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Solubilization of Aromatic Solutes in Block Copolymers

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ABSTRACT: Several factors affecting solubilization of aromatic solutes in triblock copolymers ($PEO_n-PPO_m-PEO_n$ or $PPO_m-PEO_n-PPO_m$) known to form micelles have been investigated. Solubilization isotherms of toluene, benzene, chlorobenzene, and *p*-xylene in various aqueous polymeric solutions were determined using head-space gas chromatography. The solute partition coefficient in the polymer, K_s, was shown to have a strong dependence on the solute concentration for all polymers. The amount solubilized was at its highest for the high molecular weight, hydrophobic polymers. For the less hydrophobic or lower molecular weight polymers, it was determined that solubilization capacity was a function of the polymer concentration. Comparisons between the different solute solubilization isotherms indicate that PPO−PEO, polymer−water, and polymer−solute interactions have a strong influence on aggregation and solubilization. Finally, the solubilization studies show distinct differences between conventional surfactant micelles and polymeric surfactant micelles, thereby indicating two different solubilization processes. To best understand the mechanism for solubilization in the polymeric surfactant solutions, it was postulated that (1) the addition of apolar solutes promotes aggregation of the polymeric surfactant molecules, (2) the central core of the polymeric micelles contains some water molecules, and (3) solubilization is initially a replacement process in which water molecules are displaced from the micellar core by the solubilizate.

Introduction

Polymeric surfactants that are triblock copolymers of the type ABA or BAB, where A is a poly(ethylene oxide) (PEO) chain (the hydrophilic moiety) and B is a poly(propylene oxide) (PPO) chain (the more hydrophobic moiety), are now being considered for applications for which solubilization of apolar solutes is a crucial factor. Two of these applications are micellar-enhanced ultrafiltration and surfactant-mediated ground-water restoration.[1−6] Studies of the properties of these surfactants in aqueous solutions have confirmed that certain polymeric surfactants, depending on their molecular architecture, solution concentration, and temperature, form aggregates.[7,8] Furthermore, in certain cases, the surface tension decreases with increasing concentration but abruptly reaches a plateau value over a range of increasing concentrations.[9,10] This behavior is reminiscent of "conventional" surfactants, and it is natural to regard the concentration at the transition between decreasing and constant surface tensions as a critical micelle concentration (cmc). An inflexion point has also been observed in the surface tension−concentration plot, and it has been postulated that this inflexion point corresponds to the formation of monomolecular micelles (i.e., close-packed monomolecular polymer).[9−11] However, the existence of the monomolecular micelles requires a change in the polymer configuration in aqueous solution. This transition has been questioned since the evidence is based entirely on surface tension measurements that, in fact, might relate to a conformational change at the air−water interface rather than in the bulk.[10,12] Figure 1 depicts both monomolecular (if they exist) and polymolecular micelles for which the PPO chains are assembled to form a hydrophobic core, with the PEO groups splayed into the surrounding aqueous phase.

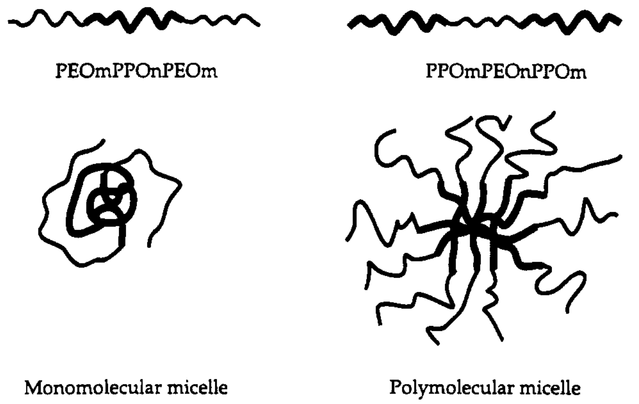

Figure 1. Polymeric surfactants and micelles.

Aggregation of the ABA polymeric surfactants has been intensively investigated, and the influence of molecular structure, concentration, and temperature on the cmc and aggregation number has been reviewed.[9,10,13−16] It is now widely accepted that the more hydrophobic block copolymers (high PPO/PEO ratios and molecular weights) exhibit low cmc and large aggregation numbers.[9,10,16] It has also been shown that, upon increasing temperature, the hydrophobicity of the polymer increases, thereby decreasing the cmc and increasing the aggregation number.[9,10,13−16] However, despite many studies, the cmc values still remain, in some cases, a matter of controversy (differences in magnitude of several orders have been reported).[7,16]

Only a few studies of BAB molecules have been reported, and the issue of micelle formation is still not yet clearly resolved.[17]

The polymer micellar structures depicted in Figure 1 have been guided by the picture of conventional surfactant micelles that has proven to be so useful, namely, a hydrocarbon core that excludes water surrounded by a palisade layer composed of the hydrophilic portions of the surfactant molecules. On the basis of this model, it has been possible to construct thermodynamic analyses that successfully predict both the cmc and the solubilization of apolar solutes from the aqueous solution into the interior of the hydrocarbon core.[18] Several thermodynamic analyses of aggregation and solubiliza-

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tion into polymeric surfactant micelles starting with the premise that such micelles are arranged as shown in Figure 1 have been reported.[15,19,20] These models which predict the influence of the polymer structure on solubilization have, however, yet to be adequately tested even though a number of their applications envisioned for polymeric surfactants relate to their solubilization capacity. The few solubilization measurements reported have been obtained in the presence of a large excess of a slightly soluble solute so that its concentration in the aqueous phase external to the micelles may be assumed to be the solubility limit[21,22] and thus at a single chemical potential. None have reported solubilization as a function of the concentration of the solute or at varying chemical potentials in the external aqueous phase which is, in fact, the type of data required to establish the validity of a thermodynamic analysis of aggregation and solubilization (such as the ones presented by Nagarajan and Ganesh[23,24] or by Hurter et al.[19,20]).

In the present study the types of data required for confirming the results of the thermodynamic studies are obtained. The approach here uses head-space gas chromatography (HSGC) and has been previously used to study solubilization in micelles composed of conventional surfactants.[25-27] The reliability of the method has been confirmed by comparing results obtained with other measurement techniques.[27] HSGC has also been successfully applied for the determination of sorption isotherms for aqueous slurries of activated charcoal and various polymeric resins.[28]

The objectives of this paper are (1) to compare solubilization isotherms of toluene and other aromatic hydrocarbons in various aqueous triblock copolymer solutions, (2) to establish the factors (such as molecular weight, structure, hydrophobicity, and the aqueous phase concentrations of solutes and polymers) governing solubilization, and (3) to compare solubilization in polymer micelles with conventional surfactant micelles.

The results are surprising in that significant differences of solubilization mechanisms for polymer surfactant micelles as compared to conventional surfactant micelles are found. These differences require that the simple configuration of polymeric micelles depicted in Figure 1 be modified. Finally, the addition of apolar solutes is shown to promote polymeric surfactant aggregation just as in the case of conventional surfactant micelles.

Experimental and Analysis

Materials. Benzene and toluene were obtained from EM Science (ACS grade; Gibbstown, NJ). Chlorobenzene was obtained from Spectrum Chemical Manufacturing Corp. (reagent grade; Gardena, CA). *p*-Xylene and sodium chloride (NaCl) were obtained from Fischer Scientific (ACS grade; Fair Lawn, NJ). The block copolymers were provided by Rhône-Poulenc (Cranbury, NJ) and BASF Corp. (Parsippany, NJ). Table 1 summarizes the properties of the block copolymers. Finally, for comparison with conventional surfactants, Rhône-Poulenc provided a nonionic surfactant, polyoxyethylene dodecylphenyl ether (RC630 or $C_{12}PhEO_{10}$), and cetyl pyridinium chloride (CPC or $C_{16}PyCl$), a cationic surfactant, was purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI). All the chemicals were used as received. Distilled water used in the experiments was further purified and deionized to a resistivity of 18 MΩ·cm by a Technic Central Systems Lab Five (Seattle, WA).

HSGC Experiments. HSGC experiments were conducted with a Hewlett Packard head-space sampler (HP 19395A) connected to a Hewlett Packard gas chromatograph (HP 5890) equipped with a capillary column and a flame ionization detector (FID). The head-space sampler consists of a valve and loop system to inject a vapor sample of a known volume (1 μL) into the gas chromatograph. Peak areas are then determined by a Hewlett Packard integrator (HP 3393A).

Table 1. Properties of the Triblock Copolymers at 25 °C

polymer	formula	PEO (%)	MW	cmc (wt %)
L61	$EO_2PO_{31}EO_2$	10	2000	
L62	$EO_6PO_{34}EO_6$	20	2500	2.4[8]
L64	$EO_{13}PO_{30}EO_{13}$	40	2900	11[10]
P65	$EO_{18}PO_{29}EO_{18}$	50	3400	8[10]
P84	$EO_{19}PO_{43}EO_{19}$	40	4200	2.6[16]
P103	$EO_{17}PO_{60}EO_{17}$	30	4950	0.07[16]–0.12[10]
P104	$EO_{27}PO_{61}EO_{27}$	40	5850	0.3[16]
P123	$EO_{19}PO_{69}EO_{19}$	30	5750	0.003[10]–0.03[16]
R172	$PO_{15}EO_9PO_{15}$	20	2100	
R174	$PO_{15}EO_{22}PO_{15}$	40	2700	
R252	$PO_{22}EO_{14}PO_{22}$	20	3100	

Table 2. Properties of the Aromatic Solutes at 25 °C

solute	C_{sat} (mg/L)	K_H (atm)[28]	V_s (Å^3)	σ_0 (dyn/cm)[29]
toluene	572	331	176	36.1
benzene	1710	320	146	35.0
chlorobenzene	510	192	170	37.4
p-xylene	206	328	206	37.8

Preparation of the standards (organic and water, only) and of the samples (organic, polymer, and water) has been reported in a previous paper.[27] Basically, 10-mL sample vials containing various concentrations of polymers and organic solutes are prepared using pipettes and microliter syringes. The use of an analytical balance (Mettler AE163), which has a reproducibility of ±0.01 mg, allows one to accurately know polymer, water, and solute weights in each vial. Sets of calibration standards (water and organic only) are prepared the same way. Samples were equilibrated at constant temperature (25 °C) in a shaker bath for at least 48 h. Equilibration times of 12, 24, and 48 h yielded the same results.

Analysis. The amount of solute solubilized in the block copolymer aggregates is obtained from the mass balance:

$$m_{sm} = m_{si} - m_{sl} - m_{sv}$$

where m_{sm}, m_{si}, m_{sl}, and m_{sv} are the amount of solute bound to the polymer, initially added to the vial, in the aqueous phase, and in the vapor phase, respectively. It is necessary to know the vapor/liquid equilibrium to determine m_{sl} and m_{sv}. The organic solutes studied have aqueous solubilities on the order of $x_{sat} = 10^{-4}$ mole fraction or less; thus, the use of Henry's law constant, K_H, with the assumption of the ideal gas law allows one to determine the amount of solute in the vapor and liquid phases in the calibration standards. Calibration curves will then give the relationship between peak areas and vapor and aqueous concentrations. These calibration curves are, in turn, used to determine m_{sl} and m_{sv} in the sample vials from the peak areas. More details are available elsewhere.[28] Solute aqueous solubilities, Henry's law constants, molecular volumes, and surface tensions for toluene, benzene, chlorobenzene, and *p*-xylene are listed in Table 2. These values were obtained from previous studies.[27,28]

Solubilization isotherms are presented as the solute mole fraction in the polymeric micelle (X_{sm}) versus the free solute concentration (C_{sl}), where X_{sm} is calculated as

$$X_{sm} = \frac{M_{sm}}{M_{sm} + M_p}$$

where M_{sm} is the moles of solute in the micelles and M_p is the total moles of polymer in solution. For solubilization in surfactant micelles, M_p is replaced by $M_a - M_o$, where M_a and M_o are the total moles of surfactant in solution and the moles of surfactant monomer dispersed in solution (M_o is assumed to correspond to the cmc of the surfactant), respectively. In the case of the polymeric surfactants, it was decided not to account for that portion of the molecules not included in micellar aggregates, since these surfactants have been reported to form both mono- and polymolecular micelles. Moreover, as noted above, there is considerable disagreement between reported cmc values. Furthermore, solubilization was observed for polymer concentrations much below the reported cmc (for instance, solubilization data in 2.5 wt % L64 and P65 solutions are presented even though their cmc has been determined to be around 8–11 wt %).[10] The most reliable cmc data obtain in the literature are found in Table 1.

The partition coefficient (units of L/mol), K_s, is defined as

$$K_s = X_{sm}/C_{sl}$$

where C_{sl} is the free (or aqueous) solute concentration (mol/L).

Finally, in some instances, results are given as solubilization capacity on a weight basis (Q_r) rather than on a molar basis (X_m). Q_r is defined as follows:

$$Q_r(\%) = 100 \times \frac{W_s}{W_p}$$

where W_s and W_p are the weight of solute solubilized and the weight of polymer in solution, respectively.

Results and Discussion

In the following, the various factors influencing the solubilization of toluene and other aromatic solutes are discussed. First, solubilization as a function of the polymer structure and molecular weight is presented. The influence of the concentration is discussed in the following section. The influence of the ionic strength of the solution and comparison between the different solutes are then presented. Finally, comparison with nonionic and cationic surfactants is discussed.

Yet, the free solute concentration is perhaps the most influential factor in determining the extent of solubilization. The following reveals that, unlike in the case of conventional surfactants, the solute partition coefficient varies greatly with the solute concentration. This trend exhibited here can best be understood by postulating the following three mechanisms for solubilization:

(1) The addition of apolar solutes promotes the aggregation of polymeric surfactant molecules that otherwise tend to be dispersed in the aqueous phase. This assumption, entirely consistent with observations of the solution behavior of conventional surfactants, has also been suggested by Malmsten and Lindman.[30]

(2) The central core of polymeric micelles, unlike conventional surfactant micelles, contains substantial quantities of water. Indeed, both Hurter et al.[19,20] and Linse and Malmsten[15] used a mean-field lattice theory of micellization to predict that PPO, PEO, and water are all present in the core. This is a reasonable hypothesis since the packing of polymer molecules to form a compact core that entirely excludes water is not entropically favored. Furthermore, PPO interacts with water by hydrogen bonding since it does have solubility in water.

(3) Solubilization initially takes place through a replacement process in which water that is readily accessible to the solute is displaced from the micellar core. This process is driven by the hydrophobic interaction of the solute in the aqueous phase. As more solute is solubilized, the free energy of the transfer process increases since the remaining water becomes more difficult to displace from the core. Furthermore, the residual water may be in positions that promote the stability of the hydrogen bonds with the PPO. Thus, the free energy of the transfer process is a strong function of the solute concentration in the micellar core. This behavior is distinctly different from solubilization in conventional surfactant micelles. There, solubilization tends to be restricted by the increase in micellar surface area required to accommodate the solute molecules in the core. Normally, the free energy change associated with this transfer process is almost independent of the amount of solute present in the core. In this case, the partition coefficient is essentially independent of the free solute concentration.

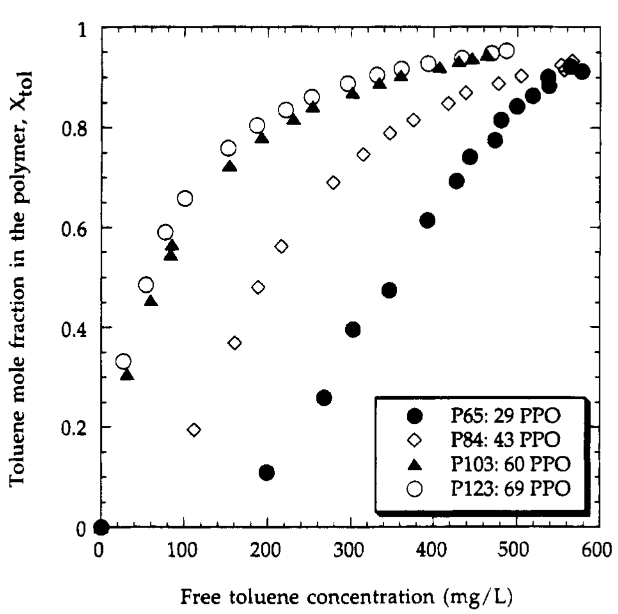

Figure 2. Influence of the number of PPO units. Toluene mole fraction in P65, P84, P103, and P123 at 25 °C. [Polymer] = 5 wt %.

Solubilization as a Function of the Polymer Structure. In this section, the influence of the polymer structure on solubilization is discussed in terms of PPO and PEO unit numbers and their percentage in the polymers and in terms of polymer molecular weight. A comparison between solubilization in ABA and BAB copolymers is also presented.

Influence of the Number of PPO Units for a Given PEO Unit Number. Figure 2 shows the mole fraction of toluene, X_{tol}, solubilized in various polymeric surfactant solutions (P65, P84, P103, and P123) for which A is approximately 19 EO units. The PPO unit numbers are 29, 43, 60, and 69, respectively. Solubilization in these block copolymers is a strong function of the free solute concentration and polymer structure. To better understand the influence of the polymer structure, the data shown in Figure 2 are replotted in Figure 3 as the partition coefficient versus the free solute concentration. First, one can observe that the solubilization capacity of these polymers increases remarkably (especially at low free solute concentration) when the number of PO units increases from 29 to 69. The high solubilization capacity in the polymers with high PPO content could be expected since increasing the PPO content decreases the cmc, therefore increasing the size or number of micelles available for solubilization. This property is similar to the one observed for solubilization in conventional surfactant micelles where it has been shown that the amount solubilized increases with the length of the hydrophobic chain. However, depending on the number of PPO units, two distinct patterns of behavior are seen for the partition coefficient. The partition coefficient for those molecules with a substan-

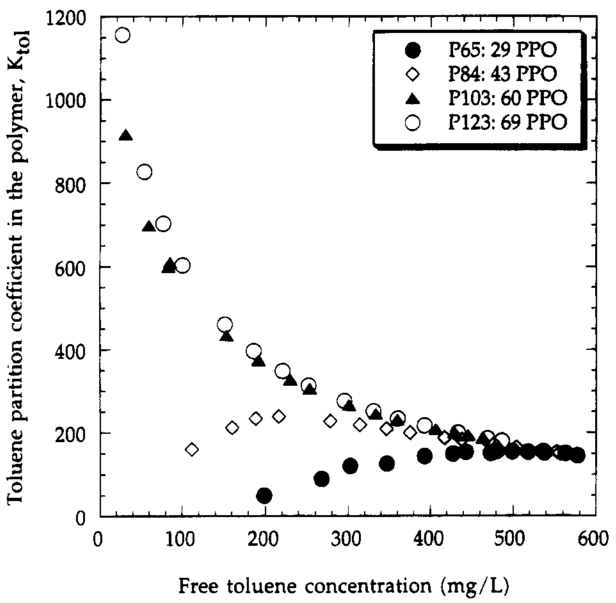

Figure 3. Influence of the number of PPO units. Toluene partition coefficient in P65, P84, P103, and P123 at 25 °C. [Polymer] = 5 wt %.

tial number of PPO units (above 60 or about 70% of the weight) decreases steadily as the free solute concentration is increased near to the solubility of toluene in water. Since the partition coefficient is a measure of the free energy of transfer, the trends observed for P103 and P123 are consistent with postulate no. 3 cited above. For polymers with low PPO content (i.e., less than 43 units), the partition coefficient increases as the first solute molecules are solubilized. At some concentration of solute, the partition coefficient reaches a maximum and then decreases. Thus, even though the polymer concentration is less than or close to the cmc, the solute promotes aggregation (see premise no. 1 above). As the aggregation number increases in the presence of free solute, solubilization is correspondingly promoted. Malmsten and Lindman have suggested such effect in their study of solubilization of *p*-xylene in another block copolymer, F127 (70% PEO or 2 × 100 EO and 65 PO).[30] Once the aggregates are formed, it becomes increasingly difficult to solubilize additional solute for the reason cited above (postulate no. 3). Hence, the maximum reflects the competition between two mechanisms—one tends to promote aggregation, while the other tends to limit further solubilization. These trends are consistent with the mechanisms of solubilization proposed above.

The partition coefficient for the two lower PPO content polymer surfactants (P65 and P84) is shown in Figure 3 to exhibit a different pattern than the one observed for molecules having the higher PPO content (P103 and P123). The reported value of cmc for P65 and P84 (2.6 and 11 wt %, respectively) is of the same order of magnitude as the polymer concentration of 5 wt % applicable to Figures 2 and 3. However, since the PEO and PPO contents cited in Table 1 are averages, it is difficult to assign a precise cmc to these molecules. As a consequence, it may be assumed that, for these polymers, micelles are not present (or, if they are, their concentration is very low) in the absence of free solute. Whereas the reported cmcs of both P103 and P123 are considerably less than 5 wt % (see Table 1). Thus, the two patterns for the partition coefficient seen in Figure 3 could result from the initial presence or absence of micelles.

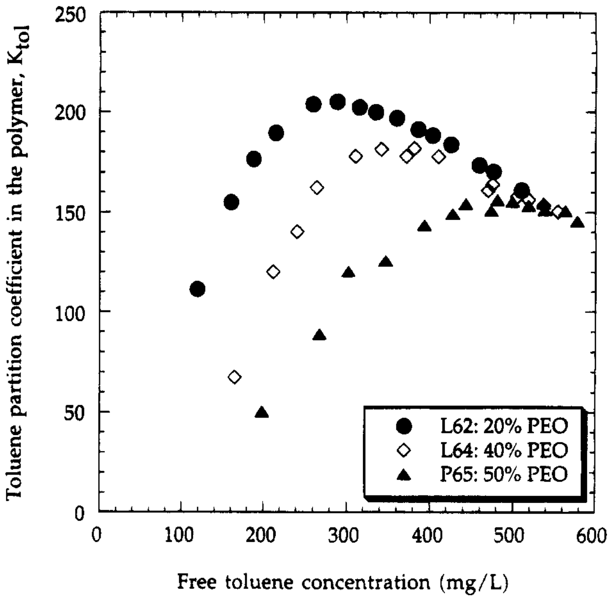

Figure 4. Influence of the PEO percentage in the polymer. Toluene partition coefficient in L62, L64, and P65 at 25 °C. [Polymer] = 5 wt %.

Finally, it is interesting to note that the partition coefficients all seem to converge, attaining nearly identical values as the solubility limit of toluene in water is approached.

Influence of the Percentage of PEO for a Given PPO Unit Number. Solubilization isotherms of toluene in polymers having similar PPO content (about 31 PO) but different PEO contents were also measured. The polymers studied were L61 (10% PEO, 31 PPO), L62 (20% PEO, 34 PO), L64 (40% PEO, 30 PO), and P65 (50% PEO, 29 PO). Results are presented in Figure 4. Because of low L61 solubility in water, the data for this particular polymer are not shown. It is observed that increasing the PEO percentage in the polymer decreases the amount of toluene solubilized. It has been reported that increasing the number of PEO units increases the cmc,[16] therefore inhibiting the aggregation process. This lower aggregation number results in a decrease of the solubilization capacity. Nagarajan and Ganesh also predicted a similar result for solubilization of benzene in PPO–PEO diblock copolymers.[23] The influence of the PEO content on solubilization of aromatic solutes is somewhat different from the EO influence observed with nonionic surfactants. While this influence is noticeable for the polymers, solubilization capacity in polyoxyethylene nonylphenyl ethers decreases only slightly with an increase in the number of ethylene oxide units when the free solute concentration is close to the aqueous solubility.[27] Figure 4 also shows that the three polymers studied exhibit a partition coefficient pattern similar to that of the polymers with lower PPO content in Figure 3: the partition coefficients reach a maximum, and all tend to converge as the free solute concentration approaches the saturation limit.

Influence of the Molecular Weight for a Given PPO/PEO Ratio. Solubilization of toluene in aqueous solutions containing 5% of L64, P84, and P104 is shown in Figure 5. These polymeric surfactants all have a PEO percentage of 40 (PPO/PEO = 1.5) and molecular weights of 2900, 4200, and 5850 for L64, P84, and P104, respectively. The same features shown in Figure 3 are again observed. High solubilization capacity at low solute concentrations is found for the polymers with

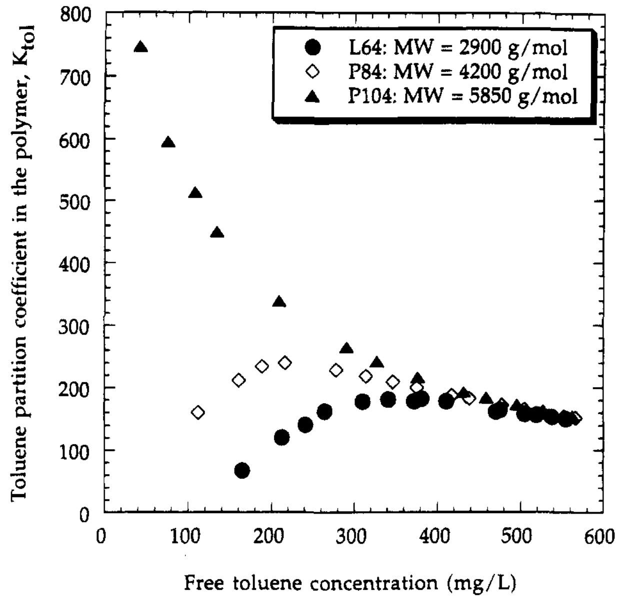

Figure 5. Influence of the polymer molecular weight. Toluene partition coefficient in L64, P84, and P104 at 25 °C. [Polymer] = 5 wt %.

high molecular weight, and almost no solubilization at these same solute concentrations is observed for the polymers with low molecular weight. It has been suggested that hydrophobicity increases with the molecular weight of the polymer, thereby decreasing the cmc and increasing self-association.[16,19,22] This hypothesis is consistent with the trends shown in Figure 5.

Comparison between ABA and BAB Triblock Copolymers. Reverse block copolymers of the type BAB, where B is the hydrophobic group, have not yet been studied extensively, and the issue of micelle formation is not resolved. Alexandridis et al. reported that the polymer R254 (70% PPO or 2 x 21 PO and 25 EO) does not form micelles for temperatures less than the cloud point.[16] Zhou et al. have shown that R174 self-associates only in a narrow temperature range and at high concentrations; furthermore, the cmc is very large and the aggregation number is small (7.5% and 10 at 40 °C, respectively).[17] Since, for these block copolymers, the PPO chains (the hydrophobic part of the micelles) surround the PEO (the hydrophilic mantle), it would not be surprising to find that steric factors inhibit micellization. No information is yet available on the aggregation of reverse block copolymers having larger hydrophobic groups, such as R172 or R252. Solubilization experiments were nonetheless carried out, and results are presented in Figure 6. On this graph, one can observe solubilization of toluene in the reverse block copolymers R172, R174, and R252. It appears that, although there is no solubilization in the low free solute concentration range (for example, solubilization starts only at a free toluene concentration of 150 mg/L for R252 or a concentration of about 250 mg/L for R174), solubilization is quite high in the polymers having 20% PEO content. Here again, the results suggest that the addition of an organic solute to the aqueous solution induces, first, aggregation of the polymer and, second, solubilization. Finally, for comparison, Figure 7 shows solubilization capacity on a weight basis of toluene in polymers having 40% PEO content (R174 and L64) and in polymers having hydrophobic groups of about 43 PO (R252 and P84). As can be seen, the amount of solute solubilized in R174 is much less than that in L64.

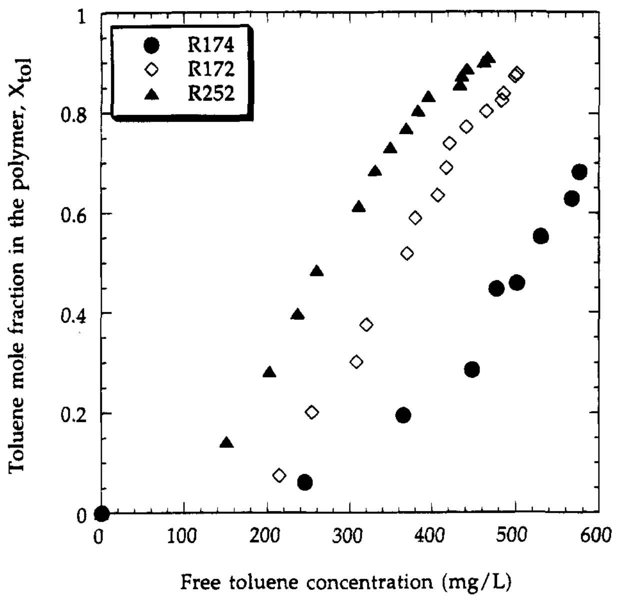

Figure 6. Solubilization in reverse block copolymers. Toluene mole fraction in R174, R172, and R252 at 25 °C. [Polymer] = 5 wt %.

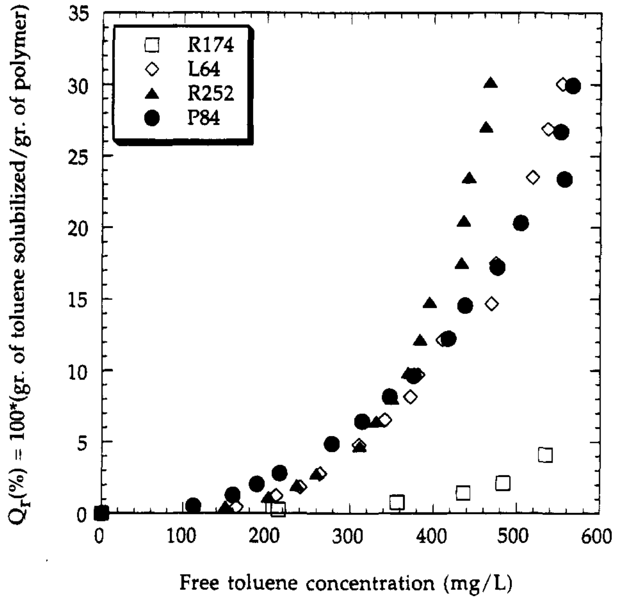

Figure 7. Influence of the polymer structure. Toluene solubilization capacity on a weight basis in R174, L64, R252, and P84 at 25 °C. [Polymer] = 5 wt %.

Although these two polymers have a similar PPO/PEO ratio and similar molecular weights, it appears that structural and steric factors hinder formation of micelles and solubilization for R174 solution. For the same reason, although the PPO/PEO ratio of R252 is greater than that of P84, solubilization capacity in R252 is lower than that in P84 at low solute concentration. However, it seems that increasing the solute concentration provides favorable conditions for the polymeric chains of R252 to self-aggregate and to form micelles with high solubilization capacity (see postulate no. 1) near the solute aqueous saturation concentration.

These different experiments indicate that solubilization is a strong function of the molecular weight and structure of the polymers. Furthermore, the amount of solute solubilized is at its highest for polymers having both high molecular weight and high PPO content (this provides a highly nonpolar environment favorable to solubilization). Yet, the most striking feature of all these results is that the solubilization isotherms for an aromatic solute in polymeric surfactants in aqueous solutions are a strong function of the free solute concentration. This characteristic differs markedly from the solubilization of aromatic solutes in conventional surfactants for which the solute partition coefficient is a weak function of the solute concentration. This issue is discussed in a later paragraph. As can be seen from the solute mole fractions, X_{tol}, and partition coefficients, K_{tol}, in Figures 2–6, solubilization capacity varies greatly with the toluene concentration. This observation is entirely consistent with our proposed mechanism of solubilization; namely, the addition of a solute promotes both aggregation (premise no. 1) and solubilization in polymeric surfactants that are otherwise dispersed in the aqueous solution, and the partition coefficient (or free energy of transfer) of the solute in the micelles decreases upon an increase in the free solute concentration (premise no. 3). These two antagonistic effects are responsible for the maximum observed for the partition coefficient of the less hydrophobic polymers. On an added note, it has been reported that incorporating a solubilizate in a micelle could change its geometry (i.e., size, shape, and aggregation number). For example, upon solubilization of *o*-xylene in L64 solutions, micelles increase in size.[31] Similar findings with hexane and L64 were also reported.[13] The authors concluded that the size increase stems not only from the presence of the solubilizate but also from an increase in the aggregation number of the polymeric micelles. This effect is also compatible with the mechanism cited in this paper. Finally, using a theoretical model, Hurter et al. predicted that the partition coefficient of naphthalene in similar polymeric surfactants should vary with the solute concentration.[19,20] However, these authors could not compare their predictions with experimental data since, until now, no data were available.

Solubilization as a Function of the Polymer Concentration. Since all the data previously reported were obtained at a polymer concentration of 5 wt %, it is important to find the influence of the polymer concentration on solubilization. It is known that cmc, shape, and size of conventional surfactants (especially for ionic molecules) can be a function of the surfactant concentration.[32-34] On the other hand, solubilization data obtained in this laboratory have shown that solubilization of aromatic solutes is essentially independent of the surfactant concentration for anionic (sodium dodecyl sulfate), cationic (cetyl pyridinium chloride), and nonionic (polyoxyethylene nonyl- and dodecylphenyl ethers) surfactants.[27] In the case of polymeric surfactants, the influence of the concentration on cmc, aggregation number, and shape of the aggregates is not fully understood. Nonetheless, it has been suggested that, at low concentrations, block copolymers could form monomolecular micelles and, as the concentration increases, the aggregates change to polymolecular micelles.[11] Moreover, increasing the concentration of the more hydrophobic polymers (i.e., high molecular weight and/or high PPO content) has been reported, in a large measure, only to increase the number of micelles and not to change the aggregation number.[35] Wanka et al.[10] also reported that the sizes of the micelles of PE6400 (corresponding to L64 of the present study), P65, P104, and P123 are independent of the concentration (for concentrations up to 10 wt %).

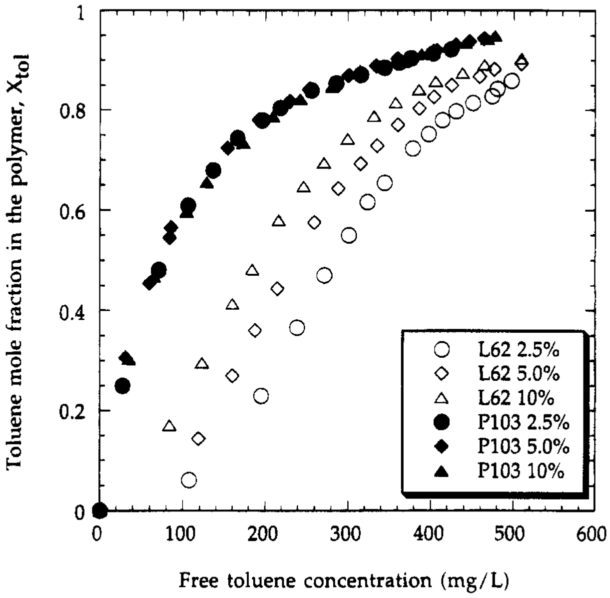

Figure 8. Influence of the polymer concentration. Toluene mole fraction in L62 and P103 at 25 °C.

Furthermore, they indicated that, above a concentration of 10 wt %, the radius of the aggregates decreases upon increasing the polymer concentration. They suggested that this decrease in size results from repulsive interactions between the micelles. Al-Saden et al.[13] reported a similar trend for L64 and other triblock copolymers: at 35 °C, the size of the micelles is constant at concentrations up to 14 wt % and then slightly decreases with increasing polymer concentration. Furthermore, the same study reports that, at 25 °C, the polymers exhibit continuous micellar growth for concentrations up to 20 wt %. Formation, first, of monomolecular micelles and, then, of micelles of very small aggregation numbers up to polymolecular micelles of constant size at and above the cmc (11 wt % for L64 at 25 °C) could be responsible for the observed aggregate growth. The partition coefficient may then be independent of the polymer concentration for the range studied for high molecular weight and hydrophobic copolymers, while solubilization in lower molecular weight may be a function of the polymer concentration. Hurter and Hatton,[22] in their study of naphthalene solubilization in various block copolymer solutions, showed that the solute partition coefficient from a saturated solution was independent of the polymer concentration for P103, P104, P105, and P123 but increased with concentration in a highly hydrophilic polymer (F108, 80% PEO or 2 × 168 EO and 61 PO), a polymer for which micelle structural properties (for example, the aggregation number) might be expected to vary with surfactant concentration. Figures 8 and 9 show solubilization isotherms for toluene in aqueous solutions of P103, P84, L62, and P65. In these experiments, the polymer concentrations were 2.5, 5, and 10 wt %. As previously reported,[22] the solubilization isotherm in P103 is independent of the surfactant concentration; this hydrophobic polymer has a high molecular weight (70% PPO, MW = 4950). Solubilization of toluene in P123 (70% PPO, MW = 5750) and P104 (60% PPO, MW = 5850) solutions was also determined to be independent of the polymer concentration. These three polymers have high molecular weights and PPO contents; their cmc is therefore relatively low (0.07 and 0.03 wt % at 25 °C for P103 and P123, respectively), and little concentration effect is antici-

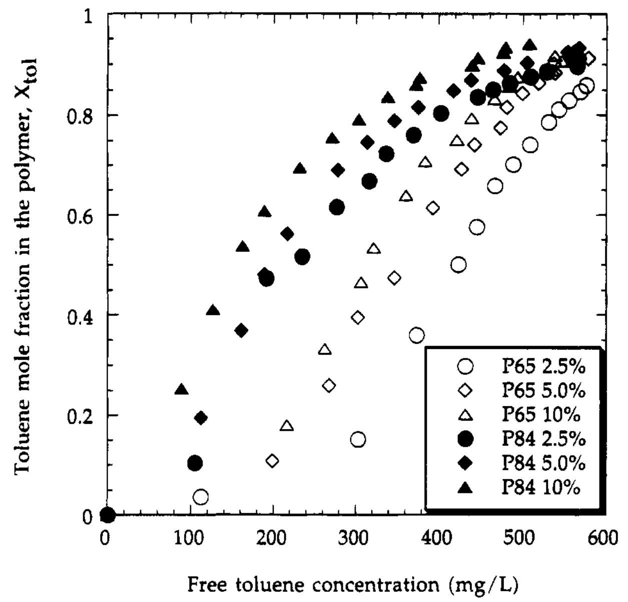

Figure 9. Influence of the polymer concentration. Toluene mole fraction in P65 and P84 at 25 °C.

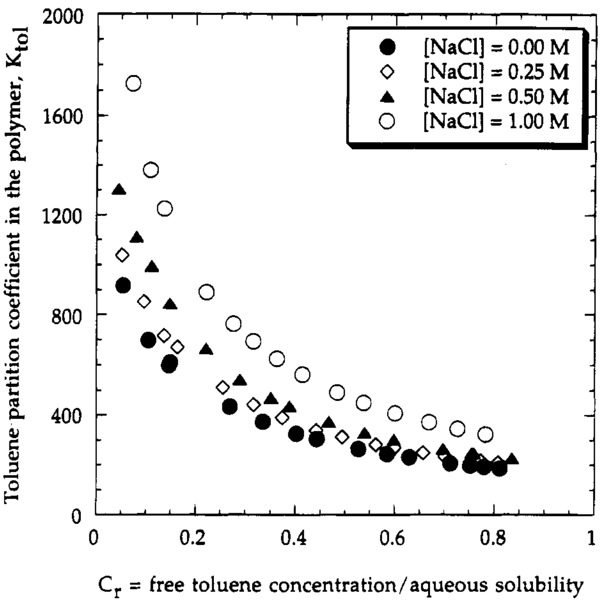

Figure 10. Influence of the ionic strength of the solution. Toluene partition coefficient in P103 and varying NaCl concentration at 25 °C. [Polymer] = 5 wt %.

pated. Conversely, it can be seen that the amount of solute solubilized in L62 and P65 solutions increases markedly with the polymer concentration. Despite being a highly hydrophobic copolymer, L62 has a low molecular weight (80% PPO, MW = 2500). This is another indication that both the PPO percentage and the molecular weight of a polymer determine the aggregation and the solubilization pattern (i.e., a partition coefficient exhibiting a maximum or a decreasing partition coefficient with an increase in free solute concentration). P65 has moderate hydrophobicity and molecular weight (50% PPO, MW = 3400) with a cmc of about 8 wt %. A similar influence of the polymer concentration was observed with L64 (40% PPO, MW = 2900) solutions and all the reverse block copolymers of the R series. These data are not presented in this study for the sake of brevity. Solubilization in P84 (60% PPO, MW = 4200) which has a reported cmc of 2.6 wt % is also shown to be sensitive to polymer concentration (for concentrations up to 10 wt %).

These results suggest that the hydrophobic polymers with high molecular weight and high PPO/PEO ratio form micelles of size and shape independent of the polymer concentration, as has been reported by others using light scattering techniques.[10] On the other hand, Figures 8 and 9 suggest that lower molecular weight polymers have an aggregate size distribution dependent on solute and surfactant concentrations. They also indicate that solubilization is observed for polymer concentration lower than the reported cmc (cf. cmc of L64 and P65) and that the addition of a solute induces aggregation (postulate no. 1). It should also be noted that similar results were obtained for solubilization of benzene, chlorobenzene, and *p*-xylene in these block copolymers.

Solubilization as a Function of the Ionic Strength of the Aqueous Solution. To study the influence of the ionic strength of the solution on solubilization, experiments were carried out in aqueous solutions of P103 and sodium chloride (NaCl). In an earlier paper,[27] it was reported that the amount of benzene solubilized in an anionic surfactant (SDS) increased upon increasing the ionic strength of the solution. The reason advanced was that, besides lowering the solute aqueous solubility, adding an electrolyte increases the free counterion concentration, thereby decreasing the energy of repulsion between charged head groups resulting in a decrease of the cmc and an increase in the aggregation number of the micelles. For nonionic surfactant solutions, salting out of the hydrophobic groups contributes to a slight decrease of the cmc upon addition of a salt.[36] It is reasonable to investigate the effect of the ionic strength on the solubilization capacity of a polymer solution. Figure 10 shows solubilization of toluene in solution of P103 and NaCl. The x-axis has been normalized with respect to the toluene aqueous solubility to eliminate the influence of the ionic strength on the solute aqueous solubility. The polymer concentration is 5 wt %, and the NaCl concentration varies from 0 to 1 mol/L. These isotherms suggest that the extent of solubilization increases with the ionic strength of the solution. However, the addition of electrolyte has a sensible effect over the entire range of solute concentrations studied only for the highest salt concentration ([NaCl] = 1 M). For the lower electrolyte concentrations, solubilization isotherms are essentially the same at high toluene concentration. At lower free solute concentrations, solubilization capacity increases slightly with the NaCl content of the solution.

Solubilization of Different Aromatic Solutes. Finally, solubilization of toluene, benzene, chlorobenzene, and *p*-xylene in block copolymer (P103) micelles was investigated to determine the influence of the solute nature. Solubilization of aromatics in conventional surfactant solutions has been shown to depend on the molar volume of the solute.[27] One might, in fact, expect a similar trend with polymeric surfactants since the solute should increase the volume of the core. Figure 11 shows the experimental data. The x-axis has been normalized with respect to the aqueous solubilities of the solutes to account for the different saturation concentrations. The agreement between volumetric isotherms, unlike with conventional surfactants, is actually not good. Two factors influencing solubilization are the molar volume and polarity (which has been sometimes evaluated from the solute interfacial tension with water) of the solute. The results reported for

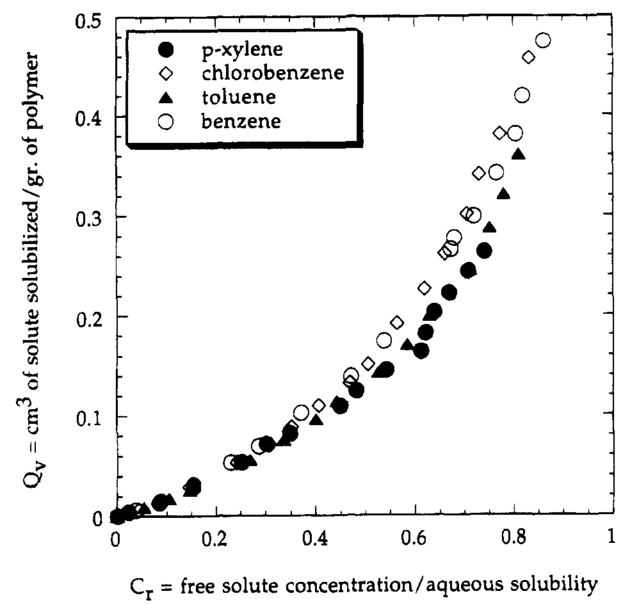

Figure 11. Influence of the aromatic solute on solubilization. Volumetric solubilization for various solutes in P103 at 25 °C. [Polymer] = 5 wt %.

Table 3. Solubility (δ) and Interaction (χ_{sp}) Parameters at 25 °C

polymer or solute	$\delta^{21,38}$	χ_{sp}(PPO)	χ_{sp}(EO)
PPO chain	9.3		
PEO chain	10.5		
toluene	8.9	0.0286	0.4563
benzene	9.2	0.0014	0.2483
chlorobenzene	9.5	0.0068	0.1711
p-xylene	8.9	0.0334	0.5355

solubilization in conventional surfactants are for aromatic solutes having relatively similar interfacial tension against water (between 35 and 37.4 dyn/cm). In this study, the interfacial tensions are, once again, roughly the same (from 35 to 37.8 dyn/cm). The results of Figure 11 then indicate that, at a constant interfacial tension, the molecular volume of the aromatic solutes is not the only factor determining the extent of solubilization in polymeric surfactants. This observation should not be surprising since micellization of block copolymers has been reported to depend more on interaction between the polymer chains than on interfacial interactions;[21] as a result, solubilization in these polymers should also be a function of solute–polymeric chain interactions. Moreover, as mentioned above (see postulate no. 2), a fundamental difference exists between conventional and polymeric surfactant micelles; the latter has a significant amount of water in the hydrophobic core. A measure of the solute–polymer interactions is the Flory–Huggins interaction parameter χ_{sp}.[15,19–21,35] This parameter is estimated as

$$\chi_{sp} = (\delta_s - \delta_p)^2 \frac{V_s}{RT}$$

where δ_s and δ_p are the Scatchard–Hildebrand solubility parameters of the solute and of the polymer, respectively.[37] V_s is the molar volume of the solute. The values for the solubility parameters[21,38] and χ_{sp} are given in Table 3.

Considering that $\delta_s \approx \delta_p$ indicates that the solute is a good solvent for the polymer, the more closely χ_{sp} approaches zero, the greater the extent of solubilization. Furthermore, solubilization should mostly take place in the PPO core of the micelles since χ_{sp}(PPO) is much lower than χ_{sp}(PEO). Toluene and *p*-xylene interaction parameters with the PPO chains are of the same order; therefore, it is not surprising to observe good agreement between their solubilization isotherms. In addition, their interaction parameters are also an order of magnitude higher than those for the two other solutes; lower solubilization capacity is then expected when compared to benzene and chlorobenzene. Further, based on the magnitude of χ_{sp}(PPO), P103 should have a greater capacity for benzene than for chlorobenzene molecules. Yet, Figure 11 shows that chlorobenzene is solubilized in slightly higher quantities than benzene. It appears that the interaction parameter between the solute and the PPO chains is perhaps insufficient to characterize solubilization in block copolymer micelles. For instance, some solubilization may take place in the PEO palisade of the aggregates where chlorobenzene has a higher affinity (i.e., lower χ_{sp}(PEO)) in comparison to the other solutes studied.

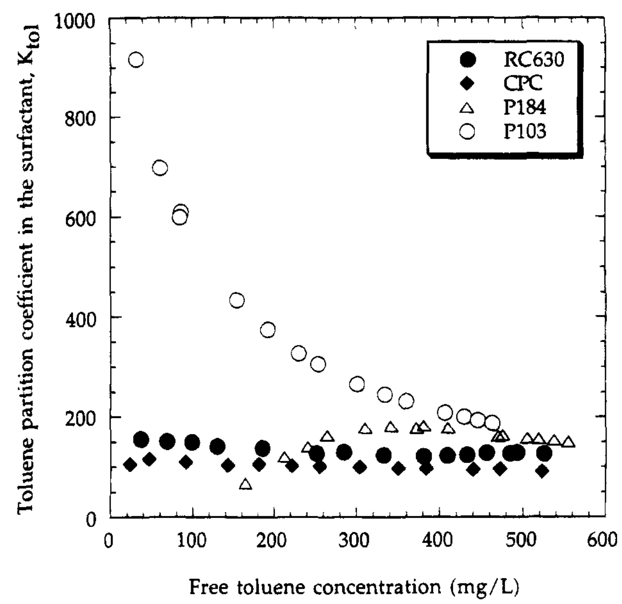

Figure 12. Comparison between conventional and polymeric surfactants. Toluene partition coefficient in RC630, CPC, L64, and P103 at 25 °C. All concentrations were at 5 wt %.

Solubilization in Polymeric and Conventional Surfactants. As mentioned in earlier paragraphs, solubilization in block copolymer micelles is a strong function of the solute concentration and may also be dependent on the polymer concentration. This result markedly differs from the results obtained in this laboratory for solubilization of aromatic solutes in low molecular weight surfactants such as sodium dodecyl sulfate (SDS), cetyl pyridinium chloride (CPC), and polyoxyethylene dodecylphenyl ether (RC630). With these surfactants, the partition coefficient is a weak function of the solute and surfactant concentrations. To emphasize the difference, the partition coefficients of toluene in block copolymers (P103 and P184) and in cationic (CPC) and nonionic (RC630) surfactants are compared in Figure 12. The partition coefficients for the two conventional surfactants are essentially constant for the entire range of solute concentration and, as already discussed, the partition coefficient of the polymers depends strongly on the aromatic solute concentration. Another noticeable difference is that, for a given PPO unit number, solubilization in the polymers

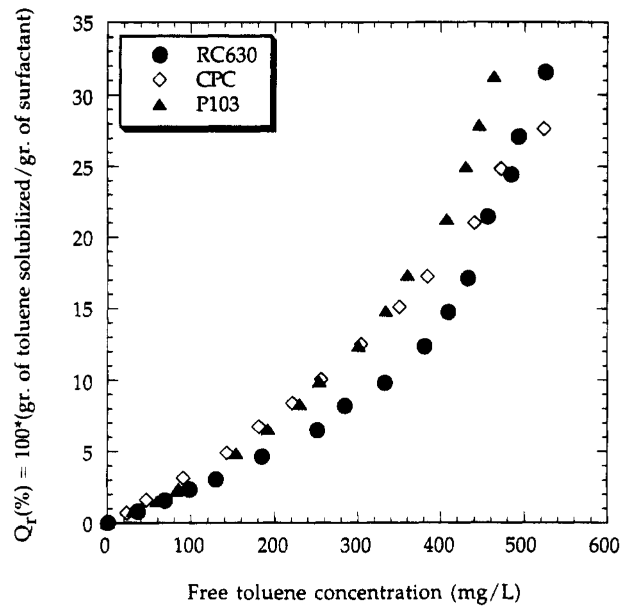

Figure 13. Comparison between conventional and polymeric surfactants. Toluene solubilization capacity on a weight basis in RC630, CPC, and P103 at 25 °C. All concentrations were at 5 wt %.

is a strong function of the PEO content (Figure 4); this is somewhat different for solubilization in low molecular weight nonionic surfactants, for which it is observed that increasing the EO number had only a moderate effect when the solute concentration was close to the aqueous saturation.[27] Likewise, the lack of agreement between volumetric solubilization isotherms of the various aromatic solutes (Figure 11) is another indication that solubilization (and micellization) in block copolymer solutions is a somewhat different mechanism when compared to solubilization in conventional surfactants. As previously assumed, the hydrophobic core of the polymeric micelles contains substantial quantities of water (postulate no. 2) and, initially, solubilization is a replacement process in which water is displaced from the core by the solubilizate (postulate no. 3). It is also thought that the formation of the polymeric micelles is directed by polymer–polymer and water–polymer interactions.[21] In contrast, the hydrophobic core of a conventional surfactant micelle is essentially void of water and the aggregation process is mostly dependent on interfacial tensions.

Finally, to compare the "true" solubilization capacity of the polymers and the conventional surfactants, a different representation of the solubilization data is given in Figure 13. The y-ordinate now gives the percentage of solute uptake by the polymer on a weight basis (Q_r) versus the free toluene concentration. Only P103 is considered for the polymers, since it exhibits one of the largest solubilization capacities; RC630 provides a high solubilization capacity at high solute concentrations, while CPC displays good solubilization power at lower solute concentrations. It is apparent that the block copolymer yields a higher solubilization capacity than the two surfactants for high toluene concentrations. On the other hand, the extent of solubilization in P103 is comparable to that in CPC for lower solute concentrations. This result indicates that some polymeric surfactants could advantageously replace conventional low molecular weight surfactants in processes where solubilization is involved.

Conclusion

Head-space chromatography has been successfully applied to determine aromatic solute solubilization in aqueous polymeric solutions. For the first time, accurate solubilization data in various triblock copolymers were obtained for a wide range of solute concentration. Furthermore, it was shown that solubilization of aromatics not only is a strong function of the solute concentration but also is highly dependent on the structure, PPO/PEO ratio, and molecular weight of the polymer, and, in some cases, of its concentration. Finally, solubilization of the different aromatic solutes and solubilization in conventional low molecular weight surfactants were compared. The data indicate that aggregation and solubilization in polymeric solutions and in conventional surfactant solutions are two significantly different mechanisms. It is postulated that water molecules are present in the hydrophobic core of polymeric micelles and that solubilization of the solute is, initially, viewed as a water replacement process. This hypothesis, which explains the solubilization results, needs confirmation. Indeed, the presence of water in the PPO core remains a matter of controversy. Therefore, it would be very interesting to develop an experimental method (perhaps NMR) to measure the amount of water in the PPO core. Polymer–polymer, polymer–solute, and polymer–water interactions are also thought to be of a major importance in this process. Next, it would be interesting to compare these experimental data with the theoretical works available in the literature. Moreover, since temperature has such an influence on micellization, another area of interest would be the study of solubilization as a function of temperature.

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