

Study of Amino Acid Interaction with a Non-Ionic Surfactant at Different Temperatures

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The surface and thermodynamic parameters iso-octyl phenoxy poly-ethoxy ethanol (TX-100) with/without α -amino acid, viz., glycine, alanine and phenylalanine have been reported at 288.15, 293.15 and 298.15 K. Thermodynamic parameters indicate that the processes are endothermic in nature but negative values of ΔG_{mic}° and positive ΔS_{mic}° favour the process of micellization.

Key Words: Amino acid, Non-ionic Surfactant.

INTRODUCTION

The interaction of surface active substances in aqueous systems has been a field of investigation. These studies are supposed to be landmarks in the field of interaction of medicinal solutions, agrochemicals, detergents, solubilizing power, enhanced oil recovery and in metallurgical processes¹⁻⁴. The interaction of surfactants with macromolecules in aqueous solutions has been studied during past several years⁵⁻¹⁰. There are several reports on various physico-chemical properties of surfactants in aqueous medium. But the data on surface and thermodynamic properties for nonionic surfactants are limited¹¹⁻¹⁶. In the present investigation we report the data for surface parameters such as surface pressure at CMC (π_{CMC}), surface excess concentration (Γ_{max}), minimum area per molecule at the air-liquid interface (A_{min}) and thermodynamic parameters for micellization of aqueous solutions of iso-octyl phenoxy polyethoxy-ethanol (TX-100) with and without amino acids at 288.15, 293.15 and 298.15 K.

EXPERIMENTAL

The nonionic surfactant isooctyl phenoxy poly-ethoxy ethanol (TX-100) and amino acids, viz., glycine, alanine and phenylalanine used were of AR grade. The chemicals were used as such without further purification. The solutions were prepared in doubly distilled water having a specific conductance of *ca.* $2.00 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$.

Surface tensions of different solutions of surfactant in water and water + amino acids were determined by the dropweight method using a specially designed stalagmometer described elsewhere¹⁷ at three different temperatures. All the measurements were made in a water thermostat whose temperature was controlled to ± 0.01 K.

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RESULTS AND DISCUSSION

Critical micelle concentration (CMC) values for TX-100 + water and water + amino acid systems have been evaluated from the plots of surface tension vs. log concentration. CMC values for the studied systems are presented in Tables 1 and 2. It is clear from Tables 1 and 2 that CMC values decrease with increase in temperature. This may be due to the dehydration of the surfactant molecule with change in temperature. It follows from Table-1 that CMC value of the surfactant decreases with the addition of amino acids in surfactant solution. The order of CMC in case of different amino acids is as glycine > alanine > phenylalanine. This order can be explained on the basis that with increase in molecular weight of the amino acid molecule salting out of surfactant increases¹⁸. The decrease in CMC values of TX-100 with addition of amino acid is because of the salting out of the hydrated ethylene oxide moiety of the surfactant molecule. Amino acid molecules behave like electrolytes and result in the salting out phenomenon^{19, 20}

TABLE-1
CMC, SURFACE EXCESS CONCENTRATION (Γ_{\max}), MINIMUM AREA PER MOLECULE (A_{\min}) AND THE SURFACE PRESSURE AT THE CMC (π_{CMC}) FOR ISO-OCTYL PHENOXY POLYETHOXYETHANOL (TX-100) IN WATER AND WATER + AMINO ACID SYSTEMS

Concentration of amino acid (mols/litre)	Temperature (K)	CMC $\times 10^3$ (mol dm ⁻³)	$\Gamma_{\max} \times 10^{10}$ (mol cm ⁻²)	$A_{\min} \times 10^2$ (nm ²)	π_{CMC} (dynes/cm)
TX 100 + water 0.000 M	288.15	0.97	1.86	89.26	37.69
	293.15	0.89	1.84	90.23	38.85
	298.15	0.81	1.71	97.09	39.17
TX 100 + glycine 0.025 M	288.15	0.92	1.83	90.73	38.49
	293.15	0.84	1.80	92.24	38.85
	298.15	0.76	1.66	105.08	39.12
TX 100 + alanine 0.025 M	288.15	0.87	1.81	91.73	39.69
	293.15	0.81	1.72	96.53	39.75
	298.15	0.75	1.55	121.19	39.82
TX 100 + phenylalanine 0.025 M	288.15	0.82	1.76	94.34	39.79
	293.15	0.79	1.63	105.08	40.05
	298.15	0.74	1.49	123.90	40.57

Maximum surface excess concentration (Γ_{\max}) values at the air-liquid interface have been obtained using Gibbs adsorption equation¹²

$$\Gamma_{\max} = 1/2.303nRT(dy/d \log C)_T \quad \dots (1)$$

where n is the number of particles released per surfactant molecule in the solution. In the present investigation $n = 1$ for nonionic surfactant, R is the gas constant (8.314 J K⁻¹ mol⁻¹) and $(dy/d \log C)_T$ represents the slope of the surface tension vs. log C plot below the CMC at constant temperature T . The calculated values for Γ_{\max} for the studied systems at three temperatures are also recorded in

Table-1. From Table -1 it is evident that Γ_{\max} values decrease with increase in temperature. This may be due to enhanced molecular thermal agitation²¹. A further decrease in Γ_{\max} values with addition of amino acids may be due to the fact that addition of amino acids causes a shift of surfactant molecules from the air-liquid interface to the bulk phase.

TABLE-2
THERMODYNAMIC PARAMETERS OF THE MICELLIZATION OF ISO-OCTYL
PHENOXY POLYETHOXY ETHANOL (TX-100) IN WATER AND WATER
AMINOACID SYSTEMS

Concentration of amino acid (moles/litre)	Temperature (K)	$-\Delta G_{\text{mic}}^{\circ}$ (kJ mol ⁻¹)	$-\Delta H_{\text{mic}}^{\circ}$ (kJ mol ⁻¹)	$-\Delta S_{\text{mic}}^{\circ}$ (kJ mol ⁻¹)
TX 100 + water 0.000 M	288.15	26.25	11.79	0.132
	293.15	26.91	12.96	0.136
	298.15	27.61	14.13	0.140
Glycine 0.025 M	288.15	26.38	12.23	0.134
	293.15	27.05	13.70	0.139
	298.15	27.77	15.16	0.144
Alanine 0.025 M	288.15	26.51	09.80	0.126
	293.15	27.14	10.68	0.129
	298.15	27.79	11.56	0.132
Phenylalanine 0.025 M	288.15	26.65	05.05	0.110
	293.15	27.20	07.35	0.118
	298.15	27.83	09.74	0.126

The minimum area per molecule A_{\min} at the liquid-air interface was calculated using the equation

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

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 and with addition of amino acid to the surfactant solution. This behaviour can be explained on the basis that the addition of an amino acids 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 (π_{CMC}) was calculated using the equation¹²

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

π_{CMC} is an index of reduction of surface tension at CMC. π_{CMC} values are presented in Table-1 and π_{CMC} increase with increase in temperature.

Thermodynamic parameters of micellization viz. $\Delta G_{\text{mic}}^{\circ}$, $\Delta H_{\text{mic}}^{\circ}$, and $\Delta S_{\text{mic}}^{\circ}$

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

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

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

The various thermodynamic parameters of micellization calculated using eqns. (4–6) are presented in Table-2. The ΔG_{mic}° values are found to be negative for the studied systems indicating that these processes are spontaneous ones. The negative ΔG_{mic}° values increase with increase in temperature and addition of the amino acids to the TX-100 solution. The negative ΔG_{mic}° values favour that addition of an amino acid to TX-100 solution facilitates micellisation and 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 amino acid.

The ΔH_{mic}° values are positive and increase with increase in temperature but ΔS_{mic}° values are also positive which favours 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. Rosen *et al.*¹² suggested that steric factor is also responsible for this positive entropy change.

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