



Conductance and ^1H NMR Studies of Some Aqueous Surfactants + Fructose Solutions

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Specific conductivity values of sodium dodecyl sulphate and dodecyl trimethyl ammonium bromide in water and fructose + water measured at 298, 308 and 318 K have been reported. From the observed conductance data the critical micelle concentration and surfactant counter ion association constant (α) values have been obtained. The thermodynamic properties of micellization *i.e.*, $\Delta G^{\circ}_{\text{mic}}$, $\Delta H^{\circ}_{\text{mic}}$ and $\Delta S^{\circ}_{\text{mic}}$ were calculated using the critical micelle concentration values for sodium dodecyl sulphate + water + fructose and dodecyl trimethyl ammonium bromide + water + fructose systems. The process of micellization of the studied systems is favoured both energetically as well as by entropy gain. ^1H NMR data of the studied systems suggest that solubilization of fructose in aqueous dodecyl trimethyl ammonium bromide micellar solutions occurs neither within micellar core nor at interface but in the bulk, while solubilization of fructose in aqueous sodium dodecyl sulphate micellar solutions occur in the vicinity of micellar surface.

Key Words: Conductance, ^1H NMR, Surfactants, Fructose.

INTRODUCTION

Ionic surfactants being amphiphilic in nature exhibit distinct characteristics in aqueous solutions¹⁻⁹. At extremely low concentrations, surface active agents behave as 1:1 simple electrolytes, followed by their adsorption at the air liquid interface. The adsorption of surfactants at the air-liquid interface followed by their aggregation in the bulk render these important in pharmaceuticals, metallurgical processes, effective petroleum recovery and solubilization of polymers in aqueous solutions^{2,3}. The physico-chemical characteristics of surfactants in solutions are sensitive to temperature and chemical nature of added co-solutes. The effect of alkyl chain length of an organic additive on the behaviour of surface active compounds in aqueous solutions have earlier been reported^{8,9}. In continuation of present studies on the effect of added co-solutes on the properties of surfactant solutions¹⁰⁻¹⁸, we report here data on specific conductance for the systems (1) sodium dodecyl sulphate + fructose + water and (2) dodecyl trimethyl ammonium bromide + fructose + water. The observed surfactant counter ion association constant (α), critical micelle concentration (CMC), thermodynamic parameters of micellization and the ^1H NMR spectral data has been analyzed in the light of intermolecular interactions in the studied systems.

EXPERIMENTAL

Sodium dodecyl sulphate (SDS) from BDH was recrystallized from hot ethanol. Dodecyl trimethyl ammonium bromide

(DTAB) (Sigma) and fructose (Sisco) were used as such. Double distilled water with specific conductance 10^{-5} $\text{Ohm}^{-1} \text{cm}^{-1}$ at 298 K was used for preparing surfactant solutions of desired compositions.

The specific conductance values of solutions (within $\pm 5 \times 10^{-6}$ S cm^{-1}) were measured using a digital conductivity meter (Naina NDC-732) and temperature around the solutions was maintained within ± 0.01 K. The samples for ^1H NMR studies were prepared in D_2O and the spectra were obtained using EM-390, 90 MHz NMR spectrometer.

RESULTS AND DISCUSSION

The CMC values and surfactant counter ion association constant (α) were obtained from the plots of specific conductance, k , as a function of surfactant concentration for the systems, SDS + fructose + water and DTAB + fructose + water are presented in Table-1. The addition of fructose to an aqueous solution of SDS causes an increase in its CMC value. However, a reverse trend is observed when the same is added to a DTAB solution. This may be explained in terms of specific ion-dipole interactions between surfactant head groups and the negative dipole of oxygen atoms of fructose. The negative dipoles of oxygen atoms from fructose molecules adsorbed at the SDS's micellar interface in the stern layer enhance the head group ion-ion repulsion leading to an increase in its CMC value. However, such ion-dipole interaction in case of cationic surfactant, DTAB, obviously leads to a diminished ion-ion repulsion

System	Mole fraction of fructose	Temp. (K)	CMC $\times 10^3$ (mol dm ⁻³)	α
SDS + H ₂ O + Fructose	0.00	298	8.00	0.61
		308	8.54	0.59
		318	8.96	0.42
	0.02	298	9.98	0.58
		308	11.43	0.40
		318	13.10	0.32
DTAB + H ₂ O + Fructose	0.00	298	14.56	0.82
		308	15.44	0.75
		318	16.62	0.70
	0.02	298	12.03	0.80
		308	13.12	0.72
		318	14.04	0.50

amongst the surfactant head groups and hence the decrease in its CMC.

The degree of surfactant counter ion dissociation constant (β) was obtained from the ratio of the slopes of the plots of specific conductance as a function of surfactant concentration in the post-micellar and pre-micellar regions, respectively. The degree of surfactant counter ion association constant (α), is equal to (1- β). The observed higher values of degree of association in case of DTAB solutions in comparison to those for the corresponding SDS solutions may be attributed to less degree of hydration of the large sized surfactant head group as well as the counter ions in the former surfactant molecules. On the other hand the small sizes of head group and counter ions, in SDS molecule, which are hydrated to a larger extent, may be responsible for its lower α values. The degree of association values are lowered on mixing fructose in the aqueous surfactant solutions. This may be due to steric hindrance of the adsorbed fructose molecules in the vicinity of stern layer at the micellar surface. The observed lowering of α values upon increasing the temperature may be attributed to the enhanced thermal agitation at higher temperatures.

Thermodynamic properties of micellization: Standard Gibbs free energy of micellization, G_{mic}° was obtained using the relation¹³:

$$\Delta G_{mic}^{\circ} = (2 - p/n)RT \ln(\text{CMC}) \quad (1)$$

where, p = number of residual charges per micelle and n = micellar aggregation number. For ionic surfactants the value of p/n has been taken equal to β , the counter ion dissociation constant, defined above. Standard entropy of micellization, ΔS_{mic}° and standard enthalpy of micellization, ΔH_{mic}° , were calculated using eqns. 2 and 3, respectively.

$$\Delta G_{mic}^{\circ} = -(\Delta S_{mic}^{\circ})/T \quad (2)$$

$$\Delta H_{mic}^{\circ} = \Delta G_{mic}^{\circ} + T\Delta S_{mic}^{\circ} \quad (3)$$

The values of thermodynamic parameters of micellization are given in Table-2.

The observed lower ΔG_{mic}° values for SDS in comparison to DTAB suggests that in aqueous medium the molecular aggregation of the former surfactant is more favourable. This may be explained in terms of: (1) more hydration of smaller head group as well as counter-ions of SDS compared to such ions

System	Mole fraction of fructose	Temp. (K)	$-\Delta G_{mic}^{\circ}$ (KJ/mol)	Temp. (K)	$-\Delta H_{mic}^{\circ}$ (KJ/mol)	$-\Delta S_{mic}^{\circ}$ (KJ/mol/K)
SDS + H ₂ O + Fructose	0.00	298	21.55	303	9.03	0.042
		308	21.97	308	8.10	0.045
		318	22.45	313	7.18	0.048
	0.02	298	22.84	303	20.75	0.007
		308	22.91	308	21.38	0.005
		318	22.93	313	22.23	0.002
DTAB + H ₂ O + Fructose	0.00	298	18.87	303	9.04	0.036
		308	19.23	308	10.73	0.032
		318	19.50	313	11.93	0.027
	0.02	298	21.91	303	12.96	0.030
		308	22.21	308	12.22	0.033
		318	22.57	313	10.97	0.036

in DTAB and (2) more steric hindrance for aggregation due to large sized DTAB head group and its counter ion.

On mixing fructose to an ionic surfactant solution ΔG_{mic}° values are lowered. This may be owing to the adsorption of the added fructose molecules at the micellar interface which causes a partial charge neutralization of surfactant ionic heads within the stern layer of micellar surface thus facilitating micellization. On raising temperature the values of G_{mic}° are decreased due to the dehydration of surfactant head groups.

¹H NMR studies: The ¹H NMR chemical shift δ , values for aqueous SDS and DTAB solutions with or without added fructose are given in Table-3.

System	Chemical shift (δ)		
	-CH ₂ SO ₄	-(CH ₂) ₁₁ -	-CH ₃
SDS + water	4.10	1.38	0.88
SDS + water + fructose	3.90	1.40	0.90
DTAB + water	-N ⁺ (CH ₃) ₃	-(CH ₂) ₁₁ -	-CH ₃
	3.25	1.32	0.86
DTAB + water + fructose	3.30	1.42	0.92

SDS + water + fructose system: In case of aqueous SDS solution the observed three peaks are: (i) a peak at $\delta = 4.10$ due to the protons of -CH₂ group adjacent to sulphate (ii) a peak at $\delta = 1.38$ for the remaining -CH₂ groups of SDS hydrocarbon chain and (iii) a peak at $\delta = 0.88$ due to the terminal methyl group. On comparing these with the corresponding three peaks observed in case of SDS solutions, mixed with fructose, it is found that the peak due to -CH₂ group adjacent to sulphate is shifted up field. This may be due to the carbonyl group present in fructose which may shield or deshield the protons of surfactant (SDS) hydrocarbon tail due to its magnetic anisotropic effect. It appears that in the present case the carbonyl group of fructose is so oriented that it enhances the actual magnetic field experienced by the -CH₂ group adjacent to sulphate and hence the observed up field signal. Further on adding fructose to an aqueous SDS solution, the remaining two ¹H NMR signals remain almost unaffected. This

lends support to the view that the fructose molecules do not penetrate the interior of the SDS micellar core and these merely solubilise near the micellar surface. A schematic representation of the solubilization of fructose in aqueous SDS micellar system is shown in Fig. 1.

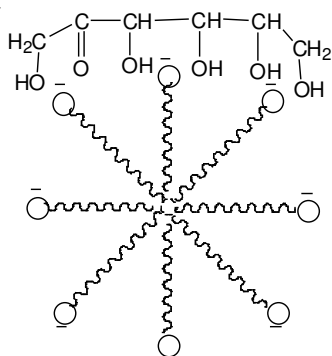


Fig. 1. Schematic representation of the solubilization site for fructose in an aqueous SDS micellar solution

DTAB + water + fructose system: Three distinct $^1\text{H NMR}$ peaks observed in case of DTAB + water system are: (i) a peak at $\delta = 3.25$ due to three methyl groups attached to the nitrogen atom of surfactant head group (ii) a peak at $\delta = 1.32$ owing to $-\text{CH}_2$ groups of hydrocarbon chain of DTAB molecule and (iii) a peak at $\delta = 0.86$ due to terminal $-\text{CH}_3$ group. On adding fructose to the aqueous DTAB solution none of these peaks exhibit an up field shift indicating no interaction of fructose molecules with any type of protons present surfactant head groups at higher temperatures which facilitate the process of micellization in surfactant molecules. It suggests that the solubilization of fructose in bulk is neither within the micellar core nor at its interface.

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