Mutual Interactions of Non-ionic & Ionic Detergents Composed of
p-(1,1,3,3-Tetramethylbutyl)phenoxypolyoxyethyleneglycol, Sodium
Dodecyl Sulphate & Cetyltrimethylammonium Bromide

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Mutual interactions of p-(1,1,3,3-tetramethylbutyl)phenoxypolyoxyethyleneglycol(Triton X-100) and a low molecular weight (mol. wt 4 00) polyethyleneglycol (PEG) with sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB) have been investigated spectrophotometrically and conductometrically. Transfer of both SDS and CTAB into the micelles of TX-100 is favoured, whereas the reverse phenomenon is difficult. Excess TX-100 thus reduces the micellization tendencies of both SDS and CTAB and forms complexes with the demicellized entities. The cmc of TX-100 decreases by the addition of SDS and CTAB, but the cmc of the latter increase by the addition of TX-100. PEG also increases the cmc of both SDS and CTAB. Association of SDS and CTAB with TX-100 and PEG has been studied conductometrically and the binding constants and the thermodynamic parameters evaluated. Free energy of transfer of the detergents from water to the additive environment has been evaluated. Thermodynamic parameters support the incorporation of the hydrophobic tails of SDS and CTAB into the interior of TX-100 micelles. The hydrophilic head of TX-100 contributes mainly to the compensation of the non-free part of the enthalpy through water structure promotion showing highly negative entropy values.

LIKE micellar solubility and micellar kinetics, the study of mutual interactions of surfactants (lipids) forming insoluble aggregates (via ion pairs) and mixed micelles has assumed importance in industrial and laboratory surface chemical works as well as in biology. It is known that oppositely charged ionic detergents form insoluble ion pairs1 (if one of the species is not in large excess3) when the solubility limit exceeds, whereas, similarly charged ions and mixtures of nonionic and ionic detergents may form soluble mixed micelles due to their mutual solubility3-6. In some cases, detergents may also exhibit phobia of mutual solubility7. It can be said in this regard that elaborate studies of mutual interactions of detergents in general, and of nonionic and ionic detergents, in particular, are very limited.

In the present paper, we describe results of studies on the interaction of a nonionic detergent, p-(1, 1, 3,3- tetramethylbutyl)phenoxypolyoxyethyleneglycol (Triton X 100) with an anionic detergent sodium dodecyl sulphate (SDS) and a cationic detergent cetyltrimethylammonium bromide (CTAB). Results of interaction of these detergents with a low molecular weight polyethyleneglycol (PEG, mol. wt 400), which is equivalent to the hydrophilic head group of Triton X 100, have also been reported to understand the role of this head group when Triton X 100 undergoes interaction with SDS and CTAB.

Materials and Methods

For the grade, purity and characteristics of the detergents, we refer to our earlier works8-9. The polyethyleneglycol (BDH) had the average molecular weight 400 and average number of the (CH₂)n-O-groups as 8.7; the head group of Triton X 100 on an average contained 9.5 oxyethylene units. Doubly distilled conductivity water (specific conductance 1-2 × 10⁻⁶ mho cm⁻¹ at 30°C) was used as the solvent medium.

Spectral measurements were made on a SPEKTROMOM apparatus (Hungary) using a silica cells of 1 cm path length. Conductance measurements were made on an ELICO conductivity bridge with dip-type and bottle-type cells of cell constants 0.7 cm⁻¹ and 1.2 cm⁻¹ respectively. Prior to measurements all the solution were equilibrated at 303 ± 0.02 K, unless otherwise stated.

Spectrophotometric determination of critical micelle concentration (cmc) of Triton X 100 was performed by recording its spectra in the presence and absence of additives and plotting the absorbance at the λmax (278 nm) of the main band against concentration of Triton X 100. Its full spectra were taken to understand the effects of additives on the nature of the native spectra in micellar and nonmicellar states of the detergents.

For the determination of the cmc of SDS and CTAB in the absence and presence of Triton X 100 and PEG, a series of solutions were prepared at a definite concentration of the additive and varying the concentrations of the ionic detergents. The conductance of each solution was measured and plotted against the concentration. The abrupt changes in the values of the initial slopes were considered as the cmc points. Such cmc was also determined performing the proton transfer complexation reaction between p-nitrosalicyclic acid and ethylene-
Results

(a) Cmc of Triton X 100 in presence of SDS and CTAB — Cmc was determined spectrophotometrically. The pure compound at concentrations above cmc (on 2.4 x 10^{-4} M at 25°C) exhibited a main peak at 278 nm and a shoulder at 285 nm. The molar extinction above cmc at 30°C was observed to be 1600 litre mol^{-1} cm^{-1} as against 1670 litre mol^{-1} cm^{-1} at 25°C reported earlier. The purity of the compound was thus good. The small peak was considered to be due to the perturbation of the electronic transition of individual non-interacting molecules upon micellization. It got prominent above cmc and also by agents that could induce micellization. Below cmc or in the presence of sufficient urea, a more or less smooth curve having indistinguishable 285 nm peak resulted (Fig. 1). A plot of absorbance at 278 nm with concentration produced two distinct linear curves that could be joined to yield the cmc (Fig. 2). The presence of SDS, CTAB, NaCl and Et₄NBr decreased the cmc of Triton X 100. In the literature, both decrease and increase of cmc of Triton X 100 in the presence of salts, urea and non-electrolytes have been reported. However, similar studies using ionic detergents are scarce. It was observed that SDS affected the cmc more than CTAB, and both the surfactants were effective at concentrations above their normal cmc levels. This has been attributed to solubilization or incorporation of the ionic detergents into the micelles of Triton X 100 forming mixed micelles.

(b) Cmc of SDS and CTAB in presence of Triton X 100 and PEG — Cmc’s of both SDS and CTAB were obtained from conductometric and proton transfer
various PEG concentrations. Curves 1-6; at 0.0M PEG; 0.1M PEG; 0.2M PEG; 0.5M PEG; and 0.75M PEG respectively

Fig. 3 - Difference specific conductance of SDS at 303 K at various PEG concentrations. Curves 1-3; at 0.0M PEG; 0.1M PEG; 0.2M PEG; 0.3M PEG; 0.5M PEG; and 0.75M PEG respectively

Fig. 4 - Effect of TX 100 on the absorbance of proton transfer complex between PNSA (3.38 x 10^(-3)M) and ED (5.63 x 10^(-3)M) to determine cmc of SDS at 303 K. Curves 1-3; at 0.13 M TX 100; 0.274 x 10^(-3) M TX 100; and 1.43 x 10^(-3) M TX 100 respectively

complexation methods. Two sets of such results are shown in Figs. 3 and 4. Cmc's of both SDS and CTAB increased in the presence of Triton X 100 and PEG. The effect on SDS was comparatively more than that on CTAB. Self-association of SDS and CTAB was hindered Triton X 100.

(c) Binding of SDS and CTAB with Triton X 100 micelles and PEG—Decrease in the conductance of both SDS and CTAB solutions at concentration below cmc indicated binding of these ionic detergents with Triton X 100 micelles as well as with PEG in such environments. In the presence of enough Triton X 100, the conductances of both SDS and CTAB at concentrations above their cmc was observed to increase, due to the breaking of micelles of these ionic detergents upon complexation with Triton X 100 micelles. Since low concentrations of the compounds were used, other factors like ionic obstruction and changed dielectric constant had, at all, minor effects on the ionic conductance. For such dilute solutions, conductance was linearly proportional to concentration (Fig. 3).

The following mass action principle may then be set up for the complexing system.

\[ (T X 100)_m + n S^{\pm} \rightleftharpoons (T X 100)_m \cdot S^{n\pm} \]  
\[ T X \text{ micelle } n(\text{surfactant}) \text{ Mixed micelle or complex} \]

In this model, \( n \), number of an ionic surfactant is assumed to be bound with a single T X 100 micelle forming the complex with association constant \( K_A \).

The thermodynamic association constant, \( K_A \) is then given by Eq. (2).

\[ K_A = \frac{\left( \gamma^*_f / \gamma^*_g \right)^n}{\left( \gamma^*_f / \gamma^*_g \right)^n} \]  
where the \( \gamma \) terms stand for the respective activity coefficients and subscript \( f \) refers to free concentration of the species at equilibrium.

For dilute solutions of ionic surfactants and the non-ionic Triton X 100 micelles as well as for the ionic complex, it may be valid to assume the activity coefficients as unity. This simplifies the situation and does not lead us far from reality. Equation (2) can then be written as

\[ \log K_A = \log [\text{Complex}] - \log [T X 100]_f - n \log [S^{\pm}]_f \]  

At relatively large proportions of Triton X 100 micelles than the ionic surfactants, concentration of the total Triton X 100 micelles can be regarded as the concentration of the free micelles.

\[ [T X 100]_m \approx [T X 100]_f \]  

Again, since below cmc the conductance-concentration-variation is practically linear, the loss in the ionic coefficients as unity. This simplifies the situation and does not lead us far from reality. Equation (2) can then be written as

\[ \log K_A = \log (\triangle S^{\pm}/n) - \log (T X 100)/W \]  

where the new term \( W \) designates the average aggregation number of Triton X 100 micelles assumed constant under the present experimental conditions.

Further rearrangement yields

\[ \log \triangle S^{\pm} = \log (K_A n[T X 100]/W) + n \log [S^{\pm}]_f \]  

In terms of solution conductance, Eq. (7) can be written as

\[ \log (k_1 - k_2/m) = \log (K_A n[T X 100]/W) + n \log (k_2/m) \]  

where \( k_1 \) and \( k_2 \) stand for the specific conductance of the ionic surfactant at any concentration in the absence and presence of T X 100 respectively, and
The thermodynamic parameters for various systems vary significantly from one another. The reflection of the non-constancy of the average aggregation number, $\bar{W}$, assumed constant in deriving $K_A$ values may although affect the absolute values, it cannot alter the observed trend or order.

(b) $n$ values obtained with different combinations at different temperatures are always close to 1.0. Non-integral values greater and lower than unity are considered due to experimental uncertainties. A fluctuation around a central value of unity has convinced us to consider $n = 1$ for the present systems.

**Discussion**

The decrease in cmc of Triton X 100 in the presence of both SDS and CTAB at concentrations above their cmc was not linear as has been observed in many cases of additives\(^9,17\). On the other hand, the increase in cmc of both SDS and CTAB with the addition of Triton X 100 followed a linear course. Such was also the case with PEG. The effect of SDS on T X 100 micellization and vice versa was more than the T X 100-CTAB pair. The cmc of SDS increases from $8.0 \times 10^{-3} M$ to $14.0 \times 10^{-3} M$ by the addition of $5.70 \times 10^{-3} M$ T X 100; whereas, the same increase of cmc of CTAB is caused by the addition of $2.85 \times 10^{-3} M$ T X 100 (Table 2). In both the cases the energy transfer from aqueous to additive environments are the same (i.e. $-1.410 \text{kJ/mol}$). The decrease of cmc of T X 100 from $2.9 \times 10^{-4} M$ to $1.0 \times 10^{-4} M$ caused by the addition of $0.15 M$ SDS; whereas, the same decrease of cmc of T X 100 is caused by $0.05 M$ CTAB additive. In both the cases the energy transfer from aqueous to additive environments are the same, i.e. $2.782 \text{kJ/mol}$). These facts clearly indicate that SDS ions are more free in the hydrophilic head group environment of T X 100 than CTAB. The special feature of conductance-temperature curves in Fig. 6 is a transition temperature (320.5K) above which sharp change in conductance is observed. Appreciable breaking of micelles at and above this temperature is envisaged. Sharpness of this transition became less as Triton X 100 was incorporated in the system similar to the addition of 50% alcohol in the medium. Demicellization by temperature, T X 100 and alcohol was considered to be the phenomenon. The use of higher concentrations of T X 100 is restricted due to a possible phase separation at elevated temperature\(^9\).

For both T X 100 and PEG, SDS get bound with greater strength than CTAB. The limited literature data available also recognizes weaker binding of cationic surfactants with PEG than anionic surfactants\(^18,19\) (quantitative picture is, however, lacking). For PEG-SDS and PEG-CTAB systems, major part of the enthalpy is utilized for the enhancement of environmental water structure showing large negative entropy change. Partial immobilization of water molecules between the polyethoxy chains on a micelle of Triton X 100 has also been reported from proton

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**Table 1 — Various Physicochemical Parameters**

<table>
<thead>
<tr>
<th>System</th>
<th>$n$</th>
<th>$K_A$</th>
<th>$\Delta G^o$ (kJ/mol)</th>
<th>$\Delta H^o$ (kJ/mol)</th>
<th>$\Delta S^o$ (J/deg. mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T X 100-SDS</td>
<td>1.20 ± 0.12</td>
<td>6230 ± 26</td>
<td>-22.14 ± 0.01</td>
<td>-71.75 ± 1.32</td>
<td>-163.73 ± 4.32</td>
</tr>
<tr>
<td>T X 100-CTAB</td>
<td>1.14 ± 0.10</td>
<td>2878 ± 24</td>
<td>-20.18 ± 0.02</td>
<td>-30.76 ± 0.50</td>
<td>-34.92 ± 1.58</td>
</tr>
<tr>
<td>PEG-SDS</td>
<td>1.00 ± 0.10</td>
<td>2.0 ± 0.08</td>
<td>-1.76 ± 0.11</td>
<td>-22.61 ± 0.38</td>
<td>-68.81 ± 0.89</td>
</tr>
<tr>
<td>PEG-CTAB</td>
<td>0.86 ± 0.10</td>
<td>1.41 ± 0.04</td>
<td>-0.87 ± 0.07</td>
<td>-66.24 ± 1.05</td>
<td>-215.74 ± 3.26</td>
</tr>
</tbody>
</table>

(a) The thermodynamic parameters for various systems vary significantly from one another. The reflection of the non-constancy of the average aggregation number, $\bar{W}$ assumed constant in deriving $K_A$ values may although affect the absolute values, it cannot alter the observed trend or order.

(b) $n$ values obtained with different combinations at different temperatures are always close to 1.0. Non-integral values greater and lower than unity are considered due to experimental uncertainties. A fluctuation around a central value of unity has convinced us to consider $n = 1$ for the present systems.

$m$ is the slope of the linear conductance-concentration line.

Equations (7) and (8) can be used to calculate $n$ and $K_A$ only from an assumed knowledge of $\bar{W}$ (this was considered 143 for T X 100 micelles\(^8\)) from other studies. In the case of PEG-SDS and PEG-CTAB system, $\bar{W}$ is unity, since PEG does not micellize.

The test for the validity of (Eq. 7) is given in Fig. 5. The calculated $n$ and $K_A$ obtained from the slope and the intercept of the linear plots in Fig. 5 are given in Table 1. By following the observations at three different temperatures, 303, 313 and 323K and plotting the log $K_A$ against $1/T$, $\Delta H^o$ of complexation has been calculated from Van't Hoff's equation which in conjunction with $\Delta G^o$ at 303K yielded the $\Delta S^o$ values for the process. These results are also given in Table 1. The standard states were considered to be the hypothetical states of ideal solutions of unit molarity.

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**Fig. 5** — Test of Eq. (7) on various systems at 303 K [Curves 1-4; T X 100-SDS, T X 100-CTAB, PEG-CTAB, PEG-SDS systems respectively].
chemical shifts. The TX 100-SDS and TX 100-CTAB systems also end up with enthalpy-entropy compensation through water structure promotion but the magnitude in these cases is comparatively less than the PEG—detergent systems. The incorporation of the ionic detergents then results in decrease in the freedom of the system as a whole. The slopes of the linear extra thermodynamic enthalpy-entropy compensation for the PEG-detergent and TX 100-detergent systems are 300 and 360 respectively. The fact that PEG interacts very weakly with both SDS and CTAB compared to TX 100 points to the insignificant role of the polar head group of the latter in fixing the ionic detergent into it. Entrapping of the ionic detergents within the micellar interior is thus considered to be the relevant model for the complex (mixed micelles): kinetically more stabilized complex is formed with SDS than with CTAB. The charge transfer possibility between the anionic detergent and the ethereal groups present in the polyoxyethylene groups may also function in cooperation with the hydrophobic interaction to ensure stronger complexation in the case of SDS than CTAB.

Conceptually, micellization can also be modelled as forming a separate phase in the solvent environment. The standard free energy change for micellization is given by the relation (9)

$$
\Delta G^\circ_m = -RT \ln (\text{cmc})
$$

Neglecting activity effects, the cmc values obtained in this study when compared with those in pure water can help in the evaluation of \(\Delta G^\circ\) free energy of transfer from water to the additive environments. Thus,

$$
(\Delta G^\circ)_t = -RT \ln \left(\frac{\text{cmc}}{\text{cmc}}\right)
$$

Such free energies of transfer are given in Table 2 with the prevailing environments. The ratio of the additives concentration and its (cmc)w has been shown in column 2; thus a comparison of the transfer process at equal number of micelles can be readily made. In the case of salts and PEG, straightforward comparison with reference to molar concentrations is only possible. It can be seen that the transfer energies become negative in the case of SDS and CTAB in TX 100 and PEG environments; whereas, the transfer of TX 100 from water to SDS, CTAB and salt (NaCl and Et4NBr) environments becomes difficult, giving positive (\(\Delta G^\circ\))t values. This suggests solubilization and separation of these materials and lipids by TX 100 micelles, an agent frequently used in the separation of proteins from cell membranes. Ribeiro and Dennis observed formation of mixed micelles of dimyristylphosphatidylecholine with TX 100 at molar ratios only above 2:1 (Triton/phospholipid) at concentrations of TX 100 well above its cmc. The present study has shown that a concentration of TX 100 well in excess than its cmc is needed for solubilizing lipid like bodies in it; the reverse process, on the other hand, is difficult.

### Table 2: Standard Free Energy of Transfer at 303K from Aqueous to Additive Environments

<table>
<thead>
<tr>
<th>Additive</th>
<th>TX 100 to SDS environment (A)</th>
<th>TX 100 to CTAB environment (B)</th>
<th>TX 100 to PEG Environment (C)</th>
<th>TX 100 to PLG environment (D)</th>
<th>TX 100 to salt environment (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[SDS]×10^4(M)</td>
<td>Micellar level</td>
<td>((\Delta G^\circ) t) (kJ/mol)</td>
<td>[CTAB]×10^4(M)</td>
<td>Micellar level</td>
<td>((\Delta G^\circ) t) (kJ/mol)</td>
</tr>
<tr>
<td>0.1</td>
<td>0.825</td>
<td>-0.297</td>
<td>0.10</td>
<td>0.25</td>
<td>0.15</td>
</tr>
<tr>
<td>0.2</td>
<td>0.064</td>
<td>-0.564</td>
<td>0.10</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>0.3</td>
<td>0.013</td>
<td>-1.013</td>
<td>0.10</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>0.5</td>
<td>0.174</td>
<td>-1.748</td>
<td>0.10</td>
<td>1.0</td>
<td>1.25</td>
</tr>
<tr>
<td>0.75</td>
<td>2.32</td>
<td>-2.32</td>
<td>0.10</td>
<td>3.0</td>
<td>3.75</td>
</tr>
</tbody>
</table>

(\(\Delta G^\circ\) t) values marked with (*) are based on conductance method, the rest are based on proton transfer complexation method. Those of C and D are based on conductance method, and of E, F and G are based on spectrophotometric method. Cmc of SDS, CTAB and TX 100 at 303 K have been taken as 8.0×10^-3M, 8.0×10^-4M and 2.9×10^-4M respectively. Micellar level=[Additive]/cmc w.
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Fig. 6—(Left) Specific conductance of detergent and detergent mixtures at various temperatures. [Curves A—E: \(5 \times 10^{-4} M\) CTAB \(\times 2.74 \times 10^{-3} M\) TX 100; \(1.4 \times 10^{-3} M\) CTAB +14.4 \(10^{-3} M\) TX 100 in 50\% methanol; \(1.4 \times 10^{-3} M\) CTAB in 50\% methanol; \(2.5 \times 10^{-3} M\) CTAB; and \(2.5 \times 10^{-3} M\) CTAB +11.4 \(10^{-3} M\) TX 100 respectively. CTAB concentration at cmc in A and above cmc in D)

(Right) Specific conductance of detergent and detergent mixtures at various temperatures [Curves A—D: \(2.5 \times 10^{-3} M\) SDS; \(2.5 \times 10^{-3} M\) SDS + 4.0 \(10^{-3} M\) TX 100; \(2.5 \times 10^{-3} M\) SDS +1.37 \(10^{-3} M\) TX 100 respectively. Ordinate scale \(k \times 10^4 \) mho cm\(^{-1}\) for curve D; open and closed points refer to heating and cooling runs].

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References