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Strong Solubilization of Small Molecules by Triblock-Copolymer Micelles in Selective Solvents

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ABSTRACT: Monte Carlo simulations on a cubic lattice were carried out to study the micellization and solubilization of a system containing ABA triblock copolymers, small molecules compatible with the A block, and solvent which selectively solvates the B blocks. The parameters varied were the amount of small molecules, the polymer concentration, the interaction parameters between A and B, A and solvent, solute and solvent, solute and B block, and the A and B block sizes. The corresponding effects on the fraction of polymers forming micelles, the aggregation number of insoluble blocks, the fraction of solutes solubilized, the micelle−solvent partition coefficient of the solubilizates, and the solubilization capacity of the insoluble block were discussed and compared with experimental and theoretical data from the literature.

Introduction

In a selective solvent which is good for one block but poor for the other block, block copolymers spontaneously form micelles with the solvent incompatible block forming the core, and the solvent compatible block forming the corona. The critical micelle concentration (cmc) can be defined as the concentration below which virtually no micelles exist and above which all additional copolymer goes into the micellar phase.[1] Among the numerous applications of a micellar system, an important one is their ability to enhance the solubility of insoluble small molecules by trapping them in the micellar core, if those small molecules are energetically compatible with the monomers of the insoluble block. Such small molecules are called solubilizates, and the related dissolution phenomena in a micellar system is called the solubilization, which is more strictly defined by[2] "the preparation of thermodynamically stable isotropic solution of a substance normally insoluble or very slightly soluble in a given solvent by the introduction of an additional amphiphilic component or components."

The phenomenon of solubilization has been studied extensively in aqueous and nonaqueous solutions of low molecular weight conventional surfactants.[2] However, block copolymers hold unusual potential compared to conventional low molecular weight surfactants because of their ability to micellize in a variety of solvents. In the last decade micellization and solubilization in block copolymer surfactant molecules have received increased attention from both a theoretical[3−7] and an experimental[8−14] point of view. Most experimental studies, using techniques such as light and neutron scattering, surface tension measurements, gas chromatography, etc., have focused on bulk properties and micellar structures, while fluorescence and NMR spectroscopy[15] provide a sensitive way of probing the microenvironment afforded by the micelles.

On the basis of their free energy model, Nagarajan and Ganesh[4,5] developed a theory of solubilization of low molecular weight compounds in micelles of AB diblock copolymer in a selective solvent. The theory predicted that the solubilization behavior of the micelles and their geometrical characteristics were significantly influenced by the interactions between the solubilizate and the solvent-compatible block of the copolymer as well as by the solubilizate−solvent interfacial tension. The scaling relationship obtained was compared to the previous experimental data[8] where the micellar core was composed of poly(propylene oxide)/polystyrene, which showed substantial solubilization of aromatic hydrocarbon solubilizates in contrast to negligible solubilization of aliphatics. The conclusion was made that the solubilizate that is more compatible with the polymer block that constitutes the core of the micelle is solubilized to a greater extent.

In dynamic light scattering studies for polystyrene−poly(ethylene oxide) (PS−PEO) block copolymers in cyclopentane, a selective solvent for polystyrene, Gast *et al.*[10−12] found that a trace amount of water has a profound effect on the structures formed in dilute solutions due to the compatibility of PEO and water. Addition of water breaks up the large aspheric aggregates, resulting in a solution of monodisperse spherical micelles and single chains. Further addition of water results in a solution of swollen micelles. Later on the self-consistent field theory[16] was applied to describe the spherical micelles in the presence of two solvents, each selective for one block, and it was predicted that the size of the core block dominates the micelle's capacity to disperse a second solvent.

Water soluble poly(ethylene oxide)−poly(propylene oxide) (PEO−PPO) triblock copolymers can aggregate in the form of micelles,[9,17−21] with a core presumably dominated by PPO and a corona dominated by hydrated PEO blocks. Hurter *et al*. developed a self-consistent mean field lattice theory[6] to predict the aggregation behavior of PEO−PPO block copolymers and the solubilization of naphthalene in these micelles as a function of polymer composition and molecular weight, both of which compared favorably with the experimental result. The dependence of the micelle−water partition coefficient on polymer composition is not simply related to the proportion of the hydrophobic constituent but depends on the details of the micelle structure. A strong effect of the molecular weight and PPO content of the polymer on the amount of naphthalene solubilized was observed.

Gadelle, Koros, and Schechter investigated the solubilization of various aromatic solutes in PEO−PPO−PEO/PPO−PEO−PPO triblock copolymers.[22] The solute partition coefficient was shown to have a strong

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dependence on the solute concentration. The amount solubilized was at its highest for the high molecular weight, hydrophobic polymers. For the less hydrophobic or lower molecular weight polymers, solubilization capacity was a function of the polymer concentration. PPO–PEO, polymer–water, and polymer–solute interactions were found to have a strong influence on the aggregation and solubilization.

In this paper, we discuss some results obtained by on-lattice Monte Carlo techniques concerning the micellization of ABA triblock copolymers and the solubilization of small molecules in the micelles. The properties include the fraction of the A blocks forming micelles, the micellar aggregation number, the fraction of small molecules solubilized, the micelle–solvent partition coefficient of the solubilizates, and the solubilization capacity of the A block. The amount of the solubilizates, the polymer concentration, the interaction parameter, and the A block and B block sizes are varied, and their influences on the properties listed above are presented.

Method

There are three kinds of molecules in the system, namely the ABA triblock copolymer, the low-mass molecules (I), and the solvent molecules (S). The copolymer is symmetric in the sense of the end block size. Each chain contains $2N_A$ beads of A and N_B beads of B, while I and S each occupy one lattice site.

Only the nearest neighbor interactions were taken into consideration while calculating the energetics. The dimensionless interaction parameter can be denoted by

$$\epsilon = E/k_B T \tag{1}$$

where k_B is the Boltzmann constant and T is the absolute temperature. The relationship between ϵ and the Flory–Huggins χ parameter is

$$\chi = z\epsilon \tag{2}$$

where z is the coordination number. All of the pairwise interactions between identical species are set to be zero. Additionally we assert that a solvent molecule is energetically equivalent to a B monomer and a solubilizate is equivalent to an A monomer by keeping ϵ_{AI} and ϵ_{BS} at zero. The nonzero interactions come from the nearest neighbor pairs of AB, AS, BI, and IS. The energy of any replica is

$$\varepsilon = \epsilon_{AB}n_{AB} + \epsilon_{AS}n_{AS} + \epsilon_{BI}n_{BI} + \epsilon_{IS}n_{IS} \tag{3}$$

where n_{XY} is the number of the nearest neighbor pairs for X and Y.

The Monte Carlo simulation was performed on a simple cubic lattice, with a box dimension of 40^3. Periodic boundary conditions were applied in all three cartesian directions. Three types of moves for generating ensembles of equilibrium configurations of the polymer chains were reptation, crankshaft, and kinkjump, while each I was moved by one lattice distance at a time. All sites not occupied by ABA or I are considered to be occupied by S. Trial moves were accepted or rejected according to the Metropolis rule[23]

$$P = \min\{1,\exp(-\Delta\varepsilon)\} \tag{4}$$

where $\Delta\varepsilon$ is evaluated using eq 3.

Simulations were started by introducing athermally a specified number of copolymer chains and solubilizates into the box. After relaxation with $\varepsilon = 0$, the specific interactions were turned on. Then more than 10^8 moves were attempted in order to attain a state where both the total energy and the properties of interest in the system fluctuated around the averaged value without any trend. This steady state was taken to be equilibrium. We than performed the calculations for 100 replicas chosen at regular intervals of 100 Monte Carlo steps. One Monte Carlo step attempts a move on every segment of the block copolymers and on every I.

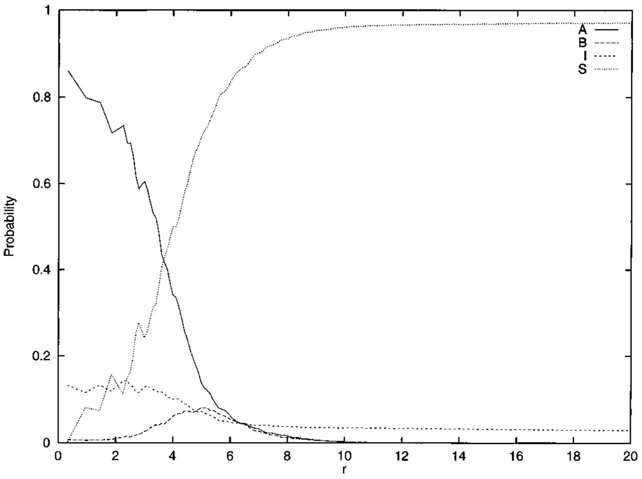

Figure 1. Radial distribution function for 96 chains of $A_{15}B_{10}A_{15}$ (I:A = 0.96, $\epsilon_{AB} = \epsilon_{AS} = \epsilon_{IS} = \epsilon_{BI} = 0.45$).

Results and Discussion

Micellar Profile. Previous simulations of block copolymers in selective solvents have identified a chain as being in a micelle if one of its A beads has an A bead from another chain as a nearest neighbor.[24,25] This contact can be written as A···A. Here we extent the definition to include A···I···A as well, where one of the solubilizates has simultaneous nearest neighbor interactions with A beads from two chains. Experimentally what is usually observed as a micelle is the whole entity including the block copolymer chains and the bound small molecules.

Figure 1 depicts the radial distributions of A, B, I, and S, from one of the simulations. The profile was averaged over all the micelles present in the system and further over 100 snapshots separated by 100 Monte Carlo steps each. In contrast to the conventional surfactant micelles, the micellar cores are substantially swollen by the continuous phase solvent, as has been reported by Van Lent and Scheutjens.[26] Compared to the profile of a diblock micelle,[24] the distribution of the insoluble block has a longer tail, which almost embraces the distribution of the soluble block. A similar distribution profile has been obtained theoretically.[6] The triblock micelles comply less strictly to the core-shell model.[3] The solubilizates contribute a significant portion of the micellar core in addition to the insoluble block. As we go further away from the micelles, the distribution of I saturates at its bulk concentration, and correspondingly, the distribution of solvent approaches some value below 1.

Characteristics. A polymer molecule either participates in a micelle or is singly dispersed in the solution. Similarly a small molecule can be in one of three states: it can be (i) trapped in a micelle, (ii) fully dissolved in the solution, or (iii) aggregated with other small molecules into clusters. Large clusters of I are never seen under the conditions employed here. Small clusters, containing two and sometimes more small molecules, are observed. Since the clusters are never large, we can simplify the three-state model into a two-state one: a solubilizate can be either absorbed in a micelle or dissolved by the solvent outside the micelles. Thus our block copolymer–solvent–solubilizate system is a multicomponent solution consisting of solvent molecules, singly dispersed copolymer molecules, dissolved solubilizate molecules and micelles of all sizes containing various possible amounts of the insoluble blocks and the solubilizates.

Several quanitites are of interest in the simulations. Suppose X_{gj} is the number of micelles with g insoluble blocks and j solubilizates, respectively. The fraction of solubilizates absorbed is the ratio of those solubilizates in the micelles to the total amount that is present in the system:

$$F_{\mathrm{I}} = \frac{\sum jX_{gj}}{J_{\mathrm{total}}} \tag{5}$$

The micelle−solvent partition coefficient is the ratio of the amount of the solubilizate inside the micelles and the amount that is dispersed in the continuous phase.

$$K_{\mathrm{I}} = \frac{\sum jX_{gj}}{J_{\mathrm{total}} - \sum jX_{gj}} \tag{6}$$

The solubilization capacity is the volume fraction of the solubilizates in the micellar core.

$$\eta = \frac{\sum jX_{gj}}{N_{\mathrm{A}}\sum gX_{gj} + \sum jX_{gj}} \tag{7}$$

With regard to the polymer behavior, the fraction of the A blocks participating in the micelle formation is defined as the ratio of the number of insoluble blocks in micelles to the overall value:

$$F_{\mathrm{A}} = \frac{\sum gX_{gj}}{\text{total number of A blocks}} \tag{8}$$

The number average aggregation number is given by the relation:

$$g_{\mathrm{n}} = \frac{\sum gX_{gj}}{\sum X_{gj}} \tag{9}$$

In the following sections we will discuss the effects on the above five properties of (1) the amount of the solubilizates, (2) the polymer concentration or the volume fraction of the copolymer (VF), (3) ϵ_{AB} and ϵ_{AS}, (4) ϵ_{IS} and ϵ_{BI}, (5) the A block size, and (6) the B block size.

Effect of the Amount of Solubilizates. In this section all parameters are kept constant except for the number of solutes, which varies from 500 to 8000, corresponding to volume fractions from 0.0078 to 0.125. Figure 2 shows the fraction of solubilizates in micelles with respect to the volume fraction of solubilizates. The fraction absorbed increases as the total number of solutes increases. The partition coefficient shown in the inset also increases markedly with the solute concentration, as observed by Hurter *et al.*,[6] which is unlike the case of conventional surfactants.

The solubilization capacity is enhanced by the presence of the solutes, which is depicted in Figure 3. The inset depicts the same property as a function of the fraction of the insoluble blocks in micelles, F_{A}. The more solutes in the system, the more insoluble blocks form micelles, which is more clearly depicted in Figure 4. Because the amount of solubilizates in the micellar core increments more dramatically than does the number of insoluble blocks in the micelles, the solubilization capacity manifests the trend of increasing slope in the inset for Figure 3. In Figure 4 F_{A} increases abruptly as more solutes are added and quickly approaches the saturation point of 1. So the addition of solutes promotes the aggregation of polymeric surfactant molecules that otherwise tend to be dispersed in the continuous phase. This observation verifies the assumption proposed by Gadelle *et al.*[22]

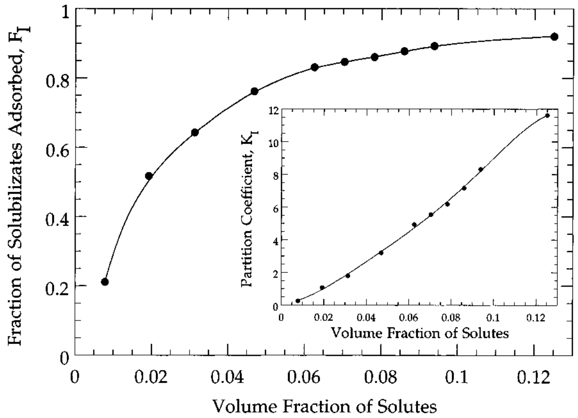

Figure 2. Fraction of solubilizates absorbed in micelles, F_{I} (and micelle−solvent partition coefficient, K_{I}, in the inset), as a function of the total number of solubilizates in the system ($A_5B_{10}A_5$, VF = 0.04, $\epsilon_{\mathrm{AB}} = \epsilon_{\mathrm{AS}} = 0.45$, $\epsilon_{\mathrm{IS}} = \epsilon_{\mathrm{BI}} = 0.8$).

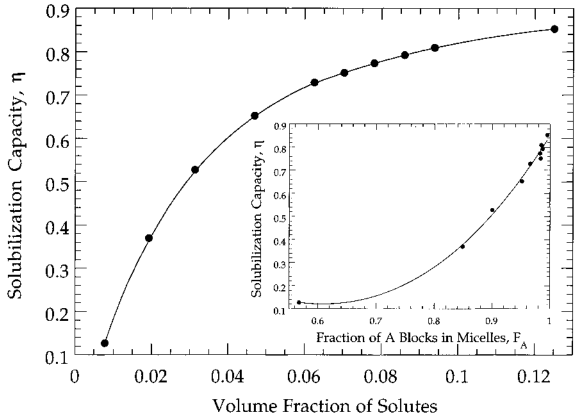

Figure 3. Solubilization capacity, η, as a function of the total number of solubilizates in the system. The inset depicts η as a function of the association number, a_n ($A_5B_{10}A_5$, VF = 0.04, $\epsilon_{\mathrm{AB}} = \epsilon_{\mathrm{AS}} = 0.45$, $\epsilon_{\mathrm{IS}} = \epsilon_{\mathrm{BI}} = 0.8$).

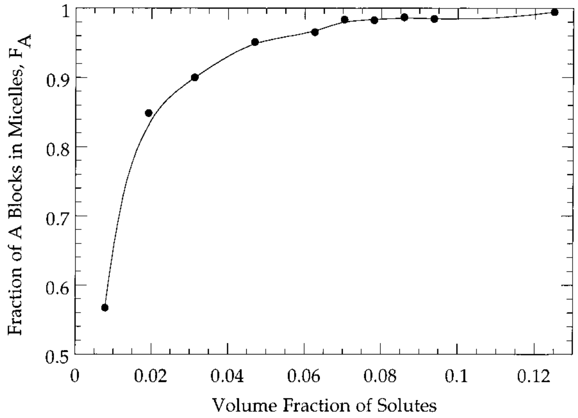

Figure 4. Association number, a_n, as a function of the total number of solubilizates in the system ($A_5B_{10}A_5$, VF = 0.04, $\epsilon_{\mathrm{AB}} = \epsilon_{\mathrm{AS}} = 0.45$, $\epsilon_{\mathrm{IS}} = \epsilon_{\mathrm{BI}} = 0.8$).

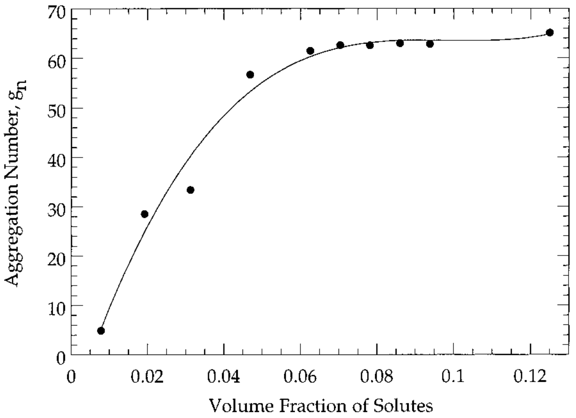

Figure 5. Aggregation number, g_n, as a function of the total number of solubilizates in the system ($A_5B_{10}A_5$, VF = 0.04, $\epsilon_{AB} = \epsilon_{AS} = 0.45$, $\epsilon_{IS} = \epsilon_{BI} = 0.8$).

The aggregation number, g_n, is also a function of solute amount, plotted in Figure 5. Although the points do not describe a smooth curve very well, the general trend is that the solubilizates facilitate the growth of micelles, which is in agreement with the prediction made by Hurter *et al.*[6] Cogan *et al.*[16] reported a very good agreement between their self-consistent field calculations and static light scattering data, both of which showed the trends of increase in aggregation with increasing probe contents. A mean field description[4] also predicted a substantial increase in aggregation number by the solubilizates. We conclude that the increase in micellar weight on solubilization does not originate simply from the incorporation of solubilizate molecules into the existing micelles but from the increased number of surfactant molecules present in the solubilizate laden micelles. In addition to swelling the micellar core and increasing the fraction of the block copolymers in micelles, the solute promotes micellization by a larger micelle aggregation.

The enhancement of micellization by solubilizates implies the lowering of cmc in the presence of the solubilizates, which has been predicted theoretically.[4] Compared to the cmc's of low molecular weight surfactant systems, the cmc is often negligibly small for the block copolymers because of the large size of the insoluble block. The cmc's cannot be determined in this study because they reside in such a low concentration regime that the detection within reasonable uncertainties is impossible.

Effect of Polymer Concentration and Interaction Parameters. In this section, the nonzero interactions, ϵ_{AB}, ϵ_{AS}, ϵ_{IS}, and ϵ_{BI} are set to be equal, and two values, specifically 1.0 and 0.45, have been chosen to address the effect of the specific interactions. The macromolecules are monodisperse with $N_A = 15$ and $N_B = 10$, and their volume fraction ranges from 0.005 to 0.13, which is well above the cmc. The certain number of solubilizates are added at various polymer concentrations, keeping the ratio between I beads and A beads at two constants, 0.19 and 0.96.

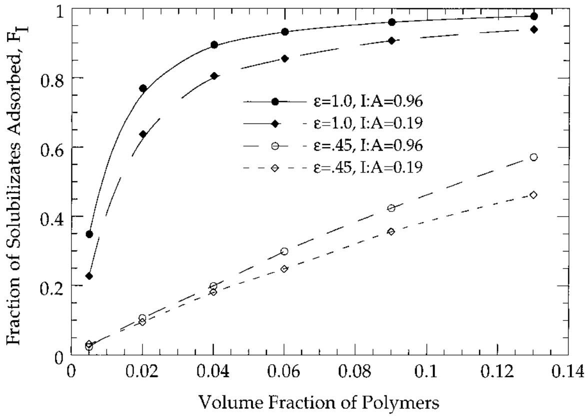

Figure 6. Fraction of solubilizates absorbed in micelles, F_I, as a function of polymer volume fraction ($A_{15}B_{10}A_{15}$).

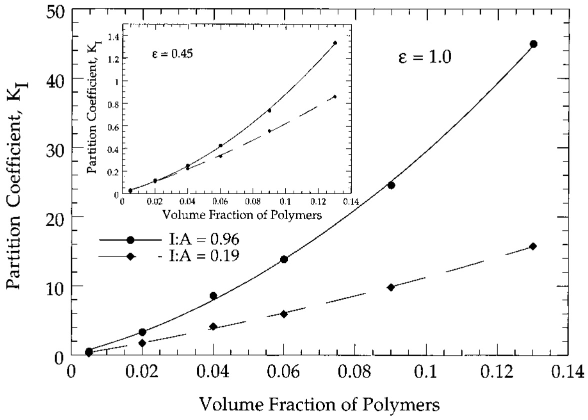

Figure 7. Micelle−solvent partition coefficient, K_I, as a function of polymer volume fraction ($A_{15}B_{10}A_{15}$).

Figure 6 depicts the fraction of solubilizates absorbed in the micelles, F_I, with respect to the volume fraction of polymer. Obviously more polymer chains provide more adsorption sites; thus the higher fraction will be solubilized. Collett and Tobin[27] have studied the solubilization of para-substituted acetanilide in a range of PEO−PPO−PEOs, and they also found that solubilization increased with polymer concentration. The more solubilizates there are, the more are picked up by the micelles, which has been observed in the previous section. The other parameter which plays a significant role is the interaction. As it jumps from 0.45 to 1.0, the curves are shifted up because the system will form bigger and tighter aggregations in order to compensate the higher energetic penalties.

The interaction also alters the partitioning behavior remarkably, as shown in Figure 7. Gadelle *et al.*[22] reported the solubilization of toluene in aqueous PEO−PPO−PEO (BAB type) solutions. They found that the partition coefficient increases monotonically as the polymer concentration increases for low molecular weight polymers. But in the range of high molecular weight and hydrophobic copolymers, the solubilization may then be independent of the polymer concentration. In our case we find that increasing polymer concentration consistently increases the partition coefficient. At low polymer concentrations, the curves for various interactions and solute-to-polymer ratios almost coincide. But as the concentration increases, the curves rise with different slopes, based on which they can be divided into two groups by different strength of interactions. At higher interactions, the micelle−solvent partition coefficients are 30−40 times larger than those at lower interactions. Additionally, the curves for higher solutes-to-polymer ratio sit above those for lower ratio under either interaction parameters, which once more justified our previous discussion about the role of the solubilizates.

The solubilization capacity, plotted in Figure 8 as a function of polymer concentration, fairly quickly reaches the saturation limits at low concentration under strong interactions. On the other hand, under weak interac-

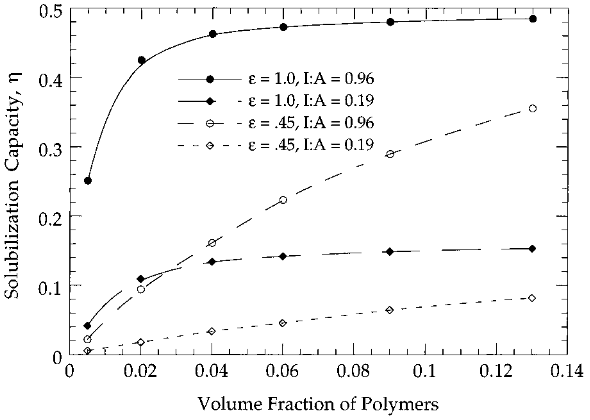

Figure 8. Solubilization capacity, η, as a function of polymer volume fraction ($A_{15}B_{10}A_{15}$).

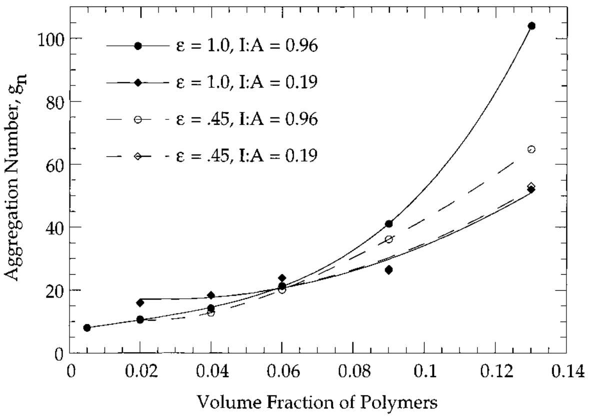

Figure 9. Aggregation number, g_n, as a function of polymer volume fraction ($A_{15}B_{10}A_{15}$).

tions, the solubilization capacities are far below the saturation value even at the highest concentration we have probed. Thus it is economically more efficient to apply the block copolymers of stronger A—B, A—S, B—I, and I—S interactions to extract the pollutes in a cleaning process.

Figure 9 depicts the aggregation number, g_n, with respect to the polymer concentration. The increase in the size of the micelles characterized by the average number of insoluble blocks in a micelle as a result of addition of more polymer chains has been predicted by Leibler,[3] although the dependence is comparatively weak for a diblock system. When concentration is decreased the entropic contributions to the total free energy become of growing importance as compared to the enthalpic terms due to the repulsions between monomers A and B; thus polymer chains drop out of the micelles and/or big micelles segregate into smaller ones, both of which result in the reduction in the aggregation number. However, there are a number of discrepancies about the concentration effect on the aggregation number. Wanka *et al.*[28] reported by light scattering that for small concentrations of the block copolymers, the aggregation number and the dimensions of the aggregates are independent of concentration, and those values decrease for concentrations above 10 wt % due to the repulsive interactions between micelles. It is also predicted theoretically[6,16] that g_n increases rapidly with polymer concentration in the dilute regime, but at concentrations far above the cmc g_n is approximately invariant with a change in the polymer concentration.

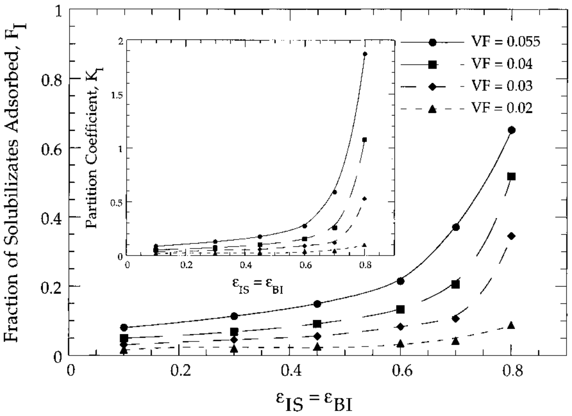

Figure 10. Fraction of solubilizates absorbed in micelles, F_I (and micelle—solvent partition coefficient, K_I, in the inset), as a function of interaction parameter, $\epsilon_{IS}/\epsilon_{BI}$ ($A_5B_{10}A_5$, $\epsilon_{AB} = \epsilon_{AS} = 0.45$, I:A = 0.96). The volume fractions of copolymers are 0.02 (▲), 0.03 (◆), 0.04 (■), and 0.055 (●).

At a certain concentration, the higher degree of incompatibility promotes the aggregation provided that a sufficient amount of solubilizates is present. Since the micellization process is a competition between entropy and enthalpy, high energetics brings about the sacrifice of entropy, and thus larger micelles are formed.

Effect of Solvent—Solute Interaction. The effect of solvent—solute interaction on the solubilization and the micellization properties can be manipulated by experimentalists through the control of the temperature and/or use of solutes of different polarities. In this section the fixed parameters are $N_A = 5$, $N_B = 10$, $\epsilon_{AB} = \epsilon_{AS} = 0.45$, and the ratio between the solutes and the A monomers is 0.96. The ϵ_{IS} and ϵ_{BI} are equal to each other and varied from 0.1 to 0.8, and the volume fraction of the polymer changes from 0.02 to 0.055 to incorporate the concentration effect.

The $\epsilon_{IS} = \epsilon_{BI}$ dependence of the fraction of solubilizates absorbed in micelles, F_I, is plotted at various polymer concentrations in Figure 10. F_I is strongly dependent on both the nature of the solutes and the concentrations. When the concentration is high, F_I increases more markedly with $\epsilon_{IS} = \epsilon_{BI}$ than at low concentrations. On the other hand, at high interaction energies, F_I is a substantially increasing function of concentration, while at weak interactions, concentration only influences F_I moderately.

As can be deduced from the behavior of F_I, the micelle—solvent partition coefficient, K_I, is very sensitive to both $\epsilon_{IS} = \epsilon_{BI}$ and polymer concentration, which is plotted in the inset of Figure 10. At high polymer concentrations, a dramatic increase in K_I occurs as the interactions reinforce. However, at low concentrations, only a small increase in K_I occurs as the temperature is lowered. Conversely, at low $\epsilon_{IS} = \epsilon_{BI}$ values, K_I decreases asymptotically to values that are nearly independent of polymer concentration.

Gadelle *et al.*[22] investigated the influence of the solute by experimenting with different aromatic solutes, such as toluene, benzene, chlorobenzene, and *p*-xylene. They were unable to rationalize the relationship between the Flory—Huggins solute—B interaction parameter and the solubilization capacity because the effect of interaction is coupled with that of the molar volume of the solutes. They are indistinguishable because one experimental entity takes both facets of the characteristics simultaneously. In conventional surfactant micelles the number of molecules solubilized decreases with increasing molecular volume of solubilizate.[29,30] The solubilization capacity, shown in Figure 11, increases monotonically

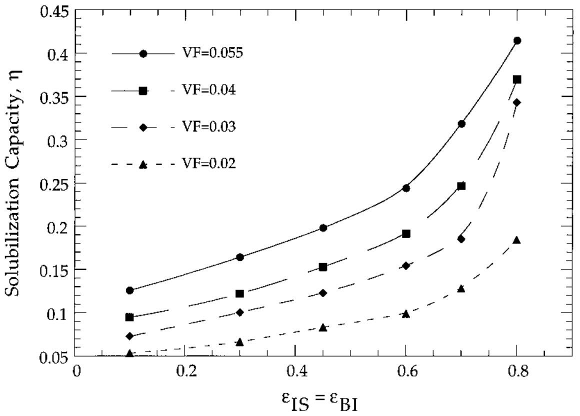

Figure 11. Solubilization capacity, η, as a function of interaction parameter, $\epsilon_{IS}/\epsilon_{BI}$ ($A_5B_{10}A_5$, $\epsilon_{AB} = \epsilon_{AS} = 0.45$, I:A = 0.96).

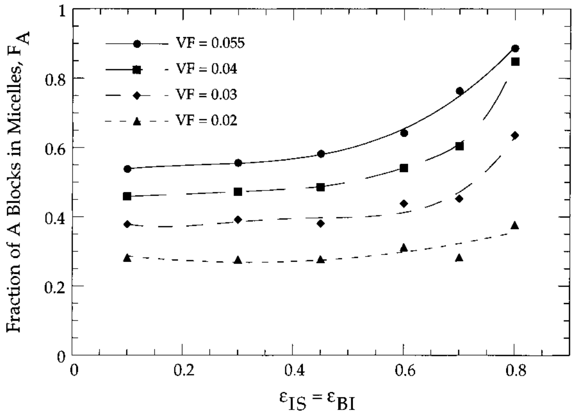

Figure 12. Association number, a_n, as a function of interaction parameter, $\epsilon_{IS}/\epsilon_{BI}$ ($A_5B_{10}A_5$, $\epsilon_{AB} = \epsilon_{AS} = 0.45$, I:A = 0.96).

with increasing immiscibility of the solutes and/or polymer concentration. This is where the distinct advantage of simulation resides, by which one can vary a specific parameter independently but keep others unchanged. Nagarajan *et al.*[8] correlated the amount solubilized per unit surfactant with the polarity parameter by comparing the solubilization of toluene and cyclohexane, which have comparable molecular volumes but belong to different chemical class. Their results showed substantial solubilization of aromatics in contrast to negligible solubilization of aliphatics because aromatics are more compatible with the polymer block that constituted the core of the micelle, or in other words, more incompatible with the solvent and the corona. Our predictions are in good agreement with their results.

As well as the properties related to the low mass molecules, the behavior of polymer chains depends on the magnitude of the interaction and the concentration. The fraction of the A blocks involved in micellication, F_A, depicted in Figure 12, remains approximately constant over the range in which $\epsilon_{IS} = \epsilon_{BI}$ varies at the lowest concentration, specifically the polymer volume fraction of 0.02. As we increase the concentration, F_A becomes more dependent on the interaction parameter. On the other hand, high interaction results in a broader change in F_A as the concentration increases the same amount. The interaction and the concentration are two factors which control the association of insoluble blocks, where strengthening one will enforce the effect of the other one.

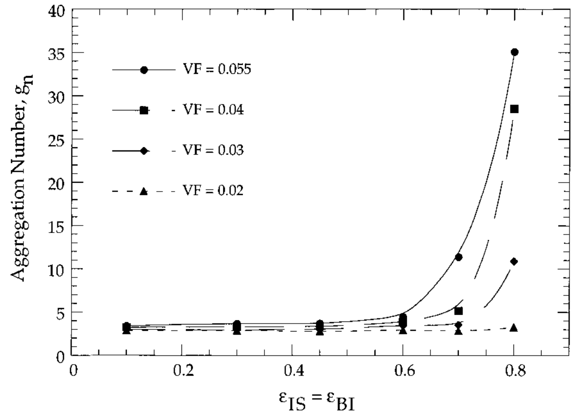

Figure 13. Aggregation number, g_n, as a function of interaction parameter, $\epsilon_{IS}/\epsilon_{BI}$ ($A_5B_{10}A_5$, $\epsilon_{AB} = \epsilon_{AS} = 0.45$, I:A = 0.96).

In Figure 13, the micelles size characterized by the aggregation number, g_n, remains almost unchanged for $\epsilon_{IS} = \epsilon_{BI}$ up to 0.6. In the range of $\epsilon_{IS} = \epsilon_{BI}$ from 0.6 to 0.8, g_n shoots up remarkably, especially at high concentrations. Compared to the much more moderate increase of the fraction of the insoluble blocks constituting micelles depicted in Figure 12 in the same range, a mechanism of micelle growth can be deduced. Provided that the concentration is sufficiently high, as the solvent–solute or B–solute incompatibility increases, the micelles start to grow by picking up more copolymer chains which were formerly dissolved in the solution. As the incompatibilities become stronger and the micelles grow bigger, at a certain point merger of micelles occurs; therefore the aggregation is enhanced dramatically.

Effect of Insoluble Block Size. The effect of A block size on the partition coefficient and the solubilization capacity is plotted in Figure 14. The ratio of I/A is 0.96. From the curves we observe that, at the same concentration of A, decreasing the insoluble block size will decrease the partition coefficient but increase the solubilization capacity. In agreement with that, Cogan and Gast[10] observed that smaller block copolymers can more easily accommodate solutes into micelles. The smaller partition coefficient indicates that less solubilizates are absorbed in the micelles, in other words, more are suspended in the solution. The larger solubilization capacity reveals that fewer A beads are required to absorb a certain amount of solubilizates. Combining the two phenomena, smaller insoluble block size results in a smaller aggregation number, brought about by the smaller χN, the effective Flory–Huggins incompatibility parameter, which has been suggested by a thermodynamic treatment[4,5] and a self-consistent mean field theory.[6,16]

Effect of Soluble Block Size. The B block size has no noticeable effect on the partition coefficient and the solubilization capacity when varied over the range 5–10 (results not shown). This is understandable since soluble blocks do not participate directly in the formation of the core of the micelle. We do not exclude the possibility that enormous variance in B block length may show some effect, but for the values we have tested, the differences in the partition coefficient and the solubilization capacity are within the uncertainty range. In fact it has been predicted in the literature[6,16] that the micelle structure is not solely determined by the core block length. Polymers with a higher proportion of the hydrophilic block tend to form smaller micelles in aqueous solution, with a lower concentration of hydrophobic block and a higher concentration of water in the core, which results in less small molecules being solu-

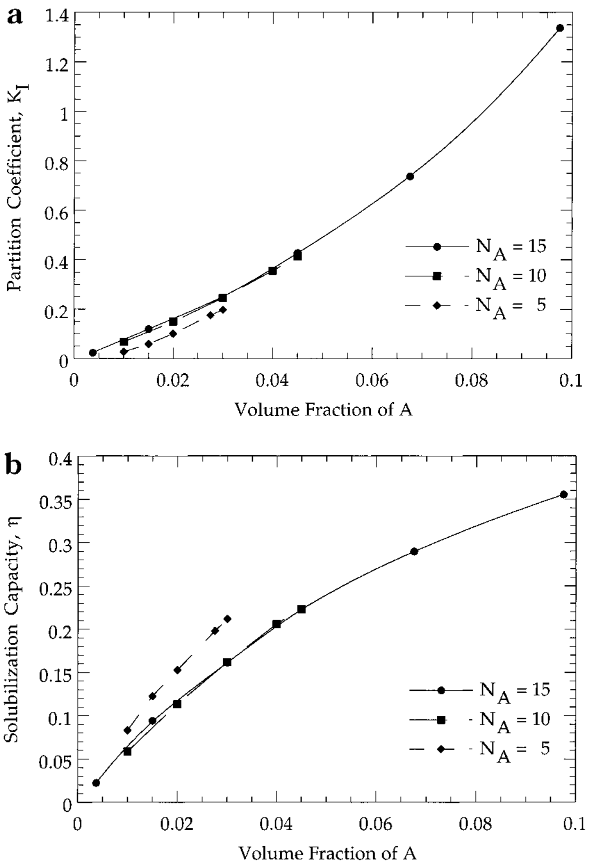

Figure 14. Effect of A block size on (a) the partition coefficient and (b) the solubilization capacity ($N_B = 10$, $\epsilon_{AB} = \epsilon_{AS} = \epsilon_{IS} = \epsilon_{BI} = 0.45$, I:A = 0.96).

bilized. Indeed the micelle features are primarily affected by the core block size; however, the corona block size can be an important factor if the size change is large enough to significantly modify the copolymer symmetry.

Conclusions

The micellization and solubilization of ABA type triblock copolymers with small solubilizate molecules in the solvents which selectively solvate the middle block are studied. The presence of the solubilizates greatly enhances the micellization of the block copolymers, which can be visualized from the fact that not only the fraction of the A blocks associated in micelles increases, but also the aggregation number increases.

The amount of solubilizates absorbed by micelles, the micelle–solvent partition coefficient, and the solubilization capacity are augmented by increasing the amount of solubilizates.

The polymer concentration is found to play a role in determining the pertinent properties. The higher the concentration, the bigger the micelles characterized by the aggregation number, the larger the partition coefficient and the solubilization capacity.

The higher the immiscibility between the incompatible entities, the larger the micelles and the stronger the solubilization. Increasing the A block–B block (ϵ_{AB}), the A block–solvent (ϵ_{AS}), the solvent–solute (ϵ_{IS}), the B block–solute (ϵ_{BI}) interaction parameters increases the micellar aggregation, the partition coefficient of the solubilizates and the solubilization capacity of the A blocks.

Longer insoluble blocks enforce the solubilization by increasing the partition coefficient, but the solubilization capacity is lowered. The soluble block size has no significant effect if a small change is introduced.

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