

Self-Aggregation of Alkyl (C₁₀-, C₁₂-, C₁₄-, and C₁₆-) Triphenyl Phosphonium Bromides and Their 1:1 Molar Mixtures in Aqueous Medium: A Thermodynamic Study

M. Prasad and S. P. Moulik*

Centre for Surface Science, Department of Chemistry, Jadavpur University,
Kolkata-700032, West Bengal, India

Amy MacDonald and R. Palepu*

Department of Chemistry, St. Francis Xavier University, Nova Scotia, Canada

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The self-aggregation of alkyl (C₁₀-, C₁₂-, C₁₄-, and C₁₆-) triphenyl phosphonium bromide surfactants (ATPBs) and their equimolar binary mixtures in aqueous medium was studied microcalorimetrically and conductometrically at different temperatures. The thermograms of C₁₀- and C₁₂TPB have shown differences in behavior from those of C₁₄- and C₁₆TPB. Their binary (1:1 mol/mol) mixtures with C₁₀- or C₁₂TPB as one of the components have also evidenced differences in behavior. Individually as well as in mixed conditions, the ATPBs have indicated formation of two states of aggregation corroborated by both calorimetric and conductometric measurements. On the basis of the results, the thermodynamic parameters, free energy (ΔG_m°), enthalpy (ΔH_m°), entropy (ΔS_m°), and specific heat ($\Delta C_{p,m}^\circ$), of micellization have been evaluated. The specific heat has been found to vary linearly with the carbon number in the ATPB chain. The ΔH_m° and ΔS_m° values for the micellization of the pure ATPBs have nicely compensated each other. The free energy of transfer of a mole of CH₂ from an aqueous environment to a micelle was found to be -2.0 kJ mol^{-1} .

Introduction

In view of important uses and applications of surfactants and micelles in chemical, biochemical, pharmaceutical, and industrial fields, detailed fundamental studies of the existing and newer amphiphilic systems are in progress. While surfactants in general find wide applications in solubilization, stabilization, and detergency,^{1,2} their cationic representatives find special uses as antifungal, antibacterial, and antiseptic agents.³ Like anionics, they can interact with synthetic and biopolymers,^{4–9} and the reacted products may form useful gels or viscous dispersions. Very recently, the interaction of cationic surfactants and lipids with DNA has been stressed with reference to transfection and gene therapy in biotechnology.^{10–14}

The majority of fundamental studies on solution behaviors of cationic surfactants have been made on alkyltrimethylammonium bromides and alkylpyridinium chlorides.^{1,15} Surface chemical studies on alkyl triphenyl phosphonium bromides (ATPBs) are very limited. Their bulky hydrophobic groups in the head are expected to play a special role in their solution and interfacial behaviors, viz., self-aggregation, interfacial adsorption, interaction with polymers, etc. Recently, Jiang et al.¹⁶ have reported the synthesis of dodecyltriphenyl phosphonium bromide and its critical micellar concentration (cmc) and micellar aggregation number. Bakshi et al.^{17–19} have studied the mixed systems of tetradecyl triphenyl phosphonium bromide with alkyl pyridinium chloride and trimethylammonium bromide with reference to cmc determination and molecular interaction. There are scanty reports in favor of two states of aggregation (considered as two cmcs) of binary mixtures of long-chain

cationic surfactants.^{20,21} Two different forms of aggregates of cetyltrimethylammonium bromide (CTAB) have been also reported.²² Evidence for more than one state of self-association (double cmcs or otherwise) is thus expected for other cationic surfactants. This issue needs substantiation, and we have contemplated that microcalorimetry could be a potential method for detection if the two micellization processes have wide differences in cmc as well as in enthalpy.

In this work, we have investigated the self-aggregation behavior of decyl, dodecyl, tetradecyl, and hexadecyl triphenyl phosphonium bromides and the thermodynamics of the process essentially by the method of isothermal titration calorimetry (ITC) with a supportive method of conductometry. For understanding the thermodynamics of a process, direct determination of enthalpy by calorimetry is a better proposition than the indirect van't Hoff procedure, for the latter often ends up with incorrect evaluation of enthalpy if the equilibrium constants (cmc for micelles) are determined within a narrow range of temperature. Along with the micellization of pure ATPBs, we have also herein examined the self-aggregation of binary (1:1 molar ratio) mixtures of the ATPBs to understand their ideality/nonideality aspects by way of mutual interaction.

Experimental Section

Materials. The ATPBs used in this study were decyl, dodecyl, tetradecyl, and hexadecyl triphenyl phosphonium bromides obtained from Caledon Laboratories, LTD, of Canada (distributors for Lancaster Synthesis of England). The C₁₀- and C₁₂TPB molecules have shown anomaly in surface tension measurements (minima in surface tension–concentration curves were observed). These compounds were purified first by partitioning between water and petroleum ether and then discarding the

* Authors to whom correspondence may be addressed. Fax: 091334146266 (S.P.M.); 9028672414 (R.P.). E-mail: spmcss@yahoo.com (S.P.M.); rpalepu@stfx.ca (R.P.).

petroleum ether fraction and collecting the aqueous fraction. The concentration of the aqueous fraction was determined from absorption measurements after proper dilution at $\lambda = 274.8$ nm (absorption maximum) in terms of Beers law. This was justified since the absorbances of the solution before and after partitioning were only minorly different so that the percentage of the nonionic surface-active impurity was very small. The compounds thus purified evidenced no minimum in surface tension, and the cmcs determined from the γ (surface tension) – $\log C$ (concentration) plots were 7.2 and 2.0 mM for C_{10} - and C_{12} -TPB, respectively (illustrations not shown).

Doubly distilled conductivity water was used for solution preparation. All measurements were taken under controlled constant temperature conditions either by placing samples in a water bath or circulating water at a constant temperature through the solution-holding compartment of the instrument.

Methods. Conductometry. The conductivity measurements were performed with an EcoScan conductivity meter series (Singapore). In this procedure, 10 mL of water was placed in a thermostated container (having a temperature accuracy of ± 0.1 °C) and surfactant solution of known concentration was progressively added using a microsyringe. The specific conductance was measured after each addition followed by thorough mixing and temperature equilibration. The cmc values were estimated from the break points in the conductance–concentration plots. The accuracy of measurements was within $\pm 2\%$.

Microcalorimetry. The ITC experiments were performed with an OMEGA isothermal titration calorimeter (Microcal, Inc., Northampton, USA). In an experiment, 1.325 and 1.8 mL of water were taken in the reaction and reference cells, respectively. The injection syringe (350 μ L) was filled with a concentrated solution of a surfactant (~ 20 times its cmc), which was injected at 4 min intervals in 32 steps (10 μ L in each step) to the pure water in the calorimeter cell under constant stirring (~ 350 rpm) conditions at a specified temperature. The heat flow in or out for each injection in the reaction cell depending on the endothermicity or the exothermicity of the dilution process was recorded in the calorimeter. The differential enthalpies of dilution per mole of the injectant were calculated with the help of MICROCAL ORIGIN 2.9 software and plotted against the [surfactant] to derive the cmc and the enthalpy of dilution and hence micellization.

Results and Discussion

Behavior of Pure Surfactant. The microcalorimetric results (differential enthalpy of dilution) of the four ATPBs (C_{10} -, C_{12} -, C_{14} -, and C_{16} -TPB) at five different temperatures, 298, 303, 308, 318, and 328 K are illustrated in Figures 1 and 2. The curves have shown different features. At lower temperatures, the profiles for both C_{10} - and C_{12} -TPB evidenced formation of maxima, as if two processes, one endothermic and the other exothermic, were coupled together. With increasing temperature, the endothermic feature diminished and the exothermic feature enhanced, making the process totally exothermic at higher temperature. The features for C_{14} - and C_{16} -TPB were all exothermic at all the studied temperatures. Since the compounds were homologues, the two opposite features at lower temperatures for the lower members (C_{10} - and C_{12} -TPB) were interesting observations. It was considered to have arisen from two kinds of self-aggregation in two concentration regions. The threshold concentrations of the aggregation states were considered as the cmcs of the two forms. The forms were entities morphologically different but distinct; the corresponding threshold concentrations were cmc_1 and cmc_2 . The thermograms of C_{14} - and C_{16} -TPB

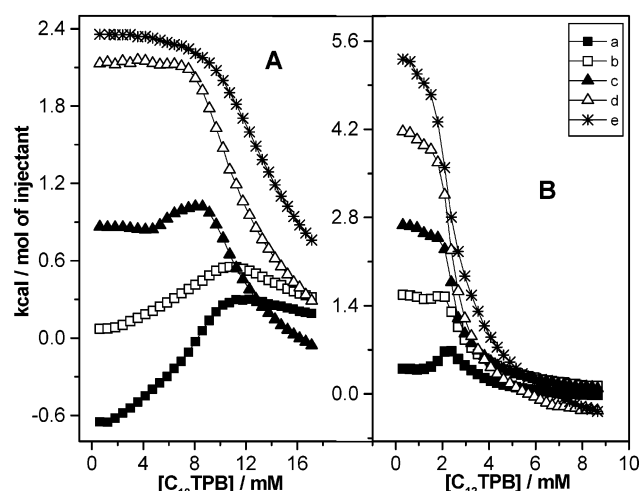


Figure 1. The differential enthalpy of dilution of C_{10} - and C_{12} -TPB at five different temperatures: (a) 298 K; (b) 303 K; (c) 308 K; (d) 313 K; and (e) 318 K.

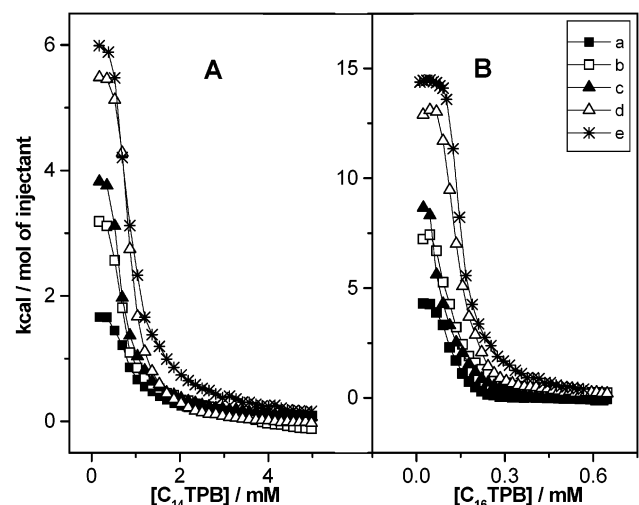


Figure 2. The differential enthalpy of dilution of C_{14} - and C_{16} -TPB at five different temperatures: (a) 298 K; (b) 303 K; (c) 308 K; (d) 313 K; and (e) 318 K.

evidenced one kind of micelle formation. On the basis of this rationale, the ITC experimental curves were processed following the Sigmoidal–Boltzmann fitting (SBF) procedure proposed by us^{23,24} to obtain the aggregation thresholds and the enthalpies of the processes. For evaluation, two halves of the profiles (left and right) were separately considered for fitting into the SBF procedure as evidenced in Figure 3. The results are presented in Table 1.

At this stage, for supportive evidence regarding two self-aggregation states, results of conductometric measurements on pure ATPBs at 298 K are presented in Figure 4. All four ATPBs have evidenced formation of two states of aggregation, which was in contrast with the calorimetric observations for both C_{14} - and C_{16} -TPB. They are illustrated in expanded forms in parts A₁ and A₂ of Figure 4 for C_{10} -TPB and B₁ and B₂ of Figure 4 for C_{12} -TPB. The results are also presented in Table 1. The two aggregation thresholds for C_{10} - and C_{12} -TPB by conductometry agreed with calorimetry. Both C_{14} - and C_{16} -TPB have evidenced formation of two breaks in the conductometric plots (parts C and D). The first corresponded fairly well with the calorimetric threshold. The second break was a manifestation of an altered association (the existing micelles might have undergone secondary aggregation or change in shape and size), which was not

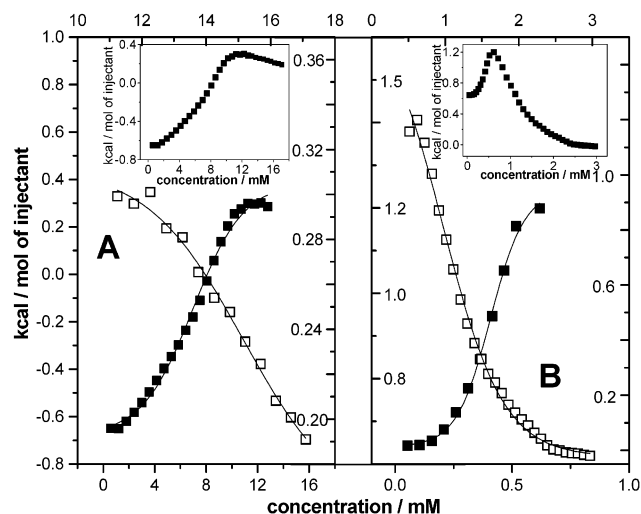


Figure 3. The differential enthalpy of dilution of (A) C_{10} TPB at 298 K and (B) TX-100, CTAB 1:1 mol/mol mixture at 298 K. Solid and open squares represent the left and right profiles of the experimental curves. Inset shows the experimental curve obtained.

TABLE 1: cmc^a and β Values of the ATPBs at Different Temperatures Obtained from Calorimetry and Conductometry

surfactant	T/K	calorimetry		conductometry	
		cmc_1	cmc_2	$cmc_1 (\beta_1)$	$cmc_2 (\beta_2)$
C_{10} TPB	298	7.26	15.1	7.21 (0.133)	15.0 (0.536)
	303	6.70	14.3		
	308	5.40	12.2		
	318		11.2		
	328		13.0		
C_{12} TPB	298	1.80	2.67	1.82 (0.396)	2.33 (0.471)
	303	1.53	2.53		
	308		2.63		
	318		2.54		
	328		3.16		
C_{14} TPB	298		0.800	0.77 (0.441)	2.30 (0.556)
	303		0.690		
	308		0.780		
	318		0.860		
	328		1.1		
C_{16} TPB	298		0.110	0.14 (0.308)	0.34 (0.520)
	303		0.095		
	308		0.070		
	318		0.125		
	328		0.134		

^a The cmc values are expressed in mM unit. From fluorescence-quenching measurements of the pure ATPBs, indication about their first stage of aggregation can be obtained. The tensiometric method has evidenced cmc of C_{10} - and C_{12} TPB as 8.0 and 2.0 mM, respectively, at 298 K.

sensed in calorimetry for a small/undetectable enthalpy change for the process.

We have tried tensiometric method to determine the cmc of the ATPBs. Evidence in favor of the first cmc was only observed. After the threshold concentration of cmc_1 was reached, the surface tension decreased to a large extent and the property lost its sensitivity at higher concentration. Thus, indication for cmc_2 was not realized. The cmc_1 values obtained from tensiometry for C_{10} - and C_{12} TPB are presented in the footnote of Table 1. We have also used the differential specific conductance (k) plots of $\Delta k/\Delta \bar{C}$ vs square root of mean concentration ($\bar{C}^{1/2}$), where $\bar{C} = (C_i + C_{i+1})/2$, to determine the cmc .²⁵ Two stage Sigmoidal curves were obtained, of which the distinct illustrations were analyzed by the SBF method to derive the $cmcs$ (plots not shown). The results agreed within $\pm 2\%$ of those obtained

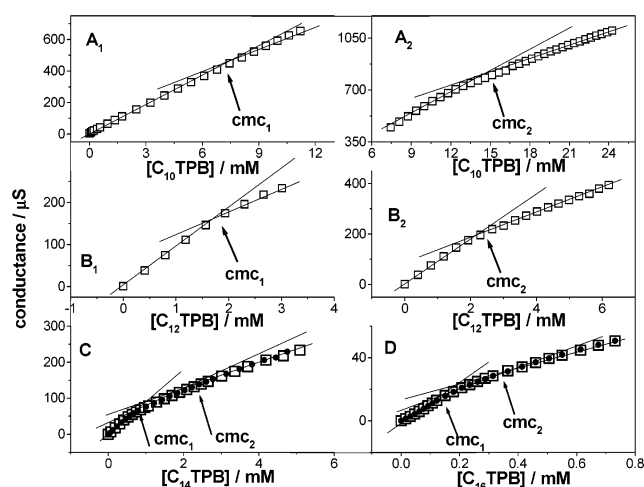


Figure 4. Results of conductometric measurements at 298 K for the four ATPBs: (A₁) cmc_1 of C_{10} TPB; (A₂) cmc_2 of C_{10} TPB; (B₁) cmc_1 of C_{12} TPB; (B₂) cmc_2 of C_{12} TPB; (C) cmc_1 and cmc_2 of C_{14} TPB; and (D) cmc_1 and cmc_2 of C_{16} TPB. Solid circles and open squares represent two different sets of experiments done.

from the specific conductance vs concentration plots. Both procedures were thus acceptable. In this study, data analysis was done based on calorimetric observations. The conductance method gave confirmation or support to the results. It has as well demonstrated the existence of a second cmc , which the thermometric method failed to resolve.

In Table 1, the fraction of counterion bound to the aggregates ($\beta = 1 - S_f/S_i$) obtained from the ratio of the post and preaggregation slopes S_f and S_i , respectively, in the conductance-concentration plots are also presented in parentheses in columns 5 and 6.

It is emphasized here that for C_{14} - and C_{16} TPB, the conductometric cmc_1 has been found to be equivalent to the single cmc obtained by calorimetry. This has been assigned as cmc_2 to be in line with the second cmc of the other two homologues C_{10} - and C_{12} TPB in terms of exothermicity of their micellization process. The related thermodynamic analysis of the studied ATPBs was, therefore, based on calorimetric results.

The threshold for the first state of association for both C_{10} - and C_{12} TPB decreased with temperature whereas the second passed through a minimum. For C_{14} - and C_{16} TPB, the threshold also passed through minima. By fitting the cmc dependence on temperature to a second-degree polynomial equation, the minimum temperatures for C_{10} -, C_{12} -, C_{14} -, and C_{16} TPB were found to be 315, 309, 305, and 308 K, respectively. Ionic surfactants are known to show a minimum in cmc in the range of 298–303 K.²⁶ Surfactants having higher hydrophobicity (like perfluorocarbons) show minimum in cmc at temperature > 303 K. The ATPBs have shown the minimum cmc temperature > 303 K (C_{10} TPB produced a higher value than others did). The three phenyl rings in the headgroups of ATPBs made them more hydrophobic, resulting in a higher temperature for cmc minimum.

The second stage of aggregation of C_{10} - and C_{12} TPB and the first stage of aggregation of C_{14} - and C_{16} TPB (by conductometry equivalent to the single stage by calorimetry) were considered as the stages for normal micelle formation of the amphiphiles. These association processes were all exothermic. The absence of another aggregation in the thermal measurements on C_{14} - and C_{16} TPB was due to low enthalpy for the other association process. The observations of the phenomenon from repeated conductometric experimentations (thrice) supported the low-

TABLE 2: Thermodynamic Parameters^a for the Micellization of the ATPBs

surfactant	T/K	10 ⁵ (cmc ₁) cmc ₂ ^b	(ΔG _{m1} ^o)	ΔG _{m2} ^o /kJ mol ⁻¹	(ΔH _{m1} ^o)	ΔH _{m2} ^o /kJ mol ⁻¹	(ΔS _{m1} ^o)	ΔS _{m2} ^o /Jmol ⁻¹ K ⁻¹	(ΔCp _{m1} ^o) ^d	ΔCp _{m2} ^o /Jmol ⁻¹ K ⁻¹
C ₁₀ TPB	298	(13.1) 27.2	(-25.1)	-31.2	(3.97)	-0.463	(97.5)	103	(-295)	-212
	303	(12.1) 25.8	(-25.3)	-32.0	(1.97)	-0.960	(91.5)	102		
	308	(9.7) 21.9	(-25.9)	-33.1	(1.02)	-2.62	(90.3)	99		
	318	20.2	-34.6		-5.84		90			
	328	23.4	-35.0		-6.10		88			
C ₁₂ TPB	298	(3.24) 4.81	(-35.7)	-36.2	(1.15)	-2.37	(123)	113	(-192)	-595
	303	(2.76) 4.56	(-36.3)	-37.1	(0.19)	-5.13	(122)	105		
	308	4.74	-37.5		-8.77		93			
	318	4.58	-39.0		-15.5		73			
	328	4.39	-39.2		-19.7		59			
C ₁₄ TPB	298	1.44	-39.8		-5.96		113			-684
	303	1.24	-41.0		-13.2		92			
	308	1.41	-41.2		-15.5		84			
	318	1.55	-42.2		-21.7		64			
	328	1.95	-42.6		-27.9		45			
C ₁₆ TPB	298	0.198	-42.6		-19.9		76			-1335
	303	0.171	-43.8		-27.4		54			
	308	0.126	-45.5		-34.7		35			
	318	0.225	-44.9		-51.4		-20			
	328	0.241	-46.1		-58.6		-38			

^a The estimated errors in free energy, enthalpy, and entropy were ± 3 , ± 5 , and $\pm 8\%$, respectively. ^b cmc expressed in mole fraction unit. ^c The β values used for calculating ΔG_m^o were β_1 for C₁₀- and C₁₂TPB and β_2 for C₁₄- and C₁₆TPB, respectively. ^d $\Delta C_{p,m1}^o$ value for C₁₂TPB contained a large error for estimation based on two temperatures.

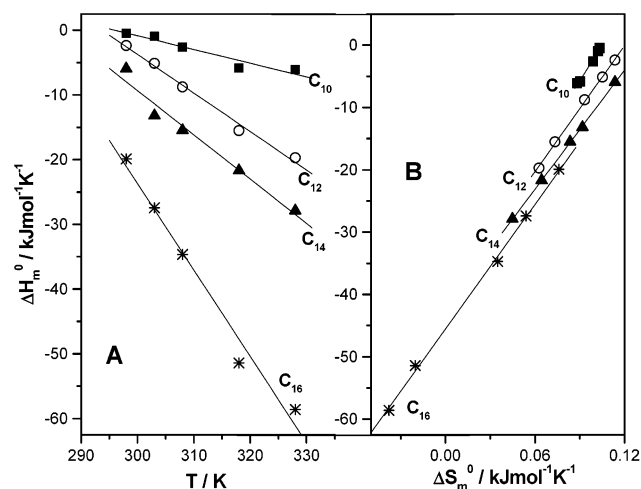


Figure 5. (A) Linear correlation of ΔH_m^o with temperature: (a) C₁₀TPB; (b) C₁₂TPB; (c) C₁₄TPB; (d) C₁₆TPB. (B) Compensation plots for the four ATPBs: (a) C₁₀TPB; (b) C₁₂TPB; (c) C₁₄TPB; (d) C₁₆TPB.

enthalpy rationale. It is to be noted that, in line with literature reports,^{27,28} the measured enthalpies by calorimetry were considered as the standard enthalpy changes for the amphiphile aggregation process. The linear correlation of the enthalpy of micellization (ΔH_{m2}^o) of C₁₀-, C₁₂-, C₁₄-, and C₁₆TPB with temperature are exemplified in Figure 5A. The slopes equivalent to the specific heats ($\Delta C_{p,m2}^o$) of micellization were -212, -595, -684, and -1335 J mol⁻¹ K⁻¹ for C₁₀-, C₁₂-, C₁₄-, and C₁₆TPB, respectively. The $\Delta C_{p,m2}^o$ values were expectedly negative, and the magnitudes increased with increasing alkyl chain length of the molecule commensurate with break down of their enhanced hydrophobically hydrated water (or iceberg) prior to monomer self-association. The $\Delta C_{p,m2}^o$ varied linearly with the carbon number in the alkyl chains of the ATPBs and fitted to a linear equation of the form

$$\Delta C_{p,m2}^o = 1.54 - 0.173C_n \quad (\text{correlation coefficient} = 0.957) \quad (1)$$

The linear dependence (Figure 6D) of $\Delta C_{p,m2}^o$ based on ΔH_{m2}^o values for C₁₀- and C₁₂TPB as well as the ΔH_{m2}^o values for C₁₄- and C₁₆TPB suggested involvement of similar energetic

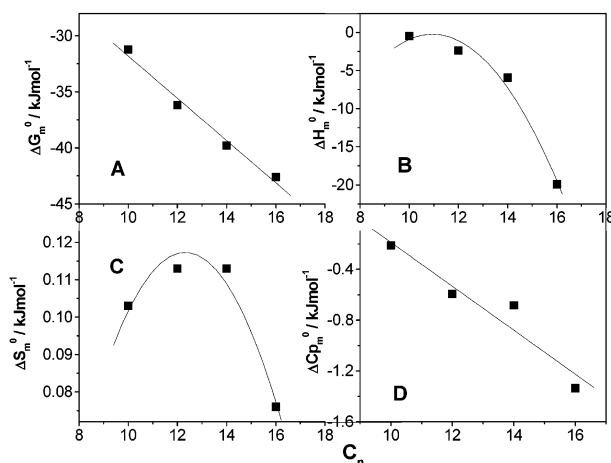


Figure 6. Profiles of (A) ΔG_m^o , (B) ΔH_m^o , (C) ΔS_m^o , and (D) $\Delta C_{p,m}^o$ vs alkyl-chain carbon number of the ATPBs.

factors for their micellization. The ΔH_{m1}^o values for C₁₀TPB at three temperatures and that for C₁₂TPB at two temperatures were also linearly correlated with temperature to evaluate the $\Delta C_{p,m1}^o$ values of -295 and -192 J mol⁻¹ K⁻¹, respectively. The explanation for the negative sign is the same as that given for $\Delta C_{p,m2}^o$. Because calculation of $\Delta C_{p,m1}^o$ for C₁₂TPB was based only on two temperatures, the value has less accuracy than the others.

On the general basis of the pseudophase principle of micelle formation,^{27,29} from the cmc and ΔH_m^o , the standard free energy and entropy of micelle formation, ΔG_m^o and ΔS_m^o were obtained from the following relations

$$\Delta G_m^o = (1 + \beta)RT \ln X_{cmc} \quad (2)$$

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

In the calculation, the cmc was expressed in mole fraction unit and the chosen standard state was the hypothetical ideal state of unit mole fraction. The results are presented in Table 2. For C₁₀- and C₁₂TPB, the thermodynamic parameters decreased with temperature. For all the ATPBs, ΔG_m^o , ΔH_m^o , and ΔS_m^o decreased with temperature, and the magnitudes of the sets, including $\Delta C_{p,m}^o$, followed the order C₁₀- < C₁₂- < C₁₄- < C₁₆TPB. Compared to the enthalpy, the decline in entropy was

mild. Thus, enthalpy was a controlling factor for the self-assembling process of the ATPBs.

Like previous reporting,²⁷ it was observed that estimation of ΔH_m° by the van't Hoff rationale from the temperature dependence of cmc resulted in values that were different from calorimetry. The higher members C_{14} - and C_{16} TPB even gave values with changed signs at lower temperature. This was in line with the report of Mukerjee and Mysels.²⁶ Since the cmc determined by calorimetry can claim better accuracy, reason for the above difference may be sought into the integral nature of the latter while the former is differential in nature as emphasized earlier.²⁷

The ΔH_{m2}° and ΔS_{m2}° of the four sets of results have evidenced a very good linear correlation (Figure 5B) with compensation temperatures (T_c) of 379, 336, 318, and 332 K for C_{10} -, C_{12} -, C_{14} -, and C_{16} TPB, respectively, which perceptibly differed from the average temperature, $T_{ave} = 311$ K. Such a compensation phenomenon has been fairly demonstrated in the literature on micellization and other processes in solution.^{30–32}

In parts A, B, and C of Figure 6, the profiles of ΔG_{m2}° , ΔH_{m2}° , and ΔS_{m2}° with C_n (the alkyl chain carbon number) for the pure ATPBs are depicted. The ΔG_{m2}° values at all the studied temperatures followed linear courses (eq 4, at 298 K) with an average slope of -2.0 kJ mol^{-1} , equivalent to the free energy of transfer of one mole of CH_2 from the aqueous environment into the micelle; the value was lower than the literature report³³ of -2.72 to $-3.00 \text{ kJ mol}^{-1}$ at 298 K

$$\Delta G_{m2}^\circ = -12.9 - 2.0C_n \quad (4)$$

The transfer of a monomer from the bulk into the micelle was hindered by the bulky headgroup barrier.

In parts B and C of the figure, the dependence of both ΔH_{m2}° and ΔS_{m2}° on C_n has been found to be nonlinear with a tendency of maximum at $C_n = 12$.

For C_{10} - and C_{12} TPB, the normal type of micelles have shown higher cmc values and degrees of counterion binding than the other ones. For C_{14} - and C_{16} TPB, the trend reversed. The surface charge density of the first kind for C_{10} - and C_{12} TPB was thus lower than the second kind; for C_{14} - and C_{16} TPB, again, reverse trend was observed. Although the second stage of micelle formation may end up in nonspherical assembly formation, the linear correlation of $\Delta C_p m^\circ$ with C_n (Figure 6D) suggested no drastic difference in solution behaviors of the lower and higher homologues.

Binary Equimolar Mixtures of TPB. Both calorimetric and conductometric measurements on equimolar binary mixtures of the ATPBs were taken for understanding their mutual interaction behaviors. The results for the C_{10} – C_{12} , C_{10} – C_{14} , C_{10} – C_{16} , C_{12} – C_{14} , C_{12} – C_{16} , and C_{14} – C_{16} combinations are illustrated in parts A, B, and C of Figure 7 and in parts D, E, and F of Figure 8. In each figure, the thermograms of the combined systems are compared with those of the two constituent pure components. The observed transitions and breaks in the plots have been sequentially designated as cmc_1 , cmc_2 , and cmc_3 . For the C_{10} – C_{12} case (Figure 7A), the thermogram of the mixed system occupied the intermediate position between the pure components. Thus, the position of the first cmc of the mixture (cmc_1^m) was $\text{cmc}_1^{12} < \text{cmc}_1^m < \text{cmc}_1^{10}$, and the second cmc of the mixture (cmc_2^m) was $\text{cmc}_2^{12} < \text{cmc}_2^m < \text{cmc}_2^{10}$. For the combination C_{10} – C_{14} (Figure 7B), the thermogram was again intermediate between C_{14} and C_{10} . Here, $\text{cmc}_1^{14} < \text{cmc}_1^m$ and $\text{cmc}_2^m < \text{cmc}_2^{10}$. Since dilution of mixed systems beyond 10 mM could not be done (due to limitation in addition for maintaining the overall concentration of the titer the same), the cmc_3^m or the shifted

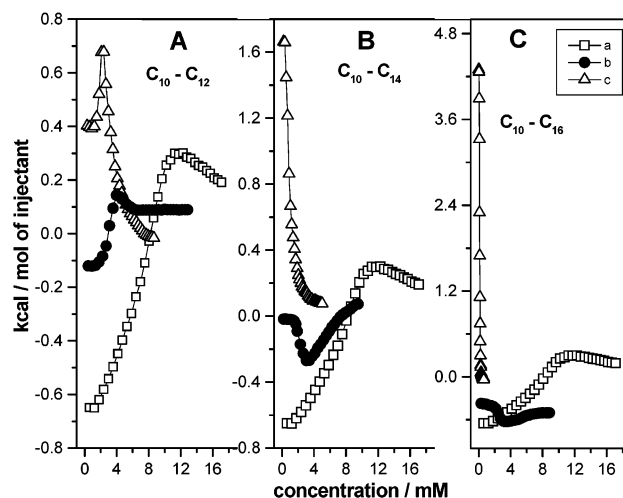


Figure 7. Thermograms of the combined systems (1:1 mol/mol mixtures) of C_{10} – C_{12} , C_{10} – C_{14} , and C_{10} – C_{16} TPB compared with that of the two constituent pure components at 298 K. (A) (a) C_{10} TPB, (b) C_{10} – C_{12} combination, and (c) C_{12} TPB. (B) (a) C_{10} TPB, (b) C_{10} – C_{14} combination, and (c) C_{14} TPB. (C) (a) C_{10} TPB, (b) C_{10} – C_{16} combination, and (c) C_{16} TPB.

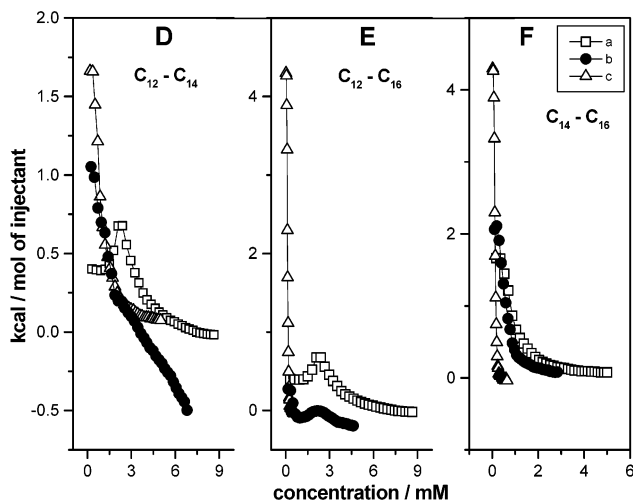


Figure 8. Thermograms of the combined systems (1:1 mol/mol mixtures) of C_{12} – C_{14} , C_{12} – C_{16} , and C_{14} – C_{16} TPB compared with that of the two constituent pure components at 298 K. (D) (a) C_{12} TPB, (b) C_{12} – C_{14} combination, and (c) C_{14} TPB. (E) (a) C_{12} TPB, (b) C_{12} – C_{16} combination, and (c) C_{16} TPB. (F) (a) C_{14} TPB, (b) C_{14} – C_{16} combination, and (c) C_{16} TPB.

second cmc of C_{10} TPB was not realized. Similarly, for the C_{10} – C_{16} combination (Figure 7C), $\text{cmc}_1^{16} < \text{cmc}_1^m$ and $\text{cmc}_2^m < \text{cmc}_2^{10}$; the cmc_3^m or the shifted second cmc of C_{10} TPB was not realized. The C_{12} – C_{14} combination (Figure 8D) did produce evidence for a single cmc; the C_{12} TPB influenced the cmc of C_{14} TPB. The exothermicity of the C_{14} TPB dilution compensated for the endothermicity of the first stage of the C_{12} TPB dilution, making the C_{14} TPB-influenced cmc of C_{12} TPB nonvisible. Thereafter, the combined negative heats of dilution monotonically declined without showing a cooperative trend for the detection of the C_{14} TPB-influenced second cmc of C_{12} TPB. The results also did not fit to the SBF procedure. The C_{12} – C_{16} combination (Figure 7E) was nearly like the C_{10} – C_{16} mixture; $\text{cmc}_1^{16} < \text{cmc}_1^m$ and $\text{cmc}_2^m < \text{cmc}_2^{12}$; here the cmc_3^m or the shifted second cmc of C_{12} TPB was realized as $\text{cmc}_3^m < \text{cmc}_2^{12}$. The C_{14} – C_{16} case (Figure 7F) was simple. Only one cmc was observed, which was of the usual sequence $\text{cmc}_1^{16} < \text{cmc}_1^m < \text{cmc}_1^{14}$. The cmc values of the mixed systems were estimated

TABLE 3: cmc^a and β Values of the Mixed Micelles Obtained from Calorimetry (cal) and Conductometry (cond) at 298 K

mixed system (1:1 mol/mol)	cmc ₁ ^m (cal) cond	β_1	cmc ₂ ^m (cal) cond	β_2	cmc ₃ ^m (cal) cond	β_3
10:12	(3.05) 3.05 (2.88) ^b	0.212	(5.07) 4.97 (4.58) ^b	0.382		
10:14	(2.19) 2.14	0.232	(5.39) 5.08	0.316		
10:16	(0.610) 0.62	0.184	(5.52) 4.94	0.488		
12:14	(0.94) 0.96	0.371	2.91	0.526		
12:16	(0.49) 0.54	0.143	(1.62) 1.56	0.362	(3.09) 3.25	0.505
14:16			(0.39) 0.38(0.193) ^b	0.466		

^a The cmc values are in mM unit. ^b Clint values.

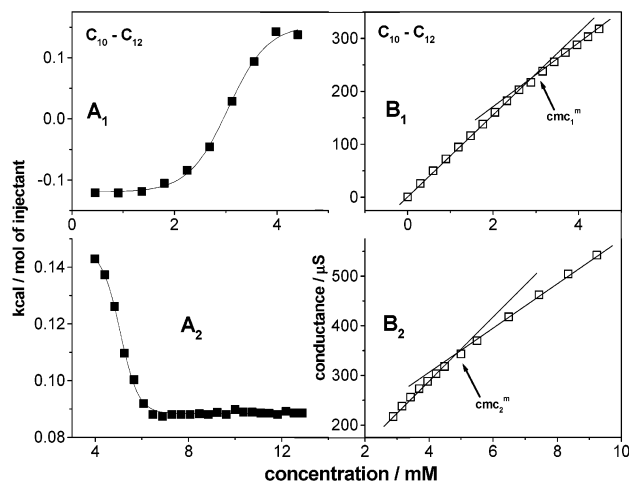


Figure 9. Dissected enthalpy-concentration profiles for the 1:1 mol mixture of C₁₀-C₁₂TPB (A₁ and A₂). Conductometric support to calorimetric findings of the same system (B₁ and B₂).

using the SBF procedure dissecting the different parts of the enthalpy-concentration profiles. This is shown in Figures 9–13, parts A₁ and A₂. The conductometric support to calorimetric findings is presented in parts B₁ and B₂ in the same figures. Of particular interest was the C₁₂-C₁₄ combination where calorimetry failed to detect the second cmc but it was distinctly observed in conductometry. Supportive evidence for cmc₃^m for the C₁₂-C₁₆ pair was also obtained from conductometry. All the cmc values realized by calorimetry and conductometry at 298 K are presented in Table 3. The cmc₃^m for the C₁₂-C₁₆ pair was greater than the pure components, which appeared to be unusual. Morphological changes of the secondary aggregates accumulating more monomers were considered to produce bigger entities with an increased cmc. The phenomenon needs verification by a suitable method such as small-angle neutron scattering.

On the basis of the measured enthalpy values, thermodynamic parameters were also obtained for the mixed systems following the same rationale used for pure ATPBs. The results are also presented in Table 3. Compared to the pure ATPBs, their binary mixtures have produced appreciable free energy and entropy; the enthalpy changes were significantly small. The self-organization of the mixed entities was thus entropy controlled.

The calorimetric results depicted in Figures 9–13 (parts A₁ and A₂) and presented in Table 3 are unique in nature for surfactants in a homologous series. While the pure lower members (C₁₀- and C₁₂-) have witnessed two energetically opposite aggregation processes, the higher homologues (C₁₄ and C₁₆) have shown only exothermic self-aggregating phenomenon in the studied temperature range of 298–328 K. Their equimolar binary mixtures have produced intermediate two to three states of aggregation with either C₁₀- or C₁₂TPB in the combinations.

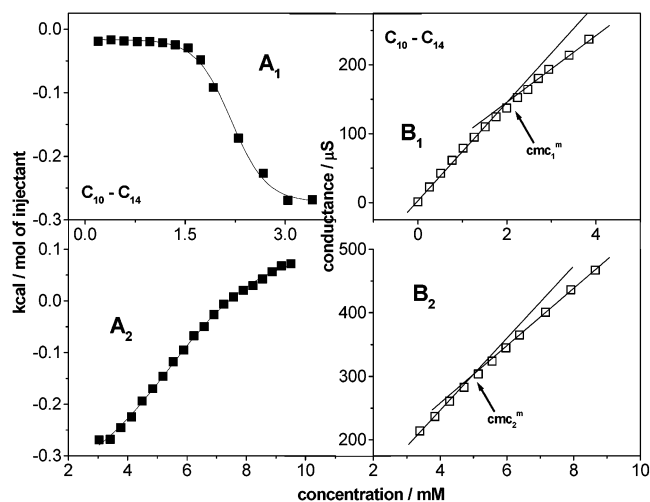


Figure 10. Dissected enthalpy-concentration profiles for the 1:1 mol mixture of C₁₀-C₁₄TPB (A₁ and A₂). Conductometric support to calorimetric findings of the same system (B₁ and B₂).

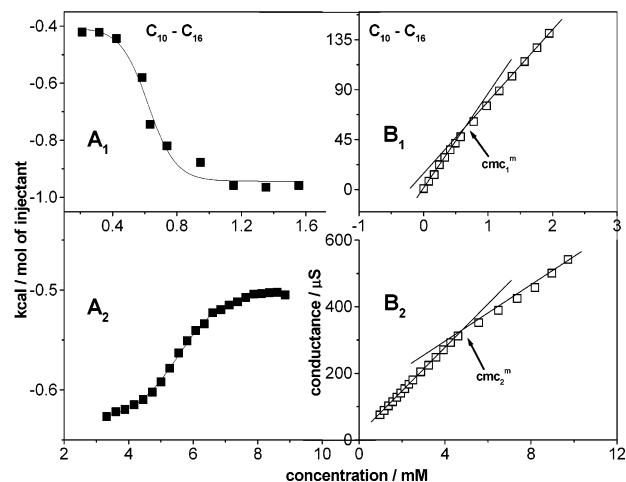


Figure 11. Dissected enthalpy-concentration profiles for the 1:1 mol mixture of C₁₀-C₁₆TPB (A₁ and A₂). Conductometric support to calorimetric findings of the same system (B₁ and B₂).

For the pairs C₁₀-C₁₂ and C₁₄-C₁₆, at 1:1 molar ratio, Clint's proposition was applicable. Thus

$$\frac{1}{\text{cmc}^m} = 0.5 \left(\frac{1}{\text{cmc}_a} + \frac{1}{\text{cmc}_b} \right) \quad (5)$$

where cmc_a, cmc_b, and cmc^m represent cmc of surfactant a, surfactant b, and their mixture, respectively.

The cmc^m_{clint} values are also presented in Table 3 in parentheses. It has been observed that the C₁₀-C₁₂ combination was close to an ideal mixture and the C₁₄-C₁₆ mixture was not, an antagonistic positive deviation of cmc was observed. A small positive deviation for 1:1 mixed surfactants of C₁₄- and C₁₆ trimethylammonium bromide has been calorimetrically reported earlier.³⁴ For other combinations, the straightforward

TABLE 4: Thermodynamic Parameters^a for the Micellization of 1:1 (mol/mol) Binary Mixtures of ATPBs at 298 K

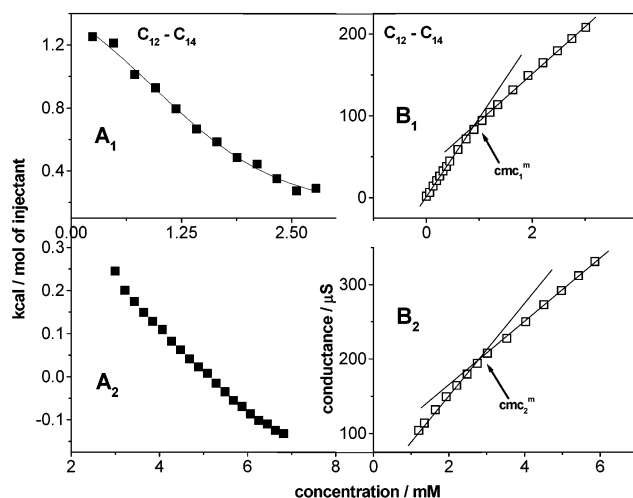
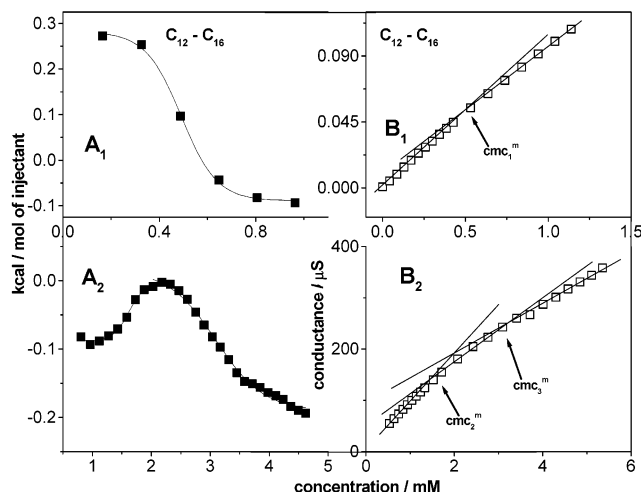
mixed micelle	$\Delta G_{m1}^{\circ M} (\Delta H_{m1}^{\circ M})$ $\Delta S_{m1}^{\circ M}/\text{kJ mol}^{-1}$	$\Delta G_{m2}^{\circ M} (\Delta H_{m2}^{\circ M})$ $\Delta S_{m2}^{\circ M}/\text{kJ mol}^{-1}$	$\Delta G_{m3}^{\circ M} (\Delta H_{m3}^{\circ M})$ $\Delta S_{m3}^{\circ M}/\text{kJ mol}^{-1}$
10:12	-29.5 (1.14) 103	-31.9 (-0.241) 106	
10:14	-31.0 (-1.07) 100	-30.1 (1.42) 105	
10:16	-33.5 (-2.25) 105	-37.4 (2.40) 134	
12:14		-41.5 (-4.62) 124	
12:16	-33.0 (-1.55) 105	-35.2 (0.354) 119	-36.5 (-0.860) 119
14:16		-43.1 (-8.41) 116	

^a The free-energy and enthalpy values are expressed in kJ mol^{-1} , and the entropy values are expressed in $\text{J mol}^{-1} \text{K}^{-1}$ units, respectively. The estimated errors in the first, second, and third parameters were ± 3 , ± 5 , and $\pm 8\%$, respectively.

application of Clint's equation was not possible. It maybe mentioned that mismatch of surfactant tails produced antagonistic behavior for tetradecyl- and hexadecyl trimethylammonium bromide.³⁵

The combined endothermic and exothermic enthalpy profiles herein obtained can also be demonstrated by judicious choice of a pair of surfactants having large differences in cmc and ΔH_m° . Results of such a measurement on an equimolar mixture of Triton X-100 and cetyltrimethylammonium bromide (CTAB) are depicted in Figure 3B. There, in the mixed condition, the lower cmc of TX-100 (0.38 mM) increased to 0.41 mM (cmc_1^m) and the higher cmc of CTAB (1.11 mM) decreased to 0.95 mM (cmc_2^m). The enthalpy of the two self-association processes (comparative illustration with pure surfactants not shown) of course considerably changed. For TX-100, the enthalpy changed from $+5.56$ to $+2.33 \text{ kJ mol}^{-1}$, and for CTAB, it changed from -8.22 to $-5.10 \text{ kJ mol}^{-1}$. Two kinds of micelle formations were thus envisaged, warranting little or no scope for application of Clint's equation.

The thermodynamic parameters $\Delta G_m^{\circ M}$ and $\Delta S_m^{\circ M}$ of the mixed binary surfactants at 298 K were on the whole comparable with the pure components, but in comparison, the $\Delta H_m^{\circ M}$ values were strikingly low. This and multiple cmc formation of the mixed ATPBs warrant detailed investigation for rationalization of the results and understanding the nature of interaction, particularly for combinations having differences in micellization trends. In a mixed surfactant solution (say of types A and B), existence of mixed micelles containing the constituent surfactants is the consensus although the possibility of existence of individual micelles or micelles of A containing B or vice versa is also a possibility. It is also considered that the micelle composition depends on the proportion of surfactants in the mixture. The geometrical state of the mixed species at different mixing proportions may also have distinction. In the present study, at 1:1 molar mixtures of the ATPBs, indication for two (even three) kinds of micelles have been observed by the methods of calorimetry and conductometry. There, by mutual interaction the lower cmc of the amphiphile species containing a higher alkyl chain increased whereas that containing a lower

**Figure 12.** Dissected enthalpy-concentration profiles for the 1:1 mol/mol mixture of C_{12} - C_{14} TPB (A_1 and A_2). Conductometric support to calorimetric findings of the same system (B_1 and B_2).**Figure 13.** Dissected enthalpy-concentration profiles for the 1:1 mol/mol mixture of C_{12} - C_{16} TPB (A_1 and A_2). Conductometric support to calorimetric findings of the same system (B_1 and B_2).

chain decreased. The first kind was considered rich in species having a higher alkyl chain while species containing a lower alkyl chain was considered for the second. The present study thus warrants a detailed exploration of mixed amphiphile systems for structural, compositional, and energetic information.

Comparison of Cationics Having $C_n = 16$. In the present context, a comparison of the micellar parameters of cationic surfactants having identical tail but different headgroups may be worthwhile. In Table 4, such a comparison for cetyltrimethylammonium bromide (CTAB), cetyldiethanol dimethylammonium bromide (CEDAB), cetyldiethanol monomethylammonium bromide (CDMAB), cetyl triphenyl phosphonium

TABLE 5: Comparison of cmc, β , and Thermodynamic Parameters for CTAB, CEDAB, CDMAB, CTPB, and CPC at 298 K

surfactant ^a	cmc/mM		cal			aggregation no. ^c	$\Delta C_{p,m}/J\ K^{-1}\ mol^{-1}$
	cond (β)	cal	$\Delta G_m^{\circ}/kJ\ mol^{-1}$	$\Delta H_m^{\circ}/kJ\ mol^{-1}$	$\Delta S_m^{\circ}/J\ K^{-1}\ mol^{-1}$		
CTAB ²⁷	0.95 (0.96)	1.05	−53.3	−10.14	138	61 ³⁶	−444
CEDAB ²⁷	0.83 (0.731)	0.86	−47.5	−12.0	119	123	−639
CDMAB ²⁷	0.76 (0.704)	0.78	−47.2	−13.3	114	105	−739
CPC ²⁷	0.96 (0.55)	1.03	−41.8	−4.5	125	-	−741
CTPB ^b	0.14 (0.310)	0.110	−42.6	−19.9	76	15 ¹⁶	−1335

^a Headgroup structure: CTAB($-\text{Me}_3\text{N}^+$); CEDAB($-\text{Me}_2-\text{N}^+-\text{C}_2\text{H}_4\text{OH}$); CDMAB($-\text{Me}-\text{N}^+-\text{C}_2\text{H}_4\text{OH}$); CPC($-\text{C}_6\text{H}_4\text{N}^+$); CTPB($-\text{P}^+\phi_3$)

^b This work. ^c By fluorescence quenching.

bromide (CTPB, C₁₆TPB member of the presently studied series), and cetylpyridinium chloride (CPC) at 298 K is presented. The headgroup structures of the surfactants are shown in the footnote of the table. The reported thermodynamic parameters were all realized by us from ITC experiments so that the comparison has equivalent basis. The cmc of CTPB was found to be significantly lower than the rest of the representatives; the cmc followed the order CTPB \ll CDMAB $<$ CEDAB $<$ CTAB \approx CPC. The aggregation number of the micelles followed the order CTPB \ll CTAB $<$ CDMAB $<$ CEDAB; again CTPB has shown characteristic difference. The CPC could not be brought into this comparison since its aggregation number is hardly available in the literature. The fraction of counterions bound to the micelles has the trend CTPB $<$ CPC $<$ CDMAB $<$ CEDAB $<$ CTAB. The aromatic ring containing headgroups (as in CPC and CTPB) offered lower counterion binding because of lower effective micellar surface charge density. The ΔH_m° values obtained for CTAB, CEDAB, and CDMAB were close, but the replacement of a methyl group by an ethanoyl group has made the self-aggregation process more exothermic. The replacement of the three methyl groups by three phenyl rings has resulted in further enhancement of exothermicity. The realization of much lower magnitude of ΔH_m° for CPC was interesting. An explanation for this observation is kept pending for future. All the ΔS_m° values were positive and large, complying with the general trend of micelle formation. The magnitudes of the $\Delta C_{p,m}^\circ$ have followed the order CTAB $<$ CEDAB $<$ CDMAB \approx CPC \ll CTPB. It was related with the nonpolarity of the headgroup region. CTPB, with three phenyl rings in the headgroup, has made $\Delta C_{p,m}^\circ$ significantly negative.

Conclusions

The results herein presented are significantly different from the normal trend manifested in amphiphile self-aggregation. At lower temperatures, C₁₀- and C₁₂TPB produced two kinds of self-aggregation; the first process was endothermic whereas the second was exothermic. At higher temperatures, only a single micellization process with exothermic heat change resulted. Equimolecular binary mixtures of C₁₀- and C₁₂TPB and their mixtures with C₁₄- and C₁₆ homologues also formed two cmcs at lower temperatures with a greatly reduced enthalpy of micellization. The phenomenon of two cmcs and associated endo- and exothermic enthalpy changes can be demonstrated with a judicious choice of a pair of surfactants as has been herein done using an equimolar mixture of TX-100 and CTAB. The observation of two kinds of self-aggregation in two different concentration regions for ATPBs by ITC and conductometry warrants corroboration and quantification by further studies.

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