

Ternary mixtures of alkyltriphenylphosphonium bromides (C_{12} TPB, C_{14} TPB and C_{16} TPB) in aqueous medium: their interfacial, bulk and fluorescence quenching behaviour

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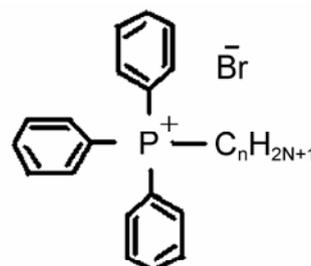
Abstract. The self-aggregation behaviour of ternary mixtures of alkyl (C_{12} -, C_{14} - and C_{16} -) triphenylphosphonium bromides was studied by conductometry and tensiometry. The pure surfactants showed two Critical Micellar Concentrations (CMCs) by conductometry, but their ternary mixtures produce single CMC both by conductometry and tensiometry. The CMC values determined were found to be lower than that obtained from Clint equation suggesting synergistic interaction among the monomers within the micelles. Their bulk properties, like fraction of counterions bound to the micelles and free energy of micellization were evaluated. Interfacial parameters, like surface excess, minimum head group area of monomer and free energy of adsorption were also assessed. Interfacial adsorption was found to be more spontaneous than micellization. The head group area per monomer in ternary systems was larger than pure systems due to stronger electrostatic repulsion among the charged head groups. The values of the packing parameters supported the pure as well as ternary micelles to be spherical. The TPB surfactants efficiently quenched pyrene fluorescence; the performances of the homologues in this respect were assessed.

Keywords. Alkyltriphenylphosphonium bromides; ternary mixed micelles; fluorescence quenching.

1. Introduction

Mixed surfactants play a promising role in surface chemical applications. Mixed systems may be less expensive and provide better performances^{1–4} that arises from judicious choice of different surfactant mixtures to induce synergistic behaviour and/or to provide different performances in a single formulation. Under this backdrop, binary mixtures of conventional and non-conventional surfactants have been liberally investigated over the past few decades.^{5–28} Reports on the bulk and interfacial properties of ternary surfactant mixtures are, however, scanty in literature.^{29,30} In a recent study, we have elaborately presented properties of the binary and ternary mixtures of tetradecyltrimethylammonium bromide (C_{14} TAB), tetradecyltriphenyl phosphonium bromide (C_{14} TPB) and tetradecylpyridinium bromide (C_{14} PyB).³¹ Interesting head group depended results were observed.

In this study, we have attempted to understand the bulk and interfacial properties of a ternary surfactant mixture comprising dodecyl-, tetradecyl- and hexadecyltriphenylphosphonium bromides C_{12} TPB, C_{14} TPB and C_{16} TPB, respectively (structures shown in scheme 1). Prasad *et al.*²³ have reported the properties of binary mixtures of alkyltriphenylphospho



n = 12, Dodecyltriphenylphosphonium bromide
14, Tetradecyltriphenylphosphonium bromide
16, Hexadecyltriphenylphosphonium bromide

Scheme 1. Schematic representation of the structures of the alkyltriphenylphosphonium bromide surfactants used in the study.

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nium bromides (C_n TPB); mutual antagonism was found to be dominating in the mixtures. We have studied the ternary C_n TPB mixtures by conductometry which probed their bulk properties, and by tensionometry which revealed their interfacial characteristics. Features like counterion binding, surface excess, minimum area of the head groups of the surfactant monomers, packing parameter, free energy of micellization and interfacial adsorption process, etc. have been evaluated and reported here.

These alkyltriphenylphosphonium bromides are known to efficiently quench emission of fluorophores.³² The alkylpyridinium halide group of surfactants also show similar properties. They are quite often used as quenchers in the determination of aggregation numbers of non-quenching surfactants by the fluorescence quenching method.^{12,24} Here, we have attempted to present a comparative investigation on the fluorescence quenching efficacies of the alkylpyridinium and alkyltriphenylphosphonium group of surfactants along with a detailed discussion on the aggregation numbers of the micelles of alkyltriphenylphosphonium bromides and their ternary mixtures.

2. Experimental

2.1 Materials

The ATPB surfactants used in this study were obtained from Caledon Laboratories, LTD. of Canada (distributors for Lancaster Synthesis of England).²² Among the alkylpyridiniumbromide surfactants, C_{12} PyC and C_{16} PyC were obtained from Merck, Germany and C_{14} PyB was also obtained from Caledon Laboratories, LTD. of Canada. The Pyridinium Hydrochloride salt was also obtained from Merck, Germany. The Cetyltrimethylammonium bromide (CTAB) and Sodium dodecylsulfate (SDS) used were purified samples of Sigma, USA. Doubly distilled water of specific conductance $2\text{--}4\ \mu\text{S cm}^{-1}$ at 303 K was used for all solution preparations and experiments.

2.2 Methods

Conductometry. A Jenway conductance bridge (UK) combined with a cell of unit cell constant was used to measure specific conductance of surfactant solutions. The concentration of surfactant solution was increased in the container by progressive addition of

a concentrated solution of it into water with a Hamilton microsyringe. Measurements were taken after thorough mixing and allowing time for temperature equilibration.

2.2a Tensiometry: A calibrated Krüss (Germany) tensiometer was used to measure the surface tension (γ) at the air/solution interface of the surfactant solutions by the du Noüy ring detachment method. The concentration of surfactant solution was increased following the same protocol as in conductometry. The surface tensions were measured allowing ~ 20 min time for equilibration after each addition. The experiments were duplicated to check their reproducibility. The mean values of the measurements were considered for the data analysis.

2.2b Fluorimetry: Fluorescence measurements using pyrene as the fluorescent probe were taken in a PERKIN ELMER (LS 55 USA) fluorimeter using a 10 mm path length quartz cuvette. Excitation was done at 332 nm and emission was recorded in the 340–450 nm range. The slit widths were fixed at 15 nm for excitation and 5 nm for emission. Pyrene concentration in solution was kept around $2\ \mu\text{M}$. The quenching efficiencies were determined in aqueous and micellar media of CTAB and SDS at concentrations 20 times their CMCs. The alkyltriphenylphosphonium bromide and alkylpyridinium bromide surfactants were used as quenchers and added progressively into the three media using a Hamilton microsyringe.

3. Results and discussion

3.1 Micellization, interfacial adsorption, micellar packing, free energy of micellization and adsorption, micellar composition

The compositions of the ternary mixtures used in this study were not arbitrarily decided. They were determined from the following rationale. For a wholesome evaluation of mixed system properties, we have chosen the points marked as 1 \rightarrow 13 in the equilateral triangle having three medians drawn from the apices to the arms (figure 1). In this figure, each axis represents the mass fraction of the labelled amphiphile. The centre point (7) thus corresponds to the 1 : 1 : 1 composition. The other ternary compositions correspond to the points 1 \rightarrow 10. The points 11, 12 and 13 are equimolar binary compositions for

the three ATPBs. The points show even spread of compositions within the triangular space. The mole ratios of the non equimolar ternary compositions (points 1–10) are given in the footnote of table 1.

CMCs of the studied ternary mixtures have been determined by the methods of conductometry and tensiometry. The former recorded the bulk property while the latter monitored the interfacial property. The agreement between the results was good. Figure 2(A and B) depicts the conductometric and tensiometric plots. The results are presented in table 1. The illustrations in figure 2 are only representative presentations. For conductometry, ternaries 6, 7 and 8 were considered, which for tensiometry, were mixtures 4, 5 and 6. Although comparable depictions of both the methods are not shown, their fair agreements can be observed from the data in table 1.

The ideal-nonideal behaviour of the mixtures by way of mutual interaction can be qualitatively examined in terms of Clint's proposition,³³

$$\frac{1}{C_m} = \sum_i \frac{X_i}{C_i} \quad (1)$$

where X_i and C_i are the stoichiometric mole fraction and CMC of the i -th component, respectively. The CMC values of the ternary mixtures were found to be lower than those obtained from Clint equation in-

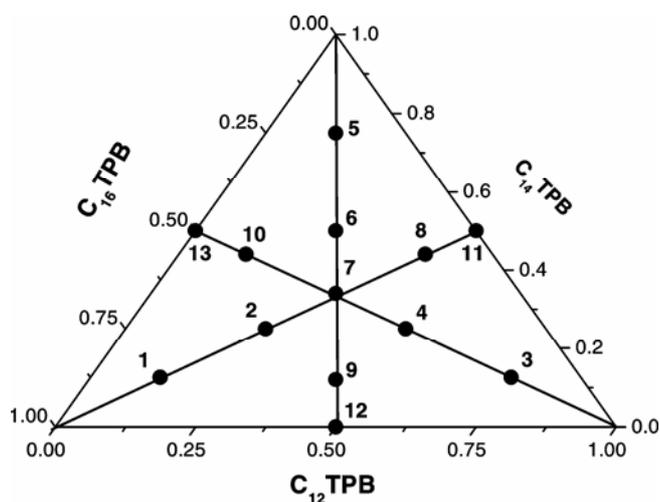


Figure 1. Equilateral triangle representation of the distribution points of the ternary compositions in the two-dimensional space. The compositions of the points marked as 1 → 13 are given in the footnote of table 1 in terms of mass percent compositions of C_{12} TPB : C_{14} TPB : C_{16} TPB.

dicating associative or cooperative interaction prevailing in the ternary mixed micelles in contrast to the predominantly antagonistic behaviour reported earlier in the binary mixtures of the ATPBs.²³ A four-coordinate, three-dimensional trajectory showing the nature of variation of CMC with the ternary compositions is presented in figure 3. Prasad *et al*^{22,23} have demonstrated earlier that surfactants with C_{10} and C_{12} alkyl chains show different behaviour from those with C_{14} and C_{16} tails; the former group has a greater possibility of double CMC formation. We have also obtained two CMCs from conductometry for all three pure TPBs (second CMCs are presented in parentheses in table 1). The latter is considered to be a consequence of changes in micellar

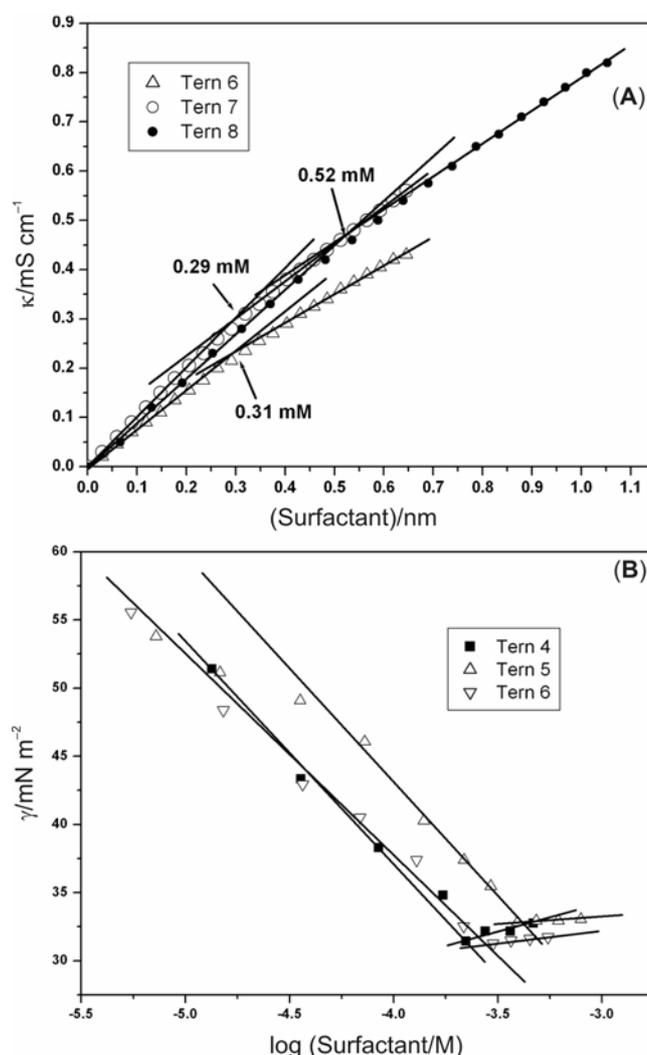


Figure 2. (A) Specific Conductance (κ) vs (surfactant) for ternary mixtures (compositions 6, 7 and 8) at 303 K. (B) Tensiometric profiles for ternary compositions 4, 5 and 6 at 303 K.

Table 1. CMCs, counterion bindings β and free energy change for micellization ΔG_m^0 for the pure TPBs and their studied ternary mixtures at 303 K.

Parameters	Pure			Ternary mixtures ^a										
	C ₁₂ TPB	C ₁₄ TPB	C ₁₆ TPB	1	2	3	4	5	6	7	8	9	10	
CMCs (mM)	Cond	1.75 (3.10)	0.57 (1.21)	0.20 (0.42)	0.15	0.23	0.55	0.34	0.43	0.31	0.29	0.52	0.35	0.26
	Tens	2.35	0.61	0.24	0.15	0.21	0.59	0.27	0.43	0.33	0.36	0.42	0.30	0.32
	Clint	—	—	—	0.27	0.35	0.87	0.55	0.53	0.47	0.45	0.66	0.41	0.36
β	0.36 (0.48)	0.38 (0.54)	0.32 (0.54)	0.245	0.242	0.266	0.260	0.309	0.202	0.267	0.251	0.239	0.284	
$\Delta G_m^0/\text{kJ mol}^{-1}$	-43.4	-39.9	-41.7	-40.2	-38.9	-36.6	-38.4	-38.8	-36.5	-38.4	-36.8	-37.6	-39.4	

^aX_{C₁₂TPB}/X_{C₁₄TPB}/X_{C₁₆TPB}: **1**, 0.125/0.125/0.75; **2**, 0.25/0.25/0.50; **3**, 0.75/0.125/0.125; **4**, 0.50/0.25/0.25; **5**, 0.125/0.75/0.125; **6**, 0.25/0.50/0.25; **7**, 0.333/0.333/0.333; **8**, 0.44/0.44/0.12; **9**, 0.44/0.12/0.44; **10**, 0.12/0.44/0.44

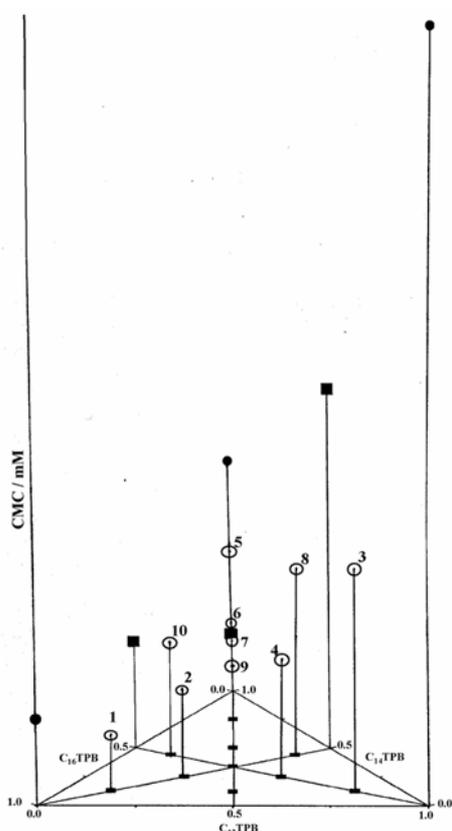


Figure 3. A four co-ordinate diagram showing the three-dimensional spatial distribution of the CMCs of the ternary compositions including the pure C₁₂TPB, C₁₄TPB and C₁₆TPB surfactants along with their 1 : 1 binary combinations at 303 K.

shapes.^{31,34} Tensiometric method could not detect the second stage of micellization for it was a bulk property. The organizational change in the mixed

systems with variation in the associated counterion binding contributed towards the mobility of the modified ionic species in solution making the conductance method sensitive to detect the two CMCs. Evidences for the second CMC were also obtained from calorimetric measurements of C_nTPB.^{22,23}

The specific conductance when plotted against [surfactant], two straight lines with distinctly different pre-micellar and post-micellar slopes, S₁ and S₂, respectively were obtained where the cutting concentration was CMC. Binding counterions to micelles lower the ionic mobility to make S₂ < S₁. The ratio S₂/S₁ is a measure of the fraction of counterions dissociated from the micelles so that the fraction bound, $\beta = 1 - S_2/S_1$. This is a simple but well-used method for determining β .^{24,28,25,31,35,36} Buckingham *et al*³⁷ have shown that β values obtained by the electrometric (ion-selective electrode) and conductometric (slope ratio) methods were in good agreement. The estimated β values for the mixed ATPB systems are given in table 1. As discussed earlier, the bulky triphenylphosphonium head group with less electronegative phosphorus moiety offered lower surface charge density, and hence lower β values. The tail lengths did not affect the charge density and the all three C₁₂-, C₁₄- and C₁₆-members have offered a comparable ~30–40% counterion binding to their micelles. The ternary mixtures had stronger head group repulsions causing decreased surface charge density as compared with the binaries²³ with a lowering of β to ~20–30% on the average.

The competence of the pure and ternary mixtures of the alkyltriphenylphosphonium bromides in ad-

sorption at the air/solution interface was assessed in the light of Gibbs adsorption equation,^{28,38}

$$\Gamma_{\max} = \frac{1}{2.303iRT} \lim_{C \rightarrow \text{CMC}} \frac{d\gamma}{d \log C} \text{ mol m}^{-2}, \quad (2)$$

where Γ_{\max} , i , R , T and C are the maximum surface excess at CMC, the number of species participate in the adsorption process, the universal gas constant, the absolute temperature and the concentration of surfactant in solution, respectively. In the pure systems, i was equal to 2 by amphiphile dissociation. In the ternary systems, $i = n_i X_i$, where n_i and X_i are the number of species the i th component of the adsorbed surfactant produced by dissociation and its mole fraction at the interface, respectively.³⁸ For any combination $n_i = 2$ and $X_i < 1$, calculations for all combinations would produce $i = 2$. For example, at the mole fraction composition of C₁₂TPB: C₁₄TPB: C₁₆TPB at the interface as 0.1 : 0.4 : 0.5, $i = (2 \times 0.1) + (2 \times 0.4) + (2 \times 0.5) = 2$ for the ternary system.

With increasing [surfactant], the surface tension value decreased due to the accumulation of the amphiphile at the interface. At a particular point, the monolayer became saturated, any further addition of surfactant resulted in micelle formation. This point was the CMC and the minimum head group area of the monomer molecule in the saturated monolayer was obtained from the relation,

$$A_{\min} = \frac{10^{18}}{N\Gamma_{\max}} \text{ nm}^2 \text{ mol}^{-1}, \quad (3)$$

where N is the Avogadro number.

Israelachvili³⁹ predicted the structural geometry of the micelles in terms of packing parameter (P) by the relation,

$$P = \frac{v}{Al_c}, \quad (4)$$

where l_c is the maximum effective length of the hydrophobic chain of a monomer, A is the surface area of the head group, and v is the volume of the hydrophobic chain considering it to be fluid and incompressible. Both l_c and v for a saturated hydrocarbon chain with n number of carbon atoms can be obtained from the proposed formulas of Tanford,⁴⁰

$$l_c = (0.154 + 0.1265C_n) \text{ nm} \quad (5)$$

$$v = (0.0274 + 0.0269C_n) \text{ nm}^3. \quad (6)$$

In line with our earlier reports,³¹ A_{\min} obtained from tensiometry was used in the evaluation of P . Since three types of monomers were involved in the ternary mixtures, we used a modified form of the Israelachvili equation,^{13,31}

$$P_{\text{effect}} = \left(\frac{v}{Al_c} \right)_{\text{effect}} = \frac{\sum v_i x_i}{\left(\sum A_i x_i \right) l_c}, \quad (7)$$

where for all combinations we have selected l_c to be equal to that of the longest component (C₁₆TPB), and x_i are the stoichiometric mole fractions of the i th component. The shape of the amphiphile aggregates can be predicted from the values of P or P_{effect} . The values for different shapes are as follows: for spherical assemblies, $P \leq 0.333$; for non-spherical shape, $0.333 < P < 0.5$; for vesicles and bilayers, $0.5 < P < 1$; and for inverted structures $P > 1$. With this rationale, all the pure alkyltriphenylphosphonium bromides as well as their ternary mixtures were observed to form spherical micelles for their P values (table 2) were all < 0.333 . The pure C₁₂TPB and C₁₄TPB produced P values of 0.283 and 0.238. The pure C₁₆TPB and all the ternary mixtures resulted P values in the range of 0.122–0.198, which were quite lower than 0.333. Much smaller P values (0.07–0.10) were observed for the ternary mixtures of C₁₄TAB/C₁₄TPB/C₁₄P_yB.³¹

The standard Gibbs free energy of micellization (ΔG_m^0) and interfacial adsorption (ΔG_{ads}^0) were also evaluated for the ternary systems. The pseudophase micellar model was considered for this purpose. Thus,

$$\Delta G_m^0 = (1 + \beta)RT \ln X_{\text{CMC}}. \quad (8)$$

The ΔG_{ads}^0 at the air/solution interface was obtained from the relation,

$$\Delta G_{\text{ads}}^0 = \Delta G_m^0 - \frac{\Pi_{\text{CMC}}}{\Gamma_{\max}}, \quad (9)$$

where Π_{CMC} is the surface pressure at CMC, and the other terms are already defined. For the pure surfactants, the process of adsorption was nearly 1.4 times more favourable than micellization; C₁₆TPB showed

Table 2. Interfacial parameters of the pure TPBs and their studied ternary mixtures at 303 K.

Parameters	Pure			Ternary mixtures									
	C ₁₂ TPB	C ₁₄ TPB	C ₁₆ TPB	1	2	3	4	5	6	7	8	9	10
$\Gamma_{\max} \times 10^7/\text{mol m}^{-2}$	22.4	18.8	10.2	4.63	7.16	4.89	5.97	7.50	6.41	5.89	5.28	8.14	6.45
$A_{\min}/\text{nm}^2 \text{mol}^{-1}$	0.74	0.88	1.63	3.59	2.32	3.40	2.78	2.21	2.59	2.82	3.14	2.04	2.57
$\Delta G_{\text{ad}}^0/\text{kJ mol}^{-1}$	-60.2	-56.0	-75.3	-116.2	-93.2	-118.8	-105.2	-90.9	-99.7	-102.6	-106.5	-79.5	-98.0
P	0.283	0.238	0.129	0.122	0.180	0.109	0.140	0.182	0.157	0.143	0.123	0.198	0.163

Table 3. Stern–Volmer constant values of C_nPX and C_nTPX surfactants in different studied media at 303 K.

Systems	C ₁₂ PC	C ₁₂ TPB	C ₁₄ PB	C ₁₄ TPB	C ₁₆ PC	C ₁₆ TPB	HPyCl
K_{SV} In H ₂ O	2.75	2.85	2.74	6.78	7.65	43.9	1.11
In CTAB	2.50	1.56	4.40	0.90	4.33	1.28	0.05
In SDS	1.47	0.82	0.60	0.50	1.20	0.99	0.99

a higher inclination towards adsorption with $\Delta G_{\text{ads}}^0/\Delta G_{\text{m}}^0 \approx 1.8$. The ternaries showed approximately three times more spontaneity towards interfacial adsorption than association in the bulk to form micelles. The ΔG_{m}^0 and ΔG_{ads}^0 values are presented in table 1 and table 2, respectively. In comparison, ΔG_{m}^0 for both the pure and mixed systems were comparable but the ΔG_{ads}^0 for the mixed systems were more spontaneous than their pure components.

3.2 Fluorescence quenching of ATPBs and related features

Bimolecular static fluorescence quenching involves deactivation of an excited molecule at the singlet state by long- or short- range interaction of it with a quencher molecule. The quenching efficiency depends on a variety of factors including, orientation and interactive (electron transfer, dipole–dipole, etc.) parameters. Quantitatively, fluorescence quenching efficiency can be scaled by determining the Stern–Volmer constant, K_{SV}^{41-43} as given in (10),

$$\frac{I_0}{I} = 1 + K_{\text{SV}}[\text{Quencher}], \quad (10)$$

where I_0 and I are the fluorescence intensities in the absence and presence of the quencher, respectively.

Surfactants with pyridinium head groups have gained recognition as fluorescence quenching candidates. The alkyltriphenylphosphonium bromides, dealt with in this study, also have considerable quenching

characteristics. The fluorescence spectra of pyrene in the presence of both C_nPyB and C_nTPB (where $n = 12, 14$ and 16 ; Py = pyridinium; TP = triphenylphosphonium; B = Br⁻) in aqueous and micellar media of SDS and CTAB (both at 20 times CMC) were measured. A representative presentation of the results is depicted in figure 4. Differences in the behaviours in the three studied media are evident from the diagram. Fair influences of C_nTPBs on the quenching of fluorescence of pyrene and tryptophan have been also reported earlier.⁴⁴ The observed quenching influences C_nPyB and C_nTPB on the fluorescence intensities of pyrene have been used in equation 10 to estimate K_{SV} . The Stern–Volmer plots are presented in figure 5. The K_{SV} values obtained are shown in table 3. It was found that in aqueous medium, $K_{\text{SV}}(\text{C}_{12}\text{PyB}) \approx K_{\text{SV}}(\text{C}_{12}\text{TPB})$; $K_{\text{SV}}(\text{C}_{14}\text{PyB}) < K_{\text{SV}}(\text{C}_{14}\text{TPB})$ and $K_{\text{SV}}(\text{C}_{16}\text{PyB}) \ll K_{\text{SV}}(\text{C}_{16}\text{TPB})$. But in CTAB solution (~20 times CMC), the C_nTPBs showed lower efficacies compared to their pyridinium homologues. In SDS medium (20 times CMC), the differences between $K_{\text{SV}}(\text{C}_n\text{TPB})$ and $K_{\text{SV}}(\text{C}_n\text{PyB})$ were lesser than that in CTAB medium. In the quenching process, the chemical interaction between the head groups of the surfactants and the quencher was of importance which for the cationic surfactants and cationic quenchers was repulsive in nature to prevent them from making molecular contact. So, CTAB micellar medium was a more suitable medium for comparing the quenching efficacies of the cationic C_nPyBs and C_nTPBs. Both have shown much lower quenching efficiencies in

SDS micellar medium, because of favourable electrostatic interaction between the anionic SDS and the cationic quenchers.

The K_{SV} data analysis has inferred that the medium dependent quenching efficiencies of C_n TPBs and C_n PyBs on pyrene fluorescence followed the trend, pure water > aqueous CTAB > aqueous SDS. In each medium, C_n TPBs quenched more than C_n PyBs. The significant quenching efficiencies of the C_n TPBs posed a serious problem for the determination of their micellar aggregation by the fluorescence quenching method. Hansson *et al*⁴⁵ suggested that the aggregation numbers of surfactants must not depend on the type of head group but on the alkyl chain length. Based on this suggestion, n for C_{12} TPB, C_{14} TPB and C_{16} TPB were expected to be 56, 74 and 95, respectively. We have used this rationale in our recent work.³¹ Bakshi *et al*⁴⁶ have

reported n values for C_n TPBs by fluorescence quenching method using Pyridinium hydrochloride (HPyC) as the quencher, and the n values of C_{14} TPB and C_{16} TPB micelles reported were 7 and 5, respectively. The values were much lower than expectation. Determination of n of C_n TPBs by fluorescence quenching method using C_{16} PyCl as the quencher has been also reported by Jiang *et al*⁴⁷; the results were also of much lower magnitudes. In the present work, we have attempted to quantify the quenching efficacy of HPyC. It was found that in all the three studied media, HPyC was a much weaker quencher compared to the C_n PyBs and C_n TPBs. Thus, at higher C_n TPB concentrations (~ 20 times CMC as normally used for n determination), the pyrene fluorescence was enormously quenched by the surfactant itself, the weak quencher HPyC was unable to show its influence. We have also attempted to find aggregation

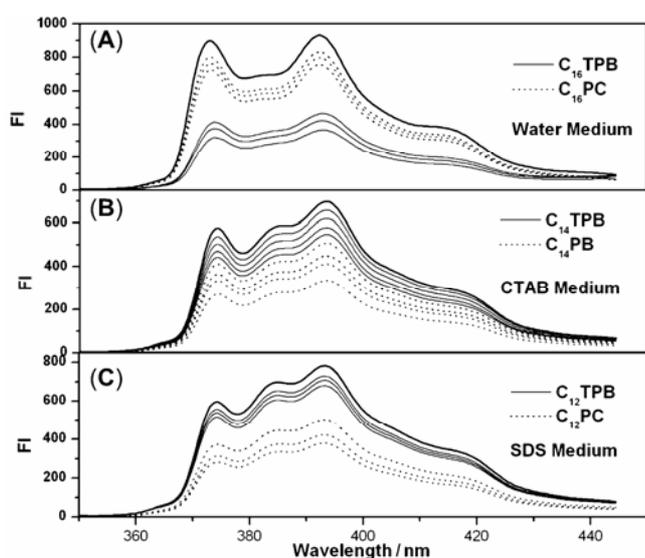


Figure 4. Illustrations of a comparison between the quenching efficiencies of C_n PyX and C_n TPX surfactants in aqueous medium, and CTAB and SDS micellar media at 303 K. The curve number increases with decreasing peak heights. (A) Aqueous medium: curve 1, pyrene spectrum in aqueous medium without quencher; curves 2 \rightarrow 4, pyrene spectra in aqueous medium with $[C_{16}PC] = 0.019, 0.029, 0.039$ mM; curves 5 \rightarrow 7 pyrene spectra in aqueous medium with $[C_{16}TPB] = 0.021, 0.029, 0.039$ mM. (B) CTAB medium (20 CMC): curve 1, pyrene spectrum in CTAB medium without quencher; curves 2 \rightarrow 5, pyrene spectra with $[C_{14}TPB] = 0.041, 0.141, 0.200, 0.295$ mM; curves 6 \rightarrow 9, pyrene spectra with $[C_{14}PB] = 0.051, 0.140, 0.200, 0.280$ mM. (C) SDS medium (20 CMC): curve 1 pyrene spectrum without quencher; curves 2 \rightarrow 4, pyrene spectra with $[C_{12}TPB] = 0.109, 0.250, 0.290$ mM; curves 5 \rightarrow 7, pyrene spectra with $[C_{12}PC] = 0.105, 0.250, 0.303$ mM.

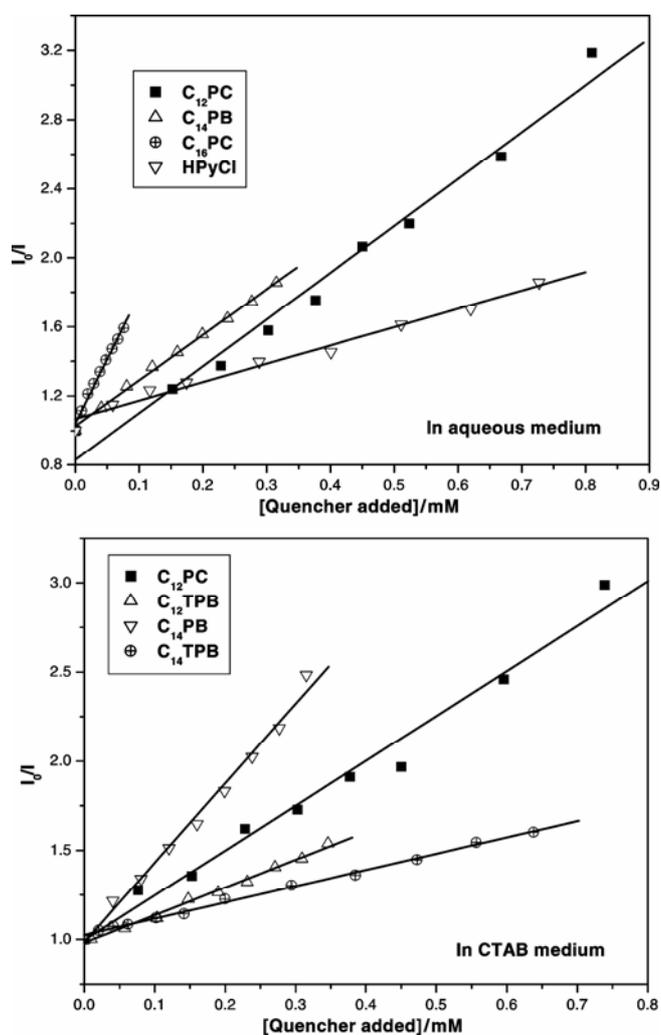


Figure 5. Comparative Stern–Volmer plots in aqueous medium and CTAB micellar medium. $[pyrene] = 2 \mu M$; Temp. = 303 K.

numbers of non photoactive surfactants by fluorescence quenching method using HPyC as the quencher, but n for CTAB could not be satisfactorily determined. SDS, however, yielded n value of 109 which was fairly higher than the reported values (~80) by us²⁸ and others. The reports in literature^{46,47} on the evaluated n of C_n TPBs by both C_{16} PyC and HPyC are thus doubtful. Uses of other techniques like light scattering, SANS etc. are required to estimate their aggregation numbers.

4. Conclusion

A brief and informative scientific narration on the bulk and surface properties of ternary mixtures of three cationic surfactants with varying chain length and identical bulky head group has been presented in this work. Interesting observations due to the low surface charge density of the bulky triphenylphosphonium head group has been reported. The observed mixed micellar CMCs of the ternary systems were considerably lower than that obtained in terms of Clint equation applicable to ideally behaved mixed systems. Thus, in solution the components fairly interacted synergistically among themselves. In addition, these surfactants showed potential fluorescence quenching behaviour and were found to be quenchers of almost equal stature as the conventional quenchers like alkylpyridinium group of surfactants. This in turn posed a serious problem for the aggregation number determination of this triphenyl phosphonium head group containing cationic surfactants by the fluorescence quenching method.

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