

# Modulation of Aggregation Behaviour of Anionic Surfactant in the Presence of Aqueous Quaternary Ammonium Salts

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**Abstract** The self-aggregation of sodium dodecylsulphate (SDS), an anionic surfactant, in aqueous solutions of tetraalkylammonium bromide salts ( $R_4NBr$ , where  $R = \text{propyl, butyl and pentyl}$ ) was determined at various temperatures in the range 288.15–318.15 K. The critical micelle concentration (CMC) determined from conductivity data was used to study the thermodynamics of the surfactant. The presence of bromide salts was found to affect the micellization of SDS in accordance with the hydrophobicity of the tetraalkylammonium cations, thus the CMC values follow the order no additive >  $Pr_4NBr > Bu_4NBr > Pen_4NBr$ . The results from conventional conductivity methods were combined with those of spectroscopic techniques like fluorescence and UV–Vis studies.

**Keywords** Micellization · Tetraalkylammonium bromide · Sodium dodecylsulphate · Hydrophobic character · Electrostatic interactions · Thermodynamic parameters · Spectroscopic techniques

## Introduction

Quaternary ammonium compounds (QUATS) have been extensively studied owing to their hydrophobic character, weak surface activity and low aqueous toxicity. They have

been widely used as phase transfer catalysts [1–3] and in detergents [4], disinfectants [5, 6] and synthetic reagents [7, 8]. QUATS, especially those containing long alkyl chains e.g. cetylpyridinium chloride, are used as hygienic adjuncts against bacterial growth in various industrial and clinical formulations [9, 10]. Among the different QUATS, tetraalkylammonium bromides are an interesting group owing to their symmetric structure having four short alkyl chains in one molecule providing a large hydrophobic volume. Hence the hydrophobic interactions between alkyl chains allow for the penetration of some alkyl chains at the micellar surface into another micelle. Qualitatively, they act as spacers between the surfactant head groups and promote self-association and micelle formation [11, 12].

Basic data on surfactant–QUATS interactions is essential for understanding the effects of interplay of solute–solute, solute–solvent and solvent–solvent interactions on micelle formation [11–15]. Such information is useful to industrial chemists, especially in the optimization and determination of various characteristic properties of surfactants. A detailed investigation of the literature reveals that studies on the effect of QUAT salts on aggregation of surfactants are scarce. In our previous study, we analysed the dependence of micellization of the cationic surfactant dodecyltrimethylammonium bromide (DTAB) on the alkyl chain length of tetraalkylammonium bromides [16]. The results show the importance of hydrophobic interactions in surfactant micellization in the presence of bromide salts. The present work analyses the effect of tetraalkylammonium bromide salts ( $R_4NBr$ , where  $R = \text{propyl, butyl and pentyl}$ ) on the micellar behaviour of the anionic surfactant sodium dodecylsulphate (SDS) by employing conventional conductivity methods in combination with spectroscopic techniques like fluorescence and UV–Vis probe studies. For conductivity measurements, temperatures ranging from

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288.15 K to 318.15 K at a regular interval of 5 K were selected, whereas the spectroscopic studies were carried out at room temperature (i.e. 298.15 K).

## Experimental

### Materials

Deionized distilled water with a conductivity of  $2\text{--}3 \times 10^{-6} \text{ S cm}^{-1}$  and pH of 6.8–7.0 (at 298.15 K) was obtained from a Millipore–Elix system and was used for all the experiments. SDS of A.R. grade was obtained from Himedia (India) and was used after purification as mentioned in the literature [17]. Tetrapropylammonium bromide ( $\text{C}_{12}\text{H}_{28}\text{NBr}$ ) from Fluka (Switzerland), tetrabutylammonium bromide ( $\text{C}_{16}\text{H}_{36}\text{NBr}$ ) from SRL (India) and tetrapentylammonium bromide ( $\text{C}_{20}\text{H}_{44}\text{NBr}$ ) from Acros Organics (Belgium) were dried in a vacuum oven at 333.15 K for 24 h before use. The probe used for the spectroscopic techniques was pyrene (A.R. grade) provided by Merck (Germany) and was used as received. The specifications of all the samples used are provided in Table 1 and their structures are given in Fig. 1.

### Methods

Conductivity measurements were carried out with a Cyberscan CON-510 digital conductivity meter. The calibration of the conductivity cell was done with 0.01 M KCl calibration solution provided by Merck Chem Ltd. The reproducibility of the conductance measurements was estimated to be  $\pm 5 \mu\text{S cm}^{-1}$ . The temperature was maintained constant at  $\pm 0.01 \text{ K}$  by circulating thermostated water through a double-walled conductivity vessel containing the solution. The specific conductance ( $\kappa$ ) of SDS solution in aqueous solutions of  $0.01 \text{ mol kg}^{-1}$   $\text{Pr}_4\text{NBr}$ ,  $\text{Bu}_4\text{NBr}$  and  $\text{Pen}_4\text{NBr}$  were measured over a wide range of temperature (288.15–318.15 K) at an interval of 5 K.

Both fluorescence and UV–Vis spectra were recorded at room temperature (298.15 K). Pyrene solution of

concentration approx.  $2 \times 10^{-6} \text{ mol kg}^{-1}$  in ethanol was used as a probe. Fluorescence measurements were carried out using a Perkin Elmer LS 55 fluorescence spectrometer at room temperature (298.15 K). The emission spectra of the solutions were recorded in the wavelength range of 350–450 nm and the excitation and emission slit widths were 8 nm and 2.5 nm, respectively. UV–Vis absorption spectra of SDS- $\text{R}_4\text{NBr}$  solutions were recorded using a Genesys 10S spectrophotometer supplied by Thermoscientific, USA using 10-mm-path-length quartz cuvettes. The absorbance spectra were obtained in the 200–400 nm wavelength range and at room temperature (298.15 K).

## Results and Discussion

### Conductivity Measurements

The conductivity data for the SDS in the absence and presence of  $0.01 \text{ mol kg}^{-1}$  tetraalkylammonium bromide salts  $\text{R}_4\text{NBr}$  are reported in Table S1 of the supplementary data. The specific conductance ( $\kappa$ ) varies linearly with [SDS] in both pre- and post-micellar regions (Fig. 2), with the slope ( $S_1$ ) in pre-micellar region always greater than that in post-micellar region ( $S_2$ ). The intersection point between two straight lines is the critical micellar concentration (CMC) while the ratio  $S_2/S_1$  gives counterion dissociation ( $\alpha$ ). Linear regression analysis of the conductivity data was used to calculate  $S_1$  and  $S_2$  values and, in this case, the correlation factor was found to be better than 0.995.

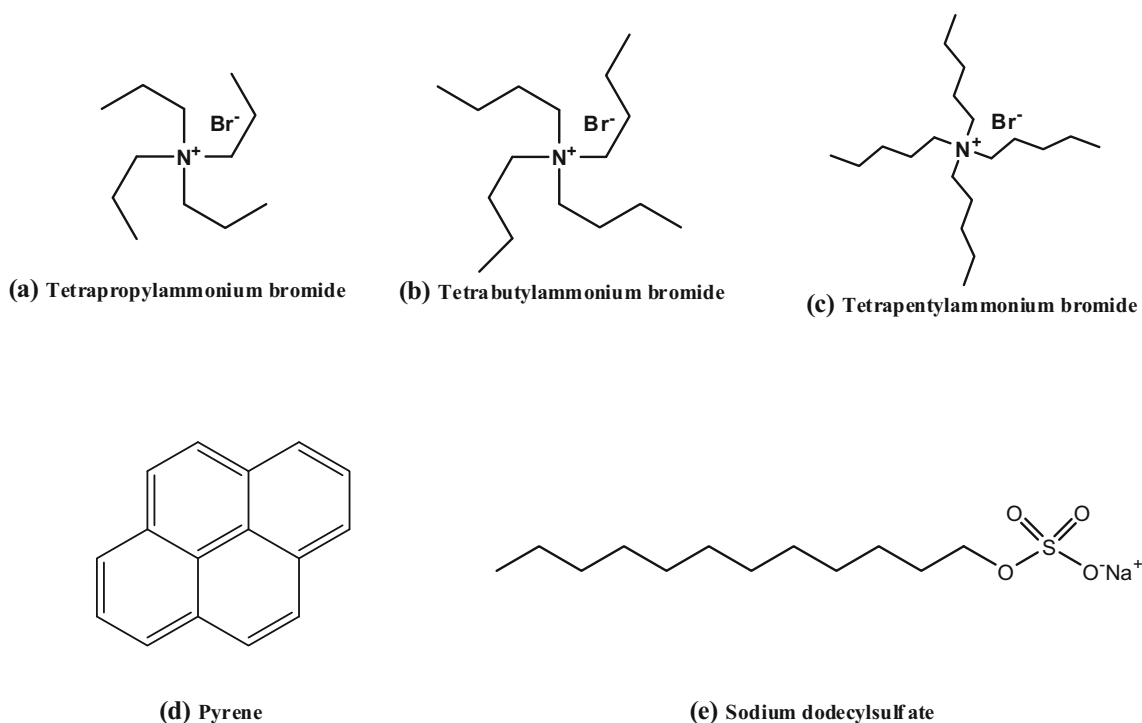
The CMC and corresponding  $X_{\text{CMC}}$  (CMC in mole fraction units) values for aqueous SDS in the absence and presence of  $\text{R}_4\text{NBr}$  are recorded in Table 2 and reveal that CMC values for the SDS ( $8.20 \text{ mmol kg}^{-1}$  at 298.15 K) in water are closer to the values reported in the literature i.e.  $8.10 \text{ mmol kg}^{-1}$  for SDS [18].

The effect of temperature on CMC values of SDS is presented in Fig. 3, indicating that CMC values first decrease to a minimum around 298.15 K and then increase with rising temperature. For most of the ionic surfactants

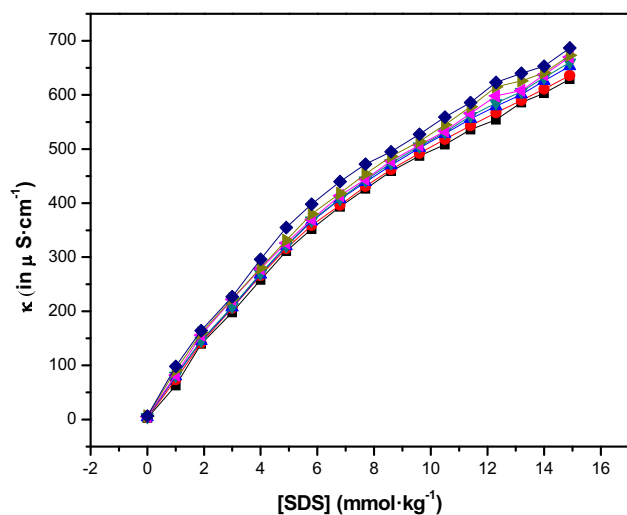
**Table 1** Specification of chemicals used in the present study

Chemical name	Source	Purification method	Mass fraction purity <sup>a</sup>
Tetrapropylammonium bromide ( $\text{C}_{12}\text{H}_{28}\text{NBr}$ )	Fluka	None	0.98
Tetrabutylammonium bromide ( $\text{C}_{16}\text{H}_{36}\text{NBr}$ )	SRL	None	0.99
Tetrapentylammonium bromide ( $\text{C}_{20}\text{H}_{44}\text{NBr}$ )	Acros Organics	None	0.99
Sodium dodecylsulphate ( $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$ )	Himedia	Recrystallization	0.98
Pyrene ( $\text{C}_{16}\text{H}_{10}$ )	Merck	None	0.99

<sup>a</sup> Provided by supplier



**Fig. 1** Structures of chemicals used



**Fig. 2** Plot of  $\kappa$  versus [SDS] in pure water at 288.15 K (black squares), 293.15 K (red circles), 298.15 K (blue triangles), 303.15 K (down-pointing green triangles), 308.15 K (left-pointing pink triangles), 313.15 K (right-pointing green triangles) and 318.15 K (blue diamonds). (Colour figure online)

such as alkyl sulphates and some non-ionic surfactants like *N*-decanoyl-*N*-methylglucamine (MEGA 10), the minimum in the CMC vs. temperature plot is a usual trend which is well documented in the literature [19–23]. In general, the temperature dependence of CMC is analysed by considering two opposite processes [24]. As the temperature increases, the hydrophilicity of the surfactant

decreases as a result of the dehydration of the monomers, which favours micellization. However, the rise in temperature also causes the disruption of water structure around the hydrophobic groups, increasing the solubilisation of surfactant monomers and hence inhibits the micelle formation.

Also as the temperature rises, the thermal motions of surfactant and solvent molecules are enhanced so that the formation of ordered micelle structures becomes difficult. The increase of temperature increases the kinetic energies and destroys the ordered micellar structures leading to an increase in the CMC value. Therefore, the higher the temperature is, the greater the degree of disaggregation and the higher the CMC are. In the case of SDS, the gradual decrease in CMC at lower temperatures and then similar increase at higher temperatures may be due to the dominance of the first and second factors, respectively.

The addition of tetraalkylammonium bromide salts decreased the surfactant CMC in the following order:  $C_{12}H_{28}NBr > C_{16}H_{36}NBr > C_{20}H_{44}NBr$ . The presence of four alkyl chains in addition to the positive charge on the nitrogen atom in the tetraalkylammonium cation allows it to interact electrostatically as well as hydrophobically with the micellar surface of anionic SDS. The strong electrostatic interactions between the anionic micelles and cationic counterions neutralize the effective charge on the head groups of the surfactant, thereby reducing the repulsions between polar head groups. These interactions result in an

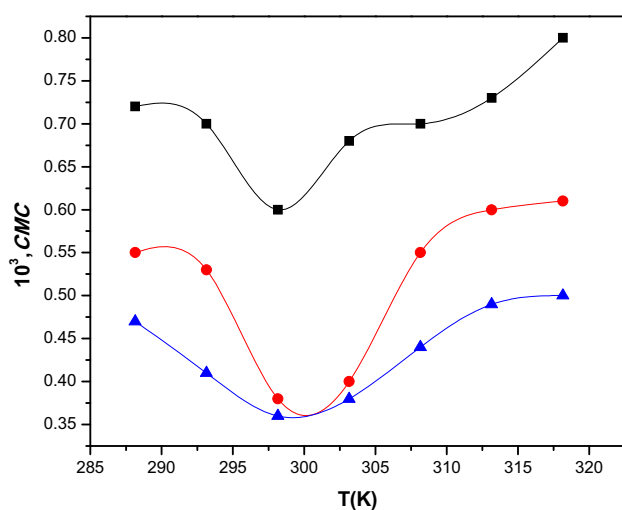
**Table 2** CMC and corresponding  $X_{\text{CMC}}$  for aqueous solutions of SDS in the absence and presence of tetraalkylammonium bromide salts at different temperatures ( $T/K$ ) and experimental pressure,  $p = 0.099$  MPa

$T/K$	Pure water		$[\text{C}_{12}\text{H}_{28}\text{NBr}] = 0.01 \text{ mol kg}^{-1}$		$[\text{C}_{16}\text{H}_{36}\text{NBr}] = 0.01 \text{ mol kg}^{-1}$		$[\text{C}_{20}\text{H}_{44}\text{NBr}] = 0.01 \text{ mol kg}^{-1}$	
	$10^{-3} \times \text{CMC}$	$10^{-4} \times X_{\text{CMC}}$	$10^{-3} \times \text{CMC}$	$10^{-4} \times X_{\text{CMC}}$	$10^{-3} \times \text{CMC}$	$10^{-4} \times X_{\text{CMC}}$	$10^{-3} \times \text{CMC}$	$10^{-4} \times X_{\text{CMC}}$
288.15	8.85	1.5915	0.72	0.1295	0.55	0.0989	0.47	0.0845
293.15	8.70 (8.40) <sup>a</sup>	1.5645	0.70	0.1259	0.53	0.0953	0.41	0.0737
298.15	8.20 (8.10) <sup>a</sup>	1.4746	0.60	0.1079	0.38	0.0683	0.36	0.0647
303.15	8.65 (8.40) <sup>a</sup>	1.5555	0.68 (0.70) <sup>b</sup>	0.1223	0.40 (0.40) <sup>b</sup>	0.0719	0.38	0.0683
308.15	8.90 (8.60) <sup>a</sup>	1.6005	0.70	0.1259	0.55	0.0989	0.44	0.0791
313.15	9.00 (8.80) <sup>a</sup>	1.6184	0.73	0.1313	0.60	0.1079	0.49	0.0881
318.15	9.10	1.6364	0.80	0.1439	0.61	0.1097	0.50	0.0899

Standard uncertainties ( $u$ ) are  $u(T) = \pm 0.1$  K,  $u(p) = \pm 0.002$  MPa,  $u(\text{CMC}) = \pm 0.1 \times 10^{-3} \text{ mol kg}^{-1}$ , and  $u(X_{\text{CMC}}) = \pm 0.02 \times 10^{-4}$  (level of confidence = 0.68)

<sup>a</sup> Reference [18]

<sup>b</sup> Reference [11]



**Fig. 3** Comparison of CMC as a function of temperature for SDS in the aqueous solutions containing  $0.01 \text{ mol kg}^{-1}$   $\text{Pr}_4\text{NBr}$  (black filled squares),  $\text{Bu}_4\text{NBr}$  (red filled circles) and  $\text{Pen}_4\text{NBr}$  (blue filled triangles)

increase of dispersion forces and therefore promote micelle formation. The dominance of this factor has been observed in the literature [25–27]. However, the presence of hydrocarbon chains in the case of quaternary ammonium salts may result in penetration of some of the alkyl chains into the micellar core of the surfactant as a result of hydrophobic interactions. The remarkable decrease in CMC of the surfactant as the size of the alkyl chain

increases also supports the dominance of hydrophobic interactions [11, 28–30].

#### Thermodynamics of Micellization

In order to further interpret the surfactant–tetraalkylammonium bromide salt interactions, various thermodynamic parameters of micellization have been calculated and explained. According to the charged pseudo-phase model of micellization, the standard free energy ( $\Delta G_m^o$ ) of micelle formation per mole of surfactant is given by

$$\Delta G_m^o = (2 - \alpha)RT(\ln X_{\text{CMC}}) \quad (1)$$

where  $R$  is the gas constant and  $T$  is the temperature in kelvin ( $K$ ).

The standard enthalpy of micelle formation ( $\Delta H_m^o$ ) can be derived by Van't Hoff equation

$$\Delta H_m^o = -(2 - \alpha)RT^2 \{d(\ln X_{\text{CMC}})/dT\} \quad (2)$$

where  $d(\ln X_{\text{CMC}})/dT$  is the slope of the plot of  $\ln X_{\text{CMC}}$  against temperature at each temperature calculated by fitting  $\ln X_{\text{CMC}}$  versus  $T$  data to a second-order polynomial and differentiation.

The standard entropy of micelle formation ( $\Delta S_m^o$ ) was calculated from the relation

$$\Delta S_m^o = (\Delta H_m^o - \Delta G_m^o)/T \quad (3)$$

The thermodynamic parameters of micellization for SDS in different aqueous solutions of tetraalkylammonium

bromides at different temperatures are presented in Table 3.

The  $\Delta H_m^o$  values for SDS were endothermic when  $T < T^*$  (where  $T^*$  is the temperature at which CMC was minimum) and became exothermic and larger in magnitude when  $T > T^*$  for all the studied systems (Table 3). At low temperatures, the positive  $\Delta H_m^o$  values were probably due to the destruction of structured (or hydrogen-bonded) water

molecules around hydrophobic alkyl chains of surfactant monomers. However, such hydrophobic interactions become increasingly insignificant and the hydration of water molecules around the hydrophilic head groups may result into negative  $\Delta H_m^o$  values at higher temperatures. The positive  $\Delta H_m^o$  values show the dominance of hydrophobic interactions in micellization, whereas negative  $\Delta H_m^o$  values suggest the importance of London dispersion interactions as an alternative force for micellization [28, 31]. The tetraalkylammonium salts seem to add to this effect which is clearly reflected by the large negative  $\Delta H_m^o$  values for these salts.

The  $\Delta S_m^o$  values are positive and show a decrease with rise in temperature. This can be explained by considering two opposing processes that occur during aggregation viz. (1) disruption of three-dimensional water structure around the hydrocarbon tails of surfactant monomers due to aggregation into micelles resulting in increased randomness and hence increase in the entropy of the system and (2) the arrangement of disordered monomers into more ordered surfactant aggregates leading to a negative change in entropy [31, 32]. As can be seen from Table 3, the decrease in  $\Delta S_m^o$  values with temperature may be due to the dominance of the latter process. Hence, it appears that the process of micellization of SDS is entropy controlled at low temperatures but enthalpy controlled at high temperatures in all the studied systems. Such an effect of temperature on  $\Delta H_m^o$  and  $\Delta S_m^o$  values of ionic surfactants has also been reported in the literature [19, 21, 22, 24].

From Table 3 it can be inferred that  $\Delta G_m^o$  values are negative in all the studied cases suggesting the spontaneous micellization of SDS [19]. Temperature as well as type of electrolytes seems to have a negligible effect on  $\Delta G_m^o$  values. However,  $\Delta G_m^o$  is the sum of the enthalpic ( $\Delta H_m^o$ ) and entropic ( $-T\Delta S_m^o$ ) contributions. As the temperature rises, the contribution of entropy to free energy decreases, whereas that of enthalpy increases (Fig. 4).

#### Enthalpy–Entropy Compensation for SDS Micellization

The dependence of the enthalpy of micellization on the entropy of micellization follows a straight line equation described by the relation

$$\Delta H_m^o = \Delta H_m^* + T_c \Delta S_m^o \quad (4)$$

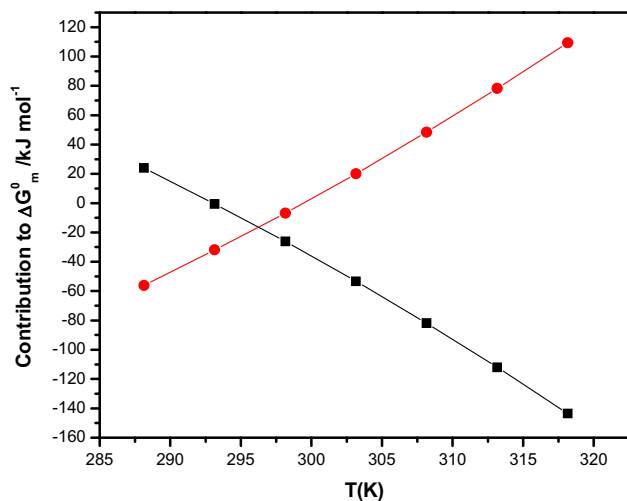
where  $T_c$ , the compensation temperature, quantifies the desolvation due to the micellization and  $\Delta H_m^*$  measures the chemical aggregation of the surfactant monomers to form the micelles. The slope,  $T_c$  from  $\Delta H_m^o$  versus  $\Delta S_m^o$  plots, characterizes both solute–solvent and solute–solvent interactions, whereas  $\Delta H_m^*$  interprets the solute–solute interactions [33].

**Table 3** Degree of counterion dissociation and standard thermodynamic parameters of micellization for aqueous solution of SDS in the absence and presence of tetraalkylammonium bromide salts at different temperatures ( $T/K$ ) and experimental pressure,  $p = 0.099$  MPa

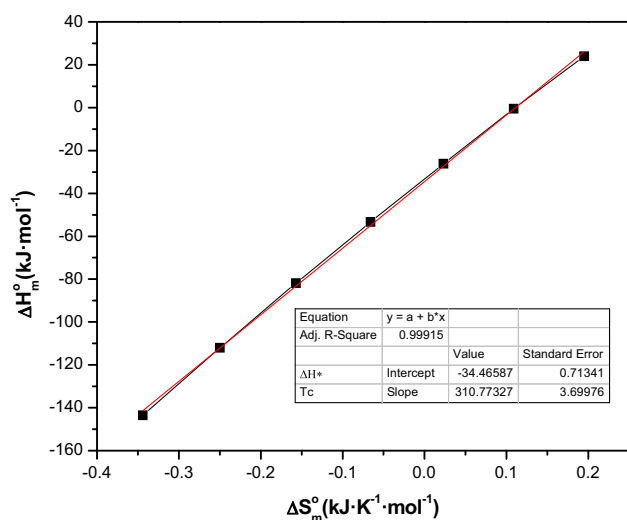
$T/K$	$\alpha$	$\Delta G_m^o$ (kJ mol <sup>-1</sup> )	$\Delta H_m^o$ (kJ mol <sup>-1</sup> )	$\Delta S_m^o$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )
0.00 mol kg <sup>-1</sup> R <sub>4</sub> NBr				
288.15	0.458	-32.31	23.96	0.195
293.15	0.474	-32.59	-0.53	0.109
298.15	0.491	-33.00	-26.20	0.023
303.15	0.499	-33.17	-53.32	-0.066
308.15	0.508	-33.41	-81.85	-0.157
313.15	0.514	-33.77	-112.05	-0.250
318.15	0.523	-34.06	-143.55	-0.344
[C <sub>12</sub> H <sub>28</sub> NBr] = 0.01 mol kg <sup>-1</sup>				
288.15	0.46	-41.52	113.45	0.538
293.15	0.45	-42.62	56.17	0.337
298.15	0.524	-41.84	-5.76	0.121
303.15	0.49	-43.05	-70.70	-0.091
308.15	0.58	-41.05	-131.48	-0.293
313.15	0.552	-42.38	-204.57	-0.518
318.15	0.553	-42.67	-279.20	-0.743
[C <sub>16</sub> H <sub>36</sub> NBr] = 0.01 mol kg <sup>-1</sup>				
288.15	0.413	-43.81	186.78	0.800
293.15	0.521	-41.67	98.79	0.479
298.15	0.419	-46.61	19.27	0.221
303.15	0.427	-46.95	-72.72	-0.085
308.15	0.443	-45.97	-169.03	-0.399
313.15	0.527	-43.86	-257.61	-0.683
318.15	0.524	-44.59	-362.09	-0.998
[C <sub>20</sub> H <sub>44</sub> NBr] = 0.01 mol kg <sup>-1</sup>				
288.15	0.548	-40.63	102.33	0.496
293.15	0.495	-43.35	48.48	0.313
298.15	0.466	-45.43	-13.50	0.107
303.15	0.377	-48.65	-85.45	-0.121
308.15	0.394	-48.33	-159.64	-0.361
313.15	0.489	-45.79	-225.33	-0.573
318.15	0.562	-44.2	-290.32	-0.774

Standard uncertainties ( $u$ ) are  $u(T) = \pm 0.1$  K,  $u(p) = \pm 0.002$  MPa,  $u(\alpha) = \pm 0.03$ ,  $u(\Delta G_m^o) = \pm 0.03$  kJ mol<sup>-1</sup>,  $u(\Delta H_m^o) = \pm 0.04$  kJ mol<sup>-1</sup> and  $u(\Delta S_m^o) = \pm 0.003$  kJ K<sup>-1</sup> mol<sup>-1</sup> (level of confidence = 0.68)

In the present study, a good correlation between  $\Delta H_m^0$  and  $\Delta S_m^0$  values of SDS in all the cases was observed with the correlation coefficient lying near to 0.998 (Fig. 5). The



**Fig. 4** Contribution of enthalpy  $\Delta H_m^0$  (black filled squares) and entropy  $-T\Delta S_m^0$  (red filled circles) to free energy of SDS in the aqueous solution



**Fig. 5** Enthalpy–entropy compensation plot for SDS in aqueous solution

**Table 4**  $\Delta H_m^*$  and  $T_c$  values from enthalpy–entropy compensation plots of SDS in the absence and presence of tetraalkylammonium bromide salts at different temperatures ( $T/K$ ) and experimental pressure,  $p = 0.099$  MPa

[R <sub>4</sub> NBr]	Regression coefficient, $R^2$	$\Delta H_m^*$ (kJ mol <sup>-1</sup> )	$T_c$ (K)
Pure water	0.9992	-34.46	310.77
[C <sub>12</sub> H <sub>28</sub> NBr] = 0.01 mol kg <sup>-1</sup>	0.9990	-46.29	306.00
[C <sub>16</sub> H <sub>36</sub> NBr] = 0.01 mol kg <sup>-1</sup>	0.9993	-50.48	305.57
[C <sub>20</sub> H <sub>44</sub> NBr] = 0.01 mol kg <sup>-1</sup>	0.9998	-48.70	309.43

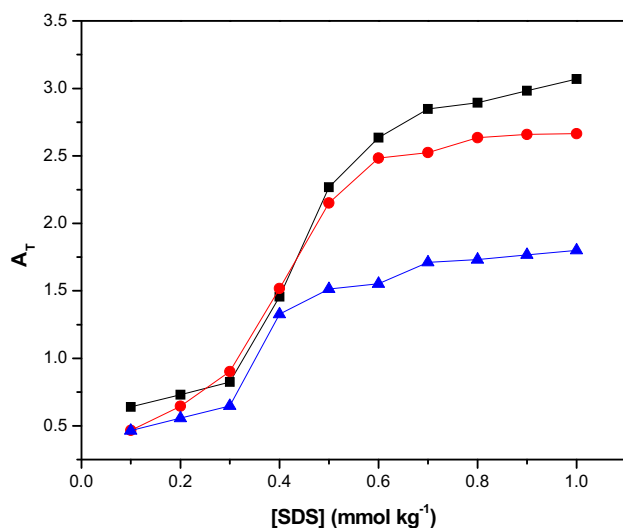
Standard uncertainties ( $u$ ) are  $u(T_c) = \pm 0.1$  K,  $u(p) = \pm 0.002$  MPa,  $u(\Delta H_m^*) = \pm 0.04$  kJ mol<sup>-1</sup> (level of confidence = 0.68)

parameter  $\Delta H_m^*$  is the enthalpy when  $\Delta S_m^0 =$  zero and indicates the stability of micelles. The stability of micelles increases with the increase in the negative values of  $\Delta H_m^*$ . It is clear from Table 4 that the value of  $\Delta H_m^*$  shows a slight increase as the length of alkyl chain of tetraalkylammonium bromide salt increases. In other words, the increase in the steric hindrance with longer chains probably reduces the contribution of the chemical part towards micellization [34]. The value for compensation temperature  $T_c$  lies in the well-documented range of approximately 301–307 K for various sodium alkylsulphate surfactants [35].

#### Spectroscopic Measurements

UV–Vis spectroscopy provides supporting evidence about the formation of micelles in solution. The spectra with varying concentration of surfactant yield important information regarding the interaction between pyrene and surfactant. The simple UV–Vis absorbance spectrum of pyrene in water gives four strong peaks at 242, 272, 320, and 336 nm due to multiple rings [36]. The total absorbance ( $A_T$ ) i.e. the sum of absorbance of all four strong peaks is plotted against the concentration of surfactant in Fig. 6. At low surfactant concentration, there is a very small increase in the absorbance as pyrene resides in a polar aqueous environment. When the concentration reaches the CMC value, there is a sudden increase in absorbance because pyrene resides in a non-polar environment provided by SDS micelles [37]. Also the lack of hydrophilicity of pyrene helps it to stay at the interface. This reduces the hydrophobic repulsions between water and pyrene [38]. It also reveals the importance of ionic interactions between the pyrene molecules and ionic headgroup of surfactant. After the micellization, there is a slight increase in absorbance. It has been observed that the absorbance of peaks increases with concentration of surfactant. In all the absorbance–surfactant concentration profiles,  $A_T$  increases sigmoidally with concentration and thus a sigmoidal Boltzmann equation (SBE) [39] can be fitted to evaluate the CMC values reported in Table 5.





**Fig. 6** Variation of sum of absorbance ( $A_T$ ) with [SDS] in the aqueous solutions containing  $0.01 \text{ mol kg}^{-1}$   $\text{Pr}_4\text{NBr}$  (black filled squares),  $\text{Bu}_4\text{NBr}$  (red filled circles) and  $\text{Pen}_4\text{NBr}$  (blue filled triangles)

#### Fluorescence Probe Study

Fluorescence probe analysis is a useful method for studying micellar aggregates and membranes [40, 41]. In the present study, pyrene has been used as a fluorescence probe to obtain the CMC of SDS in the absence and presence of tetraalkylammonium bromide salts. The ratio of the fluorescence intensity of the highest vibrational band energy to that of the third highest vibrational band energy i.e. ( $I_1/I_3$ ) has been taken as a measure of polarity of the environment and hence has been used to study the formation of the surfactant micelles [42, 43]. Figure 7 shows the plots of  $I_1/I_3$  versus [SDS] in the presence of tetraalkylammonium bromide salts  $\text{R}_4\text{NBr}$ . Pyrene senses the polar environment at low concentration of surfactant, resulting in high values of ratio  $I_1/I_3$ . The further addition of surfactant makes the environment around pyrene hydrophobic due to the formation of micelle, resulting in a drastic decrease in  $I_1/I_3$ .

**Table 5** CMC ( $\text{mol kg}^{-1}$ ) for aqueous solutions of SDS in the absence and presence of tetraalkylammonium bromide salts at room temperature ( $T/K$ ) and experimental pressure,  $p = 0.099 \text{ MPa}$

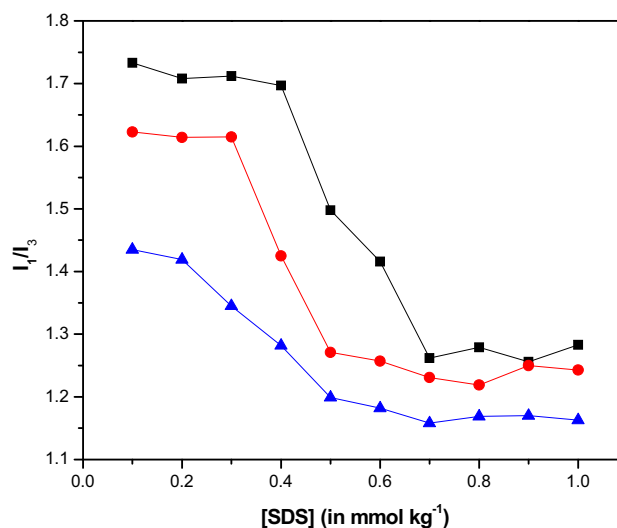
[ $\text{R}_4\text{NBr}$ ]	$10^{-3}$ CMC		
	From conductivity	From fluorescence	From UV-Vis
Pure water	8.20	8.10 (8.00 <sup>a</sup> , 8.20 <sup>b</sup> )	8.11 (7.80 <sup>c</sup> )
$[\text{C}_{12}\text{H}_{28}\text{NBr}] = 0.01 \text{ mol kg}^{-1}$	0.60	0.52	0.44
$[\text{C}_{16}\text{H}_{36}\text{NBr}] = 0.01 \text{ mol kg}^{-1}$	0.38	0.40	0.40
$[\text{C}_{20}\text{H}_{44}\text{NBr}] = 0.01 \text{ mol kg}^{-1}$	0.36	0.36	0.37

Standard uncertainties ( $u$ ) are  $u(T) = \pm 0.1 \text{ K}$ ,  $u(p) = \pm 0.002 \text{ MPa}$ ,  $u(\text{CMC}) = \pm 0.1 \times 10^{-3} \text{ mol kg}^{-1}$  (level of confidence = 0.68)

<sup>a</sup> Ref. [44]

<sup>b</sup> Ref. [45]

<sup>c</sup> Ref. [46]



**Fig. 7** Variation of ratio  $I_1/I_3$  with [SDS] in the aqueous solutions containing  $0.01 \text{ mol kg}^{-1}$   $\text{Pr}_4\text{NBr}$  (black filled squares),  $\text{Bu}_4\text{NBr}$  (red filled circles) and  $\text{Pen}_4\text{NBr}$  (blue filled triangles)

Thus the fitting of Boltzmann equation to these sigmoidal curves allows the determination of the CMC. An interesting feature is that the  $I_1/I_3$  values follow the order  $\text{Pr}_4\text{NBr} > \text{Bu}_4\text{NBr} > \text{Pen}_4\text{NBr}$ . These results showed that as the hydrophobicity of the salt increased, the electrostatic interactions decreased as discussed in conductivity studies and hence the values of  $I_1/I_3$ .

The CMC values of SDS in the absence and presence of tetraalkylammonium bromide salts obtained from the fluorescence studies are reported in Table 5 along with those from literature [44–46]. The values obtained by this method were close to those obtained by conductivity and UV-Vis spectroscopic methods. The small difference in the CMC values may be due to the different methods adopted. However, the CMC values followed the same trend: no additive  $>$   $\text{Pr}_4\text{NBr} > \text{Bu}_4\text{NBr} > \text{Pen}_4\text{NBr}$ . These results also showed that the addition of tetraalkylammonium bromide salts effectively decreased the CMC value for aqueous solution of SDS as a result of increased hydrophobicity of the salts.

## Conclusion

The addition of cationic tetraalkylammonium bromide salts to anionic SDS micelles promotes micellization of the surfactant. This may be due to the (1) strong ionic attractions between the oppositely charged ions of the surfactant and the bromide salt and (2) hydrophobic interactions due to the penetration of long alkyl chains of QUATS into the hydrophobic core of the micelles. It has been also confirmed that the longer the hydrocarbon chain of the bromide salt are, the stronger the interactions are. Furthermore, the investigation of thermodynamic parameters reveals that the micellization of SDS is spontaneous and is mainly enthalpy driven in the presence of QUATS. The enthalpy of micellization correlates well with the entropy of micellization. The results from the conductivity measurements are strongly supported by those obtained from fluorescence and UV–Vis probe studies.

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