

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Effect of Additives on the Clouding Behavior of an Ethylene Oxide-Propylene Oxide Block Copolymer in Aqueous Solution

Ketan Pandya<sup>a</sup>; Kishor Lad<sup>a</sup>; Pratap Bahadur<sup>a</sup>

<sup>a</sup> Department of Chemistry, South Gujarat University, Surat, India

**To cite this Article** Pandya, Ketan , Lad, Kishor and Bahadur, Pratap(1993) 'Effect of Additives on the Clouding Behavior of an Ethylene Oxide-Propylene Oxide Block Copolymer in Aqueous Solution', *Journal of Macromolecular Science, Part A*, 30: 1, 1 – 18

**To link to this Article:** DOI: 10.1080/10601329308009387

**URL:** <http://dx.doi.org/10.1080/10601329308009387>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# EFFECT OF ADDITIVES ON THE CLOUDING BEHAVIOR OF AN ETHYLENE OXIDE-PROPYLENE OXIDE BLOCK COPOLYMER IN AQUEOUS SOLUTION

KETAN PANDYA, KISHOR LAD, and PRATAP BHADUR\*

Department of Chemistry  
South Gujarat University  
Surat 395007, India

## ABSTRACT

Phase behavior of an ethylene oxide-propylene oxide block copolymeric surfactant Pluronic L-64 (MW = 2900, % PEO = 40) in the presence of various additives was studied from cloud point (CP) and phenol index measurements. Electrolytes with different sizes and polarizabilities of anions and cations showed an increase/decrease in cloud point; the effect of salts is discussed in terms of “salting in” and “salting out” and follows the Hofmeister series. The effect of various nonelectrolytes, viz., hydroxy compounds and amides, on the CP of L-64 was examined and discussed in terms of their influence on water structure. Ionic surfactant, viz., sodium dodecyl sulfate (SDS), increased the CP of L-64 which could be decreased drastically in the presence of small amounts of electrolytes. The clouding behavior of a mixed L-64 + SDS system in the absence/presence of salt is discussed primarily in terms of electrical charge on the micelle surface. The polyelectrolyte-like nature of the L-64 + SDS complex is shown from viscosity measurements.

## INTRODUCTION

The clouding behavior of nonionic surfactants in water is an interesting feature involving their practical usefulness. The clouding phenomenon shows the interactions between polyethylene oxide (PEO) chains become increasingly attractive

with increasing temperature in water or, in other words, water becomes a less good solvent. The molecular mechanism behind this has been disputed. A reasonable explanation is found in the conformational equilibrium of the PEO chains as suggested by Karlstrom [1]. The cloud point of nonionic surfactants can be conveniently decreased or increased in the presence of various additives, thus providing a way to use them under different conditions. Various additives have been examined for their influence on cloud point. Inorganic salts have been extensively studied, and the effect of anions and cations on the cloud point is generally expressed as "salting in" and "salting out." Studies on several nonelectrolytes, viz., hydroxy compounds, amides, saccharides, etc., have also been carried out because they provide information on the mechanism of protein denaturation. Also, a small quantity of ionic surfactant has a remarkable influence on the cloud point and micellar/adsorption characteristics of nonionic surfactants. Mixed surfactant systems, viz., ionic + nonionics, are often used in industrial formulations. The literature is exhaustive, and various studies involving different nonionic surfactants have been carried out to examine the effect of electrolytes [2-14], nonelectrolytes (like alcohols [15-18], phenols [19-26], amides [27-31], and saccharides [32-36]), and ionic surfactants [37-43].

Bahadur et al. [44-53] examined the aggregation behavior of nonionic surfactants, Pluronic (PEO-PPO-PEO block copolymers), in aqueous solutions, and they observed that the solution behavior is strongly influenced by an increase in

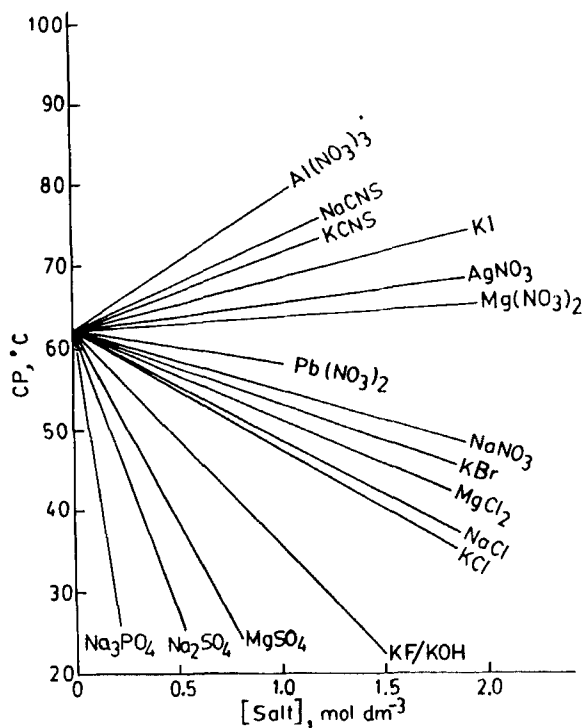


FIG. 1. Cloud point of L-64 in aqueous salt solutions.

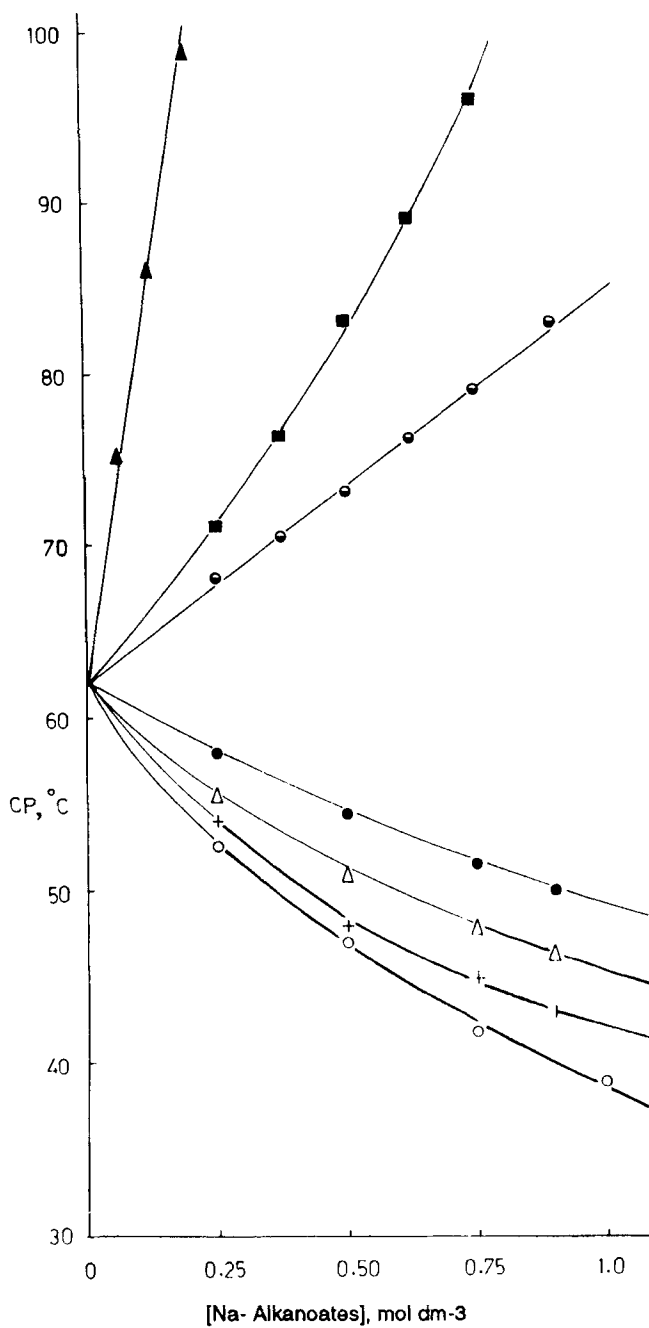


FIG. 2. Cloud point of L-64 in water in the presence of sodium alkanates: (+) Na-formate, (○) Na-acetate, (△) Na-propionate, (●) Na-butyrate, (◐) Na-valerate, (■) Na-caproate, (▲) Na-caprylate.

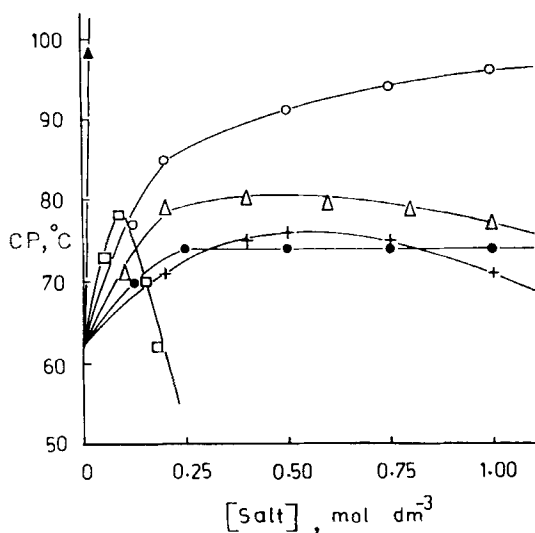


FIG. 3. Cloud point of L-64 in the presence of tetraalkylammonium bromides: (●)  $\text{NH}_4\text{Br}$ , (+)  $(\text{CH}_3)_4\text{NBr}$ , ( $\Delta$ )  $(\text{C}_2\text{H}_5)_4\text{NBr}$ , ( $\circ$ )  $(\text{C}_3\text{H}_7)\text{NBr}$ , ( $\square$ )  $(\text{C}_3\text{H}_{11})_4\text{NBr}$ , ( $\blacktriangle$ )  $\text{C}_{10}\text{H}_{23}\text{N}(\text{CH}_3)_3\text{Br}$ .

temperature in the presence of electrolytes, nonelectrolytes, and ionic surfactants. This paper reports a systematic study on clouding behavior of Pluronic L-64 in the presence of different additives.

## EXPERIMENTAL

### Materials

Pluronic L-64 (total MW = 2900, % PEO = 40) was supplied by SERVA, Germany, and used as received. Double distilled water from Pyrex glass apparatus was used. Fresh solutions filtered through  $0.45 \mu\text{m}$  Millipore filters were always used. Additives (viz., electrolytes, nonelectrolytes, and ionic surfactants) used were BDH/E. Merck chemicals of analytical reagent grade. Sodium alkanoates were prepared by neutralizing carboxylic acids (pure) with sodium hydroxide.

### Methods

*Cloud points* of 1 wt% L-64 solutions at different concentrations were measured by heating them in glass tubes immersed in a well-stirred heating bath. The solutions were stirred with a magnetic bar while being heated. The first appearance of turbidity was taken as the cloud point. The cloud point of L-64 in water agrees with the literature value. The cloud points were reproducible to  $0.5^\circ\text{C}$ .

*Phenol index:* L-64 solution (25 mL of 1.0 wt%) containing added salt/additive was titrated against 5.0% phenol in water at room temperature ( $27^\circ\text{C}$ ), and the

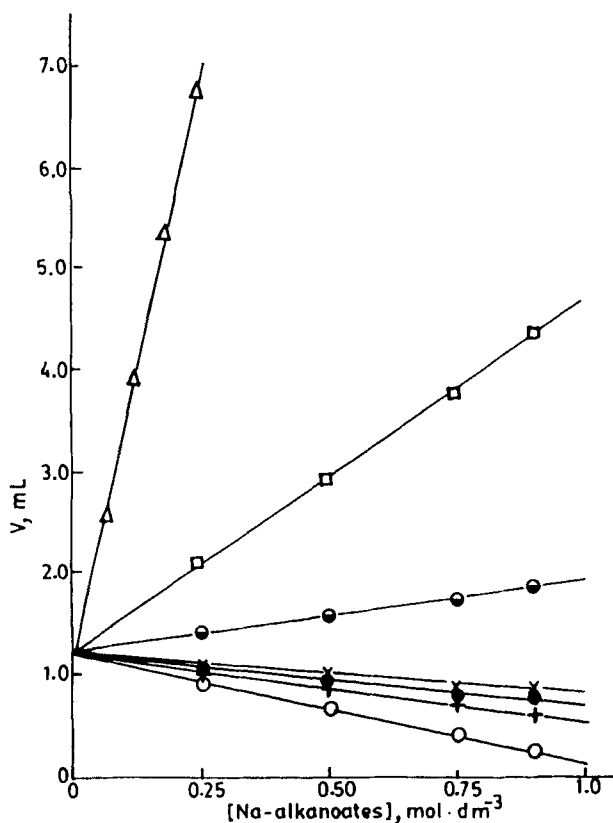


FIG. 4. Phenol index for L-64 in water in the presence of sodium alkanooates: (+) Na-formate, (○) Na-acetate, (●) Na-propionate, (×) Na-butyrate, (●) Na-valerate, (□) Na-caproate, (Δ) Na-caprylate.

milliliters of aqueous phenol solution used to bring about the first appreciable turbidity was taken as the phenol index.

*Viscosities* were measured using an Ubbelohde suspended level capillary viscometer with proper thermostating. The flow times always exceeded 150 s, and no kinetic energy corrections were necessary.

## RESULTS AND DISCUSSION

The effect of inorganic salts on the cloud point of Pluronic L-64 is shown in Fig. 1. These salts increase or decrease the cloud point (CP) depending on their nature; a CP decrease is generally due to dehydration of the ethylene oxide (EO) chain by the salt (salting out) whereas an increase reflects enhanced solubility of the EO chain in water (salting in). The influence of salts on the CP of L-64 is similar to what has been observed for polyethylene oxide (PEO) or nonionic surfactants and follows the Hofmeister or lyotropic series. Anions with a low lyotropic number,

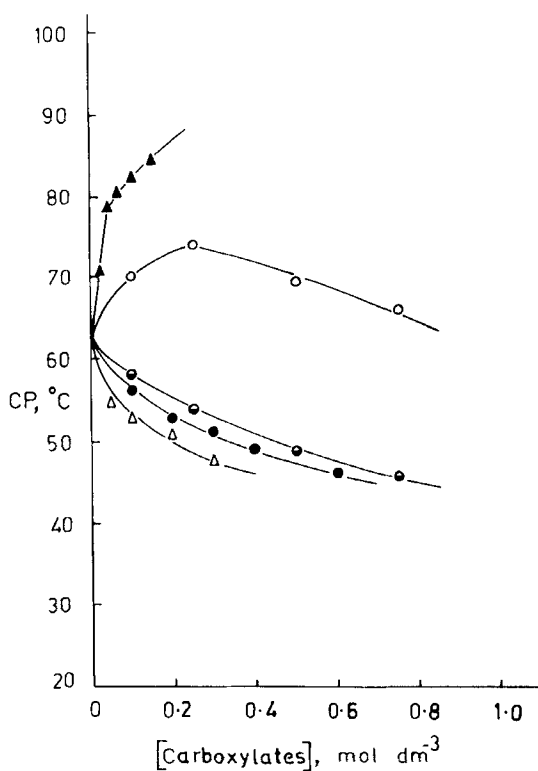


FIG. 5. Cloud point of L-64 in water-containing carboxylates: (○) Na-oxalate, (●) Na-malonate, (●) Na-succinate, (△) Na-adipate, (▲) Na-salicylate.

high hydration, or a strong water-structure-making tendency decrease the CP. Usually, the higher the valency of the anion, the more the CP decreases. Multivalent cations, due to their interaction with the ether oxygens of PEO, show a CP increase. Similarly, the ions  $\text{CNS}^-$  and  $\text{I}^-$  show an increase in the CP due to the enhanced solubility of L-64 in water. The net effect of salt on the CP of L-64 is reflected by the combined influences of both the anion and cation.

The effect of salts on the CP may be explained in terms of the polarity of the solute and the solvent. Ions prefer a water environment, and thus they increase the polarity of the solvent which decreases the solubility of L-64.  $\text{I}^-$  and  $\text{CNS}^-$  ions have a slight preference to associate with the L-64 molecule and increase its polarity, and thus they increase the solubility, resulting in an increase in the CP.

Apart from the effect of pure inorganic salts, two series of electrolytes, one with increasing anion size (carboxylates: formate, acetate, propionate, butyrate, valerate, caproate, caprylate) and the other with increasing cation size (tetraalkylammonium ions: methyl, ethyl, propyl, butyl, amyl), were also studied (Figs. 2 and 3). Figure 2 shows that smaller carboxylate ions show a CP decrease, similar to that of inorganic anions with the "salting out" effect. With an increasing chain length of carboxylate ion, the CP decreasing effect diminishes. On the other hand, higher carboxylate ions show a remarkable increase in the cloud point. This CP

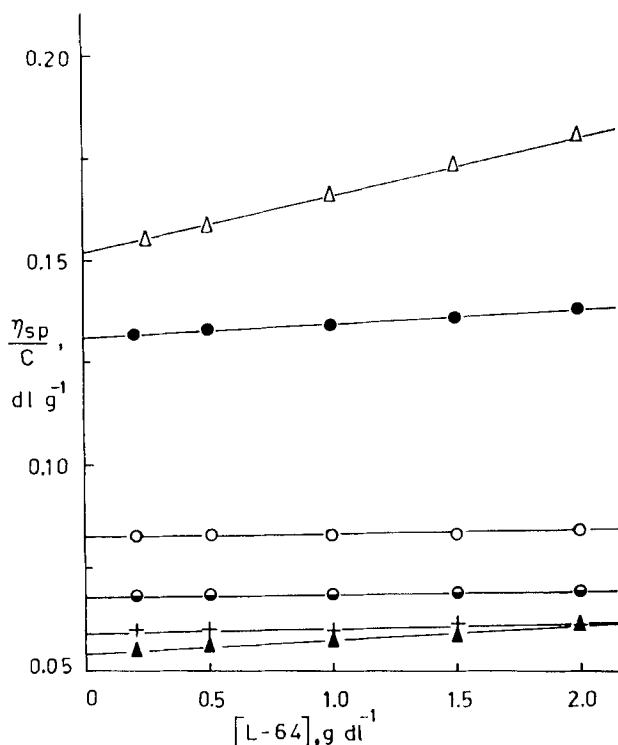


FIG. 6. Reduced viscosity,  $\eta_{sp}/c$ , of L-64 in the presence of sodium acetate as a function of L-64 concentration at 40°C: (▲)  $\text{H}_2\text{O}$ , (+) 0.1 M, (●) 0.2 M, (○) 0.4 M, (●) 0.6 M, (Δ) 0.65 M.

increase can be interpreted in the same manner as the presence of a very small amount of an ionic surfactant which co-micellizes with L-64 to form a mixed micelle (this effect will be discussed later). Valerate, caproate, and caprylate ions possess fairly long chains, and they behave like ionic surfactants. In the case of tetraalkylammonium ions, an increase in the CP was observed (which attains a constant value after a certain concentration) for all cations except tetraamylammonium ion which at low concentration first shows an increase in the CP which rapidly decreases at higher concentrations (Fig. 3). The increase in the CP by tetraalkylammonium ions can generally be considered to be due to the more favorable interaction between water and the PEO chain. The tetraamylammonium ion, due to its longer amyl chain, increases the hydrophobicity of the solvent (water) and makes the hydrophilic PEO chain less soluble, and thus the CP decreases. Figure 3 also shows the effect of a cationic surfactant, trimethylammonium bromide, for comparison. A steep rise in the CP in the presence of a small amount of cationic surfactant is anticipated.

To further examine the phase separation of L-64 solutions in the presence of salts, a few phenol index measurements were also made. The measured phenol index for L-64 in the presence of the same sodium alkanoates followed the same trend as observed in their effect on the CP (Fig. 4). The mechanism of interaction of various nonionic surfactants and phenol has been the subject of many studies [20-24].



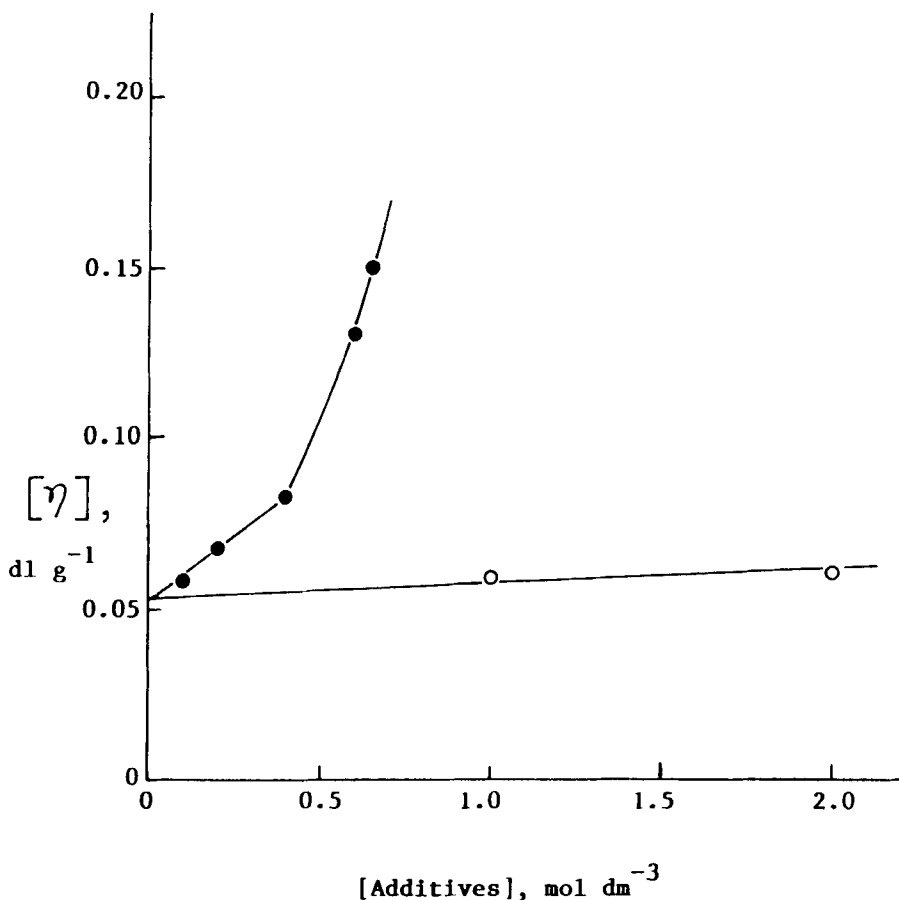


FIG. 7. Intrinsic viscosity,  $[\eta]$ , of L-64 as a function of additives concentration at 40°C: (●) Na-acetate, (○) urea.

Phenol depresses the CP of nonionic surfactants remarkably. Thus, the progressive addition of phenol causes clouding and phase separation at room temperature (27°C) before reaching the limits of solubilization in the usual meaning. The purpose of this work is to point out the qualitative similarities in two different methods of hydrophilic lipophilic balance (HLB) determination based on cloud point and phenol index measurements.

Figure 5 shows the effect of sodium dicarboxylates with an increasing number of methylene group. Their effect on the CP is opposite to that shown by monocarboxylates. The two carboxylate groups at the ends of methylene chain perhaps put constraints on the incorporation of the ion into the micelle. The dicarboxylate ions thus show a CP decrease. A remarkably steep rise in CP was observed for sodium salicylate.

A few viscosity measurements on L-64 solutions in the presence of electrolytes and at different temperatures were made. Figure 6 illustrates a representative plot for sodium acetate. The reduced viscosities of L-64 solutions at different concentra-

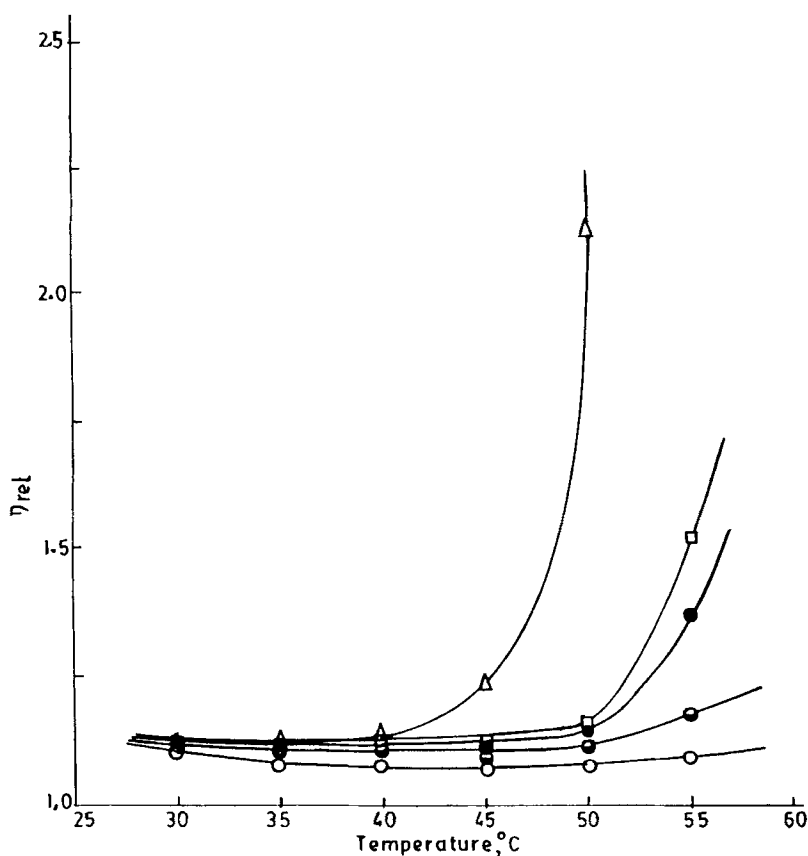


FIG. 8. Relative viscosity,  $\eta_{rel}$ , of L-64 in the presence of additives as a function of temperature: ( $\Delta$ ) 0.5 M Na-acetate, ( $\square$ ) 0.1 M Na-acetate, ( $\bullet$ ) 0.1 M TMABr, ( $\ominus$ ) 0.1 M Na-caproate, ( $\circ$ ) 0.5 M Na-caproate.

tions in water and sodium acetate (0.1–0.65 M) showed linear plots from which extrapolation yielded the intrinsic viscosity (Fig. 7). Small intrinsic viscosity  $[\eta]$  values speak in favor of spherical micelles of L-64, and they increase with increasing salt concentration; the increase is rapid at higher salt concentrations. An increase in  $[\eta]$  reflects micellar growth, particularly at temperatures close to the CP, as has been discussed earlier [45, 49]. Figure 8 shows variations in the relative viscosity as a function of temperature for L-64 solutions in the presence of various salts which show a CP decrease. They exhibit an increase in relative viscosity in the temperature range 40–55°C, which is self-explanatory. Reduced viscosity,  $\eta_{sp}/c$ , plots for L-64 in long-chain carboxylate solutions did not show linearity; an increase in  $\eta_{sp}/c$  at low L-64 concentrations shows a polyelectrolyte-like nature due to interactions between long-chain carboxylate ions and L-64 (Fig. 9).

Different kinds of nonelectrolytes were also examined for their effect on the cloud point. The effect of different amides on the CP is first considered. Five amides (viz., urea, thiourea, acetamide, formamide, and dimethylformamide) were used; each showed an increase in CP (Fig. 10). The increasing CP effect of ureas

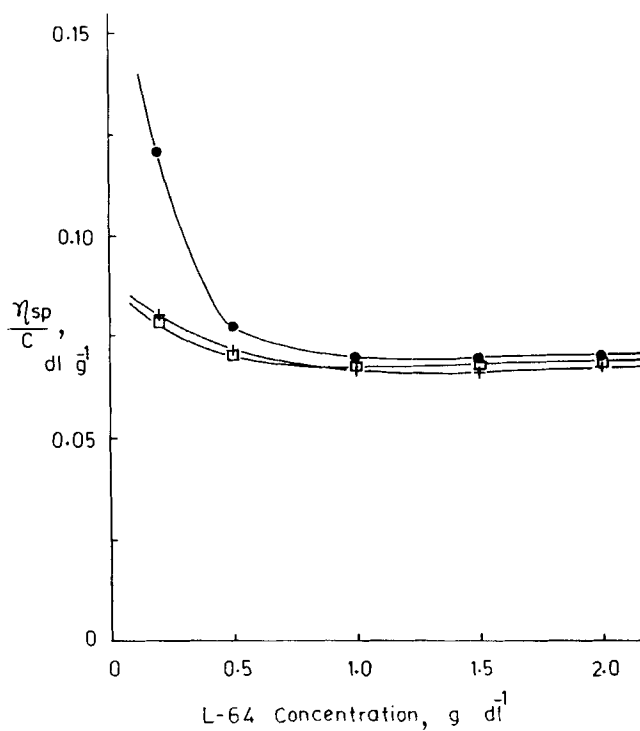


FIG. 9. Intrinsic viscosity,  $[\eta]$ , of L-64 in the presence of sodium valerate as a function of L-64 concentration at 40°C: ( $\square$ ) 0.1 M, ( $\bullet$ ) 0.2 M, ( $+$ ) 0.4 M.

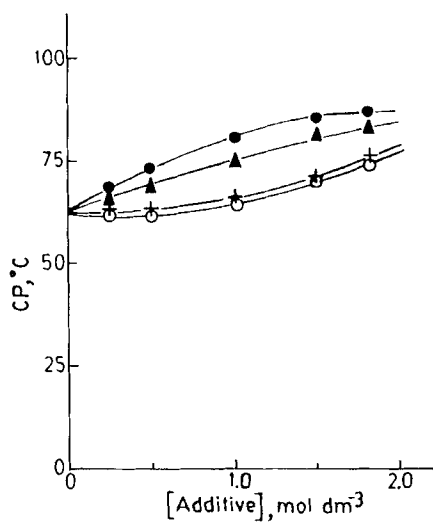


FIG. 10. Cloud point of L-64 in the presence of amides: ( $\bullet$ ) Urea, ( $\blacktriangle$ ) formamide, ( $+$ ) acetamide, ( $\circ$ ) thiourea.

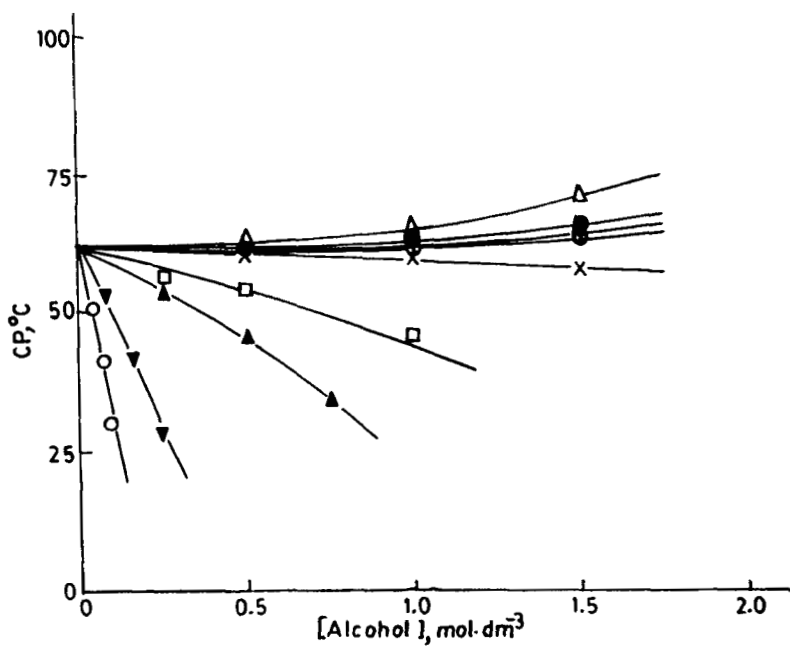


FIG. 11. Cloud point of L-64 in the presence of alcohols: (●) Methanol, (●) ethanol, (+) propanol-1, (Δ) propanol-2, (×) 2 methyl propanol-2, (▲) butanol-1, (□) butanol-2, (▼) pentanol-1, (○) phenol.

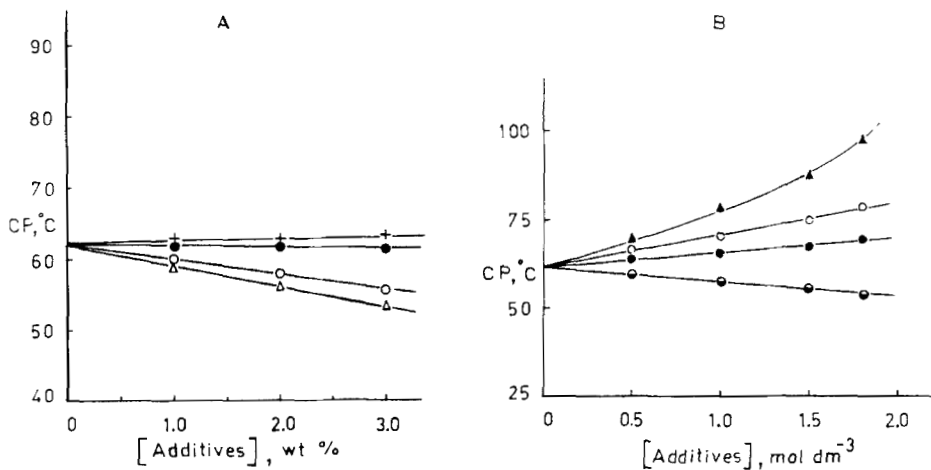


FIG. 12. (A) Cloud point of L-64 in the presence of additives: (+) Ethylene glycol, (●) diethylene glycol, (○) PEG-400, (Δ) PEG-6000. (B) Cloud point of L-64 in the presence of monoalkylethers of ethylene glycol: (●) Methyl, (○) ethyl, (▲) butyl, (◐) sorbitol.

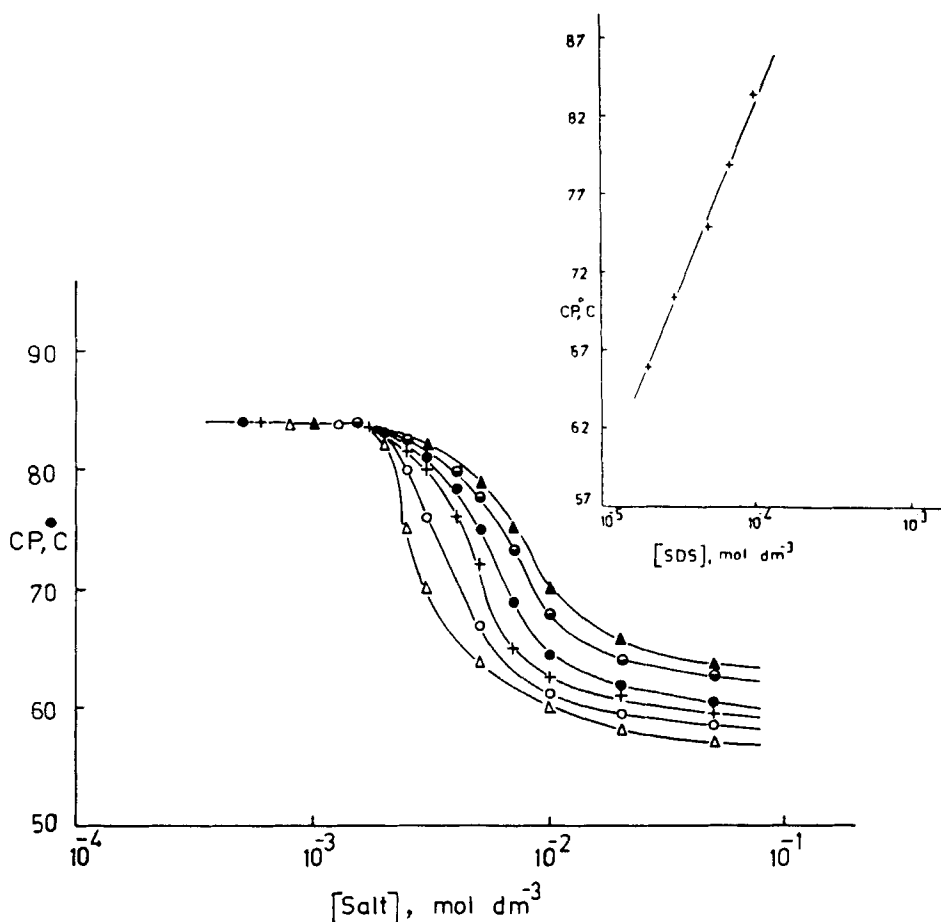


FIG. 13. Cloud point of L-64 in the presence of SDS (0.1 mM) as a function of molar concentration of added salts: (▲) KCNS, (⊖) KI, (●) KBr, (+) KCl, (○) KF, (△) K<sub>2</sub>SO<sub>4</sub>. The inset figure shows the cloud point of L-64 in the presence of SDS.

and other amides on solutions of nonionic surfactants has been examined before [30, 31]. These amides decrease the water structure and thus favor hydration of PEO chain, resulting in an increase in the CP. The viscosities of L-64 in aqueous urea solutions were measured, and the calculated intrinsic viscosities at different urea concentrations (1.0 and 2.0 M) did not show any significant change. This is expected for additives which have the tendency to increase the CP (Fig. 7).

The effect of various hydroxy compounds on the CP of L-64 was studied in detail. The effect of monohydric alcohols on the CP is shown in Fig. 11. While lower alcohols (C<sub>1</sub>-C<sub>3</sub>) have a slight increasing effect on the CP, higher alcohols decrease the CP; the longer the carbon chain in the alcohol, the stronger is the CP decrease. Furthermore, this effect weakens with branching in the chain or a shift of the -OH group from the end of the chain. The effect of added alcohols on the CP can be interpreted by assuming that short-chain alcohols prefer a water environment

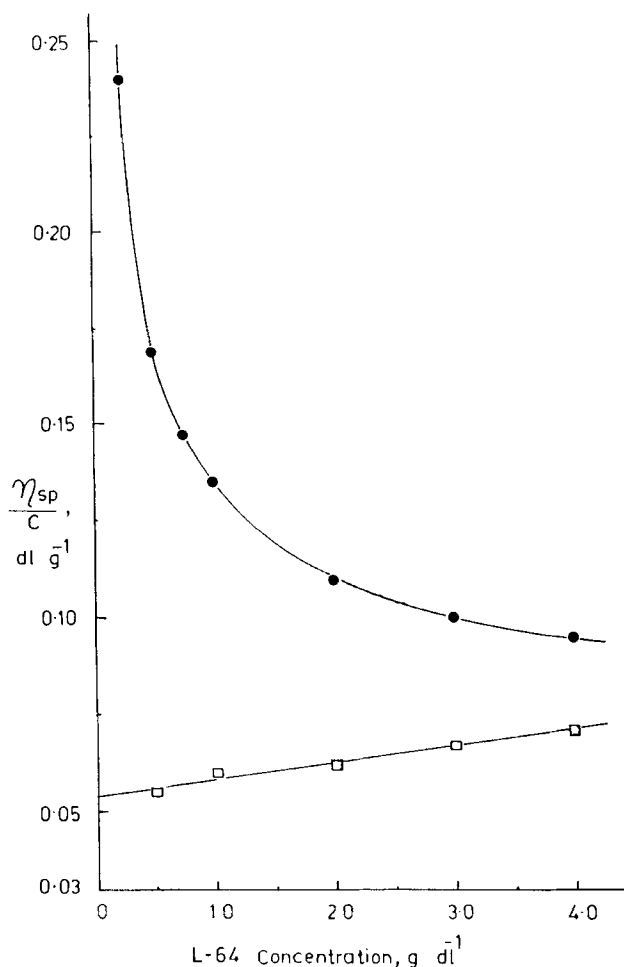


FIG. 14. Reduced viscosity,  $\eta_{sp}/c$ , of L-64 in the presence of water and SDS as a function of L-64 concentration at 40°C: (□) Water, (●) 2.0 mM SDS.

while long-chain alcohols are effectively attracted to the L-64 molecules to an extent that depends on the chain length of the alcohol. Therefore, short-chain alcohols will decrease the polarity of the solvent, thereby increasing the solubility of L-64 and also the CP. Long-chain alcohols, on the other hand, will tend to associate with the L-64 molecules, making the polymer more hydrophobic and therefore also less water soluble.

It should be noted here that long-chain ( $C_5$ ,  $C_6$ ) carboxylates show a strong CP increase in contrast to the corresponding alcohols where a steep fall in CP is seen. The main difference between the alcohols and the carboxylates is the charged head group of the latter. This leads to three consequences: 1) a longer hydrocarbon chain is needed in order to make the long carboxylate ion bind to L-64; 2) the L-64 long carboxylate complexes are charged, leading to an electrostatic repulsion between the L-64 molecules, thereby causing an increase in the CP; 3) different

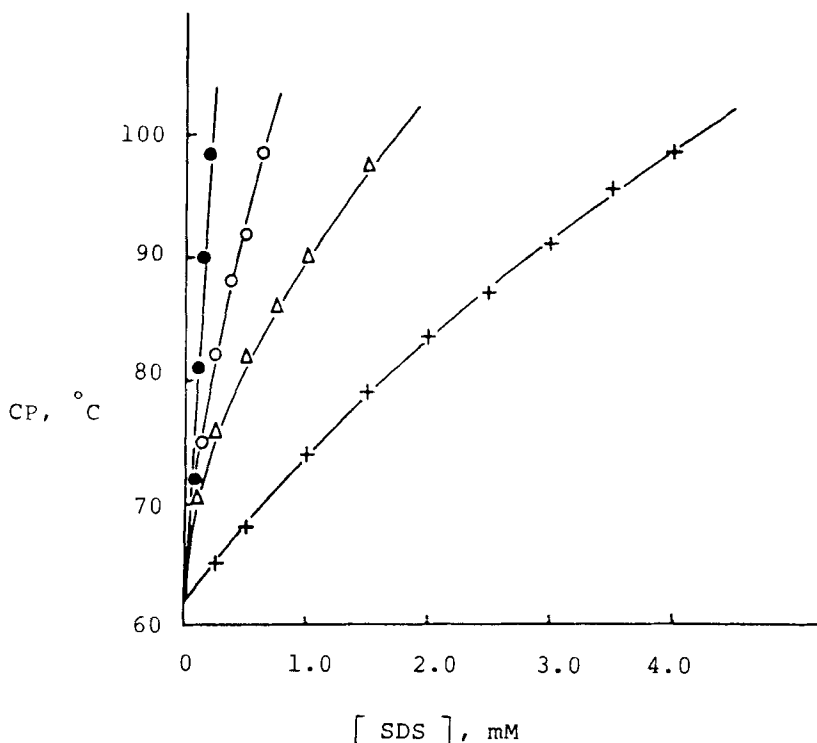


FIG. 15. Cloud point of L-64 in the presence of NaCl as a function of the molar concentrations of added SDS: (●) 5 mM, (○) 10 mM, (△) 25 mM, (+) 50 mM.

parts of the same L-64 molecule will repel one another. The overall increase in CP is, however, quite small due to the near-balance between the attractive forces caused by the hydration chains and the repulsive electrostatic forces.

A very small amount of phenol decreases the CP of L-64 significantly to room temperature (Fig. 11). A similar behavior was observed by Donbrow and Azaz [25] for cetomacrogel in the presence of various phenols. It is thought that the sharp fall in the CP of L-64 in the presence of phenols at specific solute concentrations might be due to saturation of the micelles. The influence of phenols on the CP of L-64 may be due to a combination of hydrogen bonding, favoring retention of these molecules in the ethylene oxide region of the micelles, and water structuring exercised by solubilizate molecules in this environment.

The effect of ethylene glycol, its oligomers, and its polymers on the CP of L-64 is shown in Fig. 12(A). A slight increase in CP by EG and DEG is due to preferential solvation of the surfactant molecules. Micelle formation of a nonionic surfactant in water-EG mixtures has been examined by Ray and Nemethy [54]. These authors observed an increase in critical micelle concentration (cmc) and have accounted for this effect as due to partial changes in the solvent environment of the EO chain of the surfactant. PEGs, on the other hand, showed a decrease in the CP of nonionic surfactants. The effect of PEGs on the clouding behavior of polyoxyethylene nonyl phenol ethers has been studied by Marszall [26]. Depending on the

chain length of the surfactant, the CP decreases or increases in the presence of PEGs. A decrease in the CP of L-64 upon the addition of PEGs (which are themselves very hydrophilic and have  $CP > 100^\circ\text{C}$ ) reveals some interaction between L-64 and PEG although such an interaction may be very weak.

The effect of ethylene glycol and its monoalkylether substitutes is shown in Fig. 12(B). A linear increase in the CP in the following order was always seen: MBEEG > MEEEG > MMEEG (butyl, ethyl, and methyl, respectively). The increase in the CP of L-64 by glycol and its ethers is mainly due to the weakening of hydrophobic interaction, although the interaction of the polyethylene oxide moiety of L-64 with these additives and the self-aggregating behavior of glycol ethers, particularly for monobutyl ether, may also affect the clouding phenomena. A detailed study on the effect of glycol ethers on cmc and the CP of nonionic surfactants has been made by Marszall [26]. The trend in our results resembles that observed by Marszall for polyoxyethylene nonyl phenols.

In Fig. 12 we have shown the effect of sorbitol. A gradual decrease in the CP with an increase in sorbitol concentration was observed. Some other polyhydric alcohols (including saccharides, namely mannitol, glucose, sucrose, fructose, etc.) showed a similar decrease. A decrease in CP with saccharides has been observed for polyethylene glycol (PEG) and for sorbitol on polysorbate, a nonionic surfactant [33, 36]. Sjöberg et al. [35] showed that all saccharides decrease the CP of PEG, which is well described by mean field theory. Also, an explanation was given for the difference between the saccharides in their ability to decrease the CP in aqueous PEG solutions.

The effect of sodium dodecyl sulfate (SDS) concentration on the CP of L-64 in water is shown in Fig. 13. A drastic increase in the CP of nonionic surfactants in the presence of a small amount of ionic surfactant was observed, which is in agreement with previous studies on ionic + nonionic surfactant systems [42, 43]. The incorporation of an ionic surfactant into nonionic micelles creates an electric charge on the micellar surface and thus causes repulsion between the micelles and increases the CP of L-64. It was shown earlier in fluorescence [45] and dynamic light-scattering [53] studies that a small amount of SDS (below its own cmc) incorporates into L-64 micelles.

An interesting observation on the clouding behavior of L-64 + SDS in the presence of salt was made. The added salt significantly alters the CP of L-64 in a higher concentration range (from 0.5 to 2.0 M salt, as shown in Fig. 1), but lower concentrations (up to  $10^{-2}$  M) do not change the CP by more than  $5^\circ\text{C}$ . However, when SDS is added to L-64, a CP decrease of about  $15\text{--}20^\circ\text{C}$  can be clearly seen, even at lower salt concentrations. Figure 14 shows the CP of 1 wt% L-64 (0.1 mM SDS) in the presence of potassium salts. The CP decrease with anions is of the same order as observed for L-64 in the absence of SDS at high salt concentrations. Similar observations on the CP of a nonionic surfactant, Triton X-100, in the presence of SDS and salt were made by Marszall [43].

It appears that the CP of L-64 in the presence of SDS and salt seems to be primarily electrostatic in nature. L-64 micelles in the presence of SDS possess some surface charges which could be effectively neutralized by adding a small quantity of salt, thus causing a decrease in the CP of the L-64 + SDS (0.1 mM) system ( $= 83^\circ\text{C}$ ) to a value close to about  $62^\circ\text{C}$  (the CP of L-64 in water). Furthermore, viscosity results on L-64 + SDS systems clearly depict the polyelectrolyte, indicating interaction between two surfactants (Fig. 14).



The CP of aqueous solutions of L-64 in NaCl in the presence of SDS is shown in Fig. 15. As observed before without salt addition, the CP increases steeply in the presence of SDS. A high SDS concentration is required to increase the CP in the presence of salt. However, no minimum in CP was observed, as previously noted by Karlstrom et al. [16].

## CONCLUSION

The cloud point of a nonionic surfactant is a unique characteristic that helps in deciding its function and practical utility under various conditions. Different additives (electrolytes and nonelectrolytes) have shown a marked influence on the cloud point of L-64; a decrease or an increase in the cloud point in the presence of these additives is explained. When an ionic surfactant (SDS) is present in a small amount, an abrupt increase in the cloud point leading to the formation of mixed micelles is shown. The polyelectrolyte-like nature of such entities reveals the interacting features of mixed surfactants.

## ACKNOWLEDGMENT

P.B. is thankful to CSIR, India, for financial support.

## REFERENCES

- [1] G. Karlstrom, *J. Phys. Chem.*, **89**, 4962 (1985).
- [2] M. J. Schick, *Nonionic Surfactants*, 2nd ed., Dekker, New York, 1987.
- [3] V. Degiorgio, in *Physics of Amphiphiles: Micelles, Vesicles and Microemulsions* (V. Degiorgio and M. Corti, Eds.), North Holland, Amsterdam, 1985, p. 303.
- [4] T. Warnheim, J. Bokstrom, and Y. Williams, *Colloid Polym. Sci.*, **266**, 562 (1988).
- [5] H. Fujimatsue, S. Ogasawara, and S. Kuriowa, *Ibid.*, **266**, 594 (1988).
- [6] Th. van der Boomgaard, Sh. M. Zourab, and J. Lyklema, *Prog. Colloid Polym. Sci.*, **68**, 25 (1983).
- [7] K. Weckstrom, *Chem. Phys. Lett.*, **119**, 503 (1985).
- [8] C. Holtzcherer and F. Candau, *J. Colloid Interface Sci.*, **125**, 97 (1988).
- [9] E. Florin, R. Kjellander, and C. Eriksson, *J. Chem. Soc., Faraday Trans. I*, **80**, 2889 (1984).
- [10] K. D. Collins and M. W. Q. Washabaugh, *Rev. Biophys.*, **18**, 323 (1985).
- [11] K. P. Ananthapadmanabhan and E. D. Goddard, *Langmuir*, **3**, 25 (1987).
- [12] T. Imae, M. Sasaki, A. Abe, and S. Ikeda, *Ibid.*, **4**, 414 (1988).
- [13] W. Binana-Limbele, N. M. Van Os, L. A. M. Rupert, and R. Zana, *J. Colloid Interface Sci.*, **144**, 458 (1991).
- [14] M. J. Garvey and I. D. Robb, *J. Chem. Soc., Faraday Trans. I*, **75**, 993 (1979).

- [15] M. Ueda, T. Urahata, A. Katayama, and N. Kuroki, *Colloid Polym. Sci.*, **258**, 1202 (1980).
- [16] A. Carlsson, G. Karlstrom, and B. Lindman, *Langmuir*, **2**, 536 (1986).
- [17] M. Malmsten and B. Lindman, *Ibid.*, **6**, 357 (1990).
- [18] Zs. Bedo, E. Berecz, I. Lakatos, and J. Lakatos-Szabo, *Prog. Colloid Polym. Sci.*, **82**, 229 (1990).
- [19] W. P. Evans, *J. Pharm. Pharmacol.*, **16**, 323 (1964).
- [20] D. L. Wedderburn, in *Advances in Pharmaceutical Sciences* (H. S. Bean, A. H. Beckett, and J. E. Carless, Eds.), Academic Press, London, 1964.
- [21] B. N. Kabadi and E. R. Hammarlund, *J. Pharm. Sci.*, **55**, 1069 (1966).
- [22] P. H. Elworthy, A. T. Florence, and B. Macfarlane, *Solubilization by Surface-Active Agents*, Chapman and Hall, London, 1968.
- [23] K. Thoma, E. Ullmann, and O. Fickel, *Arch. Pharm.*, **303**, 289 (1970).
- [24] J. J. Jacobs, R. A. Anderson, and T. R. Watson, *J. Pharm. Pharmacol.*, **23**, 786 (1971).
- [25] M. Donbrow and E. Azaz, *J. Colloid Interface Sci.*, **57**, 20 (1976).
- [26] L. Marszall, *Ibid.*, **65**, 589 (1978).
- [27] M. J. Shick, *J. Phys. Chem.*, **68**, 3585 (1964).
- [28] M. F. Emerson and A. Holtzer, *Ibid.*, **71**, 3320 (1967).
- [29] S. K. Han, S. M. Lee, and H. Schott, *J. Colloid Interface Sci.*, **126**, 393 (1988).
- [30] S. K. Han, S. M. Lee, M. Kim, and H. Schott, *Ibid.*, **132**, 444 (1989).
- [31] G. Briganti, S. Puvvada, and D. Blankshtein, *J. Phys. Chem.*, **95**, 8989 (1991).
- [32] M. Ueda, T. Urahata, A. Katayama, and N. Kuroki, *Colloid Polym. Sci.*, **257**, 973 (1979).
- [33] J. L. Zatz and R-Y. Lue, *J. Pharm. Sci.*, **76**, 157 (1987).
- [34] L. Cantu, M. Corti, V. Degiorgio, H. Hoffman, and W. Ulbricht, *J. Colloid Interface Sci.*, **116**, 384 (1987).
- [35] A. Sjoberg, G. Karlstrom, and F. Tjerneld, *Macromolecules*, **22**, 4512 (1989).
- [36] D. Attwood, G. Ktistic, Y. McCormick, and M. J. Story, *J. Pharm. Pharmacol.*, **41**, 83 (1989).
- [37] K. Nakamura, R. Endo, and M. Takeda, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 2087 (1977).
- [38] A. K. Jain, V. K. Velu, and R. P. B. Singh, *Indian J. Chem.*, **23A**, 308 (1984).
- [39] N. J. Turro, P. L. Kuo, P. Somasundaram, and K. Wrong, *J. Phys. Chem.*, **90**, 288 (1986).
- [40] J. H. Chang, M. Ohno, E. Kunio, and K. Meguro, *Yakagaku*, **37**, 1122 (1988).
- [41] P. Bahadur, N. V. Sastry, Y. K. Rao, and G. Riess, *Colloids Surf.*, **29**, 343 (1988).
- [42] B. S. Valaulikar and C. Manohar, *J. Colloid Interface Sci.*, **108**, 403 (1985).
- [43] L. Marszall, *Langmuir*, **4**, 90 (1988).
- [44] W. Brown, K. Schillen, M. Almgren, S. Hvidt, and P. Bahadur, *J. Phys. Chem.*, **95**, 1850 (1991).
- [45] M. Almgren, J. Alsins, and P. Bahadur, *Langmuir*, **7**, 446 (1991).
- [46] P. Bahadur, P. Li, M. Almgren, and W. Brown, *Ibid.*, **8**, 1903 (1992).

- [47] M. Almgren, J. Van Stam, C. Lindblad, P. Li, P. Stilbs, and P. Bahadur, *J. Phys. Chem.*, **95**, 5677 (1991).
- [48] M. Almgren, P. Bahadur, M. Jansson, P. Li, W. Brown, and A. Bahadur, *J. Colloid Interface Sci.*, **151**, 157 (1992).
- [49] P. Bahadur, K. Pandya, M. Almgren, P. Li, and P. Stilbs, *Colloid Polym. Sci.*, In Press.
- [50] P. Bahadur and K. Pandya, *Langmuir*, In Press.
- [51] K. Pandya, P. Bahadur, T. N. Nagar, and A. Bahadur, *Colloids Surf.*, Submitted.
- [52] K. Pandya, P. Bahadur, and A. Bahadur, *Tenside Surf. Deterg.*, Submitted.
- [53] P. Bahadur et al., Unpublished Results.
- [54] A. Ray and G. Nemethy, *J. Phys. Chem.*, **75**, 809 (1971).

Received May 27, 1992