Effect of tetraalkylammonium bromides on the micellar behaviour of ionic and non-ionic surfactants

Jay Patel, Dharmesh Varade* & Pratap Bahadur
Department of Chemistry, South Gujarat University, Surat 395 007, India
E-mail: dharmeshvarade@yahoo.co.in.

Received 5 December 2003; revised 19 February 2004

Effect of tetraalkylammonium bromides (methyl, ethyl, n-propyl and n-butyl) on the surface activity and micellar behaviour of sodium dodecyl sulfate (NaDS), tetradecyltrimethylammonium bromide (C\textsubscript{14}TABr) and dodecyl decapolyethylene glycol ether (C\textsubscript{12}E\textsubscript{10}) has been examined by surface tension, dye solubilization, viscosity and cloud point measurements. Strong decrease in critical micelle concentration (CMC) and increase in solubilization power has been observed for NaDS; the effect is more with longer tetraalkyl salts. These salts also decrease the CMCs of C\textsubscript{14}TABr, while the CMCs of C\textsubscript{12}E\textsubscript{10} remain practically unaffected even up to 0.1 M concentration. However, cloud point (CP) of C\textsubscript{12}E\textsubscript{10} increases in the presence of these salts except in tetramethylammonium bromide where it decreases above 0.05 M. Viscosity results indicate the micellar growth for NaDS and tetrabutylammonium bromide. The micellar solution of NaDS exhibits a cloud point phenomenon in the presence of tetrabutylammonium bromide. The results are discussed in the light of charge and hydrophobicity of tetraalkylammonium salts.

It is well known that surfactant molecules can organize themselves into aggregates when dissolved into water medium. The micelle formation takes place above a critical micelle concentration (CMC), below which surfactant molecules are present as monomers\textsuperscript{1-3}. The functions and properties of surfactant systems depend on their structural type, concentration and compositions in addition to other factors, viz. temperature, pressure, pH, solvent and additives. Surfactants are generally used in the presence of additives in order to improve their properties. The effect of different kinds of electrolytes both with inorganic and organic counterions on the critical micelle concentration (CMC), aggregation number (N\textsubscript{agg}) and micellar transition for surfactants has been examined in detail\textsuperscript{4-5}.

While much work has been reported on metal salts (sodium halides have been most extensively studied), relatively less is reported on salts containing organic ions. Some such electrolytes, viz. sodium salts of organic acids e.g., toluene sulfonic acids or quaternary ammonium salts, behave differently that they may even show weak surface activity and hydrotrropic action. The physical properties of aqueous solutions of tetraalkylammonium salts have been studied in water and in presence of ionic and non-ionic surfactants\textsuperscript{6-11}. The difference between tetraalkylammonium salts (R\textsubscript{n}N\textsuperscript{+}) and an ordinary salt is that R\textsubscript{n}N\textsuperscript{+} possesses four alkyl chains with a symmetrical structure. Such an organic ion has a large hydrophobic volume, and some of the short alkyl chains may penetrate into the micellar interior due to the hydrophobic interaction\textsuperscript{12}. Among these salts, tetrabutylammonium bromide is known to induce the unusual micellar growth and phase separation in ionic surfactants\textsuperscript{8-10}.

The present paper reports the effect of tetraalkylammonium bromide (TC\textsubscript{n}ABr for n = 1, 2, 3 and 4) on cationic tetradecyltrimethylammonium bromide (C\textsubscript{14}TABr), anionic sodium dodecyl sulfate (NaDS) and non-ionic surfactant dodecyl decapolyethylene glycol ether (C\textsubscript{12}E\textsubscript{10}) examined by surface tension, dye solubilization viscosity and cloud point measurements.

Materials and Methods

The anionic surfactant sodium dodecyl sulfate (NaDS) and cationic surfactant tetradecyltrimethylammonium bromide (C\textsubscript{14}TABr) were highly pure samples from Fluka and were used as received. Non-ionic surfactant dodecyl decapolyethylene glycol ether (C\textsubscript{12}E\textsubscript{10}) was from Lancaster, England. A surface tension measurement gave a sharp break point at critical micelle concentration 8.0×10\textsuperscript{-3} M for NaDS\textsuperscript{13}, 3.9×10\textsuperscript{-2} M for C\textsubscript{14}TABr\textsuperscript{14} and 0.12×10\textsuperscript{-3} M C\textsubscript{12}E\textsubscript{10} which agrees well with the literature values.
No surface tension minimum was found, indicating the absence of any surface active impurities in all the three surfactants. Tetramethylammonium bromide (TMABr), tetraethylammonium bromide (TEABr), tetrapropylammonium bromide (TPABr) and tetrabutylammonium bromide (TBABr) were from Fluka and used as received. The dye orange OT (1-o-tolyl azo-2-naphthol, mol. wt. 262.3) prepared from o-toluidine and 2-naphthol was purified twice by precipitating it from acetone solution with water followed by recrystallization from ethyl alcohol. Water used to prepare all solutions was triply distilled from alkaline permanganate.

Surface tension

The surface tension of surfactant solutions in the absence and presence of tetraalkylammonium bromide (TAABr) was measured by drop weight method using a modified stalgmometer at 30°C. The assembly consisted of Pyrex glass bulb of spherical shape with a capillary tube attached at filling and dropping ends. The capillary tube at the dropping end was blown into a 2-fold U shape and the tip of the end was grounded in the form of a fine cone. By this way, not only is the formation of drops of uniform shape and size ensured but also drops are allowed to break under their own weight. A thoroughly stoppered weighing bottle was attached to the dropping end through a rubber septum. The weighing bottle attached to a dropping capillary tube was placed suspended in another closed long glass tube. The stalgmometer assembly along with the predried and preweighed weighing bottle was thermlly equilibrated at the desired temperature (30°C) accurate to 0.1°C for 30 min. Then a known number of drops (>20) of given solution and reference triply distilled water were allowed to fall into the weighing bottle in separate runs. The weight of solutions as well as triply distilled water drawn from separate runs was instantly recorded on single pan balance. The surface tension of the individual solution was then calculated from known values of surface tension of water, densities and weight of solution and water.

Dye solubilization

The insoluble dye orange-OT was shaken with an aqueous solution of the surfactant for 48 h at room temperature and then the residue was removed by means of centrifugation and filtration. The absorbance of the resultant solution was then measured at \( \lambda = 470 \) nm using Shimadzu spectrophotometer at 30°C.

Viscosity

The viscosity measurements were carried out using an Ubbelohde suspended level capillary viscometer at 30°C. The viscometer was always suspended vertically in a thermostat with a temperature stability of ±0.1°C in the investigated region. The viscometer was cleaned and dried every time before each measurement. The flow time for constant volume of solution through the capillary was measured with a calibrated stopwatch.

Cloud point (CP)

Cloud point was determined at fixed concentration of NaDS in TBABr and C_{12}E_{10} in the absence and presence of varying amounts of added TAABr by gently heating the solution in thin 20 ml glass tubes immersed in a beaker containing water well stirred with a magnetic bar while being heated. The heating rate of the samples was controlled by less than 1°C/min. The first appearance of turbidity was taken as the cloud point. The CP values were reproducible up to 0.5°C.

Results and Discussion

Surface active behaviour of tetraalkylammonium bromide (TAABr) in aqueous solution measured over a range of concentration is shown in Fig. 1. They all showed a marked resemblance to the plots obtained by Tamaki. Tetramethylammonium bromide slightly raises the surface tension of pure water, whereas higher homologous salts reduce the surface tension of pure water, and the surface activity increases progressively with the number of carbon atoms in the
alkyl group. Tetraalkylammonium ions show a tendency to be rejected from the aqueous phase as a result of the strong cohesive force between water-water bonding, which is responsible for the adsorption of this large, hydrophobic cation at the interface in contact with their aqueous solution. The phenomenon that the dissolved substance raises the surface tension of pure water has been observed with a variety of simple salts, whether the constituent ions are electrostrictive structure makers or breakers. On the other hand, the non-polar organic solutes, which act as hydrophobic structure-makers in water, show the effect of reducing the surface tension of pure water. In view of the above results, TMABr may be considered to act as a simple salt. With TMA⁺ ion, the interaction of the ionic part with water will surpass the hydrophobic hydration due to methyl groups, while in case of higher homologous salts, the interaction of alkyl group with water surpasses the electrostrictive hydration due to the central ionic part; consequently, the transfer of these salts from the bulk phase to the surface phase is a spontaneous process. Thus they are surface active in aqueous solution.

Figures 2-4 show the surface tension (γ) of NaDS, C₁₄TABr and C₁₂E₁₀ solutions respectively measured for a range of concentrations above and below the critical micelle concentration (CMC). A decrease in surface tension for the surfactants was observed with increase in concentrations up to the CMC, beyond which no considerable change was noticed. This is a common behaviour shown by surfactants in solution and is used to determine their purity and CMCs. All four tetraalkylammonium bromides significantly lower the surface tension of ionic surfactants. The final limiting value of the surface tension is also lower than that of pure surfactants when tetraalkylammonium bromide is added; indicating an increased surface activity. The electrical atmosphere in the aqueous surfactant solution altered in presence of TAABr which neutralizes the effective head group charge for ionic surfactants resulting in reduced electrostatic repulsion between the polar head groups and the micelles are formed at much lower concentration as compared to that in pure water. The CMC of the ionic surfactant decreased in the presence of TAABr, the decrease being dependent upon the concentration of TAABr. While in case of non-ionic surfactant C₁₂E₁₀ with TAABr the effect was not much pronounced due to the absence of any electrostatic interactions. The CMC data obtained from the break point in the γ-log concentration plots

for NaDS, C₁₄TABr and C₁₂E₁₀ in absence and presence of TAABr are recorded in Table 1.

Solubilizing power is one of the most important properties of surfactants. To measure solubilizing behaviour of surfactants, the solubilization of water
insoluble dye Orange OT in the surfactant micelles was studied. The obtained results were plotted as absorbance versus concentration of the surfactants. A representative solubilization plot for NaDS in presence of TAABr is shown in Fig. 5. The results for all the three surfactants in TAABr reveal that the amount of the dye solubilized rise slowly up to the CMC of each surfactant and then after a sudden and steep rise was observed with the formation of micelles in the bulk. Thus the solubilizing power of surfactants increases in the presence of TAABr. The CMCs for all the three surfactants obtained by surface tension and dye solubilization methods are nearly the same. Variations in CMC values depending on the method of determination have been reported in literature.\textsuperscript{16,17}

Figure 6 shows the dependence of relative viscosity carried out at fixed concentration of NaDS, C\textsubscript{14}TABr (50 mM) in presence and absence of varying TAABr concentrations and for C\textsubscript{12}E\textsubscript{10} (50 mM) in presence of TEABr only. There is a sharp increase in relative viscosity of NaDS as compared to C\textsubscript{14}TABr, while a negligible change in viscosity of C\textsubscript{12}E\textsubscript{10} was observed. The effect increases with number of carbon atom in the alkyl groups. The structure of the micellar aggregates formed from surface active molecules is governed by a delicate balance between the attractive and repulsive terms of the surface free energy. As the TAABr salts used in this study are cationic in nature, adding them to NaDS results in the formation of elongated micelle by the reduction in the effective head group area because of the screening effect. Tetrabutylammonium bromide is more effective in inducing the micellar growth in NaDS as compared to other lower homologous salts. It can be explained on the basis that TBABr has large hydrophobic volume and some of the alkyl chains may penetrate into the micellar core. Geometric restriction makes it infeasible for all four chains to penetrate. Hence, two
Table 1—Critical micelle concentration (CMC) of surfactants in absence and presence of tetraalkylammonium bromides at 30°C

<table>
<thead>
<tr>
<th>Concentration M</th>
<th>TMABr</th>
<th>TEABr</th>
<th>TPABr</th>
<th>TBABr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ST</td>
<td>DS</td>
<td>ST</td>
<td>DS</td>
</tr>
<tr>
<td>NaDS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>8.00</td>
<td>7.80</td>
<td>8.00</td>
<td>7.80</td>
</tr>
<tr>
<td>0.001</td>
<td>3.16</td>
<td>-</td>
<td>2.24</td>
<td>-</td>
</tr>
<tr>
<td>0.010</td>
<td>1.80</td>
<td>-</td>
<td>1.10</td>
<td>-</td>
</tr>
<tr>
<td>0.050</td>
<td>1.40</td>
<td>1.30</td>
<td>0.85</td>
<td>0.80</td>
</tr>
<tr>
<td>0.100</td>
<td>1.10</td>
<td>-</td>
<td>0.70</td>
<td>-</td>
</tr>
<tr>
<td>C14TABr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>3.90</td>
<td>3.80</td>
<td>3.90</td>
<td>3.80</td>
</tr>
<tr>
<td>0.010</td>
<td>1.80</td>
<td>-</td>
<td>1.60</td>
<td>-</td>
</tr>
<tr>
<td>0.050</td>
<td>1.25</td>
<td>1.20</td>
<td>1.00</td>
<td>0.80</td>
</tr>
<tr>
<td>0.100</td>
<td>0.95</td>
<td>-</td>
<td>0.70</td>
<td>-</td>
</tr>
<tr>
<td>C12E10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.12</td>
<td>0.11</td>
<td>0.12</td>
<td>0.11</td>
</tr>
<tr>
<td>0.100</td>
<td>0.11</td>
<td>0.10</td>
<td>0.11</td>
<td>0.10</td>
</tr>
</tbody>
</table>

chains are located at the micellar surface layer in contact with water, which forms an iceberg structure around the chains. As the concentration of TBABr increases, the icebergs on the butyl chains penetrating toward the interior will breakdown, thereby increasing the entropy of the system. This entropy increase may be a driving force for the micellar growth.

Figure 7 shows the variation of cloud point (CP) with NaDS (50 mM) in the presence of different concentrations of TBABr. The CP decreases with increase in TBABr concentration. It is well-known that non-ionic surfactants always have CP properties while in case of ionic surfactants CP phenomenon is
rarely observed\textsuperscript{7-10}. Clouding behaviour has been attributed to dehydration of the hydrophilic group of the surfactant with increase in temperature\textsuperscript{16}. Large amounts of added salt, which screen the electrostatic repulsion is thought to be responsible for ionic micellar systems exhibiting CPs. The butyl chains of TBABr may penetrate into the micellar interior due to the hydrophobic interaction\textsuperscript{12}. Van der Waals attraction and the penetration effect will help in attracting two micelles together, while the electrical repulsion will prevent the micellar contact. Dehydration of the ionic heads of the surfactant monomers takes place on increasing the temperature which increases the interaction between anionic heads and TBA\textsuperscript{+}. At the CP the collapse of the micelle occurs, which results in the formation of two phases. More TBABr concentration will replace more structured water and the phase separation is expected to appear at a lower temperature since the NaDS concentration is constant. This is clearly reflected from Fig. 7.

The clouding phenomenon shows that 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\textsuperscript{20}. The cloud point of non-ionic 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’. In Fig. 8, the variations of CP of C\textsubscript{12}E\textsubscript{10} (1\% wt/v) as a function of TAABr concentration are shown. For C\textsubscript{12}E\textsubscript{10} in water the CP\textsuperscript{21} is 88°C. The CP of C\textsubscript{12}E\textsubscript{10} (0-10\% wt/v) decreases with increase in the concentration (inset in Fig. 8). The decrease in CP with increase in C\textsubscript{12}E\textsubscript{10} concentration is due to increase in micelle concentration. The phase separation results from micelle-micelle interaction. TMABr, which behaves like a simple salt as discussed earlier, decreases the CP of C\textsubscript{12}E\textsubscript{10}. TMABr is water structure former, hence decreases the availability of non-associated water molecules to hydrate the ether oxygen\textsuperscript{2} of the PEO chain, thus lowering the cloud point. Higher members of the series actually stabilize the polymer in solution, raising its cloud point. The hydration atmospheres of the higher TAABr cations are strongly hydrophobic in nature. Their hydration atmospheres are thus compatible with the hydrophobic hydration surrounding the polymer and enable these solutes to penetrate and profoundly alter the hydration of macromolecule, in the present case evidently strengthening that structure and enabling the polymer to remain in solution to even higher temperatures thereby increasing the cloud point.

In conclusion, the tetralkyl ammonium bromides show a remarkable decrease in surface tension and CMC and increases solubilizing power of the anionic surfactant NaDS; the effect being strong with tetralkyl...
salts with longer chains. For tetrabutylammonium bromides growth of NaDS micelles followed by phase separation was observed. These salts also decreased the CMC of cationic surfactant C\textsubscript{14}TABr but to a lesser extent. No significant change in surface tension and CMC was observed for the non-ionic surfactant C\textsubscript{12}E\textsubscript{10} though cloud points showed marked change, particularly in the presence of TBABr.

**Acknowledgement**

Financial assistance from CSIR Project No-01/1827/02/EMR-II of Dr. P. Bahadur is gratefully acknowledged.

**References**