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Thermodynamic Investigation of Anionic Dye-Cationic Surfactant Ion Pair Formation in Water-Acetonitrile Mixed Solvent

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Ion pair formation between anionic dye methyl orange and three cationic surfactants *n*-alkyltrimethylammonium bromide C_nTAB (n = 12, 14, 16) was studied by conductance technique in pre-micellar region. The specific conductance of dye-surfactant mixtures was measured at different temperatures in water-acetonitrile mixed solvent. Two theoretical models dependent on conductance were used to calculate the equilibrium constants for dye-surfactant ion pair formation. The results showed that the equilibrium constants increase by increasing chain length of the surfactant in the same solvent and temperatures while decrease by increasing both temperature and acetonitrile content. Electrostatic and hydrophobic interactions are responsible for ion pair formation, hydrophobic interaction showed a predominate effect. The standard free energy change, standard enthalpy change and standard entropy change for the process were calculated and discussed.

Keywords: Methyl orange, Surfactant, Mixed solvents, Conductance, Ion pairs, Thermodynamics parameters.

INTRODUCTION

Dye and surfactant are two important classes of organic compounds with wide industrial uses. Dyes as unsaturated organic substances have an affinity to substrates such as textile, paper, wool, nylon, silk and leather[1]. Surfactants are widely used as leveling agents for improving dying processes by increasing solubility, stabilizing the dispersed state and promoting a uniform distribution of the dye in the textile[2].

Among various dye-surfactant mixtures, oppositely charged systems have been studied to understand the contribution effects of electrostatic and hydrophobic interactions[3]. Javadian *et al.*[4] studied the interaction of Congo red with a series of alkyltrimethylammonium bromide (C_nTAB) using conductometric method. The equilibrium constant and thermodynamic parameters for ion pair formation were calculated on the basis of two theoretical models. Studies in this field are still important and interesting for the theory and technology of dying processes[5-7].

In addition, the studies of binary dye-surfactant systems are pertinent to many scientific fields including pharmaceutical science, analytical chemistry, photography, luminescence and lasers[8]. Many techniques such as spectrophotometery[9-12], tension-metry[13,14], potentiometry[15] and conductometry[16,17] have been applied for the dye and surfactant interactions in aqueous media.

Few studies have been made on the influence of varying solvent and temperature for the above interactions. The aim of recent work is to investigate the strength of ion pair formation between the anionic dye methyl orange (MO) and series of cationic surfactants *n*-alkyltrimethylammonium bromide by varying the polarity of the medium when adding acetonitrile as co-solvent with water and varying temperature. The measurements were carried out by conductance technique and applied two theoretical methods to obtain the equilibrium constant. Thermodynamic functions for dye-surfactant ion pair formation were calculated and discussed. This study indicated the important type of interaction for the formation of a dye-surfactant ion pair.

EXPERIMENTAL

Methyl orange from Sigma with purity of 99.7 % was used without more purification. All the alkyltrimethylammonium bromides (C_nTAB, n = 12, 14 and 16) (Eastman Kodak) were recrystallized twice from acetone and dried in a vacuum oven. Conductivity water was obtained by passing ordinary distilled water into Elgastat deionizer, its specific conductance k° amounted ($5\text{-}7 \times 10^{-7}$ cm^{-1}) at 25 °C. Acetonitrile (Merck AnalaR) is dried overnight in contact with 3 Å molecular sieves, then freshly distillate solvent be obtain by using fractionating column where middle fraction is only collected, its k° is taken as (5×10^{-8} S cm^{-1}). Each H_2O-CH_3CN mixed solvent is prepared by using micro burette to take the require stock volume % of acetonitrile in 250 mL measuring flask.

Surfactant solution is prepared by weighing definite amount of this surfactant in 10 mL fitted bottle then add the require dye concentration (1×10^{-5} mol/L) finally completed with the require solvent to give the desire molar concentration. Conductivity meter model Haak (HI 8819) with cell constant 0.999 cm^{-1} was used to measure the specific conductance for each solution. Conductance measurements were carried out at 25, 35 and 45 °C. Ultra thermostat with accuracy of ± 0.05 °C was used to adjust the required temperature.

Pure crystals of NaBr (BDH) was dried and used to prepare different solutions either in pure water or in water-acetonitrile mixtures at the same concentration range of the above solutions.

RESULTS AND DISCUSSION

The specific conductance (k) of dye methyl orange-surfactant C_{14}TAB mixture in 10 % CH_3CN is presented at 25, 35 and 45 °C as a function of C_{14}TAB concentration (a typical example). The measurement of k values were found to increase by increasing temperature indicating more free ions (conducting species) in the solution at high temperature (Fig. 1).

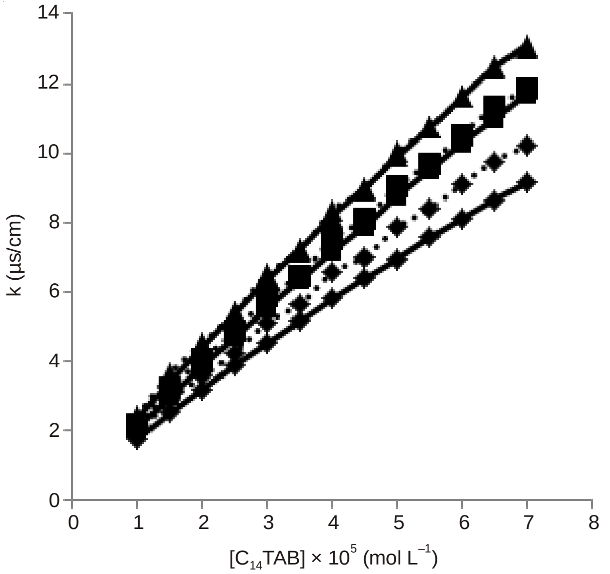

Fig. 1. Specific conductivity of methyl orange-C_{14}TAB mixture in aqueous solution as a function of the C_{14}TAB concenterations at 25 °C (◆), 35 °C (■), 45 °C (▲)

The measured conductance of methyl orange-C_{14}TAB mixtures at 25 °C, as a function of C_{14}TAB concentration is carried out at different amounts of acetonitrile as shown in Fig. 2. This plotting indicates the order of increasing k according to increasing the dielectric constant.

Bracko and Span[18] studied the system of acid orange dye with dodecylpyridinium chloride in H_2O-C_2H_5OH mixtures. The equilibrium constant was found to decrease by increasing ethanol content.

It was found that measured conductivity was not always increased linearly with the surfactant concentration. This was explained as a consequence of presence of non-conducting species in the solution[17].

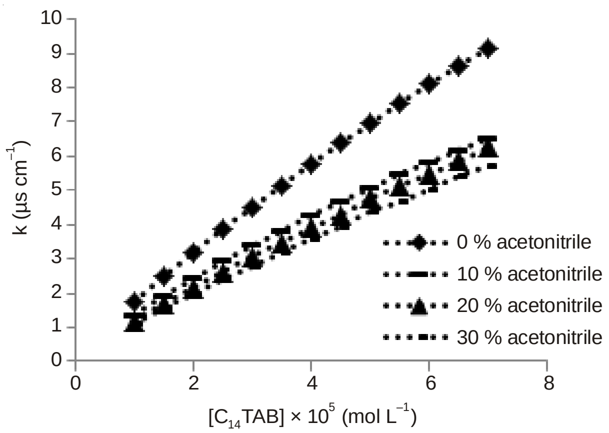

Fig. 2. Specific conductivity of methyl orange-C_{14}TAB mixture in different media as a function of the C_{14}TAB concenteration at 298 K

In present work, Fig. 2 shows deviation from linearity, this deviation refers to non-conducting species in the solution and formation of ion pair complex. The order of increasing ion pair formation follow the trend 0 > 10 > 20 > 30 % CH_3CN.

The variation of specific conductivity with surfactant concentration for different surfactants C_nTAB (n = 12, 14, 16) at 35 °C, 20 % CH_3CN was shown in Fig. 3. The most deviation from linearity indicated the ion pair formation which appeared to follow the order $C_{16} > C_{14} > C_{12}$.

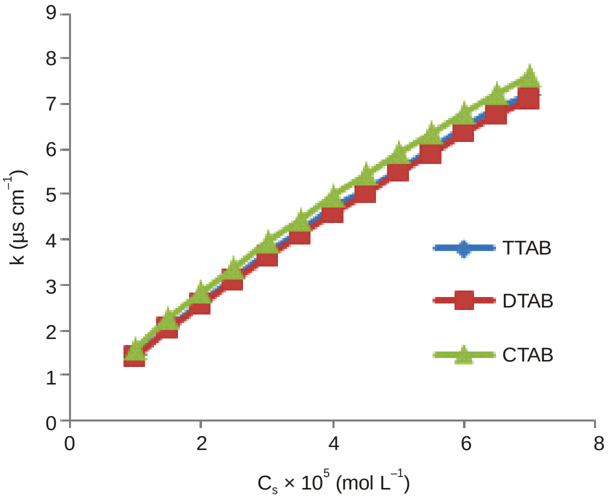

Fig. 3. Plotting of specific conductivity k against surfactants concentration at 20 % acetonitrile at 35 °C

Gökturk[16] studied the interaction of carminic acid an anionic dye with various cationic surfactants. The equilibrium constants for dye-surfactant complex formation were calculated using two methods.

Method 1 based on assumption that at the equivalent point, the dye-surfactant ion pair can be treated as a partly associated electrolyte[17]. For this case, the equilibrium constant is given by eqn. 1:

$$K = \frac{1-\propto}{\propto^2 C}\text{; where } \propto = \frac{\Lambda}{\Lambda_o} \quad (1)$$

∝ is the degree of ionization, Λ_o is the hypothetic completely ionized electrolyte equivalent conductance and Λ is that related to concentration "c".

The evaluation of Λ_{DS} and Λ^o_{DS} of dye-surfactant ion pair based on the assumption that conductance is additive value, so eqn. 2 can be written as:

$$\Lambda_{DS} = \Lambda_{NaD} + \Lambda_{SBr} - \Lambda_{NaBr} \qquad (2)$$

where Λ_{NaD}, Λ_{SBr} and Λ_{NaBr} are the equivalent conductance of dye, surfactant and sodium bromide respectively. The above Λ values are taken at each concentration where Λ_{DS} is based on the assumption that at low ionic concentration, dye and surfactant are coupled to give ion pair at definite concentration which change by varying solvent mixture and temperature.

Λ^o_{DS} also can be estimated where its individual terms be represented as shown in the following eqn. 3:

$$\Lambda^o_{DS} = \Lambda^o_{NaD} + \Lambda^o_{SBr} - \Lambda^o_{NaBr} \qquad (3)$$

where Λ^o_{NaD}, Λ^o_{SBr} and Λ^o_{NaBr} are the limiting equivalent conductance values for dye, surfactant and sodium bromide respectively.

Table-1 shows the calculated Λ^o_{DS} in addition to that of surfactant Λ^o_{SBr} for all solutions at different volume (%) acetonitrile and temperatures (25-45) °C. Table-2 shows the values of equilibrium constant K calculated by this method.

Method 2 is based[18] on a comparison between the experimental and theoretical values of specific conductivity of the dye-surfactant solution.

Assuming that the anionic dye and the cationic surfactant form a non-conducting associated ion pair (DS) in their solution, the reaction between the dye NaD with anionic moiety D^- and the surfactant SBr with cationic moiety S^+ can be described as an equilibrium reaction.

$$D + S^+ \rightleftharpoons DS \qquad (4)$$

From eqn. 4 the equilibrium constant K can be given as

$$K = C_{DS}/(C_D - C_{DS})(C_S - C_{DS}) \qquad (5)$$

If there was no interaction between them in the solution, the limiting values of their conductance would be given as the following:

$$10^3\ k = C_D\lambda_{Na^+} + C_D\lambda_D + C_S\lambda_{S^-} + C_S\lambda_{Br^-} \qquad (6)$$

where C_D and C_S are the molar concentrations of the dye and surfactant respectively, while λ_{Na^+}, λ_{D^-}, λ_{S^+} and λ_{Br^-} are limiting equivalent conductance of the ions Na^+, D^-, S^+ and Br^- respectively.

Fig. 4 shows plotting k (exp.) and k (theoretical) against surfactant concentrations (TTAB) in 10% acetonitrile and different temperatures. It is found that the experimental line is lower than the theoretical which is attributed to the occurrence of non-conducting species of ion pair.

TABLE-1
INFINITE EQUIVALENT CONDUCTANCE (S cm^{2}mol^{-1}) FOR SURFACTANT (SBr) AND SURFACTANT-DYE ION PAIR (SD) AT DIFFERENT VOLUME (%) OF ACETONITRILE AND TEMPERATURES

Temperature (°C)	CH_3CN (%)	$C_{12}TAB$		$C_{14}TAB$		$C_{16}TAB$	
		Λ^o_{SBr}	Λ^o_{DS}	Λ^o_{SBr}	Λ^o_{DS}	Λ^o_{SBr}	Λ^o_{DS}
25	0	104.27	75.50	117.37	88.60	142.88	114.11
35		107.96	76.00	121.06	89.10	159.76	127.80
45		124.84	76.70	138.42	90.65	180.10	132.33
25	10	91.17	74.32	97.25	80.40	127.69	110.84
35		101.43	75.66	107.47	81.70	139.91	114.14
45		118.77	76.60	127.20	85.03	163.09	120.92
25	20	77.41	73.81	81.80	78.20	110.55	106.94
35		86.81	74.51	91.41	79.10	123.42	111.11
45		111.14	74.80	121.04	84.70	149.86	113.52
25	30	59.42	60.20	71.32	72.10	79.22	80.00
35		62.97	60.66	75.10	72.80	82.78	80.47
45		67.30	60.80	79.50	73.00	87.36	80.85

TABLE-2
EQUILIBRIUM CONSTANTS FOR METHYL ORANGE-C_nTAB CALCULATED BY TWO DIFFERENT METHODS

Temp. (°C)	Method 1				Method 2			
	CH_3CN (0 %)	CH_3CN (10 %)	CH_3CN (20 %)	CH_3CN (30 %)	CH_3CN (0 %)	CH_3CN (10 %)	CH_3CN (20 %)	CH_3CN (30 %)
	$C_{12}TAB \times 10^{-4}$ (dm^3 mol^{-1})				$C_{12}TAB \times 10^{-4}$ (dm^3 mol^{-1})			
25	8.573	6.177	5.558	4.300	2.500	2.000	0.700	0.400
35	7.958	5.499	4.963	3.371	0.700	0.500	0.300	0.020
45	6.985	3.202	2.872	2.843	0.500	0.400	0.250	0.000
	$C_{14}TAB \times 10^{-4}$ (dm^3 mol^{-1})				$C_{14}TAB \times 10^{-4}$ (dm^3 mol^{-1})			
25	9.506	8.355	7.390	5.655	3.900	3.400	1.900	1.200
35	8.119	7.506	5.020	4.198	0.800	0.600	0.400	0.030
45	7.076	6.378	4.340	3.792	0.600	0.500	0.300	0.000
	$C_{16}TAB \times 10^{-4}$ (dm^3 mol^{-1})				$C_{16}TAB \times 10^{-4}$ (dm^3 mol^{-1})			
25	20.915	15.187	10.491	6.386	4.000	3.200	2.000	1.300
35	15.224	13.076	8.072	5.554	0.900	0.800	0.700	0.040
45	12.001	10.442	7.399	4.831	0.700	0.700	0.600	0.000

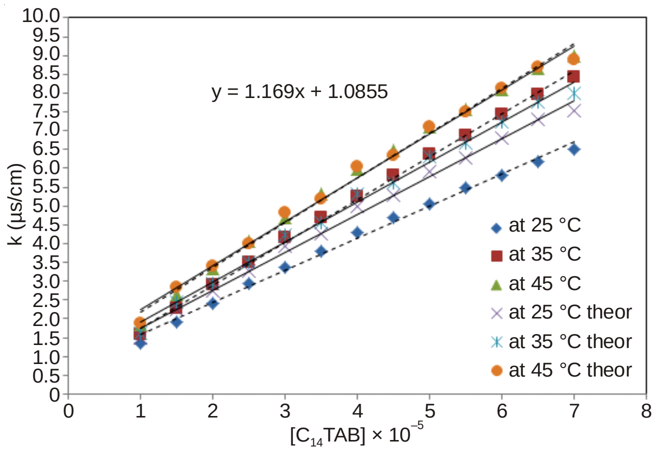

Fig. 4. Specific conductance (Exp.) and (theo.) of methyl orange-C_{14}TAB in 10 % (H_2O-CH_3CN) mixtures at differenttemperatures

Accordingly, eqn. 6 can be rewritten as:

$$10^3k = (C_D\text{-}C_{DS})\lambda_{D^-} + C_D\lambda_{Na^+} + (C_S\_C_{DS})\lambda_{S^+} + C_S\lambda_{Br^-} \quad (7)$$

where C_{DS} is the concentration of the non-conducting dye-surfactant ion pair. From eqns. 6 and 7, we obtain the following equation:

$$10^3\,\Delta k = C_{DS}\,(\lambda_{D^-} + \lambda_{S^+}) \quad (8)$$

where Δk is the difference in specific conductance between the theoretical and experimental values for each surfactant concentration.

Since the measurements were carried out in dilute solutions of dye and surfactant, so eqn. 8 can be written as:

$$10^3\,\Delta k = C_{DS}\Lambda^o_{DS} \quad (9)$$

where Λ^o_{DS} is the equivalent conductance of the dye-surfactant ion-pair at infinite dilution at given volume % acetonitrile and temperature. The C_{DS} values were calculated from the corresponding Δk and Λ^o_{DS}.

The equilibrium constant (K) for ion pair formation is given by eqn. 10:

$$K = \frac{C_{DS}}{(C_D - C_{DS})(C_S - C_{DS})} \quad (10)$$

Table-2 shows the calculated K values for all solutions estimated by method (2) where each value is taken as the average of more than one experimental run.

K values are observed to increase by increasing hydrocarbon chain of the surfactant in the order $C_{16} > C_{14} > C_{12}$ in given solvent. Also ion pairing is seen to decrease by increasing acetonitrile content as well as temperature[19].

From examining K values, it is seen that **method 1** have higher values than **method 2**. This fact is attributed to the relative different affinities between electrostatic and hydrophobic attraction forces that related to calculate the equilibrium constant.

Thermodynamic of ion pair formation: The standard thermodynamic parameters of free energy change Δ^oG_{IP} of ion pair formation, the enthalpy change Δ^oH_{IP} and the entropy change Δ^oS_{IP} can be estimated[19-21] from the following eqns. 11-13.

$$\Delta G^o_{IP} = -RT\ln K \quad (11)$$

$$\Delta H^\circ_{IP} = \frac{\partial\left(\frac{\Delta G^\circ}{T}\right)}{\partial\left(\frac{1}{T}\right)} \quad (12)$$

$$\Delta S^\circ_{IP} = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (13)$$

According to van't Hoff, a plot of (ΔG^o_{IP}/T) *versus* (1/T) gives a straight line whose slope is equal to Δ^oH_{IP}.

Table-3 listed the thermodynamic data that related to the above solutions at different concentrations. ΔG^o_{IP} is more negative by increasing the hydrocarbon chain in the order $C_{16} > C_{14} > C_{12}$ for given solvent as well as by increasing temperature. When increasing CH_3CN % ΔG^o_{IP} be less negative where the negativity is related to more spontaneous process.

The formation of the dye-surfactant ion pair is a consequence of mutual influence of electrostatic and hydrophobic interaction. The surfactant as well as dye posses a strong polar group. In aqueous solution they dissociate into ions and therefore electrostatic attractive interactions can appear between the dye anion and the surfactant cation. The non-polar part of the surfactant is a long aliphatic chain so it is very likely that hydrophobic interactions will appear in the process of ion pair formation.

The contribution of electrostatic interactions[22,23] can be estimated from eqn. 14 which describes the electrical work required for the process of transferring two charges on the distance "a"

TABLE-3
THERMODYNAMIC PARAMETERS FOR ION PAIRING OF METHYL ORANGE WITH CATIONIC SURFACTANTS IN DIFFERENT VOLUME (%) ACETONITRILE AND TEMPERATURES

Surfactant	Temp. (K)	0 %			10 %			20 %			30 %		
		ΔG (KJ mol^{-1})	ΔH (KJ mol^{-1})	ΔS (J mol^{-1} k^{-1})	ΔG (KJ mol^{-1})	ΔH (KJ mol^{-1})	ΔS (J mol^{-1} k^{-1})	ΔG (KJ mol^{-1})	ΔH (KJ mol^{-1})	ΔS (J mol^{-1} k^{-1})	ΔG (KJ mol^{-1})	ΔH (KJ mol^{-1})	ΔS (J mol^{-1} k^{-1})
C_{12}TAB	298	-28.142	-15.000	44.101	-27.330	-20.840	21.778	-27.069	-25.000	6.943	-26.433	-28.000	-5.258
	308	-28.896		45.117	-27.950		23.084	-27.687		8.724	-26.697		-4.230
	318	-29.489		45.563	-27.427		20.714	-26.286		4.044	-26.260		-5.472
C_{14}TAB	298	-28.398	-13.333	50.554	-28.078	-14.333	46.124	-27.774	-17.857	33.278	-27.112	-20.000	23.866
	308	-28.947		50.695	-28.746		46.795	-27.716		32.010	-27.258		23.565
	318	-29.524		50.915	-29.249		46.906	-28.231		32.623	-27.874		24.761
C_{16}TAB	298	-30.352	-13.043	58.084	-29.560	-14.000	52.215	-28.642	-15.000	45.778	-27.413	-17.857	32.067
	308	-30.557		56.864	-30.168		52.493	-28.932		45.234	-27.975		32.851
	318	-30.921		56.2201	-30.552		52.050	-28.710		43.113	-27.618		30.695

$$\Delta G^\circ_{eL} = -\frac{[z_1 z_2]e^2 N_A}{\varepsilon a} \qquad (14)$$

where z_1 and z_2 are the valences of cation and anion respectively, e is unit charge, N_A is Avogadro's number and ε is the dielectric constant of the solvent, "a" represents the contact distance, *i.e.* the sum of the radii of the two ions.

According to this equation, with an increase in the proportion of acetonitrile in the solution, the values of ΔG°_{eL} decrease because of the reduction in dielectric constant of the solvent. Table-3 shows the opposite, so the electrostatic contribute a minor part to standard free energy change of ion pairing ΔG°_{IP}.

The contribution of interaction effect on ΔG°_{IP} is indicated from Fig. 5 where the plotting of ΔG°_{IP} *versus* 1/ε in case of $C_{14}TAB$ at different temperatures gave a curvature or non-linear relationship. This indicate that not only electrostatic interaction but both electrostatic and non-electrostatic interaction affect on ΔG°_{IP}[24].

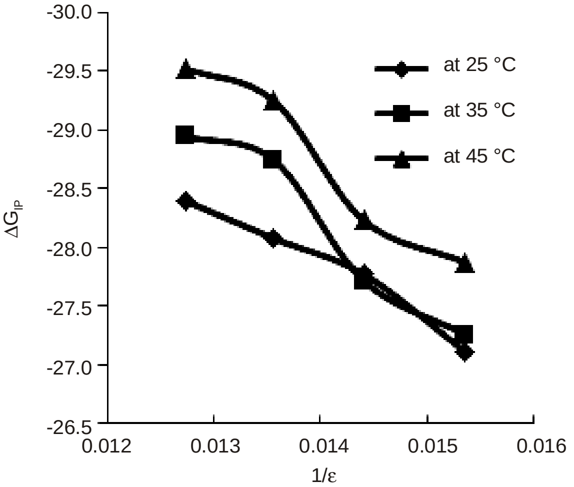

Fig. 5. Variation of the standard free energy with the revers of dielectric constant 1/ε for $C_{14}TAB$

Hence the free energy of ion pairing can be divided into two parts, eqn. 15:

$$\Delta G_{IP} = \Delta G_{el.} + \Delta G_{hyd.} \qquad (15)$$

We conclude from the values of ΔG_{IP} that the hydrophobic contribution play the major part in the formation of ion pair.

The presence of acetonitrile solvent has a negative influence on hydrophobic interaction. This is explained according to the unique behaviour of water. In water, there is a strong interaction between water molecules arising from driving dispersion forces and hydrogen bonding act cooperatively to squeeze the alkyl hydrocarbon chain out of the water. So the attraction between hydrocarbon molecules increase which lead to increasing hydrophobic interaction. In mixed solvent, this tendency becomes more weaker due to the breakdown of water structure by addition of other solvent acetonitrile[25,26].

The calculated ΔH^o_{IP} values from eqn. 12 given in Table-3 are found to be negative for all solutions. The negativity is large in water than in (H_2O-CH_3CN) mixtures indicating more exothermic interaction in water.

Finally, the entropy ΔS^o_{IP} of the interactions is positive and increase in the same solvent as increasing the chain length of surfactant. The positive values of ΔS^o_{IP} calculated for the surfactant with the longer aliphatic chain indicate the presence of hydrophobic interactions[9,27].

Conclusion

Methyl orange form a non-conducting ion pair with a series of cationic surfactants as $C_{12}TAB$, $C_{14}TAB$ and $C_{16}TAB$ at different volume (%) CH_3CN and temperatures. Two different methods relating to conductance technique were used to estimate the equilibrium constant. The estimated K values observe to give higher values by method (1) than (2) indicated that the long range and short range interactions are not taken the same chance in both calculations. The role of the solvent was found to be essentially sharing the electrostatic and hydrophobic processes in measuring K. The formation of dye-surfactant ion pair is a consequence of mutual influences of long range electrostatic force and short range hydrophobic interactions. The increase of the hydrophobicity of surfactant in the same medium increase the tendency to associate while this tendency be less when increasing acetonitrile *i.e.* by decreasing the polarity of the medium.

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