conclude that organic additives can be used as a partial substitute of salt toward viscosity thickening of surfactant solutions (which is desirable for various industrial applications/reaction media), but care should be taken in selecting an additive as regards its concentration, chain length, and compatibility with the surfactant.

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