Extraction of Naphthalene by Block Copolymer Surfactants Immobilized in Polymeric Hydrogels

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Gel/micelle materials, comprising hydrogels containing block copolymer micelles, have the potential to be very useful in a variety of extraction and controlled release applications. It is demonstrated that block copolymer surfactants can be immobilized in calcium alginate gels and that the resulting composite material preferentially solubilizes the model hydrophobic solute naphthalene. Five different polyethylene oxide-polypropylene oxide-polyethylene oxide triblock copolymer surfactants are considered, and the qualitatively different properties exhibited are interpreted in light of the properties of these surfactants in solution. Alginate gel concentrations of 22.5 and 52.5 g/L and surfactant concentrations ranging from 20.4 to 136 g/L are considered. The data indicate that micelles can be permanently immobilized for purposes of extraction or controlled release and that the extent of solute uptake or release can be altered by varying gel and surfactant concentration and the type of surfactant employed.

Introduction

It has long been recognized that hydrophobic solutes can be incorporated into aqueous surfactant aggregates known as micelles, making it possible to increase the aqueous solubility of such substances by orders of magnitude. The solute is generally accommodated within the core of the micelle, where the presence of the oil-like tail groups of the surfactant molecules provides a hydrophobic microenvironment for the solute. In this article, we explore the possibility of capitalizing on these solubilizing capabilities of micelles within a novel environment: that of micelles incorporated into an aqueous polymeric gel. The presence of the gel hinders or eliminates the transport of the micelles inside of the gel matrix, giving the system interesting possibilities both for the efficient extraction of hydrophobic solutes and toxins and for the controlled release of water-insoluble pharmaceuticals. We are thus interested in how the properties of surfactant aggregates formed within a gel are impacted by micelle/polymer interactions, coupled with the constraining nature of the gel matrix.

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We explore these interactions by measuring the capacity of various micelle/gel materials to solubilize hydrophobic solutes. To maximize the retention of the surfactant within the gel, large block copolymer surfactants are chosen as our micelle-forming molecules. We measure the solubilization properties of the micelle/gel materials as a function of surfactant type, surfactant concentration and gel polymer concentration. The aromatic hydrocarbon naphthalene is used as a model hydrophobic solute, whose concentration is measured by monitoring solution absorbance of light at a wavelength of 276 nm using an ultraviolet (UV) spectrophotometer. Naphthalene light absorbance is strong enough so that even the very low concentrations obtainable in water in the absence of micelles can be detected readily. Naphthalene also makes a useful probe because its solubility has previously been measured for block copolymer micelle solutions not containing gel (Nagarajan et al., 1986; Hurter and Hatton, 1992). Its solubility has also been measured in a variety of other surfactant solutions (Nakagawa, 1966). By comparing our results with these earlier studies, we can thus determine the impact of the gel matrix on the solute partitioning behavior.

In the following section, we discuss in some detail how such micelle/gel materials in improved extraction and controlled release technologies can play a role. However, as is the case for so many novel scientific concepts, the range of applications for such materials can be determined only after understanding their fundamental physical properties. Hence, it is also important to understand in a more fundamental way the role of interactions between surfactants and polymeric gels on the equilibrium properties of the system. In this sense, our work is an extension of the considerable literature examining micelle-polymer interactions (Saito, 1987). The influence of dissolved polymer molecules on surfactant solutions is of great interest, because in large part so many surfactant solutions in practice contain polymers as well. Existing studies of these interactions have focused on surfactant and polymer *solutions*, and it is currently unknown how transforming the solution to gel form alters micelle-polymer interactions. Thus, the studies of surfactants incorporated into gels should yield important information applicable to any system containing both surfactant and gel, including photographic films, micellar-enhanced chromatographic columns, and many foods.

Applications of Micelles Incorporated into Gels

Currently, there is substantial interest in taking advantage of the solubilizing properties of micelles to effect novel separations of water-insoluble compounds. Using an aqueous micellar solution to extract hydrophobic compounds has considerable environmental and economic advantages over organic solvent extraction. Micelles may also provide a more flexible medium from which to recover the solute than do solid adsorption methods, because micelle solubilization properties can be adjusted readily by changes in temperature, pressure, and addition of salts. The bulk of recent explorations of micellar extraction techniques have been directed toward removing hydrophobic toxins from waste or ground water. Polyaromatic hydrocarbons (PAHs) have been successfully extracted from water (Nagarajan et al., 1986; Christian and Scamehorn, 1989; Edwards et al.,1991; Garcia et al., 1992; Gotlieb et al., 1993) and from soil (Vignon and Rubin, 1989; Fountain et al., 1991; Liu et al., 1991; Bockelen and Niessner, 1993; Gotlieb et al., 1993), as have the highly toxic polychlorinated biphenyl compounds (PCBs) (Kile and Chiou, 1989; McDermott et al., 1989; Pramauro, 1990; Abdul and Gibson, 1991; Lee et al., 1991a). Phenol, which is less hydrophobic but still presents pervasive environmental concern, has also been extracted using micellar solutions (Dunn et al., 1989; Kandori et al., 1989a,b; Pramauro, 1990; Lee et al., 1991b). By using charged surfactant systems, it is also possible to extract hydrophilic metal ions, either through ion binding (Dunn et al., 1989; Ismael and Tondre, 1992; Nakamura et al., 1992; Okada, 1992) or by phase separation (Christian et al., 1989). Micellar solubilization to remove petroleum products from soil has also been investigated (Abdul et al., 1990). Finally, we should mention the important potential for novel separations outside of environmental cleanup, such as for the removal of cholesterol from milk fat (Sundfeld et al., 1993a,b).

This interest in micellar-based separations increases the need to understand and predict the solubilizing capacity of different surfactants for different types of solutes. However, also important—and less studied—is the development of techniques for separating the solute-containing micelle from the aqueous solution. To this end, two novel approaches for separating the micelles from solution have been proposed. The "micelle-enhanced ultrafiltration" technique developed by Scamehorn and coworkers (Christian and Scamehorn, 1989; Christian et al., 1989; Lee et al., 1991a) has been very influential and was employed by many of the articles cited in the paragraph above. In this approach one filters the surfactant from the solution using ultrafiltration membranes, with pore sizes smaller than the diameters of the micellar aggregates. A more recent suggestion made by Hurter and Hatton (1992) also uses a membrane to retain the micelles, but instead uses a hollow-fiber device to provide a semipermeable barrier between the surfactant aggregates and the purified water stream. The contaminated water contacts the micellar solution across the fiber membrane, allowing the toxins to pass through the membrane where they are retained within the micellar phase. Extraction and separation are therefore achieved simultaneously and continuously. Very large block copolymer surfactants are used in this approach, so that the surfactant may be retained more effectively. Both this hollow-fiber device and the ultrafiltration technique have unique advantages that warrant further study.

In this article, we explore the feasibility of incorporating the micelles within the interstices of a polymeric hydrogel and using the combined micelle/gel material for solubilization applications. Because naphthalene is itself a PAH, we felt it would be a useful choice as a model solute in our studies, while still not being toxic enough to present a hazard in our laboratory. The use of micelle/gel materials to extract toxins such as PAHs relies on the ability to immobilize the micelles in the gel, while leaving the gel structure porous enough that mass transfer of the aromatic hydrocarbons is relatively unrestricted. To maximize the retention of the surfactant, like Hurter and Hatton (1992) we focus our attention on block copolymer surfactants. These surfactants are incorporated within a gel by dissolving surfactant and gel polymer in an aqueous solution and then rapidly cross-linking the polymer fibers to form a gel. Beads of the gel/micelle material could be packed into a column similar to those now used for gel permeation chromatography. As polluted water passes through the column, the immobilized micelles solubilize the contaminants while remaining separated from the purified water. With this approach, gel retention of the micelles removes the need for an expensive separation step, such as the filtration required in micellar-enhanced ultrafiltration, while allowing good contacting between the solute solution and the micelles. This concept of large micelles immobilized within an aqueous gel bears resemblance to that of organic gels made from water-in-oil microemulsions, in which gelatin solubilized within the water pools of microemulsion droplets is used to link those droplets together in a gel (Haering and Luisi, 1986; Quellet and Eicke, 1986).

In addition to the obvious applications for cleaning contaminated water using a packed bed device, the micelle/gel system may have unique advantages in soil remediation. The currently proposed approach to surfactant cleanup of soils is to pump a surfactant solution directly through the soil, followed by a wash of pure water to remove surfactant (Fountain et al., 1991). Surfactant adsorption to the soil and other surfactant losses are a potential problem in this direct approach (Nash and Traver, 1986; Vignon and Rubin, 1989; Jafvert and Heath, 1991). An alternative method would be to embed po-

Table 1. Properties of Block Copolymer Surfactants Used in This Study

Surfactant Type	Structure*	% Polypropylene Oxide	Molec. Wt. (Total)	Molec. Wt. (PPO Only)
Tetronic 908 (T908)		20%	18,750	3,750
Tetronic 1307 (T1307)		30%	19,000	5,700
Pluronic 88 (P88)		20%	11,000	2,200
Pluronic 87 (P87)		30%	7,500	2,250
Pluronic 123 (P123)		70%	5,750	4,025

* All polymers consist of blocks of polyethylene oxide (□) and of polypropylene oxide (•).

rous columns of micelle/gel beads within the contaminated soil, followed by continuous *in-situ* contacting of those columns with groundwater. The toxins would partition from the water into the beads for easy removal, while no surfactant would contact the soil, thus saving on surfactant recovery costs and further environmental adulteration. Better contacting could be achieved by actually dredging the soil and mixing it with the beads, which could then be separated by gravitational separation or coarse filtration.

After the column of micelle/gel beads is saturated, the concentrated nature of the contaminated waste will facilitate regeneration steps. For example, supercritical oxidation requires moderately high concentrations of toxins (Tester et al., 1991). Other researchers have shown that degradative reactions to destroy nerve agents and mustards often precede faster when carried out in micellar media (Bunton and Ihara, 1977; Brown et al., 1980; Moss et al., 1986; Menger and Elrington, 1990, 1991). The micelle/gel configuration also presents interesting possibilities for *in-situ* solute degradation by permitting the coimmobilization of enzymes or cells for the destruction of toxins. Bury and Miller (1993) have recently demonstrated that biodegradation rates of hydrocarbons are enhanced when hydrocarbon is solubilized within micelles. The use of micelles in biodegradation has an added importance, since it has been noted that successful bioremediation requires moderate threshold concentrations of toxin, so that the cells do not turn to other more abundant sources of carbon (Peotrowski, 1991). Thus, by encapsulating cells within the micelle/gel, one could locate the cells in close proximity to a concentrated source of toxins. If successful, this coencapsulation would accomplish extraction and detoxification in a single step.

In addition to extraction applications, the ability of micellar aggregates to solubilize hydrophobic compounds makes them potentially useful in a variety of controlled release applications. Previous studies have shown that micelles significantly enhance the solubilities of drugs such as steroids, antibiotics, anticancer agents, and pain killers (Attwood et al., 1989; Krishna and Flanagan, 1989; Yokoyama et al., 1990; 1991; Alkan-Onyuksel and Son, 1992; Hussain et al.,1992; Kumar and Singh, 1992; Fahelelbom et al., 1993; Malcomson and Lawrence, 1993), as well as protecting them from premature degradation (Krasowska, 1979; Moro et al., 1991). Gel/micelle materials, therefore, present the possibility of improving the loading capacity and protective capabilities of a controlled release device. They also provide an additional degree of flexibility in controlling release rates, since that rate will depend strongly on the type of surfactant used. We also note that such controlled release applications are by no means limited to drug delivery, but could be extended to the delivery of vitamins (Winn et al., 1989; Canfield et al., 1990; Liu et al., 1990; 1991; Schubiger et al., 1993), perfumes (Tokuoka et al., 1992; Abe et al., 1993), and pesticides (Nassetta et al., 1991).

Materials and Methods

The block copolymer surfactants were obtained as a gift from BASF Chemical Corporation (Wyandotte, MI). The surfactants used are of the Pluronic (poloxamer) and Tetronic (poloxamine) series, and consist of triblocks of polyethylene oxide-polypropylene oxide-polyethylene oxide (Table 1). The ethylene oxide groups provide a hydrophilic character to the polymer, whereas the propylene oxide groups contribute hydrophobic portions. The two different series of surfactants differ only in their shape, with Pluronics being linear polymers and Tetronics being of the branched form. The properties of the five surfactants used in this study are given in Table 1. All surfactants used in this study came from the same production lot to maximize the uniformity of their properties.

The hydrogel matrix chosen to incorporate these block copolymer surfactants is sodium alginate, which was purchased from Sigma Corporation (St. Louis, MO). Alginate was selected because it has a simple and easily controlled gelling process, its properties are well known, and it has been widely studied for controlled release applications. The negatively charged alginate polymer is composed of primarily anhydro-β-D-mannuronic acid residues. Klein et al. (1983) examined alginate gels made with similar alginate polymers, and the pore size of the gel beads was determined to be less than 17 nm for polymer concentrations of 3, 4 and 7 wt. %. Because the gel beads used in our experiments were of similar concentrations of polymer (approximately 2 wt. % to 5 wt. %), it is expected that the beads will have a maximum pore size of the same order of magnitude. Note that a hydrodynamic diameter on the order of 20 nm has been measured for micelles made up of the block copolymer Pluronic 123 (Wanka et al., 1990). Since this surfactant is the smallest of the surfactants used in our study, we anticipate that, if micelles do form within the gel, they will be comparable to or larger than the alginate pores.

The method used to make the micelle/gel beads is similar to that for the immobilization of cells (Scott, 1987). To prepare the micelle-containing gel beads, a stock surfactant solution of known concentration (20 to 136 g/L) is made. Sodium alginate is added to a portion of the surfactant solution and

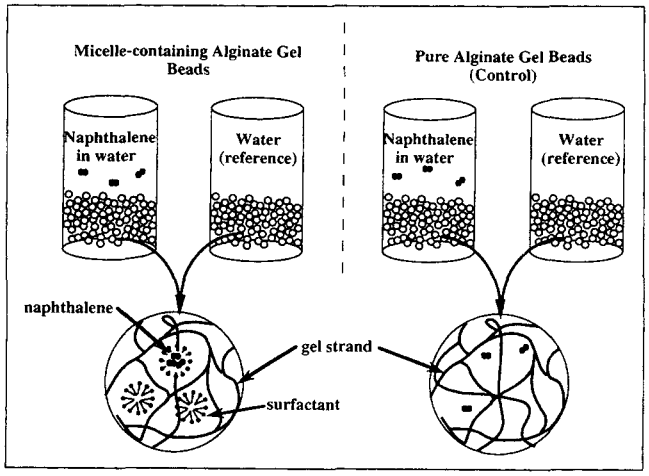

Figure 1. Naphthalene extraction experiments.

The diagram shows alginate gel beads containing the block copolymer surfactant and beads containing no surfactant which are used as a control.

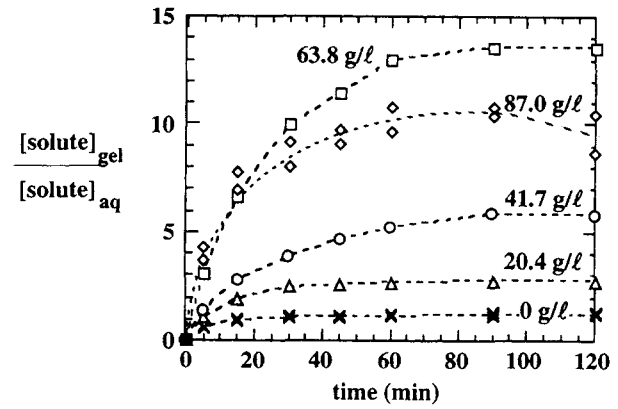

Figure 2. Experimental results for naphthalene concentration within gel beads divided by naphthalene concentration in the aqueous phase.

Results are for 52.5 g/L alginate gel beads containing various concentrations of T1307 block copolymer surfactant.

stirred overnight to make a 22.5 or 52.5 g/L mixture of alginate polymer. A 7.6 g/L solution of calcium chloride (Fisher Scientific, Fair Lawn, NJ) is also made with the stock surfactant solution as the solvent. 30 μL drops of the alginate/micelle mixture are added to the calcium chloride solution by using a syringe pump. The drops begin to gel almost immediately and are left in the cross-linking solution for at least two hours to ensure complete gelation. Because the concentration of surfactant is the same inside and outside the beads, leakage of surfactant from the beads is minimized during the process of gelation. Although some polyethylene oxide-polypropylene oxide block copolymer surfactants are "salted out" by the concentrations of calcium chloride used in this gelation process, no salting-out effects were observed with the surfactants used in the experiments discussed here. After gelling, the beads are washed repeatedly in the calcium-micelle cross-linking solution, over a period of several hours, to remove most of the ungelled alginate polymer. A second set of alginate beads, which does not contain micelles, is also prepared as a control.

The partitioning experiments are designed to allow one to compare the extraction of naphthalene by the micelle/gel beads with that of gel beads containing no block copolymer. In this way, we account for any errors caused by solute evaporation or adsorption to the glass. 10 mL quantities of beads are measured by noting the change in liquid volume when added to graduated cylinders containing 20 mL of pure calcium chloride solution. The beads are then rinsed once with 20 mL of pure calcium chloride solution to ensure the removal of any surfactant adhering to the surfaces of the beads. Before use, excess liquid is removed from the surface of the beads by drying them in a Buechner funnel over a vacuum.

The micelle-containing beads (10 mL) are added to two glass vials, and two more vials are each filled with 10 mL of pure gel beads. Over one set of each type of bead (surfactant-containing and surfactant-free) an equal volume of saturated naphthalene solution is added; to the other two vials we introduce 10 mL of pure water (see Figure 1). The naphthalene solution is tested against water in the UV spectrophotometer before it is placed over the beads to obtain an initial naphthalene absorbance at zero time. We then measure the ultraviolet absorption of the external aqueous solution using a Shimadzu 160 spectrophotometer. Each of the four vials is stirred and monitored at regular time intervals for at least two hours, using samples from the pure water solutions as references for the samples containing naphthalene. These references are needed because small amounts of leaking alginate and block copolymer also absorb some light, and hence must be subtracted from the naphthalene absorbance.

Results

From the experiments described above, we determine the concentration of naphthalene as a function of time in an aqueous solution in contact with an equal volume of alginate gel beads. By incorporating different types of block copolymer surfactant in various concentrations into the gel matrix, the effect of the surfactant presence on naphthalene extraction can be evaluated. In Figure 2, the ratio of naphthalene concentration in the gel divided by that in the external solution is plotted as a function of time. This naphthalene concentration ratio is given by:

$$\frac{c^{gel}_{naph}}{c^{aq}_{naph}} = \frac{1 - c^{aq}_{naph}/c_o}{c^{aq}_{naph}/c_o}, \qquad (1)$$

where $c^{gel}_{naph} = c_o - c^{aq}_{naph}$ and c^{aq}_{naph} and c_o are the aqueous and total concentrations of naphthalene. Hence, the concentration ratio given by Eq. 1 can be determined directly from our experimental data.

Figure 2 shows results for experiments in which the aqueous naphthalene solution is contacted with alginate gel beads containing (a) no incorporated surfactant and (b) the block copolymer surfactant Tetronic 1307 in concentrations varying between 20.4 and 87.0 g/L. The results indicated by the control experiment, in which alginate without surfactant is contacted with naphthalene solution, show a concentration ratio of unity at long times. Thus, they indicate that in the absence of surfactant, naphthalene partitioning into the gel is *nonselective*, with an approximately equal preference of the solute for the

gel and the aqueous phases. In contrast, the gel beads containing the added surfactant clearly impact the extent of naphthalene uptake, showing concentration ratios ranging from 2.8 at 20.49 g/L surfactant to nearly 14 at 63.89 g/L added surfactant. Hence, the additional presence of the surfactant within the alginate causes the solute to partition *selectively* into the gel. The extent of the partitioning appears to increase with surfactant concentration.

Effect of surfactant type

It is possible that the enhanced solubility of naphthalene within the surfactant/gel material is caused by the formation of micellar aggregates by the surfactant within the interstices of the alginate gel matrix. The hydrophobic microenvironment provided by the micelles would cause naphthalene to partition into the micellar aggregates as they do in aqueous solution (Hurter and Hatton, 1992), hence permitting much higher concentrations of the solute to be incorporated in the gel phase. Alternatively, the surfactant may simply increase the hydrophobicity of the gel matrix in some other fashion, without specifically organizing into molecular aggregates. This second possibility must certainly be considered, particularly given the large size of the block copolymer surfactants used. Whether such surfactants can still form micellar aggregates within the confined matrix of a gel is currently unknown.

To investigate the presence of micelles within the gel, as well as to explore the properties of the surfactant/gel materially generally, five different block copolymer surfactants have been employed in this study. The surfactants are all of the polyethylene oxide-polypropylene oxide-polyethylene oxide type discussed earlier, but differ in the relative amounts of these components as well as in the shape of the block copolymer. Although there is considerable debate in the literature as to the micellar properties, particularly the critical micelle concentrations, of these polyethylene oxide-polypropylene oxide-polyethylene oxide block copolymers, it is clear that these five surfactants should have distinctly varying tendencies to form micellar aggregates, at least in aqueous solution. The properties of the block copolymer surfactants we used are summarized in Table 1.

We start by comparing the two Tetronic surfactants, T908 and T1307. These two copolymers have comparable molecular weights and are both branched structures, but are distinguished by different proportions of the hydrophobic polypropylene oxide (PPO) component. T908, with only 20% PPO, is less hydrophobic than T1307. Figures 2 and 3 show the concentration of naphthalene inside the gel relative to the aqueous naphthalene concentration as a function of time for gel beads containing T1307 and T908, respectively. The gel containing the surfactant T908 promotes some selective partitioning of solute into the bead, with the effect generally increasing with increasing surfactant concentration (Figure 3). The strength of this partitioning effect is small, however, with the concentration ratio $c^{gel}_{naph}/c^{aq}_{naph} = 2$ the maximum value achieved with 63.8 g/L surfactant incorporated within the gel. This value is only slightly above the value of unity achieved by the control. In contrast, the more hydrophobic surfactant T1307 achieves much higher concentration effects (Figure 2). Here with 63.8 g/L added surfactant the maximum partitioning achieved is $c^{gel}_{naph}/c^{aq}_{naph} = 14$. This ability of T1307 surfactant/gels to solubilize naphthalene within a gel is consistent with results for

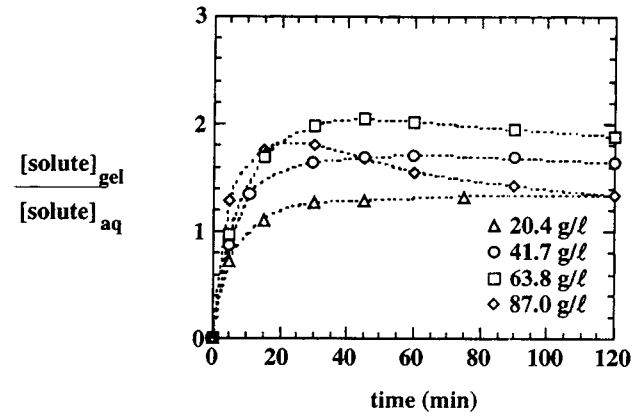

Figure 3. Concentration ratio inside and outside the gel bead for the surfactant T908 at four surfactant concentrations in 52.5 g/L alginate gel beads.

surfactant solutions reported by Hurter and Hatton (1992). This latter study found enhanced naphthalene solubility within T1307 micelles forming in aqueous solution alone.

We also compare the extraction ability of two Pluronic copolymers, P88 and P87, with the same relative proportions of PPO (20% and 30%, respectively) as the Tetronic copolymers discussed above (Table 1). These surfactants have a linear structure and a lower molecular weight than T908 and T1307. Also, P88 and P87 differ in their total molecular weight, but have comparable values for the molecular weight of the PPO portion of the molecule alone (~2,200). As demonstrated by the data in Figures 4 and 5, P87 and P88 surfactant/gels show only a slight enhancement in naphthalene solubility over a gel with no surfactant. Although the dependence on concentration differs somewhat for the two surfactants, at 87.0 g/L added surfactant both surfactants reach a maximum partitioning of $c^{gel}_{naph}/c^{aq}_{naph} = 1.8$. The enhancement is slightly less at all concentrations than that observed for T908, but is dramatically less than the solubility of naphthalene in T1307 gels. Note that the relative hydrophobic fraction is the same in T1307 as in P87.

Finally, we examine concentration ratios obtained using a significantly more hydrophobic surfactant, P123. This sur-

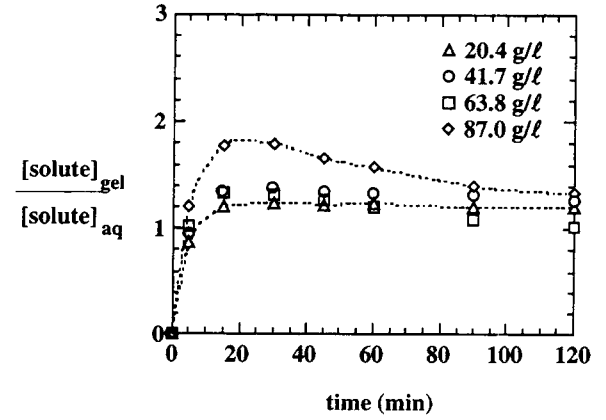

Figure 4. Concentration ratio inside and outside the gel bead for the surfactant P87 at four surfactant concentrations in 52.5 g/L alginate gel beads.

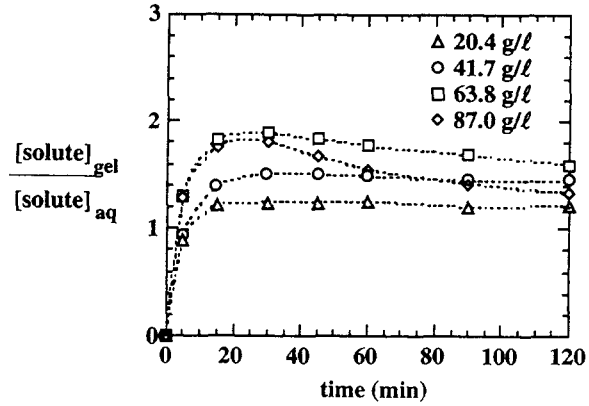

Figure 5. Concentration ratio inside and outside the gel bead for the surfactant P88 at four surfactant concentrations in 52.5 g/L alginate gel beads.

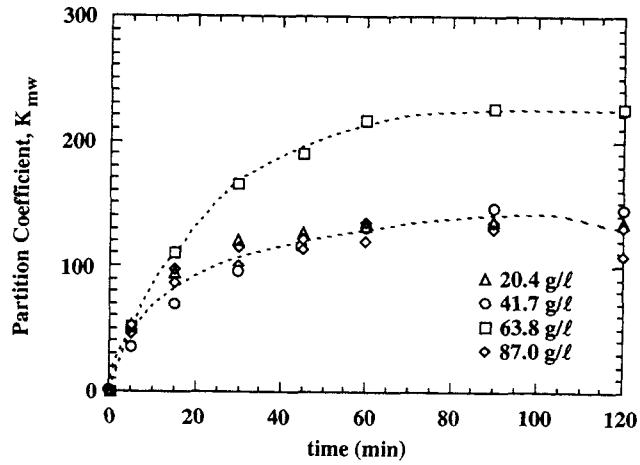

Figure 7. Partition coefficients based on block copolymer concentration, for T1307 surfactant in 52.5 g/L alginate gel beads.

factant is smaller than the other four surfactants considered, but has 70% of the molecule composed of polypropylene oxide. The remarkably high solubility of naphthalene in gels containing this surfactant is manifested by the results in Figure 6. After two hours the concentration ratio has reached $c^{gel}_{naph}/c^{aq}_{naph} = 33$ with 63.8 g/L surfactant, and the gel concentration continues to rise to a maximum ratio of 37 after four hours. Note that T1307 and P123, the two block copolymers that exhibit the highest level of partitioning, are also the two surfactants with the largest molecular weights of the hydrophobic portion of the molecule.

Effect of surfactant concentration

Figures 2 to 6 show a clear surfactant-concentration dependence for solute partitioning into surfactant/gels. For the five different surfactants utilized, the extent of partitioning into the gel increased with increasing surfactant concentrations for concentrations between 20.4 and 63.8 g/L. With the exception of the results for P87, gels containing 87.0 g/L surfactant did not perform as well as gels with 63.8 g/L surfactant. Further, for 87.0 g/L surfactant gels, values for $c^{gel}_{naph}/c^{aq}_{naph}$ generally reach a maximum value at some point within the two hour experiment, after which time this concentration ratio starts to decline.

In the study of solute partitioning into micellar aggregates, it is customary to calculate a partition coefficient based on the amount of surfactant, rather than on the entire micellar phase. This calculation allows one to consider the micelle as a "pseudophase," into which the solute partitions from the aqueous external phase. Along these lines, we define a nonequilibrium pseudo partition coefficient:

$$K_{mw} = \frac{c^{gel}_{naph}/c^{aq}_{naph}}{c^{gel}_{surf}} \qquad (2)$$

in which the concentration within the gel is normalized by the amount of surfactant within the gel. The calculated values for K_{mw} for the two surfactants T1307 and P123 are shown in Figures 7 and 8, respectively. Many of the data points for the T1307-containing gels collapse upon a single curve, indicating

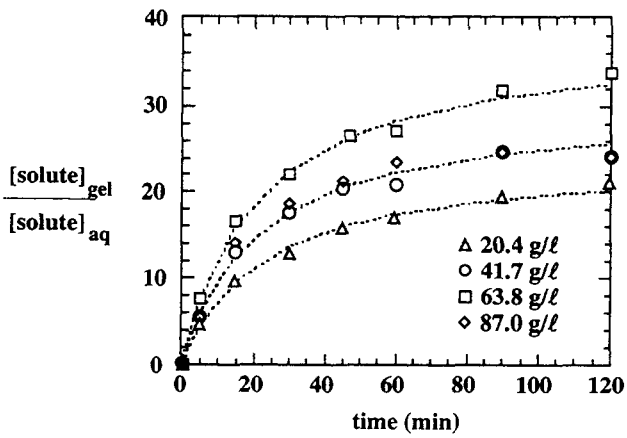

Figure 6. Concentration ratio inside and outside the gel bead for the surfactant P123 at four surfactant concentrations in 52.5 g/L alginate gel beads.

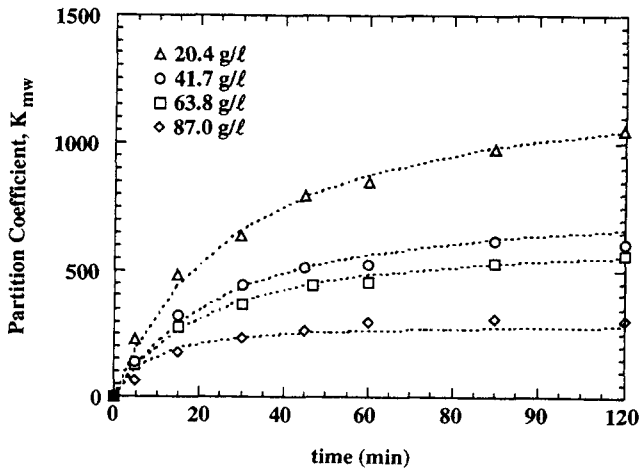

Figure 8. Partition coefficients based on block copolymer concentration, for P123 surfactant in 52.5 g/L alginate gel beads.

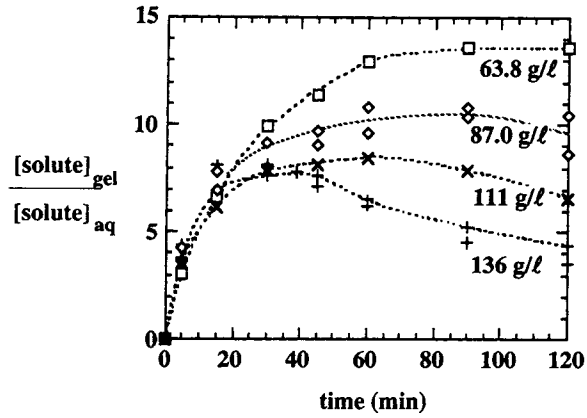

Figure 9. Concentration ratio inside and outside the gel bead for the surfactant T1307 at higher concentrations of surfactant in 52.5 g/L alginate gel beads.

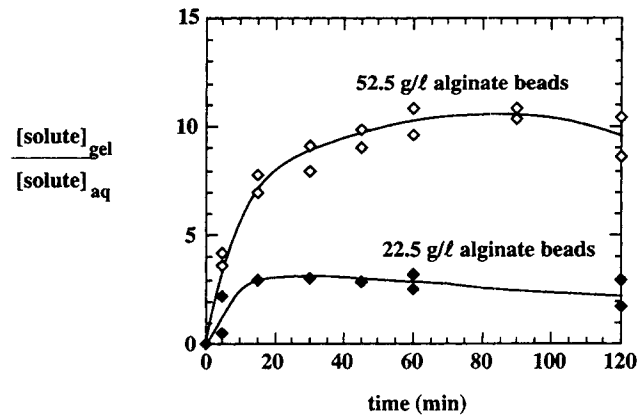

Figure 10. Concentration ratio inside and outside the gel bead for the surfactant T1307 at different alginate concentrations.

87.0 g/L of surfactant was incorporated within the alginate gel beads.

that for those concentrations and times, the solubility of naphthalene within the gel is directly proportional to the amount of surfactant present within the gel. The data at 63.8 g/L surfactant concentration does not follow such a proportional relationship, however, and manifests enhanced solubility relative to the amount of surfactant added. On the other hand, the K_{mw} values obtained from the data for the P123 surfactant/gels clearly do not collapse upon a single curve. Instead, as more surfactant is added, there is an actual decrease in gel solubility relative to the concentration of surfactant present. That is, additional surfactant appears less efficacious in solubilizing naphthalene for gels containing P123.

In examining the effect of surfactant concentration on naphthalene solubilization within gels, it is necessary to consider the anomalous solubilization behavior observed at concentrations of 87.0 g/L as mentioned above. We believe that the initial rise and then decline in the ratio of solute inside and outside the gel is caused by some diffusion of surfactant out of the gel matrix and into the surrounding solution. Such diffusion would tend towards equalizing the surfactant concentrations inside and outside the gel, and hence drive the ratio $c^{gel}_{naph}/c^{aq}_{naph}$ back towards unity. This effect is most apparent in the surfactant systems with low naphthalene solubilizing capabilities (T908, P87, and P88), with decreases at longer times seen over a range of surfactant concentrations.

The effect is also present in the T1307-containing gels, although only at 87.0 g/L surfactant concentrations. In order to explore this surfactant diffusion phenomenon further we also carried out extraction experiments at 111 and 136 g/L. Figure 9 indicates that the extent of surfactant diffusion and accompanying decrease in naphthalene concentration is augmented as we increase the surfactant concentration above 87.0 g/L. This augmentation appears to be larger than would be expected from the larger surfactant concentration gradient at those concentrations.

Finally, we note that no effect of surfactant diffusion out of the gels was observed in the gels containing P123 surfactant. Although the solubilization of naphthalene is lower at 87.0 g/L surfactant concentration relative to that at 63.8 g/L, we do not perceive any decline in the ratio at longer times. Indeed, the steady-state concentration of naphthalene in these systems was observed to remain constant over at least 24 hours.

Effect of gel concentration

To explore the ramifications of surfactant diffusion further, we measured the uptake of naphthalene by surfactant-containing gels for two different gel concentrations. In Figure 10 we show the ratio of naphthalene concentration inside to that outside the gel at alginate concentrations of 22.5 and 52.5 g/L. Both gels contain T1307 surfactant at a concentration of 87.0 g/L. The figure clearly indicates improved solubilization in the more concentrated gel, with a threefold increase in the concentration ratio and an apparent delay in the effects of surfactant diffusion.

Discussion

Results from Figures 2 and 6 clearly demonstrate the efficacy of using gels laden with block copolymer surfactant for the extraction of hydrophobic solutes such as naphthalene. Alginate gels containing the Tetronic 1307 copolymer are capable of concentrating naphthalene up to fourteen times over the aqueous concentration, and concentrations up to thirty-seven times the aqueous concentration are achieved using the Pluronic 123 copolymer. Even with the relatively inefficient contacting used in these preliminary experiments, 99.9% of the naphthalene could be removed by simply treating the solution once more in the case of P123 gels, and twice more in the case of T1307 gels. The concentrated naphthalene is retained by the surfactant within the gel for further treatment, such as incorporation in a reactor for the destruction of the solute, or contacting the beads with an organic or supercritical fluid stripping solvent. Breaking down the gel for removal of the solute is also a possibility.

Similarly, our results indicate that hydrophobic pharmaceuticals could readily be incorporated in very high concentrations within the alginate gel beads. Here the drugs could remain until the gel is destroyed, or until the solute diffuses out. Under certain conditions we have observed the gradual release of some of the surfactant—with accompanying solute—from the gel matrix, and these conditions can be further explored to enable us to control carefully the rate of solute release.

Large variations were observed between different types of block copolymer surfactants in terms of their ability to extract naphthalene from aqueous solution. There was a distinct and qualitative difference in the performance of the T1307 and P123 surfactants, as compared to the other three types of surfactants used (P87, P88, and T908). The latter three surfactants solubilized comparable amounts of solute, achieving maximum concentration ratios of close to two in all three cases, despite the considerable variation in their structure, size, and hydrophobicity. In contrast, T1307 and P123 achieved an order of magnitude higher concentration factors. This qualitatively different solubilization behavior for the two groups of surfactants suggests that they take on distinctly different forms within the gel, and that the poorly performing copolymers do not aggregate into micelles or any other self-organizing structure within the gel. The slightly enhanced solubility of naphthalene in gels containing P87, P88, and T908 would in that case be related to the presence of monomeric surfactants within the gel, which may allow some binding of solute (or incorporation into monomolecular micelles (Zhou and Chu, 1988)). The surfactants T1307 and P123, on the other hand, could be forming micelles or other aggregates within the gel, hence allowing them to take up greater quantities of solute.

The hypothesis that only P123 and T1307 are forming surfactant aggregates within the gel matrix is supported by data for block copolymer aggregates in free aqueous solution. As noted above, there is considerable debate in the literature as to critical micelle concentrations (cmc) for these block copolymers, with reported values ranging over orders of magnitude. However, the literature values show a clear difference in micelle-forming properties between the three Pluronic polymers. Critical micelle concentration values for P123 at room temperature are reported to be quite low, with values ranging between 1.5×10^{-2} g/L (Wanka et al., 1990) and 1.0×10^{-1} g/L (Alexandridis et al., 1993). Critical concentrations for P87 and P88 appear to be much higher, with values of 60 g/L (Al-Saden et al., 1982) and 99 g/L (Alexandridis et al., 1993) quoted for P87 and P88, respectively. Unfortunately, little work has been done to investigate the micelle properties of the branched Tetronic polymers, but Hurter and Hatton (1992) found that aqueous solutions of T1307 were able to solubilize large quantities of naphthalene at room temperature. The authors felt this solubilization behavior was consistent with the formation of T1307 micelles at the concentrations they used (>20 g/L). Thus it is likely that P123 and T1307 do indeed form micelles in aqueous solutions at room temperature, whereas P87, P88, and T908 do not. Qualitatively similar micelle-forming properties for these surfactants when incorporated within alginate gels would explain the dramatic differences in naphthalene solubilizing properties in Figures 2 to 6.

The solubility of naphthalene in aqueous solutions of P123 and T1307 was studied by Hurter and Hatton (1992), and it is interesting to compare their results with our solubilization experiments using the surfactant/gel materials. Based on the weight of polymer in solution, their partition coefficients K_{mw} measured in aqueous solution were 550 and 2,200 for T1307 and P123, respectively, and remained approximately constant over a concentration range of 0 to 87 g/L. Some increase in K_{mw} was observed for solutions of T1307, with about a 30% increase in partition coefficient between concentrations of 10 and 79 g/L.

In our micelle/gel studies, the maximum value measured for T1307 in a gel is $K_{mw}=225$, and for P123 is $K_{mw}=1{,}140$. These values for the gel systems are therefore approximately a factor of two smaller than those measured in solution. However, it is important to note that the coefficients measured by Hurter and Hatton (1992) were carried out on micellar solutions saturated with naphthalene. Hence, the naphthalene concentration in their experiments are orders of magnitude above the aqueous solubility of naphthalene, and are at the maximum value obtainable in a micellar solution. In contrast, our measurements determined partitioning into a micellar phase for which the total naphthalene concentration was at or lower than the aqueous solubility of naphthalene. The number of naphthalene molecules per micelle in the two experiments may therefore differ by two orders of magnitude, and may indeed affect the thermodynamics of partitioning. In addition, the nature of the surfactant/gel material means that our measured coefficients may not represent equilibrium concentration ratios, as they do in the study by Hurter and Hatton (1992). Thus, considering the differences in the way these partition coefficients are measured, the partitioning behavior of the micelles in solution and those entrapped in gels are reasonably similar.

The partition coefficients measured for T1307 and P123 block copolymers within a gel were in general not constant as we changed surfactant concentration. The marked dependence of partitioning behavior on the concentration of surfactant added to the gel is remarkable, particularly when contrasted with fairly concentration-independent results found in aqueous solutions alone (Hurter and Hatton, 1992). A value of K_{mw} that is independent of surfactant concentration is consistent with the notion of a micelle solution whose size and structure is independent of surfactant concentration. Hence adding more surfactant to such a solution merely increases the number of micelles present, and therefore increases the naphthalene solubility to a proportional extent. Variation in K_{mw} with surfactant concentration, conversely, suggests that there are structural changes in the micelle as concentration increases, as also noted by Hurter and Hatton (1992). Such changes, if significant enough, can include size and shape changes, which will therefore alter the thermodynamics of solubilization. It appears from the results of Figures 7 and 8 that such structural transformations may be occurring to a significant extent when surfactant aggregates are trapped within gels, particularly in the case of P123 copolymer surfactants. It therefore appears quite possible that the presence of the gel matrix may influence the structure of surfactant aggregates such as micelles forming within its interstices.

The effect of surfactant diffusion on naphthalene concentrations in some of the gels also raises some interesting questions about interactions between the surfactant and the surrounding gel matrix. In gels formed using T1307 surfactant, surfactant diffusion is not observed until the surfactant concentration reaches 87.0 g/L. The rate of surfactant diffusion appears to increase as surfactant concentration increases above 87.0 g/L (Figure 9), even if the concentration ratios shown in that figure are renormalized by surfactant concentration. This concentration effect on surfactant diffusion suggests: (a) that interactions between surfactant molecules, enhanced at higher concentrations, lead to more rapid diffusion; (b) that interactions between the surfactant and the polymer (either attractive or repulsive) change with surfactant concentration and

facilitate diffusion above 87.0 g/L surfactant; or (c) that higher concentrations of surfactant alter the pore structure of the alginate gel, allowing faster surfactant diffusion. The latter two possibilities gain support from the fact that no surfactant diffusion was observed in the P123-containing gels. We found this result quite remarkable, given the much smaller size of the linear P123 molecule relative to the branched T1307 surfactant. The ability of the alginate matrix to retain so completely the smallest of the surfactants we studied suggests that interactions other than steric ones must play an important role in these surfactant/gel systems.

The presence and nature of surfactant/gel interactions will provide an intriguing new area of study. As mentioned in the introduction, relatively little is known about interactions between micelle-forming surfactants and polymeric gels, nor about nonionic surfactant interactions with acidic polymers. Existing studies focus on low molecular weight surfactants (Johansson et al., 1993; Penders et al., 1993), leaving considerable work to be done on the interaction of quite large amphiphilic block copolymers with the strands of a gel matrix. The promising ability of the more hydrophobic block copolymers, contained within a gel, to extract aromatic hydrocarbons from water provides strong motivation for further interest in understanding surfactant/gel interactions.

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Notation

c_o = initial aqueous concentration of naphthalene
c_{naph}^{aq} = concentration of naphthalene in the aqueous phase external to the gel beads
c_{naph}^{gel} = concentration of naphthalene in the gel beads
c_{surf}^{gel} = concentration of block copolymer surfactant in the gel beads
K_{mw} = nonequilibrium partition coefficient based on the weight of surfactant within the gel

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