Micellization Behavior and Thermodynamic Properties of N-Alkyl Trimethylammonium Bromide Surfactants in aqueous media at different temperatures

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Abstract - Knowledge of Micellar behavior of a surfactant is essential for its wide range of applications. Studies have been done on the micellar behavior of some of the cationic surfactants individually, by different methods, which is not sufficient to correlate the trend of change of properties of the surfactants in a particular series. A comprehensive study of Critical Micelle Concentration (CMC) and thermodynamic behavior of Tetradecyl Trimethylammonium Bromide (TTAB), Hexadecyl Trimethyl ammonium Bromide (CTAB) and Octadecyl Trimethylammonium Bromide (OTAB) has been herein conducted by conductivity measurements to represent the trend of micellar and thermodynamic properties of N-Alkyl Trimethylammonium Bromide Surfactants, at different temperatures. The CMC studies have been utilized to evaluate the empirical relation (Stauff- Klevens rule), i.e. log CMC= A – Bn, for this homologous series. It was found that the value of B of this relation changes from 0.283 to 0.271 with increase of temperature. Thermodynamic parameters (the free energy, entropy and enthalpy of micellization) for these surfactants were calculated over the temperature range of 293K-328K. It was found that the free energy of micellization values become more and more negative whereas the entropy values becomes more positive with increase of chain length of the surfactants. From the thermodynamic calculations it was found that the micellization processes of these surfactants are enthalpy and entropy controlled.

Index Terms - Cationic Surfactants, Counter ion binding, Critical micelle formation, Krafft temperature, Thermodynamic Parameters, Specific conductivity, Stauff- Klevens rule

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1. INTRODUCTION

Surfactants are extensively used in the field of detergents, paints, cosmetics and pharmaceutical industry for their typical structure which consists of a polar head group and a hydrophobic hydrocarbon chain. The polar head groups of ionic surfactants want to interact with water molecules and at the same times their hydrocarbon chains want to separate the water molecules, which cause an increase in energy of the system. So the surfactant molecules present in the system arrange themselves so that the hydrocarbon

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portions can be exposed at the surface [1]. Thus a surfactant molecule dissolves in water by a balance interaction of the polar head group with water and the tendency for water molecules to expel the nonpolar group. [2]. After a certain concentration of the surfactant in the system, micellization appears which is a delicate balance between the hydrophobic interactions with in the alkyl chains and the opposing repulsive interactions between the ionic head groups of an ionic surfactant [3],[4],[5],[6]. The opposing repulsive interactions between the ionic head groups are greatly influenced (minimized) by the associated counter ions of the surfactants [4], [7], [8]. Temperature influences the degree of counter ion binding which play an important role on micelle formation. Thus micellization is greatly influenced by temperature, dielectric constant of the medium and hydrogen bonding ability of the solvent [9]. In the present work, efforts have been made to study the effect of chain length on the CMC of aqueous solutions of N-Alkyl Trimethylammonium Bromide surfactant series at wider temperature variations. To represent the series, aqueous solutions of Tetradecyl Trimethylammonium Bromide (TTAB), Hexadecyl Trimethylammonium Bromide (CTAB) and Octadecyl Trimethylammonium Bromide (OTAB) have been studied by conductance measurements.

The cmc values of these surfactants are compared to study the empirical relation, log CMC = A- Bn [3], which will give important information for the trend of change of solution behavior and other properties of the cationic surfactants in the homologous series. In addition, the thermodynamic parameters, ΔG_m^o, ΔS_m^o and ΔH_m^o have also been estimated and analyzed for these surfactants in aqueous media. Although the typical (amphipathic) structure of surfactants cause significant changes on a large number of physical properties of the solutions such as conductivity, viscosity, molecular fluorescence, surface tension etc. which is the basis of applications of the surfactants in many purposes but these applications for a surfactant becomes insignificant below a certain temperature. Because below a certain temperature solubility of the ionic surfactant becomes very limited and the surfactant loses its activities such as dispersing, emulsifying and micelle forming properties. [10], [11]. This certain temperature for a specific (ionic) surfactant is known as the Krafft temperature (T_K) which is generally considered to be the melting temperature for hydrated solid surfactant [12],[13],[14]. The present study reveals that the Krafft temperature (T_K) of TTAB, CTAB and OTAB is 12.7 ^{o}C, 24.7 ^{o}C and 36.5 ^{o}C respectively which is consistent with the reference values [3]. So in the present experiment, the temperature range selected for CTAB is 298 K – 328 K and OTAB is 313 K- 328 K.

2. METHODOLOSY

2.1 Materials. The surfactant Tetradecyl trimethyl ammonium bromide (TTAB), Hexadecyl Trimethylammonium Bromide (CTAB) and Octadecyl Trimethylammonium Bromide (OTAB) with purity 99% were purchased from Sigma –Aldrich and were used as received. For all solution preparation purposes double distilled water was used.

2.2 Methods. Conductivity was measured with a Eutech–Cyber Scan–Con–510 conductivity meter equipped with a temperature compensated cell (the cell constant provided by the manufacturer is 1.0 cm^{-1}). Temperature of the solution was controlled by using a circulating water bath (Haake B 3, Germany) with a precision of ± 0.1 K. The conductivity cell was calibrated with KCl solutions of appropriate concentration range. For Krafft temperature measurements 7.5 x 10^{-3} M TTAB, In solution, the counter ions stabilize ionic surfactant micelles by binding to the micelle surface and screening the electrostatic repulsions between the ionic head

4.0 x 10^{-3} M CTAB and 2.5 x 10^{-3} M OTAB solutions were prepared in pure water. These solutions are cooled in a refrigerator for 24 h at about 3°C to get precipitate of the hydrated surfactants. The conductivity of this solution is measured with gradual increase of the temperature at a rate of about 1°C/ 10 min with constant stirring. For each temperature the conductivity of the solution was checked for about 3 min until it reached a steady value. The T_K value was obtained at the sharp break point of the conductivity vs. temperature plot.

3. RESULTS AND DISCUSSIONS

The experimental conductivities (κ) for CTAB in pure water at different temperatures are shown in fig.1. It is observed that the κ shows a linear increase with gradual increase of concentration of the surfactant which is due to the increase of surfactant monomers. The break in the plot (which represents micelle formation) is due to the binding of some counter ions of the ionic surfactant.
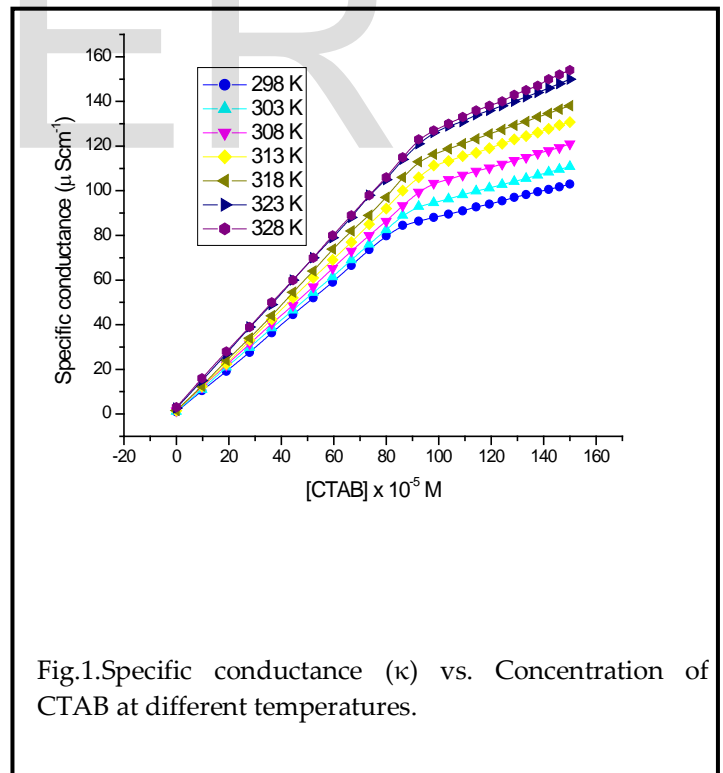

Fig.1.Specific conductance (κ) vs. Concentration of CTAB at different temperatures.

groups [15].The degree of ionization, α was determined by the ratio, S_2/S_1 of the slopes above and below the break point (i.e. post and pre micellization) [16],[17].

The fraction of counter ion binding (β) was obtained from the relation $\beta = (1 - S_2/S_1)$. Table 1 shows CMC and the fraction of Counter ion Binding (β) for TTAB, CTAB and OTAB at Different Temperature. For TTAB and CTAB it was found that the CMC, in pure water, gradually increases with increase of temperature up to a certain range and then the CMC values slightly decrease with further increase of temperature. The initial increase in CMC for increased temperature is due to the thermal solubility of the surfactant monomers and a slight decrease of the CMC with further increase of temperature is due to dehydration of the head group, resulting an increase in the hydrophobic character, which dominates over the solubility effect [18]. OTAB was found to produce two CMCs; the first has low aggregation, while the second one is higher. The second CMC values are in agreement with the reported values [3]. Both the CMC_1 and CMC_2 values for OTAB were found to increase with increase of temperature.

At each temperature The CMC values were found to decrease with gradual increase of alkyl chain length of the N-Alkyl Trimethylammonium Bromide surfactants which is due to the increased hydrophobicity.

The β values were found, from table 1, to decrease gradually with increase of temperature. This gradual decrease of β with increase of temperature indicates that the degree of dissociation of the micelle increase with increase of temperature which is caused by the decrease of aggregation number [19]. After a certain range (i.e. above 308 K), further increase of temperature causes a much greater

Table-1 CMC and the fraction of Counter Ion Binding (B) for TTAB, CTAB and OTAB at Different Temperature.

T/K	TTAB		CTAB		OTAB	
	$10^3 CMC/M$	β	$10^3 CMC/M$	β	$10^5 CMC_1/M$ ($10^4 CMC_2/M$)	β_1 (β_2)
293	3.20	0.70	--	--	--	--
298	3.43	0.69	0.84	0.70	--	--
303	3.67	0.68	0.89	0.69	--	--
308	4.02	0.67	0.93	0.68	--	--
313	4.01	0.64	0.97	0.67	2.02 (2.96)	0.58 (0.70)
318	3.99	0.62	0.96	0.66	2.22 (3.08)	0.57 (0.69)
323	3.97	0.60	0.95	0.65	2.30 (3.19)	0.56 (0.68)
328	3.95	0.58	0.94	0.60	2.41 (3.27)	0.55 (0.67)

decrease of β for TTAB compared to the other two surfactants, which indicates that the surface charge density of TTAB aggregates decreased with increasing temperature by the way of enhanced counter ion dissociation.[20]. At every certain temperature, it was found that the surfactant with larger alkyl chain length has greater counter ion binding (β) value. For OTAB, the counter ion binding (β) of second micelle was found to be greater than the first, suggesting increased surface charge density of the later.

Log CMC vs. n (number of carbon in the alkyl chain of the surfactants) plots at 313 K- 328K temperatures are shown in figure 2. Because of poor solubility of OTAB in pure water below 309.5 K and higher chance of solvent evaporation above 328 K, This temperature range is selected for the comparison study. Linear relationship between the log CMC vs. n were obtained which shows that the micellization of N- Alkyl trimethyl ammonium bromide surfactants follow the Stauff-Klevens empirical rule, log CMC= A – Bn. The values for A and B of these plots are also in good agreement with few of the reference values [3]. It was observed that both A and B values for this series decrease at increased temperature. This represents that, within this temperature range, CMC of smaller chain surfactants decrease where as CMC of larger chain surfactant increases with the increase of temperature.

Table -2 Constants for the Relation of: Log CMC = A-BN of N-Alkyl Trimthylammonum Bromides at Different temperatures.

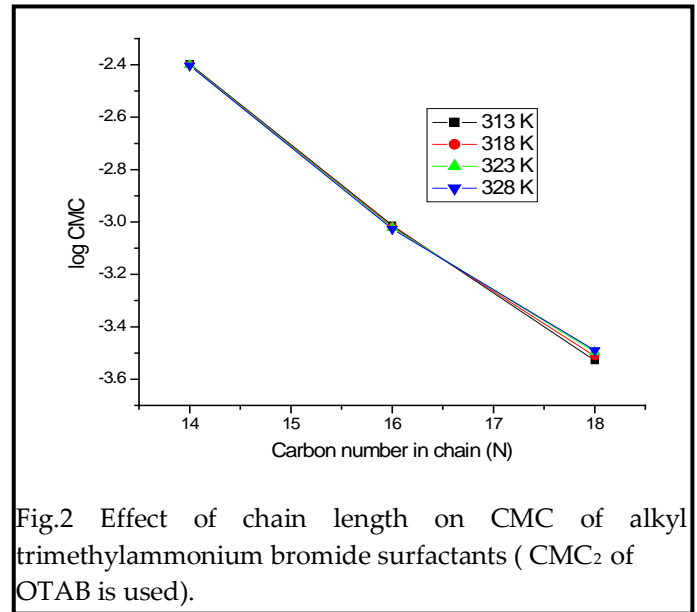| Temperature	A	B
313	1.55	0.283
318	1.48	0.278
323	1.41	0.274
328	1.36	0.271

Fig.2 Effect of chain length on CMC of alkyl trimethylammonium bromide surfactants (CMC_2 of OTAB is used).

These comparison studies, for our selected surfactants, were not possible below 313 K temperature, since the Krafft temperature of CTAB and OTAB were found to be higher than this temperature. Experimental results show that T_K of TTAB, CTAB and OTAB are 12.4 °C, 24.7 °C and 36.5 °C respectively.
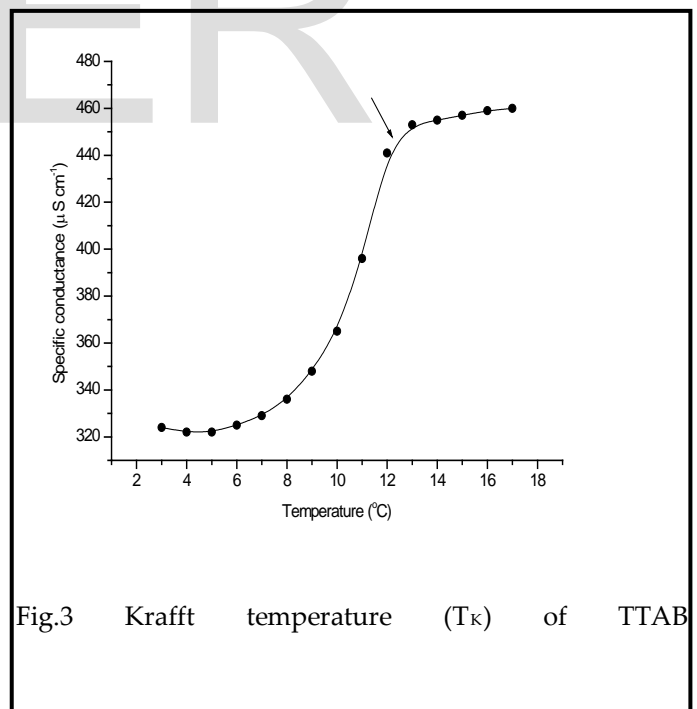

Fig.3 Krafft temperature (T_K) of TTAB

3.1 Thermodynamics of micellization of the surfactants: The free energy (ΔG_m^o) and the entropy (ΔS_m^o) changes of micellization have been calculated from the following expressions [6], [15]:

$$\Delta G_m^o = (1 + \beta) \, RT \ln X_{CMC} \dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

$$\Delta S_m^o = - \{ \delta \Delta G_m^o / \delta T \}_P \dots\dots\dots\dots\dots\dots\dots\dots(3)$$

Then the enthalpy (ΔH_m^o) of micellization have been calculated from the following expression:

$$\Delta G_m^o = \Delta H_m^o - T\Delta S_m^o \dots\dots\dots\dots\dots\dots\dots\dots\dots(4)$$

Here X_{cmc} is the mole fraction of the surfactant at the CMC. Table 3 shows thermodynamic parameters of TTAB, CTAB and OTAB, in pure water. In the present experiment the ΔG_m^o values for micellization of the surfactants in the given temperature range were found to be negative which indicates the spontaneity of the process.

The ΔG_m^o values for TTAB, CTAB and OTAB (ΔG_{m2}^o for OTAB), in pure water at different temperatures, as a function of carbon number in the alkyl chain of the surfactants are shown in fig.4a. It is observed that the negative ΔG_m^o values show a linear increase with gradual increase of alkyl chain length of the surfactants, which indicates that micellization becomes more spontaneous with increase of the alkyl chain length of the cationic surfactants. This trend is attributed to greater hydrophobic nature of the larger alkyl chain. For OTAB, ΔG_m^o values of first micelle ware found to be more negative than the second, suggesting the spontaneity of first micellization -even at the lower aggregation number. Micellization is associated with the destruction of the higher degree of hydrogen bonding around the alkyl chains which gives a positive enthalpy change [6],[23],[24]. Despite the fact the ΔH_m^o is found to be negative and becomes further negative with increase of temperature. The negative ΔH_m^o is associated by the way of (i) disruption of the hydrophobic hydration (or melting of the "iceberg") surrounding the hydrophobic tails of the monomers, and (ii) increased degree of freedom of the tails in the interior of the micelle [20] where the London dispersion force is the major attractive force and which is greater for a larger hydrocarbon chain [16], [25]. In the present study the ΔH_m^o values are found to be increasing with increase of temperature which is attributed to the disruption of greater number of hydrogen bonding between the water This arises because the "structured water layer" around

molecules at higher temperature [26],[27]. So less energy is required to break the ice berg structure around the hydrophobic alkyl chain.

On the other hand, although temperature is raised the ΔS_m^o of micelle formation is positive and its value decreases with increase of temperature.
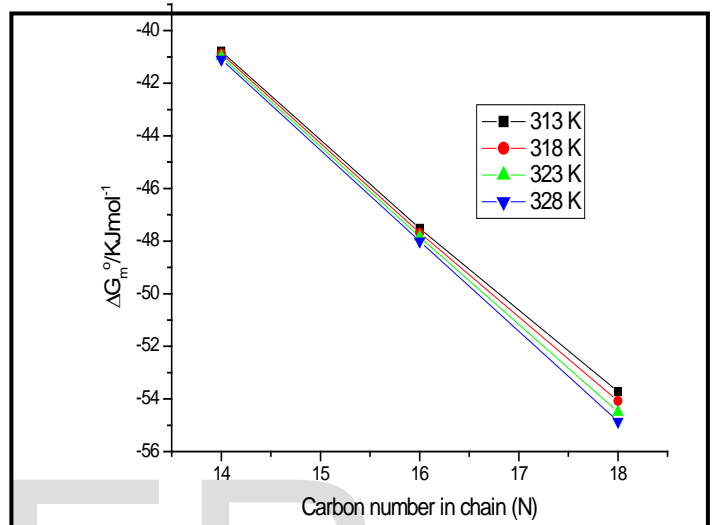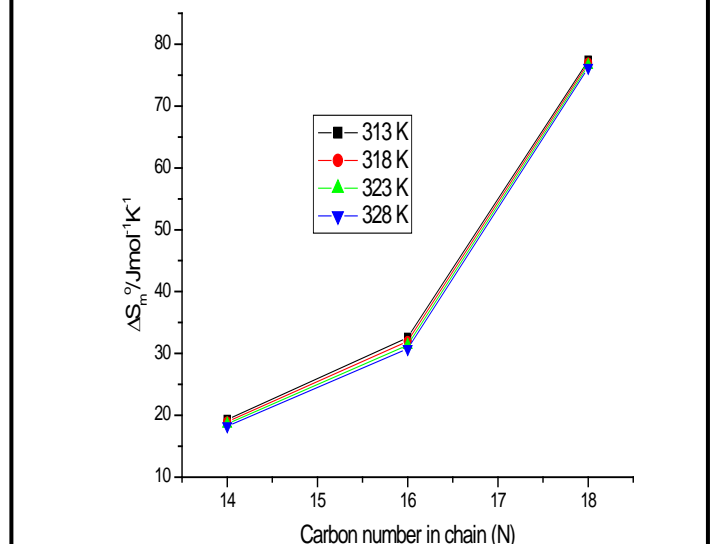

Fig. 4 Effect of chain length on **a.** ΔG_m^o and **b.** ΔS_m^o of

alkyltrimethyl ammonium bromide surfactants (ΔG_{m2}^o and ΔS_{m2}^o of OTAB is used).

the hydrophobic moiety of a monomer surfactant

becomes thinner as temperature increases or alternatively the degree of structure in the water layer decrease. Therefore the extent of randomness increased (producing a free energy gain) upon micelle formation becomes less and less with increasing temperature [28].

Greater entropy values are obtained for the surfactants with larger alkyl chain. This greater entropy of the system is obtained when the larger hydrocarbon chains are removed from aqueous medium to the interior of the micelle [3].

Table 3. Values of the free energy of micellization, ΔG_m^o, Enthalpy of micellization, ΔH_m^o and Entropy of micellization, ΔS_m^o for TTAB, CTAB and OTAB at various temperatures

T/K	TTAB			CTAB			OTAB		
	ΔG_m^o	ΔS_m^o	ΔH_m^o	ΔG_m^o	ΔS_m^o	ΔH_m^o	ΔG_{m1}^o (ΔG_{m2}^o)	ΔS_{m1}^o (ΔS_{m2}^o)	ΔH_m^o (ΔH_{m2}^o)
293	-40.37	20.72	-34.30						
298	-40.51	20.37	-34.44	-47.02	34.45	-36.75			
303	-40.62	20.02	-34.55	-47.20	33.83	-36.95			
308	-40.70	19.67	-34.65	-47.35	33.21	-37.12			
313	-40.78	19.32	-34.73	-47.52	32.59	-37.32	-60.96 (-53.72)	69.23 (77.40)	-39.29 (-29.49)
318	-40.87	18.97	-34.84	-47.69	31.97	-37.52	-61.30 (-54.08)	68.53 (77.00)	-39.51 (-29.60)
323	-40.98	18.62	-34.97	-47.84	31.35	-37.71	-61.65 (-54.50)	67.83 (76.60)	-39.74 (-29.76)
328	-41.09	18.27	-35.10	-48.00	30.73	-37.92	-61.98 (-54.86)	67.13 (76.20)	-39.96 (-29.87)

Energetic Parameters are expressed in KJ mol^{-1} for ΔG_m^o and ΔH_m^o and J K^{-1} for mol^{-1} for ΔS_m^o. Subscript 1 and 2 to the column title refer to micellization processes 1 and 2 respectively for OTAB.

The enthalpy – entropy compensation plots for bulk micellization (for CMC$_1$) of OTAB are shown in fig.5. Linear relationships are obtained for micelle formation of each surfactant, which represents that when the entropy term contributes less to the free energy, its counterpart, the enthalpy term contributes more to keep the negative free energy nearly constant. In some of the previous studies such behaviors were shown for aqueous solutions of ionic surfactants and smaller molecules [16], [29], [30], [31].
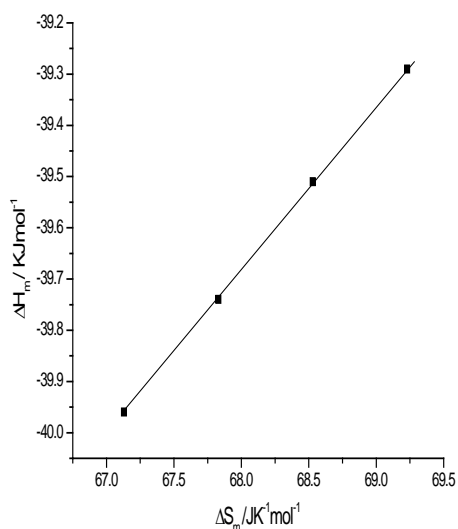
Fig. 5 Enthalpy –entropy compensation plot for 1st micellization of OTAB.

4. CONCLUSION

CMC for the surfactants in the studied homologous series were found to follow a linear relationship with the alkyl chain length. This relationship is evaluated by using the Stauff- Klevens equation i.e. log CMC= A – Bn. In the present study we observed that both the value of A and B, of this empirical equation, decrease with temperature. To carry out these comparison studies we emphasized on the Krafft temperature (T_K) of each of the surfactants because below the Krafft temperature properties and solubility of the surfactants become insignificant. ΔG_m^o and ΔH_m^o values were found to be negative whereas ΔS_m^o values were positive. ΔG_m^o and ΔS_m^o values were found to change consistently with increase of the temperature and the alkyl chain length. For each of the surfactants ΔG_m^o and ΔH_m^o values were found to increase, whereas ΔS_m^o values decrease, with increase of temperature. Greater ΔG_m^o and ΔS_m^o values were found for the surfactants with lager alkyl chain length. OTAB was found to produce two CMCs. Micellization of these surfactants are enthalpy - entropy compensated.

ACKNOWLEDGEMENTS

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