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Surface and thermodynamic studies of micellization of surfactants in binary mixtures of 1,2-ethanediol and 1,2,3-propanetriol with water

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Surface physico-chemical and thermodynamic studies of some aqueous surfactant solutions were carried out by employing conductance, surface tension and dye solubilization (UV-Vis absorption spectroscopy) techniques. From conductivity and surface tension measurements, critical micelle concentration (CMC), counter-ion association constant (α), equivalent conductance at infinite dilution (λ_o), surface exess concentration (Γ_{max}), minimum area per molecule (A_{min}), surface pressure at CMC (π_{CMC}), thermodynamic properties of micellization (ΔG^o_{mic}, ΔH^o_{mic}, ΔS^o_{mic}) and adsorption (ΔG^o_{ads}, ΔH^o_{ads}, ΔS^o_{ads}) have been obtained for an anionic (sodium dodecyl sulphate (SDS)), a cationic (hexadecyl trimethyl ammonium bromide (HTAB)) and nonionic (Polyoxyethylene (20) sorbitan mono-oleate (Tween 80)) surfactant solutions. Effect of mixing cosolvents (1,2-Ethanediol or 1,2,3-Propanetriol) on physico-chemical properties of surfactant systems at 298.15, 308.15 and 318.15K has been investigated. Surfactants micellar characteristics and their interactions with cosolvents were also investigated by Uv-vis absorption spectroscopy measurements of solutions using bromothymol blue as a probe. The inclusion of cosolvents caused an increase in CMC and degree of counterion dissociation (β) of surfactant solutions whereas the thermodynamic analysis shows that, although the micellization is less favorable in mixed solvent compared to pure water, the process is spontaneous and exothermic.

Key words: Conductance, dye solubilization, micellization, surface physico-chemical properties.

INTRODUCTION

Investigations about the micellization characteristics of different types of surfactants are still carried out mostly in water and in aqueous media containing additives that can alter the water structure. Despite extensive studies made on the micellization behavior of surfactants in different types of media, it is still not exactly clear which property of a solvent controls the micellization process. However, high cohesive energies, dielectric constants and considerable hydrogen bonding ability between the solvent molecules have been reported to be a prerequisite for aggregation of surfactants (Tharwat, 2005). In recent years there has been a renewed interest on the study of adsorption and aggregation of surfactants in solvent media containing a binary mixture of water and

a polar nonaqueous solvent as evident from published papers (Tharwat, 2005; Kabir-ud-Din and Koya, 2011; Sansanwal, 2005; Homendra and Devi, 2006; Das and Ismail, 2008; Zdziennicka, 2009; Dubey, 2008; Hideki, 2009; Zdziennicka and Jańczuk, 2010; Deepti et al., 2011; Sibani et al., 2013). Carrying out investigation on the effect of added cosolvents on the micellization of surfactants is also equally important so as to gather knowledge about the role of solvent structure on aggregation phenomenon so that it could be applied for the development of certain areas (e.g., cleaning operation, lubrication, *etc.*) which require a water-free or water-poor media (Cross and Singer, 1994; Laurier et al., 2003). Several such studies were carried out in aqueous medium and the commonly used nonelectrolytes are dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dimethyl acetamide, acetonitrile, dioxane, urea and n-alkanols (Tharwat, 2005; Kabir-ud-Din and Koya, 2011; Sansanwal, 2005; Homendra and Devi, 2006; Deepti et al., 2011; Sibani et al., 2013).

1,2-Ethanediol (ED) and 1,2,3-Propanetriol(PT) are another polyhydric organic alcohols which has poly sites for hydrogen bonding and there are few reports (Hideki, 2009; Amalia et al., 2009; Nagarajan and Wang, 2000) in the literature about the micellization of ionic surfactants in water mixed medium. The author had therefore made a detailed study of the micellization behavior of an anionic (sodium dodecyl sulphate (SDS)), a cationic (hexadecyl trimethyl ammonium bromide (HTAB)) and nonionic (Polyoxyethylene (20) sorbitan mono-oleate (Tween 80)) surfactant solutions on adding the organic solvents ED or PT to water by employing conductometric, surface tension and dye solubilization (UV-Vis absorption spectroscopy) methods.

The study has been carried out at three different temperatures, 298.15, 308.15 and 318.15K, which helped to compute thermodynamic parameters of micellization assuming equilibrium model for micelle formation.

MATERIALS AND METHODS

The surfactants SDS (BDH chemicals Ltd, England), HTAB (99+%, Acros organics Ltd, USA), Tween 80 (98+%, Acros organics Ltd, USA) and organic solvents 1,2-Ethanediol (99.5%, Breckland Scientific Supplies, U.K), 1,2,3-Propanetriol(99%, Blulux, Laboratory Ltd.) were used as received. Other chemical reagents which were used in this work were: Potassium chloride (99%, Blulux, Laboratory Ltd.), Bromothymol blue (dye content: 85%, BDH chemicals Ltd, England), Absolute ethanol (99.9%, Hayman Ltd., England), n- Hexane (BDH chemicals Ltd, England), Acetone (Sigma-Aldrich, Germany), Glacial acetic acid (Hayman Ltd., England), Toluene (HPLC grade, Analytical reagent, CDH (P) LTD, India), and 1,4- Dioxane (Blulux, Laboratory Ltd.).

Conductance measurement

Conductance of ionic surfactant solutions (SDS or HTAB) with and without cosolvents(1,2-Ethanediol or 1,2,3-Propanetriol) was measured over a wide range of surfactant concentrations, at 298,

308 and 318K. The conductivity data was obtained using a digital conductivity/temp meter (ELE International, model 4071, England) equipped with a dip cell (cell constant: 1.03 cm^{-1}) and the calibration of the instrument was made with 0.01 M KCl solutions at regular time intervals and the electrode was cleaned with distilled water after each measurement. Distilled and triply deionized water with a specific conductivity of less than 1×10^{-6} Scm^{-1}, was used throughout the experiment. All the experiments were done in a thermostated water-bath holding the solution under study. The solutions (water/surfactant or water/cosolvent/surfactant mixtures) were thermally equilibrated at the desired temperature for at least 15 min before measurement. Temperature control of thermostat was within ± 0.1°C.

Surface tension measurement

Surface tension of surfactant solutions was determined by drop weight method using a specially designed stalagmometer (Wilmad lab. Glass, LG-5050-102, USA) at the desired temperatures. The stalagmometer was calibrated by determining the surface tension of pure liquids: absolute ethanol, acetone, *n*-hexane, acetic acid (glacial), toluene, 1,4-dioxane and water as standard. The observations were made in a thermostated water bath holding the solution under study. The temperature control around the solution was maintained within ± 0.1 K.

Absorbance measurement

The absorbance of surfactant solutions with and without cosolvents was measured over a wide range of surfactant concentrations, using bromothymol blue (BTB), at 298 K. Magnetically stirred (for an hour) and filtered saturated aqueous solution of BTB was used as probe for each measurement. The absorbance data was obtained using double beam UV- Visible spectrophotometer (Sanyo, SP 75, Japan) and the base line correction was made by using water (distilled and deionized). The absorbance of solutions was noted at equilibrated temperature of 25 ± 0.1˚C.

RESULTS AND DISCUSSION

Critical micelle concentration

The critical micelle concentration (CMC) values of surfactants in various compositions of water-ethanediol (W/ED) and water-propanetriol (W/PT) mixtures, estimated through conductometric, surface tension and UV-Visible absorbance spectroscopy experiments at 298.15, 308.15 and 318.15K are listed in Tables 1 to 3. In these techniques, usually, CMC values are determined from the inflection point in the plots of specific conductance (κ) versus surfactant concentration (Figure 1), surface tension versus logarithm of surfactant concentration (Figure 2) and absorbance versus surfactant concentration (Figure 3) by plotting two straight lines in the pre and post micellar regions according to William's method (Tharwat, 2005; Maria et al., 2005).

In the studied pure aqueous surfactant solutions, CMC values are in the order: SDS > HTAB > Tween 80 (Tables 1 to 3). CMC of ionic surfactants (SDS or HTAB) are higher than nonionic surfactant (Tween 80) owing to the ion- ionic head group repulsion in case of the former

Table 1. Critical micelle concentration (CMC), surface excess concentration (Γ_{max}), minimum area per molecule (A_{min}) and surface pressure at CMC (π_{cmc}) for aqueous SDS solution with or without cosolvent systems.

System	T(K)	CMC (m moldm^{-3})			A	Λ_O x 10^{-1} (S cm^2 mol^{-1})	$\Gamma_{max} \times 10^{10}$ (mol cm^{-2})	$A_{min} \times 10^2$ (nm^2)	π_{cmc} (mN m^{-1})
		*C	*S	*A					
SDS + H$_2$O	298.15	8.11	7.98	8.14	0.62	8.72	2.38	69.78	31.07
	308.15	8.52	8.48		0.60	9.49	2.17	76.52	31.85
	318.15	9.00	8.92		0.58	10.67	2.00	83.03	31.98
SDS + ED(1M) + H$_2$O	298.15	8.98	8.76	8.95	0.59	13.28	1.74	95.43	32.29
	308.15	9.23	9.17		0.55	14.95	1.66	100.0	32.84
	318.15	9.55	9.53		0.53	17.04	1.58	105.1	32.87
SDS + ED(2.5M) + H$_2$O	298.15	9.33	9.21	9.32	0.58	15.68	1.47	112.9	32.91
	308.15	9.40	9.29		0.56	18.03	1.41	117.7	33.26
	318.15	9.71	9.67		0.55	19.30	1.30	127.7	33.54
SDS + ED(4M) + H$_2$O	298.15	9.67	9.57	9.61	0.55	15.59	1.25	132.8	34.44
	308.15	9.81	9.87		0.53	17.16	1.14	145.6	34.63
	318.15	9.99	9.94		0.50	19.45	1.05	158.1	34.71
SDS + PT(1M) + H$_2$O	298.15	8.62	8.60	8.57	0.61	7.02	2.21	75.14	32.01
	308.15	8.88	8.86		0.58	7.85	1.99	83.45	32.39
	318.15	9.21	9.20		0.56	8.39	1.83	90.74	32.47
SDS + PT(2.5M) + H$_2$O	298.15	8.98	8.91	9.00	0.59	6.05	2.17	76.52	32.77
	308.15	9.18	9.06		0.58	6.46	2.03	81.80	32.99
	318.15	9.50	9.43		0.55	7.03	1.83	90.74	33.11
SDS + PT(4M) + H$_2$O	298.15	9.44	9.30	9.45	0.59	4.35	2.03	81.80	32.97
	308.15	9.77	9.73		0.59	4.99	1.85	89.76	33.06
	318.15	9.82	9.80		0.56	5.57	1.67	99.43	33.28

*C, *S,*A are CMC values obtained from conductance, surface tension and absorbance measurements respectively.

surfactants (Tine and Bešter-Rogac, 2007). Lower values of CMC for HTAB in comparison to SDS is attributed to comparatively weaker ionic head groups repulsion in case of HTAB because of (a) steric hinderance of its larger sized head group and (b) deeply embedded N$^+$ under three methyl groups (Zdziennicka and Jańczuk, 2010).

The CMC value of an ionic surfactant solution 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 (Sansanwal, 2005; Kye et al., 2001): (a) Dehydration of surfactant ionic head groups at elevated temperature resulting in a stronger repulsion of their ionic head; and (b) Shifting of monomer ⇌ 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.

The CMC values in pure water appear to be in good agreement with literature values (Das and Ismail, 2008;

Hideki, 2009; Maria et al., 2005). On mixing ED or PT to an aqueous surfactant solution, an increase in CMC, irrespective of the nature of the surfactant, is observed (Tables 1 to 3). This may be because of lower dielectric constant of ED (ε = 36, 298.15 K) or PT (ε = 42.5, 298.15 K) as compared to water (ε = 78.36, 298.15 K). The decrease of dielectric constant (ε) of medium opposes micellization by increasing mutual repulsion of ionic heads in the micelle, hence increasing the CMC (Kabir-ud-Din and Koya, 2011;). Increase in CMC on mixing ED to a surfactant solution, being more significant compared as to PT, is due to lower dielectric constant of the former.

Counter ion association constant (α)

The post micellar and pre micellar linear plot 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:

Table 2. Critical micelle concentration (CMC), surface excess concentration (Γ_{max}), minimum area per molecule (A_{min}) and surface pressure at CMC (π_{cmc}) for aqueous HTAB solution with or without cosolvent systems.

System	T(K)	CMC (m moldm^{-3})			A	$\Lambda_O \times 10^{-1}$ (S cm^2 mol^{-1})	$\Gamma_{max} \times 10^{10}$ (mol cm^{-2})	$A_{min} \times 10^2$ (nm^2)	π_{cmc} (mN m^{-1})
		*C	*S	*A					
HTAB + H$_2$O	298.15	0.92	0.88	0.90	0.77	19.49	1.78	93.29	32.23
	308.15	0.96	0.93		0.77	21.52	1.58	105.1	32.93
	318.15	1.08	0.99		0.76	24.89	1.47	112.9	32.01
HTAB + ED(1M) + H$_2$O	298.15	0.98	0.97	0.97	0.75	82.53	1.09	158.0	35.33
	308.15	1.09	1.06		0.72	87.65	0.96	182.5	35.72
	318.15	1.25	1.20		0.70	94.47	0.91	198.4	36.06
HTAB + ED(2.5M) + H$_2$O	298.15	1.26	1.23	1.22	0.68	112.4	0.90	184.5	36.27
	308.15	1.50	1.47		0.67	119.3	0.81	205.0	36.59
	318.15	1.76	1.65		0.67	124.7	0.72	230.6	36.70
HTAB + ED(4M) + H$_2$O	298.15	1.51	1.45	1.49	0.65	115.9	0.84	197.7	37.15
	308.15	1.73	1.65		0.64	119.1	0.75	221.4	37.40
	318.15	1.97	1.90		0.62	123.4	0.67	247.8	37.68
HTAB + PT(1M) + H$_2$O	298.15	0.95	0.94	0.95	0.76	21.30	1.47	112.9	34.65
	308.15	1.01	1.00		0.73	24.18	1.33	124.8	34.80
	318.15	1.15	1.08		0.71	28.04	1.19	139.5	34.95
HTAB + PT(2.5M) + H$_2$O	298.15	1.02	1.00	0.99	0.66	19.98	1.31	126.7	35.08
	308.15	1.21	1.14		0.66	21.88	1.16	143.1	35.69
	318.15	1.49	1.45		0.71	24.82	1.03	161.2	35.50
HTAB + PT(4M) + H$_2$O	298.15	1.29	1.27	1.32	0.64	17.40	1.19	139.5	36.07
	308.15	1.67	1.60		0.63	20.92	1.08	153.7	36.41
	318.15	1.81	1.76		0.64	24.31	0.97	171.2	36.75

*C, *S,*A are CMC values obtained from conductance, surface tension and absorbance measurements respectively.

$$\alpha = 1 - \beta \tag{1}$$

Counter-ion association values, as can be seen from Tables 1 and 2, for HTAB + H$_2$O system are higher than that of SDS + H$_2$O. At a fixed temperature, the α values roughly decreased with the cosolvent composition. An increase in α with respect to solvent composition is expected due to the decrease in the polarity of the bulk phase caused by the addition of cosolvents. That is, in order to diminish the repulsion between the ionic head groups, thus more fractions of the counterions would prefer to stay at the micellar surface (Kallol and Baghel, 2008; Amalia et al., 2009). However, the opposite trend obtained could be due to decrease in average aggregation number (number of molecules present in a micelle) by the addition of cosolvents, which results in a diminution of the electrostatic repulsion (that overcomes the effect of polarity changes) and leads to a diminution in the electrical charge density at the micellar surface.

With the increase in temperature, the α values of ionic surfactants in water and water–cosolvent mixtures are decreased. However, the effects of organic cosolvents on other systems were not always regular, although in some cases, a rough disorder can be seen (Zdziennicka and Jańczuk, 2010; Sarah et al., 2006).

Equivalent conductance at infinite dilution (Λ_o)

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

$$\Lambda = \frac{1000 \times k}{C} \tag{2}$$

Where, k is specific conductance and C is concentration in g equ/dm^3. Equivalent conductance at infinite dilution Λ_o was obtained using Onsager equation (Dubey, 2008; Tine and Bešter-Rogac, 2007):

$$\Lambda = \Lambda_o - (A\Lambda_o + B)\sqrt{C} \tag{3}$$

Where A and B are constants that explain ion- ion and

Table 3. Critical micelle concentration (CMC), surface excess concentration (Γ_{max}), minimum area per molecule (A_{min}) and surface pressure at CMC (π_{cmc}) for aqueous Tween 80 solution with or without cosolvent systems.

System	T(K)	CMC (m moldm^{-3})			A	$\Lambda_O \times 10^{-1}$ (S cm^2 mol^{-1})	$\Gamma_{max} \times 10^{10}$ (mol cm^{-2})	$A_{min} \times 10^2$ (nm^2)	π_{cmc} (mN m^{-1})
		*C	*S	*A					
Tween 80 + H$_2$O	298.15		0.018	0.020			1.91	86.94	19.55
	308.15		0.017				1.83	90.74	20.23
	318.15		0.015				1.82	91.24	20.62
Tween 80 + ED(1M) + H$_2$O	298.15		0.028	0.031			1.90	87.39	26.22
	308.15		0.025				1.85	89.76	26.56
	318.15		0.022				1.83	90.74	27.10
Tween 80 + ED(2.5M) + H$_2$O	298.15		0.034	0.035			1.80	92.25	29.98
	308.15		0.032				1.70	97.68	30.22
	318.15		0.030				1.60	103.8	30.77
Tween 80 + ED(4M) + H$_2$O	298.15		0.038	0.040			1.78	93.29	32.85
	308.15		0.035				1.68	98.84	32.95
	318.15		0.034				1.58	105.1	33.15
Tween 80 + PT(1M) + H$_2$O	298.15		0.025	0.028			1.89	73.15	24.21
	308.15		0.023				1.85	75.82	24.75
	318.15		0.019				1.84	77.59	25.51
Tween 80 + PT(2.5M) + H$_2$O	298.15		0.031	0.033			1.79	75.82	25.54
	308.15		0.030				1.74	81.40	26.70
	318.15		0.026				1.71	82.61	27.77
Tween 80 + PT(4M) + H$_2$O	298.15		0.034	0.037			1.73	74.46	28.14
	308.15		0.031				1.70	77.23	28.58
	318.15		0.029				1.68	80.61	29.59

*S, *A are CMC values obtained from surface tension and absorbance measurements respectively.
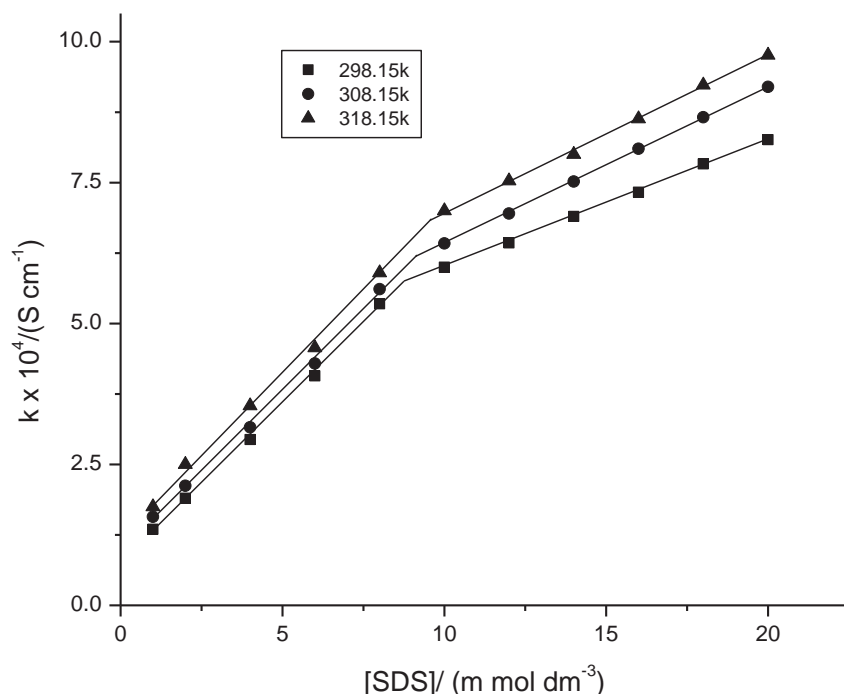

Figure 1. Plots of specific conductance (k) vs [SDS] for the system SDS + ED (1 M) + H$_2$O.
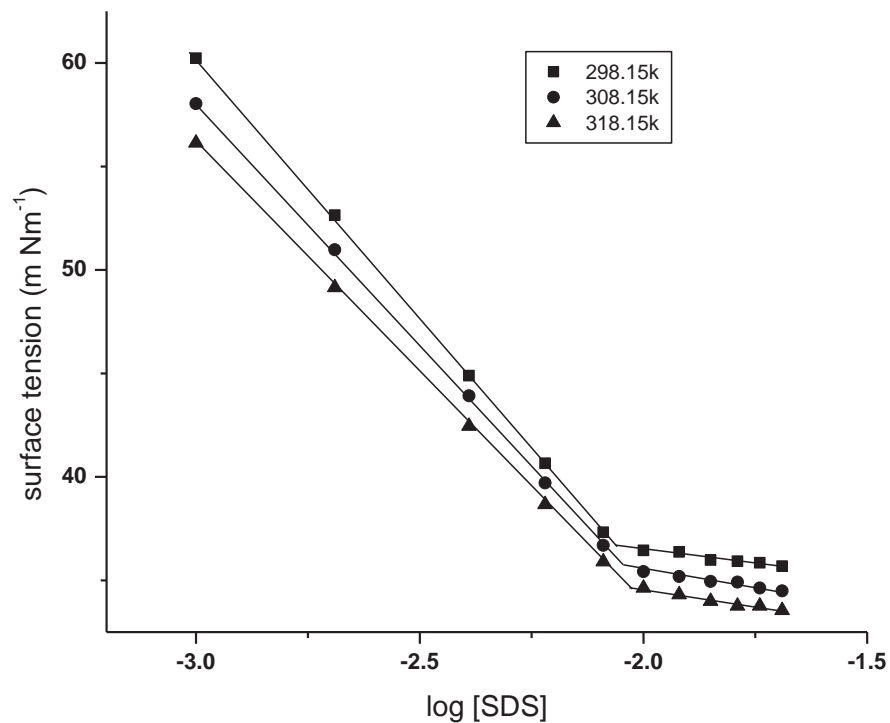
Figure 2. Plots of surface tension (γ) Vs log [SDS] for the system SDS + PT (1M) + H_2O.
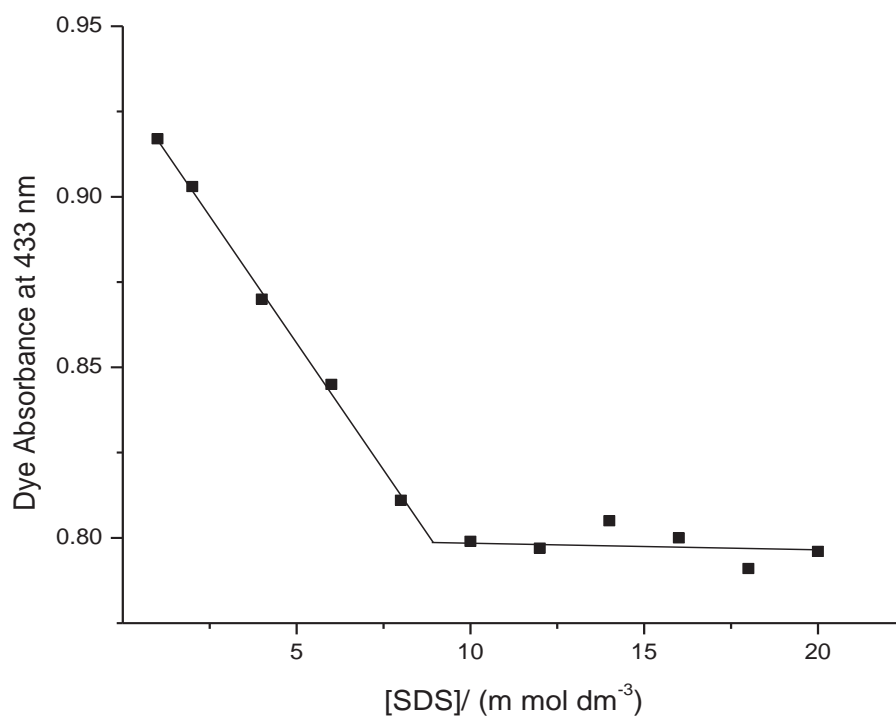

Figure 3. Plots of absorbance (*A*) Vs [SDS] for the system SDS + BTB (saturated) + ED (1 M) + H_2O, at 298.15K.

ion- solvent interaction parameters. It can be seen that (Tables 1 and 2) the observed positive temperature

dependence of Λ_o values for ionic surfactant solutions is due to the increase of ionic mobility at higher

temperature. The Λ_o values for SDS + H_2O system are lower than for HTAB + H_2O system, because of higher degree of hydration of comparatively smaller head group as well as smaller counter- ion of SDS molecule compared to HTAB. The Λ_o values slightly increase on adding ED for the surfactant systems, but the reverse is true for the case of PT that may be due to enhanced intermolecular hydrogen bonding of the later with water and thus make the water structure more viscous and lower Λ_o (Yuksel, 2003; Radhouane et al., 2008).

Surface physico-chemical properties

Maximum surface excess concentration (Γ_{max}) values at the air-liquid interface has been obtained using Gibb's adsorption equation (Huang et al., 1998; Partap and Yadav, 2008):

$$\Gamma_{max} = -\frac{1}{2.303nRT}\left(\frac{d\gamma}{d\log C}\right)_T \tag{4}$$

Where n is the number of particles furnished by each molecule of the surfactant in the solution. Since SDS and HTAB behave as univalent electrolytes in aqueous solutions, therefore, for these surfactants the values n has been taken as 2.

For nonionic surfactants n=1, R is the gas constant. $\left(\frac{d\gamma}{d\log C}\right)_T$ represents the slope of the surface tension versus log C plot below the CMC at temperature T. The calculated values for Γ_{max} for the studied systems at three temperatures are also presented in Tables 1 to 3. It may be seen that the Γ_{max} values decrease with the increase in temperature which may be due to the enhanced molecular thermal agitation at higher temperature (Partap and Yadav, 2008).

These results are in conformity with results reported elsewhere (Yuksel, 2003; Islam and Kato, 2003). A further decrease in Γ_{max} values on mixing ED or PT may be due to the fact that addition of these cosolvents cause a partial displacement of surfactant molecules from the air-liquid interface to the bulk phase.

The minimum area per molecule (A_{min}) of surfactant at the liquid-air interface (in nm^2) was calculated using the relation (Huang et al., 1998; Partap and Yadav, 2008):

$$A_{min} = \frac{10^{14}}{N\Gamma_{max}} \tag{5}$$

Where, N is Avogadro's number. A_{min} values for the studied systems are also given in the Tables 1 to 3, and for binary systems the values are in the order: HTAB > Tween 80 > SDS. An examination of these values reveals that A_{min} increases both with the increase in temperature as well as with the concentration of ED and PT in the

surfactant solution. This behavior can be explained in terms of the enhanced compatibility of surfactant with the solvent in the presence of cosolvents, thereby, causing a shift of surfactant molecules from air-liquid interface to the bulk phase (Kallol and Baghel, 2008; Sharma et al., 1996).

Surface pressure at CMC (π_{cmc}), an index of surface tension reduction at CMC, has been calculated using the equation (Tharwat, 2005; Yuksel, 2003):

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \tag{6}$$

Where γ_0 = surface tension of water and γ_{cmc} = surface tension of surfactant solution at CMC. π_{CMC} values thus calculated for various systems are recorded in Tables 1 to 3. An examination of the Tables clearly shows that π_{CMC} values for the studied systems vary in the order: HTAB > SDS > Tween 80. A similar order has been observed for the counter ion association constant (α) values for the former two. The surface pressure at CMC values are found to increase on adding a cosolvent for the studied ternary systems. This may be ascribed to the tendency of these organic cosolvents to adsorb at the air-liquid interface thereby lowering surface tension and hence increased π_{CMC} (Sansanwal, 2005). Further, π_{CMC} show marginal increase with increase in temperature.

Thermodynamic properties of micellization

Phase-separation and mass-action approaches present two models which have got wide acceptance for the interpretation of the energetics of micellization. For the ionic surfactants, however, the mass-action approach is usually preferred (Goodwin, 2004) and various thermodynamic parameters may be deduced from the temperature dependence of the CMC values. According to mass action model, the standard Gibbs free energy of micellization ($\Delta G°_{mic}$) for ionic and nonionic surfactant solutions were calculated using equations 3.7 and 3.8 respectively (Tharwat, 2005; Shaw, 1992).

$$\Delta G^o_{mic} = (2 - \beta)RT \ln X_{CMC} \tag{7}$$

$$\Delta G^o_{mic} = RT \ln X_{CMC} \tag{8}$$

Where, β is counter-ion dissociation constant, x is the surfactant mole fraction at CMC and R is gas constant (8.314 JK^{-1}mol^{-1}). The corresponding entropy and enthalpy of micellization were calculated from the following expressions respectively:

$$\Delta S^o_{mic} = \left[-\frac{d(\Delta G^o_{mic})}{dT}\right]_p \tag{9}$$

$$\Delta H^o_{mic} = \Delta G^o_{mic} + T\Delta S^o_{mic} \tag{10}$$

Table 4. Thermodynamic parameters of the micellization and adsorption for SDS system in aqueous and aqueous - cosolvent environment.

System	T(k)	$-\Delta G^0_{mic}$ (kJ mol^{-1})	ΔG^0_{trans} (kJ mol^{-1})	ΔH^0_{mic} (kJ mol^{-1})	ΔS^0_{mic} (kJ mol^{-1}K^{-1})	$-\Delta G^0_{ads}$ (kJ mol^{-1})	ΔH^0_{ads} (kJ mol^{-1})	ΔS^0_{ads}(kJ mol^{-1}K^{-1})
SDS + H$_2$O	298.15	35.46	-	-20.25		36.78	-17.40	
	308.15	35.99	-	-20.27	0.051	37.46	-17.39	0.065
	318.15	36.47	-	-20.34		38.07	-17.39	
SDS + ED(1M) + H$_2$O	298.15	34.40	1.06	-24.26		36.25	-22.54	
	308.15	34.56	1.43	-24.28	0.034	36.53	-22.36	0.046
	318.15	35.08	1.39	-24.36		37.16	-22.33	
SDS + ED(2.5M) + H$_2$O	298.15	34.05	1.41	-12.88		36.21	-23.99	
	308.15	34.48	1.51	-12.60	0.071	36.84	-23.96	0.041
	318.15	35.46	1.01	-12.87		37.03	-23.92	
SDS + ED(4M) + H$_2$O	298.15	33.26	2.20	-21.93		36.01	-24.48	
	308.15	33.87	2.12	-22.16	0.038	36.80	-24.47	0.040
	318.15	34.21	2.26	-22.22		37.01	-24.28	
SDS + PT(1M) + H$_2$O	298.15	35.00	0.46	-21.68		36.45	-18.56	
	308.15	35.38	0.61	-21.82	0.044	37.01	-18.52	0.060
	318.15	35.87	0.60	-21.87		37.64	-18.51	
SDS + PT(2.5M) + H$_2$O	298.15	34.40	1.06	-20.69		36.91	-27.67	
	308.15	35.65	0.34	-21.48	0.046	37.27	-27.72	0.031
	318.15	35.71	0.76	-21.58		37.52	-27.56	
SDS + PT(4M) + H$_2$O	298.15	34.02	1.44	-21.50		36.71	-22.70	
	308.15	35.21	0.78	-22.28	0.042	37.00	-22.52	0.047
	318.15	35.65	0.82	-22.29		37.64	-22.49	

Further, the Gibbs energy of transfer values (ΔG^0_{trans}), which can be accounted for the effect of cosolvent on the micellization process, was estimated through (Kabir-ud-Din and Koya, 2011; Sharma et al., 1996):

$$\Delta G^O_{tras} = \Delta G^O_{mic(w-cos)} - \Delta G^O_{mic(w)} \quad (11)$$

Where, $\Delta G^O_{mic(w)}$ and $\Delta G^O_{mic(w-cos)}$ stands for standard Gibbs free energy of micellization in water and water-cosolvent mixed media, respectively.

Various thermodynamic parameters of micellization calculated using Equations (7) to (11) are presented in Tables 4 to 6. The ΔG^O_{mic} values in all the cases are negative and become less negative with the increase in the cosolvent content in the mixed media. At a fixed solvent composition, the values become slightly more negative with the rise in temperature. These values show that the micellization of surfactants in water- cosolvent (ED or PT) mixed media becomes less favorable when the solvent medium contains a higher amount of ED or PT, whereas an increase in temperature slightly favors the micellization.

According to the theory of surfactant aggregation,

proposed by Nagarajan and Wang (2000), there may be various types of energy contributions to Gibbs energy of micellization. Observed positive value of ΔG^O_{tras} indicates that, it is responsible for the delay in the micellization of surfactants in the mixed media (Nagarajan and Wang, 2000) and their value depends on the transfer Gibbs free energies from pure water and the organic solvents in addition to their mutual interaction. As the addition of ED or PT modifies the bulk phase making it more favorable than pure water for dispersion of surfactant molecules, and the transfer of the hydrophobic tail from the bulk phase to the micellar region becomes less favorable, and hence ΔG^O_{mic} value increases (becomes less negative).

The standard entropy of micellization(ΔS^o_{mic}) values (Tables 4 to 6) is positive for the studied systems suggesting that the process of micellization is favored by entropy gain (16). ΔS^o_{mic} for the studied aqueous micellar solutions are in the order: Tween 80 > HTAB >SDS. On adding ED or PT, ΔS^o_{mic} values decrease due to enhanced water structure in its presence owing to intermolecular hydrogen bonding (Homendra and Devi,

Table 5. Thermodynamic parameters of the micellization and adsorption for HTAB system in aqueous and aqueous - cosolvent environment.

System	T(k)	$-\Delta G^0_{mic}$ (kJ mol^{-1})	ΔG^0_{trans} (kJ mol^{-1})	ΔH^0_{mic} (kJ mol^{-1})	ΔS^0_{mic} (kJ mol^{-1}K^{-1})	$-\Delta G^0_{ads}$ (kJ mol^{-1})	ΔH^0_{ads} (kJ mol^{-1})	ΔS^0_{ads}(kJ mol^{-1}K^{-1})
HTAB + H$_2$O	298.15	48.30	-	-15.50		50.11	-11.95	
	308.15	49.72	-	-15.82	0.110	51.80	-11.86	0.128
	318.15	50.49	-	-15.89		52.66	-11.94	
HTAB + ED(1M) + H$_2$O	298.15	47.48	0.82	-37.94		50.84	-27.29	
	308.15	47.76	1.96	-37.90	0.032	51.68	-27.24	0.079
	318.15	48.11	2.38	-37.97		52.42	-27.19	
HTAB + ED(2.5M) + H$_2$O	298.15	44.53	3.77	-26.34		47.56	-28.78	
	308.15	45.00	4.72	-26.40	0.061	49.52	-28.11	0.063
	318.15	45.75	4.74	-26.44		50.83	-28.71	
HTAB + ED(4M) + H$_2$O	298.15	42.99	5.31	-29.28		47.41	-15.81	
	308.15	43.60	6.12	-29.43	0.046	48.58	-15.80	0.106
	318.15	43.91	6.58	-29.48		49.53	-15.81	
HTAB + PT(1M) + H$_2$O	298.15	47.88	0.42	-34.46		50.23	-28.17	
	308.15	48.37	1.35	-34.50	0.045	50.98	-28.18	0.074
	318.15	48.78	1.71	-34.46		51.71	-28.17	
HTAB + PT(2.5M) + H$_2$O	298.15	44.87	3.43	-33.84		47.57	-29.99	
	308.15	45.65	4.07	-34.25	0.037	49.72	-29.99	0.064
	318.15	47.61	2.88	-35.84		51.05	-29.69	
HTAB + PT(4M) + H$_2$O	298.15	43.37	4.93	-21.90		46.40	-13.60	
	308.15	43.43	6.29	-21.94	0.072	47.80	-13.59	0.110
	318.15	44.81	5.68	-21.90		48.60	-13.60	

2006). On the other hand, ΔH^o_{mic} values for the studied systems are in the order: Tween 80 > HTAB > SDS. An exothermic standard enthalpy of micellization for ionic surfactants (SDS or HTAB) suggests that like entropy effect, the enthalpy change also favors the process of micellization. Positive ΔH^o_{mic} values, owing to the hydrophobic-hydrophobic interaction of surfactant alkyl chain in the process of micellization (Partap and Yadav, 2008), was observed for nonionic surfactant (Tween 80). Further, on adding a cosolvent (PT or ED) into surfactant solutions, there is decrease in ΔH^o_{mic} irrespective of their chemical nature, again due to its intermolecular hydrogen bonding with water.

Thermodynamic properties of adsorption

The standard free energy values of adsorption (ΔG^o_{ads}) at the air- liquid interface (a measure of the free energy of transfer per mole of surfactant at unit concentration from bulk to the surface at unit pressure) were calculated using the equation (Huang et al., 1998; Holmberg et al.,

2003):

$$\Delta G^o_{ads} = \Delta G^o_{mic} - 6.023 \times 10^{-1} \pi_{CMC} . A_{min} \qquad (12)$$

Where, π_{CMC} is in milliNewtons per meter. Values of ΔS^o_{ads} and ΔH^o_{ads} were obtained by using the corresponding Equations (13) and (14), respectively:

$$\Delta S^o_{ads} = [-\frac{d(\Delta G^o_{ads})}{dT}] \qquad (13)$$

$$\Delta H^o_{ads} = \Delta G^o_{ads} + T\Delta S^o_{ads} \qquad (14)$$

The values of ΔG°_{ads}, ΔH°_{ads} and ΔS°_{ads} are also presented in Tables 4 to 6. The lower ΔG^0_{ads} values 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: SDS > Tween 80 > HTAB. This order can be explained in terms of the order of magnitude of their intermolecular head group

Table 6. Thermodynamic parameters of the micellization and adsorption for Tween 80 system in aqueous and aqueous - cosolvent environment.

System	T(k)	$-\Delta G^0_{mic}$ (kJ mol^{-1})	ΔG^0_{trans} (kJ mol^{-1})	ΔH^0_{mic} (kJ mol^{-1})	ΔS^0_{mic} (kJ mol^{-1}K^{-1})	$-\Delta G^0_{ads}$ (kJ mol^{-1})	ΔH^0_{ads} (kJ mol^{-1})	ΔS^0_{ads}(kJ mol^{-1}K^{-1})
Tween 80 + H$_2$O	298.15	37.04	-	7.09		38.06	7.56	
	308.15	38.43	-	7.18	0.148	39.53	7.52	0.153
	318.15	39.99	-	7.20		41.12	7.56	
Tween 80 + ED(1M) + H$_2$O	298.15	35.94	1.1	6.70		37.42	7.60	
	308.15	37.44	0.99	6.63	0.143	39.04	7.49	0.151
	318.15	38.99	1.00	6.51		40.63	7.41	
Tween 80 + ED(2.5M) + H$_2$O	298.15	35.46	1.58	5.09		37.29	7.43	
	308.15	36.80	1.63	5.11	0.136	38.75	7.47	0.150
	318.15	38.17	1.82	5.10		40.28	7.44	
Tween 80 + ED(4M) + H$_2$O	298.15	35.18	1.84	4.47		37.19	6.64	
	308.15	36.57	1.86	4.41	0.133	38.71	6.59	0.147
	318.15	37.84	2.15	4.47		40.13	6.53	
Tween 80 + PT(1M) + H$_2$O	298.15	36.22	0.82	7.91		37.43	5.21	
	308.15	37.65	0.78	7.96	0.148	39.92	4.15	0.143
	318.15	39.37	0.62	7.72		40.70	4.80	
Tween 80 + PT(2.5M) + H$_2$O	298.15	35.68	1.36	7.85		36.98	9.23	
	308.15	36.97	1.46	7.99	0.146	38.42	9.14	0.155
	318.15	38.55	1.44	7.90		40.08	9.23	
Tween 80 + PT(4M) + H$_2$O	298.15	35.84	1.20	0.218		37.23	1.88	
	308.15	36.88	1.55	0.406	0.121	38.35	1.82	0.131
	318.15	38.26	1.73	0.436		39.84	1.84	

interaction at the air–liquid interface. Such interaction (repulsion) is highest in case of SDS. It has comparatively high degree of dissociation. Such head group interaction is least in case of HTAB due to steric hindrance of its comparatively larger head group. Addition of ED or PT leads to an increase (small negative) in ΔG^0_{ads} for the studied surfactant solutions. This may be attributed to the enhanced hydrophobic (nonpolar) character of the bulk on adding cosolvents, which facilitates solubilization (Sibani et al., 2013; Meghal and Parikh, 2009) of surfactant monomers in the bulk and decrease feasibility of micellization process.

The standard entropy of adsorption (ΔS^0_{ads}) values are invariably positive and correspondingly larger than standard entropy of micellization (ΔS^0_{mic}). This may be due to more degree of freedom of the surfactant molecules at the air-liquid interface compared to that in the cramped interior of micelle. Again, the endothermic (positive) standard enthalpy of adsorption,$\Delta H°_{ads}$ values observed for nonionic surfactant (Tween 80) may be due to the breaking of Hydrogen bonds between polyoxyethylene chain oxygen of surfactant and water molecules at the air-liquid interface (Hideki, 2009). Lastly,

exothermic ΔH^0_{ads} (for ionic surfactants, SDS and HTAB) and positive $\Delta S°_{ads}$ values suggest that the adsorption at air- liquid interface is favored by energy as well as entropy effect.

Nature of BTB dye absorption spectra in micellar systems

The absorption spectra of BTB in the presence of different concentration of the studied surfactant systems are shown in Figures 4 to 6. BTB in water (absence of any surfactant) shows a wavelength maximum at 433 nm. Addition of increasing concentration of surfactants with and without cosolvents led to a continuous decrease in absorbance at 433 nm. The absorption intensity at 433 nm was decreased upon further increasing the concentrations of the surfactants at constant amount of the dye indicator. That is the micellar systems altered the characteristics of the dye indicator UV spectra.

The shift in spectra is likely due to interactions between the indicators and micelles. That indicates, in micellar systems, the dye taken up by the micelles is often
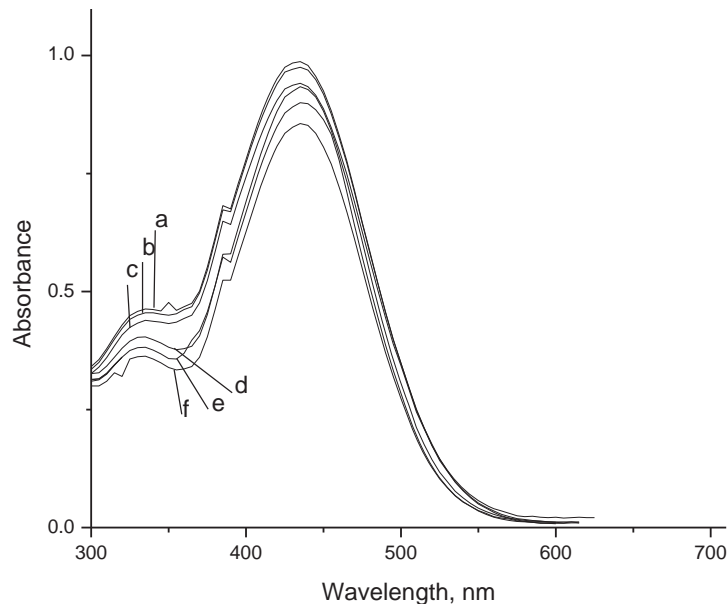
Figure 4. Absorption spectra of BTB (saturated) at various SDS concentration. [SDS]: (a) 0, (b) 0.001 M, (c) 0.005 M, (d) 0.01 M + PT (1 M), (e) 0.01 M + ED (1 M), (f) .02 M.
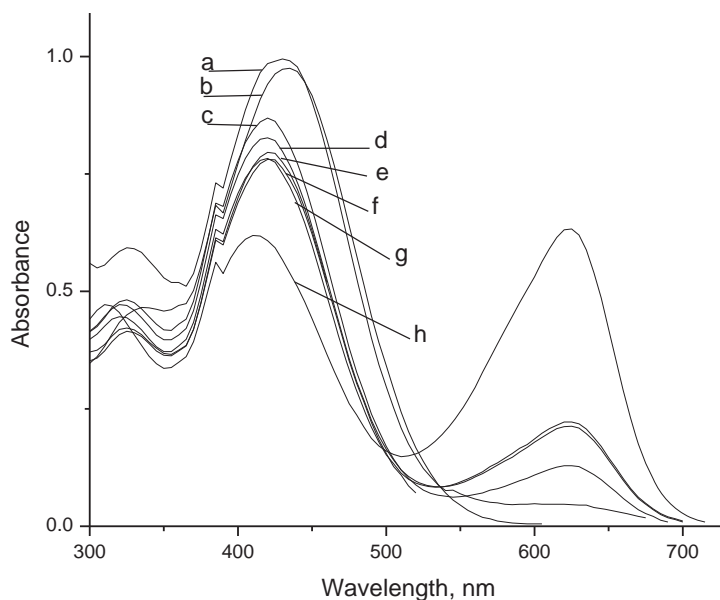

Figure 5. Absorption spectra of BTB (saturated) at various HTAB concentrations. [HTAB]: (a) 0, (b) 0.1 mM, (c) 0.5 mM, (d) 1.0 mM, (e) 1.5 mM, (f) 1.0 mM + PT (1 M), (g) 1.0 mM + ED (1M), (h) 2.8 mM.

insufficient to produce high absorbance. A similar effect of micelles on UV spectra has been reported (Jebaramya et al., 2009). In addition to that, particularly for HTAB, new peaks were appeared at 623 nm, as shown in Figure 5. Whereas absorption intensities at 623 nm are increased simultaneously with increasing the concentrations of HTAB. The development of the 623 nm band can be attributed to the conversion of the ion pair into a charge-transfer complex between the dye and micelle. Similar changes in the absorbance of the dye in the presence of oppositely charged surfactants have been reported in the past and have been attributed to the
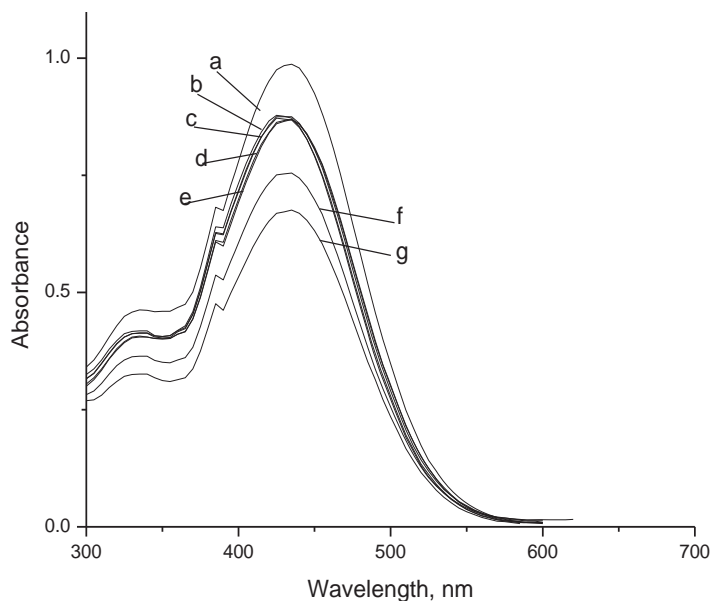
Figure 6. Absorption spectra of BTB (sat.) at various Tween 80 concentrations. [Tween 80]: (a) 0, (b) 0.005 mM, (c) 0.01 mM, (d) 0.02 mM + PT(2.5 M), (e) 0.02 mM + ED (2.5 M), (f) 0.02 Mm, (g) 0.06 mM.

formation of an ion-pair complex (Garcia et al., 2007). But as the surfactant concentration increases beyond the CMC, the absorbance of two bands (433 and 623 nm) progressively decreases with the appearance of the main dye absorption band. This indicates that the dye–surfactant complex is unstable in the micellar region, where the surfactant molecules tend to aggregate to form the micelles. The spectral changes of dye in micellar media have been suggested to be due to electrostatic interactions between oppositely charged molecules. It has been reported in the literature that the ionic dyes can form molecular complexes with oppositely charged micelles (Garcia et al., 2007). It has also been shown that aromatic compounds with sulfonic acid groups are incorporated into the Stern layer of cationic micelles in a sandwich arrangement. A van der Waals interaction between adjacent surfactant chains and the dye organic moiety (hydrophobic forces) changes the chromophore microenvironment (Jebaramya et al., 2009). The evidence that the interaction is due to oppositely charged molecules also comes from the fact that similarly charged dye-micelle systems have shown the absence of such spectral changes.

Conclusion

From the results obtained, it is possible to reach the following conclusions: Both the addition of cosolvents (ED or PT) and rise in temperature results in an increase in the critical micelle concentration (*CMC*) and degree of counterion dissociation constant (*β)* for ionic surfactants.

However, CMC of Tween 80 shows a negative temperature coefficient. Again, slight increase in CMC and *β* values of studied surfactant solutions, irrespective of their chemical nature, on mixing ED was observed compared to PT. Lower ΔG^o_{mic} of surfactants in mixed solvent containing PT compared to that containing ED suggest more feasibility of micellization on increasing hydroxy groups in a polyol. From the observed surface properties namely surface excess concentration (Γ_{max}), minimum area per molecule (A_{min}) and surface pressure at CMC (π_{cmc}): a long chain cationic surfactant (HTAB) has relatively higher π_{cmc} and A_{min} values. On the other hand, SDS and Tween 80 have higher Γ_{max} values. Further, enhancement of π_{cmc} and A_{min} values, and reduction of Γ_{max} value have been observed in the presence of studied cosolvents. For ionic surfactant solutions, with or without a cosolvent, micellization in the bulk and adsorption at the air- liquid interface are favored by exothermic enthalpy change as well as entropy gain. And, with the increase in the concentration of cosolvents in the mixed medium, micellization becomes less favorable. Therefore, on the basis of observed effect of added cosolvents (ED and PT) on CMC, surface physico-chemical properties and thermodynamic property of the studied systems, The author suggest that, addition of these cosolvents (ED or PT) would be beneficial in metallurgical process such as concentration of ores by froth floatation and other industrial application. However, they are less effective as oil spill dispersant and in detergency process.

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