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Solubilization of Polyisobutylene by Polystyrene-*block*-poly(ethylene/propylene) Micelles

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ABSTRACT: The solubilization of polyisobutylene by micelles of polystyrene-*b*-poly(ethylene/propylene) block copolymers in several ketones (dipropylketone, 5-methyl-2-hexanone, methyl isobutyl ketone, diethyl ketone, and methyl propyl ketone) has been studied. The maximum polyisobutylene concentration solubilized in the different copolymer/solvent systems has been determined by laser light scattering. The solubility curves have been found to be linear and dependent on the polyisobutylene molar mass, the chemical composition of the diblock copolymer, and the solvent. The logarithm of the maximum amount of homopolymer solubilized by gram of copolymer varies linearly with the logarithm of the homopolymer molar mass, and this variation is hardly dependent on the chemical composition of the copolymer and the precipitant character of the solvent.

Introduction

Organic compounds that are insoluble in water can often be brought into aqueous solutions by addition of suitable surfactants.[1–4] This phenomenon, called solubilization, gains significant importance when the surfactant concentration is above the so-called critical micelle concentration (cmc). This fact suggests that the solubilizate molecules enter in some way into the surfactant micelles, increasing their aggregation number, i.e., the number of surfactant molecules in a micelle.

For ionic surfactants three types of solubilization have been proposed, depending on the chemical nature of the solubilizate. Nonpolar solubilizate is located in the micelle core where the hydrocarbon tails of the surfactant are miscible with solubilizate molecules. When the solubilizate molecules consist of a hydrocarbon chain and a weakly hydrophilic group, these are placed among the surfactant molecules with the hydrocarbon tails in the core and the hydrophilic heads protruding into the aqueous medium. Finally, some solubilizates that are insoluble in hydrocarbons or in water are believed to be adsorbed on the surface of the micelle. These three modes of solubilization can probably be applied to nonionic surfactants.

When a block copolymer is dissolved in an organic solvent that is a precipitant for one block and a good solvent for the other, the block copolymer may associate in solution to form micelles,[5–7] resembling the behavior of surfactants with low molar mass. Similarly, the copolymer micelles are also capable of solubilizing homopolymers in their cores. This homopolymer must be miscible with the copolymer block which forms the micelle core and incompatible with the block which forms the micelle shell.

Although the formation of micelles by block copolymers has extensively been studied,[8–15] very few investigations have been carried out on the solubilization phenomenon of homopolymers by copolymer micelles.[16–19] Therefore, there is a need for more detailed and extensive studies on the solubilization of homopolymers by block copolymer micelles in organic solvents.

Recent investigations[20–22] have shown that polystyrene-*b*-poly(ethylene/propylene) block copolymers associate in ketones to form micelles. The micelles consist of a swollen core of poly(ethylene/propylene) blocks surrounded by a flexible shell of polystyrene blocks.

Table 1. Characteristics of Homopolymers and Copolymers Studied

sample	$M_w \times 10^{-3}$ (g·mol^{-1})	M_w/M_n	wt % styrene
PB1	1.85	1.88	0
PB2	7.76	2.00	0
PB3	10.0		0
PB4	12.6	2.18	0
PB5	20.7	3.00	0
PB6	35.0	1.76	0
PB7	105	1.79	0
SEP1	105	1.06	35
SEP2	145	1.08	26

In the present work we have investigated the solubilization of polyisobutylenes by micelles of polystyrene-*b*-poly(ethylene/propylene) block copolymers in different ketones (dipropyl ketone, 5-methyl-2-hexanone, methyl isobutyl ketone, diethyl ketone, and methyl propyl ketone). Polyisobutylene is not soluble in ketones of low molar mass but is miscible with poly(ethylene/propylene). In some experimental conditions, solutions of a polyisobutylene and a polystyrene-*b*-poly(ethylene/propylene) copolymer can become clear, suggesting that the polyisobutylene has been solubilized. The polyisobutylene molecules are placed in the micelle core.

Experimental Section

The polystyrene-*b*-poly(ethylene/propylene) block copolymers, designated SEP1 and SEP2, are commercial products kindly supplied by Shell España, S.A. The samples of polyisobutylene (PB) are commercial products of BP Chemicals and BASF.

The structural characteristics of the homopolymers and block copolymers are shown in Table 1. The mass-average molar masses, M_w, of the homopolymers and copolymers were determined by laser light scattering in tetrahydrofuran (THF) at 25.0 °C. Values of the refractive index increment of polymer solutions were measured in a Brice-Phoenix differential refractometer, using a He–Ne laser as the light source. The ratios of the weight-average to number-average molar mass were determined by size exclusion chromatography (SEC) at 25.0 °C using chloroform as solvent and a standard polystyrene calibration. Polystyrene contents of the block copolymers were determined by UV spectroscopy measurements of THF solutions.

All the solvents employed (analytical purity grade) were used without further purification. The solutions containing the copolymer and the homopolymer were prepared in sealed scattering cells. The solutions were vigorously stirred at a

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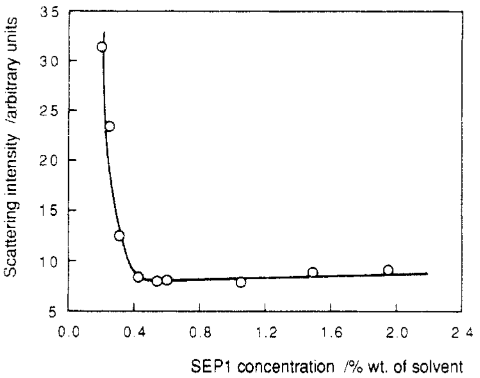

Figure 1. Light scattering intensity measured at 45° as a function of the SEP1 percentage added to a solution of 0.50% of PB4 by weight of 5-methyl-2-hexanone at 25.0 °C.

temperature just below the boiling point until a clear solution was obtained. Once polymers were dissolved, the solutions were cooled to 25.0 °C. The polyisobutylene was judged to have been completely solubilized in solutions which remained clear after being kept at 25.0 °C for several days. The measurements with such solutions were not dependent on the rate of cooling of the solutions or on the temperature at which they were prepared. Thus, the obtained micellar structures were considered as true equilibrium structures.

To determine the solubilization limit, the light intensity scattered to an angle of 45° was measured for all solutions. Laser light scattering measurements were made using a modified FICA 42000 equipped with a He-Ne laser which emits vertically polarized light at 632.8 nm with a power of 5 mW.

Results and Discussion

It has been possible to solubilize the polyisobutylenes in the copolymer micelles by heating them together in the ketones used because the high temperatures employed were located in the vicinity of the critical micelle temperatures.[22] Under these experimental conditions the solubilization occurs at a significant rate.

To carry out the study on the solubilization capability of the different micellar systems, the solubility boundaries of these systems had to be determined. The method used to measure these limits was as follows: Once a polyisobutylene concentration was fixed, several solutions with different copolymer concentrations were prepared. The solutions were heated until they were clear, and then they were kept at 25.0 °C for 1 day. Then the light intensity scattered to 45° for each solution was measured. The plot of these intensities against the copolymer concentration has a similar shape for all the systems studied (Figure 1). As the copolymer concentration decreases, the scattering intensity remains almost constant up to a given concentration where a sharp increase is observed. This high increment in the scattering intensity is attributed to the existence of unsolubilized homopolymer out of the copolymer micelles. The copolymer concentration just above the sharp increment in the scattering intensity is considered as the solubilization boundary, i.e., the minimum copolymer concentration capable of solubilizing a given homopolymer.

Results obtained in the determination of the solubilization limits for four polyisobutylenes (PB2, PB4, PB5, and PB6) in the solution system SEP1/5-methyl-2-hexanone are plotted in Figure 2. For each polyisobutylene the amount of homopolymer solubilized increases linearly with the concentration of copolymer in the ketone. Analogously with low molar mass surfactants,[4] the linear solubilization curves suggest that, at saturation, the ratio of the weight of solubilizate to the weight of copolymer in the micelle is constant,

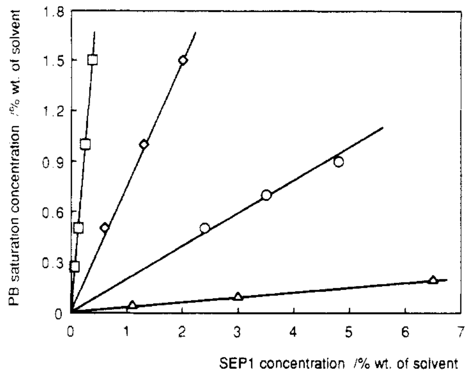

Figure 2. Solubility curves of different homopolyisobutylenes in 5-methyl-2-hexanone solutions of SEP1 at 25.0 °C ((□) PB2, (◇) PB4, (○) PB5, and (△) PB6).

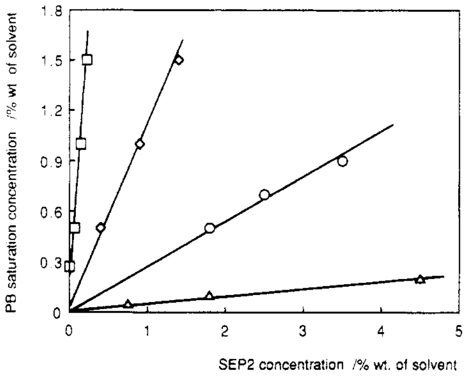

Figure 3. Solubility curves of several homopolyisobutylenes in 5-methyl-2-hexanone solutions of SEP2 at 25.0 °C ((□) PB2, (◇) PB4, (○) PB5, and (△) PB6).

The solubilization curve corresponding to PB2 shows a positive intercept because its molar mass is so low that is soluble to a certain extent in 5-methyl-2-hexanone.

Similar solubilization curves have been found for four other polyisobutylenes in the solution system SEP2/5-methyl-2-hexanone. However, the slope of the straight lines depends on the copolymer. As can be seen in Figure 3, SEP2 shows solubilization curves with larger slopes for all polyisobutylenes studied. These results suggest that copolymer SEP2 has a larger capability to solubilize homopolyisobutylene than copolymer SEP1. To explain this difference, we must take into account that whereas both copolymers have similar polystyrene blocks, the poly(ethylene/propylene) blocks are quite different (SEP1: 68 300 g·mol^{-1}; SEP2: 107 000 g·mol^{-1}). As has been pointed out in a previous work,[21] both copolymers dissolved in 5-methyl-2-hexanone form micelles with similar aggregation number (SEP1: 414; SEP2: 427). Thus, the micelles formed by copolymer SEP2 have a larger core than those formed by SEP1. These micelles with a larger core would be able to arrange a larger number of polyisobutylene chains inside their cores.

The polyisobutylene solubility is strongly dependent on its molar mass: the lower the molar mass, the higher the solubility. The experimental influence of the homopolymer molar mass, M, on the solubility, $\mathrm{d}H/\mathrm{d}C$, i.e., the maximum amount of homopolymer that a mass unity of copolymer can solubilize, can be expressed as

$$\mathrm{d}H/\mathrm{d}C = aM^b \quad (1)$$

where a and b are constants for a given system at a given temperature.

According to this equation, plots of the logarithm of $\mathrm{d}H/\mathrm{d}C$ against the logarithm of the polyisobutylene molar mass for both copolymers are shown in Figure 4. As can

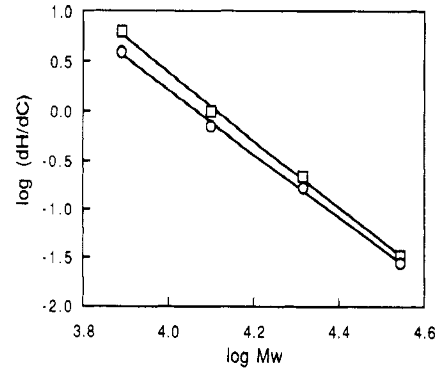

Figure 4. Plots of the logarithm of the maximum amount of polyisobutylene solubilized by mass unity of copolymer, dH/dC, as a function of the logarithm of polyisobutylene molar mass for both copolymers SEP1 (○) and SEP2 (□) in 5-methyl-2-hexanone at 25.0 °C.

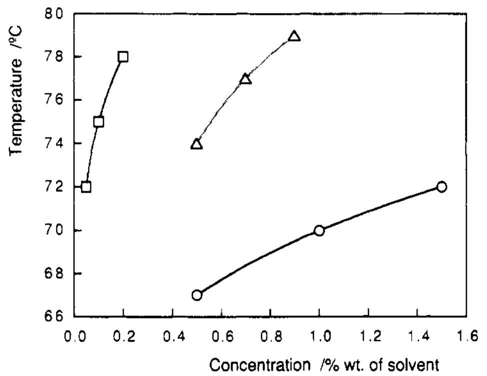

Figure 5. Aggregation temperatures against homopolymer concentration for the polyisobutylenes PB4 (○), PB5 (△), and PB6 (□) in 5-methyl-2-hexanone.

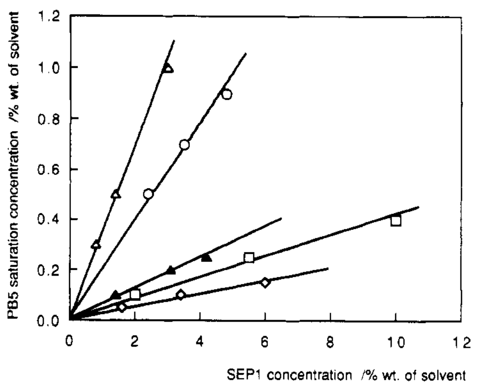

Figure 6. Solubility curves of polyisobutylene PB5 in ketone solutions of SEP1 at 25.0 °C ((△) dipropyl ketone, (○) 5-methyl-2-hexanone, (▲) methyl isobutyl ketone, (□) diethyl ketone, and (◇) methyl propyl ketone).

Table 2. Constants *a* and *b* Corresponding to Equation 1 at 25.0 °C

copolymer	solvent	$a \times 10^{-11}$	b
SEP1	methyl propyl ketone	25	−3.2
SEP1	diethyl ketone	11	−3.1
SEP1	methyl isobutyl ketone	4.4	−3.0
SEP1	5-methyl-2-hexanone	158	−3.2
SEP1	dipropyl ketone	7.9	−2.9
SEP2	5-methyl-2-hexanone	1370	−3.4

Table 3. Aggregation Temperatures of Polyisobutylene PB4 in Several Ketones at a Concentration of 0.50% in Weight of Solvent

solvent	temp (°C)
methyl propyl ketone	>100
diethyl ketone	85
methyl isobutyl ketone	87
5-methyl-2-hexanone	67
dipropyl ketone	20

be seen, the logarithm of the solubility curve slope is linearly dependent on the logarithm of the homopolymer molar mass. In the same figure it can be observed that copolymer SEP2 solubilizes a larger amount of homopolymer for all the polyisobutylenes studied. However, a light increment in its solubilization capability is observed for the polyisobutylenes of lower molar mass. The values of the constants a and b are shown in Table 2. As can be seen, both constants depend on the copolymer.

A plausible explanation for the homopolymer molar mass dependence on the solubility of the homopolymer exists. The solubilization will occur only to a significant extent when, on decreasing the temperature, there is not a phase separation of polyisobutylene before the critical micelle temperature of the copolymer is reached. The aggregation temperatures of the polyisobutylenes PB6, PB5, and PB4 in 5-methyl-2-hexanone at different concentrations are plotted in Figure 5. Aggregation temperature has been considered as that temperature at which a sharp increment in the light scattering intensity of the polyisobutylene solution is detected at an angle of 45°. This intensity increment indicates the formation of homopolymer aggregates just before a phase separation occurs. Considering a copolymer concentration, we have calculated the homopolymer saturation concentration from the solubility curves (Figures 2 and 3). With these values of concentration and the aggregation temperature–homopolymer concentration curves (Figure 5), the aggregation temperatures corresponding to the homopolymer saturation concentrations have been calculated. These temperatures are very similar for all the polyisobutylenes studied and only depend on the block copolymer and its concentration, that is to say, they depend on the critical micelle concentration of the micelles. So, for a given aggregation temperature, as the polyisobutylene molar mass increases, its concentration decreases.

Another factor that influences the solubilization phenomenon is the solvent. To study this influence several ketones have been employed: methyl propyl ketone, diethyl ketone, methyl isobutyl ketone, 5-methyl-2-hexanone, and dipropyl ketone. All these solvents are a precipitant for the polyisobutylenes and the poly(ethylene/propylene) blocks. The aggregation temperatures of polyisobutylene PB4 in the different ketones are shown in Table 3. As can be seen in this table, the ketone becomes a stronger precipitant as the number of carbon atoms in its molecule decreases and as the ketone group is placed at a more asymmetric position in the molecule. Methyl isobutyl ketone has six carbon atoms in its molecule and diethyl ketone has five. However, methyl isobutyl ketone is a stronger precipitant because whereas diethyl ketone has the ketone group at the molecule center, methyl isobutyl ketone has it at an asymmetric position.

Measurements of the polyisobutylene saturation concentration for several concentrations of copolymer SEP1 in the different ketones have been carried out. The saturation concentrations of polyisobutylene PB5 as a function of concentration of copolymer SEP1 for the different ketones are plotted in Figure 6. As can be seen in this figure, the solubility of the polyisobutylene decreases as the precipitant quality of the solvent increases. The solvent influence on the solubilization phenomenon can be explained in a similar way to the influence of the homopolymer molar mass. Thus, the stronger precipitant the solvent is, the lower the polyisobutylene concentration for a given aggregation temperature will be.

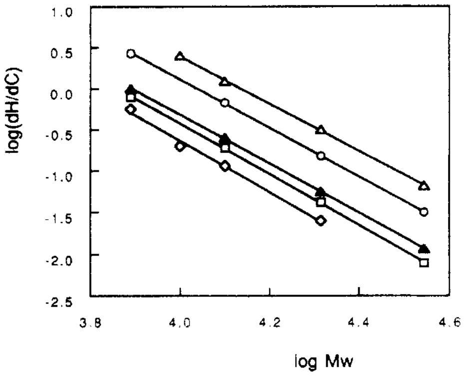

Figure 7. Plots of the logarithm of the maximum amount of polyisobutylene solubilized by mass unity of copolymer SEP1, d*H*/d*C*, as a function of the logarithm of polyisobutylene molar mass in dipropyl ketone (△), 5-methyl-2-hexanone (○), methyl isobutyl ketone (▲), diethyl ketone (□), and methyl propyl ketone (◇) at 25.0 °C.

The logarithm of the maximum amount of polyisobutylene solubilized by mass unity of copolymer SEP1, d*H*/d*C*, as a function of the logarithm of polyisobutylene molar mass for the different ketones is plotted in Figure 7. As can be observed, the homopolymer molar mass dependence on the homopolymer solubility agrees with eq 1, with all ketones showing a similar slope. The values of the constants *a* and *b* are shown in Table 2. Whereas the constant *a* is strongly dependent on the solvent, the constant *b* hardly varies with it.

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