Available online at www.sciencedirect.com

ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry 186 (2007) 166–172

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Fluorescence studies on the non-ideal mixing in triblock copolymer binary mixtures under the effect of temperature: A block hydration effect

Mandeep Singh Bakshi *, Poonam Bhandari

Department of Chemistry, Guru Nanak Dev University, Amritsar 143005, Punjab, India

Received 6 May 2006; received in revised form 29 July 2006; accepted 12 August 2006

Abstract

The fluorescence and viscosity measurements have been carried out for mixed triblock copolymers (TBP) binary mixtures such as P103 + F127 and P103 + P123 over the whole mole fraction range in the temperature range of 25–40 °C. From the fluorescence measurements mixed critical micelle concentration, micropolarity, Stern–Volmer constant, and excimer formation were determined. A variation of these parameters for pure P103, F127, and P123 components indicated that the micelles of these TBPs acquire stronger hydrophobic environment with the increase in temperature and that is proportional to the degree of hydration. Among these pure components, F127 micelles are more hydrated due to the presence of greater number of poly(ethylene oxide) units than that of P103 and P123 and hence get dehydrated at higher temperature. The components of the mixed micelles of P103 + F127 show attractive interactions at 25 °C which decrease and approach ideality as the temperature increases to 40 °C. On the contrary, the components of P103 + P123 mixtures show ideal mixing at 25 °C and the mixing becomes increasingly unfavorable with the increase in temperature. The results have been fully supported by viscosity measurements and have been explained on the basis of dehydration of oxyethylene groups with increasing temperature. The latter effect results in the unfavorable mixing of unlike components of both mixtures, which takes place at lower temperature range in the case of P103 + P123 while at higher temperature range in the case of P103 + F127.

Keywords: Triblock copolymer; Hydration; Temperature effect; Fluorescence; Viscosity

1. Introduction

Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymer (TBP) have been extensively used in various industrial formulations. Due to their potential applications, they have been thoroughly investigated in last two decades. Their nonionic nature has categorized them in the category of nonionic surfactants. Fundamentally, TBPs are more interesting systems than conventional nonionic surfactants due to their tunable PPO or PEO blocks [1,2]. Oftenly, they act as nonionic surfactants as well as neutral water-soluble polymers simultaneously [3–6]. A variation in their number of PEO or PPO units induces significant changes in their physico-chemical properties. For instance, increase in the molecular weight of PPO block provides greater hydrophobicity with the result of which various micellar parameters such as critical micelle concentration (cmc), critical micelle temperature (cmt), cloud point (C_P), etc. shift to lower concentrations and vice versa [7–9]. Due to the presence of oxyethylene groups both in PPO and PEO blocks, these blocks attain some degree of hydration even in the aggregated state, which remains quite significant for PEO blocks rather than PPO [7–9]. Thus, a change in the hydration of these groups with respect to temperature drastically influences the hydrophobicity of a TBP micelle and its stability as a whole. Fundamentally, it is, therefore, interesting to study the mixed micelle formation in binary TBP mixtures consisting of two TBP components with different molecular weights of PPO and PEO blocks under the effect of temperature variation. The physico-chemical aspects of such systems are expected to have a great potential in industrial applications [10,11] where generally more than one TBP components have been used in different formulations.

In view of these facts, in the present study, we have selected two combinations of TBP mixtures, i.e. P103 + F127 and P103 + P123. The molecular characteristics of each TBP have been listed in Table 1. In the first combination, the relative

---

* Corresponding author.
E-mail address: ms_bakshi@yahoo.com (M.S. Bakshi).

1010-6030/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2006.08.011

Table 1
Molecular characteristics of PEO–PPO–PEO triblock copolymers

TBP	General formula	Hydrophobic/ hydrophilic ratio[a]	Molecular weight
F127	$(EO)_{97}(PO)_{69}(EO)_{97}$	0.47	12,600
P123	$(EO)_{20}(PO)_{70}(EO)_{20}$	2.31	57,50
P103	$(EO)_{17}(PO)_{60}(EO)_{17}$	2.32	49,50

[a] Molecular weight.

difference between the molecular weights of PPO blocks of P103 and F127 is much less in comparison to that among PEO blocks. In the latter case, this difference is more significant for PPO blocks rather than that of PEO blocks. Hence, we want to see which combination of these two would produce greater nonideal behavior (favorable or unfavorable) in their mixed state and that too under the effect of temperature variation.

For this purpose, a steady-state fluorescence method has been applied by using pyrene as a fluorescence probe. Since we are mainly interested in the bulk physicochemical properties of the micellar aggregates of these polymers, therefore, pyrene fluorescence is considered to be the best option, which even allows us to precisely evaluate the microenvironment of these aggregates [12,13]. A change in the temperature leads to a drastic change in the hydrophobic environment of such micelles and which can be easily studied upon the solubilization of a hydrophobic fluorescence probe such as pyrene.

2. Experimental

2.1. Materials

The TBPs used in this study have the general formula $H(–OCH_2CH_2–)_n[–OCH(CH_3)CH_2–]_m(–OCH_2CH_2–)_nOH$. Table 1 lists the molecular specifications of various TBPs. Pyrene (99%) from Aldrich and quencher, hexadecylpyridinium chloride (HPyCl) (99%), from Lancaster Synthesis, UK, were used as received. Water was purified by deionization followed by double distillation. All solutions were prepared by mass within the accuracy of ±0.01 mg.

2.2. Sample preparation

Stock solutions of different pure TBPs have been made in pure water by keeping the total concentration at least fifteen times to the cmc values. These stock solutions were then mixed in different proportions to make binary combinations covering whole mixing range. All solutions were completely clear and stable within the temperature range studied, i.e. 25–40 °C. The mole fractions of each component of various such binary mixtures have been expressed only on the solute basis.

2.3. Methods

2.3.1. Fluorescence measurements

The pyrene fluorescence of the present mixtures has been measured by using Hitachi F-2500 fluorescence spectrophotometer at various temperatures using Julabo F25 thermostat within the uncertainties of ±0.01 °C. These measurements were carried out in pure water by using pyrene as fluorescence probe in the range 350–500 nm. Fluorescence emission spectra of these solutions were recorded employing an excitation wavelength of 335 nm, and the detection wavelengths were $I_1 = 373$ nm and $I_3 = 384$ nm while keeping the [pyrene] = 10^{-6} mol dm^{-3}. The excimer formation was determined at pyrene fluorescence intensity, $I_E = 470$ nm, by keeping [pyrene] = 10^{-4} mol dm^{-3}. The cmc values at each temperature for pure and mixed TBP systems have been determined by plotting the I_1/I_3 ratio with respect to [TBP] as shown in Fig. 1a. It is to be mentioned here that in some cases we observed another break before the actual cmc (as shown in Fig. 1a), which is mainly due to the pre-micellar aggregates and cannot be referred to the actual cmc behavior. The errors in cmc values were estimated to be less than 10%.

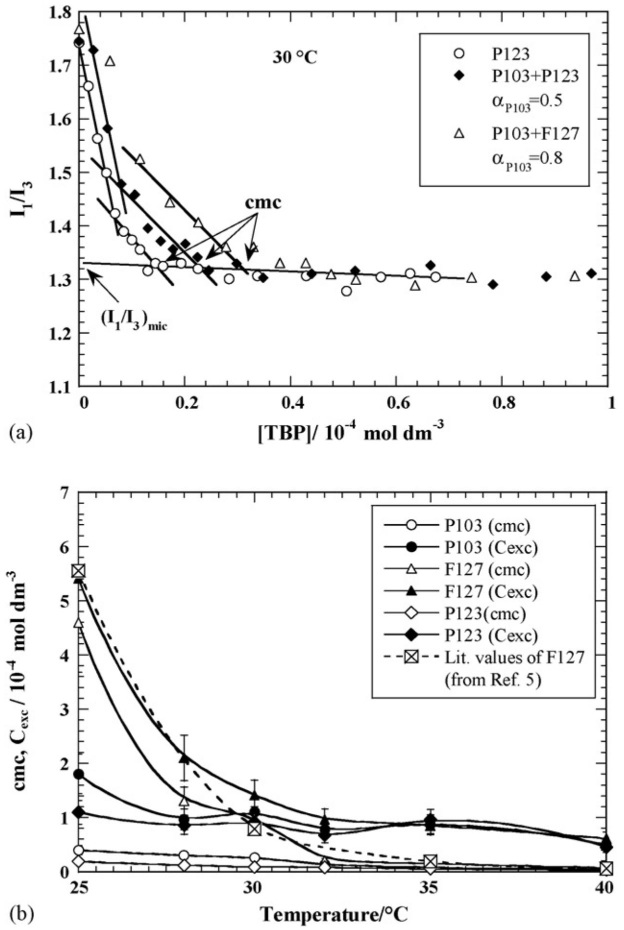

Fig. 1. (a) Plot of micropolarity (I_1/I_3) vs. concentration of TBP for some pure and mixed systems at 30 °C. (b) Plot of cmc, C_{exc} vs. temperature for all pure TBP components. The cmc data of P127 from Ref. [5] have been compared with the present values. The data for P103 and P123 from Ref. [5] even show much better agreement (not shown due to the over crowding of the figure).

2.3.2. Viscosity measurements

The efflux times of binary mixtures with [TBP] at least fifteen times the cmc were determined with the help of Ubbelohde type suspended level capillary viscometer sealed in a glass jacket to

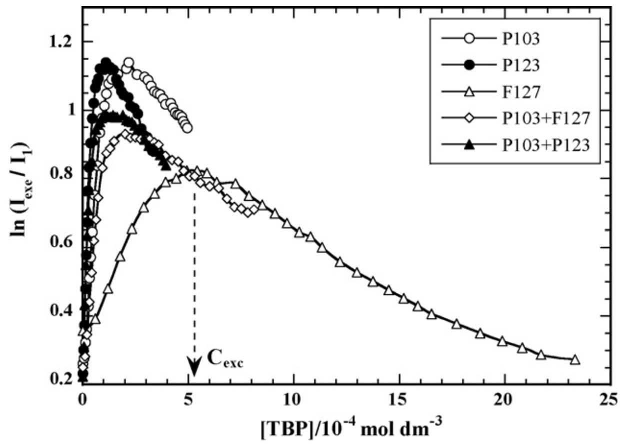

Fig. 2. Plot of $\ln(I_{\mathrm{exc}}/I_1)$ vs. concentration of TBP for some pure and mixed systems showing the excimer concentration (C_{exc}).

circulate the thermostated water. The efflux time was kept long to minimize the need for applying the kinetic corrections to the observed data. Each experiment was carried out after giving the long-time thermal stability. From the ratio of efflux times of the test solution, t, to that of the reference solution, t_0, i.e. water, the relative viscosity can be calculated, $\eta_r = t/t_0$, by ignoring the density corrections for the dilute solutions. The η_r of various mole fractions of each binary mixture have been determined over the whole mixing range. The solutions were prepared as mentioned in Section 2.2.

3. Results and discussion

3.1. Microenvironment of pure component micelles

The various micellar parameters of F127, P103, and P123 single components with respect to a change in temperature have been computed and discussed in this section. Fig. 1b shows that how cmc of pure TBP components decrease with increasing temperature. Apart from this, the difference among the cmc values becomes quite small in the temperature range of 32–40 °C, which suggests that the micelles of different TBPs attain comparable degree of dehydration within this temperature range. A steep fall in the case of F127 in comparison to P103 and P123 can be attributed to a significant higher number of hydrated PEO groups, which show greater rate of dehydration with respect to temperature. It is also possible to find out the concentration of TBP at maximum excimer formation (C_{exe}). This can be done by plotting the $\ln(I_{\mathrm{exe}}/I_1)$ versus [TBP] (Fig. 2). The C_{exe} value at a particular temperature should correspond to the cmc since maximum excimer formation would occur in a maximum hydrophobic environment when the probability of finding both the ground and excited state pyrene is maximum. The C_{exe} values are therefore plotted in Fig. 1b along with the cmc in order to show the comparison. One can see that both sets of values show good agreement with each other within the experimental uncertainties. The overall decrease in the cmc and C_{exc} values further suggests the strengthening of the micellar hydrophobic environment which shows a drastic change around 30 °C and is also evident from the decrease in the polarity of micellar microenvironment, $(I_1/I_3)_{\mathrm{mic}}$ (Fig. 3a) around 30 °C. The strength of the hydrophobic environment can further be evaluated by determining the first order quenching rate constant called Stern–Volmer constant (K_{SV}). The following relationship under the steady-state conditions can be used to explain the collision quenching constant[14–17].

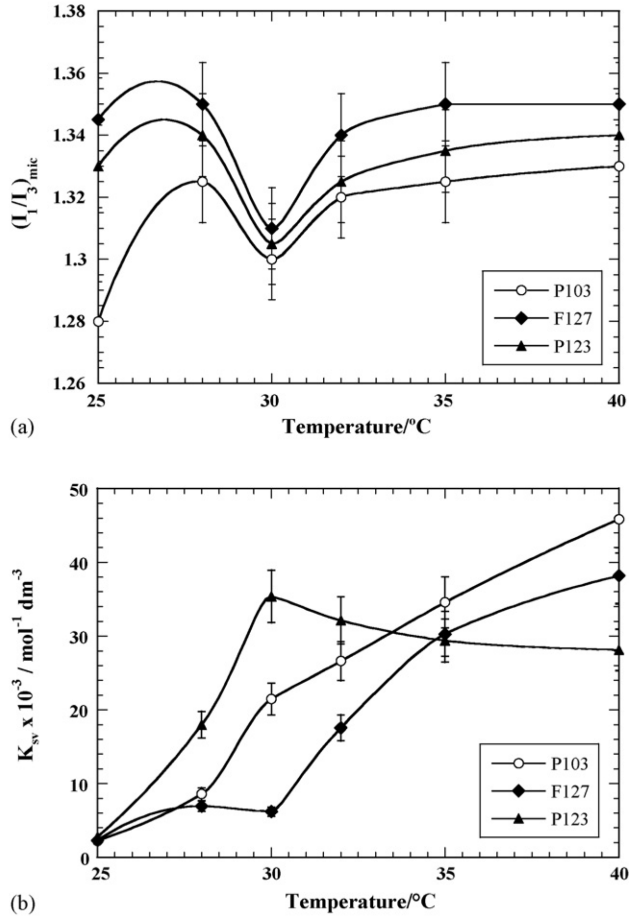

Fig. 3. (a) Plot of micelle polarity index $(I_1/I_3)_{\mathrm{mic}}$ vs. temperature for all pure TBP components and (b) plot of Stern–Volmer constant (K_{SV}) vs. temperature for all pure TBP components.

$$\frac{I_0}{I} = 1 + K_{\mathrm{SV}}[\mathrm{quencher}] \qquad (1)$$

where I_0 and I are the fluorescence intensities without and with quencher (HPyCl), respectively. A linear plot of I_0/I versus [quencher] allows us to evaluate the value of K_{SV} from the slope (not shown). The K_{SV} values thus obtained for the pure components have been shown in Fig. 3b. The K_{SV} value increases with increase in temperature for all TBPs and the increase becomes less significant beyond 30 °C for P123 while more significant for F127. The rising K_{SV} value suggests an increase in the first order quenching due to the greater probability of finding both probe and quencher in a stronger hydrophobic environment. The K_{SV} value shows a little increase in the micelles of F127 from 25 to 30 °C in comparison to that of P123 within the same temperature range. The greater hydration of F127 micelles in comparison to that of P123 seems to be responsible for this change. Thus, the micelles of P123 get more rapidly dehydrated within this temperature range in comparison to the micelles of F127. This would bring stronger hydrophobicity to the micelles of P123 and that would facilitate the quenching, which subsequently leads to an increase in K_{SV} value. But a sudden fall in the K_{SV} value for P123 beyond 30 °C suggests the inability of the quencher to approach an excited state Py which is embedded in a highly hydrophobic environment. This situation arises close to 40 °C in the case of F127 due to its greater hydration, which requires high temperature to shed its water molecules.

A relative comparison among the micellar behaviors of all three pure components demonstrates that a change in F127 micelles is directly related to the greater hydration of F127 micelles due to the presence of large number of EO groups, which loose greater amount of water thus bringing larger change in the microenvironment of the micelles. But this effect is prominent only around 30 °C and diminishes thereafter. Beyond 35 °C, the micelles of all pure components behave almost similarly. Since the aim of this study is to evaluate the nonideal behavior in the mixed micelle formation in P103 + F127 and P103 + P123 mixtures, therefore, we want to observe how an unequal dehydration process of these TBPs would influence their mixed micellar behavior.

3.2. Mixed micelle behavior

The mixed cmc values were measured over the whole mole fraction range for P103 + F127 and P103 + P123 mixtures at 25, 28, 30, 32, 35 and 40 °C. The variation of these values for both mixtures at different temperatures has been shown graphically in Supplementary figures (S1 and S2). The solid lines in these plots represent the ideal mixing based on psuedophase thermodynamic model given by Clint [18]. Fig. S1 shows that the experimental cmc values for P103 + F127 mixture are smaller than the ideal behavior at 25 °C and this difference decreases as the temperature increases from 25 to 40 °C. On the contrary, the experimental values are quite close to ideality for P103 + P123 mixture (Fig. S2) at 25 °C, but become significantly higher than ideality as temperature increases. A smaller experimental cmc value than corresponding ideal value can be explained on the basis of some sort of attractive interactions between the components, while the higher value is generally due to the unfavorable mixing. It means the mixtures of P103 + F127 actually show attractive interactions at 25 °C and the interactions decrease as the temperature increases. On the other hand, the mixtures of P103 + P123 behave almost ideally at 25 °C but show increasingly unfavorable mixing at higher temperatures. The results have been explained quantitatively by choosing the cmc value at equimolar mixing range, i.e. $\alpha = 0.5$ in both mixtures and evaluated various micellar parameters. The variation in the micellar parameters at $\alpha = 0.5$ for both mixtures has been explained as follows.

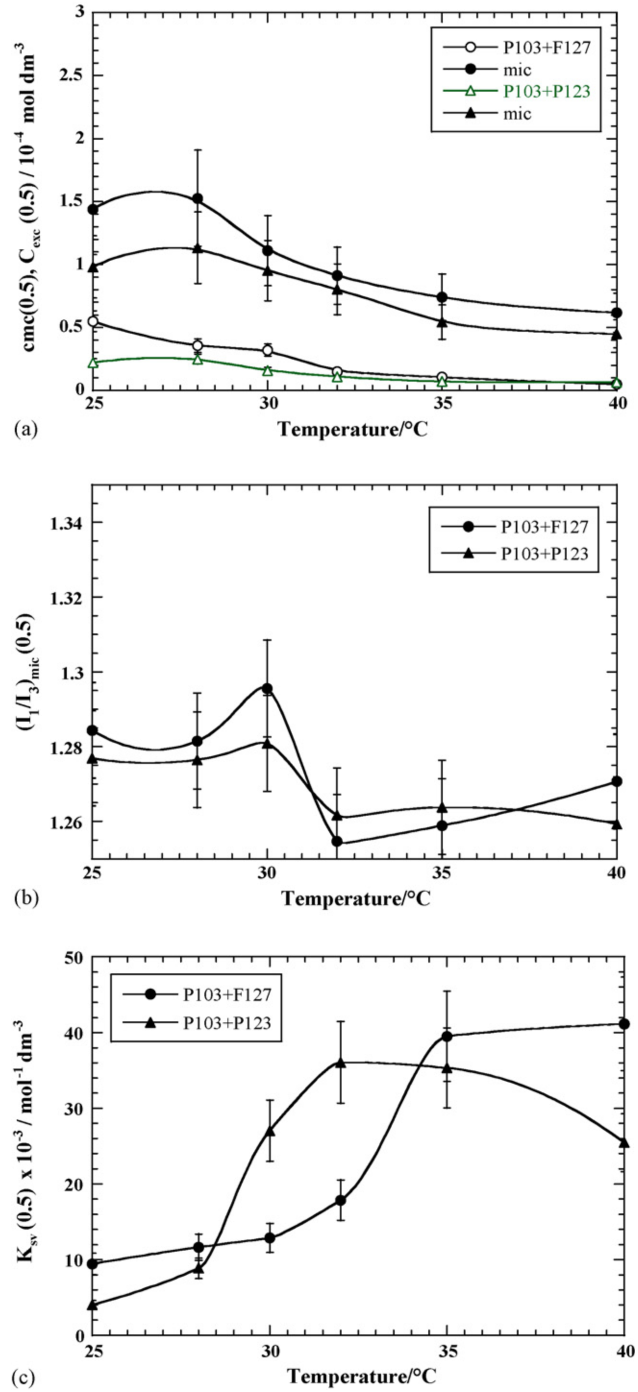

Fig. 4. (a) Plot of cmc(0.5), $C_{exc}(0.5)$ vs. temperature for P103 + F127 and P103 + P123 mixtures at $\alpha_{P103} = 0.5$; (b) plot of micelle polarity index $(I_1/I_3)_{mic}(0.5)$ vs. temperature for P103 + F127 and P103 + P123 mixtures at $\alpha_{P103} = 0.5$; (c) plot of Stern–Volmer constant, $K_{SV}(0.5)$ vs. temperature for P103 + F127 and P103 + P123 mixtures at $\alpha_{P103} = 0.5$.

A plot of cmc(0.5) and $C_{exc}(0.5)$ versus temperature (Fig. 4a) for both the mixtures shows that the values for P103 + P123 are higher than the values for P103 + F127. This indicates that the mixed micellization takes place at relatively lower [TBP] in the later case rather than in the former. It also can be explained on the basis of favorable mixed micellization in the case of P103 + F127 in comparison to that in the P103 + P123 mixtures. The results have been further evaluated by plotting the micellar polarity index, $(I_1/I_3)_{mic}(0.5)$ values for both mixtures in Fig. 4b. The micellar polarity sensed by pyrene for both mixtures lies quite close to each other within the uncertainties over the temperature studied, however the polarity decreases for both mixtures as temperature exceeds 30 °C. Similar change was also observed for single component TBPs in Fig. 3a. A plot of K_{SV} demonstrates some better picture (Fig. 4c). The $K_{\mathrm{sv}}(0.5)$ values for the mixed micellar environment of both mixtures lie more or less close to each other within the temperature range from 25 to 30 °C, but a drastic change is observed thereafter. The K_{sv} value shows an instantaneous increase for P103 + P123 mixtures up to 32 °C and then it levels off. Whereas the value for P103 + F127 increases gradually within the same temperature range before tending to constant. It means that 30–32 °C temperature range actually shows the dehydration of the mixed micelles of both the mixtures, which is quite drastic and instantaneous in the case of P103 + P123 in comparison to that in P103 + F127. If we assume that the effect of dehydration of P103 micelles remains same in both mixtures, then this difference is practically due to the difference in the dehydration of P123 and F127 micelles. Looking at Fig. 3b one would see that the K_{sv} values for P103 lie almost intermediate between those of P123 and F127 within the same temperature range. Thus the variation of K_{sv} in Fig. 4c is predominantly governed by the dehydration of P123 and F127 micelles in their respective binary mixtures. A comparison between the variations of micellar parameters of Fig. 4b and c demonstrates that $(I_1/I_3)_{\mathrm{mic}}(0.5)$ is less sensitive property than $K_{\mathrm{sv}}(0.5)$, and that is why we do not observe any significant difference between the $(I_1/I_3)_{\mathrm{mic}}(0.5)$ values for both mixtures in Fig. 4b.

The results can be further evaluated by applying the regular solution approximation [19] which can be used very comfortably for nonionic mixed surfactants. The following equation can be used for determining the micelle mole fraction of the first component, i.e. P103 (X_1) in the mixed micelles and the regular solution interaction parameter (β).

$$\frac{X_1^2\,\ln(\mathrm{cmc}\,\alpha_1/\mathrm{cmc}_1 X_1)}{(1-X_1)^2\ln(\mathrm{cmc}(1-\alpha_1)/\mathrm{cmc}_2(1-X_1))}=1 \tag{2}$$

$$\beta=\frac{\ln(\mathrm{cmc}\,\alpha_1/\mathrm{cmc}_1 X_1)}{(1-X_1)^2} \tag{3}$$

It is also possible to calculate the micellar mole fraction in the ideal state ($X_{1,\mathrm{ideal}}$) by applying the following equation derived from phase separation model [18].

$$X_{1,\mathrm{ideal}}=\frac{\alpha_1\,\mathrm{cmc}_2}{\alpha_1\,\mathrm{cmc}_2+(1-\alpha_1)\,\mathrm{cmc}_1} \tag{4}$$

where cmc, cmc_1, cmc_2, are the critical micelle concentrations of mixed TBP syetms, first, and the second pure components, respectively. α_1 is the bulk mole fraction of P103 in the bulk mixed phase.

The X_1 and $X_{1,\mathrm{ideal}}$ values thus computed have been shown as Supplementary figures (S3 and S4), respectively, for P103 + F127 and P103 + P123 binary mixtures. Fig. S3 indicates that the X_1 values are less than $X_{1,\mathrm{ideal}}$ for P103 + F127 at 25 °C but approach each other as the temperature increases. The reverse is observed for P103 + P123 where both values are close enough at 25 °C but X_1 starts decreasing with increase in temperature. Such a variation of X_1 values suggests that P103 + F127 mixtures are poor in P103 at 25 °C but show ideal mixing at higher temperature, whereas the micelles of P103 + P123 become poor in P103 at elevated temperatures. It means that the micelle dehydration process drives more hydrophobic TBP component to occupy the micelles. In the case of P103 + F127, P103 is more hydrophobic, hence increase in the temperature increases its amount in the mixed state, while the greater hydrophobicity of P123 in the second mixture reduces the amount of P103 in the mixed state. How this effect influences the synergism in both cases can be very well seen by plotting the β value at $\alpha_1 = 0.5(\beta_{0.5})$ versus temperature (Fig. 5). Both mixtures start with negative β values at 25 °C which become less negative with the increase in temperature. The values remain negative from 25 to 40 °C for P103 + F127 while those for P103 + P123 change to positive somewhere close to 30 °C. Within the framework of regular solution theory, the negative β value is explained on the basis of attractive interactions between the unlike TBP components while positive can be due the unfavorable mixing. Thus, increase in the temperature brings unfavorable mixing among both the unlike TBP components in both kind of mixed micelles. It further suggests that dehydration of the oxyethylene groups makes them less stable in the mixed state and responsible for the unfavorable mixing. The greater dehydration as in the case of P103 + P123 (due to its higher hydrophobicity) causes greater unfavorable mixing.

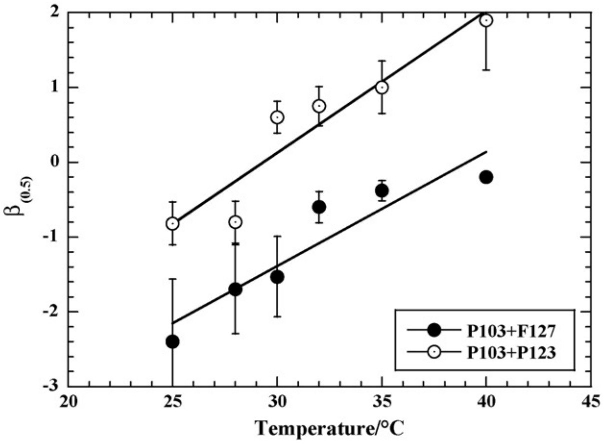

Fig. 5. Plot of regular solution interaction parameter, $\beta(0.5)$ vs. temperature for P103 + F127 and P103 + P123 mixtures at $\alpha_{\mathrm{P103}} = 0.5$.

The results have been further supported by plotting the excess relative viscosity ($\Delta\eta_{\mathrm{r}}$) of both mixtures over the whole mole fraction in Supplementary figure (S5) [20,21]. Fig. S5a demonstrates that the negative deviation of $\Delta\eta_{\mathrm{r}}$ at 25 °C of P103 + F127 decreases as the temperature increases and at higher temperature $\Delta\eta_{\mathrm{r}}$ values almost follow additivity rule. On the contrary, $\Delta\eta_{\mathrm{r}}$ values for P103 + P123 mixtures (Fig. S5b) initially show ideal behavior but increasingly have positive deviations at higher temperatures. The negative deviations in $\Delta\eta_{\mathrm{r}}$ values generally arise from the decrease in the fluidity upon mixing unlike components. It means that P103 + F127 mixed micelles reduce their size in comparison to that of pure component and which causes an increase in the fluidity. The reduction in the size of the P103 + F127 mixed micelles can be attributed to the attractive interactions as demonstrated by Fig. 5. However, increase in the temperature causes dehydration of oxyethylene groups which brings instability to the mixed micelles and thus the mixing behavior approaches ideality. On the other hand, P103 + P123 mixed micelles already show ideal mixing at 25 °C (Fig. S5b), and the dehydration process due to increase in the temperature drives the mixed micelles to an unfavorable mixing state and that brings positive deviations in $\Delta\eta_r$ values from ideal mixing.

3.3. Kinetics of excimer formation

We know that the excimer emission is produced by the collosional quenching between the excited (Py*) and ground state (Py) monomers of the fluorescence probe. Thus, the mechanism of the excimer dimer (D*) formation can be written in the following way:

$$\mathrm{Py}^* + \mathrm{Py} \xrightarrow{k_{\mathrm{EF}}} \mathrm{D}^* \qquad \mathrm{Py}^* + \mathrm{Py} \xleftarrow{k_{\mathrm{ED}}} \mathrm{D}^* \tag{5}$$

$$\mathrm{Py}^* \xrightarrow{k_{\mathrm{MF}}} \mathrm{Py} + hv \tag{6}$$

$$\mathrm{D}^* \xrightarrow{k_{\mathrm{DF}}} 2\mathrm{Py} + hv \tag{7}$$

Where k_{EF}, k_{ED}, k_{MF}, and k_{DF} are the constants of excimer formation, excimer dissociation, monomer fluorescence, and dimer fluorescence, respectively. Apart from this, there are other non-radioactive decays of Py* and D* which have been not shown here. The detailed analysis of this kinetic process has been reported by Birks et al. [22–24]. For simplification two sets of experimental conditions, i.e. low temperature and high temperature behaviors within the temperature range studied, have been discussed. At low temperature I_{exc}/I_1 ratio can be written as:

$$\frac{I_{\mathrm{exc}}}{I_1} = \frac{k_{\mathrm{EF}}^1[\mathrm{Py}]}{k_{\mathrm{MF}}} \exp\left[\frac{-W_{\mathrm{EF}}}{kT}\right] \tag{8}$$

where k_{EF}^1 and W_{EF} are the frequency factor (limiting value of k_{EF} as $T \to \infty$) and activation energy of excimer formation, respectively, and k is Boltzmann's constant. Similarly, at high temperature, the I_{exc}/I_1 ratio is given by

$$\frac{I_{\mathrm{exc}}}{I_1} = \frac{k_{\mathrm{DF}}k_{\mathrm{EF}}^1[\mathrm{Py}]}{k_{\mathrm{ED}}^1 k_{\mathrm{MF}}} \exp\left[\frac{B}{kT}\right] \tag{9}$$

where B is the excimer binding energy = $W_{\mathrm{ED}} - W_{\mathrm{EF}}$ and k_{ED}^1 is the frequency factor. Eqs. (8) and (9) suggest that $\ln I_{\mathrm{exc}}/I_1$ show increase and decrease linearly with $1/T$, respectively, at fixed [Py] [25,26]. Fig. 6 shows such a variation for P103 at different temperatures. Hence, the kinetics of pyrene solubilization in TBP micelles can be analyzed within two different sets of experimental conditions, i.e. one below 30 °C and other above. The former gives the activation energy for excimer formation (W_{EF}) by pyrene while the latter gives the binding energy (B). Both values thus obtained for various pure and mixed TBP mixtures have been listed in Table 2.

The entries of Table 2 show that W_{EF} for F127 is lowest among all three pure components. A low W_{EF} value can be explained on the basis of facilitation of the quenching process where both Py and Py* can be located in the same environment. However, a higher W_{EF} value as in the case of P123, suggests a less favorable quenching probability. A stronger hydrophobic environment (Fig. 5) is although favorable for the solubilization of both Py and Py*, it prevents the mobility among Py and Py* to approach each other for required quenching process. This is further supported by the lowest B values among Py and Py* in P103 micelles. Under the similar arguments, the quenching is more favorable in the mixed micelles of P103 + F127 rather than P103 + P123 mixtures. In fact, both W_{EF} and B values indicate two temperature regions, i.e. before and after 30 °C. The temperature range of 25–30 °C refers to the quenching behavior where quenching takes place on the basis of micellar environment. We have already observed that P103 + F127 mixtures show attractive interactions within the temperature range (Fig. 5) and due to this the mixed cmc value of this mixture deviates negatively from ideality (Fig. S1). As the temperature exceeds 30 °C even this mixture starts behaving ideal. Thus, the low W_{EF} value for P103 + F127 can be related to the mixed micellar arrangement, which proves to be favorable for the quenching process. However, beyond 30 °C, the mixed micelles of both mixtures behave ideal, and could be the reason of close values of binding energy.

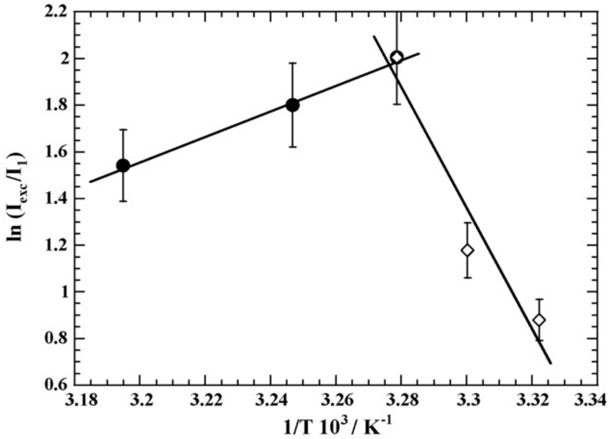

Fig. 6. Plot of $\ln(I_{\mathrm{exc}}/I_1)$ vs. $1/T$ for P103.

Table 2
Values of activation energy of excimer formation (W_{EF}, kJ mol^{-1}) and binding energy (B, kJ mol^{-1}) for pure and mixed TBP components

TBP	W_{EF}	B
F127	−18.9	11.4
P123	−20.6	9.2
P103	−25.8	5.9
P103 + F127	−9.9	14.3
P103 + P123	−20.8	13.1

4. Conclusions

The following conclusions can be drawn from this study:

1. The photophysical properties of the present pure components demonstrate that the micellar environment of the F127 micelles is predominantly hydrophilic in nature in comparison to that of P103 and P123. Due to the greater hydration of the F127 micelles, it requires longer temperature range to

get dehydrated whereas the micelles of P123 get dehydrated with a slight increase in the temperature. The temperature around 30 °C onsets a rapid dehydration of all pure TBP micelles. This difference in the behavior is mainly attributed to the greater number of PEO groups available in F127 in comparison to that of P103 and P123.

2. The predominant hydrophilic and hydrophobic nature of F127 and P123, respectively, governs the behavior of mixed micelles with P103, i.e. P103 + F127 and P103 + P123 mixtures. The greater hydration of the oxyethylene groups of P103 + F127 mixed micelles at 25 °C acquires favorable mixing which approaches to ideal behavior with increase in temperature due to the dehydration of oxyethylene groups. However, less hydration of P103 + P123 mixed micelles due to its stronger hydrophobicity, even further diminishes with the increase in temperature, which drives the unfavorable mixed micelle arrangement.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2006.08.011.

References

[1] Pluronic and Tetronic Block Copolymer Surfactants; Technical Brochure, BASF Corp., 1989.

[2] K. Mortensen, Colloid Surface A 183 (2001) 277.

[3] M. Almgren, J. Van Stam, C. Linblad, P.Y. Li, P. Stilbs, P. Bahadur, J. Phys. Chem. 95 (1991) 5677.

[4] E. Hecht, H. Hoffmann, Langmuir 10 (1994) 86.

[5] P. Alexandridis, J.F. Holzwarth, T.A. Hatton, Macromolecules 27 (1994) 2414.

[6] Y. Li, R. Xu, S. Couderc, D.M. Bloor, J.F. Holzwarth, E. Wyn-Jones, Langmuir 17 (2001) 5742.

[7] M. Almgren, W. Brown, S. Hvidt, Colloid Polym. Sci. 273 (1995) 2.

[8] I.R. Schmolka, J. Am. Oil Chem. Soc. 54 (1977) 110.

[9] P. Bahadur, G. Riess, Tenside Surf. Det. 28 (1991) 173.

[10] J.M. Harris, S. Zalipsky, Poly(ethylene glycol): Chemistry and Biological Applications, American Chemical Society, Washington, DC, 1997.

[11] D.W. Tedder, F.G. Pohland, Emerging Technologies in Hazardous Waste Management, American Chemical Society, Washington, DC, 1990.

[12] M.S. Bakshi, S. Sachar, K. Singh, A. Shaheen, J. Colloid Interface Sci. 286 (2005) 369.

[13] M.S. Bakshi, S. Sachar, T. Yoshimura, K. Esumi, J. Colloid Interface Sci. 278 (2004) 224.

[14] O. Stern, M. Volmer, Phy. Z. 20 (1919) 18.

[15] A. Wellar, Prog. React. Kinet. 1 (1976) 3246.

[16] M.R. Efthik, C.A. Gheron, J. Phys. Chem. 80 (1976) 486.

[17] H. Gorner, C. Stammel, J. Mattey, J. Photochem. Photobiol. A Chem. 120 (1997) 171.

[18] J.H. Clint, J. Chem. Soc., Faraday Trans 71 (1) (1975) 1327.

[19] D.N. Rubingh, in: K.L. Mittal (Ed.), Solution Chemistry of Surfactants, vol. 1, Plenum, NewYork, 1979, p. 337.

[20] M.S. Bakshi, P. Sharma, G. Kaur, S. Sachar, T.S. Banipal, Colloid Surface 278 (2006) 218.

[21] M.S. Bakshi, P. Bhandari, S. Sachar, R.K. Mahajan, Colloid Polym. Sci. 284 (2006) 1363.

[22] J.B. Birks, L.G. Christophorou, Proc. R. Soc. London Ser. A 274 (1963) 552.

[23] J.B. Birks, L.G. Christophorou, Proc. R. Soc. London Ser. A 277 (1964) 51.

[24] J.B. Birks, M.D. Lumb, I.H. Munro, Proc. R. Soc. London Ser. A 280 (1963) 289.

[25] M. Aoudia, M.A.J. Rodgers, W.H. Wade, J. Phys. Chem. 88 (1984) 5008.

[26] C. Honda, H. Kamizono, K.-I. Matsumoto, K. Endo, J. Colloid Interface Sci. 278 (2004) 310.