Role of Alkanols in Micellar Growth: A Viscometric Study

Sanjeev Kumar, Kirti, Krishna Kumari and Kabir-ud-Din*
Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India

ABSTRACT: We have measured the viscosity of solutions of 0.3 M sodium dodecyl sulfate (SDS) + 0.3 M NaBr + *n*-alkanols as a function of [alkanol] and temperature. When propanol was added, the viscosity of micellar solutions remained almost constant and then decreased, whereas it continuously increased with hexanol. However, with butanol or pentanol, depending upon the added concentration, increases followed by decreases in viscosity were observed. This behavior has been discussed in light of solubility of alkanols in various soluble phases of the micellar system with a resultant change in the Mitchell–Ninham parameter of the "effective surfactant" (i.e., SDS + *n*-alkanol). An increase in temperature caused a decrease in viscosity, which is related to micellar breakdown. Activation parameters (ΔG^* and ΔH^*) were computed from the temperature dependence data. ΔH^* Covered almost the total contribution to ΔG^*.
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KEY WORDS: Cosurfactant, micelle, surfactant, viscosity.

Several micellar systems have recently attracted considerable interest because of their potential use in diverse fields (1–4). An interesting aspect of micellar solutions is that they show a large change in viscosity on adding inorganic salts (5) or organic cosurfactants (6). From a practical point of view, alcohols (as cosurfactants) have been used in tertiary oil recovery because they bring about a large decrease of viscosity, strongly accelerate the rate at which these systems reached equilibrium in the polyphasic range, and appear to decrease the adsorption of the surfactants in rock pores in the oil field, thereby increasing efficiency and decreasing cost. The viscous surfactant solutions are also of industrial importance because they enhance customer appeal and economy of various formulations. Usually, inorganic salts are used as thickening agents for concentrated surfactant solutions; the role of organic molecules as thickening agents is, however, not well studied.

It has been reported that a sharp increase in the viscosity of a concentrated micellar solution is due to the formation of nonspherical micelles, which can form a network in the solution (7). The many factors that determine the shape of surfactant association structure and viscosity of the solution include temperature and the concentrations of surfactant, electrolyte, and cosurfactant. Generally, cosurfactants bind to the micelles and intercalate between the surfactant ionic head groups. This effect is correlated with a packaging parameter being governed by the hydrophilic and hydrophobic groups of the surfactant. The ratio of the average section of the hydrophobic part (V_c/l_c) to the area per head group (A_0), called the surfactant parameter, R_p (= $V_c/A_0\, l_c$), is the fundamental geometric quantity for several of the possible aggregation shapes (8). For example, critical conditions for the formation of spherical, cylindrical, bilayer, or inverted structures are: $R_p \leq 1/3$, $1/3 \leq R_p \leq 1/2$, $1/2 \leq R_p \leq 1$, $R_p \geq 1$, respectively. Surfactants with smaller head group areas (high R_p) tend to form larger aggregates. For ionic surfactants, the same area-shrinking effect may be produced by the addition of a counterion or suitable cosurfactant. Hertel and Hoffman (9) have used this packing ratio to design lyotropic nematics.

In an extensive phase study, Guerin and Bellocq (10) have shown that various phases and critical points are present in the system sodium dodecyl sulfate (SDS)/*n*-pentanol (penOH)/water/NaCl, depending on NaCl concentration and temperature. Low values of the mean aggregation number (N) of SDS in aqueous solution of penOH have been found in several studies (11–13). However, the addition of 0.1 M NaCl to solutions of SDS in pure water and to aqueous 0.2 M SDS + 0.6M *n*-penOH increases N from 65 to 93 (11,14) and from 47 to 197 (12), respectively. Thus, a larger increase of N is observed in SDS + 1-pentanol "mixed micelles" upon addition of 0.1M NaCl compared to pure aqueous SDS solution. Though it has long been reported that the variation of N of micellar solutions is governed by the solubilities of alcohols in water and the micellar phase (15), there have been few reports that are directly concerned with the effect of alkanols on concentrated SDS micellar solutions in the presence of salts (12,16–18).

These facts explain why the effect of alkanols on the properties of micellar systems is a topic of importance. Indeed, such studies constitute a necessary step toward clarification of the role of alkanols in thickening and thinning of concentrated micellar solutions. These considerations led us to pursue a systematic study of the effects of the addition of aliphatic alkanols on the viscosities of concentrated SDS micellar so-

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*To whom correspondence should be addressed.

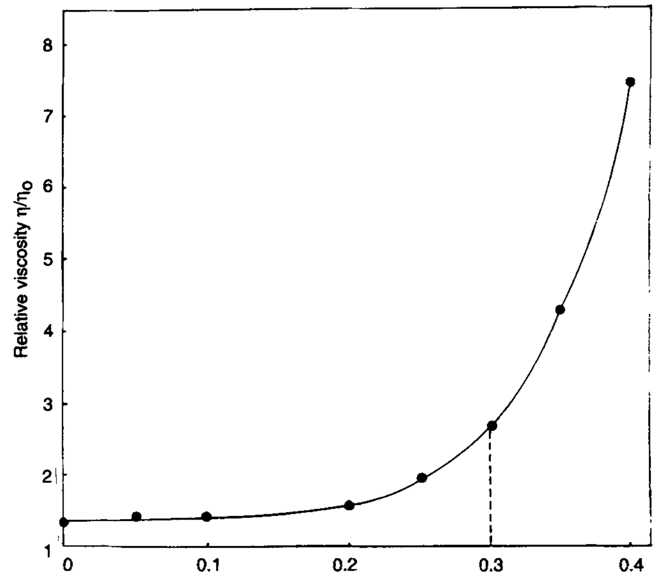

FIG. 1. NaBr concentration dependence of relative viscosity, η_r, of 0.3 M sodium dodecyl sulfate micellar solution at 298.16 K.

lutions in aqueous NaBr by capillary viscometry. The method is simple and reliable and can provide a large body of important information with respect to the change in micellar shape. The concentration of the starting sample (0.3 M SDS + 0.3M NaBr) was chosen from the study of the effect of NaBr on 0.3 M SDS aqueous solution. A distinct rise in viscosity at 0.3 M NaBr (Fig. 1) was observed, which is a possible indication of the presence of nonspherical aggregates in the solution (5,7). However, sphere-to-rod transition in aqueous micellar solution, without any added salt, is reported to occur at a higher SDS concentration (~1.16 m).

The aim of this work is to study the role of alkanols as thickening/thinning agents for surfactant solutions. The viscosity behavior has been discussed in light of preferential solubility of alkanols in micellar/water phases with a concomitant variation in the Mitchell–Ninham parameter (8) of the resultant "effective surfactant" system (i.e., SDS + *n*-alkanol).

EXPERIMENTAL PROCEDURES

Materials. "Specially pure" SDS (BDH, Poole, United Kingdom) and "pro analysi" sodium bromide (NaBr; Merck, Darmstadt, Germany) were used. All alkanols, *n*-propanol (prOH), *n*-butanol (butOH), and *n*-hexanol (hexOH) were BDH high-purity chemicals and were used as supplied. Water was distilled twice over alkaline $KMnO_4$ in an all-glass still.

Measurements. Viscosities of the solutions were measured in an Ubbelohde viscometer that was thermostated at a fixed temperature (25, 30, 35, or 40°C, accuracy ±0.01°C). The method of measurement of viscosities under conditions of Newtonian flow was the same as described by other investigators (19). Density corrections were not made because they were negligible (20).

RESULTS AND DISCUSSION

Figure 1 shows the variation of relative viscosity, η_r (=η/η_0, η and η_0 are the viscosities of solution and solvent water, respectively), of a 0.3 M SDS micellar solution at 298.1, K with NaBr concentration. The addition of NaBr induces screening of the repulsive forces, which decreases the intermicellar interactions and favors growth of the micelles as it allows the SDS molecules to approach each other more closely. This leads to a sharp rise in η_r around 0.3 M NaBr [indicating the formation of larger aggregates (5,7)].

The relative viscosities of 0.3 M SDS + 0.3 M NaBr in the presence of various concentrations of *n*-alkanols at different temperatures are given in Table 1. Typical plots of ln η_r vs. concentration of alkanols at one of the temperatures (298.16 K) are shown in Figure 2. Because lower alkanols are mainly hydrophilic molecules with excellent solubility in water and little in micelles (21), prOH will affect water structure more efficiently and will cause the larger micelles to break into smaller ones, with a resultant decrease in the viscosity of micellar solutions. Indeed, this is reflected in Figure 2. Such transitions from rod to sphere by the addition of lower alkanols to dodecyl trimethylammonium bromide–sodium salicylate micelles have been reported from light-scattering measurements (22). Medium-chain alkanols (like butOH and penOH), which are partitioned between the micelles and the bulk phase, form mixed micelles in the solution. With addition of the butOH or penOH, η_r increased up to a certain concentration and then decreased. However, no such fall in viscosity was observed with the addition of hexOH. It is worth recalling that both anionic SDS and cationic cetyl tetrammonium bromide (CTAB) micellar solutions, even without added electrolyte, show similar behavior with hexOH concentration on the whole range investigated (23,24). Also, the results of Hirsch *et al.* (25) on penOH addition to solutions of tetrammonium bromide (TTAB) + 0.1 M KBr, as well as those of Prasad and Singh (26) on butOH or penOH addition to 0.1 M CTAB + 0.1M KBr solutions are similar to the present results, namely, viscosity increase in the beginning followed by decrease. The authors have satisfactorily explained the rise in viscosity in terms of incorporation of the alkanols inside the micelle, but the explanation invoked for the observed viscosity decrease in the presence of medium-chain alkanols (butOH or penOH) at higher concentrations seems unlikely for such systems. At higher concentrations, it is possible that these medium-chain alkanols may be salted out by the added NaBr and dissolve preferentially in the micelle hydrophobic core rather than in the palisade layer; thus, the requirement of the surfactant chains to reach the center of the micelle becomes relaxed (17). Thus, it is possible that, at high alkanol contents, the rod-shaped structures revert back to spherical shapes and form the basis of a viscosity decrease.

The preceding discussion reflects that the viscosity behavior of micellar solutions in the presence of alkanols depends, in general, upon the alkyl chainlength of alkanols. Preferential incorporation of alkanols into the micelles lowers the sur-

TABLE 1
Value of Relative Viscosities, η_r, as Functions of [Alkanol] and Temperature, and Activation Parameters for the Viscous Flow *of 0.3 M + 0.3 M NaBr in H_2O*

	h_r				Activation parameters (kcal mol^{-1})		
C_A[a] (M)	298.16[b]	303.16[b]	308.16[b]	313.16[b]	ΔG*	ΔH*	r[c]
0	2.77	2.38	2.13	1.86	4.85	4.85	0.9985
n-Propanal							
0.01	3.05	2.62	2.24	1.95	5.56	5.56	0.9999
0.06	2.96	2.60	2.19	2.00	501	5.01	0.9962
0.10	2.86	2.51	2.12	1.94	4.95	4.95	0.9961
0.40	1.98	1.88	1.76	1.69	2.00	2.00	0.9967
0.60	1.85	1.77	1.73	1.66	1.31	1.31	0.9922
n-Butanol							
0.04	4.23	3.79	2.96	2.53	6.54	6.54	0.9903
0.08	5.15	4.39	3.36	2.66	8.31	8.31	0.9947
0.10	5.87	4.64	3.47	2.77	9.33	9.33	0.9989
0.15	6.51	4.88	3.72	3.02	9.46	9.46	0.9983
0.40	5.01	3.79	2.97	2.42	9.15	9.15	0.9983
0.60	2.50	2.47	2.42	2.32	9.15	9.15	0.9839
n-Pentanol							
0.04	9.97	7.00	5.15	3.63	12.34	12.34	0.9996
0.06	14.75	11.12	7.38	4.64	14.37	14.37	0.9927
0.10	56.71	21.34	12.61	7.51	24.56	24.57	0.9883
0.15	104.07	42.19	24.35	14.06	24.29	24.29	0.9927
0.20	79.44	42.54	28.23	18.43	17.79	17.79	0.9957
0.30	42.00	28.86	21.39	15.84	11.98	11.98	0.9988
0.35	25.45	21.24	17.31	14.26	7.19	7.19	0.9999
0.50	15.33	13.07	11.22	9.92	5.94	5.94	0.9991
0.65	9.09	8.75	8.21	7.93	1.78	1.78	0.9950
n-Hexanol							
0.02	8.61	6.23	4.45	3.28	12.02	12.02	0.999
0.03	19.94	10.11	6.44	4.61	17.90	17.91	0.9888
0.06	188.83	100.92	56.71	22.30	25.86	25.87	0.9925
0.08	335.45	214.03	88.08	39.41	27.00	27.01	0.9900
0.09	649.00	193.25	82.09	35.97	35.36	35.37	0.9962

[a] Molar concentration of added alkanol.
[b] Temperature (in degrees Kelvin).
[c] Correlation coefficient obtained from the linear variation of η_r with 1/T.

face charge density, which is responsible for micellar growth. This micellar growth brings about a large increase in the viscosity of the micellar aqueous solutions, with or without added electrolyte. The larger-chain alcohols would also affect the Mitchell–Ninham parameter of the surfactant molecule (8). In the present case, while the length of the SDS molecule (l_c) remains the same, alcohol (C_4–C_6) intercalation increases affect the hydrophobic volume (V_c) and decreases the cross-sectional area per SDS monomer (A_0). The result is an increase in R_p ($=V_c/A_0l_c$) value of "effective surfactant" (SDS + *n*-alkanol). The combination of SDS–alkanol could be regarded as a single surfactant with a Mitchell–Ninham parameter (R_p) higher than that of SDS alone. Therefore, SDS + medium-chain alkanol should have a tendency to form large, nonspherical micelles, and it seems to do so as reflected by an increase in viscosity (Fig. 2). Similar arguments were put forth earlier to design viscoelastic and lyotropic nematics (9,27). An increase in the chainlength of alkanol will increase the effective V_c with a concomitant increase in R_p. This explains the higher viscosity values for the SDS–hexOH combination at any particular concentration as compared to penOH or butOH. As stated earlier, micellar core solubilization at higher concentrations of alkanols brings about a decrease in viscosity. This may increase the effective l_c (V_c as well), with a simultaneous increase in A_0. The effect of l_c increase is possibly neutralized by V_c toward any variation of R_p. But, due to the increase of effective A_0, the net result is a decrease in R_p on alcohol solubilization. As a result, the smaller micelles form the basis of the viscosity decrease.

An effect of temperature variation (25–40°C) on the vis-

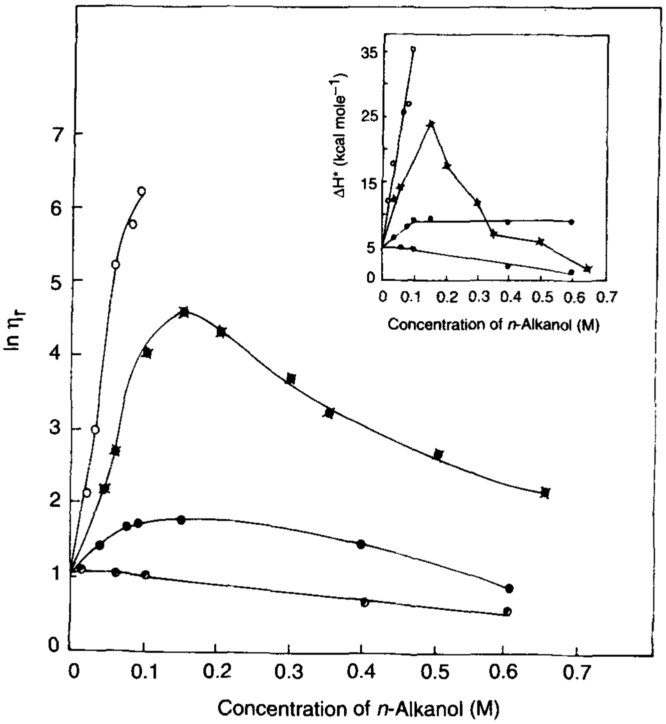

FIG. 2. Relative viscosity, ηr, as a function of alkanol concentration for 0.3 M sodium dodecyl sulfate + 0.3 M NaBr micellar solution (*n*-propanol, half-filled circle; *n*-butanol, closed circle; *n*-pentanol, circle with an X through it; *n*-hexanol, circle) at 298.16 K. Inset: Variation of ΔH* with added *n*-alkanol.

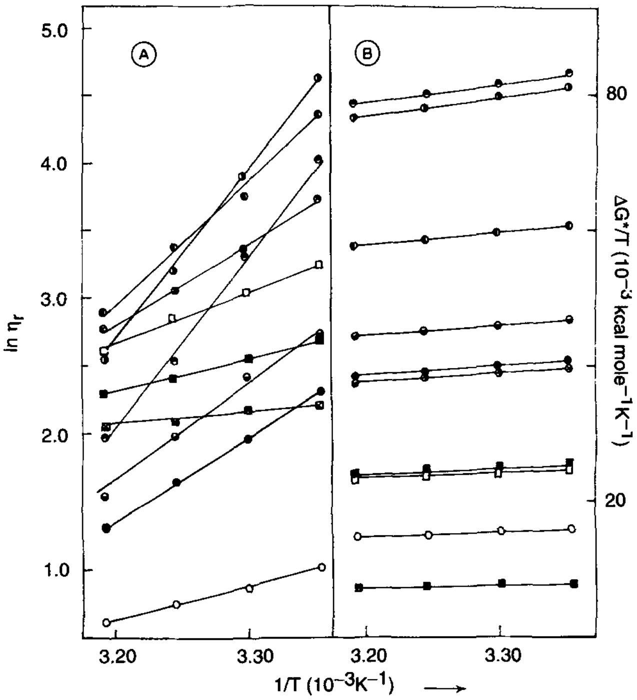

FIG. 3. (A) Logarithm of relative viscosity, η_r, as a function of 1/*T* and (B) Gibbs–Helmholtz plots for 0.3 M sodium dodecyl sulfate + 0.3 NaBr micellar solution in the presence of various *n*-pentanol concentrations (open circle, 0.0; closed circle, 0.04; circle with bottom half filled, 0.06; circle with top half filled, 0.10; circle with right half filled, 0.15; circle with left half filled, 0.20; circle with an X through it, 0.30; open square, 0.35; closed square, 0.50; and square with an X through it, 0.65 M).

cosity of the micellar system under study was also seen in the presence of alkanols. As the temperature was raised, micelles shorten and, consequently, viscosities were lowered (Table 1). With the relative viscosity data obtained as a function of temperature, plots like those shown in Figure 3A were constructed. The observed linearity follows the equation:

$$\ln (\eta/\eta_o) = l_n A + \Delta G^*/RT \qquad [1]$$

where A is a constant and ΔG* is the activation free energy of viscous flow. The densities of the solutions were close to the density of water; hence, kinematic corrections were neglected, and values of DG* were calculated from the slopes of straight lines (Fig. 3A). The DG* values are recorded in Table 1, along with the correlation coefficients (r).

The temperature dependence of DG*, according to Equation 2:

$$\delta(\Delta G^*/T)/\delta(1/T) = \Delta H^* \qquad [2]$$

was used to obtain the values of the activation enthalphy, ΔH* (Fig. 3B) (similar plots were obtained for other alkanols). All these values are recorded in Table 1. We see that DH* nearly covers the total contribution toward DG*, and, accordingly, the entropic contribution is negligible. In addition, the observed linearity in the l_n η_r/η_o vs. 1/T plots (Fig. 3A) also implies that the enthalpic and entropic contributions to DG* are independent of temperature.

The variation of ΔH* with concentration of various alkanols is illustrated in Figure 2 (inset). ΔH* seems to be the more important contribution related to the rupture of larger micelles to give smaller aggregates as its magnitude reflects the energy involved in the transition from larger aggregates to smaller ones.

The dependence of ΔG* and ΔH* on the nature and concentration of added alkanols is reflected in the data recorded in Table 1. The magnitude of these thermodynamic parameters shows that addition of hexOH promotes the micelles to larger aggregates (elongated rods) because the DH* values are higher for this alcohol, whereas prOH breaks the initially present, rod-shaped micelles into spherical shapes. However, for butOH and penOH, the size of the micelles initially increases and, then, at a certain concentration of the alcohol, the micelles break up to give smaller aggregates. Such a transfer would be determined by the energy required to create a passage (hole) for individual particles from one equilibrium position to another (28). The creation of such holes in the solvent for accepting the smallest broken micelles is not the only factor responsible for high values of DG*. The micelle reorganization in solution must require energy because the fact that the micelle breaks up implies an increase in surface area, different distribution of alkyl chains, a higher ionization degree (29) and/or repetition phenomenon. All these factors contribute to DG*. The behavior of alkanols, in general, can be looked upon as being due to the combined influence of two effects—hydrophobic interactions (intercalation and solubilization) and the nature of solvent (water + alcohol). The solubilization effect becomes operative only at higher concentrations of alkanols of four or five carbon atoms and is responsible for smaller micelles with a concomitant decrease in DH* values.

From this discussion we can conclude that organic molecules (e.g., alkanols) may be used as thickening/thinning agents in addition to inorganic salts in concentrated micellar solutions. The exact behavior depends upon temperature, chainlength, and concentration of added alkanol. Viscosity behavior of these mixed surfactant systems can be explained satisfactorily in terms of variation of R_p of "effective surfactant" (SDS + *n*-alkanol) in the same manner as used by other investigators to explain complex structures in solution (9,27,30).

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REFERENCES

1. Mittal, K.L., *Micellization, Solubilization and Microemulsions*, Vols. 1 and 2, Plenum Press, New York, 1977.
2. Shah, O.H. (ed.), *Surface Phenomena in Enhanced Oil Recovery*, Plenum Press, New York, 1981.
3. Rosen, M.J. (ed.), *Surfactants in Emerging Technologies*, Marcel Dekker, New York, 1987.
4. Armstrong, D.W., and W.L. Hinze (eds.), *Use of Ordered Media in Chemical Separations*, ACS Symposium Series 342, American Chemical Society, Washington D.C., 1987.
5. Wang, J., *Colloids and Surfaces 70*:15 (1993).
6. Kumar, S., Kirti, and Kabir-un-Din, *J. Am. Oil Chem. Soc. 71*:763 (1994).
7. Lucassen-Reynders, E.H., *Anionic Surfactant: Physical Chemistry of Surfactant Action*, Vol. 11, Surfactant Science Series, Marcel Dekker, New York, 1981, Chapter 2.
8. Mitchell, D.J., and B.W. Ninham, *J. Chem. Soc., Faraday Trans. 277*:601 (1981).
9. Hertel, G., and H. Hoffman, *Liq. Cryst. 5*:1883 (1989).
10. Guerin, G., and A.M. Bellocq, *J. Phys. Chem. 92*:2550 (1988).
11. Almgren, M., and J.E. Lofroth, *J. Colloid Interface Sci. 81*:486 (1981).
12. Lianos, P., J. Lang, C. Strazielle and R. Zana, *J. Phys. Chem. 86*:1019 (1982).
13. Almgren, M., and S. Swarup, *J. Colloid Interface Sci. 91*:256 (1983).
14. Croonen, Y., E. Gelade, M. van der Zegel, M. van der Auweraer, H. Vandendriessche, F.C. De Schryver and M. Almgren, *J. Phys. Chem. 87*:1426 (1983).
15. Hoeiland, H., O. Kvammen, S. Backlund and K. Rundt, in *Surfactants in Solution*, edited by K.L. Mittal, and B. Lindman, Plenum Press, New York, 1982.
16. Nguyen, D., and G.L. Bertrand, *J. Phys. Chem. 96*:1994 (1992).
17. Lindemuth, P.M., and G.L. Bertrand, *Ibid. 97*:7769 (1993).
18. Stephany, S.M., T.M. Kole and M.R. Fisch, *Ibid. 98*:11126 (1994).
19. Gamboa, C., and L. Sepulveda, *J. Colloid Interface Sci. 113*:566 (1986).
20. Ozeki, S., and S. Ikeda, *Ibid. 77*:219 (1980).
21. Hayase, K., and S. Hayano, *Bull. Chem. Soc. Japan 50*:83 (1977).
22. Bayer, O., H. Hoffman and W. Ulbricht, in *Surfactants in Solution*, Vol. 4, edited by K.L. Mittal, and P. Bothorel, Plenum Press, New York, 1986.
23. Backlund, S., J. Bakken, A.M. Blokhus, H. Hoeiland and I. Vikholm, *Acta Chem. Scand. A40*:241 (1986).
24. Tominaga, T., T.B. Stem and D.F. Evans, *Bull. Chem. Soc. Japan 53*:795 (1980).
25. Hirsch, E., S. Candau and R. Zana, *J. Colloid Interface Sci. 97*:318 (1984).
26. Prasad, Ch.D., and H.N. Singh, *Colloids and Surfaces 50*:37 (1990).
27. Mishra, B.K., S.D. Samant, P. Paradhan, S.B. Mishra and C. Manohar, *Langmuir 9*:894 (1993).
28. Glasstone, S., K.J. Laidler and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.
29. Lindman, B., and H. Wennerstrom, *Micelles: Topics in Current Chemistry*, Springer-Verlag, Berlin/Heidelberg/New York, 1980.
30. Rehage, H., and H. Hoffman, *J. Phys. Chem. 92*:4712 (1988).

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