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Tunning of physico-chemical characteristics of charged micelles by controlling head group interactions via hydrophobically and sterically modified counter ions.

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Abstract

Different tetraalkylammonium viz., $N^+(CH_3)_4$, $N^+(C_2H_5)_4$, $N^+(C_3H_7)_4$, $N^+(C_4H_9)_4$ along with simple ammonium salts of dodecylbenzene sulphonic acid were prepared by ion-exchange technique. The cmcs' of dodecylbenzene sulfonate salts with varied counterions were determined by electrical conductivity and surface tension measurements within the temperature range 283 – 313 K. Counterion ionization constant, α, the surface parameters Γ_{max} and A_{min} and also the thermodynamic parameters of micellization process viz., ΔG^0_m, ΔH^0_m and ΔS^0_m in aqueous solution have been determined by using pseudo-phase model. The order of cmc in aqueous solution is found to be $NH_4^+ > N^+(CH_3)_4 > N^+(C_2H_5)_4 > N^+(C_3H_7)_4 > N^+(C_4H_9)_4$ at any given temperature. On the other hand, aggregation number increases with alkyl chain length first due to increasing hydrophobic interactions and then decreases as a function of counterion size passing through a maximum for $N^+(C_2H_5)_4$. Spontaneity of micellization in aqueous solution is supported by large negative ΔG^0_m as well as the positive entropy change for the micellization process for all the above counterions. At a given temperature, ΔG^0_m for surfactant with different counterions followed the order $N^+(CH_3)_4 > NH_4^+ > N^+(C_2H_5)_4 > N^+(C_3H_7)_4 > N^+(C_4H_9)_4$. Electrostatic interaction along with effective charge screening and hydrophobicity of the surfactant head group together may give an explanation for the observed variation of aggregation behaviour and the energetics as a function of the nature of counterion.

Introduction

Surfactants form aggregates, particularly in aqueous solutions, via hydrophobic and hydrophilic interactions occurring within the same molecule. These exotic molecules have generated a great deal of interests because of their various industrial applications [1–9]. While the formation of micelles is the consequence of interplay between hydrophobic and hydrophilic parts of the surfactant molecules with water, it is mainly triggered to avoid loss of entropy due to the formation of ordered water cages around hydrophobic part disrupting the hydrogen bonds between water molecules. There are many factors which influence critical micelle concentration (cmc), size, shape and the aggregation number of ionic micelles. These factors include temperature, geometrical structure of the surfactant molecule, the length of the hydrocarbon tail, the nature and dimension of the surfactant head group, the polarity and other characteristics of the solvent including solvent structure, ionic strength of the medium and finally the nature of the counter ions. Among these factors, the surfactant head group characteristics, including the counter ion interactions, is perhaps the least studied facet, yet one of the pivotal issues which control the shape and size of the micellar aggregate. Strong binding counter ions favorably influence aggregate formation and decrease the cmc via effective charge screening of the head groups. However, the counter ion which contains fairly strong hydrophobic groups (hydrotropes) are particularly much effective in charge screening and increase the aggregation number to a great extent and promotes micellar shape transition via altering micellar surface curvature. These hydrotropes (e.g., sodium salicylate) efficiently interact with the micelle core via hydrophobic group and facilitate the formation of rod or worm-like micelles at low surfactant concentration. The aqueous solutions of this worm like micelles behave like that of linear polymers and form shear responsive viscoelastic gel which attracts many researchers in recent years[2,3]. However, symmetrical tetraalkyl ammonium counter ions with varying alkyl chain length demand special attention because one can study two opposing effects in this series of ions viz., the effect of progressively enhanced hydrophobicity and the effect of increasing dimension of the ions. Counter ion specific interactions (hydrophobic or hydrophilic) along with change in hydration energy are also very important and this has been discussed in a number of recent reports[10-15]. Different types of organized assemblies are formed in surfactant systems on varying composition, concentration and environmental conditions viz., pressure, temperature, additives and pH as well[1,3]. The fraction, α, of the counterions of an ionic surfactant which are generally dissociated from the micelles, move to the bulk of the solution leaving the micelles electrically charged[16-18]. On the other hand, at a certain temperature, the aggregation number of ionic micelles depends only on the counterion concentrations in aqueous phase, C_{aq} which can be defined as[15]:

$$C_{aq} = F\,(S_t)\,[\alpha\, S_t + (1 - \alpha)\, S_m] \qquad (1)$$

where S_t and S_m are the total and monomeric concentration of the surfactant molecules respectively present in the solution and the factor $F\,(S_t) = 1 / (1 - \theta)$, where θ relates to the volume fraction occupied by the micelles. The size of the ionic micelle in aqueous solution changes with the change of counterions and also with the electrolyte content of the surfactant solution[19]. The knowledge of the values of different thermodynamic parameters at different temperatures is also of utmost importance to understand the aggregation behavior where the structure and interactivity of counterions also play considerable role[20].

Sodiumdodecylbenzene sulfonate (SDBS) is a well known anionic surfactant widely used in the industry for manufacturing detergents, emulsions, degreaser and deinking agents and also for assisting dying processes in textile factories. Although the effect of the nature of counter ions of anionic surfactants is less significant than that of cationic surfactants, hydrophobic counter ions can bring about relatively stronger modification in the aggregation behaviour. Therefore a considerable number of literatures have been found[2,14,15,18,21] concerning micellar growth as affected by hydrotropic counter ions of both cationic and anionic surfactants. In this connection it may be anticipated that symmetrical organic counter ions might interact with the surfactant head groups more effectively via strong hydrophobic interaction with the terminal hydrocarbons of surfactant molecule. However, such ions with larger sizes could only approach towards the head group to a limited extent and fail to charge screen the head groups effectively and the micellization process becomes unfavourable. These two mutually opposite effects are operative in symmetrical tetraalkylammonium counter ions and the micellization process is regulated by one which prevails over the other. Therefore, for undertaking an in-depth study of the effect of size of the counter ion vis-à-vis its hydrophobicity on the aggregation behaviour of sodiumdodecylbenzene sulfonate, the set of symmetrical tetraalkyl ammonium counter ions with progressively larger groups may be an excellent model which one strives to investigate. This prompted us to synthesize dodecylbenzene sulfonates with tetramethyl, tetraethyl, tetrapropyl and tetrabutyl ammonium counter ions to study their aggregation properties along with the ammonium counter ion.

Experimental

Materials

All the surfactants with inorganic and organic counterions were prepared by the ion exchange technique starting from sodiumdodecylbenzene sulfonate following the procedure as mentioned below[17-18,21]. A solution of sodiumdodecylbenzene sulfonate in 1:1 (v/v) mixture of water and ethanol was prepared. The surfactant solution was then passed through an ion-exchange column (dimension of 40 cm by 2sq.cm) containing strong ion exchange resin in its H^+ form (Amberlite IR-120, 20-50 mesh, Loba Cheme, India). As a result, the aqueous solution of dodecylbenzene sulphonic acid is formed which then titrated immediately for neutralization with the hydroxides containing desired counterions. The above hydroxides were of AR grade procured either from Merck, India or Fluka, Switzerland. To enhance the extent of ion-exchange, flow rate was necessarily controlled in the column. To determine the extent of ion-exchange a portion of the sulphonic acid was titrated with standard NaOH solution which was quite satisfactorily found to be more than > 99% in all cases. In order to prepare solid salts, water was removed from the solution by freeze drying and then keeping the solute under vacuum in a constant temperature of 313 K for 7 days and then the solid was finally dried in vacuum over P_2O_5. All the dodecylbenzene sulfonic acid salts (except tetrabutylammonium dodecyl benzene sulfonate (TBADBS)) were then purified by recrystallization twice from ethanol-water (1:1) mixture and finally dried in vacuum over P_2O_5. However, TBADBS salt appeared as waxy material and could not be crystallized from ethanol-water mixture. In order to remove residual water from the sample, P_2O_5 was kept over the surfactant solution in isooctane (≥99.5% from Merck, India) at 313K for 7 days. The solvent was then removed and the TBADBS sample was used without further purification. Double distilled water having conductivity 2 μS.cm^{-1} were used throughout the experiment. For the determination of aggregation number, cetylpyridinium chloride (Fluka, Belgium) was used after recrystallization and puriss grade pyrene (Fluka, Switzerland) used as received.

As mentioned in our earlier publication that commercialsodium dodecyl benzene sulfonate contains five different isomers[21] but the manufacturer did not mention any isomeric identification of the sample. The separation of isomeric forms and also their identifications are very difficult. In the present sample, however, the cmc values and the other parameters indicate the presence of $6\phi C_{12}$ system as the major component. In order to obtain one isomeric composition with adequate purity (viz., $6\phi C_{12}$), repeated recrystallization was done of the ion-exchanged product. Therefore, it may be argued that the present surfactants are essentially $6\phi C_{12}$ system of TMADBS, TEADBS, TPADBS and TBADBS.

Methods

The critical micelle concentration (cmc) was determined by two methods viz., surface tension and specific conductance methods. The Tensiometer (K9, KRŰSS; Germany) was used to measure the surface tension at different temperatures by platinum ring detachment method at the air ⁄ water interface of the surfactant solution within the accuracy of ± 0.1 mN.m^{-1}. The ring was cleaned several times before the measurements by double distilled water and also burning in alcohol flame and the solution was progressively diluted with water keeping the experimental solution in a double-wall container. Temperature was maintained by circulating water controlled by an auto-thermostat. Similarly, a highly calibrated electrical conductivity bridge (METTLER TOLEDO, Switzerland, uncertainty limit ±1%) was used to measure the specific conductance by progressively diluting the solution. Each measurement was repeated several times throughout the experiment to maintain the accuracy.

Steady-state fluorescence quenching method was used to determine the mean aggregation number of the surfactants by using a Fluorescence spectrophotometer, (Photon Technology International Co., USA,) with slit widths of 0.20 nm, 0.60nm, 0.50 nm and 1.50 nm respectively. Pyrene solution (5 μM) was used as a probe and CPC as a quencher.

By exciting the samples at 332 nm, emission spectra of pyrene were obtained and the emission was measured in the range of 350-520 nm. The emission peak at 393 nm was considered for calculating micellar aggregation number.

Results and discussion

Critical Micelle Concentration (cmc)

As has been already mentioned that cmc is the most important parameter for an aqueous amphiphilic system to give the aggregation characteristics. We have determined the cmc of the systems by conductivity as well as surface tension measurements. The representative plots of surface tension and specific conductance as a function of concentration of tetramethylammonium dodecylbenzene sulfonate (TMADBS) at different temperatures are shown in figures 1 and 2 respectively (The plots of surface tension and specific conductance as a function of concentration of TEADBS, TPADBS and TBADBS are provided as supplementary materials). To our knowledge, the aggregation data for TMADBS, TEADBS, TPADBS and TBADBS are recorded for the first time and, therefore, to check the reliability of the measured parameters, repeated experiments have been performed for both the measurements at least for three times and the mean values are recorded for reporting within the temperature range of 283 - 313 K at 5K intervals. In table 1, the cmc values of all the surfactant systems at various temperatures with varying counterions are shown along with different surface parameters and degree of ionization, α. The values of α have been determined from the ratio of the slopes of two linear fragments of conductivity-concentration plots i.e, above and below the cmc. Though the values of α does not change appreciably within the given temperature range (table 1) and the changes in cmc values with temperature for different surfactants are small but clearly detectable. At a given temperature, the cmc values of the surfactants follow the order $NH_4^+ > N^+(CH_3)_4 > N^+(C_2H_5)_4 > N^+(C_3H_7)_4 > N^+(C_4H_9)_4$. This variation of cmc can be explained in terms of the binding ability of the counterions. Among all the counter ions, the greater binding ability of $N^+(C_4H_9)_4$ group to the polar head of DBS due to strong hydrophobic interactions reduces the electrostatic repulsive force considerably which leads to the formation of the micelle at the lowest concentration. The binding tendency decreases in the order $N^+(C_4H_9)_4 > N^+(C_3H_7)_4 > N^+(C_2H_5)_4 > N^+(CH_3)_4 > NH_4^+$ and at a particular temperature the cmc values follow the reverse order. It shows that the result exactly follows the theoretical understanding pertaining to the micellization process. In figure 3, values of cmc are plotted against temperature (variation is small with temperature) for different surfactant systems. The plots give very shallow and broad minima in some cases (linear in other cases) within the given range of temperature. Similar result of linear or near linear variation of cmc with temperature for sodiumdodecylbenzene sulfonate was also recorded by Hait et. al.[22] and this is indeed somewhat different from the general parabolic trend of the plot with a shallow minimum shown by the surfactant like SDS, AOT etc[12-15]. In the similar range of temperature, the cmc decreases in above cases due to the decrease in degree of hydration of the hydrophilic group to attain the minima with increase in temperature. But for surfactants like dodecyl benzene sulfonate, this effect is not pronounced. Here, the disruption of water cluster facilitates surfactant monomer solubilization and the result is an increase in cmc with increase in temperature[14].

In fact, the effect of temperature on the cmc of surfactant in aqueous medium is quite interesting. An increase in temperature initially favours micellization process to occur at lower concentration of surfactant. This may be explained by the lower probability of the hydrogen bond formation with temperature resulting in the considerable decrease in hydrophilicity of the surfactant molecules. But further increase of temperature also causes disruption of the structured water surrounding the hydrophobic group, an effect that disfavours micellization[23,24]. The relative magnitude of these two opposing effects, therefore, determines whether the cmc increases or decreases over a particular temperature range. In general, from the data available, the minimum in the cmc-temperature curve appears to be around 298K for ionics and around 323K for nonionics[25]. For bivalent metal alkyl sulphates, the cmc appears to be practically independent of the temperature[26,27]. Though data on the effect of temperature of zwitterionics are limited, they generally show a steady decrease in the cmc of alkyl betains with increase in temperature in the range 279-330K[28,29]. Whether further increase in temperature will cause an increase in the cmc is not evident from the data.

The micellar aggregation number was determined by the fluorescence quenching method with pyrene as the probe and cetylpyridinium chloride (CPC) as the quencher. Five predominant vibronic bands are exhibited by pyrene in water in the fluorescence spectrum. It has been observed that the ratio of intensity of the first (I_1 at 373nm) and third peaks (I_3 at 384 nm) is a sensitive parameter which characterizes the polarity of the probe environment. The solubilization of the probes in a more hydrophobic environment than water is indicated by a decrease in I_1/I_3 values. The aggregation number of the surfactant micelles was determined by using Stern-Volmer equation and also considering the usual following assumptions:

(I) Static quenching occurs between the fluorescence probe and the quencher molecules so the quenching process does not affect the fluorescence lifetime of the probe.

(II) Fluorescent lifetime of the probe is much less than the residence times of the quencher and probe inside the micelle.

(III) The probability of finding a micelle with more than one probe molecule is negligible as because the quencher concentration is very low.

Following Poisson statistics[30] for the description of probe and the quencher among the micelles, the logarithm of I_0/I takes the form

$$\ln\frac{I_0}{I} = \frac{[Q]N}{\left([S]_0 - cmc\right)} \qquad (2)$$

where, I_0 and I are the intensities of fluorescence without and with quencher. [Q] is the bulk quencher concentration, N is the mean aggregation number and $[S]_0$ is the total surfactant concentration. The aggregation number has been obtained by plotting $\ln(I_0/I)$ as a function of quencher concentration.

. In the present study, good linear plots for all the surfactants have been obtained satisfying the above equation. The representative plot of fluorescence measurement for the surfactant, TEADBS is shown in figure 4 (Similar plots of $\ln(I_0/I)$ as a function of the concentration of CPC for TMADBS, TPADBS and TBADBS are provided as supplementary materials). The aggregation number measured at 298K for all the surfactants in aqueous solutions are given in the table 2. Figure 5 shows the variation of aggregation number as a function of the size of the counter ions (in terms of the number of carbon atoms present in R of R_4N^+). Aggregation number increases with alkyl chain length of counterions and gives maximum value for tetraethylammonium ion due to hydrophobic interactions of hydrocarbon exterior of the ions with exposed hydrocarbon to the micelle surface. However, for tetrapropyl and tetrabutyl ammonium ions aggregation become increasingly unfavorable due to steric hindrance for increasing counterion size. Here, comparison of aggregation number with the ionization degree might be interesting.

The ionization degrees of all the surfactants are shown in table 1. The result shows that the values are quite high which indicates that the tetraalkylammonium counter ions are strongly bound to the micelle surface. It is also observed that the counter ion ionization degree increases in the series $NH_4^+ \leq N^+(CH_3)_4 < N^+(C_2H_5)_4 < N^+(C_3H_7)_4 < N^+(C_4H_9)_4$. This means that, as expected, the binding increases as the counter ion becomes more and more hydrophobic in nature. The values of cmc also follow the opposite trend, i.e., as the fraction of counter ion binding increases, the micelles are formed at lower concentrations. However, the aggregation number does not follow the expected trend. At 298K, the aggregation number becomes minimum in the case of NH_4^+ counter ion. But as the alkyl groups are substituted for hydrogens, the aggregation number increases because of the formation of larger aggregates which is the consequences of the increased charged screening at higher counter ion binding capacity via stronger hydrophobic interactions with the micelles. This increasing trend of aggregation number continues up to the tetra ethylammonium ions. But for tetrapropyl and tetrabutyl ammonium ions, aggregation number progressively decreases as illustrated in figure 5. This is indeed interesting. Such a complex behaviour of micelle pertaining to the aggregation number with respect to the expected trend on the basis of cmc values is, however, available in the literature[22]. It has been shown that the effect of head group size of tetradecyltrialkylammonium bromide surfactant is very important pertaining to the observed reverse trend of the aggregation number with respect to its cmc. For these surfactants the values of both the cmc and aggregation number N decrease as the size of the tetraalkylammonium head group increases. This effect has been explained in terms of the geometric steric hindrance (overlap) between the large trialkylammonium head groups at the micellar surface[15,31].

It seems apparent that in the present systems, as the hydrophobicity of counter ions increases, the counter ion binding/condensation increases due to increased hydrophobic interactions and eventually the cmc decrease. However, enhanced electrostatic charge screening of the head groups is incapable of increasing the aggregation number of the micelles for tetrapropyl and tetrabutylammonium counter ions. On the other hand, micellar surface probably does not offer sufficient surface area to accommodate all the N^+R_4 counter ions that must bind to the micelle to ensure their stability. Therefore, the micelles become smaller in size and more in number to provide larger surface area in order to pack a large number of counter ions.

Energetics of micellar processes

Using pseudo-phase separation model[32-34], different thermodynamic parameters have been determined by using temperature dependency of micellization. For uni-univalent ionic surfactants, the standard Gibbs free energy of micellization can be expressed as

$$\Delta G_m^0 = (2-\alpha)RT\ln X_{cmc} \tag{3}$$

Here, α is the counterion ionization constant for ionic surfactant and X_{cmc} is the cmc in the mole fraction scale. The standard enthalpy change of micellization ΔH_m^0 can also be obtained from the Gibbs-Helmholtz equation[20]:

$$\Delta H_m^0 = -RT^2[(2-\alpha)(\partial\ln X_{cmc}/dT)_P - \ln X_{cmc}(\partial(2-\alpha)/\partial T)_P \tag{4}$$

The second term of the equation, which is quite small as compared to the first term, is difficult to determine because the values of α do not follow any general trend of variation as a function of temperature and also due to polydispersity of the micelle[35,36]. Therefore, neglecting the second term of the above equation takes the form

$$\Delta H_m^0 = -RT^2[(2-\alpha)(\partial\ln X_{cmc}/dT)_P \tag{5}$$

Further, the values of $\partial \ln X_{cmc}/\partial T$ in equation (5) can be obtained by fitting the curve of $\ln X_{cmc}$ vs. T to a second order polynomial in the following way:

$$\ln X_{cmc} = a + bT + cT^2 \tag{6}$$

where a, b and c are the polynomial coefficients respectively.

$$\left(\partial \ln X_{cmc}/\partial T\right) = b + 2cT \tag{7}$$

The free energy of micellization, ΔS^0_m and the specific heat capacity of micellization, $\Delta_{mic}c_p^0$ are also determined by the following expressions

$$\Delta S_m{}^0 = \left(\Delta H_m{}^0 - \Delta G_m{}^0\right)/T \tag{8}$$

$$\Delta_{mic} C_p{}^0 = \left(\partial \Delta H_m{}^0/\partial T\right)_P \tag{9}$$

Here, in the table 2, the various thermodynamic quantities are presented. All the calculated properties change with the variation in temperature and counterion present with the surfactant molecule. For all the micellization processes large negative values of ΔG_m^0 support that the micellization processes are thermodynamically favourable. On the other hand, the plot of ΔG_m^0 as a function of alkyl chain length in the figure 6 suggests that with increase in alkyl chain length of the counterion, the spontaneity of the process decreases first and then remains almost constants. Furthermore, with increase in temperature, the spontaneity of the process increases by increasing ΔG_m^0 values in general. The negative ΔH_m^0 values suggest that micellization is an exothermic process and for all the surfactants it can be explained in terms of the size and hydration of the counter ions[17,18,21]. Among the different factors proposed by researchers, the hydrocarbon chains with water molecules have the major contribution to the thermodynamic factors responsible for dodecylbenzene sulfonate aggregation[37,38]. Usually the micellization process results in an appreciable positive entropy change via (i) disruption of the hydrophobic hydration surrounding the hydrophobic tails of surfactant molecules and (ii) increased degree of freedom of the tails in the oil-like interior of micelles. Plot of ΔS_m^0 as a function of alkyl chain length (figure 7) suggests that positive entropy value first increases, reaches a maximum and then decreases with alkyl chain length which may be explained with the increase in the hydrophobic effect and the binding capabilities of the alkyl chain length and after that due to the bulkiness or large size of the tetrabutyl group, decrease in entropy is observed. An opposite effect is observed as usual for ΔH_m^0 (figure 8). For tetraalkylammonium counterion, the hydration number decrease effect is also a contributing factor for the micellization process. It has been observed that $\Delta S^0{}_m$ decreases systematically with increasing temperature of a particular type of counterion that may be explained by the disruption of ordered arrangement of water dipoles around the amphiphilic part of the surfactant molecules. Heat capacity of micelle formation, $\Delta_{mic}C_p{}^0$, is the expression for the effective interactions associated with hydrocarbon chains. The general trend in heat capacity values of a surfactant increases with increase in temperature due to solvation of ions upon micellization. Here, the dodecylbenzene sulfonate shows similar trend and the values vary from -81 $J.mol^{-1}.K^{-1}$ to -249 $J.mol^{-1}.K^{-1}$ which is quite similar to the other surfactants within the temperature range 283-313 K suggesting execution of hydrophobic interaction by the hydrocarbon tail followed by dehydration in greater extent[15,22] and with the change of counterions, the reduction of number of water molecules in counterion solvation shell occurs.

Surface properties

The surface excess concentration maximum (Γ_{max}) and minimum areas per molecule (A_{min}) in the interface (aqueous/air) was calculated by the following expressions[14,15,21]:

$$\Gamma_{\max} = (1/2.303n'RT)(-\partial\gamma/\partial \log C) \qquad (7)$$

$$A_{\min} = 1/(N\Gamma) \qquad (8)$$

where γ expresses surface tension, N is the Avogadro's number and C and n′ are the surfactant concentration and number of particles per surfactant molecules respectively. For DBS moiety with different counterions, the n′ has the value of two like uni-univalent electrolytes. Generally, the Γ_{max} value decreases with increase in temperatures, but an opposite trend is also observed[20] especially in presence of additives. At a fixed temperature, the Γ_{max} values changes in the order: $(CH_3)_4N^+ > (C_2H_5)_4N^+ > (C_3H_7)_4N^+ > (C_4H_9)_4N^+$ which is due to the head group's accessibility towards counterions followed by hydration of the ions in reverse order. Further, with increase in temperature, the surfactant molecules try to form a closely packed monolayer film due to the decreased repulsion of the oriented head groups which is well established by the fact of decreasing A_{min} value is also well supported in the literature[37].

Conclusion

Different tetraalkylammonium cation changes the cmc values of dodecyl benzene sulfonate moiety to a great extent in aqueous solution. With increase in the size of tetraalkylammonium counter ion the cmc decreases owing to the increase in hydrophobicity of the head groups. Also, with increase in size, the hydration of the head groups decreases which can effectively associate the monomer into micelle at lower surfactant concentration. However, expected reverse trend of aggregation number suffers a nudge for tetrapropyl and tetrabutylammonium counter ions because of their steric hindrance due to very large sizes, which impede their binding to the micelles and limit the values of aggregation number. The surface parameter values suggest that with increase in temperature the formation of close packed monolayer film formation occurs due to repulsion of the head groups oriented at the air/liquid interface of the surfactant solution. The thermodynamic parameters calculated by using pseudo-phase model also successfully explains the thermodynamics of micelle formation of dodecylbenzene sulfonate as a function of chain length and bulkiness of the head groups associated with the counterions.

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Table 1
Micellization and Surface parameters of Dodecyl benzene sulfonate having different tetraalkylammonium counterions at various temperatures (T/K): cmc, maximum surface excess concentration, minimum areas per molecule and ionization degree.

Counterion	T/K	cmc[a]/ (mol dm^{-3} × 10^{-3})	Γ_{max}/ mol cm^{-2} × 10^{6}	A_{min}/nm^{2}	α
	283	2.28 (2.23)	3.12	0.53	0.74
	288	2.39 (2.36)	3.17	0.52	0.74
	293	2.41 (2.40)	3.23	0.51	0.73
[b]NH_4^+	298	2.52 (2.48)	3.28	0.51	0.74
	303	2.68 (2.62)	3.38	0.49	0.78
	308	2.81 (2.82)	3.41	0.49	0.74
	313	2.80 (2.82)	3.49	0.47	0.74
	283	1.31 (1.28)	3.11	0.53	0.71
	288	1.34 (1.29)	3.14	0.53	0.73
	293	1.34 (1.30)	3.17	0.52	0.74
$(CH_3)_4N^+$	298	1.37 (1.31)	3.20	0.52	0.73
	303	1.39 (1.34)	3.28	0.51	0.74
	308	1.45 (1.37)	3.30	0.50	0.75
	313	1.49 (1.45)	3.36	0.49	0.73
	283	1.27 (1.27)	3.05	0.55	0.76
	288	1.28 (1.32)	3.03	0.55	0.77
	293	1.27 (1.22)	3.02	0.55	0.79
$(C_2H_5)_4N^+$	298	1.30 (1.24)	3.10	0.54	0.79
	303	1.32 (1.25)	3.14	0.53	0.80
	308	1.32 (1.27)	3.19	0.52	0.79
	313	1.37 (1.29)	3.26	0.51	0.81
	283	1.08 (1.10)	3.02	0.55	0.79
	288	1.12 (1.15)	3.04	0.55	0.81
	293	1.14 (1.17)	3.07	0.54	0.81
$(C_3H_7)_4N^+$	298	1.18 (1.19)	3.08	0.54	0.82
	303	1.23 (1.20)	3.11	0.53	0.82
	308	1.25 (1.23)	3.16	0.53	0.82
	313	1.31 (1.25)	3.19	0.52	0.82
	283	0.79 (0.75)	2.93	0.57	0.87
	288	0.84 (0.81)	2.96	0.56	0.84
	293	0.90 (0.96)	2.99	0.55	0.84
$(C_4H_9)_4N^+$	298	0.93 (1.02)	2.99	0.56	0.83
	303	1.01 (1.03)	3.00	0.55	0.83
	308	1.06 (1.05)	3.01	0.55	0.82
	313	1.11 (1.12)	3.05	0.54	0.83

[a]The values in the parenthesis represent cmc determined by conductivity method.

bThe data are collected from [16].

Table 2

Thermodynamic parameters of micellization for Dodecyl benzene sulfonate with different tetraalkylammonium counterions at various temperatures: Standard Gibb's free energy, Enthalpy, Entropy and standard heat capacity and aggregation number.

Counterion	T/K	-ΔGm° (kJ mol^{-1})	ΔH_m° (kJ mol^{-1})	ΔS_m° (J mol^{-1})	$-\Delta C_{pm}$° (J $mol^{-1}K^{-1}$)	Aggr. No.
	283	39.9	-6.3	118.7	405	
	288	30.3	-7.7	78.5	488	
	293	31.0	-11.1	67.9	571	
NH_4^+	298	31.3	-13.2	60.7	654	08
	303	30.5	-18.0	41.2	737	
	308	32.0	-21.1	35.4	820	
	313	32.6	-25.2	23.6	903	
	283	32.4	-21.5	38.34	141	
	288	32.5	-22.4	35.05	159	
	293	32.8	-23.3	32.21	177	
$(CH_3)_4N^+$	298	33.4	-24.6	29.46	195	17
	303	33.7	-25.6	26.47	213	
	308	33.8	-26.6	23.17	231	
	313	34.7	-28.3	20.41	249	
	283	31.1	-12.2	66.68	108	
	288	31.5	-12.8	65.09	116	
	293	31.4	-13.1	62.50	124	
$(C_2H_5)_4N^+$	298	31.8	-13.8	60.81	132	34
	303	32.2	-14.3	59.08	140	
	308	32.9	-15.1	58.02	148	
	313	33.0	-15.6	55.53	156	
	283	30.9	-8.5	79.05	81	
	288	30.9	-8.7	76.93	87	
	293	31.2	-9.1	75.34	93	
$(C_3H_7)_4N^+$	298	31.6	-9.5	74.03	99	27
	303	31.9	-9.9	72.76	105	
	308	32.4	-10.3	71.64	111	
	313	32.7	-10.7	70.26	117	
	283	29.7	-17.6	43.07	245	
	288	30.9	-18.9	41.71	241	
	293	31.2	-19.8	38.93	237	
$(C_4H_9)_4N^+$	298	31.9	-20.9	36.96	233	25
	303	32.1	-21.8	33.97	229	
	308	32.8	-23.1	31.74	225	
	313	33.0	-24.0	28.98	221	

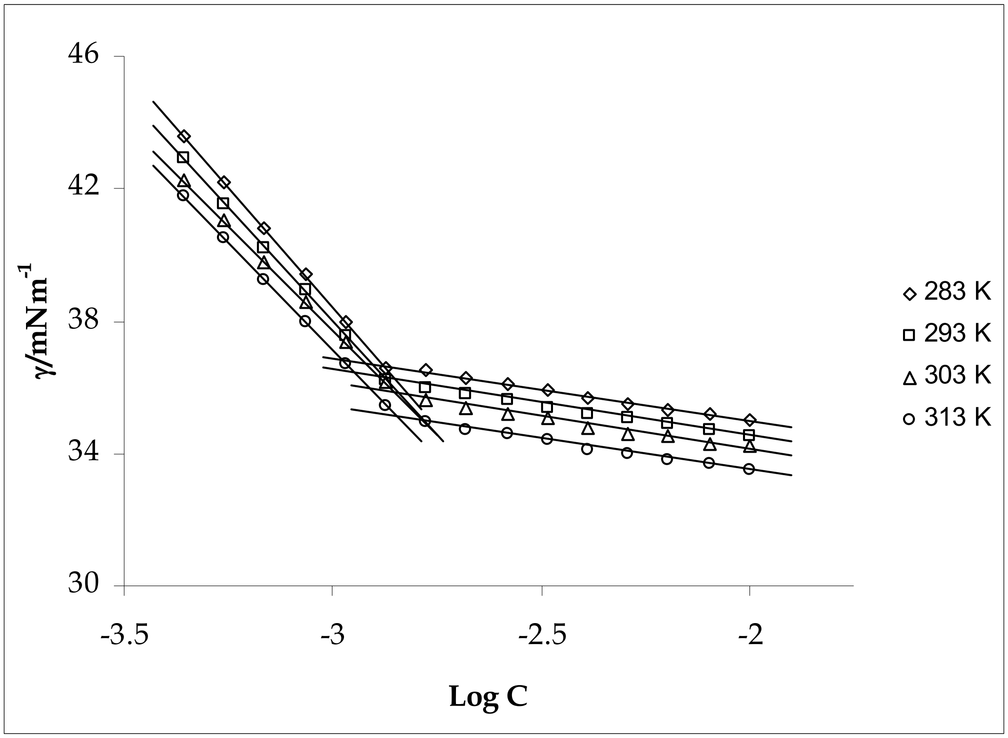

Figure 1: Plot of Surface tension vs. Logarithm of concentration with different temperatures of Tetramethylammonium dodecyl benzene sulfonate (TMADBS).

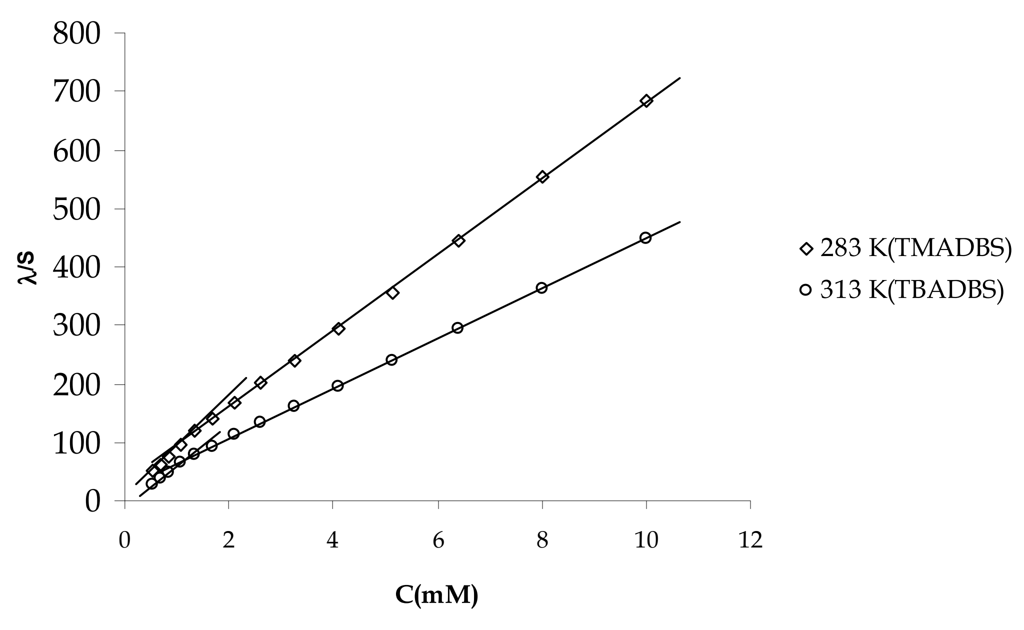

Figure 2: Plot of specific conductance, Λ vs. concentration with different temperatures of Tetramethylammonium and tetrabutylammonium dodecyl benzene sulfonates.

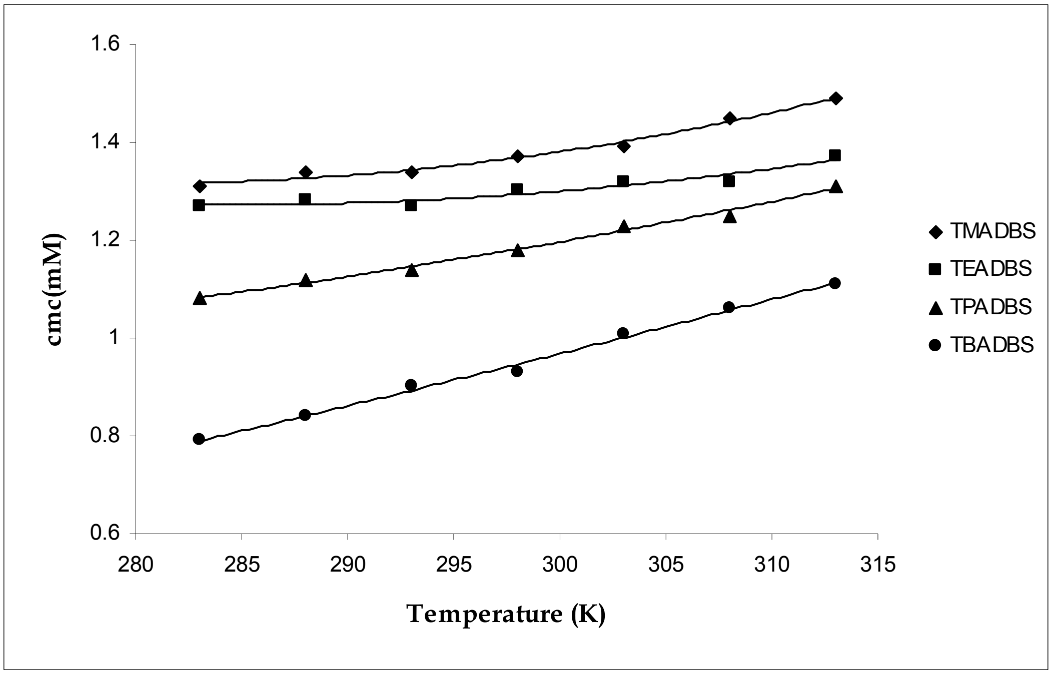

Figure 3: Plot of cmc of different surfactants as a function of temperature

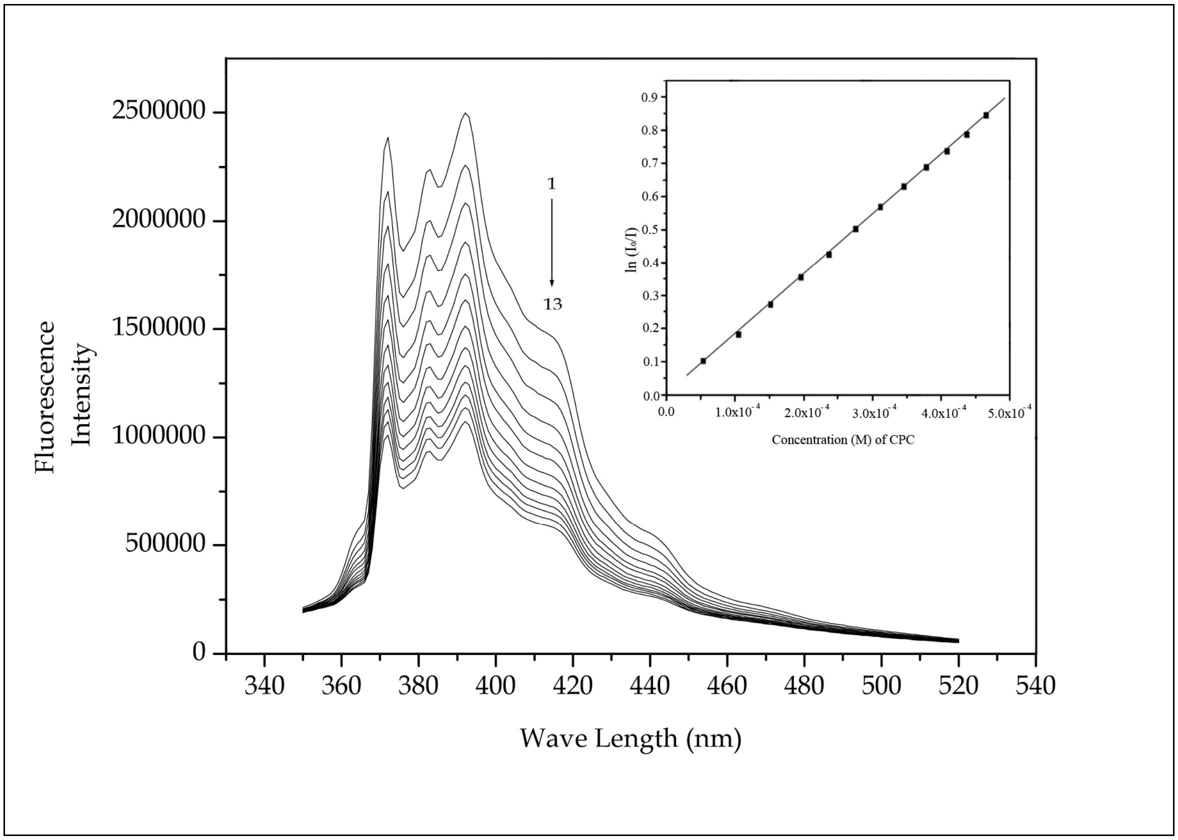

Figure 4: Fluorescence spectra of pyrene with different concentration of CPC in mM (1) 0.0 mM (2) 0.0054 mM (3) 0.105 mM (4) 0.152 mM (5) 0.196 mM (6) 0.237 mM (7) 0.276 mM (8) 0.312 mM (9) 0.346 mM (10) 0.379 mM (11) 0.409 mM (12) 0.438 mM (13) 0.466 mM; Inset – Plot of ln (I_0/I_3) vs. [CPC] to determine the aggregation number for TEADBS surfactants.

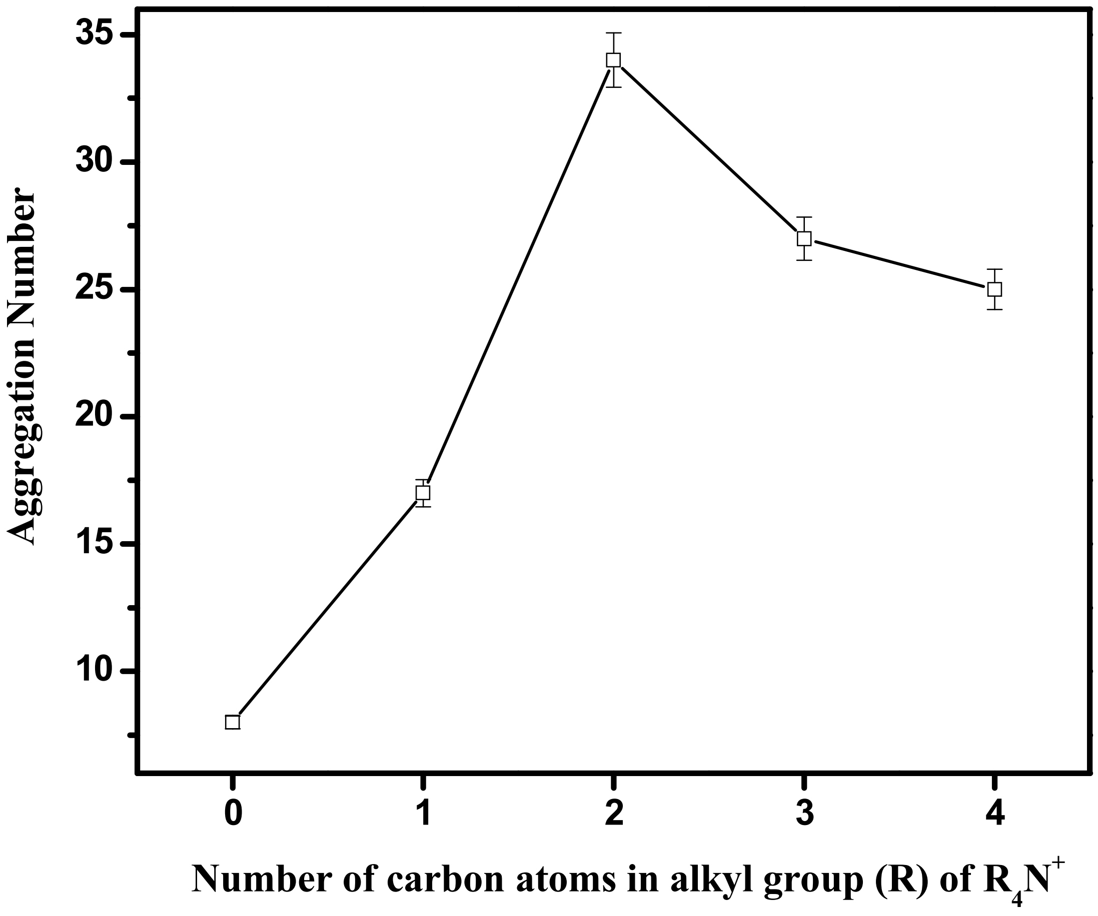

Figure 5: Aggregation Number change with the change of alkyl Chain length of R in R_4N^+ counterion.

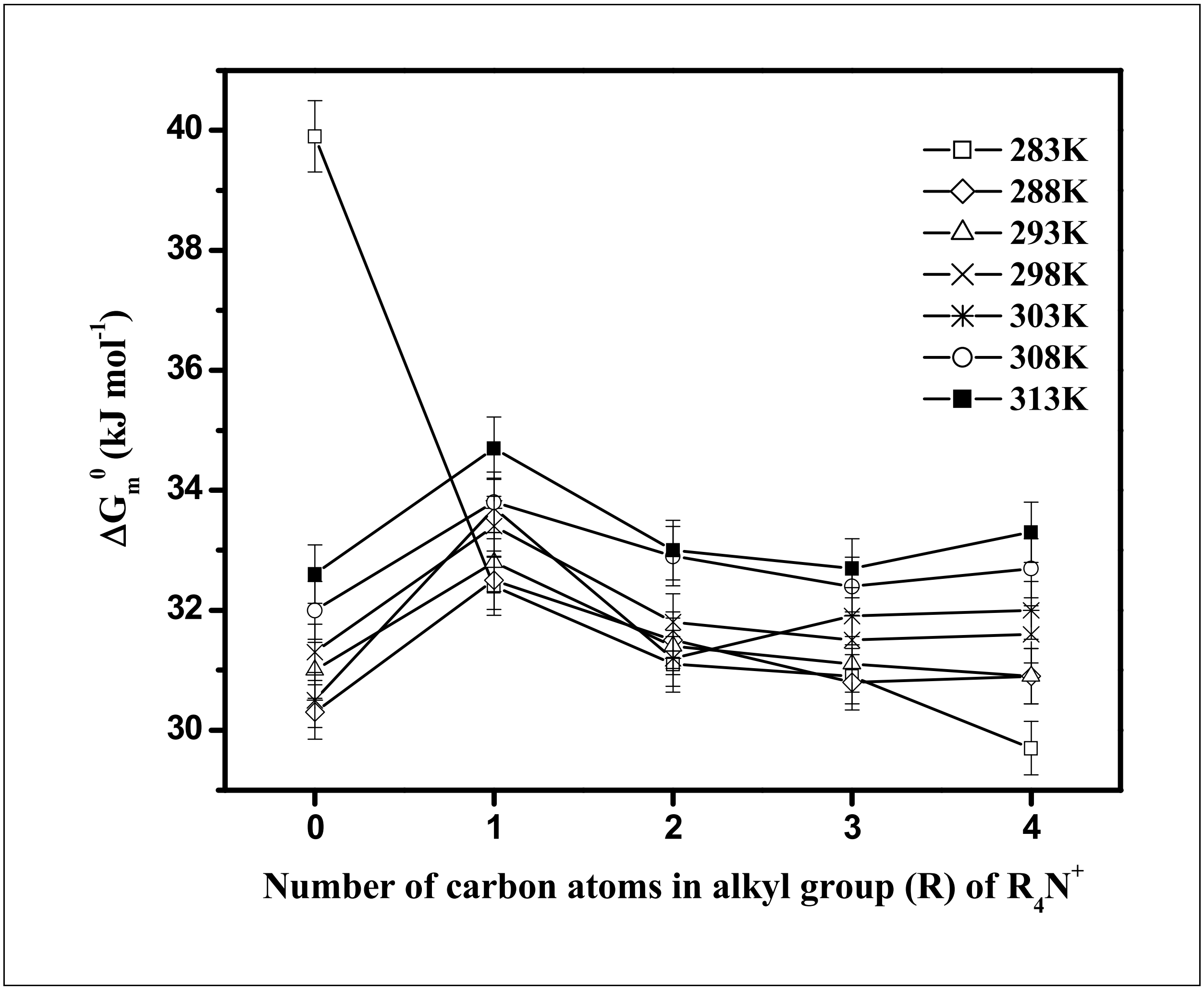

Figure 6: Gibbs free energy change with the change of alkyl chain length of R in R_4N^+ counterion.

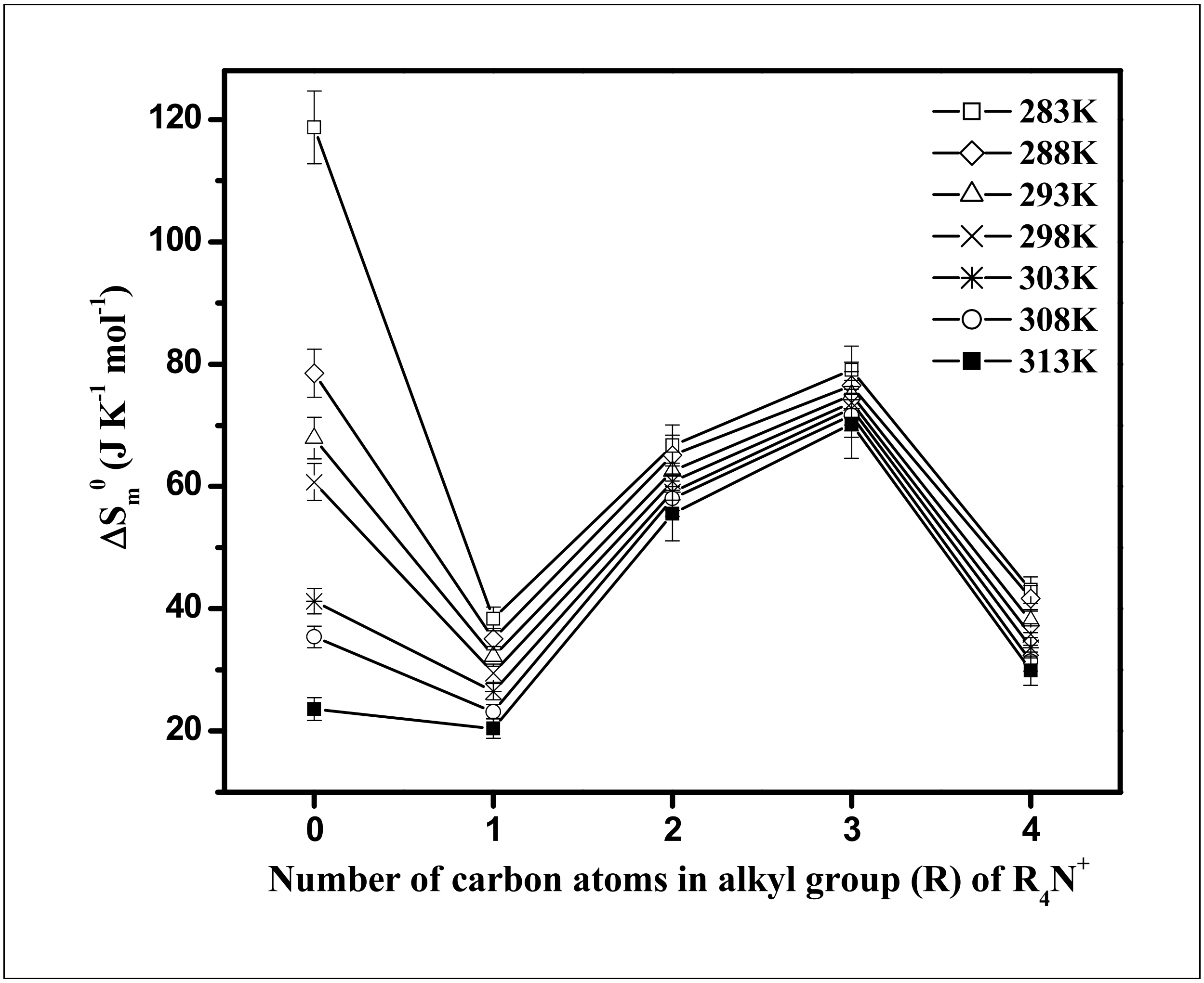

Figure 7: Entropy change with the change of alkyl chain length of R in R_4N^+ counterion.

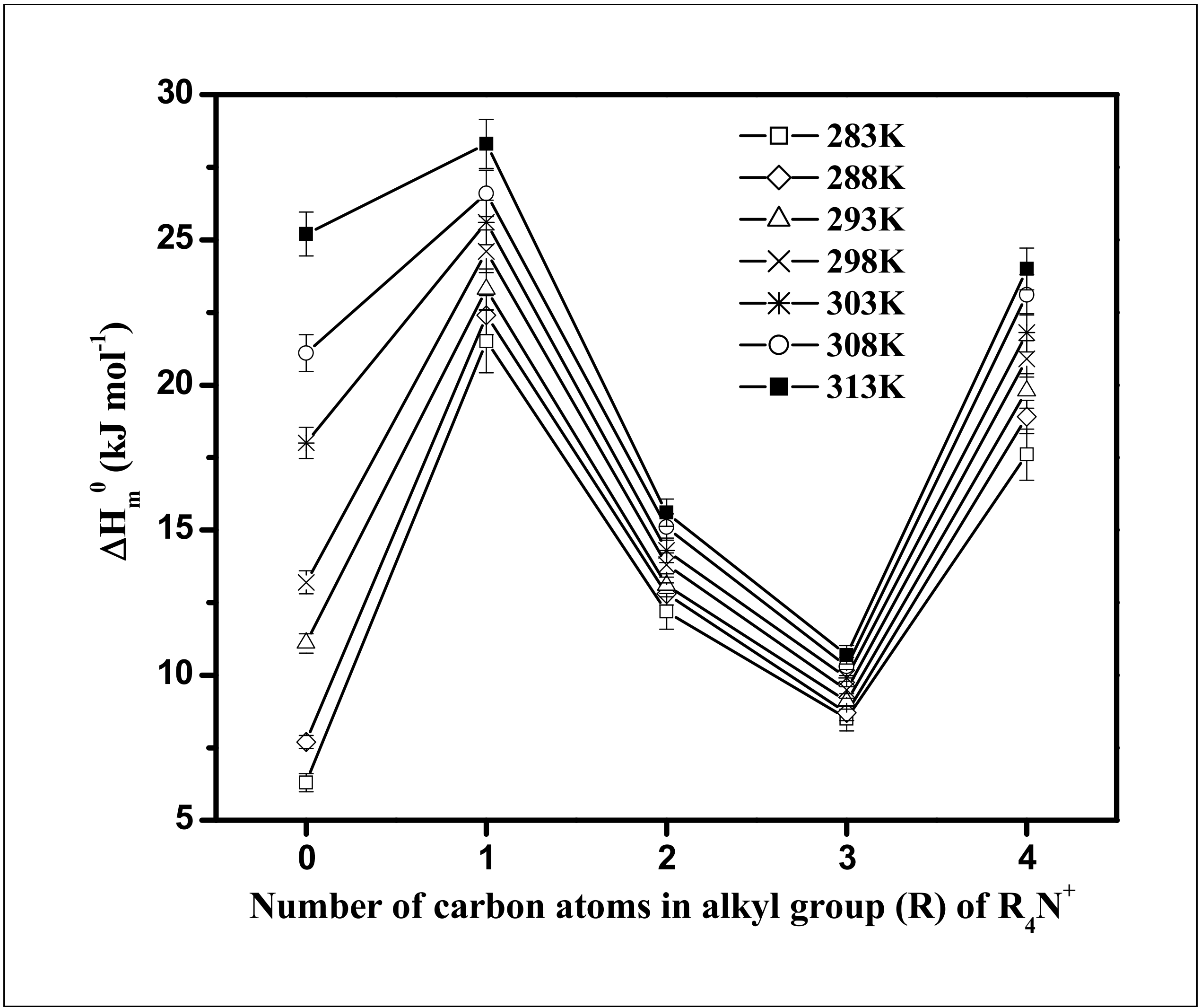

Figure 8: Entropy change with the change of alkyl chain length of R in R_4N^+ counterion.