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Effects of Temperature and Tetramethylammonium Bromide Salt on the Micellization of Cetyltrimethylammonium Bromide in Aqueous Medium: A Conductometric Studies

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Abstract

The subject of this study concerns the effect of temperature and Cetyltrimethyl ammonium bromide (CTABr) in the presence of tetramethylammonium bromide $[(Me)_4N^+Br^-]$ at different temperature using conductometric method. CTABr showed a remarkable decrease in critical micelle concentration (CMC) in the presence of $[(Me)_4N^+Br^-]$. The CMC values reduced to a certain minimum in all cases, with increase in the system temperature at different concentration of $[(Me)_4N^+Br^-]$. The thermodynamic parameters ($\Delta G_m^0, \Delta H_m^0$ and ΔS_m^0) for the micelle system were estimated by applying the phase separation model while the data obtained allowed access to their usability on the micellization process. Enthalpy – entropy compensation was observed, with a constant compensation temperature of 296K.

Keywords: *Thermodynamic parameter; micellization; enthalpy-entropy compensation; hydrophobic; tetramethylammonium bromide.*

1. Introduction

Surfactant molecules dissolve in aqueous medium and easily aggregate to form micelles. Micelles formation occurred above the point known as the critical micelles concentration (CMC), and above this point, surfactant solution are used as drug carrier [1,2], drug solubilization [3], toxic waste removal [4] etc. Below the CMC point, monomer, which has no significant influence on the solubility of water -insoluble compound are formed [5-7]. Mixtures of surfactants with additives in aqueous solutions find application in pharmaceutical industries, enhanced oil recovery and other chemical application. One of the methods used to monitor the interactions between ions in solution, is the conductometry method. Investigation has shown that, the values of electric conductivity are connected with presence of ions in solution and their mobility. Analysis of the results obtained from the conductometry study gives valuable information about the association processes in surfactant solution matrix [8, 9].

Quaternary ammonium salts are positively charged polyatomic ions of symmetrical $R_4N^+B_r^-$ structure [10] which has been used numerously in phase transfer catalysis [11-13], and as antimicrobial agents in many disinfectants, perfumes and cosmetics [14,15]. Cetyltrimethyl ammonium bromide (CTABr) micellization in aqueous solution occurs as a result of delicate balance between the favourable hydrophobic interaction between the alkyl chains and opposing repulsive interaction between the ionic head group [6,16-19]. When CMC are determined at different temperature, the thermodynamic potentials of micellization are easily determined for the characterization of micelle formation.

One of the most relevant field where n- alkyl ammonium bromide is useful, is in the study of (solute + solvent), (solute + solute) and (solvent+ solvent) interaction for the hydrophobes [20-24]. Additions of electrolyte and associated counter ion largely moderate micellization of ionic surfactants [25-27], due to decrease in electrostatic repulsion between the charge head group, which induced a decrease in CMC.

Organic electrolytes with short chain tetra alkyl ammonium salt are known to penetrate the micellar interaction of the surfactant due to the hydrophobes interaction [28]. Hence they make the micelle shrink and act as spacers between the surfactant head group [29]. Much work has been reported on the effect of metal salts and temperature on the micellization of n-alkyltrimethyl ammonium [29], while paucity of reports exist on the effects of short chain organic salts like tetramethylammonium bromide on the micellization of CTABr.

In this work, we have investigated the effects of tetramethyl ammonium bromide ($[(Me)_4N^+Br^-]$), (an organic salt) and temperature on the micellization behavior of cetyltrimethyl ammonium bromide (CTABr) in aqueous medium. The micellization parameters were evaluated and discussed from the influence of ($[(Me)_4N^+Br^-]$) concentration and temperature.

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2. Experimental

2.1 Materials

Cetyltrimethyl ammonium bromide (CTABr) having purity >99% was obtained from Merk Germany and was used without further purification. Tetramethyl ammonium bromide ([$(Me)_4N^+Br^-$]) from Fluka (Switzerand) was dried in vacuum oven at T= 333.15 K for 24 hours before use.

2.2 Method

All solutions were prepared in double distilled water and measured under thermostated condition between 298.15 – 318.15K with an accuracy of + 0.01 K. The electrical conductivity values of the solutions were determined with a digital conductivity meter (Jenway 4510). The cell constant was determined by measuring the conductivity of 0.001, 0.01, and 0.1 N solution of KCl (Across organic, purity >99%). The conductometric titration involves a gradual addition of 200 µl of CTABr in different concentration of tetramethylammonium bromide into a conductance cell that already contained 10 ml of distilled water and fixed concentration of tetramethyl ammonium bromide [$(Me)_4N^+Br^-$]. The resulting solution was thoroughly mixed, and this was followed by the measurement of the electrical conductance. This procedure was continued until the desired addition of the stock solution was made.

3.0 Results and Discussion

3.1 Determination of Critical Micelle Concentration

The CMC values of CTABr micelle at different concentrations of [$(Me)_4N^+Br^-$] and temperature (298.15–318.15) K were found from conductance measurements. The values of the CMC were determined from the intersection of the straight lines graph of the plot of electrical conductivity value against concentration of CTABr at different concentration of additive. The slope in the pre-micelle region was greater than in the post micellar region and the ratio of the slopes of the post – micellar region to that of the pre-micellar region gives the effective degree of counter- ion dissociation (α). However, as the concentration [$(Me)_4N^+Br^-$] and temperature increased, a smaller curvature appeared around the CMC, which showed that the CMC value was affected to a greater uncertainty.

This problem has been solved by different authors by an approach that is based on the analysis of the plots of the differential conductivity of first ($\partial\kappa/\partial c$) [30,31] or second order ($\partial^2 k/\partial c^2$) [17], versus surfactant concentrations. In the case of ($\partial\kappa/\partial c$) versus [CTABr] at different additive concentrations (Figure 1), it was observed that the curves obtained showed an abrupt fall, which is a reverse sigmoid. The CMC value is given by the center of the sigmoid and this can be obtained from fitting the data to a Boltzmann—type decreasing sigmoid

$$\frac{\partial\kappa}{\partial c} = A_2 + \frac{A_1 - A_2}{1+e^{(c-cmc)/d}} \qquad (1)$$

where κ is the specific conductivity c is the total concentration of surfactant A_1, and A_2 are the upper and lower limits of the sigmoid, respectively, the CMC value is the center of the sigmoid and d is the called time constant, which is directly related to the independent variable range where the abrupt change of the dependent variable occurs [27]. The CMC and the degree of counter, ion dissociation values ($\alpha = A_2/A_1$) obtained directly from the fitting of conductivity versus concentration plot to Eq. 1 are summarized in Table 1.

3.2 Effect of Tetramethylammonium Bromide on the CMC of CTABr

The CMC of CTABr, as shown in Figure 2, over the temperature range of studied, decreased on the addition of tetramethyl ammonium bromide [$(Me)_4N^+Br^-$], which is known to possess large hydrophobic volume [29]. Thus, it was assumed that tetramethyl ammonium salts were accommodated into the micellar interior, under the synergistic hydrophobic interaction [29] as shown in Figure 3. Since both, the surfactant and [$(Me)_4N^+Br^-$] have similar head group, the decrease in the CMC value was attributed to the synergistic hydrophobic interaction between the non-polar hydrogen chain of surfactant and alkyl chain of the salt [28], and effective reduction in the electrostatic repulsion between the intermolecular head group which enhanced the CTABr micellization.

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Table 1. Calculated CMC value and degree of counter-ion dissociation α for CTABr in different concentration of tetramethylammonium bromide at various temperature.

T/K	298.15		303.15		308.15		313.15		318.15	
	[CMC] Mol/dm^3	α	[CMC] Mol/dm^3	α	[CMC] Mol/dm^3	α	[CMC] Mol/dm^3	α	[CMC] Mol/dm^3	α
Water	9.45×10^{-4}	0.125	1.17×10^{-3}	0.126	1.11×10-3	0.105	1.24×10-3	0.115	1.41×10^{-3}	0.086
1.0×10^{-4}M	6.97×10^{-4}	0.150	5.39×10^{-4}	0.140	5.94×10-4	0.130	6.29×10-4	0.120	8.34×10^{-4}	0.130
2.0×10^{-4}M	5.53×10^{-4}	0.300	4.54×10^{-4}	0.170	4.91×10-4	0.220	5.01×10-4	0.130	7.94×10^{-4}	0.200
3.0×10^{-4}M	5.30×10^{-4}	0.390	4.47×10^{-4}	0.260	4.64×10-4	0.340	4.92×10-4	0.230	6.06×10^{-4}	0.220
4.0×10^{-4}M	4.41×10^{-4}	0.450	3.41×10^{-4}	0.340	3.52×10-4	0.420	3.90×10-4	0.320	5.72×10^{-4}	0.240

3.3 Effects of Temperature on the CMC or χ_{CMC} of CTABr.

The results presented in Figure 4 showed a minimum in the cmc temperature profile characteristics of temperature dependence of cationic surfactant [32, 34]. The results presented indicate that the χ_{CMC} values passed through a broad minimum at T = 303.15K. This trend can be attributed to two different factors; which are hydrophobic and hydrophilic hydration [6]. For monomers, hydrophobic and hydrophilic hydration is possible, whereas in micellized surfactant systems, only hydrophobic hydration is possible. Furthermore, both type of hydration are known to decreases with increase in temperature [35]. It is a known fact that decreases in hydrophilic hydration favors the micellization while a decrease in hydrophobic hydration disfavors the micelle formation with rise in temperature [36, 37]. Consequently the dominance of these two factors will determine whether the CMC (χ_{CMC}) values increases or decreases over a particular temperature range. In the present case of micellization of CTABr in the presence of $[(Me)_4N^+Br^-]$, the continuous decreases in χ_{CMC} values at lower temperature and increases at high temperature may be referred to (i) decrease in the hydrogen-bond formation, which entail a weaker hydration of polar heads group and consequently facilitates the formation of micelles and (ii) formation of solvation sheaths around the hydrophobic heads which impedes the self- association process. The existence of a minimum at around 303.15K (Figure 4), is thus a result of balancing of these two opposing effects. These observations have been reported extensively in the literature [34].

3.4 Thermodynamics of Micellization

In order to quantify how addition of $[(Me)_4N^+Br^-]$ affected the micellization of CTABr, the standard thermodynamics parameters of micellization for CTABr in pure water and aqueous solution of $[(Me)_4N^+Br^-]$ were determined by phase separation model[38]. The standard enthalpy of micellization for ionic surfactant is given by Eq. (2) [39,40].

According to the phase separation model of micellization [6], the activity of surfactant's monomer remains constant at and above the CMC. The free energy of micellization ΔG_m^0 is calculated from

$$\Delta G_m^0 = (2-\alpha)RT\ln(\chi_{cmc}) \tag{2}$$

The corresponding standard molar enthalpy of micellization, ΔH_m^0 is given by [6]

$$\Delta H_m^0 = -T^2\frac{\partial(\Delta G_m^0/T)_P}{\partial T} = -RT^2[(2-\alpha)(\partial\ln\chi_{cmc}/\partial T)_P] \tag{3}$$

where, χ_{cmc} is the value of CMC expressed on a mole fraction basis, and $(\partial\ln\chi_{cmc}/\partial T)$ is the slope of $\ln\chi_{cmc}$ versus T plots. The values of the degree of counter-ion dissociation (α) did not change appreciably with temperature, hence the average values of (α) were used in counting the thermodynamic parameters.

ln order to compute ΔH_m^0 , the variation of $\ln\chi_{cmc}$ with temperature was fitted to equation (3) as proposed by Kim and Lim [41].

$$\ln\chi_{cmc} = A_0 + A_1\ln(T) + \frac{A_0}{T} \tag{4}$$

The change in the standard entropy of micellization ΔS_m^0, was calculate from equation [5].

$$\Delta S_m^0 = \frac{(\Delta H_m^0 - \Delta G_m^0)}{T} \tag{5}$$

Thermodynamic parameter of CTABr in pure water and aqueous solution of $[(Me)_4N^+Br^-]$ at different temperature (298.15K, 303.15K, 308.15K, 313.15K and 318.15K.) obtained from equation (2, 3, and 5), are listed in Table 2.

The values of ΔG_m^0 are negative in all temperature considered and fall within a well define range - (31.05 to 36.0) KJ.mol^{-1} for ionic and amphoteric surfactant [42]. This showed that the micellization of CTABr in pure water and in aqueous solution of $[(Me)_4N^+Br^-]$ was spontaneous over the temperature range of studied. The $\Delta_m G^0$ is the sum of the enthalpy ($\Delta_m H^0$) and entropic (-$T\Delta_m S^0$) contributions. With increases in temperature, the enthalpy contribution to free energy increases, whereas the entropic contribution decreases as depicted in figure 5. As shown, the entropy dominance switched to enthalpy dominance at 308.15K of the temperature range exercised.

The $\Delta_m H^0$ values for CTABr which were positive and decreased as temperature increased in pure water are an indication of an endothermic process. In the presence of $[(Me)_4N^+Br^-]$, the $\Delta_m H^0$ values were positive between 298.15k and 303.15K but later became negative at higher temperature. This is an indication that at lower temperature, the reaction was endothermic and at higher temperature it became exothermic. For all the systems studied (Table 2), the positive $\Delta_m H^0$ values obtained at lower temperature were ascribed to the destruction of the structure of water molecules around the hydrophobic chain.

This showed the importance of hydrophobic interactions in the micelle formation process. The same explanation goes for the higher positive $\Delta_m S^0$ values obtained at lower temperature. The decrease in $\Delta_m S^0$, at higher temperatures (Table 2) was attributed to the dismissal of hydrogen bond of three dimensional water structures, making self – aggregation to be poorer at higher temperature because of enhanced molecular motion at higher temperature [6]. As shown in Figures 6 and 7, the values of $\Delta_m H^0$ and $\Delta_m S^0$ both decreased with increase in temperature, indicating that micellization is energy driven at higher temperature, which compensated for the contribution due to enthalpy and entropy. On this note, it could be inferred that the micellization of CTABr in aqueous $[(Me)_4N^+Br^-]$ was entropy driven, at low temperature while it is enthalpy driven at higher temperature. Similar results have been reported for ionic surfactant in the literature [42].

3.5 Enthalpy – Entropy Compensation for CTABr

The Enthalpy + entropy compensation for CTABr micellization scheme proposed was based on the concept of Lumry and Rajander [43]. For the compensation phenomenon, the micellization process can be divided into two part process (i)’’solution‘’ part and (ii) a ‘’chemical ‘’ part. Overall, this compensation phenomenon between the enthalpy and entropy change can be represented by Eq. (6):

Table 2. Thermodynamic Parameters of Micellization of CTABr in Different Concentration of Tetramethylammonium Bromide at Various Temperatures.

T/K	$\Delta_m G^0 KJmol^{-1}$	$\Delta_m H^0 KJmol^{-1}$	$-T\Delta_m S^0 (KJmol^{-1})$
	PURE WATER		
298.15	-30.03	36.47	-36.51
303.15	-31.85	30.81	-30.84
308.15	-32.76	25.44	-25.47
313.15	-34.55	14.15	-14.18
318.15	-36.61	12.13	-12.17
	1.0x10⁻⁴M		
298.15	-32.51	71.25	-103.76
303.15	-33.95	27.47	-61.42
308.15	-34.29	-16.78	-17.61
313.15	-35.74	-61.50	26.57
318.15	-35.93	-105.56	69.82
	2.0x10⁻⁴M		
298.15	-28.54	73.60	-102.14
303.15	-34.03	26.85	-60.88
308.15	-36.05	-26.42	-9.63
313.15	-36.07	-79.74	43.67
318.15	-36.56	-135.53	98.97
	3.0x10⁻⁴M		
298.15	-30.43	47.57	-78.01
303.15	-33.46	17.35	-50.81
308.15	-34.01	-13.87	-20.14
313.15	-34.98	-45.51	10.53
318.15	-35.40	-77.49	42.09
	4.0x10⁻⁴M		
298.15	-30.90	36.18	-67.08
303.15	-32.62	15.81	-48.43
308.15	-33.99	-4.80	-29.19
313.15	-34.63	-25.97	-8.66
318.15	-35.30	- 46.63	11.33

$$\Delta_m H_m^0 = \Delta_m H^* + T_c \Delta S \qquad (6)$$

where T_c is known as the compensation temperature, which provide a measure of the solvation part of micellization. The intercept of the plot (Figure 8) gives the compensation enthalpy, $\Delta_m H^*$, which gives information on the solute – solute interaction, i.e. considered as an index of the chemical part of the process of micellization. The value of the compensation temperature T_c obtained was in good agreement with the interaction values, which was in the range of 270.15 and 300.15k [43]. The parameter, $\Delta_m H^*$ is the enthalpy at $\Delta_m S^0 = 0$, indicated the stability of the micelles. Therefore, the results indicated that the contribution of the chemical part towards micellization or stability of the micelle formed was enhanced in the presence of $[(Me)_4N^+Br^-]$.

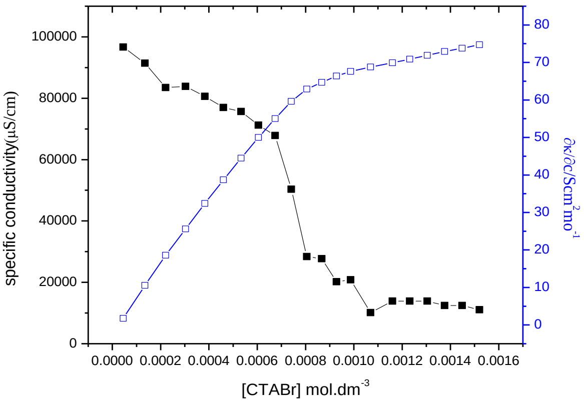

Figure 1. Plots of specific conductivity and differential conductivity against concentration of CTABr at 298.1 K (CMC = 9.45 × 10⁻⁴ mol dm⁻³).

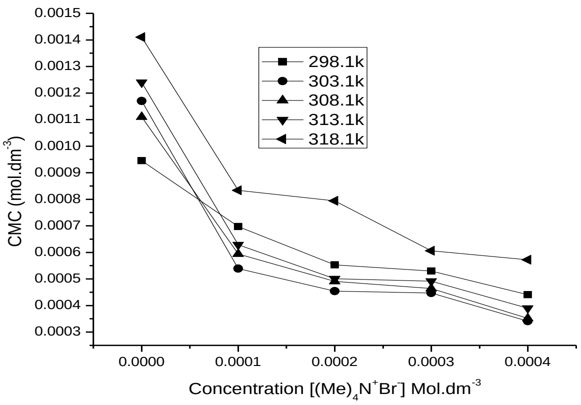

Figure 2. Plots of CMC of CTABr versus $[(Me)_4N^+Br^-]$ at different temperatures.

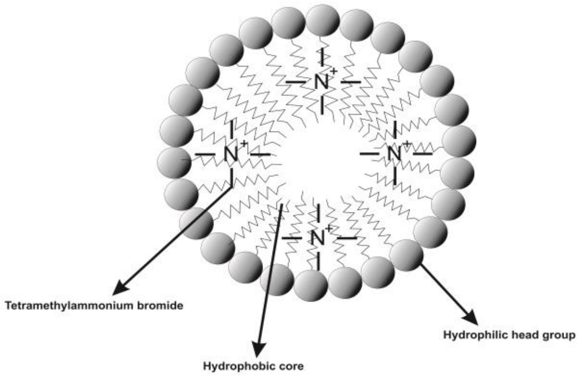

Figure 3. A tentative illustration showing the accommodation of $[(Me)_4N^+Br^-]$ salt in the CTABr micelle.

4. Conclusion

The effect of tetramethyl ammonium bromide and temperature on the micellization of CTABr has been investigated. The CMC values of CTABr decreased on the addition of different concentration of tetramethyl ammonium bromide. This was attributed to the synergistic hydrophobic interaction between the non-polar chain of

CTABr and alkyl chain of the organic electrolyte. Thermodynamic studies indicated that micellization of CTABr in the presence of $[(Me)_4N^+Br^-]$ was entropy driven at low temperature and enthalpy driven higher temperature.

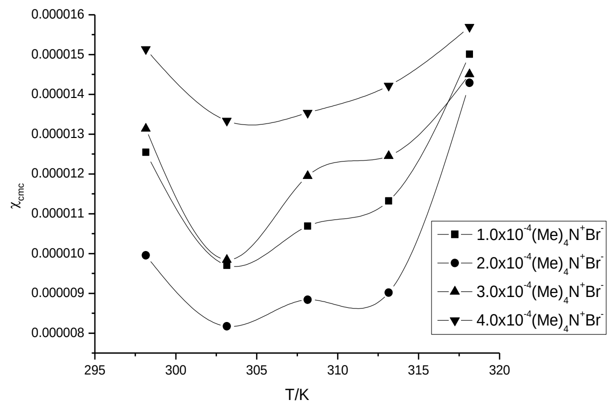

Figure 4. Comparison of χ_{cmc} *as a function temperature for CTABr in pure water at different concentration of*$[(Me)_4N^+Br^-]$.

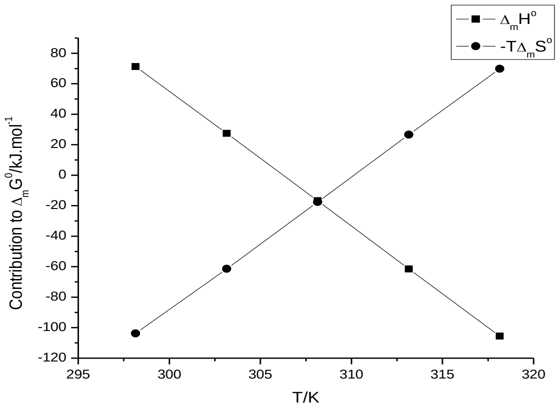

Figure 5. Representative plot for the contribution of enthalpy, Δ_mH^o *and entropy* $-T\Delta_mS^0$ *to* Δ_mG^0 *of CTABr in aqueous medium.*

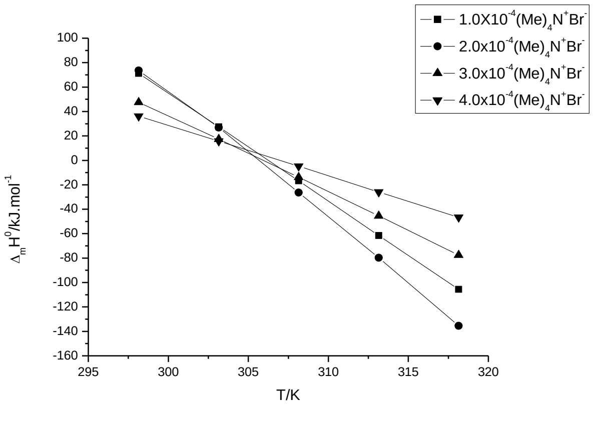

Figure 6. Temperature dependence of Δ_mH^0 *in aqueous solutions of CTABr at different concentration* $[(Me)_4N^+Br^-]$.

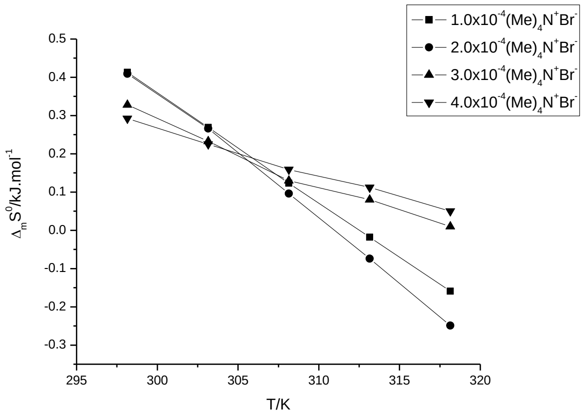

Figure 7. Temperature dependence of Δ_mS^0 *in aqueous solutions CTABr at different concentrations*$[(Me)_4N^+Br^-]$.

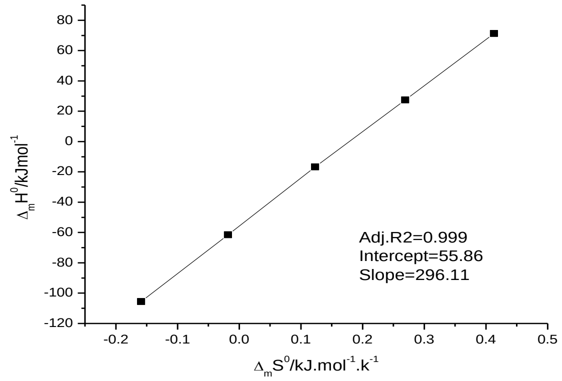

Figure 8. Representative plot for (enthalpy + entropy) compensation of CTABr in aqueous medium.

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