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# Effects of Na<sub>2</sub>SO<sub>4</sub> and Na<sub>3</sub>PO<sub>4</sub> on the surface and thermodynamic properties of an anionic surfactant: bis-(2- ethyl hexyl) sodium sulfosuccinate (AOT) in aqueous solutions

Suman Bala<sup>a</sup>, Ram Partap<sup>a,\*</sup> & O P Yadav<sup>b</sup>

<sup>a</sup>Department of Chemistry, Government College, Hisar 125 004, India <sup>b</sup>Department of Chemistry, CCS Haryana Agricultural University, Hisar 125 004, India \*E-mail: rampartap@rediffmail.com

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From tensiometric measurements, critical micelle concentration (CMC), maximum surface excess concentration, minimum area per molecule at the air-liquid interface and thermodynamic parameters of micellization have been determined for an anionic surfactant: bis-(2-ethylhexyl) sodium sulfosuccinate (AOT) in aqueous medium. Effects on the above physico-chemical properties due to added electrolytes:  $Na_2SO_4$  and  $Na_3PO_4$  over a wide range of the surfactant concentrations and at 288.15, 293.15 and 298.15 K have been described in the light of intermolecular interactions. The CMC of AOT is lowered and the micellar stability is improved upon mixing the above electrolytes in aqueous surfactant solution and the same become more pronounced when divalent  $SO_4^{2-}$  are replaced by trivalent  $PO_4^{3-}$ . These observations may be beneficial for improving efficiency of AOT as a detergent, managing oil spill problem, in froth-flotation process for concentrating ores and for efficient recovery of petroleum in the tertiary process.

Keywords: Electrolytes, Micellization, Tensiometric, Thermodynamic, Critical micelle concentration

Surfactants are a unique class of chemical compounds with amphiphilic nature exhibiting hydrophilic as well as lipophilic properties. These may exist in a solvent as monomers, can concentrate at air-liquid or liquidliquid interface and above critical micellar concentration (CMC), may aggregate to form micelles. In polar solvents these form normal micelles with their hydrophilic or ionic head group pointing towards the interior of micelle and the non-polar hydrophobic chain pointing outwards<sup>1-3</sup>. With these characteristic features the surface active compounds find several practical applications such as in detergency<sup>4</sup>, biological studies<sup>5</sup>, enhanced oil recovery<sup>6-7</sup>, cosmetic, paint, food science bioremediation, chemical transformation<sup>8</sup>, agriculture, in metallurgical processes<sup>9</sup>, drug delivery, optoelectronic and even in nanotechnology $^{10}$ .

The physico-chemical studies of surfactant solutions in aqueous medium with and without electrolyte are important from the fundamental as well as application point of view in understanding the mechanism of these interactions. There have been several reports on various physico-chemical properties of surfactants in aqueous solution<sup>11-16</sup>. Moulik et al.<sup>11</sup> studied micellar properties of some cationic surfactants in pure and mixed states and using Rubingh's theory, they found

that surfactant mixtures were non-ideal with a lower degree of counter-ion association compared to pure states. Kumar and Yadav<sup>12</sup> used equilibrium dialysis technique for studying interaction of some surfactants with Poly(N-vinyl-2-pyrrolidone) (PVP) and Bovine Serum Albumin. Titration calorimetric study of the interaction between ionic surfactants and uncharged polymers in aqueous solution were studied by Wang and Olofsson<sup>13</sup>. From the molecular dynamics computer simulations study on sodium dodecyl sulfate (SDS), Dominguez and Berkowitz<sup>14</sup> reported that the surfactant tails are less ordered at the water/vapor interface. Sukul et al.<sup>15</sup> studied polymer-surfactant interaction by excited state proton transfer method using 1-naphthol as a probe and reported that the critical association concentration of SDS for the PVP-SDS system is 10 times lower than the CMC of SDS.

A comparative adsorption of linear alkane sulfonate and benzene sulfonate surfactants at liquid interfaces was studied by Watry and Richmond<sup>16</sup> using vibrational sum frequency spectroscopy and have reported that the change in aromatic ring orientation as a function of surface concentration is quite different for the dodecyl benzene sulfonate at the air/water interface relative to that at the organic/water

interface (CCl<sub>4</sub>/water). However, the reports on physico-chemical properties of surface active compounds in aqueous electrolyte solutions are limited.<sup>17-22</sup>. Para et al.<sup>17</sup> studied the effect of electrolytes on surface tension of ionic surfactant solutions and developed an improved model of surfactant adsorption considering penetration of counter-ions into the interfacial Stern layer. Gu and Galera-Gómez<sup>18</sup> studied the effect of added electrolytes on the cloud point of Triton X-114 in the presence of ionic surfactants and have reported that the mixing of surfactants TX114 and TX100 solution shows a negative deviation from ideal additivity. Effects of some inorganic ions on surface properties of non-ionic surfactants such as iso-octyl phenoxy polyethoxy ethanol, in aqueous medium, have been reported by Ram Partap and Yadav<sup>19</sup>. Ram Partap et al.<sup>20</sup> studied surface and thermodynamic properties of a cationic surfactant: cetyl pyridinium chloride in aqueous sodium chloride solutions. They reported micellization process favoured by entropy gain as well as exothermic effect, however, the adsorption at the air-liquid interface though endothermic yet is made feasible by dominating entropy gain, Demissie and Duraisamy<sup>21</sup> studied the effects of electrolytes on the surface and micellar characteristics of SDS surfactant solution. Udoh and Vinogradov<sup>22</sup> have studied the behaviour of biosurfactants in brine solutions relevant to hydrocarbon reservoirs.

We report here surface excess concentration ( $\Gamma_{max}$ ), minimum area per molecule at the air–liquid interface ( $A_{min}$ ), surface pressure at CMC ( $\pi_{cmc}$ ) and thermodynamic parameters of micellization and interfacial adsorption of an anionic surfactant: bis-(2-ethyl hexyl) sodium sulfosuccinate (AOT) with or without added Na<sub>2</sub>SO<sub>4</sub> and Na<sub>3</sub>PO<sub>4</sub> at 288.15, 293.15 and 298.15 K.

## **Materials and Methods**

Sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>, MW= 142.04 g mol<sup>-1</sup>, BDH) and Sodium phosphate (Na<sub>3</sub>PO<sub>4</sub>, MW= 163.94; BDH) were of AR grade. Sodium bis(2-ethyl hexyl) sulphosuccinate (AOT) (C<sub>20</sub>H<sub>38</sub>NaO<sub>7</sub>S, MW: 445.57 g mol<sup>-1</sup>) was purchased from SD fine chemicals and its molecular structure is shown in Fig. 1. Doubly distilled water (specific conductance  $2.0 \times 10^{-6}$  S cm<sup>-1</sup>) was used for preparing various aqueous AOT solutions.

Surface tensions of aqueous AOT solutions, with or without added Na<sub>2</sub>SO<sub>4</sub> and Na<sub>3</sub>PO<sub>4</sub> were measured by drop-weight method using a modified stalagmometer, described elsewhere<sup>23</sup>. The stalagmometer was calibrated using standard liquids including benzene, *n*-hexane, carbon tetrachloride, acetophenone and water. Surface tensions were measured over a wide range of AOT concentrations and at temperatures 288.15, 293.15 and 298.15 K. using a thermostatic bath (Tempstar, Model KW 201 A) that ensured temperature control within  $\pm 0.01$  K. The reproducibility of measured surface tension values was within  $\pm 0.2$  m Nm<sup>-1</sup>. A digital conductivity meter (Model E.I. 601 E) was employed for conductance measurements of surfactant solutions.

# **Results and Discussion**

#### **Critical micelle concentration**

The plots of surface tension versus log [AOT], conductivity versus [AOT] and specific viscosity versus [AOT], for AOT aqueous solutions are presented in Figs 2-4, respectively. The values of CMC of AOT aqueous solutions, obtained from the break-point of such plots are recorded in Table 1. The observed values for CMC of pure surfactant at 298 K agree well with those reported in literature<sup>24-26</sup>. The CMC values have also been evaluated from the conductance and viscosity measurements and recorded



Fig. 1 — Molecular structure of sodium bis (2-ethyl hexyl) sulphosuccinate (AOT)



Fig. 2 — Plots of surface tension (m  $Mm^{-1}$ ) as a function of Log [AOT] at 288.15, 293.15 and 298.15 K for AOT+H<sub>2</sub>O system



Fig. 3 — Plot of specific conductance (k)  $\times 10^4$  (S cm<sup>-1</sup>) as a function of [AOT] at 288.15, 293.15 and 298.15 K for AOT+H<sub>2</sub>O system



Fig. 4 — Plots of specific viscosity ( $\eta_s$ ) as a function of [AOT] at 288.15, 293.15 and 298.15 K for AOT+H<sub>2</sub>O system

in parentheses in Table 1 and are in good agreement with those determined from surface tension data. Surface tension as a function of temperature at a fixed 0.1 mM AOT concentration with varying Na<sub>2</sub>SO<sub>4</sub> and Na<sub>3</sub>PO<sub>4</sub> levels are shown in Figs 5 and 6, respectively. It is observed that surface tension of aqueous AOT solution decreases both upon increasing temperature as well as on increasing an electrolyte concentration. This is obvious because the water structure disruption enhanced during both these events leading is to lowering of inter-molecular interaction at the air-liquid interface and hence the observed lowering of surface tension. The CMC of AOT in an aqueous solution increases upon raising the temperature. This may be because enhanced thermal agitation at higher temperature causes lowering of counter ion charge density resulting in an enhanced ion-ion head groups' repulsion thus shifting the surfactant monomers  $\rightleftharpoons$ micelle equilibrium in favor of the monomers leading to higher  $CMC^{27,28}$ .

Upon adding an electrolyte to an AOT aqueous solution, the CMC decreases due to (a) enhanced dielectric constant of aqueous medium (b) increased charge density of AOT counter-ion (causing a diminished inter-molecular head-group repulsion) and (c) hydrogen-bonded water structure disruption due to the added electrolyte allowing more hydrophobic

Table 1 — Critical micelle concentration (CMC), surface excess concentration ( $\Gamma_{max}$ ), minimum area per molecule ( $A_{min}$ ) and surface pressure at CMC ( $\pi_{cmc}$ ) for bis-(2-ethyl hexyl) sodium sulfosuccinate (AOT) aqueous solutions at varying molar concentrations of an added electrolyte (Na<sub>2</sub>SO<sub>4</sub> and Na<sub>3</sub>PO<sub>4</sub>)

System	Temp. (K)	$CMC \times 10^{3}$ (mol dm <sup>-3</sup> )	$\Gamma_{\rm max}  imes 10^{10}$ (mol cm <sup>-2</sup> )	$\begin{array}{c} A_{min} \times 10^2 \\ (nm^2) \end{array}$	π <sub>cmc</sub> (m Nm <sup>-1</sup> )
AOT+H <sub>2</sub> O	288.15	1.82(1.84* 1.84**)	2.68	61.9	31.7
_	293.15	2.12(2.14* 2.14**)	2.55	65.1	32-4
	298.15	2.42(2.44* 2.50**)	2.42	68.6	35.4
AOT+0.025 M	288.15	1.46(1.48)	1.80	92.2	44.7
Na <sub>2</sub> SO <sub>4</sub> +H <sub>2</sub> O	293.15	1.67(1.68)	1.64	101.2	46.4
	298.15	1.84(1.86)	1.44	115.3	47.9
AOT+0.050 M	288.15	1.30(1.34)	1.56	106.4	45.9
Na <sub>2</sub> SO <sub>4</sub> +H <sub>2</sub> O	293.15	1.50(1.52)	1.43	116.1	47.4
	298.15	1.62(1.64)	1.31	126.7	48.6
AOT+0.075 M	288.15	1.13(1.18)	1.45	114.5	47.1
Na <sub>2</sub> SO <sub>4</sub> +H <sub>2</sub> O	293.15	1.31(1.34)	1.34	123-9	48.6
	298.15	1.42(1.44)	1.24	133.9	49.6
AOT+0.025 M	288.15	1.40 (1.42)	1.56	106.4	47.5
Na <sub>3</sub> PO <sub>4</sub> +H <sub>2</sub> O	293.15	1.60 (1.62)	1.46	113.7	48.4
	298.15	1.78 (1.80)	1.38	120.3	48.9
AOT+0.050 M	288.15	1.22 (1.26)	1.51	109.9	48.3
Na <sub>3</sub> PO <sub>4</sub> +H <sub>2</sub> O	293.15	1.41 (1.44)	1.41	117.8	48.9
	298.15	1.55 (1.58)	1.30	127.7	49.6
AOT+0.075 M	288.15	1.04 (1.06)	1.39	118.6	49.4
Na <sub>3</sub> PO <sub>4</sub> +H <sub>2</sub> O	293.15	1.21 (1.24)	1.31	126.7	49.7
	298.15	1.32 (1.36)	1.19	139.5	49.9
CMC values from vi	scosity measure	ments and **CMC values fr	om conductance meas	urements	



Fig. 5 — Plots of surface tension versus temperature at a fixed 0.1 mM AOT concentration with varying  $Na_2SO_4$  levels



Fig. 6 — Plots of surface tension versus temperature at a fixed 0.1 mM AOT concentration with varying  $Na_3PO_4$  levels

interaction between surfactant alkyl chains thereby facilitating micellization<sup>29-31</sup>. All these factors also lead to contraction of electrical double layer around the micelle in the presence of an electrolyte resulting in the lowering of the CMC<sup>32</sup>. The effect of electrolyte's anionic valency upon decreasing CMC of AOT was found in the order: trivalent ( $PO_4^{3^-}$ ) > divalent ( $SO_4^{2^-}$ ).

### Maximum surface excess concentration:

The values of maximum excess concentration  $(\Gamma_{\text{max}})$  at the air-liquid interfaces have been obtained using Gibb's adsorption equation<sup>33</sup>

$$\Gamma_{\text{max}} = -1/2.303 \text{ nRT}(d\gamma/d(\log C))_{\text{T}} \qquad \dots (1)$$

where *n* is the number of particles released per surfactant molecule in the solution; R is the gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>) and C is the surfactant molar concentration. The  $(d\gamma/d \log C)_T$  is the slope

of the plot for surface tension versus log *C* below CMC, at constant *T* and for the ionic surfactant AOT, n = 2. The values of  $\Gamma_{max}$  thus obtained, at varying electrolyte concentrations as well temperatures, for the studied systems are also presented in Table 1. The  $\Gamma_{max}$  values decrease with increasing temperature which may be due to the enhanced thermal agitation at higher temperature causing a partial shifting of surfactant monomers from the air-liquid interface to the bulk<sup>34</sup>. The  $\Gamma_{max}$  values further decrease upon mixing an electrolyte in an AOT solution owing to the displacement of a fraction of surfactant molecules at the air-liquid interface by electrolyte molecules. Such decrease in  $\Gamma_{max}$  is more pronounced upon adding Na<sub>3</sub>PO<sub>4</sub> than Na<sub>2</sub>SO<sub>4</sub>.

#### Minimum area per molecule

Minimum area per molecule  $(A_{\min})$  at the liquid–air interface was calculated using the equation<sup>33</sup>

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

Where, 'N' is the Avogadro's number. The values of  $A_{\min}$  presented in Table 1, show the positive dependence on temperature as well as on the amount of added electrolyte. It may be because at a higher temperature, due to the expansion of liquid, the available free space per molecule is increased allowing it to stretch further and an added electrolyte, by causing a partial disruption of water-structure, enables further relaxing of the surfactant monomers.

## Surface pressure at CMC

Surface pressure at CMC ( $\pi_{cmc}$ ), an index of the surface tension reduction at CMC, was calculated using the relation <sup>33</sup>:

$$\pi_{\rm cmc} = \gamma_0 - \gamma_{\rm cmc} \qquad \dots (3)$$

Where  $\gamma_0$  = surface tension of pure water and  $\gamma_{cmc}$  = surface tension at CMC. The calculated  $\pi_{cmc}$  values (Table 1) increase with increasing temperature as well as on mixing an electrolyte. It may be because higher temperature and addition of an electrolyte both cause weakening of hydrogen-bonded water-structure in the bulk thus cumulatively contribute to decrease in intermolecular interaction of water molecules resulting in the observed lowering of the surface tension i.e.  $\pi_{cmc}$ .

## Thermodynamic parameters of micellization

Standard Gibb's free energy of micellization ( $\Delta G^{0}_{mic}$ ) for AOT in aqueous solution, with or without an added electrolyte, was calculated using the equation<sup>33</sup>

 $\Delta G_{\rm mic}^0 = RT \ln X_{\rm cmc} \qquad \dots (4)$ 

Where,  $\beta$  is the fraction of micellar charge un-neutralized by the counter ions and was determined from the ratio of post- and pre-micellar slopes of specific conductance versus [surfactant] plot, R are T are gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>) and temperature in Kelvin, respectively, X<sub>cmc</sub> represents the mole fraction of surfactant at CMC. The standard state for surfactant is taken as the solvated surfactant monomer at unit mole fraction referred to infinite dilute solution, and for micelle, the micelle itself is considered as its standard state.

Entropy of micellization ( $\Delta S^{0}_{mic}$ ) and enthalpy of micellization ( $\Delta H^{0}_{mic}$ ) were obtained using the following equations<sup>33</sup>:

$$\Delta S_{\rm mic}^0 = -d(\Delta G_{\rm mic}^0)/dT \qquad \dots (5)$$

$$\Delta H_{\rm mic}^0 = \Delta G_{\rm mic}^0 + T \Delta S_{\rm mic}^0 \qquad \dots (6)$$

The above thermodynamic parameters of micellization, presented in Table 2, suggest that the micelle forming process in aqueous media is favoured both by entropy gain as well as by exothermic enthalpy change. The  $\Delta G^{0}_{mic}$  values, for AOT+H<sub>2</sub>O as well as AOT+electrolyte+H<sub>2</sub>O solutions are negative. It suggests the feasibility of AOT micelle formation in

aqueous media at the studied temperatures. Plots of standard Gibbs free energy of micellization  $(\Delta G^0_m)$ versus temperature at different concentration of  $Na_2SO_4$  and  $Na_3PO_4$  are presented in Figs 7 and 8, respectively. The lowering of  $\Delta G^0_{\text{mic}}$  upon increasing temperature may be due to entropy gain because of enhanced thermal agitation as well as water structure disruption. The  $\Delta \vec{G}_{\text{mic}}^{\vec{0}}$  values decrease (i.e. become more negative) upon mixing an electrolyte in an AOT solution due to entropy gain by water structure disruption caused by the added electrolyte. The  $\Delta G^{0}_{mic}$ is further lowered upon raising the electrolyte concentration. However, mixing of trivalent PO<sub>4</sub><sup>3</sup> anion in an AOT solution caused more lowering of  $\Delta G^0_{\text{mic}}$  (or higher AOT micellar stabilization) in comparison to divalent  $SO_4^{2-}$ .

The entropy of micellization  $\Delta S^{0}_{mic}$  values are invariably positive and increase with increasing temperature as well as on mixing an electrolyte in AOT solutions. It is obvious since higher temperature and added electrolyte both cause disruption of water structure resulting in a cumulative increase of entropy gain. Enthalpy of micellization ( $\Delta H^{0}_{mic}$ ) values are exothermic for AOT aqueous solutions with or without an added electrolyte. However, the exothermicity decreases upon raising the temperature as well as upon mixing an electrolyte due to endothermic water structure breaking in both these cases.

Table 2 — Thermodynamic parameters of micellization, interfacial adsorption and transfer from water to electrolyte solution for bis-(2-ethyl hexyl) sodium sulfosuccinate (AOT) at varying molar concentrations of  $Na_2SO_4$  and  $Na_3PO_4$ 

System	Temp. (K)	$-\Delta G^0_{m.}/-\Delta G^0_{ad}/-\Delta G^0_{tr}$ (kJ mol <sup>-1</sup> )	$-\Delta H^{0}_{mic} / \Delta H^{0}_{ad} / \Delta H^{0}_{tr}$ (kJ mol <sup>-1</sup> )	$\frac{\Delta S^0_m}{(kI mol^{-1} K^{-1})}$
AOT+H <sub>2</sub> O	288.15	24.73 / 25.91 / -	21.27 /17.27 / -	0.012 / 0.030 / -
-	293.15	24.79 / 26.06 / -	20.40 /13.46 / -	0.015 / 0.043 / -
	298.15	24.88 / 26.34 / -	19.51 /09.64 / -	0.018 / 0.056 / -
AOT+0.025M	288.15	25.26 / 27.79 / 0.53	18.92 / 04.16 /2.35	0.020 / 0.082 / 0.010
Na <sub>2</sub> SO <sub>4</sub> +H <sub>2</sub> O	293.15	25.37 / 28.20 / 0.58	16.58 / 04.04 /3.82	0.030 / 0.110 / 0.015
	298.15	25.56 / 28.89 / 0.68	14.23 /12.25 /5.28	0.038 / 0.138 / 0.020
AOT+0.050M	288.15	25.53 / 28.44 / 0.79	19.77 / 0.20 / 2.09	0.022 / 0.098 / 0.012
Na <sub>2</sub> SO <sub>4</sub> +H <sub>2</sub> O	293.15	25.63 / 28.93 / 0.84	15.67 / 4.48 / 4.73	0.034 / 0.114 / 0.019
	298.15	25.87 / 29.58 / 0.99	11.56 / 8.58 / 7.95	0.048 / 0.128 / 0.028
AOT+0.075M	288.15	25.83 / 29.08 / 1.10	18.34 / 01.44 / 2.93	0.026 / 0.104 / 0.014
Na <sub>2</sub> SO <sub>4</sub> +H <sub>2</sub> O	293.15	25.96 / 29.60 / 1.17	15.12 / 04.43 / 5.28	0.037 / 0.118 / 0.022
	298.15	26.20 / 30.26 / 1.32	11.19 / 10.29 / 7.26	0.048 / 0.132 / 0.032
AOT+0.025M	288.15	25.36 / 28.40 / 0.63	19.02 / 6.50 / 2.25	0.022 / 0.076 / 0.010
Na <sub>3</sub> PO <sub>4</sub> +H <sub>2</sub> O	293.15	25.47 / 28.78 / 0.68	17.27 / 5.34 / 3.13	0.028 / 0.080 / 0.013
	298.15	25.64 / 29.20 / 0.76	15.50 / 4.16 / 4.01	0.034 / 0.084 / 0.016
AOT+0.050M	288.15	25.69 / 28.93 / 0.96	20.50 / 6.45 / 2.49	0.018 / 0.078 / 0.012
Na <sub>3</sub> PO <sub>4</sub> +H <sub>2</sub> O	293.15	25.78 / 29.32 / 0.99	17.28 / 4.10 / 3.11	0.029 / 0.086 / 0.014
	298.15	25.98 / 29.79 / 1.10	14.05 / 1.76 / 5.46	0.040 / 0.094 / 0.022
AOT+0.075M	288.15	26.06 / 29.62 / 1.31	20.87/ 4.84/ 2.72	0.018 / 0.086 / 0.014
Na <sub>3</sub> PO <sub>4</sub> +H <sub>2</sub> O	293.15	26.15 / 30.05 / 1.38	16.77 / 3.08 / 4.19	0.032 / 0.092 / 0.019
	298.15	26.38 / 30.54 / 1.50	12.67 / 1.32 / 5.66	0.046 / 0.098 / 0.024



Fig. 7 — Plots of standard Gibbs free energy of micellization  $(\Delta G^0_m)$  versus temperature at different concentrations of Na<sub>2</sub>SO<sub>4</sub>



Fig. 8 — Plots of standard Gibbs free energy of micellization  $(\Delta G^0_m)$  versus temperature at different concentrations of Na<sub>3</sub>PO<sub>4</sub>

#### Thermodynamic parameters of adsorption

Thermodynamic parameters of adsorption at liquidair interface viz.  $\Delta G^{0}_{ad}$ ,  $\Delta H^{0}_{ad}$  and  $\Delta S^{0}_{ad}$  have been evaluated using the relations<sup>35</sup>:

$$\Delta G_{ad}^{0} = \Delta G_{mic}^{0} - 6.023 \times 10^{-1} \pi_{cmc} \ .A_{min} \qquad \dots (7)$$

$$\Delta S_{ad}^{0} = -d(\Delta G_{ad}^{0})/dT \qquad \dots (8)$$

$$\Delta H_{ad}^0 = \Delta G_{ad}^0 + T \Delta S_{ad}^0 \qquad \dots (9)$$

Where, R, T,  $X_{cmc}$ ,  $\pi_{cmc}$  and  $A_{min}$  are as defined above. The values of  $\Delta G^{0}_{ad}$ ,  $\Delta H^{0}_{ad}$  and  $\Delta S^{0}_{ad}$  thus obtained are also included in Table 2. The observed lower values of  $\Delta G^{0}_{ad}$  compared to corresponding  $\Delta G^{0}_{mic}$  for AOT solutions, at studied temperatures and electrolyte concentrations, suggest that the process of adsorption of AOT monomers at the air-liquid interface is more favoured, thermodynamically, compared to their aggregation to form micelles. The higher entropies of adsorption ( $\Delta S^{0}_{ad}$ ) in comparison to  $\Delta S^{0}_{mic}$ may be due to more degree of freedom of the surfactant monomers at the liquid-air interface compared to the cramped interior of micelles<sup>36</sup>. The enthalpy of adsorption  $(\Delta H^0_{ad})$  is invariably more endothermic compared to  $\Delta H^0_{\text{mic}}$  because the energy is required in transferring surfactant monomers from the bulk to the liquid surface while during micellization, the energy is released by the system during aggregation of the monomers to form micelle. Enthalpies of adsorption at air-liquid interface increases (becomes more endothermic) upon raising temperature as well as on increasing the electrolyte concentration owing to the water structure disruption in both cases.

## Thermodynamic parameters of transfer

Standard thermodynamic parameters of transfer from binary (AOT+H<sub>2</sub>O) to ternary (AOT+ electrolyte+H<sub>2</sub>O) solution were evaluated using following relations<sup>37</sup> and these are recorded in Table 2.

$$\Delta G_{\rm tr}^0 = \Delta G_{\rm mic\,(ter\,)}^0 - \Delta G_{\rm mic\,(bin\,)}^0 \qquad \dots (10)$$

$$\Delta S_{tr}^0 = -d(\Delta G_{tr}^0)/dT \qquad \dots (11)$$

$$\Delta H_{tr}^0 = \Delta G_{tr}^0 + T \Delta S_{tr}^0 \qquad \dots (12)$$

Where,  $\Delta G^{0}_{\text{mic}(t)}$  and  $\Delta G^{0}_{\text{mic}(b)}$  are standard free energy of micellization for ternary and binary mixtures, respectively. The standard Gibb's free energy of transfer ( $\Delta G^{0}_{tr}$ ) for the studied systems are negative indicating the feasibility of the process of transfer of micelle from binary surfactant solutions to ternary solution. The  $\Delta G^{0}_{tr}$  value decreases further upon raising the temperature as well as on increasing the concentration of the added electrolyte. This is obvious since in both these cases the entropy is gained because of disruption in water structure. Further, though the enthalpy of transfer is endothermic, yet the process of such transfer becomes feasible due to dominating larger entropy gain.

## Conclusions

This paper reports the effects on surface and thermodynamic properties of AOT in aqueous solution due to added  $Na_2SO_4$  and  $Na_3PO_4$ , respectively. It is found that replacing divalent  $SO_4^{2-}$  by trivalent  $PO_4^{3-}$  leads to more stability as well as further lowering of critical micelle concentration of

AOT in aqueous media. This would be beneficial for improving the efficiency of AOT in its application as solubilizing agent for organic material in water, laundry detergent and efficient petroleum recovery and the management of oil spill problem.

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