

## Synthesis and Interaction Investigation of a Non-ionic Surfactant in Aqueous Medium at Different Temperatures

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The surface tension data have been utilized for evaluation of surface and thermodynamic parameters. Isooctylphenoxy polyethoxy ethanol (TX-100) with/without aqueous  $\text{Na}_2\text{SO}_4$  has been reported at 288.15, 293.15 and 298.15 K. Thermodynamic parameters indicate that processes are endothermic in nature but negative values of  $\Delta G_{\text{mic}}^0$  and positive  $\Delta S_{\text{mic}}^0$  favours the process of micellization.

**Key Words:** Non-ionic surfactant, Interaction, Synthesis.

### INTRODUCTION

The interaction of surface active substances in aqueous system have been a field of investigation. These studies are supposed to be landmarking in the field of interaction of medicinal solution, agrochemicals, detergency, solubilizing power, enhanced oil recovery and in metallurgical process<sup>1-4</sup>. There are several reports on various physicochemical properties of surfactants in aqueous medium. However, the data on surface and thermodynamic parameters for non-ionic surfactant are limited<sup>5-9</sup>. In the present investigation) the data for surface parameters such as critical micelle concentration (CMC), surface pressure at CMC ( $\pi_{\text{cmc}}$ ), surface excess concentration ( $\Gamma_{\text{max}}$ ), minimum area per molecule at the air-liquid interface ( $A_{\text{min}}$ ) and thermodynamic parameter for micellization of aqueous solution of isooctylphenoxy polyethoxy ethanol (TX-100) in the presence and absence of sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) at 288.15, 298.15 K are reported.

### EXPERIMENTAL

**(a) Synthesis of surfactant:** The non-ionic surfactant isooctylphenoxy polyethoxy ethanol (TX-100) was synthesized by the reaction between recrystallized *t*-octyl phenol and ethylene oxide following the Crook *et al.*<sup>10</sup> and Mansfield *et al.*<sup>11</sup> methods. The ethylene oxide content of the compound was determined by weight increase and chemical hydroxyl methods. The surfactant was purified with hot ethanol. The purity of material was checked by thin layer chromatography and hydroxyl number analysis<sup>12</sup>. Purity of the sample was also checked by determining the CMC from surface tension method.

The electrolyte  $\text{Na}_2\text{SO}_4$  obtained from S.D. Fine Chemicals was of AR grade and used without further purification. The various solutions of surfactant and

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electrolyte were prepared in doubly distilled water having specific conductance of  $2.00 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ .

(b) **Methods:** Surface tensions of different solutions of surfactant in water and aqueous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) were determined from the dropweight method using stalagmometer described elsewhere<sup>13</sup> at three different temperatures. The stalagmometer was calibrated by determining the surface tension of pure liquids and reproducibility of results was within  $\pm 0.2\%$ . All the measurements were made in a water thermostat whose temperature was controlled within  $\pm 0.01 \text{ K}$ .

## RESULTS AND DISCUSSION

Critical micelle concentration (CMC) values for the TX-100 in water and aqueous  $\text{Na}_2\text{SO}_4$  systems have been obtained from the plots of surface tension vs.  $\log [\text{surfactant}]$ . CMC values for the studied systems are presented in Table-1.

TABLE-1  
CRITICAL MICELLE CONCENTRATION (CMC), SURFACE EXCESS CONCENTRATION ( $\Gamma_{\text{max}}$ ), MINIMUM AREA PER MOLECULE ( $A_{\text{min}}$ ) AND THE SURFACE PRESSURE AT THE CMC ( $\pi_{\text{cmc}}$ ) FOR ISO-OCTYLPHENOXYPOLYETHOXY ETHANOL (TX-100) IN WATER AND WATER + ELECTROLYTE SYSTEMS

$\text{Na}_2\text{SO}_4$ (mol/L)	Temp. (K)	$\text{CMC} \times 10^3$ (mol dm <sup>-3</sup> )	$\Gamma_{\text{max}} \times 10^{10}$ (mol cm <sup>-2</sup> )	$A_{\text{min}} \times 10^2$ (nm <sup>2</sup> )	$\pi_{\text{cmc}} \times 10^3$ (Nm <sup>-1</sup> )
0	288	0.49	2.18	72.6	35.8
	293	0.42	2.09	79.4	36.9
	298	0.36	2.01	82.6	38.1
0.025	288	0.42	1.85	89.7	41.9
	293	0.35	1.70	97.7	41.4
	298	0.28	1.58	105.1	41.8
0.050	288	0.37	1.80	92.2	42.2
	293	0.30	1.60	103.8	42.5
	298	0.22	1.50	110.7	42.8
0.075	288	0.31	1.63	101.9	42.6
	293	0.25	1.51	109.9	43.2
	298	0.19	1.40	118.6	43.5

Table-1 shows that CMC values of TX-100 agree well with those reported in literature<sup>14</sup>. It is clear that CMC of aqueous surfactant decreases with increase in temperature. This may be due to the dehydration of the surfactant molecule with change in temperature. The further decrease in CMC values of the surfactant (TX-100) with the successive addition of sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) in surfactant solution may be partly due to the salting out of the hydrated ethylene oxide

condensate of the surfactant<sup>15</sup> and partly due to ion-dipole interaction of Na<sup>+</sup> and negative dipole of the hydroxyl group of the surfactant.

Maximum surface excess concentration ( $\Gamma_{\max}$ ) values at the air-liquid interfaces have been obtained using Gibbs adsorption equation<sup>6</sup>

$$\Gamma_{\max} = -1/2.0303 nRT (d\gamma/d \log C)_T \quad (1)$$

where  $n$  is the number of particles released per surfactant molecule in the solution;  $R$ , is the gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and  $(d\gamma/d \log C)_T$  represents the slope of the surface tension vs.  $\log C$  plot below the CMC at constant temperature  $T$ . In the present investigation  $n = 1$  for non-ionic surfactant. The calculated values for  $\Gamma_{\max}$  for the studied systems at three temperatures are also recorded in Table-1. From Table-1 it is evident that  $\Gamma_{\max}$  values decrease with increase in temperature, which may be due to enhanced molecular thermal agitation<sup>16</sup>. A further decrease in  $\Gamma_{\max}$  values with addition of electrolyte may be due to displacement of surfactant molecules from the air-liquid interface to the bulk phase.

The minimum area per molecule  $A_{\min}$  at the liquid-air interface has been calculated using the following equation<sup>6</sup>:

$$A_{\min} = 10^{14}/N\Gamma_{\max} \quad (2)$$

where  $N$  is Avogadro's number.  $A_{\min}$  values for the studied systems are given in Table-1. An examination of these values reveals that  $A_{\min}$  increases with increase in temperature as well as with addition of sodium sulphate to the surfactant solution. This behaviour can be explained on the basis that the addition of an electrolyte makes the surfactant more compatible with the solvent and thereby causes a shift of surfactant from air-liquid interface to the bulk phase.

Surface pressure at the CMC ( $\pi_{\text{cmc}}$ ) was calculated using the following equation<sup>6</sup>:

$$\pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}} \quad (3)$$

$\pi_{\text{cmc}}$  is an index of reduction of surface tension at CMC.  $\pi_{\text{cmc}}$  values are presented in Table-1 and  $\pi_{\text{cmc}}$  increase with increase in temperature.

Thermodynamic parameters of micellization, viz.,  $\Delta G_{\text{mic}}^0$ ,  $\Delta H_{\text{mic}}^0$  and  $\Delta S_{\text{mic}}^0$  have been calculated using the eqns.<sup>6</sup> (4–6).

$$\Delta G_{\text{mic}}^0 = RT \ln X \quad (4)$$

$$\Delta S_{\text{mic}}^0 = -d(\Delta G_{\text{mic}}^0)/dT \quad (5)$$

$$\Delta H_{\text{mic}}^0 = \Delta G_{\text{mic}}^0 + T \Delta S_{\text{mic}}^0 \quad (6)$$

The various thermodynamic parameters of micellization calculated using equations (4–6) are presented in Table-2. The  $\Delta G_{\text{mic}}^0$  values are found to be negative for the studied systems indicating that these processes are spontaneous ones. The negative  $\Delta G_{\text{mic}}^0$  values increase with increase in temperature and addition of the Na<sub>2</sub>SO<sub>4</sub> to the TX-100 solution. The negative  $\Delta G_{\text{mic}}^0$  values favour that addition of Na<sub>2</sub>SO<sub>4</sub> to TX-100 solution facilitate the micellization. This can be attributed to the fact that there is decreased hydration of the surfactant molecule in the more structured water in the presence of an electrolyte.

TABLE-2  
THERMODYNAMIC PARAMETERS OF MICELLIZATION OF ISOCTYLPHENOXY-POLYETHOXY ETHANOL (TX-100) IN WATER AND WATER + ELECTROLYTE SYSTEMS

Na <sub>2</sub> SO <sub>4</sub> (mol/litre)	Temp. (K)	-ΔG <sub>mic</sub> <sup>0</sup> (kJ mol <sup>-1</sup> )	ΔH <sub>mic</sub> <sup>0</sup> (kJ mol <sup>-1</sup> )	ΔS <sub>mic</sub> <sup>0</sup> (kJ K <sup>-1</sup> mol <sup>-1</sup> )
0	288	27.9	18.2	0.16
	293	28.7	21.1	0.17
	298	29.6	24.0	0.18
0.025	288	28.3	23.5	0.18
	293	29.2	29.4	0.20
	298	30.3	35.3	0.22
0.050	288	28.5	34.9	0.22
	293	29.6	37.8	0.24
	298	30.9	46.6	0.26
0.075	288	29.0	40.1	0.24
	293	30.2	46.0	0.26
	298	31.6	51.8	0.28

The ΔH<sub>mic</sub><sup>0</sup> values are positive and increase with an increase in temperature but ΔS<sub>mic</sub><sup>0</sup> values are also positive which favour the process of micellization. A positive entropy change indicates that the micellization process is mainly controlled by the entropy gain rather than by an energy effect.

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#### REFERENCES

1. M.J. Schwuger, *J. Colloid Interface Sci.*, **43**, 491 (1973).
2. P. Dutta and S.P. Moulik, *Indian J. Biochem. Biophys.*, **35**, 1 (1998).
3. D.O. Shah, *Surface Phenomena in Oil Enhanced Recovery*, Plenum Press, New York (1991).
4. A. Kahn and J. Lynn, in: *Encyclopedia of Technology*, Wiley, New York, p. 332 (1993).
5. B.W. Barry and G.F.J. Russel, *J. Colloid Interface Sci.*, **40**, 174 (1972).
6. M.J. Rosen, A.W. Cohen, M. Dahanayaki and X. Hua, *J. Phys. Chem.*, **86**, 541 (1982).
7. M.S. Bakshi, *J. Chem. Soc. Faraday Trans. 1*, **89**, 4223 (1993).
8. K. Mukherjee, D.C. Mukherjee and S.P. Moulik, *J. Phys. Chem.*, **98**, 4713 (1994).
9. S. Ghosh and S.P. Moulik, *Indian J. Chem.*, **38A**, 10 (1999).
10. E.H. Crook, D.B. Fordyce and G.F. Trebbi, *J. Phys. Chem.*, **67**, 1987 (1963).
11. R.C. Mansfield and J.E. Locke, *J. Am. Oil Chemists Soc.*, **41**, 267 (1964).
12. C.L. Hilton, *Anal. Chem.*, **31**, 1610 (1959).
13. D.V.S. Jain and S. Singh, *Indian J. Chem.*, **10**, 629 (1979).
14. W.W. Sukow, H.E. Sandber, E.A. Lewis, D.J. Eatough and L.D. Hansen, *Biochem.*, **19**, 912 (1980).
15. M.J. Schick, S.M. Atlas and F.R. Eirich, *J. Phys. Chem.*, **66**, 1326 (1962).
16. S. Nandi, S.C. Bhattacharya and S.P. Moulik, *Indian J. Chem.*, **39A**, 589 (2000).