Organization of amphiphiles, Part-II—Surface activity of polyoxyethylated alkyl phenols at air-water interface

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The surface properties of a series of polyoxyethylated alkyl phenols, \( \text{[C}_9\text{H}_17\text{O} \text{(CH}_2\text{CH}_2\text{O})_n\text{H}, n=10, 30 \text{]} \) and \( \text{[C}_4\text{H}_9\text{O} \text{(CH}_2\text{CH}_2\text{O})_n\text{H,} \text{ n=10, 15, 20, 40} \text{]} \) have been studied through surface tension measurement by Wilhelm plate method. The surface pressure values calculated from surface tension data have been fitted to Gibbs adsorption equation and the standard free energies of micellization and adsorption at air water-interface have been calculated. The minimum area per surfactant molecule and critical micellar concentration reveal that both steric constraints and hydrophobicity of the surfactant play a major role in micelle formation.

We have earlier studied the aggregation behaviour of some polyoxyethylated alkyl ethers and anionic surfactants in aqueous medium using fluorescence spectroscopy. Both surface tension and fluorescence spectroscopy have been successfully utilized to study the interfacial and thermodynamic properties of nonionic surfactants mixtures, maltoside and sodium dodecyl benzyl sulphonate. In the present study the surface activity of polyoxyethylated alkyl phenols have been investigated by surface tension measurement. These surfactants are chosen because of their ability to adsorb selectively on silica surface and applications in processes such as detergent, cosmetics, enhanced oil recovery etc. The surface activity of these surfactants has been correlated with their structure.

Experimental

All the polyoxyethylated surfactants were obtained from Nikko Chemicals, Japan under the product name OP-X/la, \( X=10, 30 \text{]} \) and NP-X/la, \( X=10, 15, 20 \text{]} \) where \( X \) represents the number of poly(oxyethylene) group present in the surfactants. Polyoxyethylated(nonyl) phenol was obtained from GAF corporation (product name Igepal CO890) and referred in the note as NP-40 for convenience. These surfactants were used as received. The absence of minimum in the surface tension concentration curve confirmed the high purity (>99%) of these surfactants.

Sodium chloride used for maintaining constant ionic strength was supplied by Fisher Scientific Co., USA (A.C.S. grade, purity>99%). It was used without further purification.

Pyrene obtained from Aldrich Chemicals, USA was used as such.

The solutions of surfactants in triply distilled water having conductivity 1-2×10^6 ohm{cm}^{-1} containing 0.01 M NaCl and 3×10^{-7} M of pyrene were prepared afresh for surface tension measurements. Constant ionic strength (containing 3×10^{-7} M of pyrene) was maintained to carry out further studies like adsorption of the surfactants from solutions at solid-liquid interface and related phenomena.

Method

The solutions containing 0.01 M NaCl and 3×10^{-7} M of pyrene were subjected to surface tension measurement using Wilhelm plate method (designed at Columbia University, New York). The appearance of break in the surface tension concentration curve is referred to as formation of micelle and the concentration at the break is referred as the critical micellar concentration as shown in Figs 1 and 2. The CMC of the surfactants are given in Table 1. The CMC does not change with the addition of 0.01 M NaCl and 3×10^{-7} M of pyrene. The CMC of nonionic surfactants is found to be independent of change in salt concentration in presence of low concentration of pyrene. The surface tension values were converted to surface pressure \( \pi \) by Eq. 1 (ref.3):

\[
\pi = \gamma_{\text{water}} - \gamma
\]
and the surface pressure at the break are given in Table 1. In this equation, is the surface tension of water and is the surface tension of the surfactant solution.

**Results and discussion**

In order to understand the effect of the variation in hydrophobicity and hydrophilicity on the aggregation behaviour of surfactants, selectively two sets of surfactants are used; alkyl= nonyl; poly(oxyethylene) (POEO) unit= 10, 15, 20, 40 and alkyl= octyl; POEO unit= 10 and 30. Since in each series the alkyl chain length remains same, the effective hydrophobicity decreases with increase in degree of ethoxylation i.e. increase in number of POEO unit. This has been clearly reflected in the CMC data (Table 1). The hydrophobicity of the surfactant decreases with increase in POEO unit and hence micelle formation occurs at higher concentration similar to our earlier observation. This is observed in both OP and NP series. Between two surfactants, NP-10 and OP-10, NP-10 is more hydrophobic than OP-10 since one unit of -CH₂- group contributes about 0.5 unit of hydrophobicity to the surfactant. Hence micelle formation is expected to occur at a higher concentration for OP-10 as compared to NP-10, which is observed to be true. The following quantitative relationship (Eq. 2) has been proposed to correlate CMC with the POEO unit for NP series of surfactants.

\[
\log \text{CMC} = -4.2886 + 0.01913 R
\]

where \( R \) = No. of poly(oxyethylene) unit. \( n =4 \) and \( r = 0.99997 \)

**Evaluation of thermodynamic parameters**

The surface pressure values as calculated using Eq.1 are plotted against logarithm of the concentration of the surfactants. The values of surface pressure at the CMC(\( \pi_{\text{CMC}} \)) are given in Table 1. In order to calculate the amount of surfactant adsorbed per unit area at air/water interface, these surface pressures are fitted to the Gibbs adsorption equation. Assuming the adsorption density of water to be zero, the Gibbs adsorption equation may be written as

\[
d\pi = \Gamma d\mu = \Gamma R T d\ln C
\]

where \( d\pi \) = the change in the surface pressure in the solution, \( \Gamma \) = the adsorption density of the surfactant, \( d\mu \) = the change in the chemical potential of the surfactant, \( R \) = universal gas constant, \( T \) = absolute temperature, \( C \) = concentration of the surfactant in aqueous solution.

Since the surfactant solutions are dilute, the activity is comfortably replaced by concentration. Eq. 3 can be written as

\[
\Gamma = \frac{1}{RT} \left( \frac{d\pi}{d\ln C} \right)
\]

Maximum adsorption density is calculated by limiting the concentration in the above equation to CMC of the surfactant.

Hence Eqn.4 can be expressed as.

\[
\Gamma = \frac{1}{2.303RT} \lim_{C \to \text{CMC}} \left( \frac{d\pi}{d\ln C} \right)
\]

The minimum area per molecule (\( A_{\text{min}} \)) in \( \AA^2 \) can be calculated from Eq. 6.
Surfactant CMC, M $\pi_{\text{CMC}}$ $\Gamma_{\text{max}} \times 10^6$ $\Lambda_{\text{min}}$ $\Delta G_m^\circ$ $\Delta G_m^\circ$ (dyne/cm) (mol m$^{-2}$) (Å$^2$) (kJmol$^{-1}$) (kJmol$^{-1}$)
NP-10 8.000x10$^{-5}$ 42.38 3.16 52.84 -33.10 -46.51
NP-15 1.000x10$^{-4}$ 35.58 2.40 69.47 -32.56 -47.36
NP-20 1.234x10$^{-3}$ 30.69 1.90 87.66 -32.04 -48.15
NP-40 3.000x10$^{-3}$ 24.10 0.83 202.42 -29.85 -59.07
OP-10 4.000x10$^{-3}$ 41.20 2.70 61.78 -29.12 -44.36
OP-30 1.000x10$^{-3}$ 28.69 1.25 133.46 -26.89 -49.83

$A_{\text{min}} = 10^{20}/N \Gamma_{\text{max}}$. ... (6)

where $N$ is the Avogadro's number. The values of $\Gamma_{\text{max}}$ and $A_{\text{min}}$ are given in Table 1. The standard free energies of micellization are obtained from the Eqs 7 and 8 respectively.

$\Delta G_m^\circ = RT \ln(CMC/55.5)$ ... (7)

$\Delta G_m^\circ = \Delta G_m^\circ - (\pi_{\text{CMC}}/\Gamma_{\text{max}})$ ... (8)

and the values are given in Table 1.

It is seen from Table 1 that the area per molecule increases and maximum adsorption density decreases with increase of POEO unit in both nonyl and octyl series. Since the alkyl chain length in a series does not vary, the change in the maximum adsorption density with change in number of poly(oxyethylene) group can be attributed to the change in the latter which ultimately affects the size of the surfactant. Less number of molecules are accommodated per unit area with increase in the size of the molecule and hence adsorption density decreases. The minimum area per molecule also increases with increase in POEO unit because of the same reason. Assuming the change in minimum area per molecule to be due to change in number of POEO unit in a series (having constant alkyl chain length), the area per unit number POEO molecule is calculated. Interestingly, it is found that the minimum area per POEO unit decreases with increase in number of POEO unit. For compact adsorption at the air-water interface, two forces are operating; the hydrophobic interaction of the alkyl chain and the cross sectional area of the POEO unit (since the surfactant anchors at the interface through hydrogen bonding between POEO unit and the water molecule). For the same hydrophobic interaction between two hydrophobic chains of the adjacent surfactant molecules the space available for the POEO chain should be nearly the same. So the surfactants with longer POEO chain are forced to be accommodated more compactly than those with the shorter chain. Hence the area per POEO unit decreases as we go from NP-10 to NP-20. In the case of NP-40, however, the area per POEO unit increases. Probably the size of its POEO units is playing a significant role leading to a less compact packing at the interface. This is also supported from the fluorescence behaviour of pyrene in the presence of NP surfactant micelles.

The emission spectrum of pyrene consists of five peaks out of which the relative intensity of the first ($I_1$) and third ($I_3$) shows greater solvent dependency. Qualitatively the ratio ($I_1/I_3$) decreases with solvent polarity (eg 1.65 for hexane and 0.6 for water) and increases with the formation of micelle. In NP-series all three surfactants except NP-40 micelles have $I_1/I_3$ around 0.85, whereas in case of NP-40 micelles the value is 0.74. This indicates the loose packing of the surfactants in NP-40 micelles leading to the penetration of water into the micelle, thereby increasing the micropolarity of the micelle. Due to loose packing of the surfactants the area per POEO unit increases. Our proposition is also strengthened as we compared the area per unit POEO unit obtained from OP-10 surfactant. Since the surfactant has a shorter alkyl chain length, the hydrophobic interaction becomes relatively less compared to NP-10 (one unit of $\text{CH}_2$ group contributes about 0.5 unit of hydrophobicity to the surfactant). Hence OP-10 is under less strain than NP-10. Consequently the area per POEO unit for OP-10 is more than that of NP-10.

To investigate the type of arrangement of POEO units on the water surface during the monolayer formation the area/molecule is plotted against the powers of the number of POEO unit in NP series. A straight line is obtained with correlation coefficient = 0.9997 when area per molecule is plotted against square of the POEO unit. This indicates that the
POEO units cover the water surface in a flat on position as shown in Fig. 3.

The $\Delta G^m$ values are all negative which indicates that the formation of micelle is a spontaneous processes. The $\Delta G^m$, however, becomes less negative and hence relatively less spontaneous with increase in number of POEO unit in both series. This indicates that the increase in poly(oxyethylene) units has an adverse effect on micellization. Each POEO unit is found to increase $\Delta G^m$ value by $0.108 \pm 0.010$ kJ mol$^{-1}$. Similarly, with decreasing methylene group in the hydrophobic chain, $\Delta G^m$ increases due to decrease in hydrophobicity. Each methylene unit has a contribution of $3.982$ kJ mol towards the micellization process. The $\Delta G^ad$ values is in a reverse trend to that of $\Delta G^m$. It looks reasonable since with the increase in number of POEO unit, binding of the hydrophobic units with water increases and $\Delta G^ad$ values therefore, decrease. The $\Delta G^ad$ values are found to be more negative compared to $\Delta G^m$ values. This is attributed to the fact that work has to be done to transfer the surfactant molecule in the monomeric form from surface to the micelle.

However, the decrease in $\Delta G^ad$ with decrease in methylene units in the hydrophobic tail is attributed to a co-operativity in the adsorption phenomena. With varying alkyl group in the hydrophobic tail with the same hydrophilic unit, the surfactant with longer hydrophobic chain is found to bind more strongly at the air-water interface thus decreasing $\Delta G^ad$. Thus binding is supported by greater co-operativity of nonyl chain than that of the octyl chain.

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