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Polymer surfactant interactions: Surface tension, conductance and spectrofluorometric studies

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Abstract

Surface tension and electrical conductivity data have been measured for aqueous solution of anionic [*bis* (2-Ethylhexyl) sulphosuccinate sodium salt (AOT)], cationic [cetyl trimethyl ammonium bromide (CTAB)] and non-ionic [polyethylene (23) lauryl ether (Brij-35)] surfactants with inulin (carbohydrate polymer) at 298.15, 308.15 and 318.15 K temperature. The observed data has been utilized to evaluate the critical micelle concentration (CMC), counter-ion association (β), surface excess concentration (Γ), minimum area per molecule (A_{min}), surface pressure at CMC (p_{CMC}), thermodynamic properties of micellization ($\triangle G°_{mic}$, $\triangle H°_{mic}$, $\triangle S°_{mic}$) and adsorption ($\triangle G°_{ads}$, $\triangle H°_{ads}$ and $\triangle S°_{ads}$). Intermolecular interactions of inulin-surfactant mixture in water were also studied spectrofluorometrically using pyrene as a fluorescence probe.

Keywords: Surfactants, surface tension, electrical conductance, fluorescence, inulin

Introduction

In the recent years, there has been a considerable interest in the studies on the interaction between polymers and amphiphilic molecules in aqueous solutions [1-3]. Aqueous solutions containing surfactants and polymers find extensive applications in various fields such as, pharmaceutical [4], enhanced oil recovery [5], metallurgical process for concentrating ores [6], cosmetic and food industries [7] and a number of biological and environmental systems [8]. Polymer-surfactant interaction studies give valuable information pertaining to (a) the modification in the micellar properties of surfactants when a polymer is added to a surfactant solution [9], (b) conformational changes of the polymer chain in the presence of surfactant [10].

Most of the studies pertaining to surfactant-polymer systems have been concered with the interactions of surfactant with water soluble synthetic polymers [11, 12]. However, physico-chemical characterizations of the surfactant-biopolymer systems are few [13]. The present work focuses on the change in conductance, surface tension and spectrofluorometric properties of aqueous solution of anionic surfactant (AOT), a cationic surfactant (CTAB), and a non-ionic surfactant (Brij-35) in the presence of inulin.

Inulin, a carbohydrate polymer, belonging to the family of fructuns which after starch, is the most abundant polysaccharide found in nature [14]. Inulin has sweet taste and is present in several vegetables and fruits, including onions, garlic, bananas, asparagus, chicory and Jerusalem artichokes. Structurally, Inulin consists of fructosyl fructose units with terminal glucose.
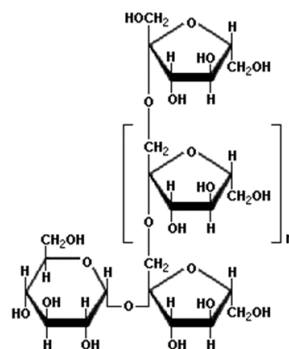
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Structure of Inulin

Inulin-surfactant solutions are being used in various pharmaceuticalapplications [15-16]. Inulin is being used as an active ingredient as well as a drug carrier for the prevention and/or treatment of colon in human [17]. Inulin-surfactant coating on drug tablets/capsules are useful for delivery of drugs to specific site in body.

Materials and Methods

The surfactants, *bis* (2-ethylhexyl) sulphosuccinate sodium salt (Sigma), cetyltrimethyl ammonium bromide (Lancaster, UK), polyoxyethylene (23) lauryl ether (Merck, Germany), inulin (Sigma) and pyrene (Merck) were used as such. Doubly distilled water of specific conductance of order: 2 μS cm^{-1} at 298.15 K was used for solution preparation.

Surface tension was measured by drop weight method [18] and specific conductances of solutions using Digital Conductivity -meter-306 (Systronics). The temperature around the sample was maintained within ±0.01 K using a water thermostat. Spectrofluorometric measurements were carried out at 298.15K temperature on a spectrofluorometer (SL 174 ELICO) using pyrene (10^{-6} M) as a probe (λ_{excit} = 338 nm).

Results and Discussion
Critical micelle concentration

The CMC (Table 1) obtained from different techniques for surfactant + H$_2$O system agree well with literature values [19-21]. On adding inulin, CMC value increases in case of AOT system while it decreases for CTAB and Brij-35 systems. The representative plotfor one case(CTAB +Inulin (0.2% w/v) + H$_2$O) regarding surface tension (γ) versus log[CTAB] is shown in fig. 1. for the system Higher CMC for AOT + inulin + H$_2$O system compared to AOT + H$_2$O system is due to the initial binding of surfactant (AOT) with inulin through ion dipole interactions between AOT and inulin molecules, which raises the CMC [22]. Decrease in CMC of CTAB in the presence of inulin is attributed to diminished positive charge of N of CTAB head group caused by ion-dipole interaction between CTAB head group and negative dipole of carbonyl group of inulin. In case of Brij-35 the decrease in CMC is due to dipole-dipole interaction between surfactant head group and inulin.

Counter-ion association constant (β)

Prior to the micelle formation as well as at the post micellar stage the dependence of specific conductivity upon surfactant concentration is linear. The ratio of the slopes of these post-micellar and premicellar linear plots is taken equal to counter-ion dissociation constant (α). The counter-ion association constant (β) is obtained using the relation:

$$\beta = 1- \alpha. \qquad \text{eq.(1)}$$

Addition of inulin to AOT or CTAB solution invariably causes an increase in β values. This may be attributed to (a)

decrease in the dielectric constant of aqueous surfactant solution in the presence of inulin and (b) enhanced water structure on mixing inulin resulting in diminished surfactant head group as well as counter ion solvation leading to more degree of counter ion association.

Surface properties

Surface excess concentration (Γ) at air-liquid interface was calculated by using Gibb's Adsorption equation [23]

$$\Gamma = - (2.303\ nRT)^{-1} (d\ g / d\ \log C) \qquad (2)$$

where, R = gas constant (8.314 J K^{-1} mole^{-1}), T is absolute temperature,(d g /d logC) = slope value of the plot between 'g' and log [surfactant] at pre-micellar stage, n = number of particles per molecule of the surfactant whose surface concentration varies with change in surfactant concentration in bulk phase. Since AOT and CTAB behave like uni-univalent electrolyte in solutions, therefore, values of n has been taken as 2. However, for Brij-35 the value of n is taken as 1. The Γ values for binary (surfactant + water) solutions (Table 1) are in the order: Brij-35 > AOT > CTAB. On adding inulin to surfactant solutions the surface excess concentration is increased. This may be attributed to the water structure making effect of inulin, which promotes the accumulation of surfactant at the air-liquid interface.

Minimum area per molecule (A$_{min}$) of surfactant at air-liquid interface was calculated using equation [23].

$$A_{min} = 10^{14}/ N\ \Gamma \qquad (3)$$

where, N is Avogadro number. Addition of inulin causes a decrease in A$_{min}$ (Table 1). It is obvious since a fraction of interface is also occupied by inulin molecules, which diminished available surface area for surfactant molecules.

Surface pressure at CMC (p$_{CMC}$), a measure of surface tension reduction at CMC, was calculated by using equation[24]

$$p_{CMC} = g_0 - g_{CMC} \qquad (4)$$

where, g$_0$ is the surface tension of water, g$_{CMC}$ is the surface tension of solution at CMC.

The magnitude of surface pressure at CMC (p$_{CMC}$) for the surfactant + water systems are in the order Brij-35>AOT>CTAB (Table 1). The highest value of p$_{CMC}$ in case of Brij-35 indicates more effective adsorption of non-ionic surfactant at the interface due to the absence of ion-ion head group repulsion at the interface, which causes more reduction in surface tension. The surface pressure at CMC is found to increase on adding inulin for the studied ternary systems. This may be ascribed to the tendency of inulin to adsorb at the air-liquid interface thereby lowering the surface tension and hence increasing p$_{CMC}$.

Table 1: Critical micelle concentration (CMC), Surface excess concentration (Γ) minimum area per molecule of surfactant (A$_{min}$) and surface pressure at CMC(л $_{cmc}$) for studied Surfactant systems.

System	Temp./K	[CMC]/ m mol dm^{-3}			B	Γ x 10^{10}/ mol cm^{-2}	A$_{min}$ x10^2 / nm^2	л $_{cmc}$ /mNm^{-1}
			* SCF					
AOT+ H$_2$O	298.15	2.60	2.77	2.60	0.59	2.53	65.50	37.72
	308.15	2.81	2.94	----------	0.54	2.34	70.80	42.16
	318.15	3.00	3.12		0.50	2.11	78.62	43.65
AOT+ Inulin(0.2%w/v)+ H$_2$O	298.15	3.81	3.55	3.53	0.69	2.64	62.92	50.19
	308.15	4.46	4.66	----------	0.61	2.53	65.57	53.44

	Temp./K	S	C		F			
	318.15	5.73	5.08		0.54	2.36	70.25	55.62
CTAB+H$_2$O	298.15	1.02	1.09	1.08	0.51	1.54	107.77	32.37
	308.15	1.13	1.28		0.46	1.32	125.08	35.37
	318.15	1.24	1.41	---------	0.42	1.21	136.44	36.07
CTAB+ Inulin(0.2%w/v)+ H$_2$O	298.15	0.58	0.67	0.61	0.54	1.64	102.89	38.85
	308.15	0.81	0.86		0.50	1.47	112.44	45.29
	318.15	0.98	1.03	---------	0.41	1.36	121.54	49.12
Brij-35+H$_2$O	298.15	0.10	-----	0.09	---------------	4.10	40.45	39.10
	308.15	0.08	-----			3.76	44.06	40.03
	318.15	0.07		---------		3.54	46.88	41.18
Brij35+ Inulin(0.2%w/v)+ H$_2$O	298.15	0.08		0.70		4.99	33.22	42.08
	308.15	0.07	---------------		---------------	3.96	41.86	43.28
	318.15	0.06		---------		3.63	45.75	43.65

Where S, C, F are CMC values obtained from conductance, surface tension and fluorescence measurements.

Table 2: Thermodynamics parameters of micellization and adsorption at air/liquid interface.

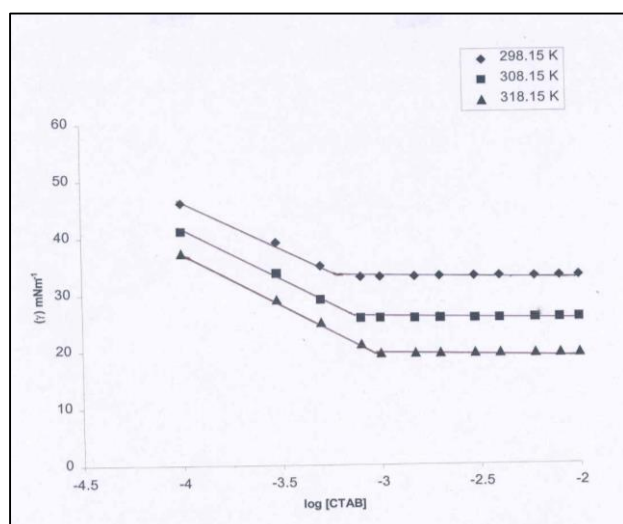| System	Temp./K	$-\Delta G^{\circ}_{mic}$ /kJ mol^{-1}	$-\Delta H^{\circ}_{mic}$ /kJ mol^{-1}	ΔS°_{mic} /kJ mol^{-1} K^{-1}	$-G^{\circ}_{ads}$ /kJmol^{-1}	$-\Delta H^{\circ}_{ads}$ /kJmol^{-1}	ΔS°_{ads} /kJmol^{-1} K^{-1}
AOT+ H$_2$O	298.15	39.08	26.04		40.57	8.48	
	308.15	39.92	26.45	0.043	41.72	8.29	0.102
	318.15	40.55	26.64		41.62	7.89	
AOT+ Inulin (0.2% w/v)+ H$_2$O	298.15	39.93	30.76		42.16	9.56	
	308.15	40.56	31.43	0.030	43.36	9.17	0.101
	318.15	41.05	31.47		44.19	8.64	
CTAB+H$_2$O	298.15	39.91	23.56		42.01	10.51	
	308.15	40.60	23.60	0.050	43.27	10.22	0.098
	318.15	41.23	23.65		44.19	9.85	
CTAB+ Inulin (0.2% w/v)+ H$_2$O	298.15	43.89	33.80		46.44	10.28 9.24	
	308.15	43.98	33.85	0.032	47.34		0.112
	318.15	44.55	34.10		48.69	8.68	
Brij-35+H$_2$O	298.15	27.63	8.80		28.37	6.60	
	308.15	28.26	8.88	0.063	29.09	6.52	0.070
	318.15	28.90	8.99		29.78	6.46	
Brij35+ Inulin (0.2% w/v)+ H$_2$O	298.15	28.80	18.33		29.64	13.16	
	308.15	29.01	18.40	0.034	30.10	12.85	0.052
	318.15	29.49	18.53		30.69	12.80	

Figure caption

Fig 1: Plots of surface tension (γ) versus log [CTAB] for the system: CTAB +Inulin (0.2% w/v) + H$_2$O

Thermodynamic properties

The standard Gibb's free energy of micellization (ΔG°_{mic}) for ionic and non-ionic surfactant solutions were calculated using the equations (5) and (6) respectively [25, 26].

$$\Delta G^{\circ}_{mic} = (2-\alpha)\, RT \ln X_{CMC} \qquad (5)$$
$$\Delta G^{\circ}_{mic} = RT \ln X_{CMC} \qquad (6)$$

where, R is the gas constant (8.314 JK^{-1} mole^{-1}), T is absolute temperature and α is counter-ion dissociation constant and X$_{CMC}$ is the mole fraction of surfactant at CMC.

Standard entropy of micellisation (ΔS°_{mic}) was calculated from the temperature dependence of Gibbs's free energy of micellization using the relation [27]

$$\Delta S^{\circ}_{mic} = -\,\delta(\Delta G^{\circ}_{mic})/\delta T \qquad (7)$$

Standard enthalpy of micellization (ΔH°_{mic}) was obtained from Gibb's Helmoltz equation [27]

$$\Delta H^{\circ}_{mic} = \Delta G^{\circ}_{mic} + T\Delta S^{\circ}_{mic} \qquad (8)$$

ΔG°_{mic} values are negative for the studied systems indicating that at CMC micelle formation in aqueous solution is more feasible than dispersion of surfactant monomers in the bulk. On adding inulin ΔG°_{mic} values decrease irrespective of the nature of surfactant. It may be due to the ability of inulin to penetrate into hydrophobic micellar core of surfactants, polar ends of inulin being situated at micellar-water interface and non-polar carbon chain directing towards the micellar hydrophobic interior core which favour micellization.

The standard entropy of micellization (DS$^{\circ}_{mic}$) values is positive for the studied systems suggesting that the process of micellization is favoured by entropy gain [44]. On adding inulin DS$^{\circ}_{mic}$ decreases due to enhanced water structure in its presence owing to intermolecular H-bonding. Standard enthalpy of micellization (DH$^{\circ}_{mic}$) being negative throughout suggest that like the entropy effect, the exothermic enthalpy

change also favors the process of micellization. Further, on adding inulin into a surfactant solution there is further decrease in DH^o_{mic}.

Thermodynamic quantities of adsorption

Standard Gibb's free energy of adsorption (DG^o_{ads}) values were obtained using the equation [23]

$$DG^o_{ads} = DG^o_{mic} - 6.023 \times 10^{-1}\, p_{CMC} \times A_{min.} \qquad (9)$$

The values of DG^o_{ads} are lower than the corresponding DG^o_{mic} indicating more feasibility of adsorption of surfactant molecule at air-liquid interface than their aggregation to form micelles. Hence, the process of micellization in bulk solution always follows the adsorption of surfactant molecules at the air-liquid interface. Decrease in ΔG^o_{ads} on adding inulin to a surfactant solution may be due to specific intermolecular interaction between the inulin and surfactant at the air-liquid interface.

Standard entropy of adsorption (DS^o_{ads}) and standard enthalpy of adsorption (DH^o_{ads}) were calculated [27] from the relations (10) and (11) respectively.

$$DS^o_{ads} = -\partial\,(DG^o_{ads})/\partial T \qquad (10)$$

$$DH^o_{ads} = DG^o_{ads} + T\,DS^o_{ads} \qquad (11)$$

From exothermic DH^o_{ads} and positive DS^o_{ads} values it is evident that like micellization in bulk the process of adsorption at air-liquid interface is favored both by energy as well as entropy effects.

Spectrofluorometric studies

Surfactants micellar characteristics and their interaction with inulin were also investigated by means of fluorescence measurements using pyrene as a fluorescence probe [28]. Pyrene exhibits a polarity dependent characteristic [29] in its fluorescence spectrum with I_1/I_3 (The ratio of virbonic band intensity of first peak [at 373 nm] to that of third peak [at 384 nm]) as the indicator of polarity of medium. The dependence of I_1/I_3 value on solvent polarity has also been used to obtain the CMC of surfactant. The point of inflexion in I_1/I_3 versus [surfactant] plot determines the CMC of surfactant. Below CMC, the values of I_1/I_3 are high indicating water-like polar environment around the probe. At CMC, abrupt fall in I_1/I_3 is due to entrapping of pyrene in the hydrophobic micellar core. As observed from conductance and surface tension measurements, the fluorescence results also show that interaction of anionic (AOT) surfactant with inulin occurs in three stages.

References

1. Esumi K, Saika R, Miyazaki M & Torigoe K, Collids Surf. 2000; 166:115.
2. Michiotti P, Mese C La, Bonicelli MG, Ceccaroni GF, Ferragina C, Cifarellai P. Colloid Polym Sci. 2003; 281-431.
3. Itri R, Caetano W, Barbora LRS, Baptista MS, Braz J Phys, Rainbow B R, Nature Reviews, 2004, 34-58.
4. Pillai V, Kanicky JR, Shah DO. In Handbook of micro emulsion science and technology Edited by P Kumar & KL Mittal, (Marcel Dekker, Inc. New York, Basel). 1999, 743.
5. Schwuger MJ, Stickdon K, Schomacker R, Chem Rev, 1995; 95:849.
6. Goddard ED, Padmanabhan KPA, Leung PS, J Soc Cosmet Chem. 1991, 42:19.
7. Garcia JM, Wick LY, Harms H, Environ Sci Technol. 2001, 35:2033.
8. Kresheck GC, Hargraves WA, J Colloid and Interface Science. 1981, 83:1.
9. Satake I, Yang J, Biopolymers. 1976; 15:2263.
10. Aprano AD, Mesa C La, Persi L, Langmuir. 1997; 13:5876.
11. Shimabayashi S, Uno T, Nakagaki M, Collids and Surfaces A: Physicochem.Eng. Aspects. 1997; 123-124
12. Zana R, Limbela WB, Kamanka N, Lindman B, J Phys Chem. 1992; 96:5461.
13. Rosen MJ, Choen AW, Hua XY, J Phys Chem. 1982; 86-541.
14. Mareshessault RH, Bleha T, Deslandes Y, Revol IF, Can J Chem. 1980; 58-2415.
15. Wu H, Ramachandran C, Weiner ND, Rossler BJ, International Journal of Pharmaceutics. 2001; 220-63.
16. Wall DA, Pierdomenico DA, Wilson G, Journal of Controlled Release. 1993; 24-227.
17. Vandamme Th F, Lenourry A, Charrueau C, Chaumeil JC, Carbohydrate Polymers. 2002; 48-219.
18. Jains DVS, Singh S, Indian J Chem. 1974; 10-629.
19. Biggs S, Selb J, Candau F, Langmuir. 1992; 8-838.
20. Neugebauer JM, Methods Enzymol. 1990; 182-239.
21. Alli A, Nain AK, J Surface Sci Technol. 1997; 13-1.
22. Minatti E, Zanette D, Colloids Surf. 1996; 113-237.
23. McDonald J, J Pharm Pharmac, 22(1970)774.
24. Das Gupta PK, Moulik SP, Colloid Ploym Sci, 1987; 246-267.
25. Moulik SP, Curr Sci, 1996; 71-368.
26. Pratap R, Swaoop N, Yadav OP, tyagi DK, J. Idian Chem Soc. 2005; 82-111.
27. Yoshimura T, Yoshimura H, Ohno A & Esumi K, Journal of colloid and interface science. 2003; 267:167.
28. Ananthapadamanabhan KP, Goddard GD, Turro NJ, Kuo PL. Langmuir. 1985; 1:352.