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ORIGINAL CONTRIBUTION

Interfacial and aggregation properties of the binary mixture of decanoyl-*N*-methyl-glucamide and hexadecyltriphenylphosphonium bromide

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Abstract The interfacial and aggregation behavior of the nonionic surfactant decanoyl-*N*-methyl-glucamide (Mega-10) with the cationic surfactant hexadecyltriphenylphosphonium bromide (HTPB) have been studied using interfacial tension measurements and fluorescence techniques. From interfacial tension measurements, the critical micellar concentrations (cmc) and various interfacial thermodynamic parameters have been evaluated. The experimental results were analyzed in the context of the pseudophase separation model, the regular solution theory, and the Maeda's approach. These approaches allowed us to determine the interaction parameter and composition in the mixed state. By using the static quenching method, the mean micellar aggregation numbers of pure and mixed micelles of HTPB+Mega-10 were obtained. It was found that that the aggregation number decreases with increasing mole fraction of HTPB. This behavior is attributed to the presence of the bulky head group of HTPB, which creates steric head group incompatibility and/or electrostatic repulsion. The micropolarity of the micelle was monitored with pyrene fluorescence intensity ratio. It was observed that the increasing participation of HTPB induces the formation of micelles with a hydrated structure. The polarization of the fluorescent probe Rhodamine B was monitored in micellar medium and found to increase with the increase of ionic content. This behavior suggests the formation of mixed micelles with a more ordered or rigid structure.

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Introduction

Surfactants are surface-active agents that have unique structure due to the presence of a polar and a nonpolar part. They have extremely important physiochemical properties at the air–water interface and in the bulk solutions. These properties make surfactants versatile for use in the field of physical, biophysical, pharmaceutical, agricultural and other industrial applications [1–3]. During the last decade, the increase of interest in the mixed surfactant systems has increased due to their favorable interactions. These interactions increase the surface activity, solubilization, spreading, wetting, and foaming properties of surfactant solutions [4–6]. When different kinds of surfactants are mixed, they form mixed micelles, which are of interest as good models for the study of molecular interactions on complex supramolecular aggregates and simplified models of biological membranes. Mixed micelles of ionic and nonionic surfactant mixtures show expanded colloidal stability in comparison to pure nonionic surfactant. Mixed micellar behavior of conventional surfactant mixtures has been investigated in detail [5]. However, studies of nonconventional surfactant mixtures such as di, tri, poly block polymer and sugar-based surfactants are rather scarce.

Nonionic surfactants are a class of amphiphiles, which are used extensively in different industrial and pharmaceutical formulations and found to be very useful in biotechnology for purification, solubilization, and crystallization of membrane proteins. Alkylpolyglycosides (APG's), e.g., *n*-

dodecylmaltoside, are a class of nonionic surfactants consisting of one or more carbohydrate units as the polar head group. They have received considerable attention due to their improved solution properties compared to ethoxylated surfactants [7–9]. APG's have both stronger hydrophobicity and hydrophilicity, and the temperature dependence of their solution properties is less pronounced than for ethoxylated surfactants. Furthermore, they do not show the clouding phenomenon (i.e., formation of phase separation at elevated temperature) [10, 11]. These kinds of surfactants are biodegradable and safe for the skin, and hence used widely in cosmetic, cleaning, and food products [12]. The self-aggregation of Mega-10 and the physicochemical characterization of the process have been investigated [13, 14]. But, interactions of Mega-10 with other surfactants are limited [3, 15–17].

In this work, we have presented experimental results of pure HTPB and Mega-10 and their binary mixtures in different ratios. First, we performed the interfacial tension measurements to determine the mixed cmc's and the interfacial thermodynamic parameters of pure and binary mixture of HTPB+Mega-10. Mixed cmc's data were analyzed in the light of different thermodynamic models. Second, steady-state fluorescence measurements were performed to determine the aggregation number and polarity of the micelle and their Stern–Volmer binding constant depending on the solution composition. Finally, we studied the polarization of Rhodamine B (RB) to monitor the rigidity of the mixed micelle at different HTPB mole ratios.

Experimental

Materials

Hexadecyltriphenylphosphonium bromide (HTPB) (>98% pure) from Avocado, England; cetylpyridinium chloride (CPyCl), (>98% pure) from TCI, Japan; decanoyl-*N*-methyl-glucamide (Mega-10) (98% pure) and Rhodamine B (RB) (approximately 95% pure) from Sigma; and pyrene (>99% pure) from Nacalai Tesque, Japan were used without further purification. All solutions were prepared in Milli-Q water obtained from the Direct-Q Millipore system with a resistivity of 18.2 MΩcm.

Interfacial tension

The interfacial tension was measured with an EZ-PI interfacial tensiometer from Kibron, Finland. This instrument is equipped with a sensor probe and a cuvette holder. Four milliliters of surfactant solution was introduced in the cuvette and placed onto the cuvette holder. Surfactant solutions were prepared from the surfactant stock solutions. Before starting the measurements, the instrument was calibrated with Milli-Q water. All measurements were carried out at 24.0±1°C.

Steady-state fluorescence

Steady-state fluorescence experiments were performed with a Perkin-Elmer LS 50B luminescence spectrometer to evaluate the mean aggregation number for the solutions of pure and mixed micelles at 24.0±1°C. A quartz cell with an optical path of 10 mm was used for the measurements. Both the excitation and emission band slits were kept at 5 nm, and the scan rate was chosen at 300 nm/min. Pyrene was used as a fluorescence probe and CPyCl was chosen as a static quencher. The concentration of pyrene was kept at 0.5 μM, while the quencher concentration was varied from 0 to 100 μM. The excitation wavelength for pyrene was 335 nm, while the emission spectra were recorded between 360 and 460 nm. The first and third vibronic peaks of pyrene appeared at 374 and 384.26 nm, respectively. In all experiments, the total surfactant concentration was kept at 12 mM. Because the quencher CPyCl is a surfactant itself, its concentration was kept below 1% of the total surfactant concentration so that the quencher does not interfere with the assembly of pure and mixed micelles. The emission spectrum was scanned two times and the average was taken. The uncertainty in N_{agg} values obtained was less than 3%.

Fluorescence anisotropy

All the fluorescence anisotropy measurements were carried out at 25.0±0.2°C with a fluorescence polarization instrument system (Beacon-2000) from USA. This apparatus is equipped with a 100 W halogen lamp as excitation source. Rhodamine B (RB) was used as a fluorescence probe and its concentration was kept at 1 μM. We have also performed the anisotropy measurements from 10 nM to 2 μM probe concentration at 12 mM of pure surfactant concentration (data not shown). The probe concentration (1 μM) at saturated r value (where the probe completely associates with the micelles) were chosen for the experimental condition. The total surfactant concentration of pure and binary mixtures was 12 mM. Fluorescence anisotropies were measured using excitation and emission wavelengths of 570 and 630 nm, respectively. When the emission polarizer is oriented parallel or perpendicular to the direction of the polarized excitation, each fluorescence intensity is called $I_{\|}$ or $I_{\perp}$, respectively. Anisotropy is the ratio of intensity difference $\left(I_{\|}-I_{\perp}\right)$ to the total intensity $\left(I_{\|}+2I_{\perp}\right)$ as shown by Eq. 1:

$$r=\frac{I_{\|}-I_{\perp}}{I_{\|}+2I_{\perp}} \tag{1}$$

The anisotropies values given are the average of 10 readings.

Results and discussion

Micellar and interfacial adsorption parameters

We have obtained the critical micellar concentration (cmc) and interfacial adsorption parameters of the mixed system of HTPB and Mega-10. Figure 1 shows the representative plots of the interfacial tension γ vs log C_s for the pure and binary surfactant mixture where C_s is the total surfactant concentration. Each plot shows a decline in γ with an increase in surfactant concentration reaching a specific break point, which was taken as the cmc value. The cmc values are shown in Table 1 and Fig. 2. The obtained cmc values for the pure components are in good agreement with previously reported values [3, 16, 17]. Apart from evaluating cmc from the γ vs log C_s plots, we have evaluated the interfacial adsorption parameter of the pure and mixed surfactants at the air–water interface. The surfactant surface excess at cmc, $\Gamma_{\max}$, can be determined for the dilute solutions by the Gibbs equation [1]:

$$\Gamma_{\max}=-\frac{1}{2.303RT\left(1+X_{1,\mathrm{mon}}\right)}\left[\frac{\partial\gamma}{\partial\log C}\right]_{T,P} \tag{2}$$

where γ, C, R, T, P, and $X_{1,\mathrm{mon}}$ are the interfacial tension, concentration of surfactant, ideal gas constant, temperature, pressure and monolayer composition of cationic surfactant (HTPB), respectively. In Eq. 2, we have considered the adsorption of counterions at the interface to calculate the $\Gamma_{\max}$. The average minimum area occupied by the surfactant species at the interface, $A_{\min}$, was then evaluated by the equation:

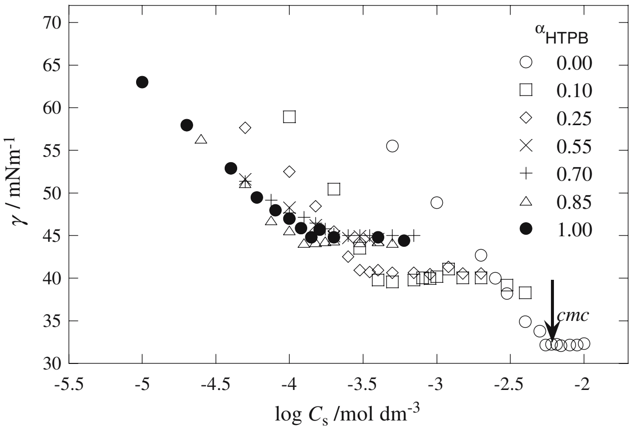

Fig. 1 Plot of interfacial tension γ vs log C_s/mol dm^{-3} at different α_{HTPB} for HTPB+Mega-10 mixed system

$$A_{\min}=1/N\Gamma_{\max} \tag{3}$$

where N is Avogadro's number. The values of $\Gamma_{\max}$ and $A_{\min}$ for the mixed system of HTPB and Mega-10 are listed in Table 1. The value found for $\Gamma_{\max}$ of pure Mega-10 agreed with the reported value [3]. The value found for $\Gamma_{\max}$ of Mega-10 is higher than that of HTPB. This behavior suggests that the amphiphilic Mega-10 is arranged more compactly than HTPB. This is a consequence of the presence of a charge leading to electrostatic repulsion and the presence of the bulky triphenyl group in the HTPB molecule inducing steric hindrance preventing a tight packing of HTPB molecules at the interface. The $\Gamma_{\max}$ for the binary mixture decreases with increasing mole fraction of HTPB. This effect can be considered due to electrostatic repulsion of the ionic head group of HTPB or the existence of thermal motion at the air–water interface leading to the destabilization of the monolayer. On the other hand, the values of $A_{\min}$ obvious show reverse behavior, Eq. 3.

From the cmc values, it is also possible to evaluate the standard free energy of micellization $\left(\Delta G_{\mathrm{m}}^{\mathrm{o}}\right)$ from the following equation [1]:

$$\Delta G_{\mathrm{m}}^{\mathrm{o}}=RT\ \mathrm{In}X_{\mathrm{cmc}} \tag{4}$$

where R, T, and X_{cmc} are the ideal gas constant, temperature, and cmc is at molar fraction unit, respectively. These values are listed in Table 1. The $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ value for HTPB is more negative than Mega-10, indicating that micelle formation is more favorable for HTPB than for Mega-10. For both binary mixtures, the values of $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ remain constant due to not much variation in the mixed cmc values. Apart from that, we have evaluated the standard free energy of interfacial adsorption $\left(\Delta G_{\mathrm{ad}}^{\mathrm{o}}\right)$ at the air–water interface from the following relation [18]:

$$\Delta G_{\mathrm{ad}}^{\mathrm{o}}=\Delta G_{\mathrm{m}}^{\mathrm{o}}-0.6023\ A_{\min}\ \pi_{\mathrm{cmc}} \tag{5}$$

In this equation, π_{cmc} is the surface pressure at cmc and given by $\gamma_0-\gamma_{\mathrm{cmc}}$ where γ_0 and γ_{cmc} are the interfacial tension of the solvent and of the micellar surfactant solution at the cmc, respectively. The $\Delta G_{\mathrm{ad}}^{\mathrm{o}}$ values are computed and listed in Table 1. However, both the $\Delta G_{\mathrm{m}}^{\mathrm{o}}$ and the $\Delta G_{\mathrm{ad}}^{\mathrm{o}}$ values are negative, indicating that both processes are spontaneous.

Mixed cmc and interaction parameter

To discuss the properties of mixed micelles formed from both binary mixtures, i.e., whether the mixed micelles reveal either ideal or nonideal behavior, we have used the

Table 1 Value of the ideal critical micellar concentration (cmc*), the experimental critical micellar concentration (cmc), the surface excess ($\Gamma_{\max}$), the area minimum per molecule ($A_{\min}$), the surface pressure (π_{cmc}), the free energy of micellization $\left(\Delta G^{\mathrm{o}}_{\mathrm{m}}\right)$, and the free energy of interfacial adsorption $\left(\Delta G^{\mathrm{o}}_{\mathrm{ad}}\right)$ for the HTPB+Mega-10 surfactant binary mixture

α_{HTPB}	cmc* (mM)	cmc (mM)	$\Gamma_{\max}$ (μ mol m^{-2})	$A_{\min}$ (nm^2)	π_{cmc} (mN m^{-1})	$-\Delta G^{\mathrm{o}}_{\mathrm{m}}$ (kJ mol^{-1})	$-\Delta G^{\mathrm{o}}_{\mathrm{ad}}$ (kJ mol^{-1})
0.00	5.50	5.50	3.9_1	0.42	$39._8$	$22._8$	$32._9$
0.10	1.20	0.40	3.6_4	0.46	$32._2$	$29._3$	$38._3$
0.25	0.55	0.30	2.5_5	0.65	$31._1$	$30._1$	$42._2$
0.40	0.36	0.30	1.7_1	0.97	$28._1$	$30._1$	$46._5$
0.55	0.27	0.25	1.1_0	1.5_1	$27._1$	$30._5$	$55._2$
0.70	0.21	0.20	0.95	1.7_5	$26._8$	$31._1$	$59._3$
0.85	0.18	0.13	1.6_8	0.99	$27._9$	$32._2$	$48._9$
1.00	0.15	0.15	1.3_9	1.1_9	$27._2$	$31._8$	$51._3$

pseudophase separation model [19]. According to this model, micelles are considered to be a macroscopic phase in equilibrium with a solution containing corresponding monomers. For binary surfactant mixtures, the ideal cmc's are related by the equation [19]:

$$\frac{1}{\mathrm{cmc}^*}=\frac{\alpha_1}{\mathrm{cmc}_1}+\frac{(1-\alpha_1)}{\mathrm{cmc}_2} \tag{6}$$

Because the structure of the head groups of the surfactant are quite different from each other, a nonideal behavior is expected. The mixed cmc and ideal cmc* values for pure HTPB and Mega-10, and their binary mixtures are presented in Fig. 2 and Table 1. The experimental cmc values deviate significantly from the ideal cmc* values in the whole mixing range, indicating that a strong synergism exist in the mixed micelle formation process.

These results could be confirmed by using the regular solution theory (RST), which characterizes not only the interaction parameter, $\beta_{12}^{\mathrm{mic}}$, in the mixed micelles, but also accounts for the deviation from the ideality [20]. According to the RST, the activity coefficients in the mixed micelles are expressed as follow:

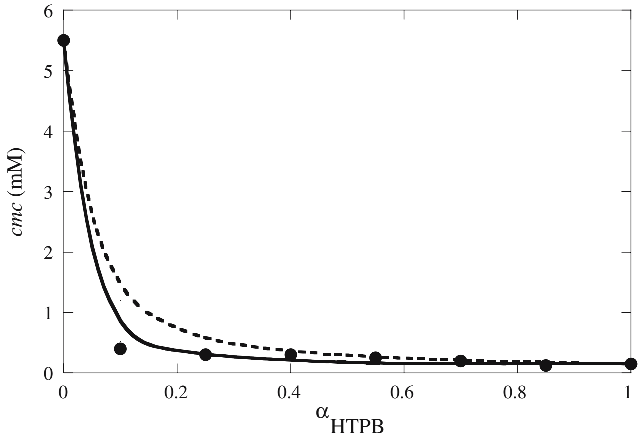

Fig. 2 Plot of mixed critical micelle concentration (cmc) vs α_{HTPB} for HTPB+Mega-10 mixed system. *Filled circle* represents experimental cmc. The *dashed line* represents the phase separation model of an ideal behavior for HTPB+Mega-10 mixed system, whereas the *solid line* is the best fit to the data according to RST with $\beta_{12}^{\mathrm{mic}}=-3.91$

$$\ln f_1=\beta_{12}^{\mathrm{mic}}\left(1-X_{1,\mathrm{mic}}\right)^2 \tag{7}$$

$$\ln f_2=\beta_{12}^{\mathrm{mic}}X_{1,\mathrm{mic}}^2 \tag{8}$$

where f_1, f_2, and $X_{1,\mathrm{mic}}$ are the activity coefficients of the ionic, nonionic, and micelle composition of the ionic component (i.e., HTPB), respectively. $X_{1,\mathrm{mic}}$ an be iteratively computed from the following equation:

$$\frac{X_{1,\mathrm{mic}}^2\ln\left(\mathrm{cmc}\alpha_1/\mathrm{cmc}_1X_{1,\mathrm{mic}}\right)}{\left(1-X_{1,\mathrm{mic}}\right)^2\mathrm{In}\left\{\mathrm{cmc}(1-\alpha_1)/\mathrm{cmc}_2\left(1-X_{1,\mathrm{mic}}\right)\right\}}=1 \tag{9}$$

The $X_{1,\mathrm{mic}}$ values are graphically shown in Fig. 3. From the $X_{1,\mathrm{mic}}$ values, the interaction parameter, $\beta_{12}^{\mathrm{mic}}$, can be computed by the following equation:

$$\beta_{12}^{\mathrm{mic}}=\ln\left(\frac{\mathrm{cmc}\alpha_1}{\mathrm{cmc}_1X_{1,\mathrm{mic}}}\right)\Big/\left(1-X_{1,\mathrm{mic}}\right)^2 \tag{10}$$

The $\beta_{12}^{\mathrm{mic}}$ value demonstrates the extent of the interaction between the two surfactants, which leads to a deviation from ideal behavior. A negative $\beta_{12}^{\mathrm{mic}}$ value indicates attractive interactions between two surfactants in a mixed micelle and vice versa. For ideal mixing, $\beta_{12}^{\mathrm{mic}}=0$. From Eq. 10, we have obtained a $\beta_{12}^{\mathrm{mic}}$ of −3.91 for the present mixed system. This value demonstrates that a significant synergism exists in the mixed micelle formation. The occurrence of synergistic effects can be taken into account by explaining the reduction of electrostatic repulsive interactions upon the intercalation of nonionic surfactant molecules in between the ionic species. Thus, the greater the incorporation of nonionic species in the mixed micelle, the higher the stability of the mixed micelle. In addition, contributions from hydrophobic interactions between the

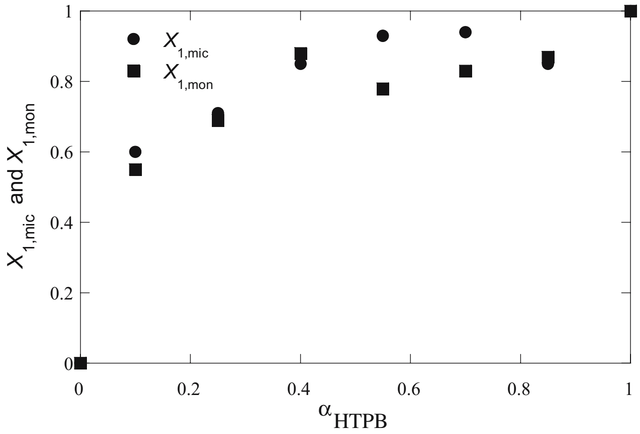

Fig. 3 Plot of micellar ($X_{1,\mathrm{mic}}$) and monolayer ($X_{1,\mathrm{mon}}$) composition vs α_{HTPB} for HTPB+Mega-10 mixed system

hydrocarbon chain of the surfactants and the occurrence of ion–dipole interactions between the surfactant head groups will contribute to the stability of the mixed micelles (see later section) [17, 21, 22]. Figure 3 shows the variation of composition of the ionic surfactant in the mixed micelle, $X_{1,\mathrm{mic}}$ as a function of α_{HTPB}. The $X_{1,\mathrm{mic}}$ values show that mixed micelles are rich in HTPB due to the greater hydrophobicity of the ionic surfactant than those of Mega-10. For example, the composition of HTPB in the mixed micelle reaches more than 70% at $\alpha_{\mathrm{HTPB}}=0.25$.

On the other hand, in the mixed micelle formation process, the existence of synergism in mixtures containing two surfactants depends not only on the strength of the interactions between them, but also on the relevant properties of the individual surfactant component of the binary amphiphilic mixture [23]. Thus, the condition required for synergism in the mixed micelle formation are that $\beta_{12}^{\mathrm{mic}}$ must be negative (see above section) and $\left|\beta_{12}^{\mathrm{mic}}\right| > |\ln(cmc_1/cmc_2)|$ (Table 2). Both conditions are satisfied for the present binary mixtures. The degree of synergism possible in mixed micelle formation is measured by the maximum decrease in molar concentration of the mixed surfactant in comparison to that of individual components, i.e., $(\mathrm{cmc}_1 - \mathrm{cmc}_{12,\mathrm{min}})$ / (cmc_1) where $\mathrm{cmc}_{12,\mathrm{min}}$ is the minimum cmc of the mixed surfactants and is given by:

$$\mathrm{cmc}_{12,\mathrm{min}} = \mathrm{cmc}_1 \exp\left(\frac{\left[\beta_{12}^{\mathrm{mic}} - \ln\left(\mathrm{cmc}_1/\mathrm{cmc}_2\right)\right]^2}{4\beta_{12}^{\mathrm{mic}}}\right) \tag{11}$$

The greater the value of $(\mathrm{cmc}_1 - \mathrm{cmc}_{12,\mathrm{min}})$ / (cmc_1), the greater the degree of synergism. This value is listed in Table 2 and comparable with the reported values for other binary mixtures [23].

The mixed micellar regular solution theory can be extended to the mixed monolayer. To evaluate the interaction parameter in the mixed monolayer, $\beta_{12}^{\mathrm{mon}}$, the analogous equation to that of mixed micelles can be derived at a constant γ value as follows [24, 25]:

$$\frac{X_{1,\mathrm{mon}}^2 \ln\left(C_{12}\alpha_1/C_1^0 X_{1,\mathrm{mon}}\right)}{\left(1 - X_{1,\mathrm{mon}}\right)^2 \ln\left\{C_{12}(1-\alpha_1)/C_2^0\left(1 - X_{1,\mathrm{mon}}\right)\right\}} = 1 \tag{12}$$

and

$$\beta_{12}^{\mathrm{mon}} = \ln\left(\frac{C_{12}\alpha_1}{C_1^0 X_{1,\mathrm{mon}}}\right)\Big/\left(1 - X_{1,\mathrm{mon}}\right)^2 \tag{13}$$

where $X_{1,\mathrm{mon}}$ is the mole fraction of cationic surfactant 1 (i.e., HTPB) in the total surfactant in the mixed monolayer at the interface. C_1^0, C_2^0, and C_{12} are the bulk phase molar concentrations of surfactants 1 and 2 and their mixtures at a given interfacial tension, respectively. The $\beta_{12}^{\mathrm{mon}}$ value evaluated from the above equation at 50 mN m^{-1} for the present binary mixture is −2.95. In comparison to $\beta_{12}^{\mathrm{mic}}$, it is suggested that the interaction are more favorable in the mixed micelles than at the air–water interface. The variation of the monolayer composition ($X_{1,\mathrm{mon}}$) of binary mixtures of HTPB and Mega-10 as a function of α_{HTPB} is shown in Fig. 3. The value of $X_{1,\mathrm{mon}}$ shows the same behavior as seen for micellar composition ($X_{1,\mathrm{mic}}$).

To complement the stability of mixed micelle analysis, we have also used Maeda's approach, which also takes hydrophobic chain–chain interactions in the mixed micelle into consideration, particularly when the chains are of different lengths [21]. In brief, according to Maeda's model, the transfer of ionic species to the nonionic micelle consists of two different contributions: the interaction between the polar head groups and the interaction between the hydrophobic chains. When the hydrophobic chains are similar, the first contribution is predominant, however, when there is difference in the hydrophobic chain lengths, the interactions between these chains becomes more predominant. Maeda's approach emphasizes that apart from the interaction parameter obtained from the regular solution theory, there could be

Table 2 Value of average interaction parameter in the micelle, $\beta_{12}^{\mathrm{mic}}$, $|ln(cmc_1/cmc_2)|$, degree of synergism, $(\mathrm{cmc}_1 - \mathrm{cmc}_{12,\mathrm{min}})$ / (cmc_1), and interaction parameters according to Maeda's approach for HTPB+Mega-10 surfactant binary mixture

Surfactants	$\lvert\beta_{12}^{\mathrm{mic}}\rvert$[a]	$\lvert\ln(\mathrm{cmc}_1/\mathrm{cmc}_2)\rvert$[a]	$(\mathrm{cmc}_1 - \mathrm{cmc}_{12,\mathrm{min}})$ / (cmc_1)	B_0	B_1	B_2
HTPB+Mega-10	3.91	3.60	0.14	−9.21	−7.51	3.91

[a] Absolute value.

another parameter (B_1), which contributes to the stability of the mixed micelle upon replacement of a nonionic surfactant monomer in the nonionic pure micelle with an ionic monomer. This process arises due to short-range interactions of the components. In this model, the free energy of micellization (ΔG_{mic}) is given as a function of the mole fraction of the ionic species in the mixed micelle as follows [21, 24]:

$$\frac{\Delta G_{\text{mic}}}{RT} = B_0 + B_1 X_2 + B_2 X_2^2 \tag{14}$$

where B_0 is an independent term related to the cmc of the nonionic component (C_1) and given by:

$$B_0 = \ln C_1 \tag{15}$$

B_2 is an analog of β_{12}^{mic} in regular solution theory as follows:

$$B_2 = -\beta_{12}^{\text{mic}} \tag{16}$$

B_1 and B_2 are related to the cmc values of pure systems by:

$$\ln\left(\frac{C_2}{C_1}\right) = B_1 + B_2 \tag{17}$$

By using Eq. 16, the parameter B_2 is obtained and, subsequently, B_1 can be obtained from Eq. 17. Table 2 shows the values of B_0, B_1, and B_2. The B_1 value that is reported for the present mixed system is −7.91. The large negative value of B_1 indicates that the hydrocarbon chain–chain interaction also plays an important role for the stability of the mixed micelles. Maeda has also reported negative and positive B_1 values for the different binary mixtures and concluded that chain–chain interactions and steric incompatibility of the head group are responsible for these variations [21]. From Eq. 14 and the parameters of Table 2, we evaluated the free energy of micelle formation (data not shown). These evaluated values are close to the values obtained from the pseudophase separation model (Table 1).

Aggregation number (N_{agg})

To evaluate N_{agg}, we have used the steady-state fluorescence quenching of a probe (pyrene) by a quencher (CPyCl) as stated in the experimental section [26]. This method is based upon the quenching of a luminescent probe by a known concentration of a quencher. This probe–quencher pair has been found to be suitable for evaluating the N_{agg} of several micellar systems [3, 15–17, 24, 27]. The quenching experiments were analyzed using the following equation [26]:

$$\ln\frac{I_{1,0}}{I_1} = \frac{N_{\text{agg}}}{C_s - \text{cmc}} C_Q \tag{18}$$

In this equation, $I_{1,0}$, I_1, C_Q, and C_s represent the fluorescence intensity of the first vibronic peak of pyrene in the absence of quencher, in the presence of quencher, total quencher concentration, and total surfactant concentration, respectively. Figure 4 shows the quenching plots of the HTPB/Mega-10 system as a function of α_{HTPB}. Solid lines in Fig. 4 represents the best fit to Eq. 18 with a correlation factor ≥0.990. In all the quenching plots, we have obtained linear behavior. From the slopes of the quenching plots (Fig. 4) and the cmc value, we evaluated the N_{agg} value along with the partial contribution of each component $N_{1,\text{agg}}$, $N_{2,\text{agg}}$, and the ideal $N_{\text{agg}}^{\text{id}}$ value as shown in Fig. 5. Partial contribution is the product of mixed aggregation number and micelle composition. The ideal behavior is estimated from the equation as follows [28, 29]:

$$\frac{1}{N_{agg}^{id}} = \sum_i \frac{X_i}{N_{agg,i}} \tag{19}$$

The N_{agg} for the pure surfactant is in good agreement with the reported values [17]. Figure 5 shows the positive deviation of the mixed aggregation number from ideality. In Fig. 5, we observe the significant reduction in the aggregation number of the mixed micelles upon the incorporation of ionic surfactant up to α_{HTPB}=0.55 where after remain constant and close to the aggregation number of ionic micelles. This behavior can be explained by considering the electrostatic interactions between the ionic head group of the surfactants in the micelle. As incorporation of ionic species increases, the electrostatic repulsion also increases, leading to an increase in the electrostatic free energy. This effect should lead to the increase in the area per head group of surfactants with the consequence that the aggregation number decreases. From fluorescence quenching data, it is also possible to evaluate the Stern–Volmer (K_{SV}) constant, which reflects the accessibility of the fluorophore to the quencher, from the following relation [24]:

$$\frac{I_{1,0}}{I_1} = 1 + K_{\text{SV}}[Q] \tag{20}$$

The values of K_{SV} are evaluated from the slope of Eq. 20 (data not shown) and presented in Fig. 6. Figure 6 shows that the value of K_{SV} decreases with the increase in the

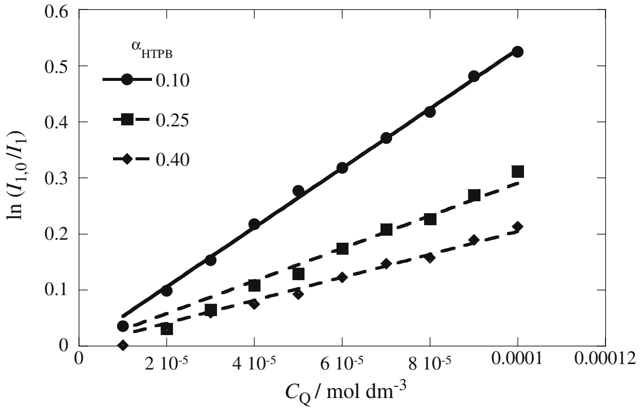

Fig. 4 Plot of $\ln\left(\frac{I_{1,0}}{I_1}\right)$ vs C_Q/mol dm^{-3} at different α_{HTPB} for HTPB+Mega-10 mixed system

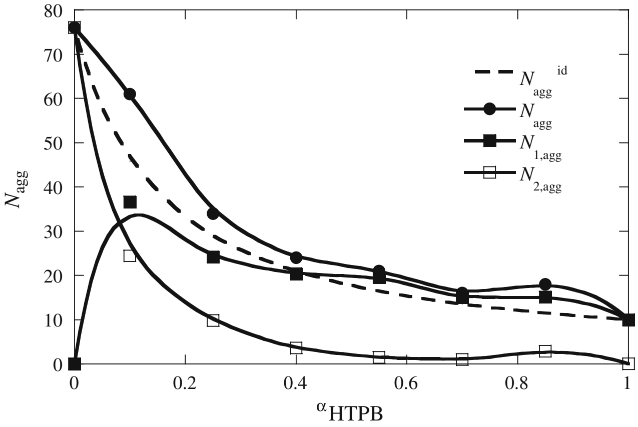

Fig. 5 Plot of N_{agg}, $N_{1,agg}$, $N_{2,agg}$, and N_{agg}^{id} vs α_{HTPB} for HTPB+Mega-10 mixed system

content of HTPB composition, reflecting that the fluorophore becomes less accessible to the quencher. A decrease in K_{SV} has been reported with the increase in the molar composition of cationic gemini surfactants [24].

Micropolarity

Micropolarity study provides information about the local environment of the pyrene probe in the micellar state where pyrene is solubilized [30]. This has been done by monitoring the I_1/I_3 ratio at a 12 mM total surfactant concentration, which is above the cmc at different α_{HTPB}. The value of I_1/I_3 reflects the polarity of the environment, viz, a higher value reveals a higher polarity. Therefore, this parameter can be used to monitor the change in the local polarity induced by hydration in this region of the micelle. The values of I_1/I_3 are shown in Fig. 7. It is observed that the polarity of pure Mega-10 micelles is less than that of HTPB micelles, indicating that the accessibility of the palisade layer of Mega-10 micelles to water is less than the HTPB micelles. It is seen that the I_1/I_3 ratio increases systematically with the increase in α_{HTPB}. It can be an indication of that the residing pyrene probe in different environments, as the micellar composition changes, may be in the central area of the micelle.

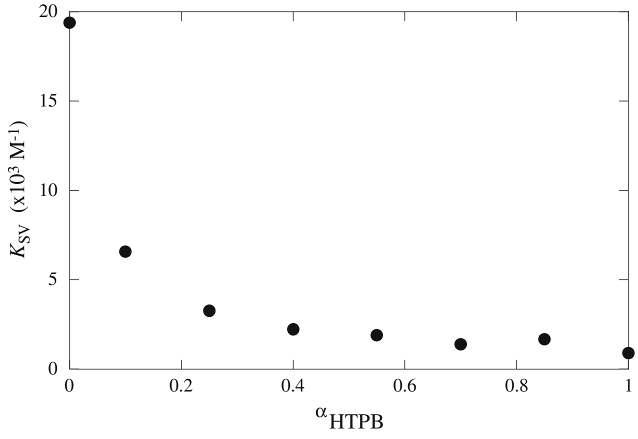

Fig. 6 Plot of K_{SV} vs α_{HTPB} for HTPB+Mega-10 mixed system

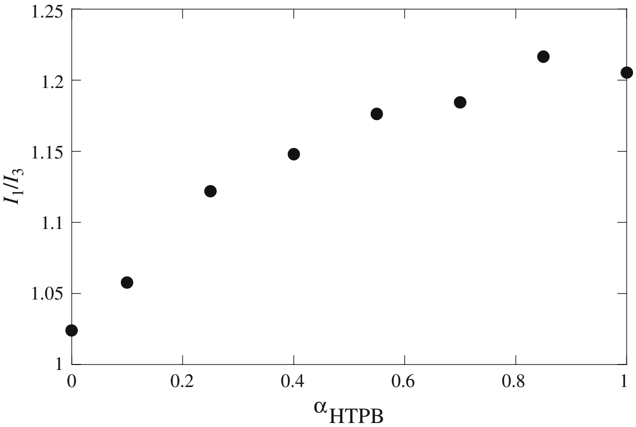

Fig. 7 Plot of I_1/I_3 ratio of pyrene fluorescence intensity vs α_{HTPB} for HTPB+Mega-10 mixed system

Fluorescence anisotropy (r)

To study the behavior of two unlike components in a mixed micelle, we have also performed polarized fluorescence measurements using Rhodamine B as a fluorescence probe. This probe in micellar medium has been well-characterized [31]. The degree of depolarization of the fluorescence emission of a probe is a measure of its rotational diffusion during the excited state lifetime. Fluorescence anisotropy (r) is related to the viscosity around the probe by Perrin's equation as follows [32]:

$$\frac{r_0}{r} = 1 + \frac{kT\tau}{V\eta} \tag{21}$$

where r_0 is the limiting value of emission anisotropy obtained in the absence of rotational freedom, k is the Boltzmann constant, T is the temperature, τ is the average lifetime of the fluorophore excited state, V is the effective

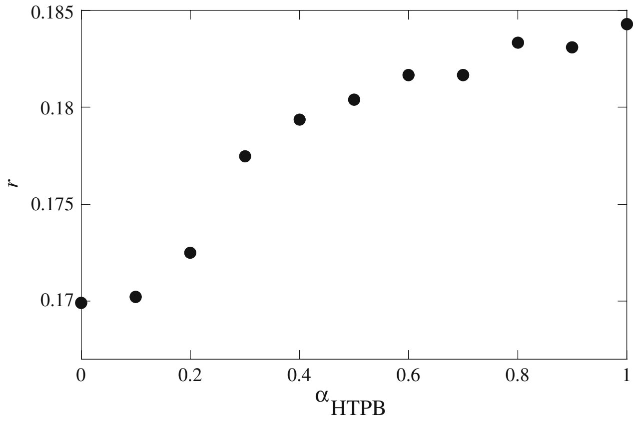

Fig. 8 Plot of fluorescence anisotropy, r, vs α_{HTPB} for HTPB+Mega-10 mixed system

molecular volume of the probe, and η is the viscosity around the probe. From Eq. 21, it is clear that a higher r value corresponds to a higher rigidity and vice versa. Observed values of fluorescence anisotropies are shown in Fig. 8. Figure 8 clearly shows that the micelles of pure HTPB have a higher rigidity than those of Mega-10. This behavior can be explained by the packing arrangement of surfactant molecules in the micelle, indicating that the packing is more tightened in ionic micelles. This behavior can be explained due to the presence of a three-phenyl group on the phosphonium ion of the polar head group of HTPB, which might be responsible for providing rigidity to the micelles. We have observed the instantaneous increase of the r value from α_{HTPB}=0.2 to α_{HTPB}=0.4 where after it remains increasing but in a steady fashion with the increase of α_{HTPB}. A rapid increase in the r value may indicate that the probe RB experiences a more viscous environment due to the formation of rigid mixed micellar structure. However, the overall increase in r value should be interpreted in the sense that the microviscosity in the micellar interface is enhanced as the participation of the ionic component increases. These increase in the r value of the HTPB/Mega-10 mixed system is in contrast with results obtained from Mega-10/HTAB/HPyBr binary mixtures (unpublished data).

Conclusions

In the present study, the interfacial and the micellar physiochemical properties of the mixed system of HTPB and Mega-10 were explored. The surface excess value of the surfactant declined with the increase of ionic surfactant composition in the aqueous solution. This behavior corresponds to the electrostatic repulsion between ionic surfactants and the existence of thermal motion at the interface. Stability of mixed micelle was discussed with regard to their cmc, and negative deviation from ideal behavior was observed for the HTPB/Mega-10 mixed system, indicating that mixed micelle formation takes place due to the synergistic effect. The interaction parameters in the mixed micelle ($\beta_{12}^{\mathrm{mic}}$) and in the mixed monolayer ($\beta_{12}^{\mathrm{mon}}$) were negative, indicating that surfactants have attractive interactions at the interface and in the micelle, however, $\beta_{12}^{\mathrm{mic}}$ is slightly more favorable than $\beta_{12}^{\mathrm{mon}}$. Mixed monolayer composition ($X_{1,\mathrm{mon}}$) and the mixed micelle composition ($X_{1,\mathrm{mic}}$) showed almost identical values at various α_{HTPB}. The negative B_1 value obtained from Maeda's approach shows that favorable short-range attractive interactions exist in the mixed micelle formation. The micellar aggregation number decreases with the increase of α_{HTPB}. This behavior was attributed to the higher participation of the ionic surfactant in the mixed micelle and led to the electrostatic repulsion between the ionic components. Micropolarity data reveal that pyrene resides in different local environments in the micelle by varying the mole fraction of the ionic surfactant. Fluorescence anisotropy results show the presence of rigid and ordered micelle structure with the increase in ionic composition.

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References

1. Rosen MJ (1989) Surfactants and interfacial phenomena, 2nd edn. Wiley, New York, pp 1–122
2. Treiner C, Makayassi A (1992) Langmuir 8:794
3. Ray GB, Chakraborty I, Ghosh S, Moulik SP (2007) J Colloid Interface Sci 307:543
4. Abe M (1993) In: Ogine K, Abe M (eds) Mixed Surfactant Systems. Marcel Dekker, New York, p 1
5. Hill RM (1993) In: Ogino K, Abe M (eds) Mixed Surfactant Systems. Marcel Dekker, New York, p 317
6. Desai TR, Dixit SG (1996) J Colloid Interface Sci 177:471
7. Kresheck GS, Hwang J (1995) Chem Phys Lipids 76:193
8. Patra KS, Alonso A, Goni FM (1998) Biochim Biophys Acta 1373:112
9. Saito S, Tsuchiya T (1984) Biochem J 222:829
10. Söderman O, Johanson I (2000) Curr Opin Colloid Interface Sci 4:391
11. Shinoda K, Carlsson A, Lindman B (1996) Adv Colloid Interface Sci 64:253
12. Garcia MT, Ribosa I, Campos E, Sanchez L (1997) Chemosphere 35:545
13. Okano T, Tamura T, Abe Y, Tsuchida T, Lee G, Sugihara G (2000) Langmuir 16:1508
14. Okano T, Abe Y, Tanaka M (1987) Bull Chem Soc Jpn 60:2718
15. Hierrezuelo JM, Aguiar J, Ruiz CC (2004) Langmuir 20:10419
16. Hierrezuelo JM, Aguiar J, Ruiz CC (2006) J Colloid Interface Sci 294:449
17. Hierrezuelo JM, Aguiar J, Ruiz CC (2005) Mol Phys 103:3299
18. Rosen MJ, Dahanayake M, Cohen AW (1982) Colloids Surf 5:159
19. Clint JH (1975) J Chem Soc Faraday Trans 71:1327
20. Rubingh DN (1979) In: Mittal KL (ed) Solution chemistry of surfactants, vol 1. Plenum, New York, p 337
21. Maeda H (1995) J Colloid Interface Sci 172:98
22. Nishikido N (1992) Langmuir 8:1718
23. Rosen MJ, Zhu ZH, Gao T (1993) J Colloid Interface Sci 157:254
24. Sharma KS, Rodgers C, Palepu RM, Rakshit AK (2003) J Colloid Interface Sci 268:482
25. Holland PM, Rubingh DN (eds) (1992) Mixed Surfactant Systems. ACS Symposium Series 501. American Chemical Society, Washington DC
26. Turro N, Yekta JA (1978) J Am Chem Soc 100:5951
27. Moulik SP, Haque MdE, Jana PK, Das AR (1996) J Phys Chem 100:701
28. Atwood D, Elworthy PH, Kayne SB (1971) J Phys Chem 75:2212
29. Bucci S, Fagotti C, Degiorgio V, Piazaa R (1991) Langmuir 7:824
30. Kalyanasundaram K, Thomas JK (1977) J Am Chem Soc 99:2039
31. Jobe DJ, Verrall RE (1990) Langmuir 6:1750
32. Lakowicz JR (2006) Principles of fluorescence spectroscopy, 3rd edn. Springer, New York, p 353