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Interaction parameters and micellisation constant of SDS and DTAB in aqueous and mixed solvents

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ABSTRACT

CMC values of ionic surfactants SDS and DTAB, were determined conductometrically in water, water + propanol and water + fructose systems at different concentrations of propanol and fructose at 298.15, 308.15 and 318.15 K. From CMC values micellisation constant (K_M), Setchenov constant (K_S^N) and interaction parameters 'P' and 'q' were calculated. K_M values are positive for 2-propanol + water system and negative for fructose + water system. K_S^N values in 2-propanol system are more as compared to fructose system. It suggests that nature of polar group of additive plays major role in solubilisation process. The high 'P' and 'q' values in presence of 2-propanol suggests that 2-propanol penetrates in the interior of micelle, while larger 'P' and 'q' values for DTAB in presence of fructose are indicative of adsorption of fructose on the micellar surface.

Keywords: SDS (Sodium dodecyl sulphate), DTAB (Dodecyl trimethyl ammonium bromide), K_M (Micellisation constant), K_S^N (Setchenov constant), q (Ideal partition coefficient), P (Real partition coefficient).

INTRODUCTION

Role of surfactants in the field of agriculture and food technology, energy, environment, biology, pharmaceuticals, textiles and metallurgy is well known[1-2]. The added co-solutes/co-solvents significantly affect the physicochemical properties of surfactants and these provide a potential tool to investigate structural changes in these solutions[3-4]. In the present studies micellisation and interaction parameters of the systems; SDS + water, SDS + water + 2-propanol, SDS + water + fructose, DTAB + water, DTAB + water + 2- propanol and DTAB + water + fructose, have been measured at different concentrations and temperatures. These parameters helped in investigating the effect of added co-solute/co-solvents on the structure of the studied systems.

MATERIALS AND METHODS

SDS, a BDH sample was purified by recrysatallisation from hot ethanol. The purified crystals were then extracted with dry and distilled petroleum ether to remove any adsorbed alcohol and finally dried under vacuum over phosphorous pentaoxide. DTAB, a Sigma product was used as supplied.2-Propanol was from Ranbaxy laboratories and fructose from Sysco research laboratories. These were used as supplied. Double distilled water having specific conductance of the order of 10^{-6} S cm^{-1} at 298 K was used for preparing solutions. The specific conductance values of solutions (within + 5 × 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.

RESULTS AND DISCUSSION

Critical micelle concentration (CMC) values determined conductometrically for the various studied systems are presented in Table-1 and 2.

Table-1: CMC values of SDS in SDS + water, SDS + water + 2-propanol and SDS + water + fructose systems at different temperatures.

System	Mole fraction of 2-propanol/fructose	Temp./ K	CMC × 10^3 (mol dm^{-3})
SDS + water	-	298.15	8.00
		308.15	8.54
		318.15	8.96
SDS + water + 2-propanol	0.0936	298.15	4.12
		308.15	4.63
		318.15	5.04
	0.1906	298.15	3.08
		308.15	3.25
		318.15	3.57
SDS + water + fructose	0.01	298.15	9.48
		308.15	10.52
		318.15	12.06
	0.02	298.15	9.98
		308.15	11.43
		318.15	13.10

Table-2: CMC values of DTAB in DTAB +water, DTAB +water +2-propanol and DTAB +water +fructose systems at different temperatures

System	Mole fraction of 2-propanol/fructose	Temp./ K	CMC × 10^3 (mol dm^{-3})
DTAB + water	-	298.15	14.56
		308.15	15.44
		318.15	16.62
DTAB + water + 2-propanol	0.0936	298.15	16.00
		308.15	17.12
		318.15	18.09
	0.1906	298.15	16.92
		308.15	18.05
		318.15	19.16
DTAB + water + fructose	0.01	298.15	13.11
		308.15	14.13
		318.15	15.17
	0.02	298.15	12.03
		308.15	13.12
		318.15	14.04

Although DTAB and SDS have equal hydrocarbon chain length, yet CMC of DTAB is higher than SDS. This is due to less tight binding of bulky DTA^+ ion with counterion (Br^-), owing to steric effects, compared to stronger binding of DS^- ion with counterion (Na^+) in case of SDS. The decrease in CMC of SDS in 2-propanol + water may be attributed to the ability of 2-propanol to penetrate into the micellar interior i.e. palisade layer[5-6]. An increment in the CMC value of DTAB in presence of 2-propanol might be due to larger head group of DTAB (in comparison to SDS) which hinders penetration of 2-propanol molecules into the micelle. In presence of fructose, CMC values of SDS are more in comparison to aqueous SDS solution. It may be due to enhanced hydration of surfactant ionic head owing to water structure breaking effect of fructose. The decrease of CMC values of DTAB in presence of fructose is partly due to steric effect and partly due to diminished positive charge at N of DTAB. The classical Setchenov equation which relates variation of the solubility of solute in a given solvent to the molality of third component is applicable, to a good approximation to the surfactant solutions in presence of additives[7].

$$K_M.\mathrm{m} = \ln\left[\frac{\mathrm{CMC}_W}{\mathrm{CMC}_{\mathrm{w+A}}}\right]$$

where 'm' is the molality of the additive, CMC_W and CMC_{W+A} are critical micelle concentrations of surfactant in water and mixed solvent respectively. K_M is known as micellisation constant, which may be expressed by the equation.

$$K_M = \frac{1}{2}\left[K_S^N + \frac{qM1}{2.303x\,1000}\right]$$

Where M_1 is molecular weight of the solvent, 'q' is ideal partition coefficient. K_S^N is the Setchenov constant and may be calculated by this empirical relation.

$K_S^N = 0.637\text{-}0.014n(CH_2) – 0.1464\sigma$

Where $n(CH_2)$ is the number of methylene groups in the linear hydrocarbon chain and σ is the hard sphere diameter of the solute which can be calculated from Vanderwaal's volumes using Deligny's relation[8].

$1/6\ \pi N\ \sigma^3 = -10+1.13V_W$

Where 'N' is Avogadro's number and V_W is Bondi's Vanderwaal's volumes[9].

The real partition coefficient (P) was calculated using the relation. P = q.F

where q is ideal partition coefficient of co solute in surfactant bulk solution and the micellar phase. F is a constant, named as activity coefficient which includes all nonideal interactions between solutes and micelles. F is taken equal to 0.64[10].

Micellisation constant (K_M) values for the studied systems are presented in Tables 3 and 4.

Table-3: Micellisation constant (K_M) for SDS in 2-propanol+water and fructose + water systems

System	Mole fraction of 2-propanol/fructose	Temp./ K	K_M (kg mol^{-1} at 298.15K)
2-propanol + water	0.0936	298.15	0.118
		308.15	0.109
		318.15	0.103
	0.1906	298.15	0.073
		308.15	0.074
		318.15	0.071
Fructose + water	0.01	298.15	-0.302
		308.15	-0.372
		318.15	-0.529
	0.02	298.15	-0.166
		308.15	-0.218
		318.15	-0.285

Table-4: Micellisation constant (K_M) for DTAB in 2-propanol+water and fructose + water systems

System	Mole fraction of 2-propanol/fructose	Temp. / K	K_M (kg mol^{-1}at 298.15K)
2-propanol + water	0.0936	298.15	-0.170
		308.15	-0.218
		318.15	-0.285
	0.1906	298.15	-0.011
		308.15	-0.012
		318.15	-0.010
Fructose + water	0.01	298.15	0.187
		308.15	0.158
		318.15	0.163
	0.02	298.15	0.143
		308.15	0.122
		318.15	0.126

K_M values are positive for SDS + water + 2-propanol and DTAB + water + fructose systems, while for SDS + water + fructose and DTAB + water + 2-propanol systems, K_M values are negative. Positive K_M values correspond to a decrease of CMC upon addition of solute, while negative K_M values correspond to an increase of CMC.

Setchenov constant (K_S^N) is proportional to a pair wise interaction coefficient between surfactant monomers and the additive molecule. Value of K_S^N for both SDS and DTAB in presence of 2-propanol and fructose are calculated equal to -0.429 and -0.558 respectively. The identical K_S^N values for both SDS and DTAB systems is due to same number of methylene groups in the hydrocarbon tail of SDS and DTAB. But size of surfactant head groups and nature of polar group of additive plays major role in solubilisation process[7]. In cases where K_M is still negative but less than K_S^N, one could assume that there is some penetration of solutes in the micelles. This type of behavior is shown by DTAB + water + 2-propanol and SDS + water + fructose systems. So there is no correlation, on one hand, of strength of interaction between surfactant monomers and additives, on the other hand, of the sign and amplitude of variation of CMC.

The ideal partition coefficient (q) and real partition coefficient (P) gives an indication of penetrating nature of additive molecules. The 'P' and 'q' values for the studied systems are listed in Table-5 and 6.

Table-5: The ideal partition coefficient (q) and real partition coefficient (P) of 2-propanol and fructose in SDS at different temperatures

System	Mole fraction of 2-propanol/fructose	Temp. / K	'q' value	'P' value
2-propanol + water	0.0936	298.15	70.23	44.94
		308.15	68.29	43.70
		318.15	66.89	42.80
	0.1906	298.15	23.63	15.12
		308.15	23.70	15.16
		318.15	23.42	14.98
Fructose + water	0.01	298.15	-5.49	-3.51
		308.15	-21.78	-13.89
		318.15	-58.78	37.62
	0.02	298.15	24.54	15.70
		308.15	13.14	8.41
		318.15	-2.94	-1.88

Table-6: The ideal partition coefficient (q) and real partition coefficient (P) of 2-propanol and fructose in DTAB at different temperatures

System	Mole fraction of 2-propanol/fructose	Temp. / K	'q' value	'P' value
2-propanol + water	0.0936	298.15	41.69	26.68
		308.15	41.35	26.46
		318.15	42.05	26.91
	0.1906	298.15	16.68	10.67
		308.15	16.64	10.65
		318.15	16.73	10.71
Fructose + water	0.01	298.15	109.37	69.99
		308.15	102.56	65.64
		318.15	103.65	66.34
	0.02	298.15	91.51	58.56
		308.15	86.96	55.65
		318.15	87.91	56.26

The high 'P' and 'q' values of aqueous SDS system in presence of 2-propanol suggests that 2-propanol penetrates in the interior of micelle[11], while such values in case of aqueous DTAB in presence of 2- propanol are low The negative values of SDS in case of fructose supports the view that fructose is highly hydrophobic and non penetrating additive. The larger 'P' and 'q' values for DTAB in presence of fructose are indicative of adsorption of fructose on the micellar surface.

REFERENCES

[1] M V Kaulgud; K S M Rao; *J. Chem. Soc. Faraday Trans.*,**1979**, 75, 2237.
[2] B Mandal; S Ray; A M Biswas; S P Moulik; *J. Phys. Chem.*, **1980**, 84, 856.
[3] S W Wettig; R E Verrall; *J. Colloid and Interface Sci.*, **2001**, 235, 310.

[4] S K Yadav; Arch. Appl. Sci. Res.**2012,** 4(3), 1220.
[5] E Vignola; G Person; J E Desnoyers; *Langmuir*, **2002,**18,6035.
[6] S K Shah; A Bhattarai; G Shrivastava; S K Chatterjee*; J. Nepal Chem. Soc*., **2009**, 24, 24.
[7] CTreiner; *J. Colloid Interface Sci*., **1982,** 90, 444.
[8] C L Deligny; N G Vanderveen;*Rev. Trav. Chim*.,**1971**, 90, 984.
[9] A Bondi; *J. Phys. Chem*., **1964**, 68, 441.
[10] C Treiner; *J. Colloid Interface Sci*., **1983**, 93, 33.
[11] P Bhattacharya; I N Basumallick; *Ind. J. Chem*., **1987**, 26A, 25.