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ORIGINAL CONTRIBUTION

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Mixed micelles of binary triblock polymer mixtures in pure water at 30 °C

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Abstract This is the first report on the mixed micelles of binary triblock polymer (TBP) mixtures. The steady-state fluorescence and viscosity measurements have been carried out for the various binary combinations of TBP (i.e., P103 + F127/P84/L64/P104/P123) in pure water at 30 °C. All the TBP components selected for the study show clear micelle formation process. The pyrene fluorescence has been used to determine the critical micelle concentration. As micelle-forming TBP can also be termed as nonionic surfactants; therefore, their mixed micelle formation has been evaluated by applying the regular solution theory. It has been observed that this theory very well predicts the nature of mixed micelles. The P103 + F127/P84/L64 binary mixtures undergo mixed micelle formation due to the synergistic interactions while P103 + P104/P123 show antagonistic behavior. The results clearly show that the mixtures with greater number of poly(ethylene oxide) units undergo favorable mixing.

Keywords Triblock polymers · Mixed micelles · Synergistic effects · Fluorescence measurements

Introduction

Triblock polymers (TBP) belong to the category of water-soluble neutral polymers. During the last one or two decades, they have achieved a considerable importance due to their wide industrial applications. These polymers have unique applications in cosmetic industry where they have been used either in single or mixed form [1]. They are made up of ethylene oxide and propylene oxide repeating units [2]. The presence of ether oxygens available among these repeating units makes them soluble in aqueous phase due to electrostatic interactions. A block of poly(propylene oxide) (PPO) units is predominantly hydrophobic in nature while that of poly(ethylene oxide) (PEO) shows hydrophilic interactions [3–5]. A systematic variation in the number of PPO and PEO units makes the whole TBP predominantly hydrophobic or hydrophilic. The TBP with a larger number of PPO units are therefore less soluble in water, while the solubility increases with an increase in the number of PEO units. Such a dual property allows it to undergo hydrophobic as well as hydrophilic interactions just like conventional surfactants.

Thus, TBP have the capacity to aggregate in aqueous phase and behave like nonionic surfactants. A typical micelle of TBP consists of a hydrophobic core made up of PPO units while PEO units occupy the corona [6–10]. In industrial applications, the usage of more than one TBP requires the fundamental understanding of their micellar behavior. The present study is a step forward in this direction where different TBP binary combinations have been selected to understand the nature of their mixed micelles. Unlike that of binary mixtures of conventional nonionic surfactants, the mixtures of TBP are expected to show the non-ideal behavior as a difference in the number of PEO or PPO units of unlike TBP components in the mixed state is expected to induce significant influence on the mixed micelle behavior. At this end, different combinations of TBP components have been selected by varying their PPO/PEO ratios and their mixed micelle behavior has been studied with the help of pyrene fluorescence measurement. We have recently applied this technique for various combinations of ionic + TBP mixtures and have observed that it works very well even

in determining the critical micellar concentration (cmc) of pure TBP components [11–14]. However, there are also a few reports showing the micelle formation of TBP with the help of surface tension measurement, but most of the TBP are generally very weakly surface active and, hence, do not give the clear break in the surface tension vs concentration plots [15, 16]. This is probably due to the weaker hydrophobic properties of PPO groups in comparison to the completely saturated hydrocarbon tails of conventional surfactants. In aqueous bulk phase, well-defined aggregates of TBP exist though they possess a slight degree of polydispersity. Thus, pyrene, being hydrophobic in its nature, solubilizes in the PPO core of the TBP micelle and, hence, gives a clear indication of the micellar process.

Experimental

Materials

The TBP 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 is a list of the molecular specifications of various TBP used in the present study and all the components have been used without further purification. Pyrene was obtained from Aldrich and was 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. The mole fractions were accurate up to ±0.0001 units.

Sample preparation

Stock solutions of different pure TBP have been made in pure water by keeping the total concentration at least 15 times to the cmc values. This would allow covering of the pre- as well as post-micellar regions of both components of binary mixtures during the titration process. These stock solutions were then mixed in different proportions to make binary combinations covering the whole mixing range. All solutions were completely clear and stable. The mole fractions of each component of such various binary mixtures have been expressed only on the solute basis.

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

TBP	General formula	Hydrophobic/ hydrophilic ratio[a]	Molecular weight
P103	$(EO)_{17}$ $(PO)_{60}$ $(EO)_{17}$	2.32	4,950
F127	$(EO)_{97}$ $(PO)_{69}$ $(EO)_{97}$	0.47	12,600
P84	$(EO)_{19}$ $(PO)_{43}$ $(EO)_{19}$	1.49	4,200
L64	$(EO)_{13}$ $(PO)_{30}$ $(EO)_{13}$	1.52	2,900
P104	$(EO)_{18}$ $(PO)_{58}$ $(EO)_{18}$	2.12	5,900
P123	$(EO)_{20}$ $(PO)_{70}$ $(EO)_{20}$	2.31	5,750

[a]Molecular weight

Methods

Fluorescence measurements

A constant amount of pyrene (less than 10^{-6} mol dm^{-3}) has been maintained in all solutions. The fluorescence titrations were carried out by the addition of appropriate amounts of various mixed solutions in water + pyrene reference solutions covering the pre- to post-micellar range. The desired temperature was maintained by circulating the thermostated water by using Julabo F25 thermostat within the uncertainties of ±0.01 °C.

Fluorescence emission spectra of these solutions were recorded by employing an excitation wavelength of 334 nm, and the intensities I_1 and I_3 were measured at the wavelengths corresponding to the first and third vibronic bands located at ca. 373 and 384 nm. The ratios of I_1/I_3 were plotted as a function of total TBP concentration. The errors in cmc values were estimated to be less than 10%. All measurements were recorded on a Hitachi F-2500 fluorescence spectrophotometer at 30 °C.

Viscosity measurements

The efflux times of binary mixtures of TBP solutions have been determined with the help of Ubbelohde-type suspended level capillary viscometer sealed in a glass jacket to circulate the thermostated water at 30 °C. 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. Good reproducibility can be obtained by properly cleaning the viscometer with concentrated chromic acid each time before starting a set of experiments to avoid the formation of air bubbles in the viscometer. 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 the "Sample preparation" section.

Results and discussion

All present pure triblock polymers, i.e., P103, P104, F127, P84, L64, and P123, show clear micelle formation process demonstrated by the change in I_1/I_3 pyrene ratio vs concentration plots (Fig. 1). In each case, the I_1/I_3 ratio

value starts from approximately 1.75 (which is the value in pure water) and, after a series of decreases, it becomes constant at around 1.3. The latter value is slightly higher than that of the micellar phase of conventional nonionic surfactants and can be attributed to the less hydrophobic environment of TBP micelles. Similar plots were also obtained when the binary combinations of these TBP with P103 have been taken. The cmc values of pure and binary mixtures have been obtained by fitting the data in linear equations before and after the breakpoints as demonstrated in Fig. 1. The values of pure components have been in listed in Table 2 and compared with those available in literature. A graphical representation of these values over the whole mixing range can be seen in Fig. 2, where all plots show clear nonlinear variation. As the present TBP can also be considered as nonionic surfactants, therefore, a pseudophase thermodynamic model can be applied on such binary systems to evaluate the deviation in experimental cmc values from the ideal behavior. Clint's [17] equation in the following form can be used to observe the deviation from ideality,

$$\frac{1}{cmc*} = \frac{\alpha_1}{cmc_1} + \frac{(1-\alpha_1)}{cmc_2} \tag{1}$$

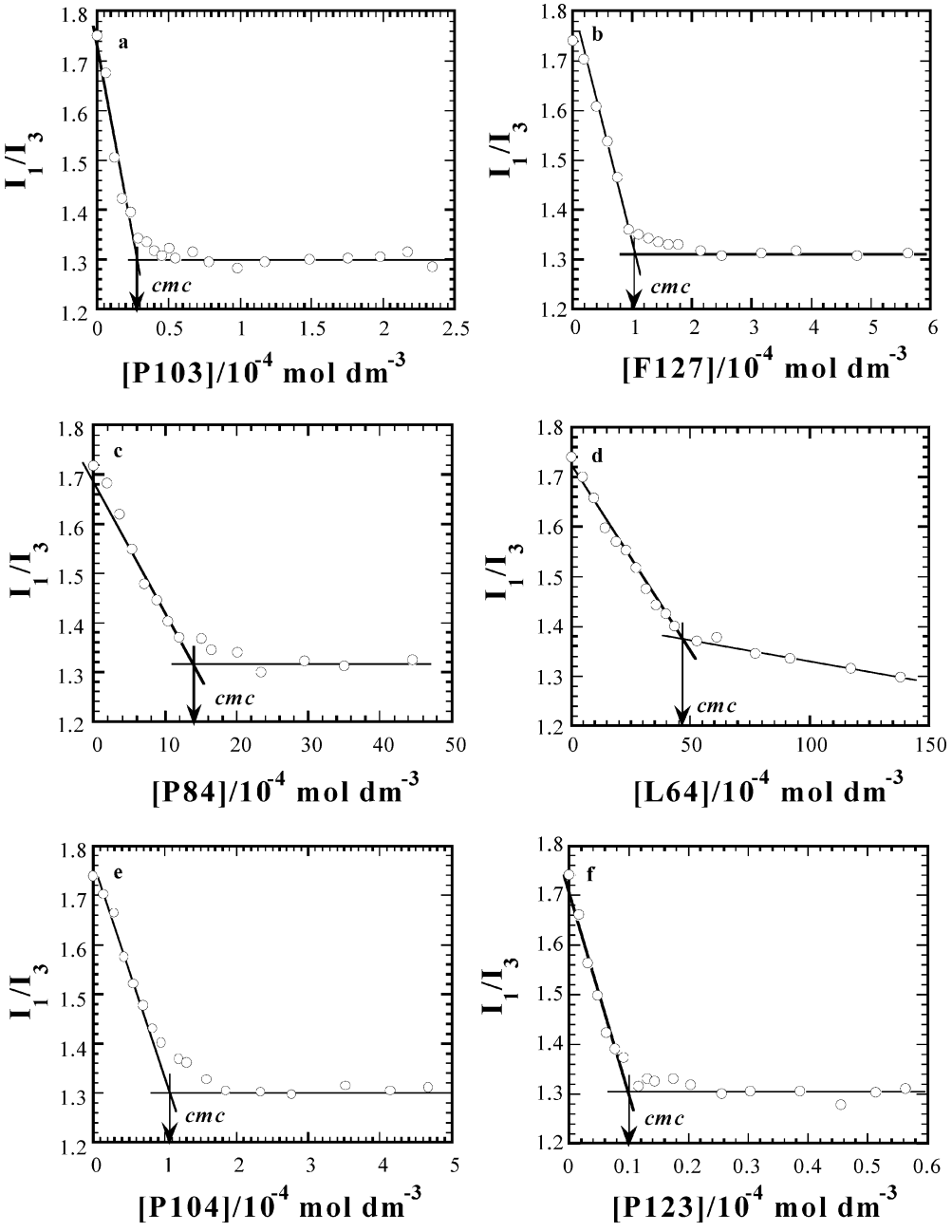

Fig. 1 Variation of the pyrene intensity; I_1/I_3 ratios with the total concentration of pure triblock polymers at 30 °C

Table 2 Values of cmc (10^{-4} mol dm^{-3}) of different triblock polymers at 30 °C

TBP	cmc	Literature values
P103	0.26	0.20 [6]
F127	1.00	0.79 [6]
P84	14.0	14.3 [6]
L64	46.0	51.7 [6]
P104	0.67	0.67 [6]
P123	0.09	0.09 [6]

where α_1 is the mole fraction of component 1 (P103) in total mixed solute and cmc_1 and cmc_2 are the critical micellar concentrations of pure components 1 and 2, respectively. Eq. 1 can be used to evaluate the cmc in ideal state (cmc*), and thus the values evaluated have also been plotted in Fig. 2 for comparison.

One would see that the cmc values are mostly lower than the corresponding cmc* values in the case of binary mixtures of P103 + F127/P84/L64 (Fig. 2a–c). On the other hand, cmc values are higher than the cmc* values in the case of P103 + P104/P123 mixtures (Fig. 2d,e). The

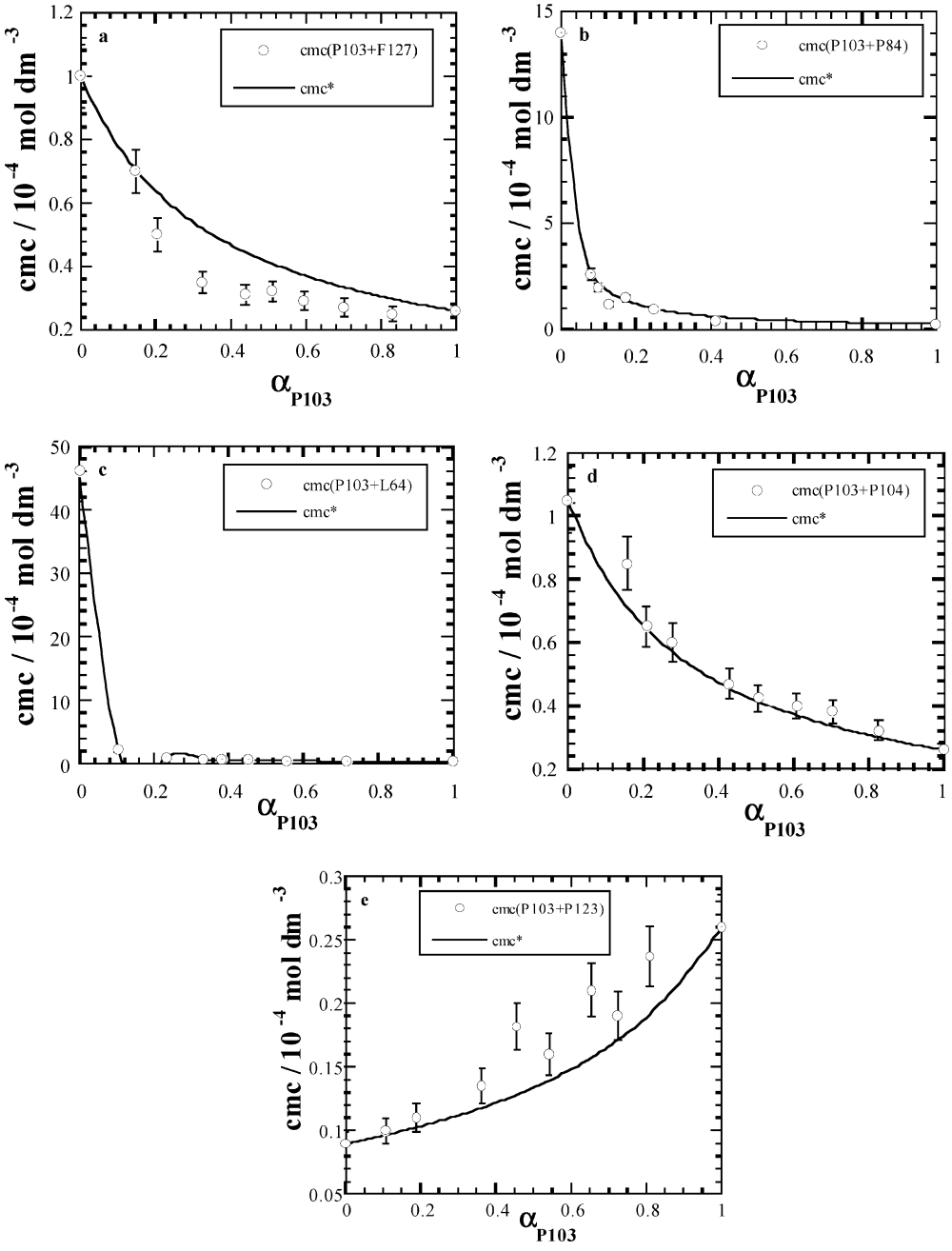

Fig. 2 Critical micelle concentration vs mole fraction of P103 for **a** P103 + F127, **b** P103 + P84, **c** P103 + L64, **d** P103 + P104, and **e** P103 + P123 binary mixtures. Experimental cmc (*points*); predicted cmc* (*line*)

negative and positive deviations in the cmc values from that of cmc* in the former and latter cases, respectively, can be attributed to the micelle formation due to the favorable and unfavorable mixing. It is to be mentioned here that the binary mixtures of conventional nonionic surfactants generally exhibit ideal or close-to-ideal mixing behavior. However, the nonideal mixing in all the binary mixtures of present TBP thus indicates a much different mixing behavior from that of traditional conventional nonionic surfactants. This nonideal behavior can be attributed to the varying degree of PPO/PEO in the mole fractions among different TBP components. A quantitative interpretation on the basis of the nature of the mixed micelles can be carried out by using the regular solution theory [18], which allows us to calculate the micellar mole fraction of the first component, i.e., P103 (X_1), and regular solution interaction

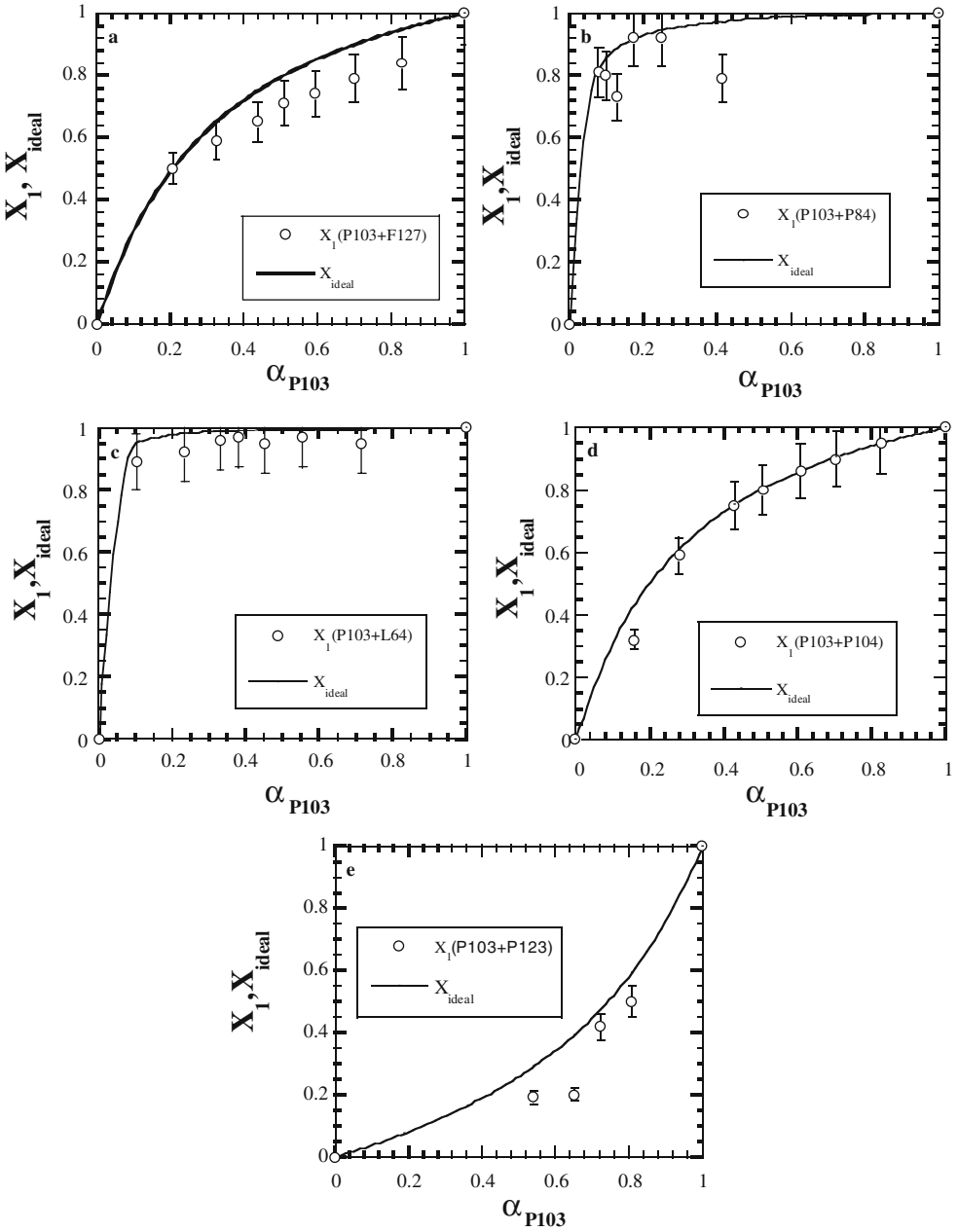

Fig. 3 Micellar mole fraction, X_1, from regular solution theory (*points*) and X_{ideal} (*line*) vs mole fraction of P103 for **a** P103 + F127, **b** P103 + P84, **c** P103 + L64, **d** P103 + P104, and **e** P103 + P123 binary mixtures

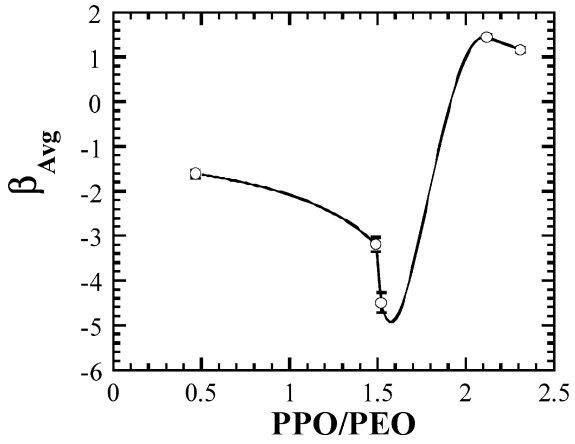

Fig. 4 Plot of interaction parameter, β_{Avg}, vs PPO/PEO ratio of the triblock polymers

parameter, β, by using the following set of Eqs. 2 and 3, respectively.

$$\frac{X_1^2 \ln\left(cmc\alpha_1/cmc_1X_1\right)}{(1-X_1)^2 ln\left(cmc(1-\alpha_1)/cmc_2(1-X_1)\right)} = 1 \tag{2}$$

$$\beta = \frac{\ln\left(\frac{cmc\alpha_1}{cmc_1X_1}\right)}{(1-X_1)^2} \tag{3}$$

It is also possible to calculate the micellar mole fraction in the ideal state (X_{ideal}) by applying the following equation derived from phase separation model.

$$X_{1,ideal} = \frac{\alpha_1 cmc_2}{\alpha_1 cmc_2 + (1-\alpha_1)cmc_1} \tag{4}$$

Both X_1 and X_{ideal} values have also been shown graphically in Fig. 3. All the frames of Fig. 3 indicate that the micelle mole fraction of P103 is mostly smaller than its intended ideal state value. It means that the mixed micelles of all mixtures possess less amount of P103 and greater amount of the co-TBP component. In other words, all mixed micelles are rich in the co-TBP component. It means that the nature of the latter governs the mixed micelle process whether it is favorable or unfavorable. The results have been further evaluated by plotting the average β (β_{Avg}) value vs PPO/PEO molecular weight ratio (Table 1) of co-TBP component in each binary mixture (Fig. 4). A close inspection of Fig. 4 suggests that, as the PPO/PEO ratio increases, the value of β_{Avg} becomes more negative as PPO/PEO approaches 1.5. Further increase in the PPO/PEO ratio instantaneously increases β_{Avg} and it becomes positive in magnitude. It is to be noted that a negative β value can be attributed to the synergistic interactions between the unlike components of the binary mixtures while a positive β value can be attributed to the unfavorable mixing. A relative comparison between the results of Figs. 3 and 4 suggests that the dependence of β_{Avg} on the PPO/PEO ratio of co-TBP component can be related to the latter's greater amount in the mixed micelles. It means that the greater amount of co-TBP component decides the fate of the mixed micelle. The component with lower PPO/PEO ratio (i.e., F127, P84, and L64) shows attractive interactions with P103 while the component with greater PPO/PEO ratio (i.e., P104 and P123) shows unfavorable mixing with P103.

The results are further supported by plotting the η_r values of these binary mixtures in Fig. 5. The dotted lines in Fig. 5 demonstrate the additivity rule. The binary mixtures with negative β values, i.e., P103 + F127/P84/L64, clearly show a significant negative departure in the η_r values from the additivity rule, while this is not so significant in the case of P103 + P104/P123 binary mixtures with positive β_{Avg} values. Furthermore, there is very little difference between the η_r values of the components of the latter binary mixtures. A large negative departure in the η_r values can be related to the formation of compact micellar aggregates with greater fluidity and less viscous drag, which can be very well related to the attractive interactions between the unlike components of these mixtures.

Thus, the nature of mixed micelles in all these five combinations depend very much on the PPO/PEO ratios of co-TBP component with respect to that of P103. In those cases where this ratio is smaller than that of P103 (i.e., in the combinations of P103 + F127/P84/L64), the mixed micelles are produced due to the attractive interactions between the unlike components. On the other hand, the co-TBP component with PPO/PEO ratio close to that of P103 (i.e., in the case of P103 + P104/P123) demonstrates unfavorable mixing. These conclusions are very well supported by the variation of η_r in Fig. 5. The origin of this behavior can only be ascribed on the basis of the greater amount of co-TBP component in the mixed micelle as demonstrated in Fig. 3. Thus, in conclusion, it can be said that the mixed micelles of binary TBP components with greater number of PPO units do not show synergistic effects. This could be due to the poor solubility of PPO units in aqueous phase and, at the same time, it is also expected that these groups may create greater steric hindrances in the mixed state. This situation, however, is expected to be not so significant when less number of PPO groups from different TBP components are mixed in the core of the mixed micelles. It means that the synergism in a particular TBP binary mixture can be related to the greater solubility in aqueous phase. Thus, the mixtures with lesser number of PPO units would be more soluble than that with greater number. Therefore, the greater number of PPO units in the mixed micelles induces insolubility in the aqueous phase and that is the driving force for the unfavorable mixed micellization.

Conclusions

The following conclusions can be drawn from this study:

1. Unlike that of conventional nonionic binary surfactants mixtures, the present triblock polymer combinations show clear non-ideal mixing which is significantly dependent upon the varying degree of PPO/PEO ratios of unlike triblock polymer components.
2. The triblock polymer components with relatively smaller PPO/PEO ratio produce mixed micelles due to synergistic interactions, while the components with higher ratios undergo unfavorable mixing. This has been attributed to the favorable solubilization of mixed micelles with smaller ratios in aqueous phase in comparison to that of mixed micelles with greater ratio.

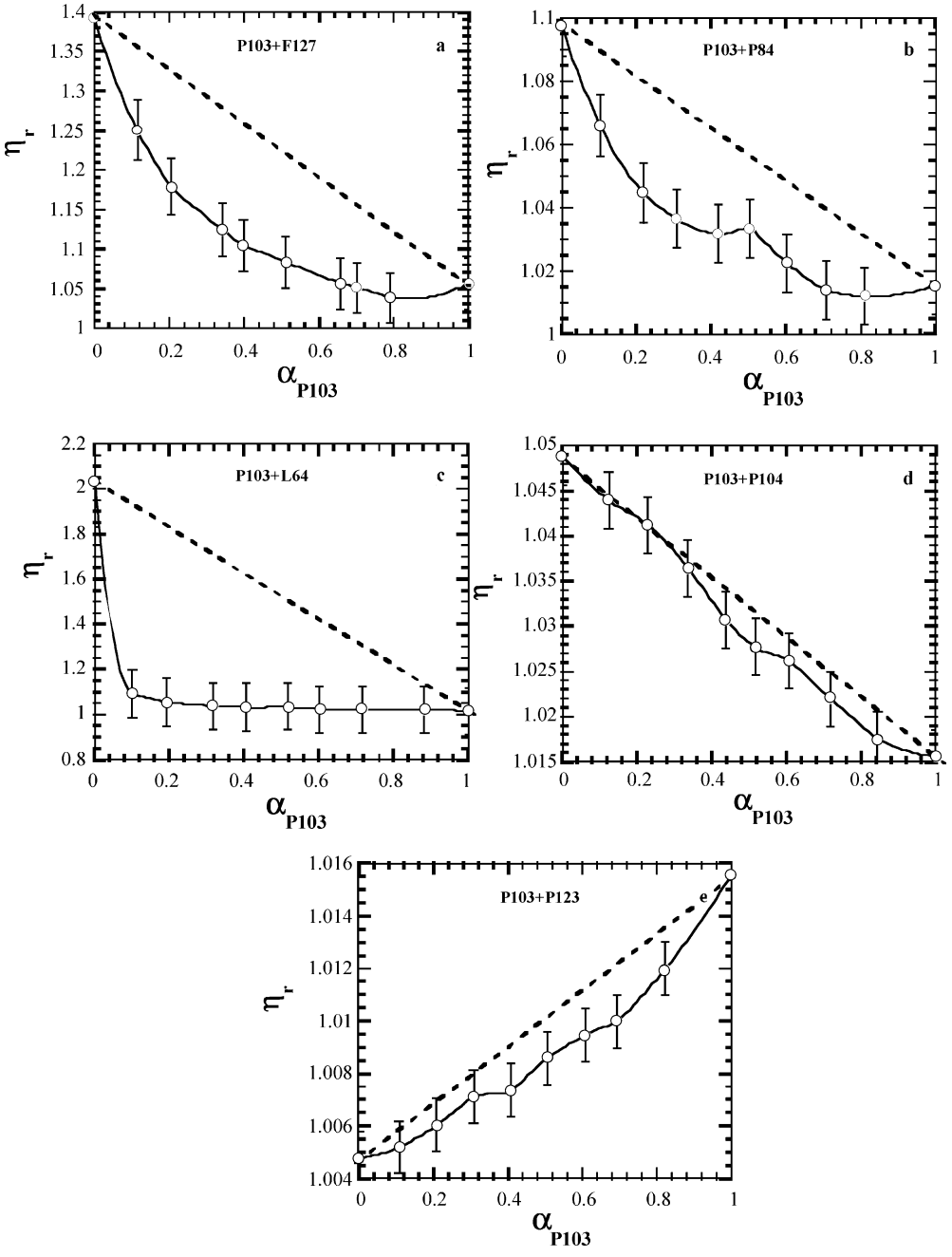

Fig. 5 Relative viscosity, η_r, vs mole fraction of P103 for **a** P103 + F127, **b** P103 + P84, **c** P103 + L64, **d** P103 + P104, and **e** P103 + P123 binary mixtures. *Dotted lines* represent ideal mixing

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