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Thermodynamic Parameters of Quaternary Ammonium Salts TMAC,TEAB,TBAB and TBAI in Aqueous and Methanolic Solutions at 298.16K,303.16K,308.16K and 313.16K by Conductivity Measurements

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Abstract:
The Critical Micelle Concentration(CMC) of Tetramethyl ammonium chloride(TMAC), Tetraethyl ammonium bromide(TEAB), Tetrabutyl ammonium bromide(TBAB), and Tetrabutyl ammonium iodide(TBAI) in aqueous and methanolic solutions were determined at 298.16K, 303.16K, 308.16K and 313.16K by conductivity measurements. Enthalpy (ΔH°_{m}), Entropy (ΔS°_{m}) Free energy (ΔG°_{m}) and Heat capacity ($C_{p)}$ were calculated from temperature dependence at CMC. The results indicate that value of CMC increased with increasing the temperature consequently thermodynamic parameter of micellization at CMC also changed.

Keywords: Critical micelle concentration, TMAC, TEAB, TBAB, TBAI, Conductance, Enthalpy, Entropy, Free energy.

I. INTRODUCTION:

Surfactants are amphiphilic molecules that possess both hydrophobic and hydrophilic properties. Surfactant molecule consists of a long hydrocarbon tail that dissolves in hydrocarbon and other nonpolar solvents and a hydrophilic head group that dissolves in polar solvents, Surfactntsare interfacially active compound and several bulk solution properties are significantly changed. The polar head group may be anionic, cationic, non ionic and zwitterionic. Surfactants have been used extensively for the enhancement or inhibition of industrially and biologically important free radical processes[1-5]. The physical properties of the solution for a amphiphile show an abrupt change into cooperative formation of micelle in the bulk solution at the CMC which is anarrow concentration[6]range. The knowledge of CMC is very important for the calculation of the thermodynamic parameters.The CMC of narrow concentration range depends on the physical property observed and measured accurately. Therefore it is essential to employ physical methodologies which are highly sensitive to structural changes for determination of the CMC[7]. The determination of thermodynamic parameters, the Gibbs free energy (ΔG°_{m}), the enthalpy (ΔH°_{m}), the entropy (ΔS°_{m}) and the heat capacity (ΔCp°) of micelle formation is very important because they qualify the relative importance of hydrophobic interactions. These parameters can be derived from the temperature dependence of the critical micelle concentration[8]. Quaternary ammonium salts have numerous uses in various industries. They are used as disinfectants, surfactants, fabric softeners, antistatic agents, and wood preservatives. Various products that contain Quaternary ammonium salts and other disinfectants are commonly used in homes, workplaces, and publicplaces. Disinfectants have an important role in preventing the spread of serious infectious diseases. Health care facilities, day care centers, and restaurants may be centers for transmission of bacterial and viral illnesses where use of disinfectants is important. On the other hand, use of these disinfectants is not recommended in places such as homes and offices when there is no elevated risk of infection, or where plain detergents would be effective in removing infectious organisms[9]. The main property of quaternary ammonium salt systems is that their aggregation phenomenon arise from various non-covalent interactions (such as, H-bonding, vanderwaals interactions) operating at the molecular level[10].The study has been carried out at four different temperatures 298.16K, 303.16K, 308.16K and 313.16K with the solutions of TMAC, TEAB, TBAB, TBAI to compute thermodynamic parameters of micellisation assuming equilibrium model for micelle formation.

II. EXPERIMENTAL:-

Requirements:- Conductivity water was obtained by distilling distilled water first with acidified $KMNO_4$ and secondly with very small amount of NaOH pellets and vapours were condensed and collected as conductivity water. Methanol was purified by keeping over Potassium Hydroxide for a day and distilled. The distillate was refluxed with 1% of Calcium metal for about eight hours and redistilled. All the reagents used were of analytical grade. The quaternary ammonium salts TEAB (98.0% CDH central drug house (P) Ltd.), TMAB (98.0% CDH), TBAB (99.0% CDH) and TBAI (99% CDH) were used as received. All solutions were prepared using conductivity water and methanol.
Methods:- Solutions were prepared by weight usingKeroy digital balance. Initial concentration was kept 0.5 N and subsequent solutions were prepared by dilution method in each solvent. The solutions were kept for ten minutes at desired temperature before use.
Conductance measurements:- Conductances of cationic surfactants quaternary ammonium salts TMAC,TEAB,TBAB and TBAI were measured in aqueous and methanolic solutions over a wide range of salt concentrations at 298.16K, 303.16K, 308.16K and 313.16K.
Conductivity data was obtained using a CM 180 digital conductivity meter equipped with a dip cell (cell constant $0.99cm^{-1}$) and the calibration of the instrument was made with 0.01 M KCL solutions at regular time intervals. The electrode was cleaned with dilute acid, distilled water and then was rinsed with conductivity water before measurement. All the experiments were performed in a High Precision thermostatic water-bath. The solutions were thermally equilibrated at the desired temperature for at least 10 minutes before

measurement. Temperature control of thermostatic water bath was within ±0.01^0

III. RESULTS AND DISCUSSION:-

The critical micelle concentration (CMC) values of quaternary ammonium salts in various compositions in aqueous and methanolic solutions were found out through conduct ometricmea surments at 298.16K,303.16K,308.16K and 313.16K. CMCs were determined from the inflection points in the plots of specific conductance versus concentration.

Table.1. CMC values of TMAC, TEAB, TBAB and TBAI in aqueous and methanolic solutions at various Temperatures

Temperat ure(K)	CMC(mol/l) in aqueous solution			CMC(mol/l) in methanolic solution			
	TMAC	TEAB	TBAB	TMAC	TEAB	TBAB	TBAI
298.16	0.2420	0.2500	0.2500	0.2610	0.2632	0.2720	0.2710
303.16	0.2600	0.2630	0.2632	0.2777	0.2820	0.2880	0.2840
308.16	0.2940	0.2940	0.2810	0.2900	0.2941	0.3120	0.2960
313.16	0.3180	0.3125	0.3040	0.3100	0.3260	0.3333	0.3120

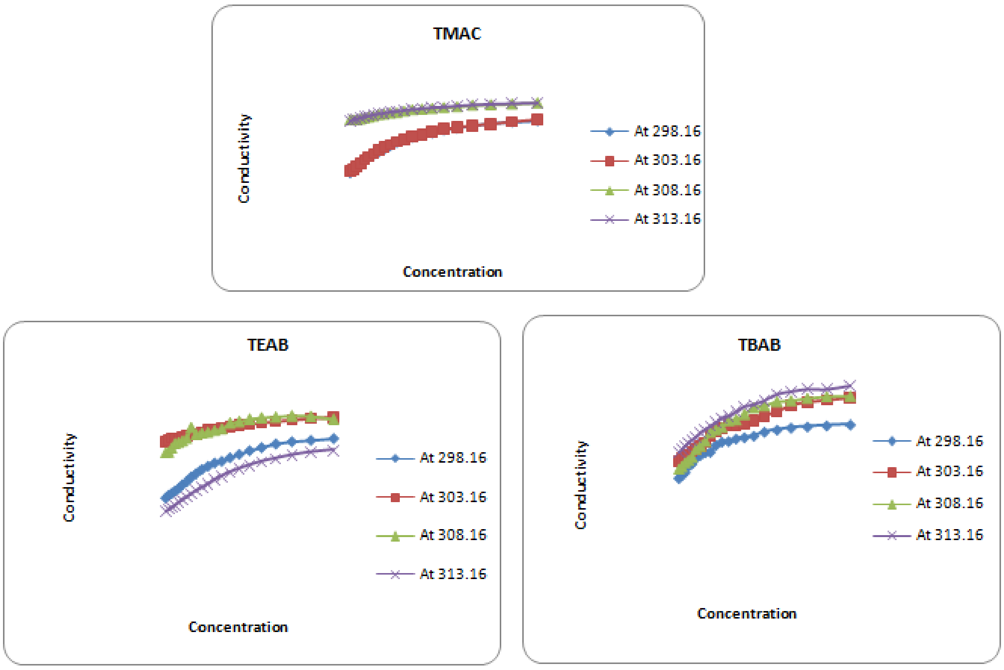

Figure.1. Plots of specific conductance versus concentration in aqueous solutions

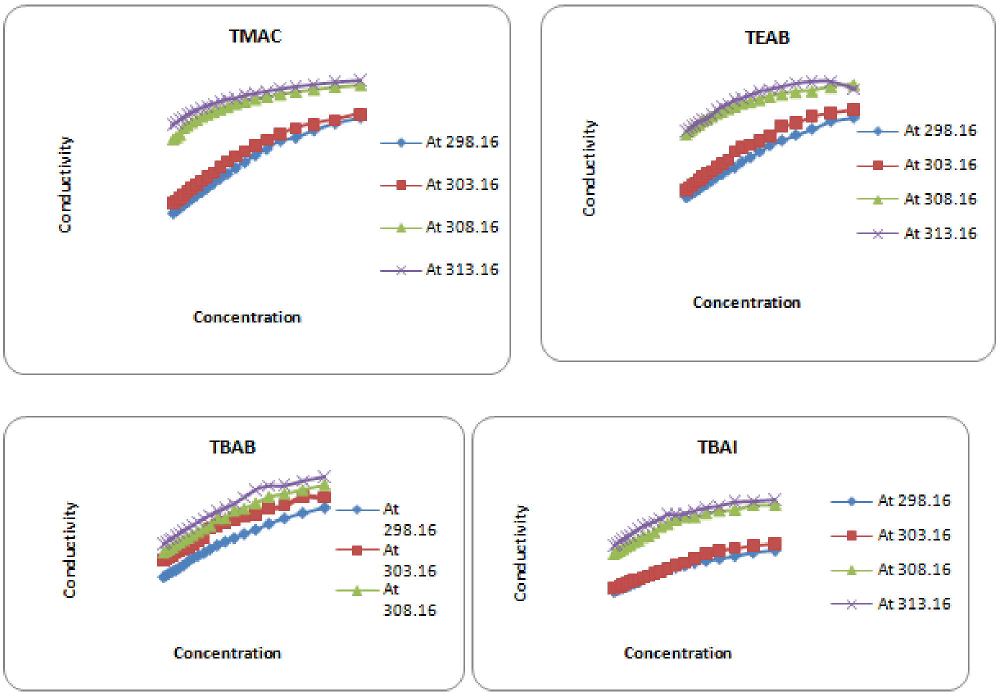

Figure.2.Plots of specific conductance versus concentration in methanolic solutions

The figures show the variation of conductivity with increasing concentration for various salts at various temperatures. The slopes of curves below the CMC values are higher than those after CMC values. This can be explained by the fact that beyond the CMC condensation counter-ions are formed on the micelles. Following equations were used for finding various thermodynamic parameters[11].

The free energy of micellizationΔG°_m is obtained using relation.

ΔG°_m = RT lnCMC- (1)

From the temperature dependence of the CMC, the enthalpy of micellizationΔH°_m is obtained through the van’t Hoff relatation.

$\Delta H^{\circ}_m = - RT^2 d\ln CMC/dT$ - (2)

Entropy of micellization$\Delta S^{\circ}_m$is obtained from the equations

$\Delta G^{\circ}_m = \Delta H^{\circ}_m - T\Delta S^{\circ}_m$ - (3)

The molar heat capacity for micelle formation ΔCp° can be obtained from this equations

$\Delta Cp^{\circ}=(\Delta H^{\circ}_m/\Delta T)$ - (4)

Table.2. Thermodynamic parameters as a function of temperature in aqueous solutions at CMC

Surfactant	T/K	$-\Delta G^{\circ}_m/10^3$ J/mol	$-\Delta H^{\circ}_m/10^3$ J/mol	$-\Delta S^{\circ}_m/10^3$ J/mol.K^{-1}	$-T\Delta S^{\circ}_m$ J/mol	$-\Delta C_p$ J/mol
TMAC	298.16	3517.11	10598.83	23.751	7081.72	35.5475
	303.16	3395.26	10957.29	24.944	7562.03	36.1436
	308.16	3136.39	12395.45	30.046	9259.06	40.2241
	313.16	2982.97	12800.95	31.351	9817.98	40.8767
TEAB	298.16	3436.49	7494.57	13.610	4058.08	25.1361
	303.16	3366.35	7748.04	14.219	4381.69	25.5576
	308.16	3136.39	9632.13	21.079	6495.74	31.2569
	313.16	3028.39	9947.24	22.094	6918.85	31.7641
TBAB	298.16	3436.49	7612.83	14.007	4176.34	25.5327
	303.16	3364.43	7870.30	14.863	4505.87	25.9609
	308.16	3252.26	12427.03	29.773	9174.77	40.3266
	313.16	3100.19	12800.95	30.977	9700.76	40.8767

Table.3. Thermodynamic parameters as a function of temperature in methanolicsolutions at CMC

Surfactant	T/K	$-\Delta G^{\circ}_m/10^3$ J/mol	$-\Delta H^{\circ}_m/10^3$ J/mol	$-\Delta S^{\circ}_m/10^3$ J/mol.K^{-1}	$-T\Delta S^{\circ}_m$ J/mol	$-\Delta C_p$ J/mol
TMAC	298.16	3329.75	9164.96	19.571	5835.21	30.7384
	303.16	3229.26	9474.92	20.602	6245.66	30.7468
	308.16	3171.49	10532.18	23.886	7360.69	34.1776
	313.16	3049.31	10876.73	24.995	7827.42	34.7322
TEAB	298.16	3308.94	10199.71	23.111	6890.77	34.2088
	303.16	3190.54	10544.67	24.258	7354.13	34.7825
	308.16	3135.52	16248.30	42.552	13112.8	52.7268
	313.16	2918.28	16779.85	44.264	13861.6	53.5824
TBAB	298.16	3227.41	8455.41	17.534	5228.00	28.3586
	303.16	3137.47	8741.38	18.485	5603.91	28.8342
	308.16	2984.14	10437.44	24.186	7453.30	33.8702
	313.16	2860.62	10778.89	25.285	7918.27	34.4198
TBAI	298.16	3236.55	6918.06	12.3474	3681.51	23.2025
	303.16	3172.72	7152.04	13.1261	3979.32	23.5916
	308.16	3119.02	8305.74	16.8313	5186.72	26.9527
	313.16	3032.56	8577.45	17.7063	5544.89	27.3900

The results show that the ΔG°_m is negative. The negative value is in accordance with many workers[12-13]. It can be generalized that the micellization is exothermic in the all temperature range studied .The negative value of ΔG°_m confirm the feasibility of the process and the spontaneous nature of adsorption. The decrease in the negative value of ΔG°_m with an increase in temperature indicates that the adsorption process becomes more favourable at higher temperature[14].

The variation of ΔH°_m with temperature for TMAC, TEAB, TBAB in water as well as in methanol and TBAI in methanol shows two behaviour:

(i) The values of $\Delta H^{\circ}_m$are negative and become more negative with the temperature range [298.16K – 313.16K], indicating that the micellization process becomes exothermic.

(ii) The formation of micelles becomes increasingly exothermic and become larger in magnitude as the temperature increased. The entropy of micellization though negative in all temperature range, increases with increase in temperature, indicating that with the formation of micelles the molecules are taking increasingly ordered position. This is due to the fact that the head group is less hydrated than the hydrophobic tail with increase in temperature which leads to an overall ordering of the system hence, the lowering of the entropy with increase in temperature[15]. Several chemical processes exhibit a linear relation between ΔH°_mandΔS°_m. This phenomenon is known as the enthalpy-entropy compensation[16-17]. The enthalpy –entropy compensation plot for TMAC,TEAB,TBAB,and TBAI is shown in figure no.5,6 Heat capacities are also very important properties which can be used in several thermodynamic calculations[18-19]. Heat capacities are becoming more negative with increasing temperature.

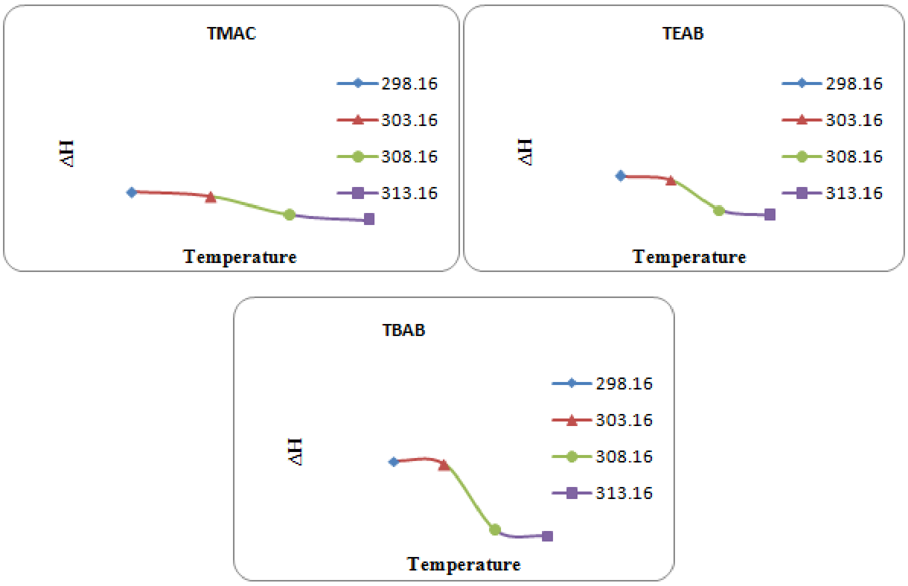

Figure 3. The plots of ΔH°_{m} with temperature for the micellization of TMAC,TEAB and TBAB in aqueous solution

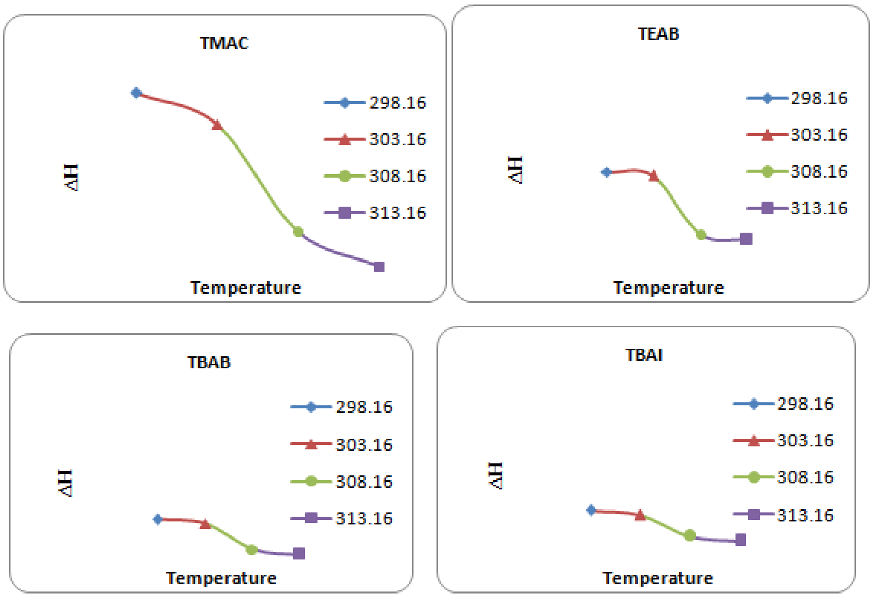

Figure 4: The plotsof $\Delta H^{\circ}_{m}$with temperature for the micellization of TMAC,TEAB,TBAB andTBAIin methanol.

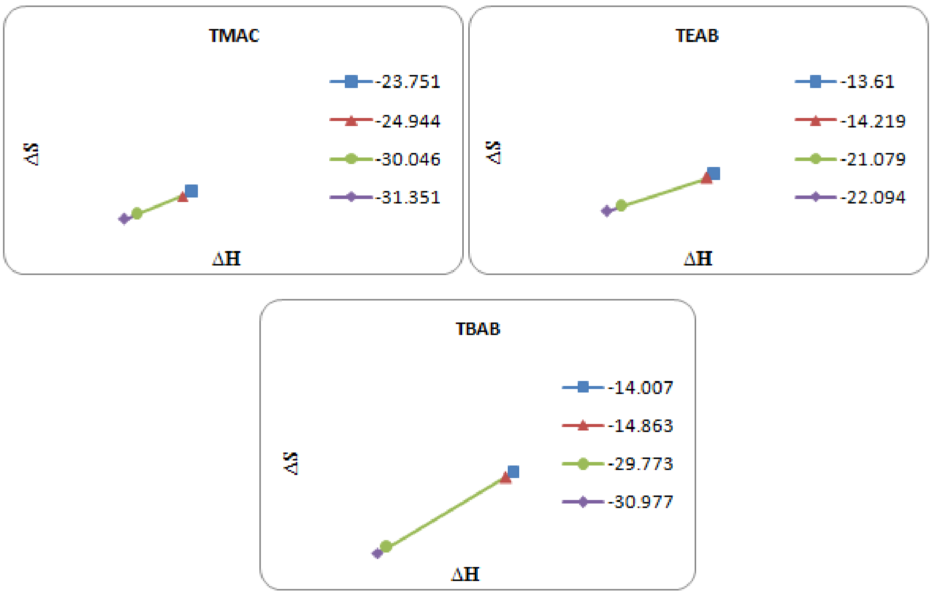

Figure .5. Typical enthalpy-entropy compensation plots for TMAC,TEAB and TBAB in water.

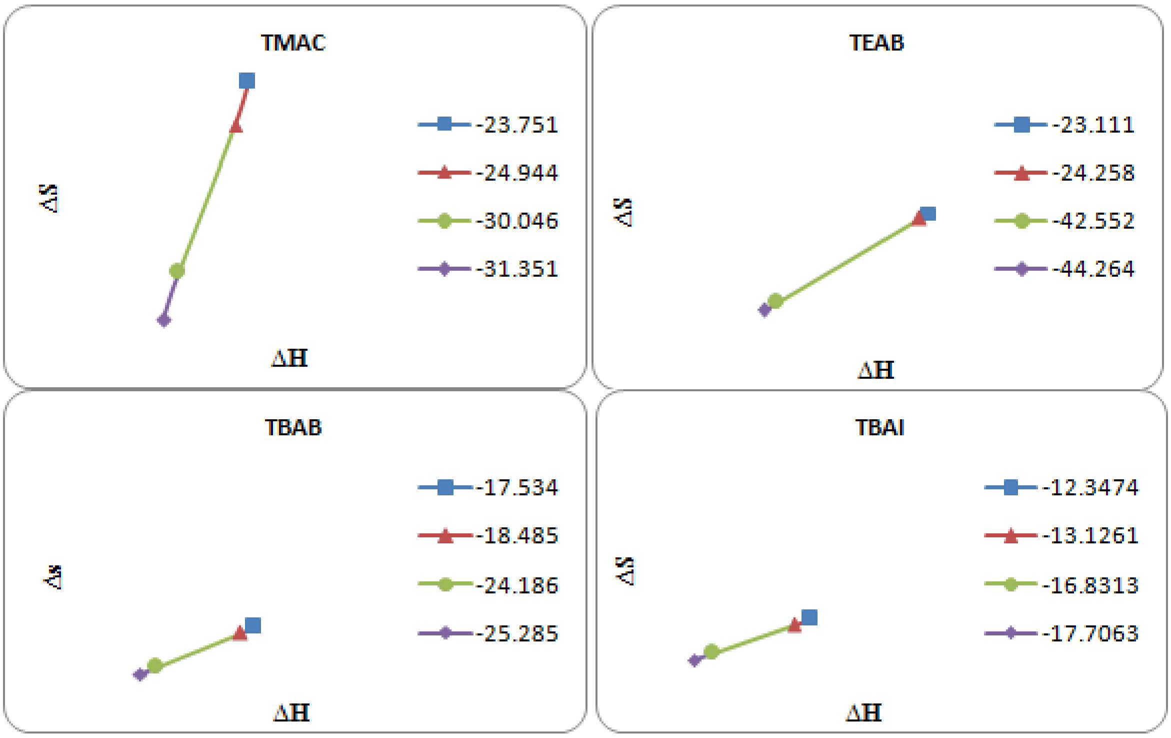

Figure.6. Typical enthalpy-entropy compensation plot for TMAC, TEAB,TBAC and TBAI with methanol.

IV. CONCLUSION

The results of these investigated cationic surfactants show that: The negative value of enthalpy indicates the exothermicmicellization process and micellization becomes more exothermic with increasing temperature. TheΔ $H^{\circ}_{m}$are found to be negative and its negative magnitude decreases with increase temperature in all the surfactants. negative value of entropy indicates the disorder of an isolated system has decreased. We have been able to show that the variation of enthalpy and entropy of micellization compensate each other.

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