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ORIGINAL CONTRIBUTION

Micellar and associated thermodynamic properties of binary mixtures of alkyl triphenyl phosphonium bromides in ethylene glycol and water mixtures

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Abstract Micellar properties of binary combinations of a family of cationic alkyl triphenyl phosphonium bromides with varying chain length (C_{10}–C_{16}) were investigated in aqueous and aqueous ethylene glycol mixtures employing conductometric technique. The results of the mixed systems were analyzed in the light of the Regular Solution Theory and the Gibbs–Duhem equation to evaluate the composition of the mixed micelle, the activity coefficients, and the interaction parameter (β). The excess free energy and the other related thermodynamic parameters of mixing were calculated and discussed in terms of the stability of the mixed micelles in the presence of an ethylene glycol additive.

Keywords Mixed micelles · Interaction parameter · Thermodynamic properties · Gibbs–Duhem equation · Regular Solution Theory

Introduction

The micellization process of various ionic and nonionic surfactants in polar organic solvents such as formamide, *N*, *N*-dimethyl formamide, dimethyl sulfoxide, glycerol and ethylene glycol, and in some, aqueous–organic mixed systems has been investigated in the past to characterize how the solvent characteristics influence the aggregation process [1–12].

Ethylene glycol (EG) is one of the most commonly used additives, as it possesses a high cohesive energy, a fairly high dielectric constant, and has many characteristics similar to water. EG has the ability to form hydrogen-bonded networks similar to water, although differing in the details of the structure [7–12].

In many industrial applications, binary surfactant mixtures are proven to be superior in their properties compared to a single surfactant solution. The physicochemical properties of these systems are dependent on environmental condition such as the presence of additives. Different additives behave differently in mixed surfactant systems. The overall polarity, as well as viscosity, of the medium is affected by the addition of the additives [13–17]. At the present time, an extensive amount of research on mixed systems has been conducted, and to this date, we have not encountered studies on mixed alkyl triphenylphosphonium bromides in the presence of EG.

The application of micellar systems as a medium in the study of rates of reaction and equilibrium processes in several organic processes has attracted considerable interest [18–20]. Micelles are known to influence reaction rates by depletion of reactants in the interfacial region and can also exert a medium effect that influences reactivity. The medium effects depend on the transfer of the substrate from the bulk to the micelle and on the properties of the interfacial region such as local charge, polarity, and the solvation of the head groups. Recently, effects of mixed surfactant systems on the rates of hydrolysis, nucleophilic substitutions, and other reactions have received considerable interest in the literature [21–25]. As a part of the

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program dealing with the micellar and mixed micelle systems in the presence of additives [26], we report in this investigation the effects of EG additive on micellar properties of pure and mixed systems of alkyl triphenyl phosphonium bromides, employing the conductivity technique.

The results were analyzed in terms of the Regular Solution Theory (RST) [27] and the Gibbs–Duhem equation [28–30] to evaluate the composition of the mixed micelles, the activity coefficients, and the nature of the interaction between the surfactants in the mixture. Also, thermodynamic parameters associated with the mixed micelle formation and the influence of EG on the properties were deduced.

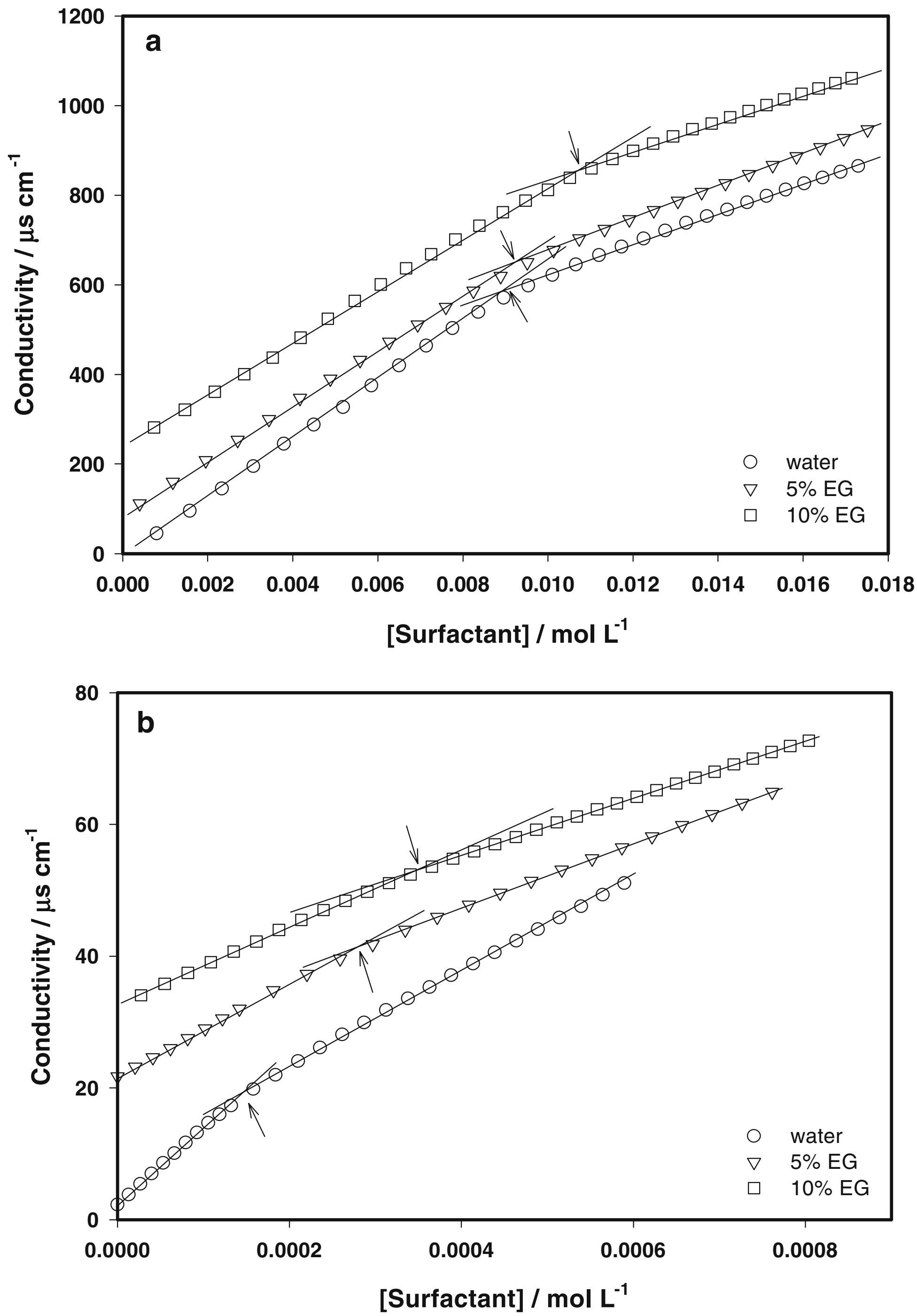

Fig. 1 Conductometric method for the determination of cmc for **a** C_{10}TPB in water, 5% EG and 10% EG, and **b** 0.3 C_{10}TPB and 0.7 C_{16}TPB in water, 5% and 10% EG, respectively

Experimental

Materials

The surfactants employed in this study are decyl (C_{10}TPB), dodecyl (C_{12}TPB), tetradecyl (C_{14}TPB), and hexadecyl (C_{16}TPB) triphenylphosphonium bromides, and were obtained from Caledron Laboratories of Canada (distributors of Lancaster Synthesis of England). The surfactants were purified as described earlier [31]. Freshly opened bottles of EG (Aldrich, 99%) were employed in the study. Binary solutions were prepared employing triply distilled and deionized water.

Methods

The conductivity technique was employed to determine the critical micellar concentration (cmc) of the pure and mixed systems in aqueous EG solutions. Conductivity measurements were made in a thermostated, jacketed beaker with a dip cell having a cell constant of 1.01 cm^{-1} and an automatic conductivity CDM 83 bridge operating at 1,000 Hz. The conductivity titrations containing at least 25 different concentrations of surfactant at a fixed solvent composition were carried at 298 K. The error in each specific conductivity measurements was estimated to be ±0.5 μs cm^{-1}.

Results and discussion

The cmc values were estimated from the break points in the plots of specific conductance (κ) vs the concentration of surfactant in surfactant binary mixtures (Fig. 1a and b). In the presence of EG, the cmc values were found to increase in both pure and binary surfactant mixtures. The cmc values in water and aqueous EG are numerically fitted into polynomial equations as a function of bulk mole fraction (α_i). The parameters of the fitting polynomial equations are presented in Table 1a and b.

The values of the counter-ion binding ($\delta = 1 - S_2/S_1$), calculated from post- (S_2) and pre- (S_1) micellar slopes of the plots of κ vs α_i, decreased with the addition of the additive (EG) in the case of pure surfactant micelles and effected to a lesser extent in the case of binary mixed micelles (data not shown). The decreased in charge density can be attributed to the penetration of the additive into the micellar interior and also due to the decrease in the aggregation number [7].

In mixed surfactant systems, the micelles are in equilibrium with the monomeric species in the bulk solution and normally considered in the context of pseudophase separation model. Clint [32] proposed a relationship to calculate the ideal cmc_i* of the mixed micelle as a function of mole fraction of the individual surfactants (α_i) in the bulk phase as follows:

$$\frac{1}{cmc_i^*} = \sum \frac{\alpha_i}{cmc_i}, \tag{1}$$

Table 1 Values for the fitting parameters for the cmc values of the mixture vs the bulk mole fraction

System	Solvent	*a*	*b*	*c*	*d*	r^2
A. Values using the polynomial equation $y=a+bx+cx^2+dx^3$						
C_{10}TPBr+C_{12}TPBr	H_2O	2.08	3.8638	−13.276	16.174	0.992
	5% EG	2.15	4.7426	−10.867	13.291	0.999
	10% EG	2.17	5.7105	−16.000	17.985	0.990
C_{12}TPBr+C_{14}TPBr	H_2O	0.572	0.7701	−2.0498	2.7641	0.996
	5% EG	0.652	0.3385	−0.481	1.6487	0.988
	10% EG	0.707	0.5702	−1.4793	2.2614	0.969
C_{14}TPBr+C_{16}TPBr	H_2O	0.156	0.1229	−0.1076	0.3956	0.996
	5% EG	0.224	0.1699	−0.1786	0.4694	0.986
	10% EG	0.280	0.3157	−0.5312	0.6452	0.990
B. Values using the polynomial equation $y^{-1}=a+bx+cx^2+dx^3$						
C_{10}TPB+C_{14}TPB	H_2O	1.4567	3.2307	−9.2009	4.6238	0.994
	5% EG	1.4600	0.8885	−3.5118	1.2703	0.997
	10% EG	1.0069	2.4074	−6.4597	3.1434	0.997
C_{10}TPB+C_{16}TPB	H_2O	5.7467	4.6840	−19.0145	8.6942	0.999
	5% EG	3.8860	6.3578	−15.9859	5.8490	0.999
	10% EG	2.5419	6.5287	−16.6463	7.6737	0.990
C_{12}TPB+C_{16}TPB	H_2O	6.1916	−3.4909	−3.6012	1.3811	0.999
	5% EG	3.600	12.6431	−32.3952	16.6111	0.992
	10% EG	3.2727	−0.6743	−3.0397	0.9010	0.998

where cmc_i is the critical micelle concentration of the pure surfactant i.

The lower experimental values of cmc* of the mixed micelles compared to the calculated cmc_i* is attributed to the attractive interactions between the component in the mixed micelles. Figure 2a–c represents the plots of cmc* and cmc_i* vs the bulk mole fraction for $C_{10}TPBr/C_{14}TPBr$ system in water, 5 and 10% EG solutions, respectively. In all cases, the lower values of cmc* indicate that the binary systems deviated from the ideal behavior.

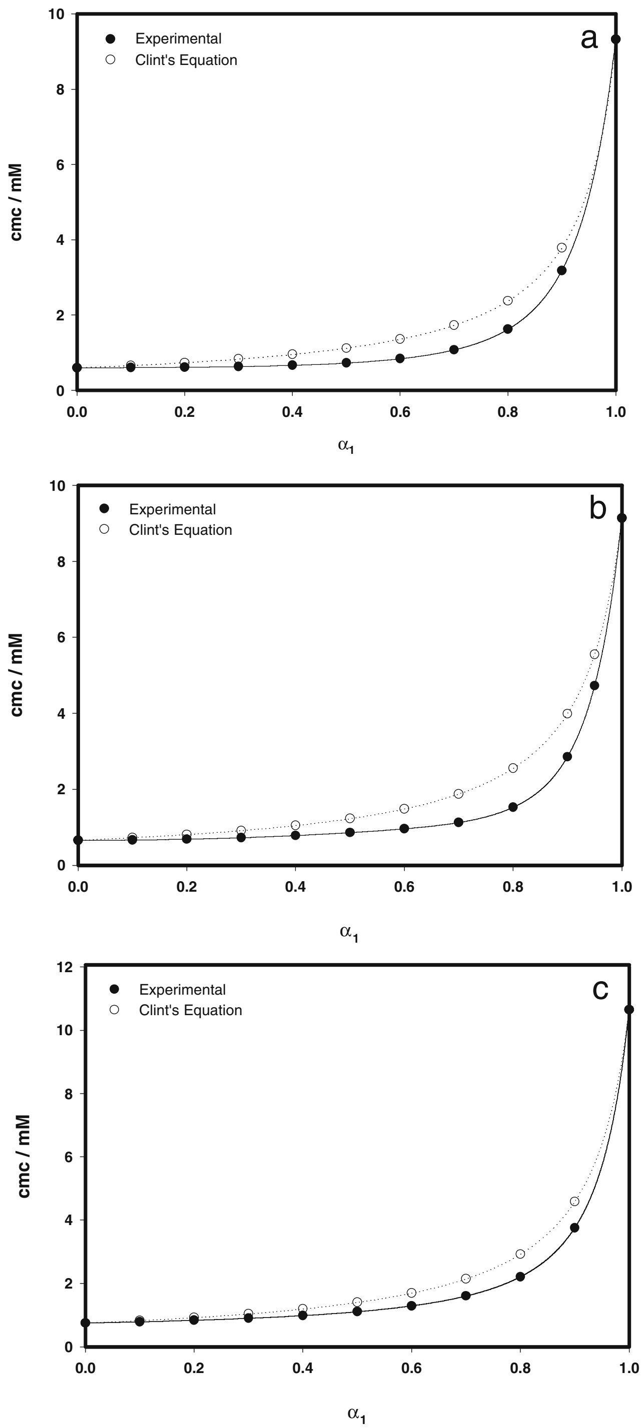

Fig. 2 Plots of the experimental cmc vs the bulk mole fraction for **a** $C_{10}/C_{14}TPB$ in water, **b** $C_{10}/C_{14}TPB$ in 5% aqueous EG, and **c** $C_{10}/C_{14}TPB$ in 10% aqueous EG

To account for the non-ideality, Clint's equation is further modified by Rubingh [27] by introducing activity coefficients (f_i).

$$\frac{1}{\mathrm{cmc}^*} = \frac{\alpha_i}{\mathrm{cmc_i\ f_i}}. \tag{2}$$

Based on the RST, Rubingh's model relates the activity coefficient values to a micellar interaction parameter (β_m) as follows:

$$f_1 = \exp\beta_m (1 - X_1)^2 \tag{3}$$

$$f_2 = \exp\beta_m (X_1)^2, \tag{4}$$

where X_1 represents the mole fraction of component 1 in the mixed micelle. The sign and magnitude of β_m is an indication of the nature and relative strength of the interaction between the individual components in the mixed micelle. The composition of the mixed micelle (X_1) can be calculated by solving the following equation iteratively:

$$X_1^2 \ell n \left[\frac{\alpha_1 \mathrm{cmc}^*}{X_1\ \mathrm{cmc}_1}\right] = (1 - X_1)^2 \ell n \left[\frac{(1-\alpha_1)}{(1-X_1)} \frac{\mathrm{cmc}^*}{\mathrm{cmc}_2}\right] \tag{5}$$

The value of β_m is obtained as follows:

$$\beta_m = \ell n \left[\frac{\mathrm{cmc}^*\alpha_1}{\mathrm{cmc}_1\ X_1}\right] \Big/ (1 - X_1)^2 \tag{6}$$

The ideal mole fraction value X_1^{ideal} in the mixed micelle is calculated by assuming β_m=0 in Eq. 6 and is given by

$$X_1^{ideal} = \frac{\alpha_1\ \mathrm{cmc}^*}{\mathrm{cmc}_1}. \tag{7}$$

The calculated values of various parameters β_m, X_1, f_1, and f_2 as a function of the bulk mole fraction for C_{14}–C_{16}, C_{12}–C_{16}, and C_{10}–C_{16} systems in water, 5% EG and 10% EG, are presented in Tables 2, 3, and 4, respectively. The data for the rest of the combinations can be found in the Supplementary Material 1. The values of X_1 as a function of the bulk mole fraction (α_1), along with the ideal values (X_1^{ideal}, solid line), are presented in Fig. 3a–c for the $C_{10}TPBr/C_{12}TPBr$ system. The values of β_m are found to vary with composition, and such behavior was previously reported [26]. In all cases, the average values are negative

Table 2 Micellar parameters for systems with varying chain lengths in water as obtained from the Rubingh and the Gibbs–Duhem methods

System		Rubingh's model				Gibbs–Duhem model		
	α_1	β	X_1	f_1	f_2	X_1	f_1	f_2
$C_{14}TPB+C_{16}TPB$	0.1	−0.171	0.035	0.853	1.000	0.041	0.742	1.040
	0.2	−0.294	0.082	0.780	0.998	0.091	0.682	0.998
	0.3	−0.324	0.132	0.783	0.994	0.130	0.799	1.021
	0.4	−0.282	0.182	0.828	0.991	0.156	0.936	0.953
	0.5	−0.184	0.236	0.898	0.990	0.182	1.149	0.936
	0.6	−0.053	0.300	0.975	0.995	0.230	1.207	0.883
	0.7	−0.023	0.396	0.992	0.996	0.328	1.275	0.979
	0.8	−0.021	0.528	0.995	0.994	0.495	1.111	0.998
	0.9	−0.011	0.715	0.999	0.995	0.731	0.975	1.079
		β_{ave}=−0.151						
$C_{12}TPB+C_{16}TPB$	0.1	−1.458	0.034	0.256	0.998	0.033	0.246	0.996
	0.2	−1.407	0.064	0.292	0.994	0.058	0.300	0.991
	0.3	−1.330	0.093	0.335	0.989	0.077	0.396	1.026
	0.4	−1.222	0.120	0.388	0.983	0.088	0.543	1.046
	0.5	−1.073	0.147	0.458	0.977	0.093	0.741	1.014
	0.6	−0.873	0.176	0.553	0.973	0.097	0.928	0.886
	0.7	−0.617	0.212	0.682	0.973			
	0.8	−0.311	0.272	0.848	0.977			
	0.9	−0.018	0.422	0.994	0.997			
		β_{ave}=−0.923						
$C_{10}TPB+C_{16}TPB$	0.1	−3.707	0.053	0.036	0.990	0.059	0.034	1.110
	0.2	−3.811	0.093	0.043	0.968	0.103	0.035	0.938
	0.3	−3.861	0.125	0.052	0.941	0.130	0.038	0.774
	0.4	−3.852	0.152	0.063	0.915	0.137	0.069	0.959
	0.5	−3.757	0.175	0.077	0.891	0.121	0.108	0.864
	0.6	−3.531	0.194	0.101	0.876			
	0.7	−3.081	0.207	0.144	0.876			
	0.8	−2.211	0.210	0.252	0.907			
	0.9	−0.513	0.186	0.712	0.982			
		β_{ave}=−3.147						

and indicative of synergestic interactions. The synergism is found to be stronger with increasing differences in the alkyl chain length of the individual surfactants. Maximum synergestic interactions are observed for C_{10}–C_{16} systems, and in all cases, the presence of 5% EG enhanced the effects. The synergism in the mixtures of surfactants depends on the relevant properties of the individual surfactant components as well as on the strength of the interaction between them [33]. Recently, Maeda [34] proposed that in addition to electrostatic interactions, the chain/chain interactions play a major role in the formation of mixed micelles, especially for the dissimilar chain lengths. In the present study, hydrophobic chain/chain interactions contribute to the synergism, whereas the head group contributions may be both synergistic as well as antagonistic in nature. Steric hindrance and electrostatic repulsions contribute to the antagonistic nature and hydrophobic hydration of phenyl moieties, and solvent penetration in the head group region may interact favorably to contribute to synergism. It is apparent that the relative contributions depend on the amounts of additive EG. It is well known in the literature that the higher the content of additive EG, the smaller micelles with low aggregation numbers thereby decreasing in the synergistic contributions and increasing in antagonistic effects, leading to a slightly lower interaction parameter value for 10% EG aqueous surfactant mixtures.

The experimental data is also analyzed, employing the Gibbs–Duhem equation to compute the composition of the mixed micelle. The composition X_1 is related to the bulk mole fraction (α_1) as follows:

$$X_1 = \alpha_1 - \alpha_1(1-\alpha_1)\frac{\mathrm{d}\,\ell\mathrm{n\ cmc}*}{d\alpha_1} \qquad (8)$$

The composition X_1 was determined from the values of the derivative of the fitting equation at various values of α_1

Table 3 Micellar parameters for systems with varying chain lengths in 5% aqueous EG as obtained from the Rubingh and the Gibbs–Duhem methods

System		Rubingh's model				Gibbs–Duhem model		
	α_1	β	X_1	f_1	f_2	X_1	f_1	f_2
$C_{14}TPB+C_{16}TPB$	0.1	−1.247	0.035	0.313	0.998	0.046	0.878	1.112
	0.2	−1.521	0.084	0.279	0.989	0.109	0.707	1.010
	0.3	−1.683	0.132	0.282	0.971	0.161	0.740	0.965
	0.4	−1.769	0.177	0.302	0.946	0.197	0.957	1.024
	0.5	−1.805	0.220	0.334	0.916	0.229	1.060	0.918
	0.6	−1.827	0.266	0.374	0.878	0.282	1.187	0.906
	0.7	−1.900	0.321	0.417	0.822	0.380	1.104	0.845
	0.8	−2.136	0.394	0.456	0.718	0.540	1.127	0.963
	0.9	−2.830	0.492	0.482	0.504	0.759	1.066	1.085
		β_{ave}=−1.857						
$C_{12}TPB+C_{16}TPB$	0.1	−2.254	0.071	0.143	0.989	0.079	0.123	0.912
	0.2	−2.368	0.128	0.165	0.962	0.146	0.148	0.970
	0.3	−2.453	0.175	0.188	0.928	0.195	0.179	0.970
	0.4	−2.490	0.216	0.216	0.890	0.218	0.213	0.852
	0.5	−2.447	0.252	0.255	0.856	0.205	0.313	0.775
	0.6	−2.266	0.285	0.314	0.832			
	0.7	−1.855	0.316	0.420	0.831			
	0.8	−1.100	0.355	0.633	0.870			
	0.9	−0.059	0.475	0.984	0.987			
		β_{ave}=−1.921						
$C_{10}TPB+C_{16}TPB$	0.1	−3.683	0.062	0.039	0.986	0.073	0.033	0.966
	0.2	−3.878	0.109	0.046	0.955	0.138	0.036	0.965
	0.3	−4.058	0.149	0.053	0.914	0.194	0.043	1.001
	0.4	−4.219	0.184	0.060	0.867	0.238	0.043	0.840
	0.5	−4.352	0.217	0.069	0.815	0.265	0.061	0.914
	0.6	−4.432	0.248	0.082	0.761			
	0.7	−4.404	0.279	0.101	0.710			
	0.8	−4.121	0.310	0.141	0.672			
	0.9	−3.117	0.350	0.268	0.682			
		β_{ave}=−4.029						

and by fitting ln cmc* vs α_1. The corresponding values of the activity coefficients f_1 and f_2 are calculated by employing the following equation based on the pseudophase separation model:

$$\alpha_1\,\mathrm{cmc}^* = X_1 f_1 \mathrm{cmc}_1 \tag{9}$$

$$(1-\alpha_1)\mathrm{cmc}^* = (1-\mathrm{X}_1)\mathrm{f}_2\mathrm{cmc}_2 \tag{10}$$

The corresponding values of X_1, f_1, and f_2 obtained are also presented in Tables 2, 3, and 4 for C_{16}TPB with C_{14}, C_{12}, and C_{10} TPB systems in water and aqueous EG. The rest of the analyzed data is presented in the Supplementary Material 1. In the case of the binary surfactants C_{10}–C_{12}, C_{12}–C_{14}, C_{14}–C_{16}, acceptable agreement between the values X_1, f_1, and f_2 was obtained by both methods. However, in the case of C_{10}–C_{14}, C_{10}–C_{16}, C_{12}–C_{16}, only acceptable agreement was observed in the lower values of α_1.

Applying the RST approach, the thermodynamic functions of mixing for the binary systems were computed (Fig. 4). Assuming the excess entropy of mixing to be equal to zero [35], the excess free energy (ΔG^E), excess enthalpy (ΔH^E), and enthalpy of mixing is given by

$$\Delta G^E = \Delta H^E = \Delta H_M = RT\sum X_i\,\ell n f_i \tag{11}$$

$$\begin{aligned}\Delta \mathrm{G}^{\mathrm{E}} &= \Delta \mathrm{G}_{\mathrm{M}} - \Delta \mathrm{G}_{\mathrm{M}}^{\mathrm{ideal}} \\ &= \mathrm{RT}\left[\sum_{\mathrm{i}} \mathrm{X_i}\,\ell\mathrm{n}\,\mathrm{X_i}\,\mathrm{f_i} - \sum \mathrm{X_i}\,\ell\mathrm{n}\,\mathrm{X_i}\right] \\ &= \mathrm{RT}\sum_{\mathrm{i}} \mathrm{X_i}\,\ell\mathrm{n}\,\mathrm{f_i}.\end{aligned} \tag{12}$$

The value of $T\Delta S_M = \Delta H_M - \Delta G_M = RT\sum_i X_i\,\ell n f_i - RT\sum X_i\,\ell n X_i f_i$ or $\Delta \mathrm{S_M} \equiv -R\sum_{\mathrm{i}} \mathrm{X_i}\,\ell n\,\mathrm{X_i}$.

Table 4 Micellar parameters for systems with varying chain lengths in 10% aqueous EG as obtained from the Rubingh and the Gibbs–Duhem methods

System		Rubingh's model				Gibbs–Duhem model		
	α_1	β	X_1	f_1	f_2	X_1	f_1	f_2
$C_{14}TPB+C_{16}TPB$	0.1	−0.502	0.062	0.643	0.998	0.043	0.933	0.954
	0.2	−0.224	0.103	0.835	0.998	0.075	1.194	0.976
	0.3	−0.107	0.151	0.926	0.998	0.137	1.081	1.011
	0.4	−0.099	0.214	0.941	0.995	0.224	0.974	1.066
	0.5	−0.144	0.290	0.930	0.988	0.321	0.860	1.025
	0.6	−0.207	0.378	0.923	0.971	0.413	0.854	1.013
	0.7	−0.263	0.476	0.930	0.942	0.501	0.879	0.955
	0.8	−0.296	0.593	0.952	0.901	0.600	0.972	0.919
	0.9	−0.294	0.750	0.982	0.848	0.746	1.056	0.870
		β_{ave}=−0.237						
$C_{12}TPB+C_{16}TPB$	0.1	−0.310	0.019	0.742	1.000	0.014	1.022	1.044
	0.2	0.080	0.029	1.078	1.000	0.061	0.515	1.041
	0.3	−0.484	0.077	0.662	0.997	0.129	0.379	1.016
	0.4	−0.778	0.132	0.557	0.986	0.200	0.377	1.095
	0.5	−0.978	0.191	0.527	0.965	0.251	0.426	1.106
	0.6	−1.079	0.249	0.545	0.935	0.267	0.496	0.934
	0.7	−1.043	0.309	0.608	0.905			
	0.8	−0.835	0.385	0.729	0.884			
	0.9	−0.472	0.530	0.901	0.876			
		β_{ave}=−0.655						
$C_{10}TPB+C_{16}TPB$	0.1	−3.407	0.058	0.049	0.989	0.042	0.072	1.030
	0.2	−3.116	0.083	0.073	0.979	0.062	0.115	1.106
	0.3	−3.148	0.116	0.085	0.959	0.166	0.065	1.098
	0.4	−3.498	0.162	0.086	0.913	0.291	0.050	1.119
	0.5	−3.810	0.205	0.090	0.852	0.272	0.072	0.974
	0.6	−3.753	0.233	0.110	0.816			
	0.7	−3.348	0.251	0.153	0.810			
	0.8	−3.107	0.288	0.207	0.773			
	0.9	−2.852	0.356	0.307	0.696			
		β_{ave}=−3.338						

Various thermodynamic parameters of mixing were computed and tabulated in Table 5 for C_{10} with C_{12}, C_{14}, and C_{16} surfactants. The parameters for the rest of the systems are found in Supplementary Material 1.

The mixing parameters are of the same order as reported in the literature [30]. The values of ΔG_M are negative, indicating that mixed micellar formation is spontaneous and micellar formation is accompanied by an increase in ΔS_M with α_i. The additive EG acted as a structure breaker, disrupting the water structure, resulting in a decrease in the hydrophobic effect thereby increasing the cmc values [7].

The synergistic effects observed in the present study can be attributed to the additive penetration into the micelle, lowering the headgroup/headgroup repulsions due to the solvation of the polar head groups by the solvent acting as a bridge between the surfactant head groups, resulting in an attractive interaction. In addition to the headgroup/headgroup interactions, Mukherjee [36] explained the stability of hydrocarbon/fluorocarbon mixed micelles in water by the term "contact hydrophobic interaction." Because the hydrophobicity depends on the chain length, contact hydrophobic interaction may be responsible for the stronger synergestic effects observed in the case of the C_{10}/C_{16}, C_{10}/C_{14}, C_{12}/C_{16} systems compared to C_{10}/C_{12}, C_{12}/C_{14}, and C_{14}/C_{16}.

Conclusions

The mixed systems of alkyl triphenylphosphonium bromides in water and aqueous EG mixtures exhibited synergism in the formation of mixed micelles. The synergistic effects are found to decrease as the difference in the carbon chain lengths decrease from six to four to two. The synergistic effect can be attributed to headgroup/headgroup interactions brought about by the solvent

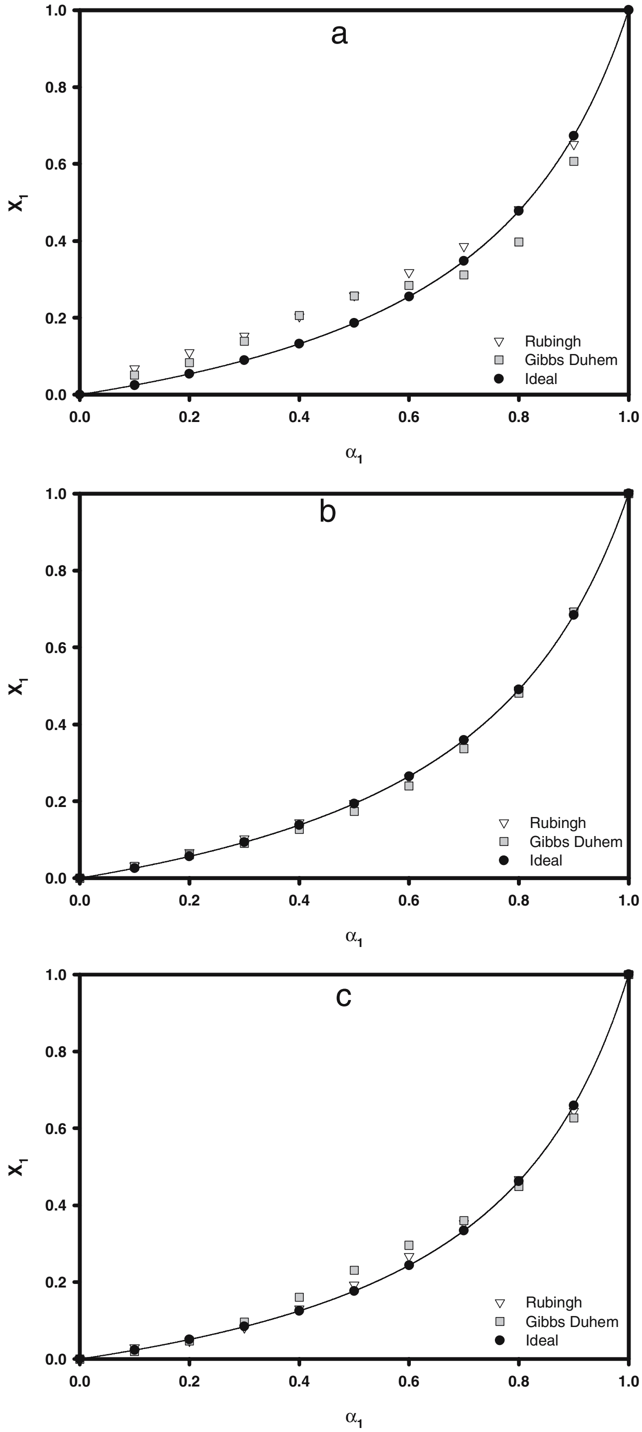

Fig. 3 Plots of micellar composition (X_1) vs bulk mole fraction for **a** C_{10}/C_{12}TPB in water, **b** C_{10}/C_{12}TPB in 5% aqueous EG, and **c** C_{10}/C_{12}TPB in 10% aqueous EG

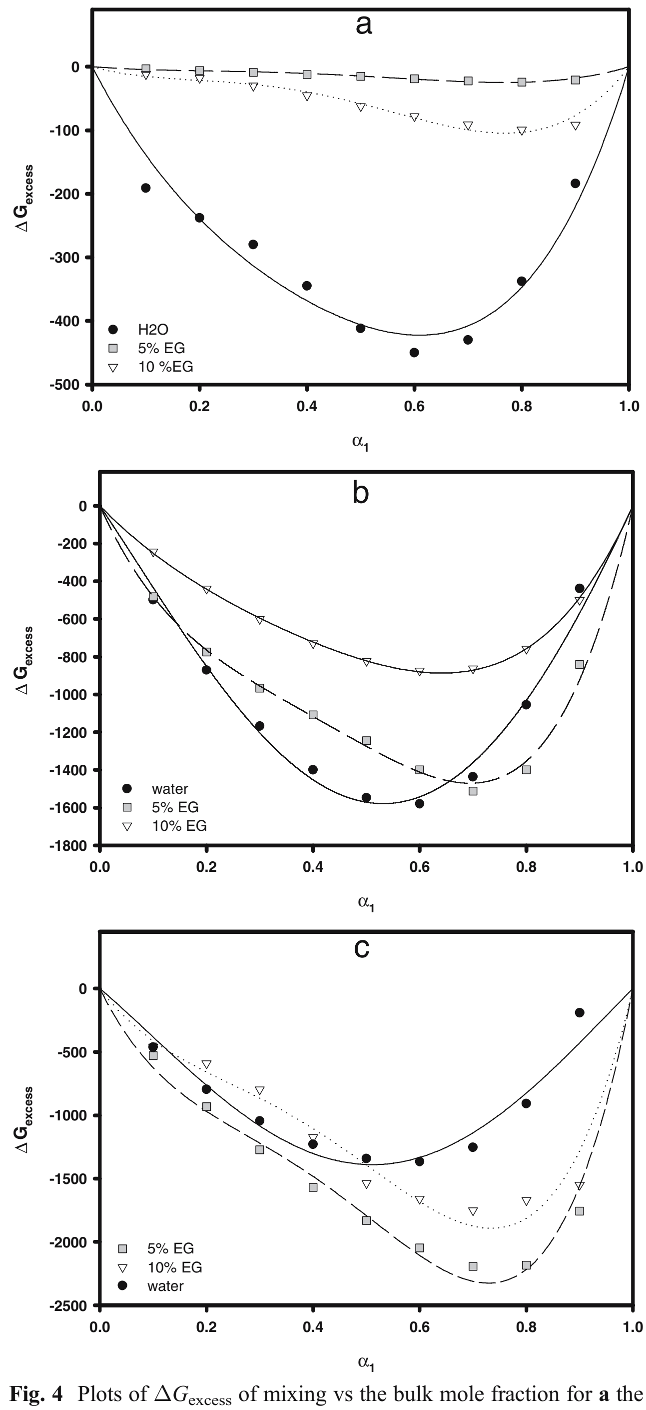

Fig. 4 Plots of $\Delta G_{\mathrm{excess}}$ of mixing vs the bulk mole fraction for **a** the C_{10}/C_{12}TPB system, **b** the C_{10}/C_{14}TPB system, and **c** the C_{10}/C_{16}TPB system

penetration thereby acting as a bridge and decreasing the headgroup/headgroup repulsions. The contact hydrophobic interactions between the chains in the mixed micelle also contribute to the favorable mixed micelle formation. All the thermodynamic parameters determined in the investigation indicate spontaneous formation of the mixed micelles. The composition of the mixed micelle evaluated from Rubingh's and Gibbs–Duhem methods are in agreement, except at higher mole fractions when the alkyl chain lengths differ by four or six carbon atoms. In all cases, the activity coefficient values of the longer chain surfactant are closer to the standard state in the mixed micelle.

Table 5 Thermodynamics of mixed micellar systems in water, 5% EG, and 10% EG, as determined by Rubingh's model

System	α_1	Water			5% Ethylene glycol			10% Ethylene glycol		
		ΔG_M	ΔS_M	G^E	ΔG_M	ΔS_M	G^E	ΔG_M	ΔS_M	G^E
C_{10}TPB/C_{12}TPB	0.1	−806	2.06	−191	−368	1.21	−3.1	−345	1.12	−11.8
	0.2	−1093	2.87	−238	−626	2.04	−6.0	−487	1.57	−17.9
	0.3	−1338	3.55	−280	−847	2.76	−9.0	−733	2.36	−30.0
	0.4	−1593	4.19	−345	−1,060	3.44	−12.0	−1,008	3.23	−45.3
	0.5	−1826	4.75	−412	−1,266	4.10	−15.2	−1,278	4.08	−62.1
	0.6	−1998	5.19	−450	−1,523	4.92	−18.7	−1,516	4.82	−77.9
	0.7	−2082	5.54	−430	−1,692	5.46	−22.2	−1,701	5.40	−91.1
	0.8	−2053	5.75	−338	−1,786	5.76	−24.2	−1,812	5.74	−99.2
	0.9	−1786	5.38	−184	−1,608	5.19	−20.6	−1,704	5.41	−91.2
C_{10}TPB/C_{14}TPB	0.1	−1162	2.23	−498	−1,149	2.24	−481	−729	1.63	−243
	0.2	−1838	3.25	−871	−1,719	3.17	−774	−1,196	2.54	−439
	0.3	−2330	3.90	−1,168	−2,083	3.75	−966	−1,553	3.20	−600
	0.4	−2696	4.35	−1,399	−2,352	4.17	−1,108	−1,836	3.72	−729
	0.5	−2942	4.68	−1,547	−2,601	4.55	−1,245	−2,057	4.14	−823
	0.6	−3046	4.92	−1,579	−2,859	4.90	−1,399	−2,217	4.51	−874
	0.7	−2958	5.10	−1,436	−3,060	5.20	−1,511	−2,308	4.85	−863
	0.8	−2625	5.27	−1,055	−3,020	5.44	−1,399	−2,308	5.20	−758
	0.9	−2105	5.59	−438	−2,536	5.69	−840	−2,184	5.65	−499
C_{10}TPB/C_{16}TPB	0.1	−977	1.73	−462	−1,105	1.93	−530	−1,006	1.84	−459
	0.2	−1562	2.57	−796	−1,785	2.86	−932	−1,301	2.39	−590
	0.3	−1979	3.13	−1,046	−2,313	3.49	−1,272	−1,684	2.98	−797
	0.4	−2285	3.54	−1,229	−2,752	3.97	−1,570	−2,270	3.68	−1,174
	0.5	−2490	3.85	−1,342	−3,125	4.35	−1,830	−2,792	4.21	−1,536
	0.6	−2583	4.08	−1,366	−3,434	4.65	−2,047	−3,002	4.51	−1,659
	0.7	−2516	4.24	−1,253	−3,657	4.92	−2,192	−3,144	4.68	−1,750
	0.8	−2181	4.27	−908	−3,718	5.15	−2,184	−3,158	4.99	−1,671
	0.9	−1382	3.99	−192	−3,361	5.38	−1,757	−3,232	5.41	−1,620

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