

Effect of co-solutes on the physico-chemical properties of surfactant solutions

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Received 08 April 2005; revised 13 September 2005; accepted 26 October 2005

Physico-chemical studies of some aqueous surfactant solutions were carried out by employing conductance, surface tension and spectrofluorometric techniques. From conductivity and surface tension measurements, critical micelle concentration (CMC), counter-ion association (α), equivalent conductance at infinite dilution (Λ_0), surface excess concentration (Γ), minimum area per molecule (A_{min}), surface pressure at CMC (π_{CMC}), thermodynamic properties of micellization (ΔG_{mic}^o , ΔH_{mic}^o , ΔS_{mic}^o) and adsorption (ΔG_{ads}^o , ΔH_{ads}^o and ΔS_{ads}^o) have been obtained for an anionic [*bis* (2-ethylhexyl) sulphosuccinate sodium salt (AOT)], a cationic [cetyl trimethyl ammonium bromide (CTAB)] and a nonionic [polyethylene (23) lauryl ether (Brij-35)] surfactant solutions. Effect of mixing co-solutes (dioxane and glycerol) on the physico-chemical properties of surfactant systems at 298.15, 308.15 and 318.15 K has been investigated. Surfactants micellar characteristics and their interaction with co-solutes were also investigated by fluorescence measurements of solutions using pyrene as a fluorescence probe.

Keywords: Conductance, Dioxane, Glycerol, Physico-chemical properties, Pyrene fluorescence, Surface tension, Surfactants

Introduction

The study of physico-chemical properties of aqueous surfactant solutions, their relevance in biological systems, and intriguing and fascinating features displayed by such systems, continuously provide new challenges to the scientific community¹⁻⁴. Surface-active compounds possess valuable characteristics (emulsification, wetting, water proofing, repellency and spreading^{5,6} etc.) used in detergents⁷, food industries⁸, pharmaceutical⁹, enhanced oil recovery¹⁰, metallurgical process for concentrating ores^{11,12}, solubilization of water insoluble dyes, hydrocarbons^{13,14}, analytical chemistry¹⁵ and a number of biological and environmental systems.

Surface, thermodynamic and fluorescence investigations of aqueous surfactant solutions provide valuable information regarding structural changes in constituent molecules in such systems¹⁶⁻¹⁸. Solubilizing capacity, surface and micellar characteristics and detergency of amphiphilic compounds are sensitive to the nature of added co-solutes and temperature^{19,20}.

Although micellar aggregates have been characterized by using various physico-chemical techniques²¹⁻²³, micellar structure is not yet clearly understood. Present study reports on conductance, surface tension, and fluorescence for aqueous solution of *bis* (2-ethylhexyl) sulphosuccinate sodium salt (AOT, anionic surfactant), cetyltrimethyl ammonium bromide (CTAB, cationic surfactant) and polyoxyethylene (23) lauryl ether (Brij-35, non-ionic surfactant), with or without dioxane and glycerol as co-solutes.

Experimental Details

Materials

AOT (Sigma), CTAB (s. d. fine-chem), Brij-35 (Merck) and pyrene (Merck) were used as such. The 1,4 dioxane and glycerol were Lancaster (UK) product. Water was doubly distilled and had specific conductance ($2 \times 10^{-6} \text{ S cm}^{-1}$) at 298.15 K.

Methodology

Surface tensions of solutions were determined by drop weight method²⁴ and specific conductance using digital conductivity meter (Model 306, Systronics). The temperature control around the sample was maintained within $\pm 0.01 \text{ K}$ using a water thermostat. Fluorescence measurements for solutions were carried out on spectrofluorometer (SL 174 ELICO) using pyrene (10^{-6} M) as probe ($\lambda_{excit} = 338 \text{ nm}$).

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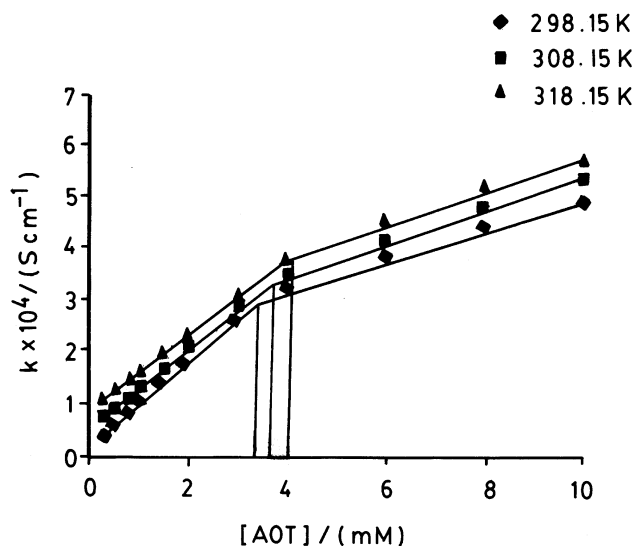


Fig. 1— Plots of specific conductance (k) vs $[AOT]$ for the system: AOT + glycerol (3.52 M) + H_2O

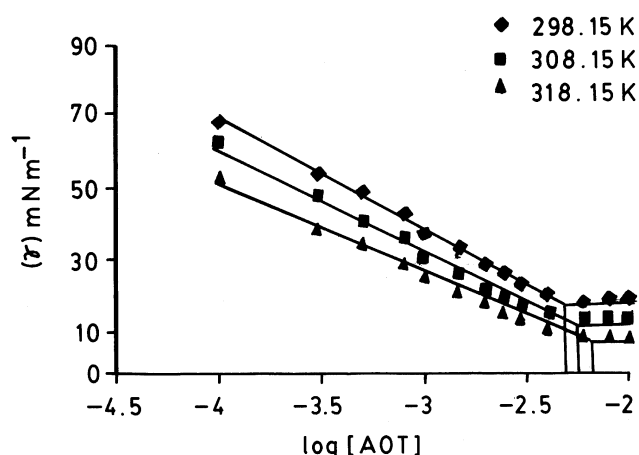


Fig. 2 — Plots of surface tension (γ) vs $\log [AOT]$ for the system: AOT + dioxane (3.52 M) + H_2O

Results and Discussion

Critical Micelle Concentration (CMC)

The point of intersection of two linear portions in the plot of specific conductance vs surfactant (Fig. 1) and surface tension vs $\log$ [surfactant] (Fig. 2) for studied systems correspond to CMC for the aqueous surfactants solution. For the pure aqueous surfactant solutions, CMC values are in the order: AOT > CTAB > Brij-35 (Table 1). CMC of ionic surfactants (AOT or CTAB) are higher than for non-ionic surfactant (Brij-35) owing to the ion-ion head group repulsion in case of the former surfactant. Lower values of CMC for CTAB in comparison to AOT is attributed to a comparatively weaker ionic head groups repulsion in

case of CTAB because of (a) steric hindrance of its larger sized head-group and (b) deeply imbedded N^+ under three methyl groups. The CMC value of an ionic surfactant solutions increases on raising temperature. However, opposite trend of temperature dependence of CMC was observed in case of non-ionic surfactant solutions. The positive temperature coefficient of CMC for ionic surfactants may be due to: (a) Dehydration of surfactant ionic heads at elevated temperature resulting in a stronger repulsion of their ionic heads; and (b) Shifting of monomer $\rightleftharpoons$ micelle equilibrium in favour of monomer at higher temperature. The negative temperature coefficient of CMC in case of non-ionic surfactant is due to phase separation referred to as clouding at higher temperature^{25,26}. On mixing dioxane or glycerol to an aqueous surfactant solution, an increase in CMC, irrespective of the nature of the surfactant, is observed. This may be because of lower dielectric constant of dioxane ($\epsilon=2.209$, 298.15 K) or glycerol ($\epsilon=42.5$, 298.15 K) as compared to water ($\epsilon=78.36$, 298.15 K). The decrease of dielectric constant of medium opposes micellization by increasing mutual repulsion of ionic heads in the micelle, hence increasing the CMC^{20,27}. Increase in CMC on mixing dioxane to a surfactant solution, being more significant compared to glycerol, is due to lower dielectric constant.

Counter-Ion Association Constant (α)

The pre-micellar and post-micellar linear plots between specific conductivity and surfactant concentration is taken equal to counter-ion dissociation constant (β). The counter-ion association constant (α) is obtained using the relation:

$$\alpha = 1 - \beta \quad \dots(1)$$

Counter-ion association values for AOT + H_2O system are higher than that of CTAB + H_2O system (Table 1), because of smaller size of surfactant head group as well as its counter-ion (Na^+) in case of AOT. This allows closer approach of two oppositely charged ions. In case of CTAB, due to bulkier surfactant head group as well as its counter-ion (Br^-), their association is diminished owing to the steric hindrance. Addition of a co-solute invariably causes increase in α values for the studied ionic surfactants, attributed to the lowering of dielectric constant of aqueous solution in presence of organic co-solute.

Table 1— Critical micelle concentration (CMC), surface excess concentration (Γ), minimum area per molecules of surfactant ($A_{\min}$) and surface pressure at cmc (π_{cmc}) for studied surfactant systems

System	Temp K	CMC m mol dm ⁻³			α	$\Lambda_0 \times 10^2$ Scm ² mol ¹	$\Gamma \times 10^{10}$ mol cm ⁻²	$A_{\min} \times 10^2$ nm ²	π_{cmc} mNm ⁻¹
		*C	S	F					
AOT+ H ₂ O	298.15	2.60	2.65	2.60	0.59	2.24	2.53	65.50	37.72
	308.15	2.81	2.79		0.57	3.96	2.34	70.80	42.16
	318.15	3.00	2.96		0.54	5.14	2.11	78.62	43.65
AOT+ dioxane (3.52 M)+ H ₂ O	298.15	5.41	5.45	5.44	0.64	1.75	2.62	63.61	52.73
	308.15	6.29	6.25		0.63	3.42	2.42	68.48	57.15
	318.15	7.41	7.38		0.61	4.51	2.21	74.98	58.96
AOT+ glycerol (3.52 M)+ H ₂ O	298.15	3.20	3.24	3.45	0.62	1.25	2.62	63.36	51.26
	308.15	3.51	3.55		0.60	2.56	2.36	70.36	54.95
	318.15	4.01	4.14		0.59	3.43	2.20	75.35	55.62
CTAB+H ₂ O	298.15	1.02	1.08	1.08	0.47	3.05	1.54	107.77	32.37
	308.15	1.13	1.28		0.46	3.83	1.32	125.08	35.37
	318.15	1.24	1.42		0.45	4.82	1.21	136.44	36.07
CTAB+ dioxane (3.52 M)+H ₂ O	298.15	4.11	4.13	4.24	0.54	2.95	2.01	82.44	51.08
	308.15	4.80	4.78		0.52	4.52	1.81	91.45	55.10
	318.15	5.51	5.47		0.51	5.24	1.63	101.82	56.33
CTAB+glycerol (3.52 M)+ H ₂ O	298.15	2.50	2.56	2.65	0.60	2.51	1.86	88.98	50.45
	308.15	3.31	3.35		0.59	3.53	1.72	96.11	54.91
	318.15	4.09	4.14		0.58	5.53	1.53	108.06	57.31
Brij-35+H ₂ O	298.15		0.10	0.96			4.10	40.45	39.10
	308.15		0.09				3.76	44.06	40.03
	318.15		0.08				3.54	46.88	41.18
Brij-35+dioxane (3.52 M)+H ₂ O	298.15		0.30	0.27			4.20	39.51	39.73
	308.15		0.24				3.90	42.56	40.44
	318.15		0.19				3.63	45.73	42.95
Brij35+glycerol (3.52 M)+ H ₂ O	298.15		0.25	0.21			4.30	38.61	36.78
	308.15		0.18				4.01	41.37	38.21
	318.15		0.14				3.63	45.70	38.63

*C, S, F are CMC values obtained from conductance, surface tension and fluorescence measurements respectively

Equivalent Conductance at Infinite Dilution (Λ_0)

Equivalent conductance (Λ) of surfactant solutions were calculated as:

$$\Lambda = \frac{1000 \times k}{C} \quad \dots(2)$$

where, k = specific conductance and C = g equ/dm³
Equivalent conductance at infinite dilution (Λ_0) was obtained using Onsager equation²⁸:

$$\Lambda = \Lambda_0 - (A\Lambda_0 + B) C^{1/2} \quad \dots(3)$$

where A and B are constants.

The observed positive temperature dependence of Λ_0 values (Table 1) for ionic surfactant solutions is due to the increase of ionic mobility at higher temperature²⁹. The Λ_0 values for AOT + H₂O system are lower than for CTAB + H₂O system, because of higher degree of hydration of comparatively smaller

head-group as well as smaller counter-ion of AOT molecule. The Λ_0 values decrease on adding a co-solute for the surfactant systems, co-solutes form intermolecular H-bonding with water and thus make the water structure more viscous and lower Λ_0 .

Surface Properties

Surface excess concentration (Γ) at air-liquid interface were calculated using Gibb's adsorption equation¹⁷

$$\Gamma = - (2.303 nRT)^{-1} (d \gamma / d \log C) \quad \dots(4)$$

where, R = gas constant (8.314 J K⁻¹ mole⁻¹), T is absolute temperature, $(d \gamma / d \log C)$ = slope value of the pre-micellar plot between ' γ ' and $\log$ [surfactant], n = number of particles furnished by each molecule of the surfactant in solution. Since AOT and CTAB behave as uni-univalent electrolytes in aqueous solutions, therefore, for these value n has been taken

as 2. However, for Brij-35, the value of n has been taken as 1.

The Γ values for binary (surfactant + water) solutions are in the order: Brij-35 > AOT > CTAB, which decrease on increasing the temperature both for binary as well as ternary solutions owing to thermal agitation. On adding dioxane or glycerol at constant temperature, the Γ values increase irrespective of the nature of surfactant. It may be due to the enhanced hydrophobic character of solution near the interface in the presence of a co-solute facilitating the accumulation of surfactants monomer at air-liquid interface hence the observed increase in surface excess concentration.

The values of minimum area per molecule (A_{min}) of surfactant at air-liquid interface (Table 1) were obtained using equation¹⁷:

$$A_{min} = \frac{10^{14}}{N \Gamma} \quad \dots(5)$$

where, N is Avogadro number and A_{min} is minimum area per molecule in nm^2 . For binary system A_{min} values are in the order: CTAB > AOT > Brij-35. Further A_{min} values increase with increase of temperature. Addition of a co-solute causes a decrease in A_{min} . It is obvious since co-solute molecules, which diminished available surface area for surfactant molecules, also occupy a fraction of interface.

Surface pressure at CMC (π_{CMC}), a measure of surface tension reduction at CMC, was calculated using equation³⁰

$$\pi_{CMC} = \gamma_0 - \gamma_{CM} \quad \dots(6)$$

where, γ_0 is the surface tension of water, γ_{CMC} (Table 1) is the surface tension at CMC.

The magnitude of surface pressure at CMC (π_{CMC}) for the surfactant + water systems are in the order: Brij-35 > AOT > CTAB. The highest value of π_{CMC} in case of Brij-35 indicates more effective adsorption of non-ionic surfactant at the interface due to absence of ion-ion repulsion at the interface, which causes more reduction in surface tension. Higher values of π_{CMC} in AOT + H_2O compared to CTAB + H_2O system is due to smaller counter ion (Na^+) of AOT, which interacts more intimately with negative ion of surfactant head at the air-liquid interface, whereas in CTAB, because of hindrance of larger Br^- counter-ion and also the larger surfactant ionic head, result in diminished

accumulation of these ions at the interface and hence lower π_{CMC} . The surface pressure at CMC values are found to increase on adding a co-solute for the studied ternary systems. This may be ascribed to the tendency of these organic co-solutes to adsorb at the air-liquid interface thereby lowering surface tension and hence increased π_{CMC} .

Thermodynamic Properties

The standard Gibb's free energy of micellization (ΔG_{mic}^o) for ionic and non-ionic surfactant solutions were calculated using Eqs (7) and (8) respectively^{31,32}:

$$\Delta G_{mic}^o = (2-\beta) RT \ln X_{CMC} \quad \dots(7)$$

$$\Delta G_{mic}^o = RT \ln X_{CMC} \quad \dots(8)$$

where, R is the gas constant ($8.314 \text{ JK}^{-1} \text{ mole}^{-1}$), T is absolute temperature and β is counter-ion dissociation constant.

Standard entropy of micellization (ΔS_{mic}^o) was calculated from the temperature dependence of standard Gibb's free energy of micellization using the relation.

$$\Delta S_{mic}^o = - \left(\frac{\partial \Delta G_{mic}^o}{\partial T} \right) \quad \dots(9)$$

Standard enthalpy of micellization (ΔH_{mic}^o) was obtained from Gibb's Helmholtz equation:

$$\Delta H_{mic}^o = \Delta G_{mic}^o + T \Delta S_{mic}^o \quad \dots(10)$$

ΔG_{mic}^o values are negative (Table 2) for the studied systems indicating that at CMC micelle formation in aqueous solution is more feasible than dispersion of surfactant monomers in the bulk. The magnitude of ΔG_{mic}^o in aqueous surfactant solution is in the order: Brij-35 > AOT > CTAB. On adding dioxane and glycerol as a co-solute, ΔG_{mic}^o values increase irrespective of the nature of surfactant. This may be owing to enhanced hydrophobic character (less dielectric constant) of the aqueous surfactant solution in the presence of dioxane or glycerol, which shifts the micelle $\rightleftharpoons$ surfactant monomer equilibrium in favor of monomers²⁷. The standard entropy of micellization (ΔS_{mic}^o) values (Table 2) is positive for the studied systems suggesting that the process of micellization is favored by entropy gain³³. ΔS_{mic}^o for the studied aqueous micellar solutions are in the order: Brij-35 > CTAB > AOT. On adding a co-solute (dioxane or glycerol), ΔS_{mic}^o decreases due to enhanced water structure in its presence owing to

Table 2— Thermodynamic parameters of micellization and adsorption for AOT, CTAB and Brij-35 in aqueous and aqueous co-solute environment

System	Temp K	$-\Delta G^{\circ}_{mic}$ kJ mol ⁻¹	$-\Delta H^{\circ}_{mic}$ kJmol ⁻¹	ΔS°_{mic} kJ mol ⁻¹ K ⁻¹	$-\Delta G^{\circ}_{ads}$ kJ mol ⁻¹	$-\Delta H^{\circ}_{ads}$ kJ mol ⁻¹	ΔS°_{ads} kJ mol ⁻¹ K ⁻¹
AOT+ H ₂ O	298.15	39.08	26.04		40.57	8.48	
	308.15	39.92	26.45	0.043	41.72	8.29	0.102
	318.15	40.55	26.64		41.62	7.89	
AOT+ dioxane (3.52 M)+ H ₂ O	298.15	37.70	26.96		39.72	17.39	
	308.15	37.94	26.85	0.036	40.30	16.95	0.068
	318.15	38.42	26.98		41.08	16.75	
AOT+ glycerol (3.52 M)+ H ₂ O	298.15	38.90	27.05		41.86	9.98	
	308.15	39.57	27.32	0.039	42.82	9.67	0.097
	318.15	40.06	27.42		43.80	9.20	
CTAB+H ₂ O	298.15	39.91	23.65		42.01	10.51	
	308.15	40.60	23.56	0.050	43.27	10.22	0.098
	318.15	41.23	23.65		44.19	9.85	
CTAB+ dioxane (3.52 M)+H ₂ O	298.15	36.31	20.87		38.85	11.95	
	308.15	36.63	20.66	0.051	39.66	11.45	0.081
	318.15	37.03	20.55		40.48	11.04	
CTAB+glycerol (3.52 M)+ H ₂ O	298.15	39.56	24.48		42.27	21.09	
	308.15	39.63	24.05	0.050	42.81	20.54	0.061
	318.15	39.78	24.70		43.51	20.09	
Brij-35+H ₂ O	298.15	27.63	8.90		28.37	6.60	
	308.15	28.26	8.88	0.063	29.09	6.52	0.070
	318.15	28.90	8.79		29.78	6.46	
Brij-35+dioxane (3.52 M)+H ₂ O	298.15	25.36	15.99		26.31	8.43	
	308.15	25.64	15.76	0.031	26.68	8.14	0.056
	318.15	25.94	15.69		27.17	7.92	
Brij35+glycerol (3.52 M)+ H ₂ O	298.15	26.24	16.00		27.10	19.49	
	308.15	26.34	15.76	0.034	27.29	19.36	0.022
	318.15	26.47	15.54		27.53	19.26	

intermolecular H-bonding. An exothermic standard enthalpy of micellization (ΔH°_{mic}) suggests that like entropy effect, the enthalpy change also favors the process of micellization. Further, on adding a co-solute into a surfactant solution, there is decrease in ΔH°_{mic} again due to its inter molecular H-bonding with water.

Thermodynamic Quantities of Adsorption

Standard Gibb's free energy of adsorption (ΔG°_{ads}) values were obtained using the equation¹⁷:

$$\Delta G^{\circ}_{ads} = \Delta G^{\circ}_{mic} - 6.023 \times 10^{-1} \pi_{CMC} \times A_{min}. \quad (11)$$

The lower values of ΔG°_{ads} (Table 2) compared to the corresponding ΔG°_{mic} suggests that the process of adsorption of surfactant molecules at the air-liquid interface proceeds the micellization in the bulk. Standard Gibb's free energy of adsorption values for studied binary systems are in the order: Brij-35 > AOT > CTAB. Higher ΔG°_{ads} for non-ionic surfactant (Brij-35) compared to an ionic surfactant is attributed to more hydrophobic-hydrophobic interaction of surfactant monomer at the air-liquid interface.

Addition of dioxane or glycerol leads to an increase in ΔG°_{ads} for the studied surfactant solutions. This may be attributed to the enhanced hydrophobic/non-polar character of the bulk on adding co-solute, which facilitates solubilization of surfactant monomers in the bulk.

Standard entropy of adsorption (ΔS°_{ads}) and standard enthalpy of adsorption (ΔH°_{ads}) were calculated (Table 2) from Eqs (12) and (13) respectively:

$$\Delta S^{\circ}_{ads} = \frac{-\partial (\Delta G^{\circ}_{ads})}{\partial T} \quad \dots(12)$$

$$\Delta H^{\circ}_{ads} = \Delta G^{\circ}_{ads} + T \Delta S^{\circ}_{ads} \quad \dots(13)$$

Exothermic ΔH°_{ads} and positive ΔS°_{ads} values suggest that the adsorption at air-liquid interface is favored by energy as well as entropy effect.

Spectrofluorometric Studies

Surfactants micellar characteristics and their interaction with co-solutes were also studied by means of fluorescence measurements of their

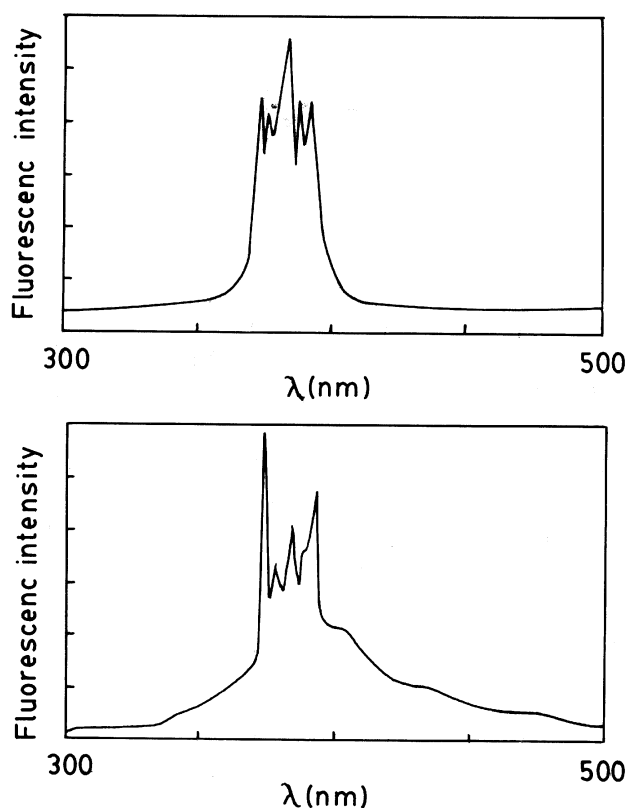


Fig.3 — Fluorescent spectra of pyrene in some solvents (a = n-hexadecane, b = water), [pyrene] = 10^{-6} M, λ_{excit} = 338 nm

solutions using pyrene as a fluorescence probe³⁴. Pyrene being hydrophobic has very low solubility in water (10^{-6} mol/l). In the presence of micelles, pyrene is preferentially solubilized in their interior hydrophobic regions, hence is used to assess micellar properties. Vibronic band spectra³⁵ undergoes significant perturbation on transferring from a non-polar to a polar environment. Pyrene exhibits a polarity dependent characteristic in monomer fluorescence spectrum with I_1/I_3 [ratio of vibronic band intensity of first peak (at 373 nm) to that of third peak (at 384 nm)] as the indicator of polarity of medium (Fig. 3). I_1/I_3 of pyrene in some solvents is as follows: n-hexadecane, 0.70; n-heptane, 0.76; n-hexane, 0.78; benzene, 0.82; n-propanol, 0.98; isobutanol, 1.01; n-butanol, 1.04; ethanol, 1.16; acetonitrile, 1.27; and water, 1.45. Lower I_1/I_3 values indicate less polar solvent environment, around the probe (pyrene). Below CMC, I_1/I_3 values are nearly same as in pure water as solvent. It indicates that at low concentration (below CMC) surfactant molecules exist as monomer dispersed in the bulk water. However, at or above CMC, the observed I_1/I_3 values

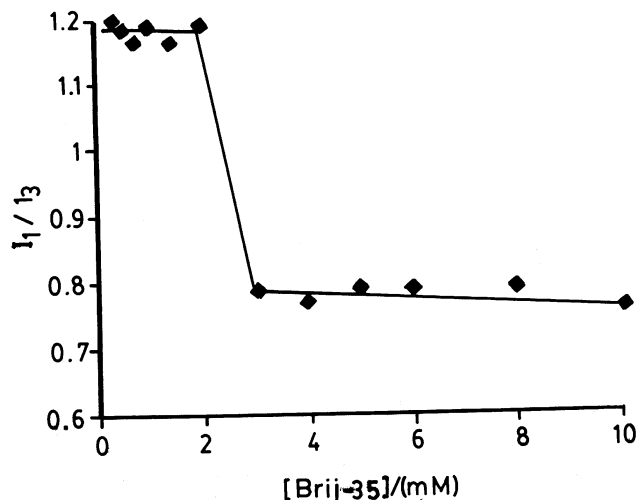


Fig. 4(a) — Plot of I_1/I_3 for of aqueous Brij-35+ dioxane (3.52 M) solution as a function of [AOT]

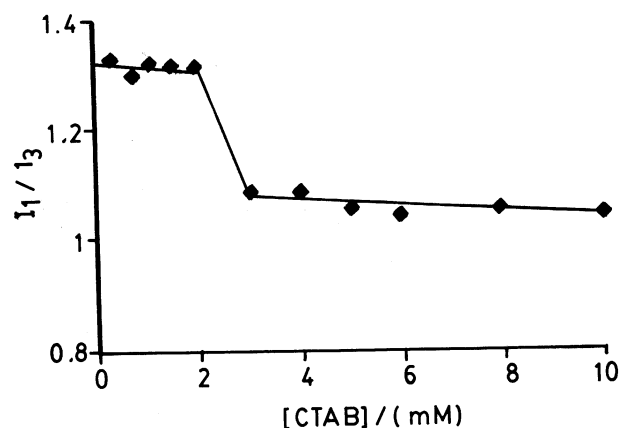


Fig. 4(b) — Plot of I_1/I_3 for of aqueous AOT + glycerol (3.52 M) solution as a function of [AOT]

is nearly the same as is observed for non-polar solvent, since the probe is entrapped within micellar non-polar hydrophobic interior/core. The observed I_1/I_3 value is slightly higher compared to such ratio in n-Hexadecane. It suggests that pyrene is located somewhere between the micellar core and the stern layer of micelle. The dependence of I_1/I_3 values on solvent polarity has been used to obtain the CMC of surfactant solution. Surfactant concentration where there is an abrupt decrease of I_1/I_3 value represents the CMC of the solution (Fig. 4). The CMC values obtained by fluorescence agree well with those observed from conductance and surface tension measurements (Table 1).

Conclusions

From physico-chemical properties of aqueous surfactants solutions studied using conductance,

surface tension and fluorescence techniques, it is concluded that the non-ionic surfactant (Brij-35) has better detergency, emulsification, wetting characteristics, hence, acts as a better surface active agents in various field like metallurgy, pharmacy, food industries and other applications involving surface phenomena, than cationic (CTAB) or anionic (AOT) surfactant. The CMC of surfactants, irrespective of their chemical nature, increases on mixing dioxane or glycerol. Such enhancement in increase in CMC values of surfactant becomes more on lowering the dielectric constant of co-solute. Whereas CMC of ionic surfactant (AOT or CTAB) shows a positive temperature coefficient, the reverse is true in case of non-ionic surfactant (Brij-35). From the observed surface properties namely surface excess concentration (Γ), minimum area per molecule (A_{min}) and surface excess concentration at CMC (π_{CMC}), it is obvious that surface activity of co-solute is more significant in an aqueous non-ionic surfactant solution compared to an ionic surfactant solution. Further, enhancement of the Γ and (π_{CMC}), in the presence of studied co-solutes, suggest that addition of these co-solutes would be beneficial in metallurgical and other industrial applications. For the studied surfactant solutions, with or without a co-solute, micellization in bulk and adsorption at the air-liquid interface are favored both by exothermic enthalpy change as well as entropy gain. Polarity dependent vibronic band intensity ratio, I_1/I_3 , may be used to assess the molecular status of surfactant in solution and also for determining the CMC of surfactants.

Acknowledgements

Author thanks Prof O P Yadav and Prof J K Nepal, Department of Chemistry, CCS Haryana Agricultural University, Hisar for their valuable suggestions during this work.

References

- Chand J, Chakraborty S & Banyopadhyay S, Monolayer of Aerosol-OT surfactants absorbed at the air-water interface: an atomistic computer simulation study, *J Phys Chem B*, **109** (2005) 471-479.
- Rainbow B E, Nano suspensions in drug delivery, *Nature Reviews*, **3** (2004) 785-7963.
- Zana R & Levy H, Micellar properties of ω -Hydroxyalkyldodecyldimethylammonium bromides in aqueous solutions, *J Interface Sci*, **170** (1995) 128-133.
- Srivastava R C, Liquid membrane phenomena: Biological implications, *Indian J Chem*, **42A** (2003) 2792.
- Dack M R J, Bird K T & Parker J, Solution of ions XXV. Partial molal volumes of single ions in protic and dipolar solvents, *Aust J Chem*, **26** (1975) 955-963.
- Sherwani M R K, Shama R, Gangwal A & Bhutra R, Micellar features and other solution properties of copper(II) soaps in benzene, *Indian J Chem*, **42A** (2003) 2527-2530.
- Schick M J, Detergency, in *Nonionic Surfactants Physical Chemistry* (Marcel Dekker Inc Press, New York) 1987, 753-833.
- Garcia J M, Wick L Y & Harms H, Influences of non-ionic surfactant Brij -35 on the bio-availability of solid and sorbed dibenzofuran, *Environ Sci Technol*, **35** (2001) 2033-2039.
- Horter D & Dressman J B, Influence of physicochemical properties on dissolution of drugs in the gastrointestinal tract, *Advanced Drug Delivery Reviews*, **46** (2001) 75-87.
- Shah D O, *Surface Phenomena in Enhanced Oil Recovery* (Plenum Press, New York) 1981, 19-48.
- Shah D O, The world of surface science, *Chem Eng Edn*, **14** (1977) 367-383.
- Schwuger M J, Stickdon K & Schomacker R, Microemulsions in technical process, *Chem Rev*, **95** (1995) 849-864.
- Saito S, Solubilization properties of polymer-surfactant complexes, *J Colloid Interface Sci*, **24** (1967) 227-234.
- Sinha S, Bahadur P & Jain N, Effect of organic counter-ions on the surface activity, micellar formation and dye solubilization behaviour of cationic surfactants, *Indian J Chem*, **41A** (2002) 914-920.
- Berthod A, Tomar S & Dorsey J G, Polyoxyethylene alkyl ether nonionic surfactants: physicochemical properties and use for cholesterol determination in food, *Talanta*, **55** (2001) 69-83.
- Zana R, Lanos P & Lang J, Fluorescence probe studies of the interactions between poly (oxyethylene) and surfactant micelles and microemulsion droplets in aqueous solutions, *J Phys Chem*, **89** (1985) 41-44.
- Rosen M.J, Choen A W , Dahanayaki M & Hua X Y, Relationship of structure to properties in surfactants. 10. Surface and thermodynamics properties of 2-dodecyloxypoly(ethanoxylethanol)s, $C_{12}H_{25}(OC_2H_4)_x OH$, in aqueous solutions, *J Phys Chem*, **86** (1982) 541-545.
- Matzinger S, Husey D M & Fayer M D, Fluorescent probe solubilization in the head-group and core regions of micelles: Fluorescence life time and orientational relaxation measurements, *J Phys Chem*, **102 B** (1998) 7216-7224.
- Yadav S K, Kumar A & Yadav O P, Physico chemical studies of 2-propanol in some micellar solutions *Indian J Chem*, **38A** (1999) 529-532.
- Hek S R, Chetry S, Jayasree V & Bhat S N, Effects of solvents and temperature on critical micellar concentration of sodium dodecyl sulfate and cetylpyridinium chloride, *J Indian Chem Soc*, **77** (2000) 478-481.
- Yoshino A, Okabayashi H, Vchida T, Ogasawara T & Yoshida T, Thermally induced structural change of D_2O - solubilized AOT reversed micelles and base-catalyzed H-D exchange reaction between solubilized D_2O deuterium and AOT- 1CH proton, *J Phys Chem*, **100** (1996) 8418-8424.
- Joshi H D, Joshi K H & Dasai C M, Study of CMC values of binary mixtures of surfactants, *Indian J Chem*, **42 A** (2003) 2749-2750.
- Onori G & Santucce A, IR investigations of water structure in Aerosol-OT reverse micelle aggregates, *J Phys Chem*, **97** (1993) 5430-5434.
- Jains D V S & Singh S, Thermodynamics of n- alkane solutions: part VII- activity coefficients of components in

- liquid-vapour interface of n-hexane-carbon tetrachloride system, *Indian J Chem*, **10** (1974) 629-631.
- 25 Durham K, *Surface Activity and Detergency* (MacMillan Press, London) 1961, 1-25.
- 26 Nakagawa T & Shinoda K, *Colloidal Surfactants* (Academic Press, New York) 1963, 45-89.
- 27 Alli A & Nain A K, Investigation of micellization properties of some ionic surfactants in water + formamide solutions at various temperatures, *J Surface Sci Technol*, **13** (1997) 1-9.
- 28 Miyata I, Jakada A, Yonese M & Kishimoto H, Solution behavior of sodium dodecyl sulfate in methanol, *Bull Chem Soc Jpn*, **63** (1990) 3502-3507.
- 29 Sharma V K, Singh J & Yadav O P, Conductance, surface tension and thermodynamic studies of aqueous sodium dodecyl benzene sulphate in pyridine and isomeric picolines, *Indian J Chem*, **35 A** (1996) 1056-1061.
- 30 McDonald J, Thermodynamics of micellization of some non-ionic surfactants in mixed solvents *J Pharm Pharmac*, **22** (1970) 774-777.
- 31 Patil S R & Rakshit A K, Physicochemical properties of anionic-nonionic surfactant mixture: α -sulfonatomyristic acid methyl ester (MES)-nonaoxyethylene monododecyl ether ($C_{12}E_9$), *J Indian Chem Soc*, **80** (2003) 345-350.
- 32 Moulik S P, Micelles: self-organized surfactant assemblies, *Curr Sci*, **71** (1996) 368-376.
- 33 Sulthana S B, Bhat S G T & Rakshit A K, Studies of the effect of additives on the surface and thermodynamics properties of poly (oxyethylene (10)) lauryl ether in aqueous solution, *Langmuir*, **13** (1977) 4562-4568.
- 34 Goddard G D, Turro N J & Kuo P L, Fluorescence probe for critical micelle concentration determination, *Langmuir*, **1** (1985) 352-357.
- 35 Yoshima T, Yoshida H, Ohno A & Esumi K, Physicochemical properties of quaternary ammonium-bromide type trimeric surfactants, *J Colloid & Interface Sci*, **267** (2003) 167-172.