Notes

Mean-Field Study of Interactions between Block Copolymer Micelles and Homopolymers

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Introduction

The micelle formation of triblock copolymers of the PEO−PPO−PEO type [PEO and PPO denoting poly(ethylene oxide) and poly(propylene oxide), respectively], often referred to as Pluronic (trademark of BASF Corp.), has been studied extensively over the past few years, both experimentally[1,2] and theoretically.[3,4] The PEO−PPO−PEO copolymers are in many respects similar to low molecular weight nonionic EO-containing surfactants, showing self-aggregation into micelles and liquid crystalline phases at higher temperature and higher concentration and clouding at high temperatures.[1,5] The phase- and aggregation behavior are strongly dependent on temperature, concentration, and molecular architecture.[2] In particular, a temperature increase (at fixed concentration) promotes the PEO−PPO−PEO chains (unimers) in an aqueous solution to self-assemble into micellar-like aggregates, in which the core is dominated by PO segments and the corona is composed of hydrated EO segments. The temperature at which the triblock copolymers start to aggregate is referred as to the critical micellization temperature (cmt).

Aqueous solutions of two different nonionic polymers often separate into two different phases, where the phases are enriched in different polymers. Such two-phase systems have been used to separate biomaterials such as amino acids, enzymes, and other proteins.[6−8] We have previously investigated the phase behavior of the ternary Pluronic P105/dextran T500/water system[9] and the partitioning of hydrophobic amino acids and oligopeptides in this polymer system[10] above and below the cmt of the PEO−PPO−PEO triblock copolymer. In the former work, the experimental phase diagrams were compared to simple theoretical predictions based on an extended Flory−Huggins theory.[11] The polymer micelle was modeled by increasing the molecular weight of the model species representing the self-assembling polymer. A similar approach has for some time been used to model the phase behavior of polymer−surfactant solutions.[12]

Here, we report on model calculations on ternary PEO−PPO−PEO/dextran/water systems using a spherical lattice model which explicitly takes into account the self-assembly of the PEO−PPO−PEO triblock copolymer. The results demonstrate that the use of the Flory−Huggins theory for describing self-assembling systems with concentration-independent interaction parameters can at most give qualitatively correct results.

Theoretical Model

A mean-field lattice model initially developed by Scheutjens and Fleer[13] is employed. In our application, the space is divided into concentric shells and each shell is further divided into lattice cells. One lattice cell contains either a polymer segment or solvent. The random-mixing (mean-field) approximation is applied within each layer separately. The lattice model is extended with a conformational model[14] for describing the reduced solubility of EO and PO in water at increasing temperature.[15] The triblock copolymer is represented as $(EO)_{37}(PO)_{56}(EO)_{37}$ and dextran with a chain of 1000 units. All conformational parameters and all the Flory−Huggins interaction parameters except those involving the PO−dextran pair are taken from previous investigations.[15,16] According to the conformational model, the polar and apolar conformers of PO (as well as of EO) have different interaction parameters. For the PO−dextran pair we assumed the interaction to be more repulsive compared to the EO−dextran pair, and we have employed $RT\chi_{\mathrm{POpolar,dextran}} = 0.68$ and $RT\chi_{\mathrm{POapolar,dextran}} = 1.858$ kJ mol^{-1} where R is the gas constant and $T = 325$ K, the absolute temperature.

The numerical solution of the model has two branches, one resulting in homogeneous concentration profiles throughout the lattice (corresponding to $c <$ cmc) and one corresponding to a single micelle formed at the center of the lattice in equilibrium with specified bulk concentrations of the components (corresponding to $c >$ cmc). In the latter case, the micelles formed are characterized by radial density profiles of the components and by the micellar aggregation number, which all are predictions of the model. The micellar, and hence the PEO−PPO−PEO, concentration is directly related to the volume of the subsystem containing one micelle and the surrounding solution and this volume is determined from the equilibrium conditions. A more detailed description of the model can be found elsewhere, see e.g. ref 4.

Results and Discussion

Seven compositions of the PEO−PPO−PEO/dextran/water system have been modeled. The composition of the systems are given in Table 1 and Figure 1 displays their relation to the cmc-curve predicted from the same model. Figure 1 shows that the presence of dextran reduces the cmc of the PEO−PPO−PEO triblock copolymer and Table 1 shows that the reduction of the cmc is accompanied with an increase in the aggregation

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Table 1. Composition and Data of the Systems Investigated[a]

no.	composition $\phi_{PEO-PPO-PEO}$	 $\phi_{dextran}$	N_{agg}	f_{EO}	f_{PO}	f	N_{agg}/N_{tot}
1	0.04	0.001	35.3	0.35	0.77	0.66	0.39
2	0.04	0.015	42.1	0.51	0.83	0.75	0.57
3	0.04	0.035	50.6	0.64	0.89	0.82	0.73
4	0.023	0.001	24.4	0.02	0.64	0.48	0.02
5	0.017	0.015	25.9	0.01	0.64	0.47	0.02
6	0.012	0.035	34.2	0.03	0.64	0.48	0.03
7	0.023	0.035	45.9	0.43	0.80	0.70	0.49

[a] The symbols are defined in the text.

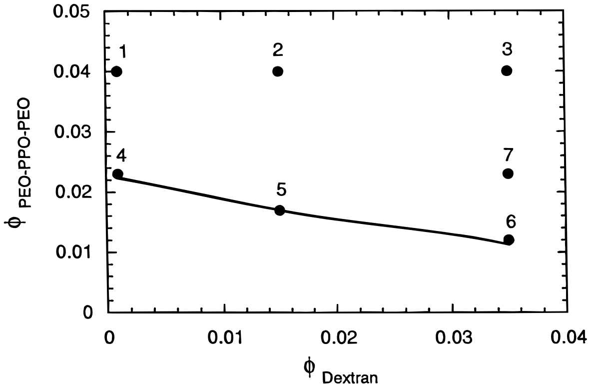

Figure 1. Compositions of the investigated PEO−PPO−PEO/dextran/water systems (circles) and the cmc of the PEO−PPO−PEO triblock copolymer as a function of the dextran concentration (curve) at 325 K. Concentrations in volume fraction.

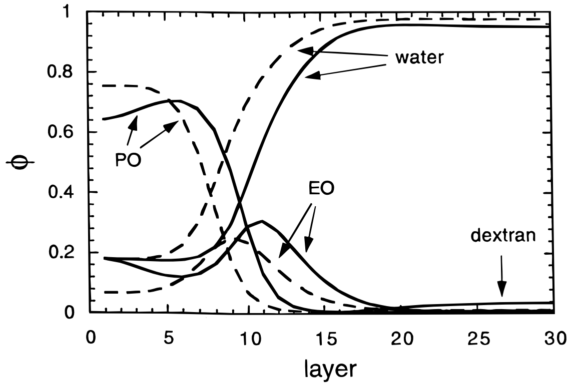

Figure 2. Radial volume fraction profiles of EO, PO, dextran, and water for $\phi_{PEO-PPO-PEO} = 0.023$ and $\phi_{dextran} = 0.035$ (filled curves, composition 7), and $\phi_{PEO-PPO-PEO} = 0.023$ and $\phi_{dextran} = 0.0$ (dashed curves) at 325 K.

number, N_{agg}, of PEO−PPO−PEO. These two trends are normally coupled,[4] and we attribute the enhanced tendency of the self-assembly to the PEO−PPO−PEO−dextran incompatibility.

Typical radial volume profiles for the different species are shown in Figure 2. The shape of the profiles is the same for all compositions examined with a high fraction of PO segments in the core of the micelle and with hydrated EO segments located in the corona. It is also seen that the dextran chains are almost totally expelled from the interior of the aggregate and the volume fraction of dextran increases to its bulk value outside the micelle.

The effect of the self-assembly on the energetics will now be considered by comparing the interaction energy arising from EO−dextran and PO−dextran contacts with the corresponding energy in a model where all components are homogeneously distributed (the Flory−Huggins theory). The total PEO−PPO−PEO−dextran interaction energy per unit volume (for a self-assembled state) in the heterogeneous model is divided as

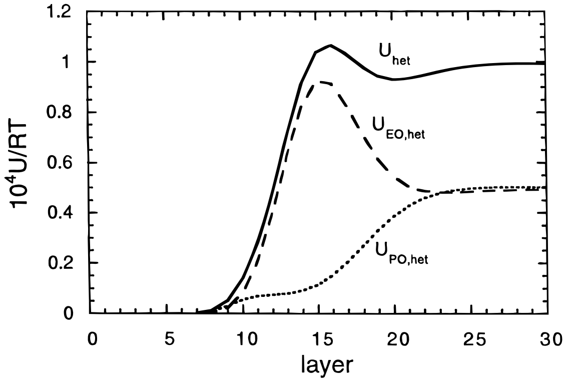

Figure 3. EO−dextran ($U_{EO,het}$) and PO−dextran ($U_{PO,het}$) interaction energies per unit volume calculated according to eq 3 and their sum (U_{het}) as a function of the layer number (distance from the micelle) for $\phi_{PEO-PPO-PEO} = 0.023$ and $\phi_{dextran} = 0.035$ at 325 K.

$$U_{het} = U_{EO,het} + U_{PO,het} \qquad (1)$$

where $U_{EO,het}$ and $U_{PO,het}$ are the contributions from the EO−dextran and PO−dextran contacts evaluated according to

$$U_{A,het} = \sum_i U_{A,het,i}L_i / \sum_i L_i \qquad (2)$$

$$U_{A,het,i} = RT(\chi_{Apolar,dextran}\langle\phi_{Apolar,i}\rangle\phi_{dextran,i} + \chi_{Aapolar,dextran}\langle\phi_{Aapolar,i}\rangle\phi_{dextran,i}) \qquad (3)$$

with A being either EO or PO. $\chi_{A,dextran}$ is the Flory−Huggins interaction parameter between segment of type A (in specified conformation) and dextran, $\phi_{A,i}$ the volume fraction of segment of type A in layer i, where brackets ($\langle...\rangle$) indicate an average over the present and two adjacent layers. L_i is the number of lattice cells in layer i. In Figure 3, $U_{EO,het,i}$, $U_{PO,het,i}$, and $U_{het,i}$ are shown vs layer number. The peak in the $U_{EO,het}$ curve around layer 15 is caused by the penetration of dextran chains in the PEO corona of the micelle, leading to a large positive energy contribution. The expulsion of dextran from the micelle makes the contribution from PO−dextran contacts in the micellar region to the total interaction energy very small. The corresponding energy expressions in the homogeneous model are given by

$$U_{hom} = U_{EO,hom} + U_{PO,hom} \qquad (4)$$

$$U_{A,hom} = RT(\chi_{Apolar,dextran}\phi_{Apolar}\phi_{dextran} + \chi_{Aapolar,dextran}\phi_{Aapolar}\phi_{dextran}) \qquad (5)$$

We will now use the relative energy difference

$$f_A = (U_{A,hom} - U_{A,het})/U_{A,hom} \qquad (6)$$

as a measure of the reduction of the PEO−PPO−PEO−dextran interaction energy upon the micellization, and f may range from zero (no shielding) to one (complete shielding). Table 1 shows that f_{EO} varies from 0.01 to 0.64 and the PO−dextran shielding from 0.64 to 0.89, where the higher shielding corresponds to higher PEO−PPO−PEO concentrations. The overall energy shielding

$f(=(U_{\mathrm{hom}} - U_{\mathrm{het}})/U_{\mathrm{hom}})$ falls between f_{EO} and f_{PO}. The obvious explanation for the large $\phi_{\mathrm{PEO-PPO-PEO}}$ dependence of the shielding is the fact that close to the cmc only a small fraction of the polymers are self-assembled and hence most of them are free and exposed to dextran, whereas at high $\phi_{\mathrm{PEO-PPO-PEO}}$ a larger fraction of the PEO−PPO−PEO molecules is self-associated. Table 1 also shows the fraction of PEO−PPO−PEO which are self-assembled, $N_{\mathrm{agg}}/N_{\mathrm{tot}}$, and indeed this ratio displays a concentration dependence similar to f_{EO}. Thus, the enhanced shielding upon micellization of the water-soluble EO units is closely related to the fraction of self-assembled polymers, whereas the shielding of the less soluble PO units is stronger and nearly complete at high polymer concentrations. Of course, in real systems the shielding upon (polymolecular) self-association becomes smaller since the unimers are partly folded.

In our previous modeling of the phase behavior of the ternary Pluronic/dextran T500/water system[9] using a homogeneous Flory−Huggins model, we found it necessary to remove all PO−dextran contacts and to reduce the interaction parameters for the EO−dextran pair to obtain reasonable agreement between calculated and experimental critical points of the binodal curves. In the case of Pluronic P105 (critical point at 6% Pluronic P105 and 3% dextran T500), $\chi_{\mathrm{EO,dextran}}$ was reduced to 30% of its original value. Composition 3 in the present study is close to the experimental situation and the calculated shielding factors $f_{\mathrm{EO}} = 0.64$ and $f_{\mathrm{PO}} = 0.89$ are indeed close to the reduction factors 0.70 and 1.0, respectively, for the interaction used in the previous study, indicating a consistency between the two approaches.

To conclude, the random-mixing approximation in the Flory−Huggins theory makes the theory only appropriate for phase calculations where there are at most weak concentration gradients within the phases. In the previous study[9] we showed that if we still use the Flory−Huggins theory for calculating phase diagrams in self-assembling systems, the χ-parameters have to be drastically changed to account for the shielding of contacts due to the self-association. Moreover, the present study clearly illustrates that the use of fixed χ-parameters for calculating full phase diagrams can at best be only qualitatively correct. The reason is that the shielding varies in the phase diagram, and hence the χ-parameters used in a Flory-type approach for modeling self-assembling systems ought to be concentration dependent.

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