

Clouding Phenomenon in Ionic Micellar Solutions: Role of the Counterion

Sanjeev Kumar, Ziya Ahmad Khan, and Kabir-ud-Din*

Department of Chemistry, Aligarh Muslim University, Aligarh 202 002, India

ABSTRACT: Clouding is rarely observed with ionic surfactants. Herein we report the occurrence of clouding in sodium dodecyl sulfate (SDS, an anionic surfactant) solutions on addition of different symmetrical and unsymmetrical quaternary phosphonium bromides (tetra-*n*-butylphosphonium, tetraphenylphosphonium, and *n*-propyltriphenylphosphonium). Cloud point (CP) measurements were made with solutions having different SDS/salt combinations. The nature of the counterion had a crucial role in the occurrence of the phenomenon, whereas substitution of an alkyl chain by a phenyl ring made the salt more effective near ambient temperature. A linear relationship between the SDS and salt concentrations was obtained. It is proposed that both the electrostatic charge and the hydration state of the headgroup region are influenced by counterion addition and that the net charge or volume of the counterion has a key role to play in the overall phenomenon. The effect of the addition of some hydroxy compounds on CP variations in these SDS + salt systems was also studied, and the data were interpreted on the basis of incorporation of these compounds in the micellar headgroup region. The nature of the counterions influenced this incorporation.

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KEY WORDS: Cloud point, counterion, micellar solution, quaternary salts, SDS.

Phase separation on heating is a general phenomenon that has been investigated in great detail in the context of non-ionic surfactants (1–3). Beyond a characteristic temperature called the cloud point (CP), these micellar solutions turn cloudy. The results have been discussed on the basis of developing attractive interactions in micelles on heating (1). These studies showed that removal of interfacial water from the micellar surface is the key requirement (4,5) for the clouding phenomenon in surfactant solutions. The removal of water changes the local dielectric constant (d_c) (6,7), which may have a role to play in the clouding phenomenon as a whole. The d_c of water is known to decrease as the temperature increases (8). However, the molecular origin of such attractions is a matter of speculation, and it is not evident that hydrogen-bonding interactions play a role (9).

*To whom correspondence should be addressed.

E-mail: kabir7@rediffmail.com

Abbreviations: Bu₄PBr, tetra-*n*-butylphosphonium bromide; CP, cloud point; ϕ_4 PBr, tetraphenylphosphonium bromide; Pr ϕ_3 Br, *n*-propyltriphenylphosphonium bromide; SDS, sodium dodecyl sulfate.

Under ordinary conditions of use, surfactants are not present in isolation; other ingredients, such as electrolytes (commonly present in surfactant products), strongly affect their clouding behavior. The CP plays a vital role in indicating the limit of their solubility and hence the end use in physicochemical processes. The practical importance of the phenomenon lies in its application to separations or pre-concentrations and to the fact that detergency reaches a maximum just below the CP (10–13). The separation based on the CP phenomenon offers a simple, rapid, sensitive, and inexpensive alternative to other separation or pre-concentration techniques based on organic solvents.

Ionic surfactant solutions are complex. Since the micelles are charged, there must be an electrostatic repulsion between the micelles in addition to the van der Waals attraction force. Mikulich *et al.* (14) reported that the degree of solvation increases with increasing surfactant headgroup size. Solvation counteracts the CP phenomenon. However, the occurrence of CP in ionic surfactant solutions under special conditions [high salt concentration (15), presence of a specific counterion (16–19), or special molecular architecture of the surfactant (20)] has been reported. Reports on the clouding behavior of anionic surfactants in the presence of cationic surfactants also have appeared (21–25). Yu and Xu (26) suggested that the CP phenomenon occurs owing to penetration of the alkyl chains of the counterion into the surface layers of two neighboring micelles, whereas Raghavan *et al.* (18) suggested that highly hydrophobic counterions (that can bind strongly to ionic headgroups) are prone to cause phase separation. Appell and Porte (15) interpreted the phenomenon as being analogous to the phase separation of polymers in poor solvents. Buckingham and coworkers (20) gave a mechanism involving hydration shells to account for CP.

It was observed that salts with four or more carbon atoms in the alkyl chain (R) caused clouding in sodium dodecylsulfate (SDS) + tetra-*n*-alkylammonium bromide (R₄NBr) systems, whereas the lower numbers of carbons failed to produce the phenomenon (16). Also, quaternary cationic surfactants with tri-*n*-butyl ammonium headgroups showed CP in aqueous solutions (20). Thus, the nature of the headgroup and the counterion seems to be of prime importance to observe the clouding phenomenon. In this work, the CP behavior of anionic SDS in the presence of quaternary phosphonium salts is described, and the effect of the presence

of phenyl rings in the quaternary counterion is compared with the counterion having butyl chains. For this purpose, tetra-*n*-butylphosphonium bromide (Bu_4PBr), tetraphenylphosphonium bromide ($\phi_4\text{PBr}$), and *n*-propyltriphenylphosphonium bromide ($\text{Pr}\phi_3\text{PBr}$) were used. The effect of the addition of some hydroxy compounds on CP variation in the foregoing systems was also considered.

EXPERIMENTAL PROCEDURES

SDS (99%; Sigma, St. Louis, MO), Bu_4PBr ($\geq 98\%$; Fluka, Buchs, Switzerland), $\phi_4\text{PBr}$ (98+%; Lancaster, Morecambe, England), and $\text{Pr}\phi_3\text{PBr}$ (99%; Lancaster) were used as received. Ethanol, ethanediol, propanediol, and glycerol were of the highest available purity. All the salts were dried for at least 72 h before use in a vacuum drying oven. The water used to prepare the solutions was deionized and doubly distilled.

Samples were prepared by taking requisite amounts of SDS and a particular salt. The sample container was a 1.0-cm diameter Pyrex glass tube, with a ground glass stopper to prevent evaporation.

The sample container was placed in a temperature-controlled water bath with a stability of $\pm 0.1^\circ\text{C}$. The CP was measured by cycling the bath temperature above and below the actual CP. The actual CP was found by starting the run with the sample in one phase-visually transparent region. The temperature was then increased until the sample became visibly cloudy; this temperature was noted. The temperature was then lowered until the sample became clear again. The temperature was cycled (at least three times) in this way to obtain the CP temperature (reproducibility: $\pm 0.5^\circ\text{C}$). Increments of temperature change near the CP were $0.1^\circ\text{C}/\text{min}$. After determining the CP at a given salt concentration, the system was diluted to a lower salt concentration with the respective aqueous solution of SDS, and this procedure was repeated. It is important to note that the CP was determined from the appearance of clouding without waiting for macroscopic phase separation to occur, which would take longer for a given sample.

RESULTS AND DISCUSSION

The CP observed with 50 mM SDS + quaternary phosphonium bromides are shown in Figure 1 as CP vs. salt concentration for the three salts used. It was seen that the salt concentration needed to observe the CP with SDS (50 mM) depended upon the nature of the salt. In SDS, the CP occurred at a lower concentration of Bu_4PBr than for the other two salts, but the rate of decrease of CP per mole of salt was higher with $\phi_4\text{PBr}$. The nature of the counterion and its possible effect on the micellar surface charge should be considered when interpreting the effect of added salts on the CP of SDS micellar solutions.

The appearance of a CP in SDS solutions with quaternary bromides has been described before (16,17); however, a few

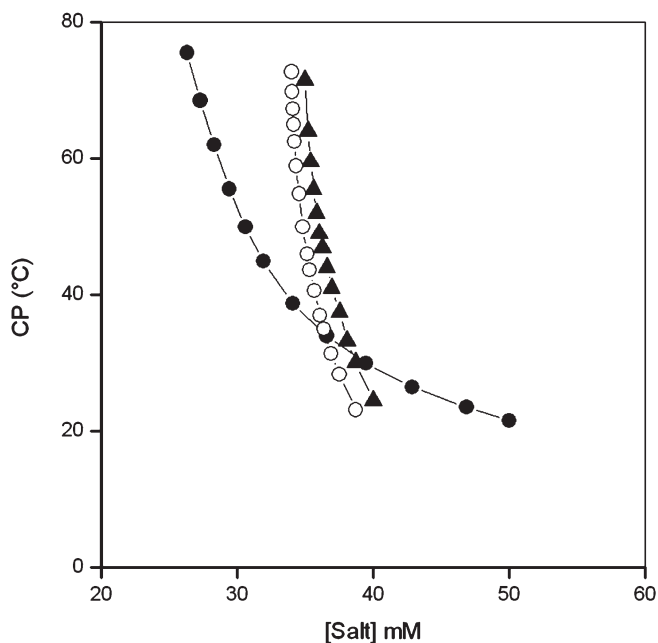


FIG. 1. Variation of the cloud point (CP) with salt concentration for 50-mM sodium dodecylsulfate (SDS) solutions: ●, tetra-*n*-butylphosphonium bromide (Bu_4PBr); ○, tetraphenylphosphonium bromide ($\phi_4\text{PBr}$); ▲, *n*-propyltriphenylphosphonium bromide ($\text{Pr}\phi_3\text{PBr}$).

features of the micellar region require elaboration. The micellar surface region is accompanied by the presence of water of hydration. Also, in addition to having a positive charge, a quaternary counterion carries four hydrophobic chains/rings. Therefore, it can interact with surfactant micelles hydrophobically as well as electrostatically. At a high temperature ($\sim 75^\circ\text{C}$), the micellar interfacial region is comparatively less hydrated, and therefore electrostatic interaction would be dominant. The absolute value of the charge on the phosphonium ion should be considered in comparing the effects of Bu_4P^+ and $\phi_4\text{P}^+$ on CP. With $\phi_4\text{P}^+$, the P would be under the environment of a delocalized π -electron cloud of the phenyl rings. This would reduce the net positive charge on $\phi_4\text{P}^+$ and the resultant interaction with the anionic head groups. This may explain why more $\phi_4\text{PBr}$ is needed for the occurrence of CP at any particular temperature in comparison with Bu_4PBr . A similar explanation can be used for the growth of cationic micelles in the presence of aromatic hydrocarbons (27), where interaction of the delocalized π -electron cloud of the phenyl ring with the former produces grown micelles. However, substitution of only one phenyl ring with a propyl chain has a marginal effect on the amount of salt needed for the first appearance of CP in the 50-mM SDS micellar solutions. As the salt concentration increases, the CP vs. salt concentration plots (Fig. 1) demonstrate that the phenyl salts are more effective in decreasing the CP (especially in the lower temperature range). The hydration of interfaces for SDS micelles would be different at lower and higher temperature ranges. Therefore, electrostatic interactions at lower temperatures would be less significant. In addition, the volume of the counter-

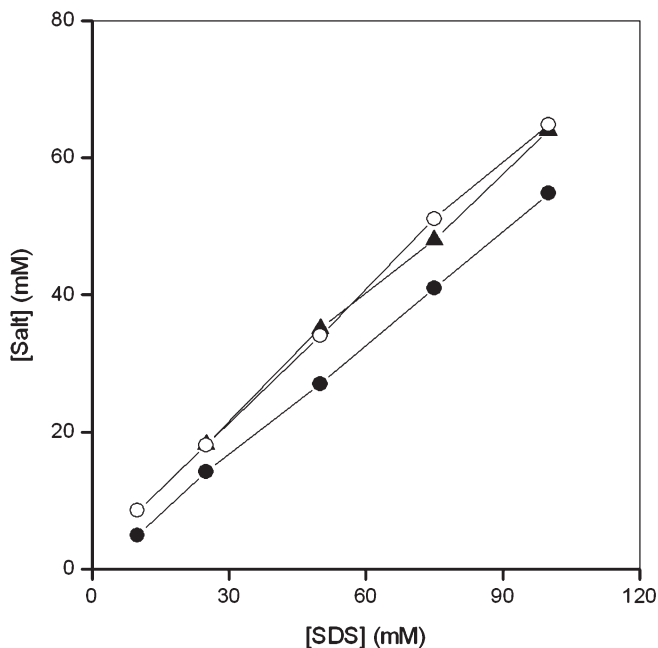


FIG. 2. Plots between SDS concentration vs. the minimum salt concentration needed for the appearance of CP at 70°C: ●, Bu₄PBr; ○, ϕ_4 PBr; ▲, Pr ϕ_3 PBr. For abbreviations see Figure 1.

ion would play a dominant role in removing the interfacial water. As the phenyl ring has more volume than the butyl chain, one can expect removal of more water from the interfacial region with ϕ_4 P⁺. This is further confirmed with Pr ϕ_3 PBr where one phenyl ring is replaced by a propyl chain.

Previously, a correlation was established between surfactant and salt concentrations to the CP in the SDS solutions (7). For the systems investigated here, Figure 2 shows the variation of SDS concentrations with salt concentration to reach the CP in solutions at 70°C (similar data were obtained for 30°C also). Measurements were taken at different SDS concentrations, and the regression data for straight-line plots are recorded in Table 1, showing that at 70°C, a lower molar ratio of Bu₄PBr to SDS (S) than of ϕ_4 PBr or Pr ϕ_3 PBr is needed to reach the CP. These results demonstrate that temperature has its own importance for the effectiveness of a salt in reaching the CP, which corroborates the earlier explanations (*vide supra*). However, the

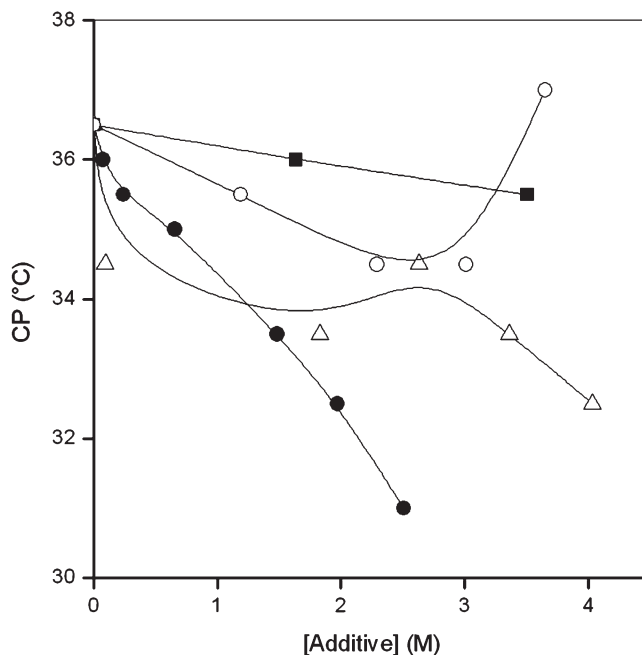


FIG. 3. CP variation in a system of 50 mM SDS + 36 mM Bu₄PBr as a function of the concentration of various hydroxy compounds (●, glycerol; △, ethanol; ■, ethanediol; ○, propanediol). For abbreviations see Figure 1.

data were not comparable because it was not possible to perform studies at 90°C (7). The phase boundaries were surpassed very quickly at approximately 75°C, which made it practically impossible to record CP and concentration above 75°C.

These studies could prove useful in CP extraction methods for the separation and preconcentration of different compounds (25). Various hydroxy compounds (ethanol, ethanediol, propanediol, and glycerol; Figs. 3–5) were added to see how they would influence CP behavior of 50 mM SDS + 36 mM salt systems. These systems were chosen as references because they provided wide temperature windows below and above the CP. A CP-decreasing effect was observed with Bu₄PBr (Fig. 3), whereas the opposite was true with phenyl salts (ϕ_4 PBr or Pr ϕ_3 PBr) (Figs. 4 and 5). The variation in critical micelle concentration of surfactants with such solvents was attributed to partial changes in the solvent environment of hydrophilic groups of the surfactant (28–30). That the solubility of hydrocarbons increases with

TABLE 1
Linear Regression Data^a for Plots of SDS vs. Salt Concentrations for Observing CP in SDS + Symmetrical/Unsymmetrical Quaternary Phosphonium Bromide Solutions at 30 and 70°C.

| Temp. (°C) | Bu ₄ PBr | | | ϕ_4 PBr | | | Pr ϕ_3 PBr | | |
|------------|---------------------|--------|-------|--------------|--------|-------|-----------------|--------|-------|
| | S | I (mM) | r | S | I (mM) | r | S | I (mM) | r |
| 30 | 0.719 | 3.404 | 0.999 | 0.676 | 3.360 | 0.999 | 0.732 | 2.235 | 0.999 |
| 70 | 0.548 | -0.146 | 0.999 | 0.632 | 2.405 | 0.999 | 0.602 | 3.7 | 0.998 |

^aS, slope; I, intercept; r, regression coefficient; SDS, sodium dodecylsulfate; CP, cloud point; Bu₄PBr, tetra-*n*-butylphosphonium bromide; ϕ_4 PBr, tetraphenylphosphonium bromide; Pr ϕ_3 PBr, *n*-propyltriphenylphosphonium bromide.

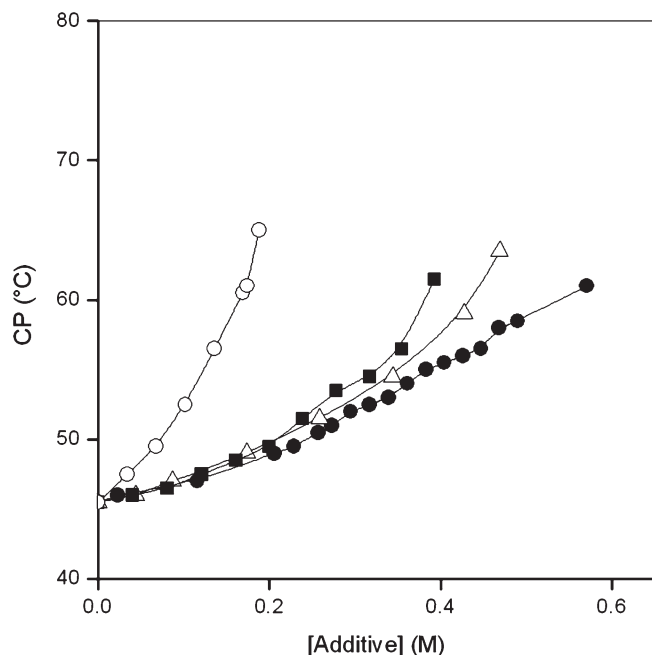


FIG. 4. CP variation in a system of 50 mM SDS + 36 mM ϕ_4 PBr as a function of the concentration of various hydroxy compounds (●, glycerol; Δ , ethanol; ■, ethanediol; ○, propanediol). For abbreviations see Figure 1.

increasing ethanediol content in ethanediol/water mixtures is also known (30). These interrelated factors seem to be responsible for the present CP behavior with ϕ_4 PBr or $\text{Pr}\phi_3$ PBr systems.

The effect of these compounds on the CP behavior of the Bu_4 PBr system invites comment. As mentioned earlier, the

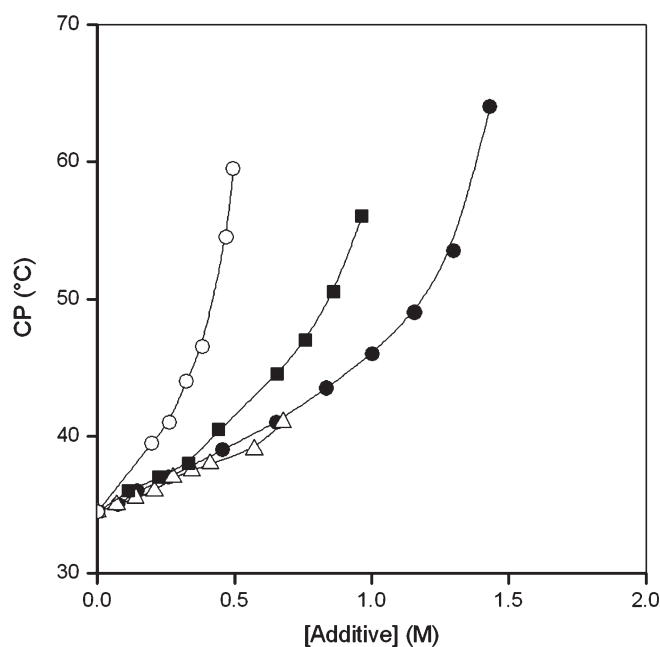


FIG. 5. CP variation in a system of 50 mM SDS + 36 mM $\text{Pr}\phi_3$ PBr as a function of the concentration of various hydroxy compounds (●, glycerol; Δ , ethanol; ■, ethanediol; ○, propanediol). For abbreviations see Figure 1.

phosphonium counterion with phenyl rings is bulkier than its *n*-butyl counterpart. Since most of the additives have a three-dimensional structure (31) and are comparatively bulky (32), their incorporation in the headgroup region is dependent upon the available volume of the surface region. Hence, it seems that incorporation of these compounds in the headgroup region would be easier in the case of Bu_4P^+ with the concomitant dehydration of the headgroup region and decrease in CP. This indeed is observed in Figure 3. In contrast, the incorporation is hindered by the presence of bulky phenyl rings in ϕ_4 PBr or $\text{Pr}\phi_3$ PBr; as a result, an increased solvation effect dominates and may be the reason for the continuous increase in CP temperature (Figs. 4 and 5).

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Dr. Kabir-ud-Din is a Professor of Physical Chemistry in the Department of Chemistry, Aligarh Muslim University, Aligarh, India. He received his M.Sc. (1965) and Ph.D. (1969) degrees from the same university. He had several years of postdoctoral research experience in Czechoslovakia (Charles University), the United Kingdom (Keele University), and the United States (University of Texas at Austin) and also worked as an associate professor in Libya (1985–1990). His name has been listed in several biographical books, such as Marquis Who's Who in the World (USA), Dictionary of International Biography (United Kingdom), and Eminent Personalities of India (India). He has authored over 139 research papers. His main scientific activities concern electrochemistry, micellar catalysis, kinetics, micellar growth through additives, and clouding phenomena in ionic surfactant solutions.

Ziya Ahmad Khan currently works as a senior research fellow (CSIR, New Delhi) at Aligarh Muslim University, Aligarh, India, with Kabir-ud-Din.

Dr. Sanjeev Kumar works as a senior research associate at Aligarh Muslim University, Aligarh, India. He has several years of postdoctoral research experience. His research interests lie in micellization, microemulsions, micellar growth, micellar catalysis, and clouding phenomena.