Thermodynamics of Micellization of n-Alkyltriphenylphosphonium Bromides: A Conductometric Study

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Accepted: February 3, 2011; Published: June 27, 2011

Abstract

The electrical conductivity of aqueous solutions of decyl- (C_{10}), dodecyl- (C_{12}), tetradecyl- (C_{14}) and hexadecyl- (C_{16}) triphenylphosphonium bromides (TPPBr) was measured at various temperatures. From the conductivity data the critical micelle concentration *cmc*, and the effective degree of counter-ion binding β, were obtained at various temperatures using a simple non-linear function obtained by direct integration of a Boltzmann-type sigmoidal function. The thermodynamic parameters ΔG_m^o, ΔH_m^o and ΔS_m^o were estimated from the temperature dependence of the equilibrium constants for the micellization of each surfactant using the phase separation model. The stability of the micellization process for these surfactants is both enthalpy and entropy controlled. The resulting ΔH_m^o and $T\Delta S_m^o$ plots showed significant correlation, an indication of enthalpy-entropy compensation in the micellization process. The intrinsic enthalpy of micellization ΔH^* varies linearly with the number of carbon atoms in the chain length of the surfactants.

Keywords: Triphenylphosphonium bromides; conductivity; micellization; enthalpy-entropy compensation.

1. Introduction

Micellar properties of cationic surfactants in bulk aqueous system have been extensively studied [1, 2]. These studies are justified from both theoretical interest and the large number of their industrial applications. The quaternary ammonium salts are known for their germicidal and antifungal properties [3, 4]; there is also the possibility of employing cationic amphiphiles as vectors in gene delivery [5, 6].

Majority of fundamental studies on cationic surfactants were on those with quaternary ammonium and pyridinium head groups [7-12]. Studies on the alkyltriphenylphosphonium bromides are rather scanty. The present work is of interest because these surfactants possess a bulky and highly hydrophobic triphenylphosphonium head group which is expected to play a significant role in their micellar properties.

The critical micelle concentration (*cmc*) appears to be the most important property in the study of the micellization of surfactants and the two models commonly employed in the theoretical thermodynamic treatment of micelles, namely the mass action and the phase separation models both required the knowledge of the *cmc* which is often obtained from the abrupt change in the physical property-concentration curve.

The synthesis and the micellar properties of dodecyltriphenylphosphonium bromide (C_{12}TPPBr) have been studied by Jiang et al [13]. The thermodynamics of the micellization of decyl- (C_{10}), dodecyl- (C_{12}), tetradecyl- (C_{14}) and hexadecyl (C_{16}) - triphenylphosphonium bromides by the method of isothermal titration calorimetry had been reported [14]. Their micellar properties in binary water-glycols mixtures [15] as well as study on their mixed surfactants systems have also been reported [16]. In most of these studies, conductometric method was employed and the *cmc* determined from the break point in the conductance-concentration plots. A frequent problem arising from the conductivity method is that it is usually difficult to determine the *cmc* for systems in which the conductance-concentration plot does not show a sharp transition from the pre-micellar to the post-micellar region, but rather exhibits a curvature. Consequently, the *cmc* and the degree of counter-ion binding (β) obtained will be affected to a greater uncertainty.

In the present work, we have investigated the thermodynamics of aggregation of these surfactants by Conductometric methods in aqueous medium, and over a temperature range between 15 to 40^{o}C.To solve the problem mentioned above, we have adopted the procedure proposed by Carpena et al [17] for the accurate determination of the *cmc* and β which are necessary for calculating the thermodynamic parameters of aggregation.

2. Methods

The surfactants C_{10}TPPBr, C_{12}TPPBr, C_{14}TPPBr and C_{16}TPPBr of the highest purity commercially available were purchased from Lancaster Synthesis of England and used as received. All solutions were prepared using glass-distilled water with conductivity not greater than 3μScm^{-1} at 25^{o}C. The conductivity measurements were made with CMD 210 from Walden Precision Apparatus, UK. The cell constant was determined by calibration with several standard solutions of KCl of known specific conductivities. Conductometric titration method involving the titration of a known volume of surfactants into a fixed volume of water contained in a thermostatted beaker. All measurements were made in a thermostatted water bath (Grant Y14) maintaining the temperature constant within ±0.1 ^{o}C. In analysing the curves, we have used the TableCurve 2D software version 5.01 by Systat Software, USA.

3. Results and Discussion

3.1. Determination of the Critical Micelle Concentration (*CMC*) of the Surfactants

For both C_{10}TPPB and C_{12}TPPB, the conductivity-concentration plots gave a sharp change from the pre-micellar to the post micellar regions at all temperatures studied, but C_{14}TPPB and C_{16}TPPB systems present a more gradual transition from the pre-micellar to the post-micellar region, in which the break in the conductivity-concentration plots was usually more difficult to determine because the conductivity-concentration plots exhibit a weak curvature. To surmount this difficulty we have used the method proposed by Carpena and others [17] based on fitting the raw experimental conductivity data to a simple non-linear function obtained by direct integration of the Boltzmann type sigmoidal function which is characteristic of the first derivative of the conductivity-concentration plot. The Boltzmann sigmoid can be analytically expressed as

$$\frac{d\kappa(c)}{dc} = \frac{A_1 - A_2}{1 + \exp^{(c-c_o)/\Delta c}} + A_2 \qquad 1$$

Where A_1 and A_2 represent the asymptotic values for small and large values of concentration *c* of the surfactant respectively, c_o represents the centre of the transition and the Δc stands for the width of the transition. A direct integration of equation 1 yields:

$$\kappa(c) = \kappa(c=0) + A_1 c + \Delta c\left(A_2 - A_1\right)\ln\left[\frac{1 + e^{(c-c_o)/\Delta c}}{1 + e^{-(c_o/\Delta c)}}\right] \qquad 2$$

The degree of counter-ion binding β is obtained from (1- A_2/A_1). A typical plot of specific conductivity versus surfactant concentration using both differential conductivity and Carpena's method is shown in Figures 1 and 2.

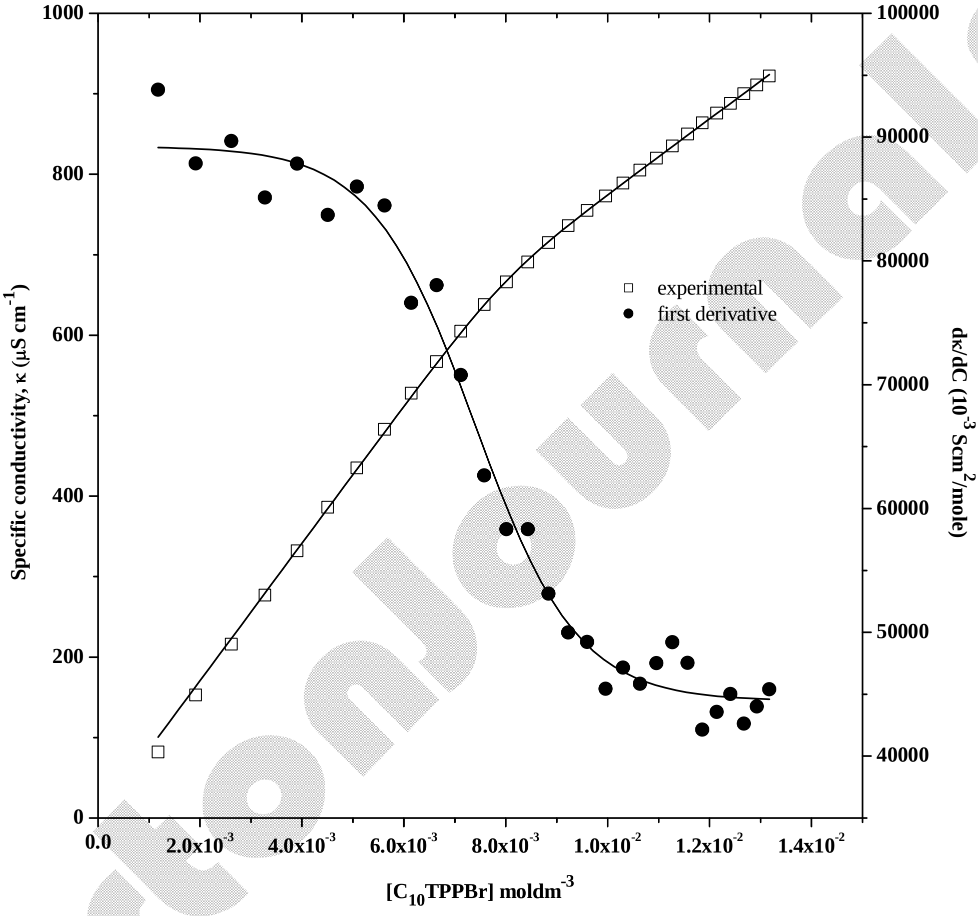

Figure 1: Plots of specific conductivity and differential conductivity against concentration of C_{10}TPPBr at 298 K (cmc = 7.54 × 10^{-3} mol dm^{-3})

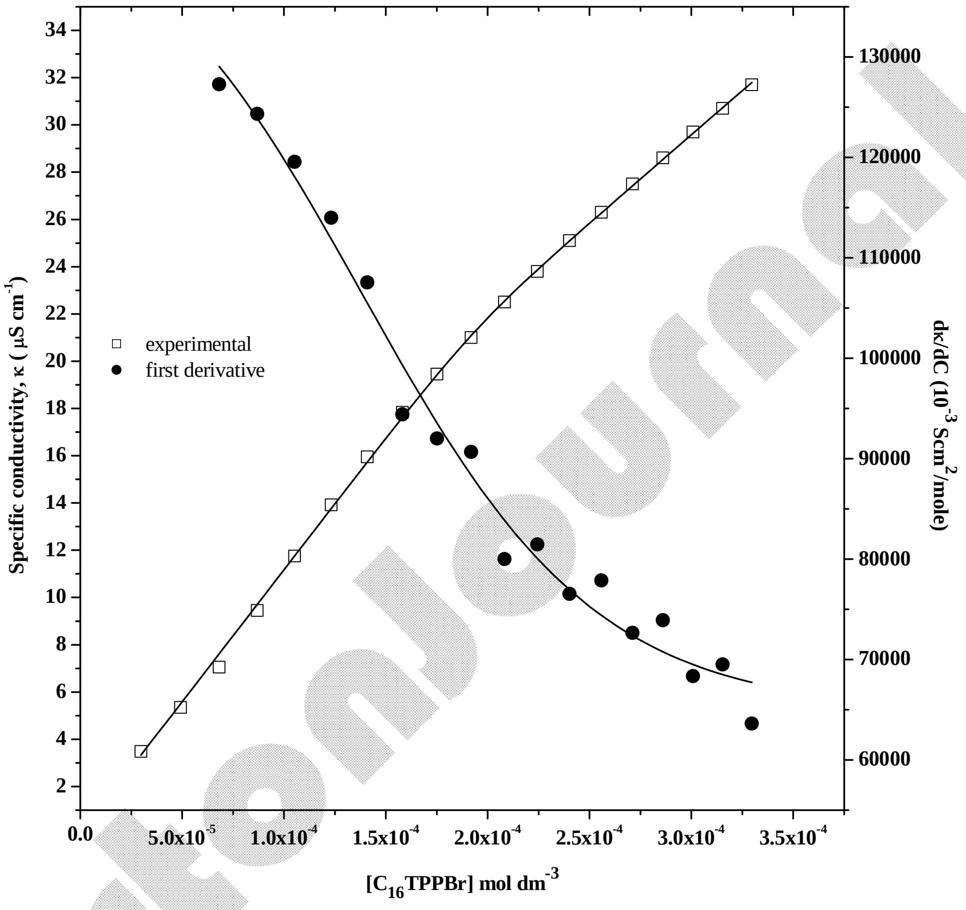

Figure 2: Plots of the specific conductivity and differential conductivity against the concentration of C_{16}TPPBr at 298 K (cmc = 1.46×10^{-4} mol dm^{-3})

Table 1: Micellization parameters of the surfactants obtained using equation 2.

Surfactant	T/K	*cmc* (mM)	β	$\beta_{average}$
C_{10}TPPBr	288	7.37±0.06*	0.52	0.47
	293	7.50±0.04	0.49	
	298	7.54±0.03	0.48	
	303	7.64±0.04	0.46	
	308	8.10±0.06	0.45	
	313	8.38±0.04	0.42	
C_{12}TPPBr	288	1.74±0.01	0.52	0.45
	293	1.79±0.02	0.45	
	298	1.81±0.02	0.44	
	303	1.84±0.02	0.45	
	308	1.96±0.02	0.42	
	313	2.11±0.04	0.40	
C_{14}TPPBr	288	0.49±0.01	0.36	0.37
	293	0.49±0.01	0.34	
	298	0.55±0.01	0.39	
	303	0.62±0.01	0.37	
	308	0.63±0.02	0.31	
	313	0.77±0.03	0.45	
C_{16}TPPBr	288	0.14±0.01	0.37	0.34
	293	0.14±0.02	0.34	
	298	0.16±0.01	0.38	
	303	0.16±0.01	0.31	
	308	0.19±0.01	0.30	
	313	0.20±0.02	0.36	

*Standard error in *cmc* as determined using equation 2.

The values of the *cmc* obtained by other investigators of the micellar behaviour of these surfactants using conductometric method and adopting the conventional method of cmc determination differed significantly from each other. For example, Palepu et al reported values of 2.15mM, 0.57mM and 0.15mM for C_{12}TPPBr, C_{14}TPPBr and C_{16}TPPBr from conductivity study at 298 K in [16] and in another article reported values of 1.80mM, 0.77mM and 0.14mM for the same surfactants at the same temperature respectively in reference [15]. Similarly, Bakshi in [18] reported a value of 9.89mM for C_{14}TPPBr and 8.18mM for the same surfactant in reference [19] at 298 K using the conventional method of *cmc* determination from conductivity method. These are few of instances of problems associated with the conventional treatment of conductivity-surfactant concentration data. However, the *cmc* values obtained in this work compared favourably with those in reference [15]. Also, some of those reports showed the occurrence of two regions of micellization corresponding to two *cmc* values [14], it should be noted that the second *cmc* values were as a result of the weak curvature in the conductivity-concentration plot at very high surfactant concentration and it may not be due to any structural changes of the micelle, but rather as a consequence of inter-ionic and micelle-micelle interactions [20]. The adopted method in this work did not show any occurrence of a second *cmc* within the concentration range employed.

3.2. Thermodynamics Parameters of Micellization

On the basis of the phase separation model of Koshinuma and Sasaki [21] for ionic surfactants, to calculate ΔG_m^o it is necessary to consider not only the transfer of surfactant molecules from the bulk to the micellar phase but also the transfer of (1-α) moles of counter-ions, where $\alpha$is the degree of counter-ion dissociation which is equal to 1-β. Hence,

$$\Delta G_m^o = RT\ln a_s + (1-\alpha)RT\ln a_{Br^-} \qquad 3$$

where a_{Br^-} is the activity of the bromide counter-ion. Equation 3 can be written as

$$\Delta G_m^o = (2-\alpha)RT\ln a_{\pm CMC} \qquad 4$$

with $a_{\pm CMC}$ as the mean activity of the counter-ions at the *cmc*. It should be noted that, in most of the thermodynamics of ionic surfactants, the $a_{\pm CMC}$ is replaced by χ_{CMC} that is,

$$\Delta G_m^o = (2-\alpha)RT\ln \chi_{CMC} \qquad 5$$

where χ_{CMC} is the *cmc* of the surfactants expressed in mole fraction. From the temperature dependence of the *cmc*, the enthalpy of micelle formation can be obtained from the Gibbs-Helmoltz equation;

$$\Delta H_m^o = -T^2 \frac{\partial\left(\Delta G_m^o / T\right)}{\partial T} \qquad 6$$

The entropy change associated with the micellization process is then obtained from equation 6:

$$\Delta S_m^o = \frac{\Delta H_m^o - \Delta G_m^o}{T} \qquad 7$$

The change in the molar heat capacity for micelle formation $\Delta_{mic}C_p^o$ can then be obtained from the slope of the plot of ΔH_m^o versus temperature

$$\Delta_{mic}C_p^o = \left(\frac{\partial H_m^o}{\partial T}\right)_p \qquad 8$$

The variation of ΔH^o_m with temperature in all the systems investigated is shown in Figure 3. In all cases the formation of micelles becomes increasingly exothermic with increase in temperature. For both C_{10}TPPBr and C_{12}TPPBr, the formation of micelles is an endothermic process at low temperature, this change in the sign of ΔH^o_m had been observed for number of ionic surfactants [22]. At all temperatures, the ΔH^o_m become increasingly negative with increase in the number of carbon atoms in the alkyl chain of the surfactants (except for C_{16}TPPBr whose enthalpy values are slightly less than that of C_{14}TPBr) indicating that the micellization process becomes more exothermic as the chain length increases. In all cases, the ΔH^o_m is a linear function of temperature and the heat capacities at constant pressure ΔC^o_m were determined from the slopes in Figure 3. All ΔC^o_m values are negative.

This is the usual trend for self-aggregating amphiphiles and it is ascribed to the removal of large areas of non-polar surface from contact with water on micelle formation [23]. The magnitude increases with increase in the alkyl chain length of the surfactant molecules.

The large changes in entropy and enthalpy with increasing temperature result in moderate decrease in the Gibbs energy. The profiles of ΔG^o_m at 298K (Figure 4) for all the surfactants followed a fairly linear correlation with carbon chain length (r = 0.977) with an average slope of -2.17kJmol^{-1}.

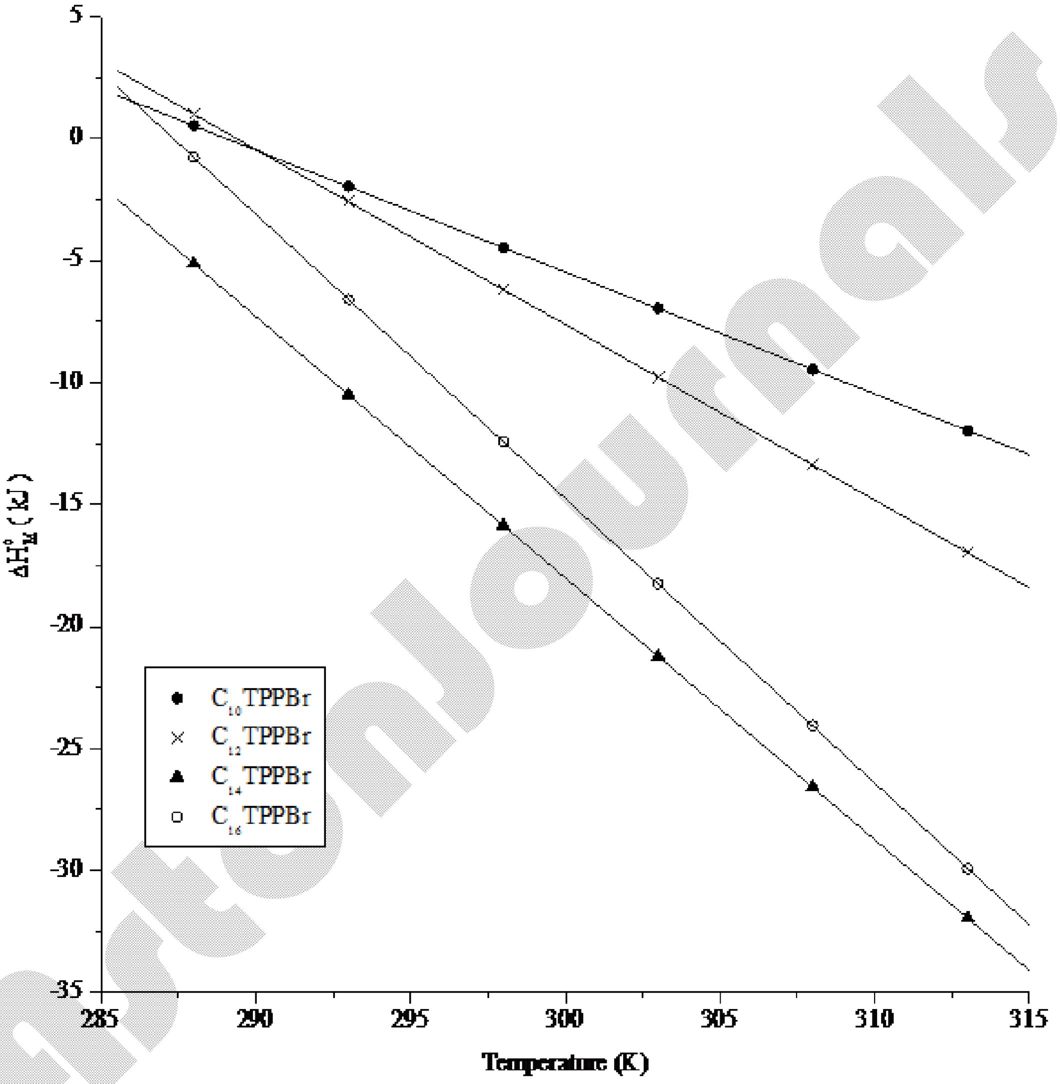

Figure 3. The plot of ΔH_m^o with Temperature for the micellization of C_nTPPBr

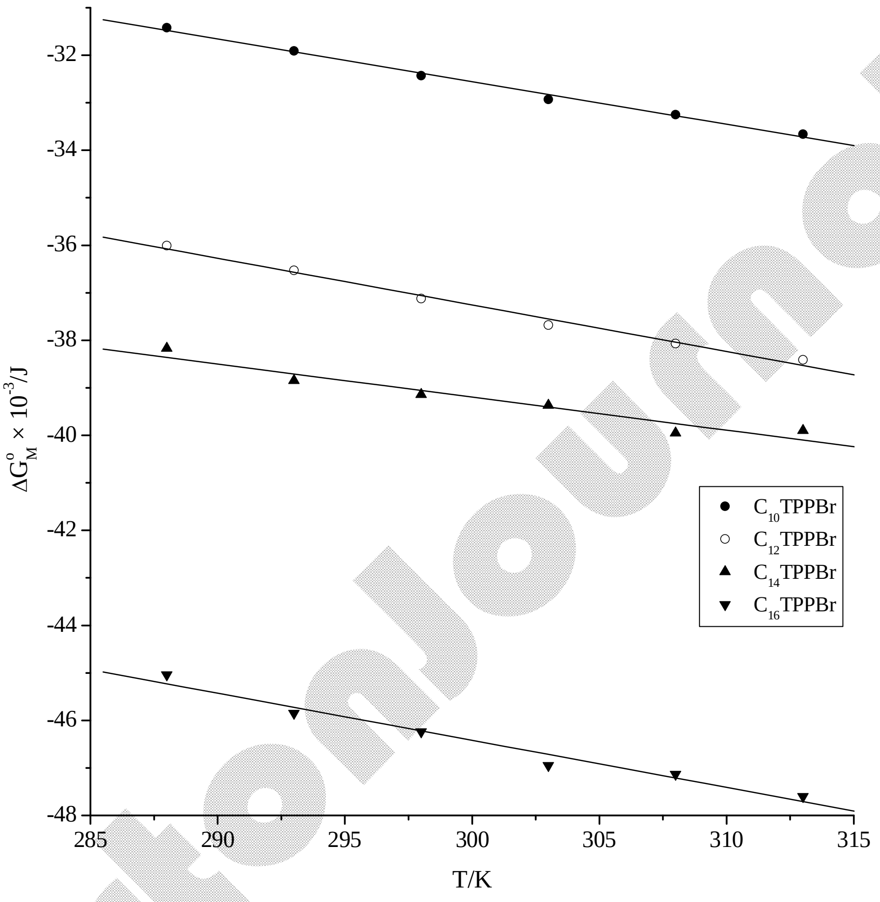

Figure 4. Plot of ΔG^o_m against temperature at different alkyl chain of the surfactants.

Table 2: Thermodynamic parameters for the micellization of C_nTPPB obtained using the equations above.

Surfactant	**T/K**	$-\Delta G_m^o / 10^3 J$	$-\Delta H_m^o / 10^3 J$	ΔS_m^o $\text{Jmol}^{-1}K^{-1}$	$-\Delta_{mic} C_m^o$
$C_{10}TPPBr$	288	31.42	-0.53	110.94	499.65
	293	31.91	1.97	102.17	
	298	32.43	4.47	93.83	
	303	32.93	6.97	85.68	
	308	33.25	9.47	77.21	
	313	33.66	11.96	69.33	
$C_{12}TPPBr$	288	36.01	-1.01	128.54	719.33
	293	36.53	2.59	115.86	
	298	37.12	6.19	103.79	
	303	37.68	9.78	92.07	
	308	38.07	13.38	80.15	
	313	38.41	16.97	68.48	
$C_{14}TPPBr$	288	38.17	5.13	114.73	1072.89
	293	38.85	10.49	96.78	
	298	39.14	15.86	78.13	
	303	39.37	21.23	59.88	
	308	39.95	26.59	43.37	
	313	39.90	31.95	25.41	
$C_{16}TPPBr$	288	45.04	3.28	145.00	1085.01
	293	45.85	8.70	126.78	
	298	46.24	14.13	107.74	
	303	46.95	19.56	90.39	
	308	47.13	24.98	71.94	
	313	47.60	30.41	54.94	

Based on the results presented in Table 2 it can be generalized that the micellization is exothermic and free energy ΔG^o_m is negative in the whole temperature range studied. The entropy of micellization though positive in all the temperature range, decreases with increase in temperature. This is due to the fact that that the head group is more 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. The value of ΔG^o_m is the sum of the enthalpic and entropic contributions. As the temperature increases the enthalpic contribution to the free energy increased, whereas the entropic contribution decreased.

Several chemical processes exhibit a linear relation between ΔH^o and ΔS^o. This phenomenon is known as the enthalpy-entropy compensation [24, 25]. The enthalpy-entropy compensation plot for $C_{10}TPPBr$ is shown in Figure 5. The compensation effect can be described by equation 9:

$$\Delta H^o = T_c \Delta S^o + \Delta H^* \qquad 9$$

where T_c, the compensation temperature is the slope of the compensation plot and ΔH^* is the intercept. The values of T_c are 300.3K for $C_{10}TPPBr$ and $C_{12}TPPBr$ and 300.2 K for $C_{14}TPPBr$ and $C_{16}TPPBr$. These results fit well into the general framework of T_c ranging from 299K to 315K proposed by Sugihara and Hisatomi [24]. The values of ΔH^* are -32.70kJ, -37.46kJ, -39.48kJ and -46.71kJ respectively and these emphasize that the micellization process is favoured even in the absence of any gain in entropy. It is noteworthy that the values of ΔH^* vary fairly linear with the number of carbon atoms in the alkyl chain length of the surfactants as can be seen in Figure 6. T_c had been interpreted as a characteristic of solute-solute and solute-solvent interactions, and it is a measure of the de-solvation part of the process of micellization, while the ΔH^* characterizing the solute-solute interaction is an index of the chemical part of the process of micellization [25]. The fact that the T_c is constant with chain length of these surfactants implies that the de-solvation part of micellization is independent of the alkyl chain length. The increase in ΔH^* corresponds to a decrease in the stability of the structure of the micelles.

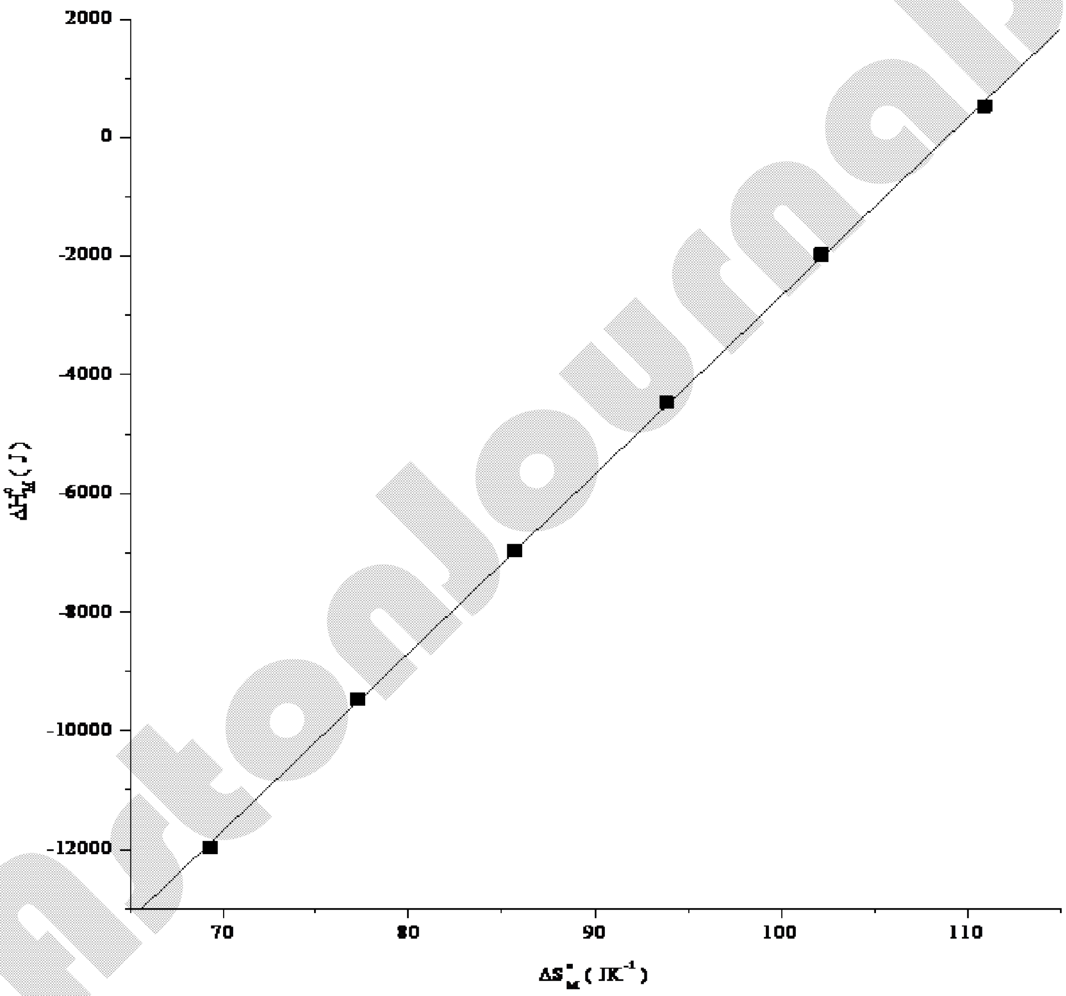

Figure 5. Typical enthalpy-entropy compensation plot for C_nTPPBr

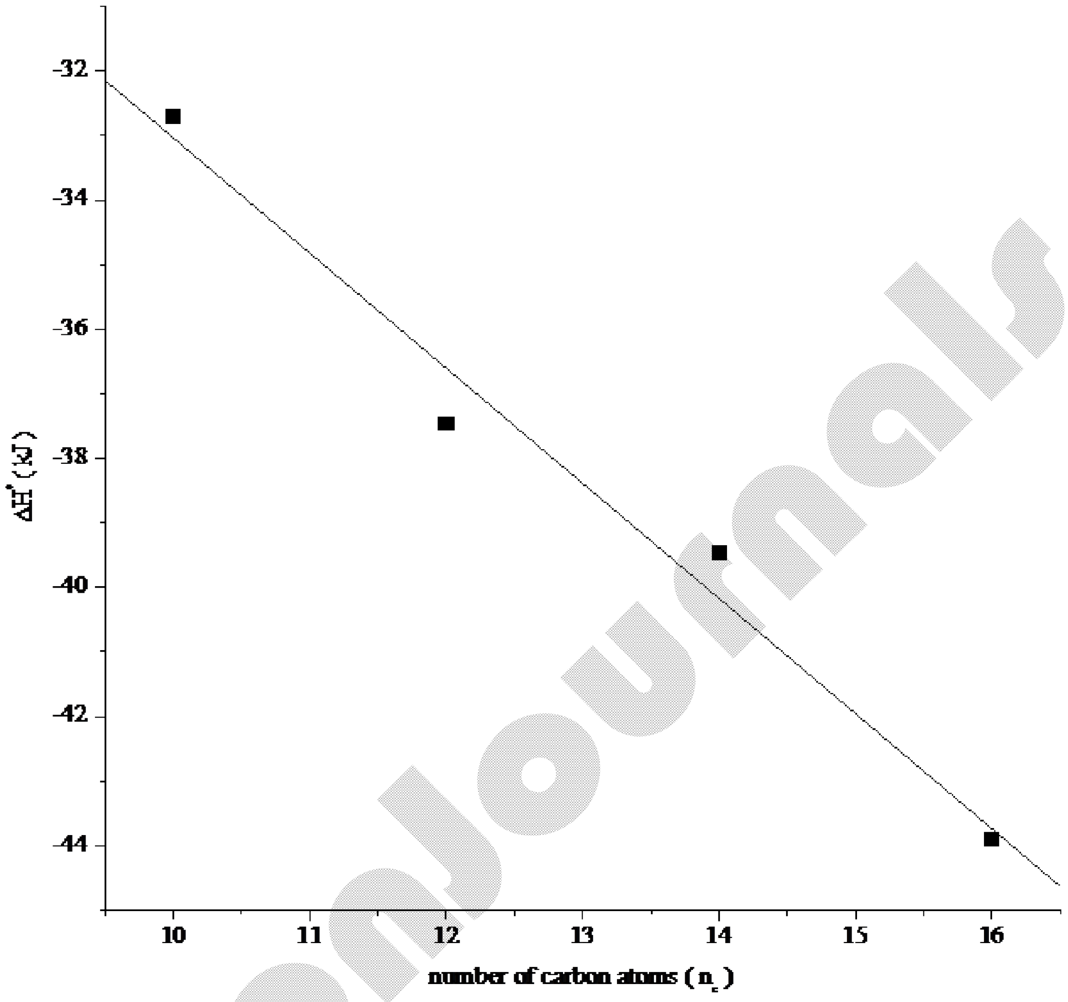

Figure 6: Variation of ΔH^* ,the intercept of the compensation plot with the number of carbon atoms in the alkyl chain length of the surfactants

4. Conclusion

The micellization behaviour of the cationic surfactants, the alkyltriphenylphosphonium bromides (C_{10}-C_{16}) as a function of temperature has been studied by electrical conductivity method. This has made the calculation of the thermodynamic functions of micellization possible. The *cmc* at a given temperature decreases with increase in the chain length of the surfactants. At a lower temperature the micellization of C_{10} and C_{12} is endothermic. With the pseudo-phase separation model, we have been able to show that the variation of enthalpy and entropy of micellization compensate each other. The large changes in entropy ΔS_m^o and enthalpy ΔH_m^o with increasing temperature result in moderate decrease in the Gibbs energy. The enthalpy change at all temperatures varied linearly with temperature and the number of carbon atoms in the alkyl chain length of the surfactants at any given temperature.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

JI developed the project and supervised the preparation of the manuscript; SOO assisted with the preparation of the manuscript; OO carried out the project and the data analysis.

Acknowledgement

The authors gratefully acknowledge the management of the Central Science Laboratory of the Obafemi Awolowo University for provision of technical support for this work.

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