### Solubilization of Homopolymers in a Solution of Diblock Copolymers

**D. Izzo\***,<sup>†</sup> and C. M. Marques<sup>‡</sup>

Instituto de Física, U.F.R.J., Caixa Postal 68528, 21945-970, Rio de Janeiro, Brazil, and LDFC UMR 7506, CNRS-ULP, 3 rue de l'Université, 67084 Strasbourg Cedex, France

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We study theoretically mixed solutions of homopolymer and diblock copolymer chains. The solvent is a poor solvent for the homopolymers and a selective solvent for the copolymers. We find that the formation of copolymer micelles containing also the insoluble chains allows for an increased solubility of the homopolymers in the solution. In agreement with experiments, we find also that the solubilization power of the micelles, that is, the maximum amount of total homopolymer weight solubilized per unit weight of copolymers in solution, decreases strongly with the homopolymer index of polymerization.

#### 1. Introduction

Diblock copolymers in selective solvents are the macromolecular analogues of low molecular weight surfactants.<sup>1,2</sup> At low concentrations, they self-assemble in a variety of micellar shapes as spheres, cylinders, disks, and other, more complex equilibrium and nonequilibrium geometries.<sup>3</sup> At higher concentrations, copolymer dense phases exhibit also many of the fascinating liquid cristalline symmetries found in dense surfactant solutions.<sup>4</sup> The reverberation of amphiphilic behavior in the size range of tens to hundreds of nanometers, typical of copolymers, paved the way to many studies of self-assembly based on the powerful tools developed within the context of polymer theory. These studies successfully predict micellization and the associated characteristic quantities as critical micellar concentrations or aggregation numbers,<sup>5-7</sup> liquid cristalline geometries and orderdisorder transition temperatures,<sup>8</sup> the effect of charges,<sup>9</sup> and comicellization.<sup>10</sup> Surprisingly, much less attention was devoted to one of the key functions played by surface and interface active molecules: solubilization. Indeed, in detergency, arguably the most important practical field for amphiphilic molecules, one needs to optimize the amount of, say, lipophilic material that is dispersed in, and washed by, the micelles formed in the solution. There is thus a need to understand the solubilizing power of micellar solutions with respect to moieties of different molecular weights and chemical composition.

Previous theoretical studies on solubilization<sup>11–13</sup> concentrated on mean-field calculations, well adapted to describe compatibilization in polymer blends or on Monte Carlo simulations,<sup>14</sup> limited by size and parameter range. On the experimental side, we were struck and inspired by the work of Quintana et al.,<sup>15</sup> investigating the solubility of a homologous series of polyisobutilene (PB), in a micellar solution of polystyrene-*b*-poly-(ethylene/propylene) copolymers (SEP) in ketones. The authors show that the total mass of homopolymer solubilized in a single micelle decreases with homopolymer molecular weight and suggest that the maximum amount of homopolymer that a unit mass of copolymer can solubilize follows a decreasing power law with the homopolymer index of polymerization. In this paper we investigate the physical reasons for such solubilization limits by considering A–B diblock copolymers in a selective solvent in equilibrium with a reservoir of insoluble C homopolymers. The paper is organized as follows. In the next section we review the thermodynamics of micellization and present a few simple limits that will help to build intuition for the main concepts developed in this work. Section III fully describes the solubilization of homopolymers in diblock micelles. Section IV summarizes our main results and discusses their relevance for homopolymer solubilization experiments.

## II. Thermodynamics of Association: Micellization and Solubility Limit

We consider a solution of homopolymers and diblock copolymers with number densities of chains  $\phi_h$  and  $\phi_d$ , respectively. The homopolymer has degree of polymerization  $M_A$  whereas the copolymer has blocks with degrees of polymerization  $N_A$  and  $N_B$ . The homopolymer is compatible only with the A-block of the copolymer; the solvent is poor for both of them but good for the B-block.

Parameters such as the molecular mass of each segment, the degree of asymmetry of the diblocks and the polymer concen-



**Figure 1.** Possible configurations of an homopolymer and a diblock copolymer in dilute solution: (a) single chains in a solution; (b) collapsed homopolymers in a poor solvent; (c) diblock copolymer chains forming micelles; and (d) diblock copolymers forming micelles with homopolymers in the core.

<sup>&</sup>lt;sup>†</sup> U.F.R.J.

<sup>‡</sup> CNRS-ULP.

tration in solution determine the state of association of the system, as illustrated in Figure 1. The energy per unit volume of the full system is written as

$$\mathcal{F} = \sum_{p_{h,p_d}} c_{ph,pd} (\ln c_{ph,pd} + F_{ph,pd})$$
(1)

where  $c_{ph,pd}$  and  $F_{ph,pd}$  are the number density and the energy of an aggregate having  $p_h$  and  $p_d$  homopolymer and diblock copolymer chains, respectively. All the energies are expressed in units such that  $k_BT = 1$ . The equilibrium values  $c_{ph, pd}^0$  are obtained minimizing  $\mathscr{F}$  with respect to  $c_{ph, pd}$  under the constraints of mass conservation:

$$\sum_{p_{h,p_d}} p_d c_{ph,pd} = \phi_d \tag{2}$$

$$\sum_{p_h, p_d} p_h c_{ph, pd} = \phi_h \tag{3}$$

leading to

$$c_{ph,pd}^{\quad 0} = \mathrm{e}^{-\left[\mathrm{F}_{ph,pd} - \mu_h \mathrm{p}_h - \mu_d \mathrm{p}_d\right]} \tag{4}$$

where  $\mu_h$  and  $\mu_d$  are the homopolymer and block copolymer chemical potentials which are determined from the mass conservation eqs 2 and 3. Hereafter we will refer to the equilibrium values of the number density by  $c_{ph, pd}$ , dropping the superscript 0. The function  $F_{ph,pd}$  carries the thermodynamically relevant information about the aggregate considered, concerning in particular its structure and the miscibility properties of each component. In the following sections we will consider the forms of the different  $F_{ph,pd}$ 's appropriate to describe solubility, micellization and solubilization by micelles.

A. Solubility of Homopolymers in a Poor Solvent. When homopolymers are exposed to a poor solvent, the few solubilized chains that can be dissolved adopt a collapsed configuration.<sup>16–18</sup> In this case the main contribution to the energy  $F_{ph} = F_{ph,pd=0}$ is due to the surface tension of the collapsed chain droplet:

$$F_{ph} = 4\pi R^2 \gamma \tag{5}$$

where  $\gamma$  is the interfacial tension between the solvent and the homopolymer in units of  $k_BTa^{-2}$  and  $R = (3p_hM_A/4\pi)^{1/3}$  is the radius of the spherical aggregate with  $p_h$  homopolymers. We further choose dimensionless length units where the monomer size *a* has a value unity a = 1. Note that when the solvent is not completely expelled from the core, new renormalized units can be introduced such that the present description still holds.<sup>7</sup> The expression above can be written as

$$F_{ph} = \alpha_h p_h^{2/3} \tag{6}$$

with  $\alpha_h \equiv (36\pi)^{1/3} M_A^{2/3} \gamma$ . With the minimization procedure described in the last section one obtains the number density of micelles with  $p_h$  chains  $c_{ph} = c_{ph,pd=0}$ ,

$$c^{ph} = \mathrm{e}^{-\Omega_{ph}} \tag{7}$$

where  $\Omega_{ph}$  is the grand-potential defined as

$$\Omega_{ph} = \alpha_h p_h^{2/3} - \mu_h p_h \tag{8}$$

Figure 2a shows the dependence of  $\Omega_{ph}$  on the aggregation number  $p_h$ . Because the first term is sublinear, the second, linear term always dominates for large aggregation numbers. When



**Figure 2.** (a) Grand-canonical potential as a function of the aggregation number for the homopolymer system. (b) The homopolymer chemical potential as a function of the volume fraction of homopolymers.  $\phi_h^{max}$  corresponds to the solubility limit,  $\mu_h = 0$ .

the chemical potential is positive, there is an exponential size distribution of the larger aggregates. When  $\mu_h < 0$  one has the formation of aggregates of infinite size  $(p_h \rightarrow \infty)$ . The point of zero chemical potential  $\mu_h = 0$  thus represents the solubility limit for this system, <sup>19</sup> a point that has been argued to bare some analogy to the Bose-Einstein condensation.<sup>20</sup> We define  $\phi_h^{max} = \phi_h(\mu_h = 0)$ , the maximum concentration of homopolymer which can be solubilized, see Figure 2b.  $\phi_h^{max}$  decreases strongly with homopolymer mass: for large polymers, there are almost only single collapsed chains homopolymers present in the solution. Within the framework used in this paper to describe aggregation, this states a classical result concerning the low mutual solubility of two strongly phase separated liquids.

**B.** Solubility of Diblock Copolymers in a Selective Solvent: Micellization. In the case where only diblock copolymers are present in the solution, the energy of the aggregates depends on their geometry. Here we consider spherical micelles in the so-called "star regime"<sup>6,7,21</sup>, corresponding to  $N_A \ll N_B^{15/11}$ . These micelles are described by the energy  $F_{pd} = F_{ph=0, pd}$  given by

$$F_{pd} = \alpha_d p_d^{2/3} + A p_d^{3/2}$$
(9)

where  $\alpha_d = (36\pi)^{1/3} N_A^{2/3} \gamma$  with  $\gamma$  being the core-solvent interfacial tension. In the star regime *A* can be taken as a constant, of order unity. We consider also that both blocks are flexible chains, and that the monomers of both blocks have the same size. More general conformal asymmetries with different monomer sizes and different Kuhn lengths can also be accounted for but are beyond the scope of the paper. The first term on the right of eq 9 is the driving force for assembly. The second term on the right is the contribution from the corona osmotic pressure. Because this contribution grows with a power larger than one, it dominates the energy for large aggregation numbers. In fact, such terms are crucial for micellization to occur because they frustrate the formation of infinite aggregates, thus preventing macroscopic phase separation. Minimization under the constraint of mass conservation, with the energy function (9), provides



**Figure 3.** (a) Number density of chains in an aggregate with aggregation number *p* chains as a function of *p*. *p*\* is the equilibrium aggregation number.  $N_A = 100$ ,  $M_A = 100$ , and  $\gamma = 0.3$ . (b) Chemical potential as a function of the diblock copolymer volume fraction. For  $\phi_d \ge \phi_{CMC}$ ,  $\mu_d$  remains virtually locked at  $\mu_{CMC}$ . The dashed-dotted lines correspond to the asymptotic limits of eqs 12 and 15. The dotted lines are guides to the eye.  $N_A = 100$ ,  $M_A = 100$ , and  $\gamma = 0.3$ .

the number density of aggregates with  $p_d$  chains  $c_{pd} = c_{ph=0,pd}$ ,

$$c_{pd} = \mathrm{e}^{-\Omega_{pd}} \tag{10}$$

with

where

$$\Omega_{pd} = A p_d^{3/2} + \alpha_d p_d^{2/3} - \mu_d p_d \tag{11}$$

and

$$\mu_d = F_1 + \ln c_1 \tag{12}$$

with  $F_1 = F_{pd=1}$  and  $c_1 = c_{pd=1}$ .

To study the micellization we follow Sens et al.<sup>10</sup> and rewrite the constraint of mass conservation as

$$\frac{c_1}{\phi_{CMC}} + \left(\frac{c_1}{\phi_{CMC}}\right)^{p_d^*} = \frac{\phi_d}{\phi_{CMC}}$$
(13)

where  $p_d^*$  is the equilibrium number of diblock copolymer chains in a micelle, obtained by minimizing the grand potential (11), and the critical micelle concentration  $\phi_{CMC}$  is written as

$$\phi_{CMC} = \frac{1}{p_d^*} \exp\left\{-\frac{p_d^* F_1 - F_{pd^*} + \log\Delta}{p_d^* - 1}\right\}$$
(14)

with  $\Delta$  the width of the size distribution, related as usual to the second derivative of the micelle free energy at its minimum point  $p_d^*$ . Solving (13) for the unimer concentration  $c_1$  one gets

$$c_{1} = \begin{cases} \phi_{d} & \phi_{d} \ll \phi_{CMC} \\ \phi_{CMC} \left( \frac{\phi_{d}}{\phi_{CMC}} \right)^{1/p_{d}^{*}} & \phi_{d} \gg \phi_{CMC} \end{cases}$$
(15)

Figure 3a,b illustrates the micellization of diblock copolymers. The distribution of the aggregates size is bimodal above the micellization concentration, as depicted in Figure 3a: single chains coexist with aggregates of  $p_d^*$  chains. The dependence of  $c_1$  on  $\phi_{CMC}$  is obtained from (14) and (15) showing that above micellization,  $\mu_d$  remains almost "locked" at  $\mu_d = \mu_{CMC}$ . Indeed  $\mu_d$  is a function only of unimer concentration  $c_1$  as shown in eq 12 and, in this region the amount of unimers is nearly constant  $c_1 \approx \phi_{CMC}$ ; see eq 15 and Figure 3b.

Contrary to homopolymers in poor solvents, diblock copolymers in selective solvents do not experience a solubilization limit. Indeed, at low concentrations, precipitation is prevented by the soluble block, while above the CMC, the formation of finite size aggregates protects a large fraction of the insoluble block from contact with the poor solvent. The solution can thus accommodate a high density of diblock copolymers by creating an increasing number of micelles. This micellization scenario is only compromised at very high diblock concentrations where excluded volume effects between different micelles come into play. We now deal with the simple case of solubilization of the homopolymer chains by the diblocks below the CMC, where only single chains of homopolymers and diblock copolymers are present in the solution.

C. Below the CMC: Dilute Mixtures of Diblock Copolymers and Homopolymers. We now consider a dilute solution of homopolymers and diblock copolymers. In the solution one has homopolymer and diblock unimers at concentrations  $c_h = c_{ph=1,pd=0}$  and  $c_d = c_{ph=0,pd=1}$ , respectively, and also dimers of one homopolymer and one copolymer. Equations 2–4 lead to

$$c_d(1 + \beta c_h) = \phi_d$$

$$c_h(1 + \beta c_d) = \phi_h^{max}$$
(16)

$$\beta = e^{-\alpha_h [1 + x^{2/3} - (1 + x)^{2/3}]}$$

 $x = N_A/M_A$  and  $\phi_h^{max} = \phi_h|_{\mu h=0}$ . Equations 16 are solved for  $c_d$  and  $c_h$ , yielding

$$\phi_h^{max} = \phi_h^{max}(\phi_d = 0) + \frac{\beta e^{-\alpha_h}}{1 + \beta e^{-\alpha_h}} \phi_d$$
(17)

In the absence of diblock copolymers,  $\phi_d = 0$  and one has from equations 7 and 8:  $\phi_h^{max}(\phi_d = 0) = e^{-\alpha_h^{2/3}}$ . Upon the addition of copolymer chains, the solubility limit increases lineary with the concentration of diblock chains. As we will see below, such linear dependence holds quite generally for the solubilization cases described in this paper and it is also observed experimentally.<sup>15</sup> It allows also to define the solubility  $\Theta$  as the maximum amount of homopolymer that can be solubilized by one block copolymer chain,

$$\Theta = \frac{M_A}{N_A} \frac{\partial \phi_h^{max}}{\partial \phi_d} \tag{18}$$

In the present case it is given by

$$\Theta = \frac{M_A}{N_A} \frac{\beta^{e-\alpha_h}}{1+\beta^{e-\alpha_h}} \tag{19}$$

Figure 4 shows the dependence of  $\Theta$  on the homopolymer molecular mass  $M_A$ . It is clear that the co-solubilization power of the diblock is reduced as the homopolymer mass increases, hindering the formation of homopolymer—copolymer doublets.

# III. Co-Solubilization of Homopolymers by Diblock Micelles

For large concentrations of diblock copolymers, the solution has many different aggregates: single diblock copolymers, some



Figure 4. Solubilization as a function of the homopolymer molecular mass.  $N_A = 100$  and  $\gamma = 0.3$ .

homopolymers or homopolymer aggregates and the dominant species, diblock copolymer micelles with solubilized homopolymer. For these later species, we consider spherical geometries for which the energy is written as

$$F_{ph,pd} = F_g + F_{brush} + F_{core} + F_{\chi}$$
(20)

The first term on the right-hand side of the equation above,  $F_{\gamma}$ , is as before, the interfacial energy between the collapsed core and the solvent:

$$F_{\gamma} = (36\pi)^{1/3} M_A^{2/3} \gamma (xp_d + p_h)^{2/3}$$
(21)

with  $\gamma$  being the core-solvent interfacial tension and x defined as above by  $x = N_A/M_A$ .  $F_{brush}$  is the osmotic contribution from the corona that prevents the micelles aggregation number from growing indefinitely

$$F_{brush} = A p_d^{3/2} \ln \left[ \frac{5(4\pi)^{2/9} N_B p_d^{1/3}}{3^{14/9} M_A^{5/9} (x p_d + p_h)^{5/9}} + 1 \right]^{3/5}$$
(22)

This form, similar to eq 9, conveniently interpolates between the so-called star geometry where the corona size is much larger than the core size and the "crew-cut" geometries where the corona size is smaller than the core, thus allowing to numerically explore a rather large region of polymer parameters.  $F_{\gamma}$  and  $F_{brush}$  are the key ingredients to study solubilization. They allow, after minimization, to obtain the equilibrium distributions of aggregation numbers sketched in Figure 6. As the figure shows, the size distribution along the copolymer axis exhibits the usual micellar structure, with a well defined aggregation size. The homopolymer axis also keeps the size distribution structure of a collapsed homopolymer solution, however enhanced by the presence of the micelles. It can indeed be easily shown from the conservation equations that, in the limit where  $\phi_d \gg \phi_h$  one has

$$\phi_h = \frac{\phi_d}{p_d^*} \frac{\overline{p_h}}{\overline{p_h}} \tag{23}$$

where  $p_h$  is the average number of homopolymer chains in the micelle. Each micelle thus acts as little reservoir for the homopolymers. To compute the solubilization power, which is of course also a measure of  $p_h$  at the solubility limit, we will numerically integrate the volumer under the distribution surfaces  $c_{ph,pd}$ , and determine the copolymer chemical potential  $\mu_d$  from eqs 2 and 3. Since we will be looking for the homopolymer solubility limit, the homopolymer chemical potential  $\mu_h$  is set to its limit value  $\mu_h = 0$ . Before reporting on the results of such procedure, we present the last two terms in the right-hand side of eq 20,  $F_{core}$  and  $F_{\chi}$ , that account respectively for the elastic



**Figure 5.** Maximum amount of homopolymer that can be solubilized as a function of the diblock copolymer volume fraction for different values of the homopolymer molecular mass.  $N_A = 100$ ,  $N_B = 105$ ,  $\gamma = 0.3$ , and  $\chi = 0$ .

stretching energy of the core blocks and for the possibility of attractive interactions ( $\chi < 0$ ) between the core blocks and the solubilized homopolymers:<sup>23</sup>

$$F_{core} = \frac{\pi^2}{80} \left(\frac{3}{4\pi}\right)^{2/3} \frac{M_A^{5/3}}{N_A^2} (xp_d + p_h)^{5/3} \left[1 - 10\left(\frac{p_h}{xp_d + p_h}\right) + 15\left(\frac{p_h}{xp_d + p_h}\right)^{4/3} - 6\left(\frac{p_h}{xp_d + p_h}\right)^{5/3}\right] (24)$$
$$F_{\chi} = \chi \frac{p_h p_d M_A N_A}{p_h M_A + p_d N_A} (25)$$

Although these two terms are not essential for discussing the general features of micellar solubilization of collapsed homopolymers, they allow for a more accurate representation of the solution thermodynamics. The elastic contribution from the core is also important because it induces, in the appropriate parameter range, a shape transition from spheres into cylinders. Exploration of this particular aspect is however beyond the scope of the present work. The interaction term trivially enhances polymer solubility, bringing as we will see, the solubilization power into much higher values.

The numerical analysis explained above provides for curves similar to those in Figure 5: the maximum solubilizable homopolymer amount  $\phi_h^{max}$  still varies linearly with copolymer number density  $\phi_d$ , allowing for the definition of the solubilization power  $\Theta$  as in eq 18. We first consider a typical case with no attractive interactions  $\chi = 0$ , in the intermediate regime  $(N_B^{15/11} \ll N_A \ll N_B^{18/11})$  where the diblock copolymer chains are not very asymmetric. Figure 7 displays the variation of the solubilization power of the micellar solution as a function of the homopolymer molecular weight. As the figure clearly shows, the solubilization power of the micelles is rather insensitive to the molecular weight of the smaller homopolymers, but decreases strongly above some value  $M_A^*$ . This limit can be understood as follows. For small homopolymers, the average number of homopolymer chains in one micelle  $p_h$  can be extracted from a small  $p_h$  expansion of eq 21 leading to  $\overline{p_h} \sim (N_A p_d^*)^{1/3}/(M_A \gamma) \sim N_A^{3/5}/(\gamma M_A)$ . When  $M_A$  increases, one reaches the limit where only one chain fits in the micelle. Above this limit, given by  $M_A^* \sim \gamma N_A^{3/5}$ , diblock copolymer micelles can still hold a single, large homopolymer chain, but only at the cost of a strong modification of the micelle dimensions. It is such thermodynamic cost that leads to a strong decrease of



Figure 6. Solubilization features of the systems considered.



**Figure 7.** Solubilization as a function of the homopolymer molecular mass, for a micelle in the intermediate regime  $(N_B^{15/11} \ll N_A \ll N_B^{18/11})$ .  $N_A = 100, N_B = 20, \gamma = 0.3, \chi = 0$ , and  $\mu_d = 10.41$ . The dashed line displays the asymptotic behavior,  $\Theta \sim M_A^{-0.25}$ , showing that the saturation effect is weak for almost symmetric diblock chains. Note that for comparison with experiments  $\Theta$  is here defined as solubilization of homopolymer unit mass per unit mass of copolymer.

the solubilization power. Contrary to the suggestion of ref 15, we did not find that the solubilization power reaches an asymptotic power law regime. However, in a limited range of homopolymer mass, one might be tempted to interpret the decrease of  $\Theta$  as a power law. For the case displayed in Figure 7, one gets for instance an apparent power law with exponent 0.25. A much stronger exponent is obtained for asymmetric micelles, in the so-called star regime ( $N_A \ll N_B^{15/11}$ ). Here, the apparent exponent is comparable to experiments—see Figure 8—but the absolute amount of polymer solubilized by the micelles is predicted, in absence of attractive interactions between the homopolymers and the chains in the core ( $\chi = 0$ ), to be rather small. Trivially, a decrease of  $\chi$  toward strong negative values leads to an increase of the solubilization power.

### **IV. Conclusion**

Inspired by solubilization studies<sup>15</sup> on an homologous series of PB in a micellar solution of SEP copolymers in ketones, we considered the problem of solubilization of homopolymers in a solution of diblock copolymers. The homopolymers are in a poor solvent and have thus a very small degree of solubility. When the same solvent is selective for the diblocks, micellar structures can been formed above the critical micellar concentration. If the solution contains both diblock copolymers and



**Figure 8.** Solubilization as a function of the homopolymer molecular mass.  $N_A = 100$ ,  $N_B = 105$ ,  $\gamma = 0.3$ . From top to bottom:  $\chi = 0$ ,  $\chi = -0.02$ , and  $\chi = -0.05$ . The dashed line shows the asymptotic behavior for  $\chi = 0$ :  $\Theta \sim M_A^{-4.80}$ . Note that for comparison with experiments  $\Theta$  is here defined as solubilization of homopolymer unit mass per unit mass of copolymer.

homopolymers, the solubility of the homopolymers is largely enhanced, due to insertion of the homopolymer chains in the micellar cores. Although homopolymer solubilization in the micella cores formed in blends have been previously considered,<sup>11–13</sup> we believe that we presented for the first time a thermodynamic framework to describe such mixtures in a selective solvent. In particular, we account for good solvent conditions in the corona and appropriate stretching of the core chains. We also provide aggregation number distributions that allow for a geometric representation of the solubilization case considered. In particular, these distributions could be in principle compared to Monte Carlo simulation results such as those of ref 14.

We found some striking similarities with the experimental results of ref 15. Similarly to experiments, we found that the maximum amount of homopolymer that can be solubilized in the micellar solution increases linearly with the concentration of diblock copolymer chains. Also in agreement with experiments, the solubilization power, that is, the mass of homopolymer solubilized in 1 g of copolymer decreases as the polymerization index of the homopolymer increases. Contrary to suggestions from experiment, we did not find a power law decrease of solubilization power. However, a limited range analysis of the solubilization power curves might be interpreted as apparent power laws. The exponents of such laws for asymmetric micelles are close to those quoted experimentally.

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