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dioxide surface sites, characteristics of water at the interface, and chemical structures of specifically adsorbed molecules. Also, ATR-CIR spectroscopy can qualitatively describe the influence of pH and "inert" electrolyte ions on reactions that occur at/or near the solid-solution interface. Finally, since signal intensity is not necessarily proportional to the concentration of goethite (unless two systems have the same degree of dispersivity), this technique can be regarded as semiquantitative if and only if IR absorption bands coming from chemical bulk groups of the solid are used as internal standards.

Consequently, ATR-CIR spectroscopy offers an in situ means of studying some very important reactions which occur at the solid-water interface such as photocatalysis, surface redox reactions, interfacial complexation, and ion-exchange reactions. By using such an analytical tool as ATR-CIR we should eventually be able to understand the complex nature of surface reaction stoichiometries

which will in turn lead to better predictive models. Since aqueous interfacial reaction chemistry is important to a broad array of processes including mineral dissolution and flotation, corrosion, heterogeneous catalysis, and micro-contaminant transport, this technique promises to be used a great deal more in the future.

**Acknowledgment.** This work was funded in part by a contract from the Ecological Research Division, Office of Health and Environmental Research, U.S. Department of Energy, in part from an grant by NSF and from funds made available through the University of Wisconsin Graduate School, the Engineering Experiment Station, and the University Industrial Research Program. We gratefully acknowledge all support received.

**Registry No.** FeO(OH), 20344-49-4; PO<sub>4</sub><sup>3-</sup>, 14265-44-2; NO<sub>3</sub><sup>-</sup>, 14797-55-8; Cl<sup>-</sup>, 16887-00-6; ClO<sub>4</sub><sup>-</sup>, 14797-73-0; H<sub>2</sub>O, 7732-18-5; goethite, 1310-14-1.

## Unusual Selectivity in Solubilization by Block Copolymer Micelles

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*Received July 31, 1985. In Final Form: November 5, 1985*

Solutions of block copolymer micelles can be designed to achieve highly selective solubilization of components from a mixture of solubilizates. Illustrative experimental results are presented for poly(ethylene oxide-propylene oxide) and poly(*N*-vinylpyrrolidone-styrene) copolymer solutions and for aromatic and aliphatic hydrocarbon solubilizates. The results show substantial solubilization of aromatics in contrast to negligible solubilization of aliphatics. The solubilize that is more compatible with the polymer block that constitutes the core of the micelle is solubilized to a greater extent. The experimental data on the amounts of hydrocarbon solubilized are correlated with the molecular volume of the solubilize, with a volume-polarity parameter characterizing the solubilize as well as with the Flory-Huggins interaction parameter between the solubilize and the polymer block constituting the micellar core.

### Introduction

Copolymer molecules are obtained via the polymerization of more than one type of monomer. The resulting polymer is a block copolymer when it consists of sequences of blocks of each monomer. It is a random copolymer when it consists of a random distribution of monomeric units. The diblock AB copolymers are of interest in the present paper. Since the blocks A and B are of different types, they exhibit a certain degree of mutual incompatibility among them and interact in different ways with any solvent. A solvent that is good for one of the blocks will inevitably be a poor solvent for the other block. A good example of a block copolymer is one in which one of the blocks is hydrophobic while the other is hydrophilic. These features of the block copolymer lead to interesting properties of their solutions in various solvents.<sup>1-10</sup> These properties arise as a result of the molecular organization of the block copolymer in solution. Two types of molecular organization are displayed by them (Figure 1). An isolated molecule can organize itself in such a way as to minimize

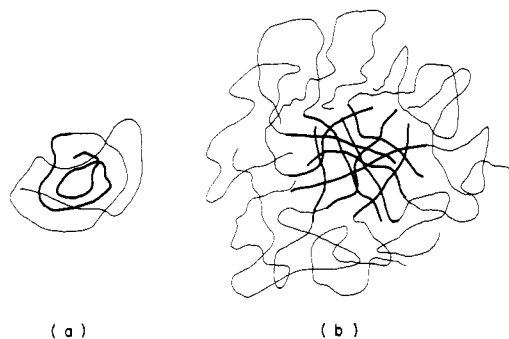
the contacts between the solvent and the block that is most incompatible with it. This intramolecular self-organization does not eliminate all the unfavorable block-solvent contacts but reduces them. The second type of organization involves the association of a number of molecules to form an aggregate in which the solvent-incompatible blocks constitute the core and the solvent-compatible blocks constitute the interfacial region. This structure is analogous to that of a micelle made up of the relatively small conventional surfactant molecules. In contrast to the

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**Figure 1.** Self-assembly of an AB type of block copolymer in aqueous solution. Block A is hydrophobic (darker lines) and block B is hydrophilic (light lines). (a) Intramolecular self-organization of a single molecule; (b) intermolecular self-organization of a number of molecules.

conventional surfactants in which the hydrophobic and hydrophilic parts are usually rather small, the surface-active block copolymers are characterized by large molecular weight blocks of solvophobic and solvophilic monomers. The formation of block copolymer micelles has been studied in a number of polar as well as nonpolar solvents and the solution characteristics, such as the occurrence of a critical micelle concentration, the size of the aggregate, etc., have been to some extent investigated as a function of the molecular features of the copolymer and solvent.<sup>1-10</sup>

A distinguishing feature of self-organizing systems is their ability to enhance the solubility of molecules which otherwise display very low solubility in the pure solvent. The solubilization in aqueous and nonaqueous conventional surfactant micellar solutions has received much attention in the literature.<sup>11-18</sup> In aqueous solutions, these surfactant molecules self-assemble to form micelles or vesicles and these aggregates provide a nonpolar micro-environment for the accommodation of hydrophobic solute molecules. The availability of such a compatible micro-environment in the aqueous phase is responsible for the increased solubility of hydrophobic solutes which are otherwise only sparingly soluble in water. In addition, a molecular thermodynamic treatment<sup>19-22</sup> has suggested and direct gas chromatographic measurements<sup>21</sup> have confirmed that aromatic solubilizes are preferred over aliphatic solubilizes. For example, when mixtures of benzene and hexane are solubilized in various conventional surfactant solutions benzene is preferred over hexane. The selectivity ratio for benzene over hexane is a function of

the composition of the hydrocarbon phase in equilibrium with the aqueous micellar solution.

In contrast to the considerable attention paid to the solubilization in conventional surfactant micelles, only the solubilization of the homopolymers of the insoluble block has been investigated<sup>1</sup> in the case of block copolymer micelles. That such a solubilization is possible can be anticipated intuitively, since the core of the block copolymer is made up of the insoluble block which provides a compatible environment for the homopolymer of the same monomer.

The main goal of the present work is to explore experimentally the solubilization in block copolymer micelles of hydrophobic solutes, both as pure components and as mixtures. The results reveal an unusually large selectivity for aromatic molecules compared to aliphatic molecules in the two block copolymer micelles examined.

## Experimental Section

**Materials.** The following hydrocarbons were utilized as solubilizes: benzene, toluene, *o*-xylene, ethylbenzene, *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, and cyclohexane. These solubilizes were chosen such as to cover a range of molecular volumes, to belong to different chemical families (aliphatic and aromatic), and to be characterized by different values of the Hildebrand-Scatchard solubility parameter.<sup>23</sup> As discussed later, there are physical reasons to use these parameters to correlate experimental solubilization data. All the hydrocarbons were obtained from commercial sources in the reagent grade and were used as received. Two block copolymer molecules were employed. They are poly(ethylene oxide-propylene oxide (70:30) of molecular weight 12500 (Polysciences Inc.) and poly(*N*-vinylpyrrolidone-styrene) (40:60) of unspecified molecular weight (Scientific Polymer Products Inc.). The latter polymer was obtained as an aqueous solution containing 40 wt % polymer. The two polymer samples were also used as received.

**Experimental Procedure.** Samples were prepared by combining 3 mL of the aqueous polymer solution and 3 mL of the hydrocarbon phase to be solubilized in glass sample bottles. These were then sealed to prevent any evaporation. The samples were allowed to equilibrate at 25 °C while being agitated on a mechanical shaker for 1 h. Some emulsification was found to occur for certain concentrations of the solubilizes and polymer. The samples were centrifuged to separate the aqueous micellar phase and the remaining hydrocarbon phase.

The amount of solubilization in the aqueous micellar phase was determined by direct gas chromatographic measurements. In the case of solubilization of mixtures, both the aqueous and the hydrocarbon phases were chromatographically analyzed for their compositions and for the amount of solubilizes in the aqueous phase. Samples were injected directly into the injection port of a dual-column Perkin-Elmer Model 900 gas chromatograph equipped with a flame ionization detector. The columns used were of 1/8-in. internal diameter and 12 ft in length. The column packing was 1,2,3-tris(2-cyanoethoxy)propane supported on calcined diatomaceous earth (Applied Science Laboratories Inc.).

Helium was used as the carrier gas at a flow rate of 30 mL/min. The column temperature was kept roughly 10–20 °C below the normal boiling point of the analyzed solubilizes. The amount of sample injected varied between 4 and 8  $\mu$ L of the aqueous phase depending upon the amount of hydrocarbon solubilized. For the analysis of the hydrocarbon phase composition, 1  $\mu$ L was injected. The output signal from the detector was recorded on a strip chart recorder and the peak areas were determined and translated into amounts of solubilizes by using the calibrations prepared. The water and the polymer present in the aqueous samples posed no problem during the analysis because of the insensitivity of the flame ionization detector to water and deposition of the polymer at the injection port of the chromatograph in the form of a solid residue. This solid polymer residue was removed periodically by

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Table I. Extent of Solubilization of Hydrocarbons at 25 °C

solubilize	mol solubilized/g of polymer or surfactant			
	poly(ethylene oxide-propylene oxide)	poly( <i>N</i> -vinylpyrrolidone-styrene)	SDS	CPC
benzene	$3.5 \times 10^{-3}$	$1.8 \times 10^{-2}$	$5.8 \times 10^{-3}$	$8.8 \times 10^{-3}$
<i>o</i> -xylene	$1.2 \times 10^{-3}$	$1.9 \times 10^{-2}$	$2.6 \times 10^{-3}$	$3.5 \times 10^{-3}$
ethylbenzene	$1.7 \times 10^{-3}$	$1.6 \times 10^{-2}$		
toluene	$1.9 \times 10^{-3}$	$8.9 \times 10^{-3}$	$4.7 \times 10^{-3}$	$6.6 \times 10^{-3}$
cyclohexane	$5.9 \times 10^{-4}$	$1.8 \times 10^{-3}$	$2.7 \times 10^{-3}$	$3.4 \times 10^{-3}$
<i>n</i> -hexane	$2.0 \times 10^{-4}$	$4.6 \times 10^{-4}$	$1.4 \times 10^{-3}$	$2.3 \times 10^{-3}$
<i>n</i> -heptane	$1.7 \times 10^{-4}$	$2.8 \times 10^{-4}$		
<i>n</i> -octane	$1.5 \times 10^{-4}$	$1.1 \times 10^{-4}$		
<i>n</i> -decane	$9.2 \times 10^{-5}$	$4.3 \times 10^{-5}$	$6.9 \times 10^{-4}$	$9.4 \times 10^{-4}$

cleaning the injection port (otherwise it may clog the port and prevent the hydrocarbon from being properly analyzed). Errors in the experimental determination of the amounts of solubilized hydrocarbons arise from a number of sources. These include the variations in the sample volume injected, the determination of the chromatographic peak areas, the preparation of the samples, and the determination of the calibration curves. The upper bound of the uncertainty in the amount of solubilization reported in this paper is estimated to be about 12%.

## Results and Discussion

**Single-Component Solubilization.** The extent of solubilization of various hydrocarbons was determined in aqueous solutions containing 10 wt % poly(ethylene oxide-propylene oxide) or 20 wt % poly(*N*-vinylpyrrolidone-styrene). One may note that the hydrophobic block constitutes only 30% of the copolymer in the first case and 60% of the copolymer in the latter case. The amount of hydrocarbon solubilized per gram of copolymer determined from the gas chromatographic measurements are listed in Table I. Also shown for comparison are the results for the conventional surfactants sodium dodecyl sulfate (SDS) and cetylpyridinium chloride (CPC) obtained earlier in our laboratory.<sup>21</sup> The most notable feature of these results is the large difference in the amounts solubilized of aromatic hydrocarbons compared to aliphatic hydrocarbons. While important differences in solubilization were observed earlier in the conventional surfactant micellar solutions, the magnitude of the difference in block copolymer solutions is remarkably large. Indeed the 4-fold difference between the solubilized amounts of benzene and hexane in conventional surfactant micelles is replaced by an almost 20–50-fold difference in block copolymer micelles.

The amount of solubilization in conventional surfactant micelles has been correlated in the literature<sup>11,12</sup> with the molecular volume of the solubilizes. The number of moles solubilized decreases with increasing molecular volume of the solubilize. This is because, as one can show on the basis of the theory developed in ref 19 and 20, the equilibrium area of the micelle per surfactant is determined by the interactions at the interface. For this reason it is independent of the size of the solubilize for a homologous family of solubilizes. Consequently, the micelles formed are of practically identical volume and the volume available for the solubilizes is fixed and independent of their size. Therefore solubilizes of larger size are solubilized in smaller numbers. However, such a correlation with the molecular volume cannot explain the differences, for example, between toluene and cyclohexane or between ethylbenzene and *n*-hexane which have comparable molecular volumes but belong to different chemical classes. One can, however, still explain these differences in terms of the interactions at the micelle-water interface. Because the aromatic molecules exhibit a lower interfacial

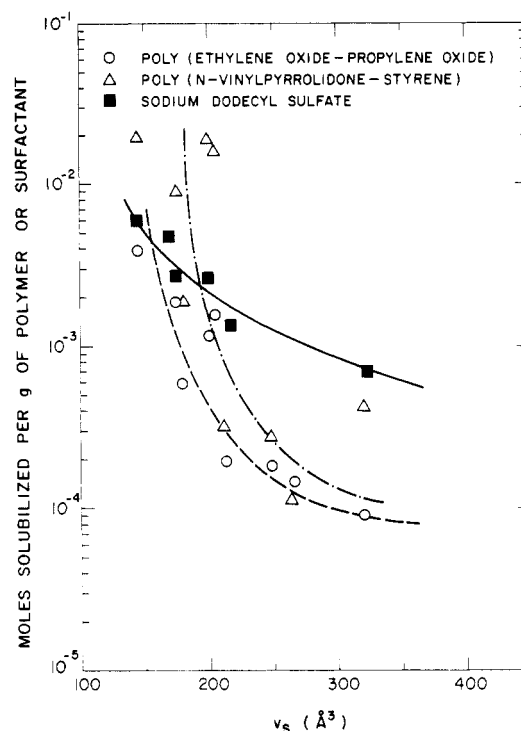


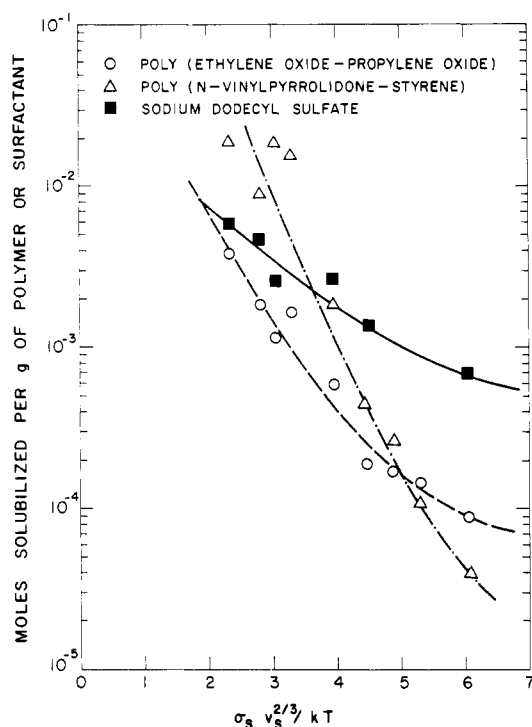
Figure 2. Dependence of the amount of hydrocarbon solubilized on the molecular volume of the solubilize. The solubilizes involved are those of Table I: (—) SDS; (---) poly(ethylene oxide-propylene oxide); (-·-) poly(*N*-vinylpyrrolidone-styrene).

tension against water, the free energy of formation per unit area of the micellar core-water interface is smaller. Consequently, for a given free energy of formation of an aggregate, containing a given number of surfactant molecules, a larger aggregate incorporating a larger number of aromatic solubilizes is possible compared to aliphatic molecules of similar size. Therefore, a new correlating parameter was proposed<sup>21</sup> which incorporates the volume of the solubilize as well as its interfacial tension against water. In this parameter ( $\sigma_s v_s^{2/3} / kT$ ),  $\sigma_s$  is the interfacial tension of the solubilize against water (erg/cm<sup>2</sup>),  $v_s$  is the molecular volume of the solubilize (cm<sup>3</sup>),  $k$  is the Boltzmann constant (erg/K), and  $T$  is the absolute temperature (K). For the SDS and CPC micellar solutions, a good correlation between the amount of solubilization and the volume-polarity parameter was obtained:<sup>21</sup>

$$\text{mol solubilized/g of surfactant} = 0.0676(\sigma_s v_s^{2/3} / kT)^{-2.3} \text{ for CPC}$$

$$\text{mol solubilized/g of surfactant} = 0.0458(\sigma_s v_s^{2/3} / kT)^{-2.3} \text{ for SDS}$$

In Figures 2 and 3, the amounts of hydrocarbon solubilized in the two block copolymer solutions are plotted against



**Figure 3.** Dependence of the amount of hydrocarbon solubilized on the volume-polarity parameter of the solubilize. The solubilizes involved are those of Table I: (—) SDS; (---) poly(ethylene oxide-propylene oxide); (-.-) poly(*N*-vinylpyrrolidone-styrene).

**Table II. Properties of Solubilizes<sup>21</sup>**

solubilize	Hildebrand solubility param <sup>23</sup> $\delta_s$ , (cal/cm <sup>3</sup> ) <sup>1/2</sup>	molecular vol $v_s \times 10^{24}$ , cm <sup>3</sup>	interfacial tension against water $\sigma_s$ , erg/cm <sup>2</sup>	volume-polarity param ( $\sigma_s v_s^{2/3} / kT$ )
benzene	9.2	146	33.93	2.33
<i>o</i> -xylene	9.0	200	36.10	3.05
ethylbenzene	8.8	204	38.40	3.29
toluene	8.9	176	36.10	2.80
cyclohexane	8.2	179	50.20	3.94
<i>n</i> -hexane	7.3	217	50.70	4.52
<i>n</i> -heptane	7.4	243	51.20	4.94
<i>n</i> -octane	7.6	270	51.50	5.32
<i>n</i> -decane	7.7	323	52.00	6.05

the molecular volume of the solubilize and against the volume-polarity parameter, respectively. The relevant molecular parameters for all the solubilizes examined are summarized in Table II.

One may observe that the correlation with the molecular volume is not completely satisfactory while the volume-polarity parameter provides an improved correlation. However, the exponent -2.3 on the volume-polarity parameter which was found to describe the solubilization in conventional surfactants is not found to be satisfactory in accounting for the solubilization in block copolymers. For the same incremental change in the volume-polarity parameter the extent of solubilization varies more dramatically in block copolymer micelles compared to conventional surfactant micelles. An alternate correlating parameter is suggested by the comparison between the micelles of conventional surfactants and those of the block copolymers. There are some important differences between the two. They arise from the fact that the polymer blocks consist of a large number of monomers and therefore can have many configurations. In order to achieve a greater entropic freedom each of the polymers tends to occupy a relatively large area at the interface. (A fraction

**Table III. Solubility Parameters for Polymers and Surfactant Tails at 25 °C**

polymer (or) surfactant tail	solubility parameter $\delta_c$ , (cal/cm <sup>3</sup> ) <sup>1/2</sup>
poly(ethylene oxide)	10.5
poly(propylene oxide)	9.3
poly( <i>N</i> -vinylpyrrolidone)	10.5
polystyrene	9.1
C <sub>12</sub> chain of SDS	7.8
C <sub>16</sub> chain of CPC	8.0

of this area is probably protected by the chains of the block copolymer that are compatible with the solvent.) The entropy due to the numerous configurations inside the micellar core compensate in this case for the increased interfacial free energy. In contrast, the short chains of the conventional surfactants can have much fewer configurations and therefore the corresponding entropic effect is relatively small. As a result, the area occupied by each conventional surfactant molecule should be relatively small for the free energy of the interface to be sufficiently small. Consequently, micellization of the conventional surfactant molecules depends strongly on the interfacial interactions and leads to relatively rigid structures while that of the block copolymer molecules leads to less rigid structures. For the above reasons it is expected that the interfacial interactions will affect the solubilization in conventional surfactant micelles while the interactions inside the micellar core between the solubilize and the polymer block will affect the solubilization in block copolymer micelles. Therefore, the Flory-Huggins interaction parameter  $\chi_{sc}$  could constitute an adequate correlating quantity for solubilization in block copolymer micelles. One expects the degree of solubilization to increase when the value of the  $\chi_{sc}$  parameter decreases. This is because, for a small positive enthalpic effect (small  $\chi_{sc}$ ) the entropic effect overcomes the enthalpic effect thus leading to larger solubilization. The magnitude of  $\chi_{sc}$  is computed<sup>24</sup> here in terms of the Hildebrand-Scatchard solubility parameters:

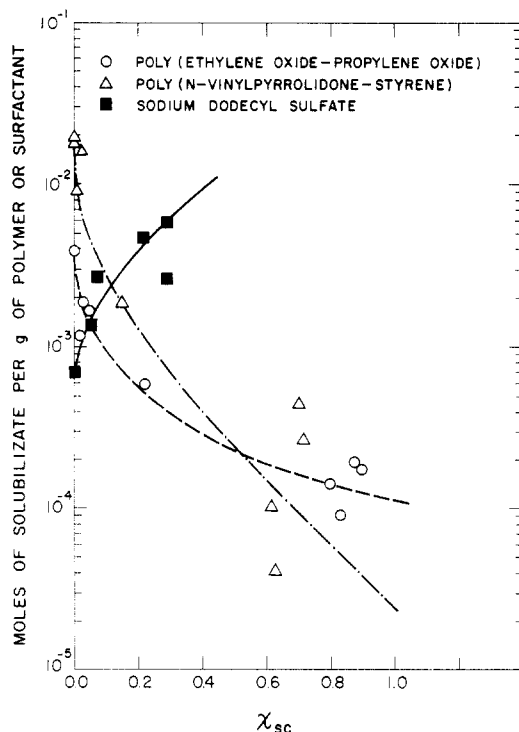
$$\chi_{sc} = (\delta_s - \delta_c)^2 v_s / kT$$

where  $\delta_s$  and  $\delta_c$  are the solubility parameters for the solubilize and the polymer block constituting the micellar core, respectively. In the case of conventional surfactants,  $\delta_c$  refers to the aliphatic tail of the surfactant. Table III lists the solubility parameters for different polymer blocks and conventional surfactant tails while Table IV presents the calculated values of the  $\chi_{sc}$  parameter for the solubilizes in the different systems that are considered here. One can see that the aromatic solubilizes are characterized by very small values of  $\chi_{sc}$  close to zero implying that these solubilizes would constitute good solvents for both polypropylene oxide and polystyrene blocks. The aliphatic solubilizes are found to be poor solvents for the above two blocks. Cyclohexane has intermediate values of  $\chi_{sc}$  implying that it is a better solvent for the above two nonpolar blocks than hexane. The amounts of hydrocarbons solubilized are plotted against the  $\chi_{sc}$  parameter for the two block copolymers in Figure 4. As anticipated, the aromatic solubilizes which have smaller values for  $\chi_{sc}$  are solubilized to a much greater extent than the aliphatic solubilizes for which the values for  $\chi_{sc}$  are larger. Also shown in Figure 4 are the data points for the surfactant SDS. In this case, although the aliphatic solubilizes are more compatible with the aliphatic tail of the surfactant, the aromatic molecules are solubilized in larger

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**Table IV. Interaction Parameter  $\chi_{sc}$  for Solubilizates with Polymers and Surfactant Tails**

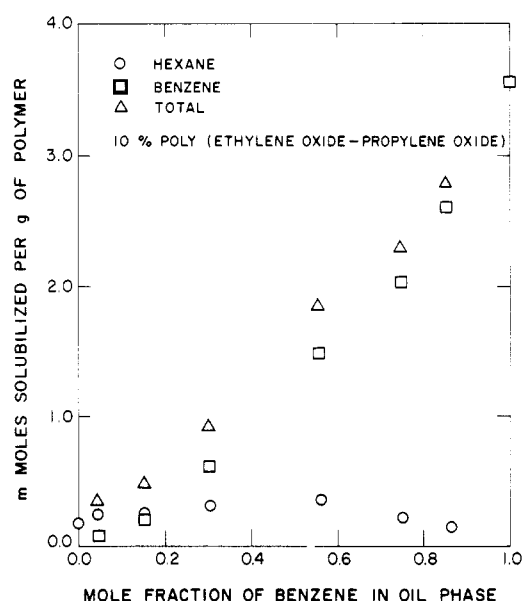
solubilizate	poly(propylene oxide) (nonpolar block)	poly(ethylene oxide) (polar block)	poly( <i>N</i> -vinylpyrrolidone) (polar block)	polystyrene (nonpolar block)	SDS	CPC
benzene	0.0015	0.25	0.249	0.0015	0.288	0.212
<i>o</i> -xylene	0.018	0.45	0.453	0.002	0.290	0.201
ethylbenzene	0.051	0.59	0.594	0.0184	0.205	0.131
toluene	0.028	0.45	0.454	0.007	0.214	0.144
cyclohexane	0.218	0.95	0.953	0.146	0.072	0.007
<i>n</i> -hexane	0.874	2.24	2.237	0.708	0.055	0.107
<i>n</i> -heptane	0.894	2.38	2.38	0.716	0.040	0.089
<i>n</i> -octane	0.794	2.31	2.31	0.618	0.011	0.044
<i>n</i> -decane	0.832	2.55	2.549	0.637	0.003	0.029



**Figure 4.** Dependence of the amount of hydrocarbon solubilized on the Flory-Huggins interaction parameter for the system consisting of the solubilizates and the polymer block constituting the micellar core. The Flory-Huggins interaction parameter is calculated in terms of the Hildebrand-Scatchard solubility parameters. The solubilizates involved are those of Table I: (—) SDS; (---) poly(ethylene oxide-propylene oxide); (-.-) poly(*N*-vinylpyrrolidone-styrene).

amounts. This happens because the solubilization is affected by the interactions at the micelle-water interface. This is represented by the parameter  $(\sigma_s v_s^{2/3}/kT)$  which provides a satisfactory correlation of conventional surfactant micelles. (While the plot in Figure 4 for SDS may appear to suggest an acceptable correlation, the increase in the amounts solubilized with increasing values of  $\chi_{sc}$  is physically unreasonable.)

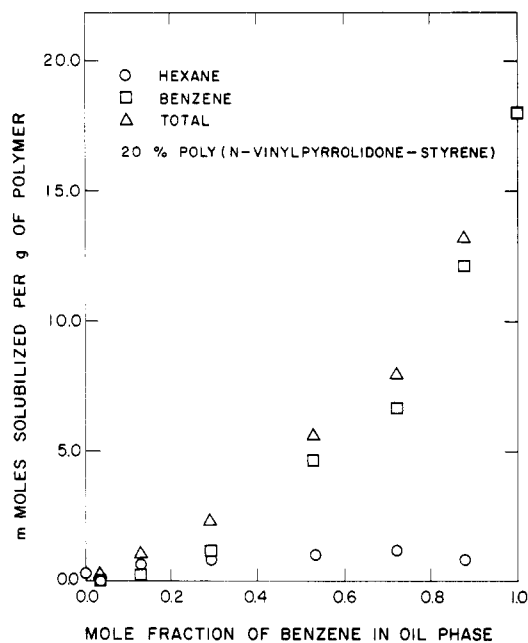
While the  $\chi_{sc}$  parameter serves as a reasonable correlating parameter for a qualitative description of solubilization in block copolymer micelles, some caution should be exercised from a quantitative point of view in using this parameter alone to fully describe the extent of solubilization. As can be seen in Figure 4, when the  $\chi_{sc}$  parameter is large corresponding to poor solvents (in this case, the aliphatic solubilizates) a quantitative correlation between the amount of solubilization and the  $\chi_{sc}$  parameter is not obtained. A possible explanation is the occurrence of some solubilization in the interfacial region of the polar blocks of the copolymer molecule. The  $\chi_{sc}$  parameters calculated for the polar polyethylene oxide and poly *N*-vinylpyrrolidone blocks and the various solubilizates are also presented in Table IV. Although the values of  $\chi_{sc}$  for the



**Figure 5.** Amounts of benzene and hexane solubilized as a function of the composition of the hydrocarbon phase in equilibrium with the aqueous poly(ethylene oxide-propylene oxide) solution.

aromatic solubilizates are larger in the polar blocks than in the nonpolar blocks, they can still allow for some solubilization to take place in the polar blocks. The values of  $\chi_{sc}$  for the aliphatic solubilizates in the polar blocks are too large, indicating that the aliphatics are not likely to be solubilized in the interfacial region of the polar blocks at all. A more plausible explanation is that one should consider other parameters in addition to  $\chi_{sc}$  such as the molecular volume  $v_s$  of the solubilize suggested by the theory of swelling of polymers. One may note that although the volume-polarity parameter  $(\sigma_s v_s^{2/3}/kT)$  provides a satisfactory correlation of the solubilization data in block copolymer micelles, we are inclined for physical reasons to consider the compatibility parameter  $\chi_{sc}$  as a more suitable correlating parameter. Some caution, however, should be exercised in using  $\chi_{sc}$  for a quantitative description of the extent of solubilization because the evaluation of  $\chi_{sc}$  (in this paper) on the basis of solubility parameters is perhaps not entirely adequate and also because as mentioned above variables other than  $\chi_{sc}$  may also be important.

**Solubilization of Binary Mixtures.** The single-component solubilization data suggest that the solubilization will be selective for aromatic molecules when mixtures of aromatic and aliphatic molecules are solubilized. As an illustrative example, mixtures of benzene and hexane were solubilized in both block copolymer solutions. The amounts solubilized were determined as a function of the composition of the hydrocarbon mixture in equilibrium with the aqueous micellar solution. These data are plotted in Figure 5 and 6. The most remarkable feature of the



**Figure 6.** Amounts of benzene and hexane solubilized as a function of the composition of the hydrocarbon phase in equilibrium with the aqueous poly(*N*-vinylpyrrolidone-styrene) solution.

experimental results is the significantly small extent of solubilization of hexane in the entire composition range of the hydrocarbon mixture. Of course, this behavior parallels the solubilization characteristics of the pure hydrocarbons. The selectivity for benzene compared to hexane suggests that the aromatic molecules can be selectively removed from a mixture with aliphatic molecules using the above block copolymer micelles. Selectivity for aromatics was reported earlier<sup>19-22</sup> in conventional surfactant solutions as well. The significant difference from a practical point of view between the conventional surfactant micelles and the block copolymer micelles can be understood from Figure 4. In surfactant micelles, the largest selectivity is displayed by those mixtures that have the largest difference in the amounts of pure components solubilized. Therefore, benzene is selectively solubilized compared to hexane. But for aromatic molecules of larger

size (e.g., toluene or xylene), this selectivity over hexane considerably decreases and is no longer of much practical value. In contrast, in the block copolymer micelles examined here, all the aromatic solubilizes exhibit a comparable degree of solubilization and, more importantly, the aliphatic solubilizes are negligibly solubilized. Therefore, the block copolymer solutions will be suitable for separating a variety of aromatic molecules from aliphatics. Also sufficiently large quantities of solubilizes can be handled by increasing the concentration of the polymer in solution.

## Conclusions

Experimental data on the solubilization of hydrocarbons in aqueous block copolymer micellar solutions have been obtained by direct gas chromatographic measurements. The solubilizes that are good solvents (small values for  $\chi_{sc}$ ) for the block constituting the micellar core are solubilized in large quantities. In contrast, the solubilizes that are poor solvents (large  $\chi_{sc}$ ) dissolve only sparingly in the block copolymer solution. For the poly(ethylene oxide-propylene oxide) and the poly(*N*-vinylpyrrolidone-styrene) block copolymers examined, the aromatic hydrocarbons are good solvents for the nonpolar blocks while the aliphatic hydrocarbons are poor solvents. Consequently, significant solubilization of the aromatics and negligible solubilization of the aliphatics are achieved. When mixtures of the aromatic benzene and the aliphatic hexane are solubilized, the block copolymer micelles selectively solubilize benzene. The selectivity is large and remains so for other aromatic-aliphatic solubilize mixtures. The present results provide a practical means for the separation of various aromatic-aliphatic mixtures using carefully chosen block copolymer molecules. Moreover, by the proper selection of block copolymers, one can separate various kinds of mixtures of polar and/or nonpolar molecules.

**Acknowledgment.** This work was supported by the National Science Foundation.

**Registry No.** Benzene, 71-43-2; toluene, 108-88-3; *o*-xylene, 95-47-6; ethylbenzene, 100-41-4; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-decane, 124-18-5; cyclohexane, 110-82-7; poly(ethylene oxide-propylene oxide) (copolymer), 9003-11-6; poly(*N*-vinylpyrrolidone-styrene) (copolymer), 25086-29-7.