

SOLUBILIZATION OF TRACE ORGANICS IN BLOCK COPOLYMER MICELLES FOR  
ENVIRONMENTAL SEPARATION USING MEMBRANE EXTRACTION PRINCIPLES

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## ABSTRACT

The solubilization of a range of polycyclic aromatic hydrocarbons in block copolymer micelles has been studied as a function of polymer composition, architecture, and temperature. Micelle formation is favored at high temperatures, leading to significant enhancements in solubilization capacity. At low temperatures, however, micelles do not form and the solubilization capacity of the block copolymer solution for the organics is low; this provides a convenient method for the regeneration of micellar solutions used as "solvents" in the treatment of contaminated feed streams using membrane extraction principles. Other experiments and analysis point to the effectiveness of block copolymer micellar solutions as water-based absorbents for the removal of trace organics from air streams.

Theoretical calculations of the structure of block copolymer micelles in the presence and absence of solutes using self-consistent mean-field lattice theories and lattice Monte Carlo methods have successfully captured the trends observed with changing polymer composition and architecture, often quantitatively. The temperature and composition dependence of the micellar properties were determined by allowing the individual polymer segments to assume both polar and non-polar conformations.

## INTRODUCTION

Pollution of the nation's harbors, waterways and groundwater resources owing to urban runoffs, waste disposal policies and industrial and domestic effluents has reached critical proportions, and poses many serious environmental, health and economic problems. Among the more ubiquitous pollutants are the polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and heavy metal ions. The increasing awareness of the need to address these problems has focused attention on the need to identify effective and energy-efficient means for the removal of toxic substances from water resources and industrial effluents. A novel approach to this problem was investigated in this research project.

Two large-scale processes that can be used for treatment of contaminated aqueous sources are solvent extraction and activated carbon adsorption. Solvent extraction relies on the strong partitioning of solutes towards a water-immiscible solvent phase for removal and concentration of the contaminant. A drawback of this technology is the problems associated with solvent losses caused by the finite, albeit very small, solubility of traditional solvents in water, and because of the invariable entrainment of finely dispersed solvent droplets by the water leaving the extractor. Indeed, countercontamination of the water feed by the solvent may pose as severe a problem as that being treated. Adsorption using activated carbon and other adsorbents could be considered. However, the materials handling characteristics are such that fixed bed processes may not be favourable because of the sheer bulk of the materials to be treated, the high costs associated with pumping the water through the beds, and the energy-intensive adsorbent regeneration.

The work undertaken in the present project was to develop and characterise a novel concept for the removal of trace contaminants from aqueous solutions with specific applications in environmental technology. This approach, which exploits the strong power of micelles coupled with membrane extraction principles, could minimize the limitations inherent in solvent extraction and adsorption processes, and could be effective in large-scale reduction of contaminants in water sources.

## CONCEPT

Block copolymers are high molecular weight polymers having two or more distinct regions of differing properties. If one or more of these blocks is hydrophilic while the remaining blocks are hydrophobic, then under certain conditions the molecules will begin to aggregate to form structures, often spherical, in which the hydrophobic blocks cluster together within a non-polar hydrocarbon-like core. The core is protected from the more polar solvent by the hydrophilic blocks, which extend into the surrounding aqueous solvent forming a corona around the micelle interior. The copolymer concentration at which this occurs is identified as the critical micelle concentration, or CMC. In some cases, polymers begin to form micelles only at certain temperatures, known as the critical micelle temperature, or CMT. The number of copolymer molecules participating in one of these micelles is known as the aggregation number, and is typically on the order of 20 to 100.

The non-polar cores of these micelles can take up significant quantities of hydrophobic solutes, the solubilization efficiency being dependent on the relative sizes of the lyophilic and lyophobic blocks, and on the overall block copolymer molecular weight. We have investigated the possibility of exploiting the unusually high capacity of block copolymer micelles for aromatic hydrocarbons in the development of an effective way to remove trace contaminants from aqueous waste streams and contaminated sources. In particular, we have contacted aqueous solutions to be decontaminated with high concentrations of the block copolymers, and have relied on the strong partitioning of the hydrophobic solutes to the non-polar cores of the micelles for the removal of the contaminants from the water feed. This permits the contaminants to be concentrated significantly to facilitate their subsequent disposal.

The micelles are supramolecular aggregates dissolved in an aqueous solution that is completely miscible with the water to be treated. To overcome this obvious problem, the solution was prevented from mixing with bulk water feed by retention within the lumens of hollow fiber membranes of sufficiently low molecular weight cut-off that even the individual polymer molecules themselves did not pass through the membrane pores (conventional surfactant micelles are not considered suitable for this application, because the monomers with which they are in equilibrium would be lost through the membranes to the feed stream). The membrane is permeable to the solutes, which are able to transfer from the solution external to the hollow fibers to the micellar solution, where they are solubilized by, and concentrated within the micelles. The high capacity of the micelles for the organic solutes ensures that the driving force for mass transfer is high, and that the water phase concentrations can be reduced significantly with only a small "volume" of the solvent phase relative to the bulk volume of water being treated. The large interfacial areas for the efficient contacting of the micellar solution with the water feed can be achieved readily using hollow fiber membrane modules.

Once the micelles are laden with solute, they are processed to regenerate the "solvent" (i.e., the block copolymer solution) phase by removing the extracted organic compounds. We discuss in this report several possible ways to go about accomplishing this step.

## EXPERIMENTAL

**Partitioning Experiments:** Saturated micellar solutions of polycyclic aromatic hydrocarbons were prepared using the generating column technique in which the polymer solution was pumped continuously through a generating column packed with solute crystals or flakes. A small stream of the polymer solution was diverted to a continuous flow spectrophotometer cell after passing through the generating column. Flow cells with path lengths of 0.01 mm and 0.1 mm were used to maintain the level of absorbance below unity. The absorbance was measured on a Lambda 3B UV/VIS Spectrophotometer at the wavelength of maximum absorbance for pyrene, 272 nm.

The generating column and the reservoir containing the polymer solution were immersed in a constant temperature water bath, monitored by a CH/P temperature control system circulator. To maintain accurate temperature control throughout the system, tubing leading to and from the pump and to the spectrophotometer was insulated. The temperature of the polymer solution was recorded using a thermometer in the solution reservoir.

Once equilibrium was reached at the desired temperature, a small sample of the polymer solution was taken and analyzed on a Waters 410 Differential Refractometer to determine polymer concentration. The refractometer was connected to a Shimadzu CR3A integrator which measured both the area and height of the peak. The temperature control system was then adjusted to raise the temperature of the water bath and the process was repeated for a select temperature range for each of the polymer solutions. At the conclusion of each experiment, temperature was decreased to its initial value. When equilibrium was reached the pyrene and polymer concentrations were measured. Three block copolymers were tested at three different concentrations.

With benzene or toluene, saturated aqueous solutions in equilibrium with the bulk organic liquids were cloudy, owing to the formation of large microemulsion drops stabilized by the polymeric surfactants; some of the polymer was also lost to the organic phase. In an attempt to overcome this limitation, head-space gas chromatography was used to estimate the partition coefficient between the micelle core and the water phase as a function of the solute concentration.

**Membrane Extraction Experiments:** Two different techniques were used to explore the feasibility of using the membrane extraction concept for the removal of organic solutes from aqueous streams. For the heavier aromatics such as naphthalene, we circulated the feed stream over naphthalene flakes to ensure it was saturated and then extracted the naphthalene in a membrane extractor using block copolymer micellar solutions as the extractant. The feed phase concentration was maintained at saturation levels, while the increasing concentration in the recirculated polymer phase was monitored. For toluene, this was not a feasible route, as the micelles would grow indefinitely to form emulsions. In this case, an aqueous feed phase was spiked with toluene at the beginning of the experiment, and the feed and extractant phases were circulated continuously through the shell and lumen sides of the hollow fiber membrane unit, respectively. The concentrations were measured on-line using UV spectrophotometry.

**Gas Absorption Experiments:** Attempts were made to use the hollow fiber modules for gas absorption experiments, but the wetting of the membrane pores by the block copolymer surfactants resulted in unstable operation with breakthrough of the water phase to the gas side of the membrane. Consequently, laboratory-scale packed bed gas absorption experiments were performed using a 0.75 in ID vacuum jacketed column (provided by Artisan Industries, Waltham, MA) filled with 29 cm of Goodlow® packing (provided by Otto York Inc., Parsippany, NJ). The total scrubber volume was 225 ml, with a contact surface area of  $1920 \text{ m}^2/\text{m}^3$  for interphase mass transfer. Nitrogen was bubbled through liquid toluene to produce the feed gas, a small fraction of which was sent for toluene concentration measurement to a gas chromatograph (GC) equipped with gas sampling valves. The scrubbed nitrogen exited the column at the top where a fraction of

the stream was sent to the GC for analysis. The liquid feed was pumped through the reference UV spectrophotometer cell through a flowmeter and into the top of the column where the feed flowed downward by gravity. A portion of the liquid effluent was pumped through the sample flowcell to measure the VOC concentration using UV spectrophotometry.

## RESULTS AND DISCUSSION

The polymers used in this study are listed in Table 1, together with their physical properties.

### Thermodynamics

The critical micellization temperature (CMT) and critical micellization concentration (CMC) values of twelve PEO-PPO-PEO block copolymers, covering a wide range of molecular weights (2900 to 14600 Da) and PPO/PEO ratios (0.19 to 1.79), have been determined employing a dye solubilization method. Copolymers with a larger hydrophobic (PPO) domain formed micelles at lower concentrations, or, for a given copolymer concentration, have lower CMTs. For groups with the same PPO/PEO ratio, copolymers of higher molecular weight form micelles more readily, e.g. at lower concentrations and temperatures. The hydrophilic group appears to play a smaller role in the micellization process.

In general, micellization of block copolymers, as in the case of conventional detergents, obeys the closed association model, which assumes an equilibrium between molecularly dispersed copolymer (unimer) and multimolecular aggregates (micelles). The standard free energy change for the transfer of one mole of amphiphile from solution to the micellar phase (free energy of micellization),  $\Delta G^\circ$ , in the absence of electrostatic interactions (nonionic surfactants) is given by

$$\Delta G^\circ = R T \ln (X_{\text{cmc}}) \quad (1)$$

where  $R$  is the gas law constant,  $T$  the absolute temperature, and  $X_{\text{cmc}}$  is the critical micellization concentration in mole fraction units. Applying the Gibbs-Helmholtz equation we can express the standard enthalpy of micellization,  $\Delta H^\circ$ , as

$$\Delta H^\circ = R [ \partial \ln(X_{\text{cmc}}) / \partial (1/T) ]_p = R [ \partial \ln(X) / \partial (1/T_{\text{cm}}) ]_p \quad (2)$$

where  $X$  is the concentration expressed as mole fraction, and  $T_{\text{cm}}$  the critical micellization temperature. The inverse CMT values were plotted as a function of the logarithm of copolymer concentration for a number of copolymers (Figure 1), in accordance with equation (2). The CMT data, plotted in this manner, are generally described well by a straight line; we consequently employed the closed association model for estimating  $\Delta H^\circ$  (from the slopes in Figure 1) and  $\Delta S^\circ$  of the micellization process. The standard enthalpy of micellization,  $\Delta H^\circ$ , is positive, indicating that the transfer of unimers from solution to the micelle is an enthalpically unfavorable endothermic process. The free energy,  $\Delta G^\circ$ , is negative, since thermodynamically stable micelles are formed spontaneously. Thus it is clear that a negative entropy contribution must be the driving force for micellization of the block copolymers. In contrast to the entropy-driven micellization in water, the micellization of copolymers in nonpolar solvents originates from enthalpy interactions between the copolymer segments and the solvent.

Free energies of micellization, normalized with respect to the total number of monomer units in the polymer,  $N_{\text{eo}} + N_{\text{po}}$  and calculated at the critical micellization temperatures for the various copolymers at different solution concentrations, are shown as a function of Pluronic molecular weight in Figure 2. It can be seen clearly that the lower molecular weight, more hydrophobic Pluronics correspond to more negative  $\Delta G^\circ$  per monomer unit values. The normalization of the data in this fashion enables the composition ratio effects to be decoupled from the effects of overall molecular weight and copolymer concentration on the micellization process. The unfavorable entropic effects associated with the localization of the polymers within the micelles could be reflected in the molecular weight dependency, as the absolute value of the free energy per monomer becomes smaller with increasing polymer molecular weight. To further probe the origin of micelle formation in Pluronic copolymer solutions, the dependence of the thermodynamic

parameters  $\Delta H^\circ$  and  $\Delta G^\circ$  on the PPO/PEO ratio was examined. Figure 3 shows that the normalized  $\Delta H^\circ$  (expressed in kJ per mole of average monomer unit) approaches zero as the PPO/PEO ratio goes to zero. It can thus be inferred that the micellization process is dominated by the PPO (hydrophobic) part of the copolymer. A plot of  $\Delta G^\circ$  of micellization (expressed in kJ per mole of average monomer unit) as a function of PPO/PEO (plot not shown), again shows the  $\Delta G^\circ/\text{unit}$  values approaching zero as the PPO/PEO ratio goes to zero. The unit free energy, however, decreases (becomes more negative) with decrease in molecular weight for Pluronics with a constant PPO/PEO ratio.

### Micropolarity of micelle core

The  $I_1/I_2$  intensity ratio of the pyrene vibrational fine structure is an attractive spectroscopic tool which has been widely used to study micellar solution properties. Many studies focused on the variation of  $I_1/I_2$  with surfactant concentration but little is known about its temperature dependence. We conducted a systematic investigation of  $I_1/I_2$  as a function of temperature in PEO-PPO-PEO copolymer aqueous solutions, water, and PEO, PPO homopolymers. As shown in Figure 4, the ratio decreases linearly with temperature for water and homopolymers, with slope characteristic of the system studied. For P104 and F108 copolymer solutions a sharp decrease in  $I_1/I_2$  was observed at the CMT, as pyrene partitioned in the hydrophobic (PPO) core of the micelles; a smoother linear decrease was observed after the CMT. The composition of the micelle core can be estimated assuming that the  $I_1/I_2$  ratio in copolymer solutions after the CMT is a linear combination of the ratios observed in pure water and homopolymers. This led to PPO:PEO:H<sub>2</sub>O = 76:24:0 for P104, and 68:28:4 for F108, indicating a decrease of PPO and increase in water in the micelle core as the copolymer becomes more hydrophilic.

### Solubilization of Aromatics

The enhanced solubility of pyrene in P104 with changes in temperature is shown in Figure 5. At low temperatures, there was effectively no enhancement in solubility. Above some transition temperature, there was a rapid increase in enhancement over a short temperature range, followed by a third regime in which the increase in solubility became less significant. This second transition temperature increased with decreasing polymer concentration, being 28.2, 27.5 and 24.1°C for the 1%, 4% and 8% solutions, respectively. The increase in solubility at higher temperatures was predominantly a result of an increase in the water solubility of pyrene. Figure 6 shows the solubility of pyrene in the polymer solution normalized by its solubility in water. Above the transition temperature the normalized concentration of pyrene was independent of temperature, which indicates a constant partition coefficient for the solute between the micelle core and the bulk water.

The solubilizing behavior of the P104 solution as temperature increases can be attributed to the enhanced tendency of the polymer to aggregate and form micelles, which grow in size as water becomes a poorer solvent for PPO and PEO. Below the first transition temperature, the polymer has not yet become sufficiently hydrophobic for micelle growth to occur, and thus the solubilisation of pyrene is not enhanced. Above the second transition temperature, the micelle size (aggregation number) remains constant, and provides an effectively unchanging environment for the solute, leading to a constant partition coefficient in this regime. The strong changes observed in solubility enhancement in the intermediate region are a result of the rapid growth of the micelles in this region.

Similar behavior was observed for aqueous solutions of F108 and L64. For F108, regions of micellar growth and constant micellar size were observed for both 4 and 7% solutions, the transition temperature decreasing from 34.3 to 31.7°C with the increase in polymer concentration. A transition temperature was not observed for the 1% solution of F108 within the range of the experiments; it is possibly above 40°C. The normalized pyrene solubility curve showed micellar saturation for both the 4% and 7% solutions above their transition temperatures. A uniform increase in solubilization of pyrene with temperature for L64 was observed, which suggests that this copolymer exhibits only the two regions of no micellar formation and micellar growth, respectively, no transition from micellar growth to constant micelle size being observed for any concentration in the temperature range of the experiments. The micelles formed with L64 never showed a region in which the pyrene partition coefficient was constant at any of the concentrations studied.

Figure 7 compares the solubility of pyrene in 8% solutions of P104, F108 and L64 at various temperatures. The P104 solution demonstrated the greatest solubilization of pyrene with a maximum  $C/C_{sat}$  of approximately 6600. The maximum solubility of pyrene in F108 was significantly lower at 1200, while the L64 micelles did not reach a maximum level of pyrene solubilization. P104 both has a higher molecular weight and is more hydrophobic than either L64 and F108, and therefore solubilized the most pyrene. Partition coefficients were calculated for the three polymers and are reported in table 2, where

$$K_{mw} = c_m^s / c_w^s$$

and  $c_m^s$  and  $c_w^s$  are the concentrations of pyrene in the micelle (based on total polymer mass) and in the water, respectively. The  $K_{mw}$  was determined from the slope of the plot of pyrene solubility vs. polymer concentration. The  $K_{mw}$  at 40°C for L64 was approximately half that of P104, while the  $K_{mw}$  for F108 was lower by a factor of almost 5.

The effect of solute on partitioning can be explored by a comparison to the results of the naphthalene partitioning experiments. Solubilization was more greatly enhanced for pyrene than for naphthalene. The maximum pyrene solubility ( $C/C_{sat}$ ) was 6600 for a 8% solution of P104, while the naphthalene solubility enhancement was 200 in a 10% P104 solution. This increased solubilization was expected since the two additional benzene rings in pyrene cause it to have a lower aqueous solubility and higher hydrophobicity than naphthalene. We have established that

$$\log K_{mw} \propto \log K_{ow}$$

where  $K_{ow}$  is the octanol/water partition coefficient for the solute and is generally used as a measure of hydrophobicity. The results from the pyrene temperature experiments are consistent with this relationship. Although solubility enhancement is greater, the solute load in the micelle (g solute/g polymer) is less for pyrene. The micelle load was 0.015 g pyrene/g P104 and 0.1 g naphthalene/g P104.

The L64 solubility curve has a lower position relative to the P104 and F108 curves for pyrene than naphthalene, indicating that L64 has a lower potential for solubilizing pyrene than naphthalene relative to P104 and F108. This difference is most likely due to the low molecular weight of L64. Since pyrene is a larger molecule than naphthalene, the smaller hydrophobic core of L64 may hinder the solubilization of pyrene over naphthalene (the PPO molecular weight for L64 is half that of P104 and F108).

### Membrane Extraction Experiments

The early membrane extraction experiments were carried out by maintaining a saturated feed naphthalene solution, and following the change in naphthalene concentration in the copolymer solution as it was circulated through the membrane unit. Such an approach could not be used effectively with solutes such as toluene, as the high concentrations in solution led to membrane deterioration and failure. In later runs, we spiked the feed solution at the beginning of the run, and monitored the solute concentrations in both the feed and the copolymer solutions as a function of time. From these results, we were able to infer suitable values for the overall mass transfer coefficients, as indicated in Figure 8. These experiments were not without their ambiguities, however. Shown in Figure 9 are the concentrations in the two phases as a function of time. Also shown is the sum of these two concentrations, which, because the flow rates were equal, should have been constant over time. We note, however, that this was not the case, there being an initial drop in this total concentration early in the extraction process, followed by an increase at the later times. This was attributed to initial adsorption of the solute on the surfaces of the extraction unit, followed by desorption as the solute was taken up by the polymer solution. This points to the difficulty in performing precise experiments using hydrophobic solutes - in most cases, however, the concentration deviations were not more than ten to fifteen percent. The partition coefficients for toluene estimated from the final concentrations in the two streams are shown as a function of the polymer concentration in Figure 10. From these results we can estimate the micelle-water partition coefficient to be about 130; this value is in agreement with predictions afforded by the correlation of PAH partition coefficients with the octanol/water partition coefficient reported earlier.

### Gas Absorption Results

Continuous countercurrent gas absorption experiments at 25°C with water and with aqueous Pluronic® solutions showed significant differences in the steady state toluene removal, as shown in Figure 11. For water, and 2% P104, 5% P104 and 5% P123 solutions, the steady state toluene removal efficiencies were  $29\pm0.7\%$ ,  $60\pm1.8\%$ ,  $72\pm3.1\%$ , and  $75\pm1.1\%$ . respectively. The small difference between the 5% P104 and P123 solution absorption efficiencies belies the large differences in their solubilization capacities owing to the more hydrophobic character of the P123 copolymer. This is attributed to the increasing importance of the gas-side resistance to mass transfer as the partitioning to the liquid phase grows stronger. The overall gas-side mass transfer coefficients were calculated to address this issue. The results are shown in Figure 12 as a function of the Henry's law constant obtained from headspace chromatography measurements. From these results it is apparent that for the higher removal rates the gas side mass transfer is limiting.

### Stripping Experiments

The countercurrent air stripping at 25°C of toluene from P104 solutions demonstrated strongly the effect of micelles on stripping effectiveness. The percent toluene removal rates were  $40\pm2.6\%$ ,  $53\pm0.6\%$  and  $67\pm3.5\%$  for 2%, 1% and 0.5% P104 solutions respectively, while that for water was  $68\pm3.3\%$ . In the first two solutions (2% and 1%), micelles are known to be present, while the 0.5% P104 solution is below the CMC at the temperature of the experiment. Thus, the presence of micelles inhibits the stripping of the solute from the aqueous solution, as expected, while the in the absence of micelles, there is no effect of the polymer on the solute removal efficiency relative to that for removal from water. Clearly, it is important when attempting to remove solute by stripping from the aqueous block copolymer solution that the temperature be below the CMT to ensure the highest possible solute activity in the liquid phase.

### Solution Regeneration

For naphthalene and pyrene solubilized in all polymers, precipitates were observed upon cooling the solution and the maximum absorbance corresponded with that measured as temperature was increased. The polymer concentration was also consistent with that measured throughout each experiment. These results indicate that the polymer can be regenerated by cooling the solution to a

temperature at which micelle formation is not observed. At this temperature, naphthalene or pyrene solubility is low, causing the additional solute released on break-up of the micelles to precipitate out of solution. Furthermore, the solid solute can be easily removed so that the polymer solution can be reused. Not all block copolymers will exhibit this behaviour, however; some may be able to be regenerated by increases in temperature, while if polyampholytic polymers are used, changes in pH may be effective for the recovery and recycle of the polymers.

The loaded micellar solution can be contacted with a low molecular weight solvent having a high capacity for the solutes to remove the contaminating species. Any residual solvent left with the micellar phase can then be flashed off before the micelles are recycled. In collaboration with Professor K.P. Johnston at the University of Texas, we have shown that supercritical  $\text{CO}_2$  can be used effectively for micellar regeneration. Shown in Figure 13 are the extraction efficiencies for a single stage as a function of pressure. Approximately 85-90% of the naphthalene was removed in this operation, which is sufficient for the regeneration and recycling of the solvent phase. In practical applications it may be advantageous to first ultrafilter the micellar solution to remove much of the suspending water to reduce the volume of aqueous micellar solution to be regenerated.

More volatile species, such as toluene and styrene, have higher solubilities in water than the polycyclic aromatic hydrocarbons, and the only effect of the break-up of the micelles on cooling may be to cause their activity in the water phase to increase by a factor equivalent to the solubility enhancement afforded by the micelles. In this case,

## THEORETICAL

The Scheutjens-Fleer theory is an extension of the Flory-Huggins analysis of homogeneous polymer solutions in which the polymer chains are allowed to assume different conformations on a lattice. In the Flory-Huggins analysis, a first-order Markov approximation is used, so that the position of a segment depends only on that of the preceding segment in the chain, the result being that the chain conformation follows the path of a random walk. In addition, a mean field assumption is invoked to describe the interactions between unlike segments. The free energy of the system is minimized in order to calculate the equilibrium thermodynamic properties of the polymer solution.

For spatially inhomogeneous systems such as those containing interfaces, the mean field approximation can be restricted to two dimensions, i.e., within parallel or concentric lattice layers, and a step-weighted random walk applied to account for the inhomogeneities normal to the layers. The polymer and solvent molecules are assumed to be distributed over a lattice, such that solvent molecules and polymer segments occupy one lattice site each. Each polymer chain can assume a large number of possible conformations, defined by the layer numbers in which successive segments are found. There can be many different arrangements for each conformation. If the number of polymer chains in each conformation is specified, the configurational entropy contribution to the system free energy can be evaluated, the other contributions to this free energy being due to the interactions between the polymer molecules, solvent molecules and the surface, which are characterized by Flory-Huggins  $\chi$ -parameters. If the free energy of the system is minimized with respect to the number of polymer chains in each conformation, it is possible to calculate the equilibrium segment density profiles. The self consistent field theory can be used to calculate the segment density profiles in a micelle once the aggregation number of the micelle is known, for which small system thermodynamics can be used. The change in the free energy due to the change in the number of micelles (at constant temperature, pressure and number of molecules) must be zero at equilibrium. This "excess free energy" is the sum of the energy required to create micelles, and the energy due to the translational entropy of the micelles. Since the segment density profiles are required in order to calculate the energy of micelle formation, an iterative process is required.

For aggregation structures, the detailed segment density profiles are obtained, and macroscopic quantities such as the critical micelle concentration (CMC), aggregation number and micelle size can be calculated. We have extended this theory to study the formation of micelles by linear and branched, star-like amphiphilic block copolymers, and the solubilization of naphthalene in these micelles has been analyzed as a function of polymer structure, composition and molecular weight. The micellar solubilization of PAHs was investigated, by modelling the PAHs as chains of benzene molecules.

Figure 15 compares the volume fraction profiles of micelles formed by Pluronic (triblock) and Tetronic (branched) PEO-PPO copolymers. These calculations indicate that there is a finite, though small, concentration of water in the core, and that there is a diffuse interface between the core and the corona, and between the corona and the bulk solution. These effects could become particularly important when dealing with the solubilization of molecules that would favor the interfacial region. The branched Tetronic molecules are less flexible than the linear Pluronic molecules, particularly at low molecular weight. Steric hindrance in the core of the micelle leads to the Tetronic molecules forming a "looser" structure, with a higher degree of mixing of PEO and PPO segments in the core. The Tetronic micelle is also smaller than the Pluronic micelle.

Figure 16 compares the experimental results for the micelle/water partition coefficient,  $K_{mw}$ , of naphthalene solubilized in aqueous solutions of Pluronic polymers, with model predictions. The theory reproduces the experimental finding of a strong correlation between the PPO content of

the polymer and  $K_{mw}$ . As the polymer becomes more hydrophobic, the micelle-water partition coefficient increases, as expected for hydrophobic naphthalene. The molecular weight effect is reproduced qualitatively by the theory, but the experimental results show a far larger dependence of  $K_{mw}$  on polymer size. The calculations show that higher molecular weight polymers form larger micelles. The formation of larger micelles will result in a decrease in the interfacial volume compared to the core volume. If naphthalene is effectively excluded from the interfacial region, larger micelles would result in higher micelle-water partition coefficients.

Both the experimental and theoretical results show that the Tetronic polymers with a higher proportion of PPO solubilize more naphthalene, which confirms the effect demonstrated in Figure 16. Thus for both the Pluronic and Tetronic molecules, the PPO content of the polymer has a strong effect on the micelle-water partition coefficient. The theory confirms the experimental finding that naphthalene partitions more favorably into the linear Pluronic polymers than into the branched Tetronic molecules. As is illustrated in Figure 14, the Tetronic molecules form micelles with a lower concentration of PPO in the core, resulting in a less hydrophobic core environment, which would inhibit naphthalene solubilization. In addition, the Tetronic molecules form smaller micelles, which is expected to result in a lower micelle-water partition coefficient, as discussed above.

Lattice Theory for Monomers with Internal Degrees of Freedom: The simple lattice theory for flexible chain molecules cannot capture effects such as the phase behavior of poly(ethylene oxide) and poly(propylene oxide) in water, where a lower critical solution temperature is observed. To predict such behavior, the gauche and trans bond orientations of the polymer chain must be accounted for. An approach which is computationally simpler than the rotational isomeric state scheme, but which accounts for the temperature and composition dependence of the interaction parameter  $\chi$  in a physically acceptable manner recognizes that certain sequences of the gauche trans orientations in a PEO monomer will lead to a polar conformation, while others will be essentially nonpolar. Using this model, the solubility gap in PEO-W and PPO-W phase diagrams can be reproduced.

A model for solubilization in block copolymer micelles has been, which incorporates Karlstrom's model to account for the conformational distribution in PEO and PPO. Using this model, the effect of temperature and the solubilization of naphthalene on the micelle structure have been investigated, and the results compared to experimental observations. An increase in temperature caused the model-predicted aggregation number of the micelles to increase, and the critical micelle concentration (CMC) to decrease. The aggregation number increased rapidly with polymer concentration in the dilute regime, but was approximately invariant to polymer concentration at concentrations far from the CMC. Raising the PPO content or the molecular weight of the polymer increased the aggregation number, and decreased the CMC. The conformation of the polymer was affected by both the temperature and the composition of the surrounding solution; both PEO and PPO had a lower fraction of polar segments in the core of the micelles, and the polar fraction decreased with an increase in temperature.

The micelle aggregation number was found to increase with an increase in the solute bulk concentration, in accordance with published results.

The presence of free polymer in the bulk solution enhances the solubility of naphthalene in this region to some extent, indicating that it associates with the naphthalene to some degree and enhances the naphthalene solubility in water. The concentration of polymer in the bulk increases with increasing ethylene oxide content of the polymer, so that the naphthalene bulk concentration is higher for the polymers with higher ethylene oxide content, despite the fact that naphthalene is more compatible with PPO than with PEO. The polymer bulk concentration decreases with increasing solute concentration, probably because the addition of a hydrophobic solute increases

the aggregating tendencies of the polymer, resulting in a higher aggregation number, and a lower concentration of polymer in the bulk solution. The fact that the polymer bulk concentration changes with solute concentration is one of the contributing factors leading to the nonlinear relationship between the overall solute concentration, and the equilibrium concentration of naphthalene in water. This nonlinear relationship indicates that the partition coefficient between water and the micelles changes with the solute concentration, and aspect of the problem that has yet to be investigated experimentally. Again, the theory reproduces the experimental finding that there is a strong correlation between the PPO content of the polymer and its propensity to solubilize naphthalene, although it overpredicts the magnitude of the PPO effect. The agreement could possibly be improved by taking such factors as the statistical segment length and the difference in molecular volumes of the individual segments into account.

To summarize, our theoretical analysis predicts that the partition coefficient of naphthalene increases with an increase in solute concentration, owing to the fact that the uptake of solute changes the structure of the micelle. The polymer aggregation number increases, and a more hydrophobic core is formed, with a lower water concentration and higher PPO concentration. The concentration of polymer in the bulk also decreases upon solute addition. On the other hand, an increase in the polymer concentration results in more micelles being formed, with the same aggregation number, so that for a given bulk concentration of naphthalene, the partition coefficient remains constant with an increase in polymer concentration. The addition of solute causes the micelles to become larger, as a result of the swelling due to solute addition, as well as an increase in the polymer aggregation number. Water is excluded from the core of the saturated micelles, and the concentration of solute in the core increases. It has been observed that the micellar profiles for naphthalene solubilized in 1.5% P105 and in 10% P105 are essentially indistinguishable.

Effect of copolymer molecular weight on solubilization: It was shown experimentally that the molecular weight of the polymer has a significant effect on the partitioning behavior of naphthalene in Pluronic and Tetronic polymers. The lattice theory for flexible chain molecules significantly underpredicted the magnitude of the molecular weight effect. The modified lattice theory improves upon this prediction. The theory overestimates the molecular weight effect somewhat, though the agreement is reasonable. In addition to showing that naphthalene solubilization increases with polymer molecular weight, the theory is able to reproduce the nonlinear relationship between the naphthalene solubilized and the polymer concentration for low molecular weight polymers, that was observed experimentally in both Pluronic and Tetronic polymers. An analysis of the theoretical results shows that the polymer bulk concentration is not constant for the low molecular weight polymers. For the P94, the bulk concentration initially increases, but then above about 4% polymer becomes constant. For the low molecular weight polymers, micelles form at a higher critical concentration, and micelle properties change near the critical micelle concentration, but are essentially constant far from it. The bulk polymer concentration is higher for lower molecular weight polymers, which means less of the polymer aggregates to form micelles, which decreases the amount of naphthalene solubilized and provides a partial explanation for the molecular weight effect. The lower molecular weight polymer forms a smaller micelle, with a large interfacial region, and a heterogeneous core with a high PEO and water content. The core environment is thus much less hydrophobic for the lower molecular weight polymer, resulting in significantly less solubilization of naphthalene. It was also shown that the higher concentration of polymer in the bulk solution results in less polymer being available to form micelles.

### **Lattice Monte Carlo Simulation of Block Copolymers in Solutions Containing Hydrophobic Solutes**

The self-consistent mean field lattice theory described above has the disadvantage that the aggregate structural shape must be assumed before the calculations can be made. Thus, it is possible that important structural features and growth of the micelles as they take up extra solute may not be captured in the analysis, unless the appropriate structure is used as the basis for the calculations.

Also, statistical information on the sizes and size distributions of the aggregates are not forthcoming. We have therefore initiated a Monte Carlo study of small surfactant systems to address these issues, and to determine the effect of solute loading on the morphology of the surfactant aggregates, as described below.

A lattice Monte Carlo simulation method has been developed for investigating block copolymers in solutions containing hydrophobic solutes. The simulation results discussed below were conducted on a 40x40x40 fcc lattice using periodic boundary conditions. The block copolymer is a diblock containing two hydrophilic head beads and two hydrophobic tail beads. The lattice contains 1200 block copolymers and 120 monomeric hydrophobic solutes. The remainder of the lattice is filled with hydrophilic solvent. There is a single interaction parameter  $\chi$  characterizing the strength of the interaction between hydrophilic and hydrophobic beads, all other interactions are like-like interactions and are set to zero. The scaled temperature for the simulation is  $kT/\chi = 2.0$ .

The equilibrium size and shape distributions of the block copolymer micelles are shown in Figure 17. The size distribution is plotted as the number of polymers ( $n_A$ ) as a function of aggregation number. This distribution has a single peak at an aggregation number of about 40. The peak corresponds to "spherical" micelles and is separated from monomers and "premicelles" by a deep minimum at an aggregation number of about 10. There is a long tail in the size distribution extending to aggregation numbers many times that of the "spherical" micelles reflecting the polydispersity of the size distribution.

The micellar shapes are represented by the square root of the eigenvalues of the mean square radius of gyration tensor of the micelles at each aggregation number. These have been ordered such that for each micelle  $X_g > Y_g > Z_g$ . For example, a cylinder of length  $2L$  and radius  $R$  has values  $Y_g = Z_g \sim R$  and  $X_g \sim L$ , for  $L > R$ . The smallest eigenvalue of the micelles,  $Z_g$ , increases up to the aggregation number of "spherical" micelles and remains approximately constant.

The peak in the distribution shifts to higher aggregation numbers as oil is added to the surfactant/water mixture (Figure 18). This indicates that the spherical aggregates become larger and the oily core of the micelle is expanded by the absorbed oil, thereby increasing the surface area available for the surfactant molecules. The height of the peak decreases with oil concentration while the width increases and there is an increasing proportion of surfactant in the tail portion of the distribution, which consists of cylindrical micelles. These changes are consistent with the swelling and growth of micelles upon addition of small amounts of oil. Typical aggregate morphologies at high oil concentrations are shown in Figure 19.

The ability of the surfactant solutions to dissolve more oil than aqueous solutions can be quantified by the partition coefficient or solubility enhancement factor,  $K$

$$K = c_m/c_w$$

where  $c_m$  is the concentration of oil in the surfactant solution at the same thermodynamic activity as in a surfactant-free aqueous solution at concentration  $c_w$ . The solubility enhancement factor is shown as a function of oil concentration in Figure 20. At low oil concentrations, the enhancement factor increases slowly with  $c_w$ , but increases rapidly as  $c_w$  approaches the bulk solubility of the oil in water, in agreement with experimental observations. With increasing oil content, the concentration of free surfactant monomers in solution decreases, as the oily contents of the swollen micelles provide a favourable environment for the surfactant tails. These results can also be interpreted as a decrease in the critical micelle concentration (cmc) or critical microemulsion concentration (cmc) with increasing oil concentration.

## CONCLUSIONS

The solubilization of aromatic from toluene through to pyrene by poly(ethylene oxide-propylene oxide) block copolymer micelles is enhanced with increasing temperature. A greater hydrophobicity of the polymer solution contributes to the increased partitioning of the organic compounds to the micelles. High molecular weight and high PPO:PEO ratio both result in high hydrophobicity, with an increase in % PPO content having a greater effect on enhancing solubilization than an increase in molecular weight. As the concentration of the polymer solution increased, the temperature for the cessation of micellar growth decreased, a manifestation of the temperature effect on the critical micelle concentration.

These observations were exploited in the development of new processes for removal of organic contaminants from air emission and aqueous discharge streams. The polymeric micellar solution was fed to the lumen of a hollow fiber membrane module, while the contaminated feed solution was introduced to the shell side of the module. The solute transferred through the membranes to be picked up and concentrated by the micelles. In gas absorption processes, standard packed beds can be used to effect the contact between the two phases. The regeneration of the block copolymer micellar solutions was shown to be possible using either temperature swings or supercritical CO<sub>2</sub> extraction.

Molecular modelling of the micelle-forming block copolymer solutions and their propensity to enhance the solubility of trace organics using self-consistent field and lattice Monte Carlo theories was found to be very successful. In many cases semi-quantitative predictions of partitioning results were obtained. The effect of oil concentration on the growth and morphological changes in the micelles was observed quantitatively using the Monte Carlo simulations.

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Table 1 Properties of the copolymers used in this study.

Polymer	Mol. Weight	PPO segm. weight	number of PO units	number of EO units
L64	2900	1740	30	2x13
P65	3400	1700	29	2x18
F68	8400	1680	29	2x76
P84	4200	2520	43	2x19
P85	4600	2300	40	2x26
F88	11400	2280	39	2x103
P103	4950	3465	60	2x17
P104	5900	3540	61	2x27
P105	6500	3250	56	2x37
F108	14600	2920	50	2x132
P123	5750	4025	69	2x19
F127	12600	3780	65	2x100

Table 2. Pyrene partition Coefficients measured at 40° C

Polymer	$K_{mw}$
P104	81 000
L64	49 000
F108	18 000

Figure 1. Reciprocal CMT vs copolymer concentration for the determination of micellization enthalpy

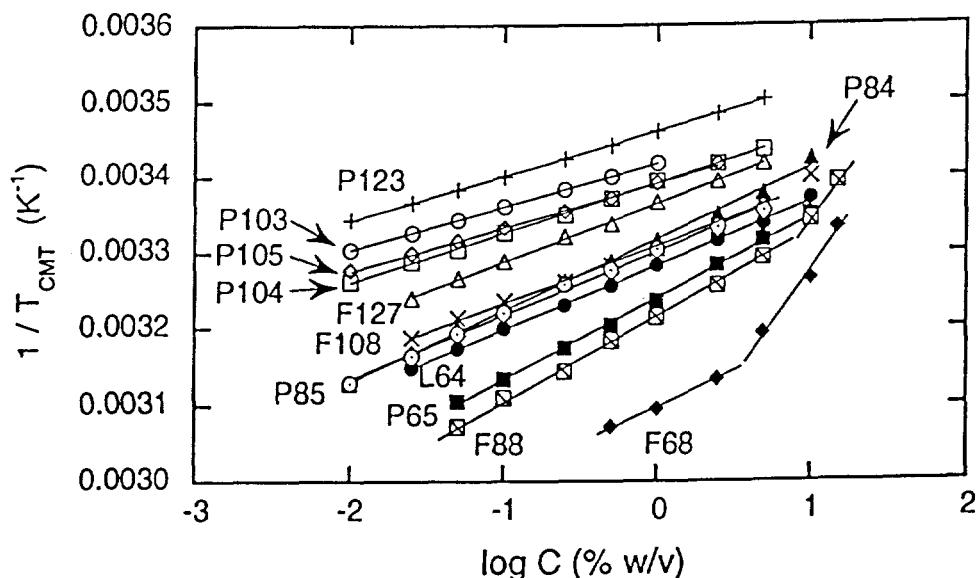


Figure 2. Effect of copolymer molecular weight on free energies of micellization for various copolymer concentrations

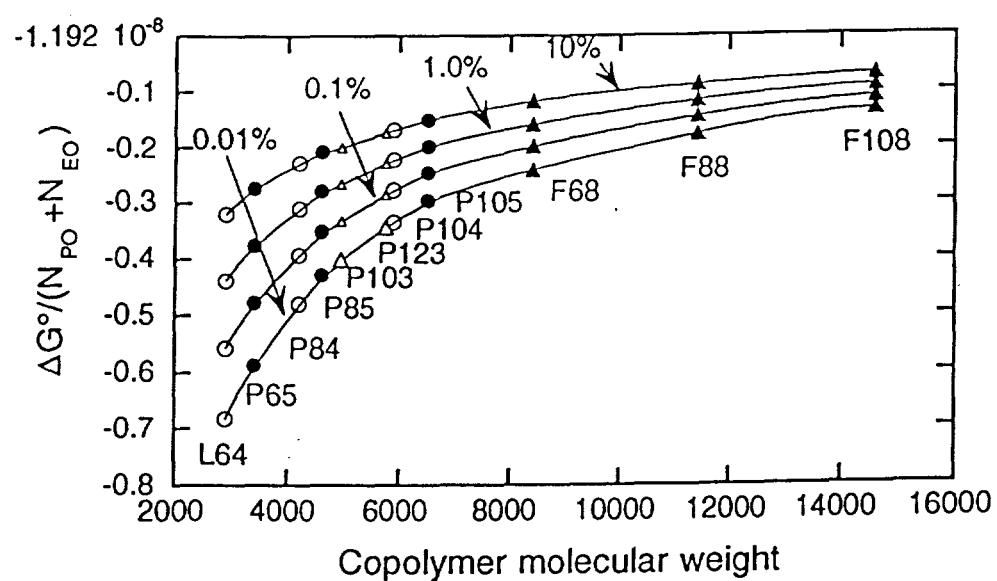


Figure 3. Effect of copolymer composition ratio (PPO/PEO) on the micellization enthalpy per unit monomer concentration

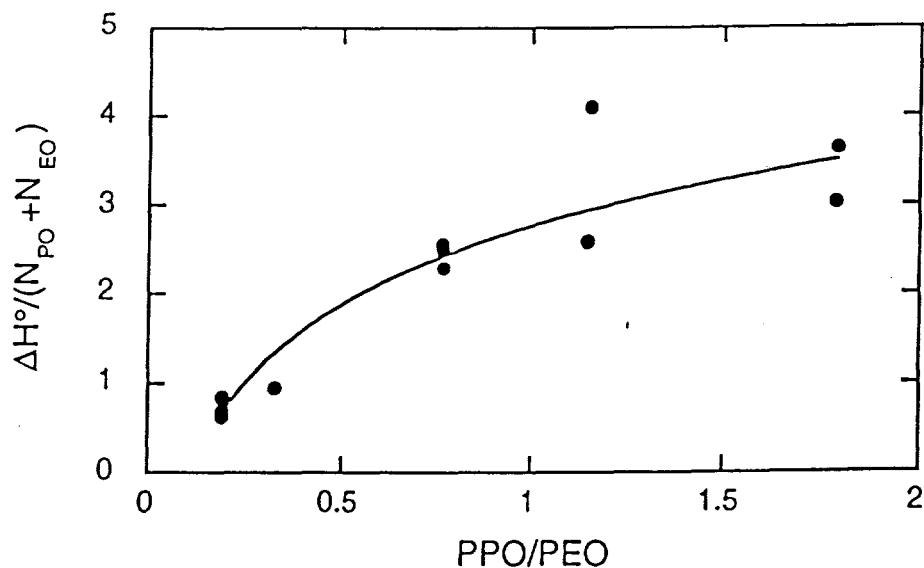


Figure 4. Effect of temperature on micropolarity (pyrene  $I_1/I_3$  ratio) for various solution environments.

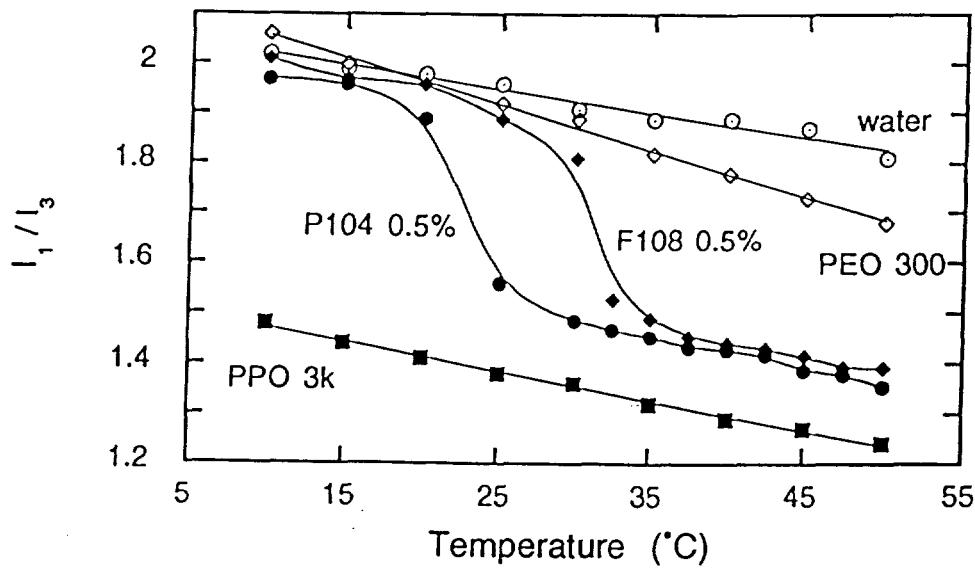


Figure 5. Effect of temperature and P104 concentration on solubilization of pyrene

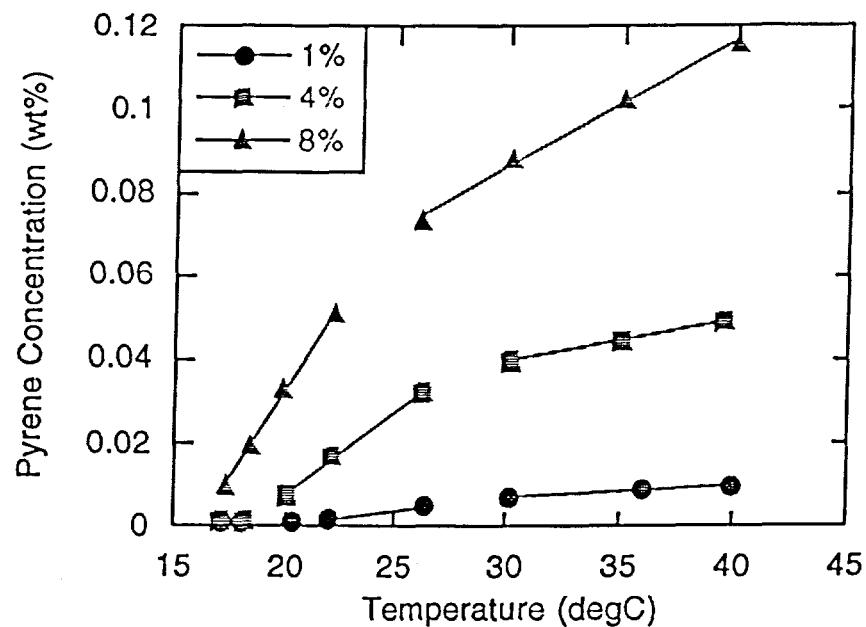


Figure 6. Relative solubility of pyrene in solutions of P104 as a function of temperature

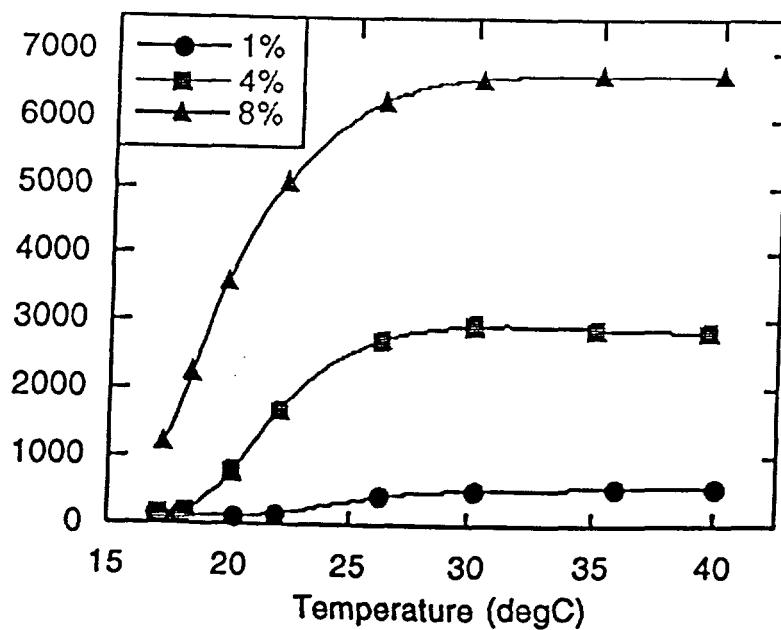


Figure 7. Enhanced solubilisation of pyrene in solutions of block copolymers of different molecular weights and PPO

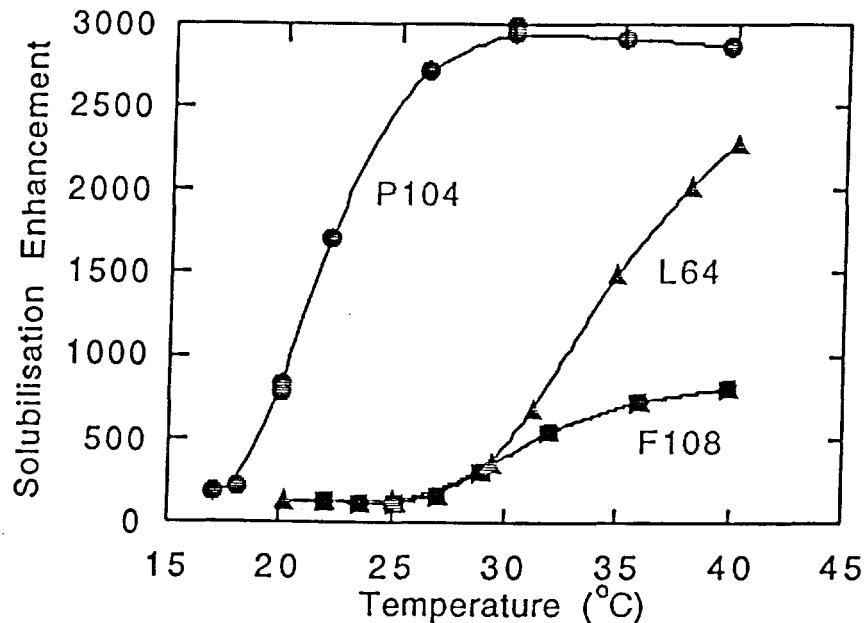


Figure 8. Extraction profiles for different feed flow rates, and mass transfer coefficients derived therefrom

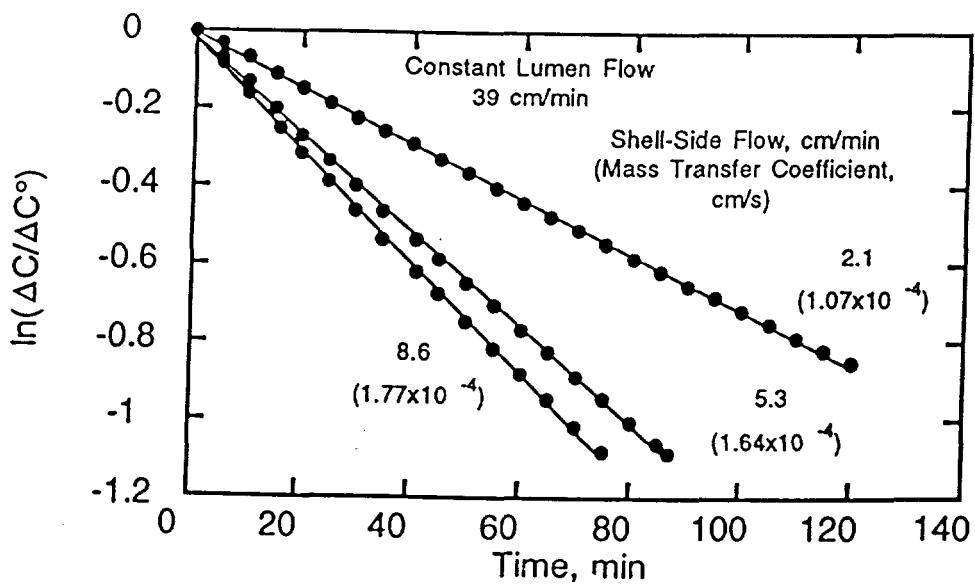


Figure 9. Extraction profiles for toluene into a 4% P104 solution. Volumetric flowrates were the same for both phases.

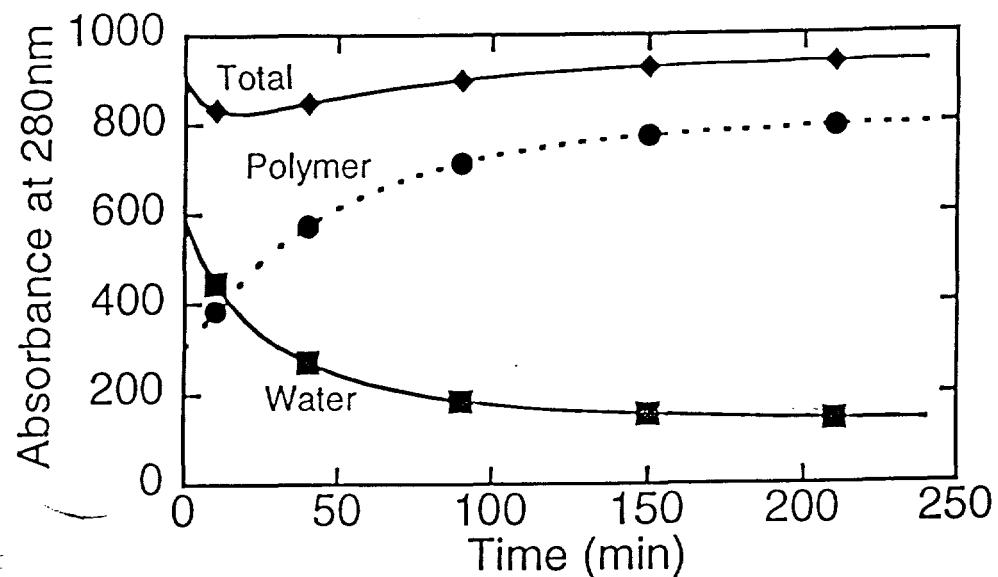


Figure 10. The partition coefficient for toluene between P104 copolymer solutions of differing concentration and water

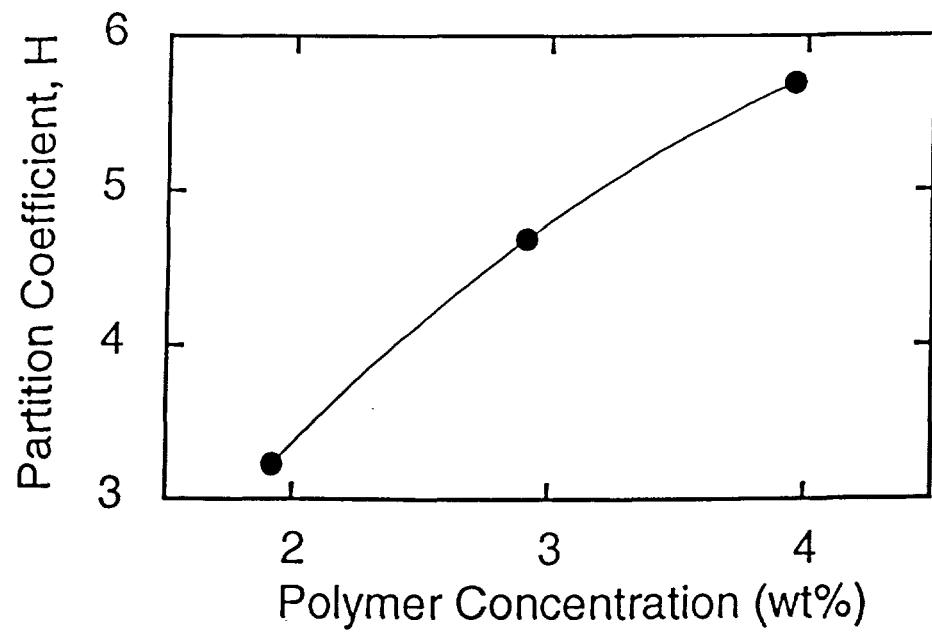


Figure 11.

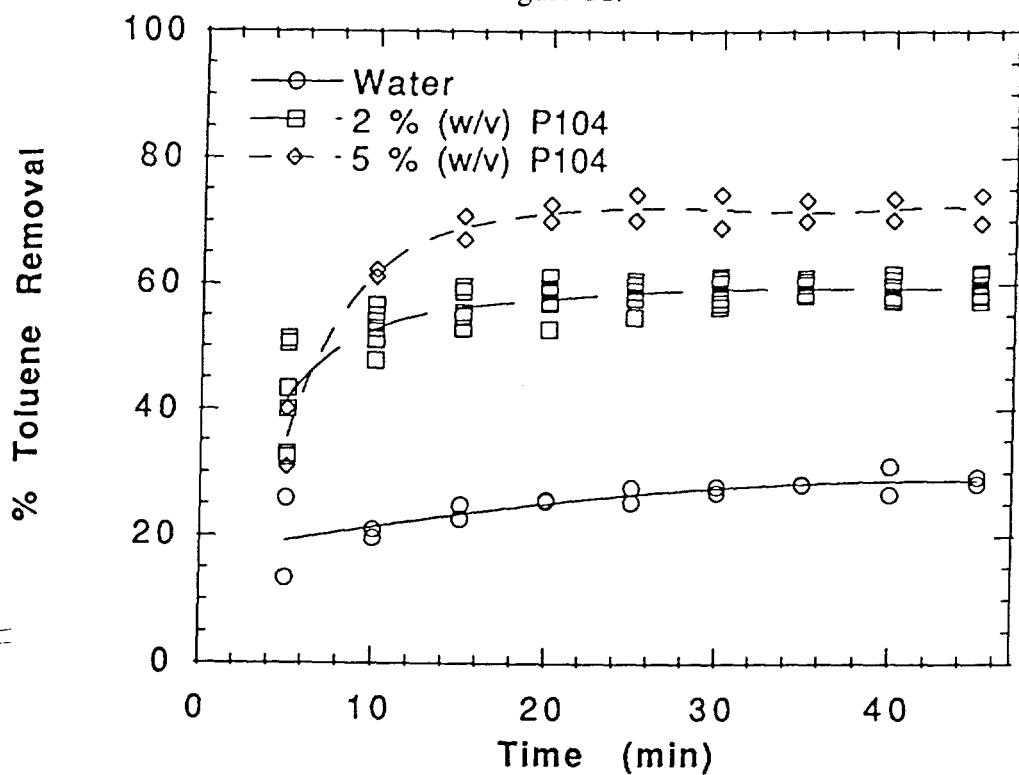


Figure 12

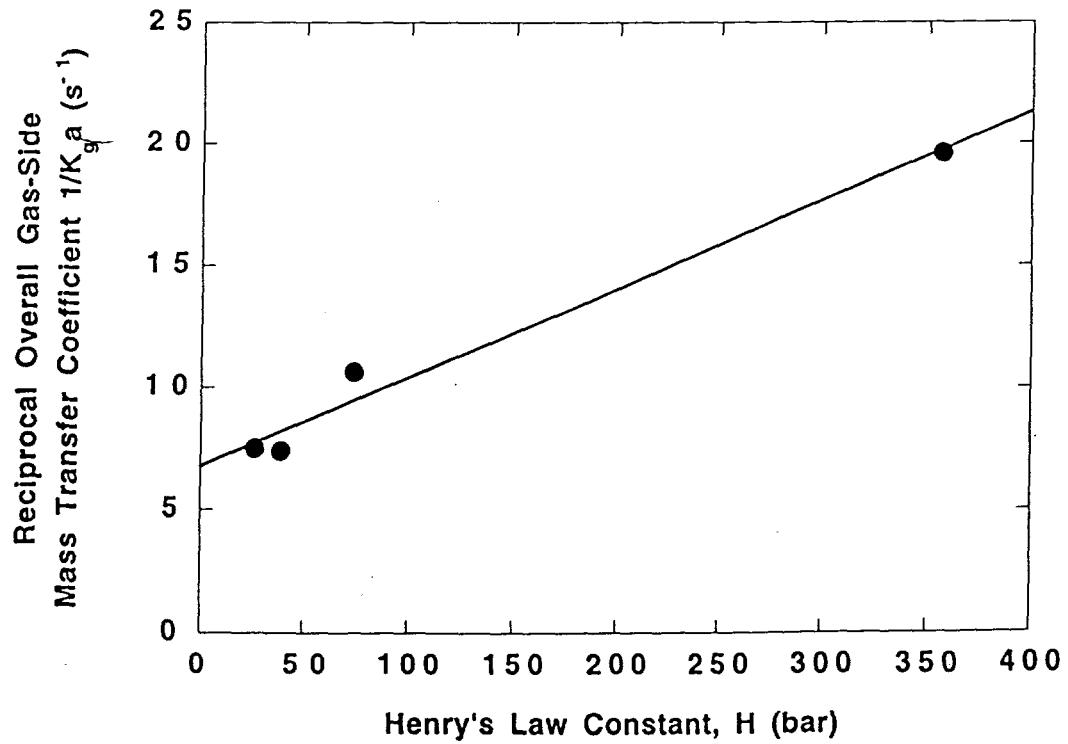


Figure 13. The percent extraction of pyrene from P104 micelles in a single stage extraction using supercritical carbon dioxide

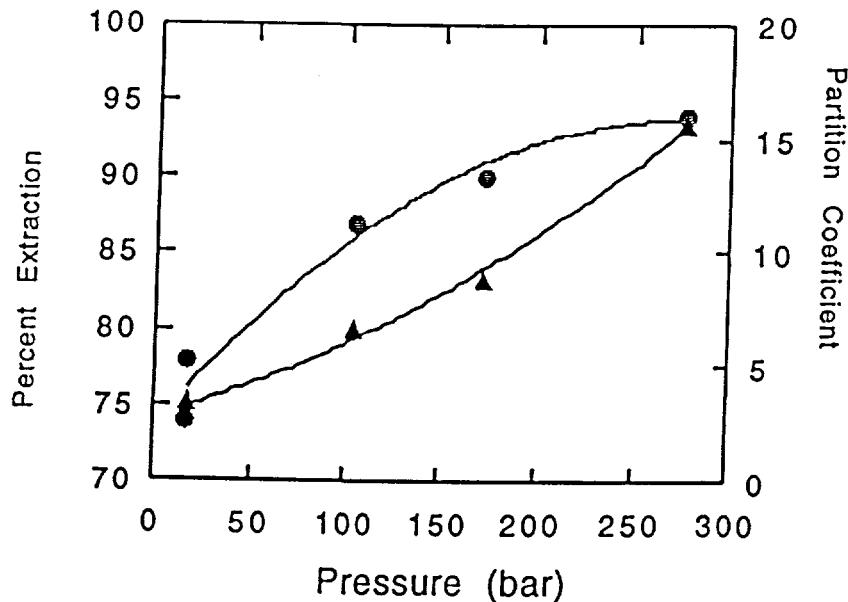


Figure 14. A schematic of a membrane extraction process coupled with micelle disruption and steam stripping of released solutes for block copolymer solution regeneration.

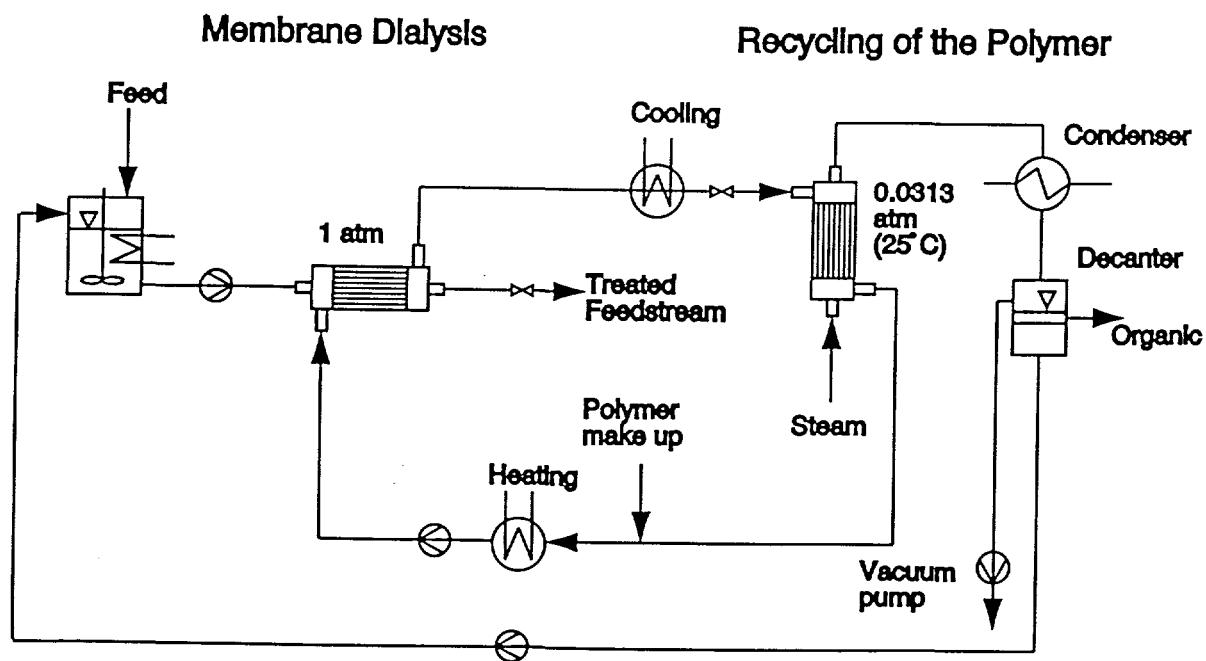


Figure 15. Volume fraction profiles for micelles formed by Pluronic (triblock) and Tetronic (Star) PEO-PPO block copolymers

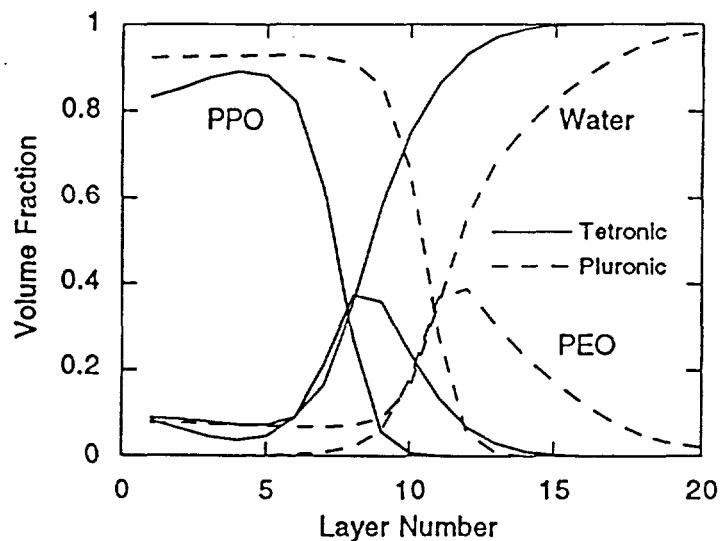


Figure 16. Comparison of experimental micelle/water partition coefficients for naphthalene solubilised in PEO-PPO-PEO block copolymer micelles with model predictions

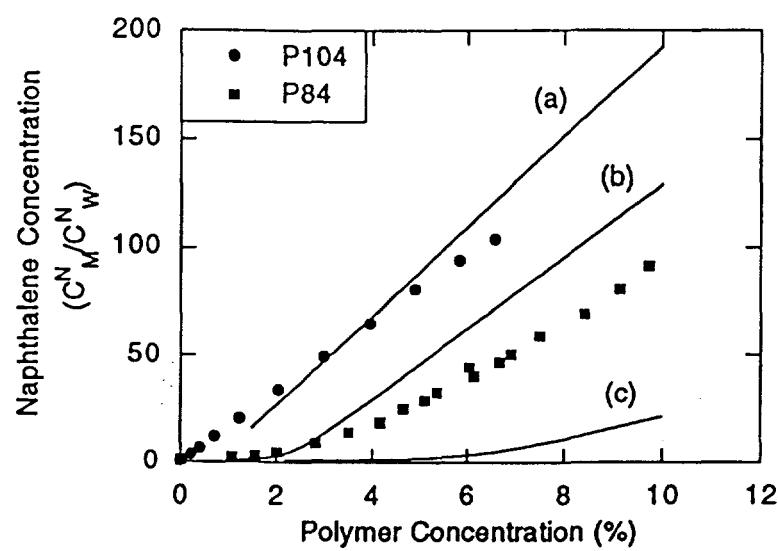


Figure 17. Micelle size distribution and mean square radii of gyration for short diblock copolymers in solution as determined by Monte Carlo simulations

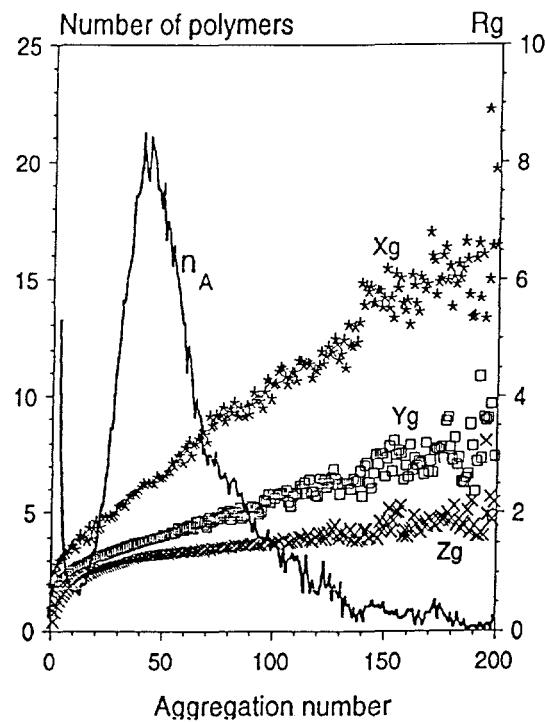


Figure 18. Effect of oil content on the short diblock copolymer micelle size distributions as determined by Monte Carlo simulations.

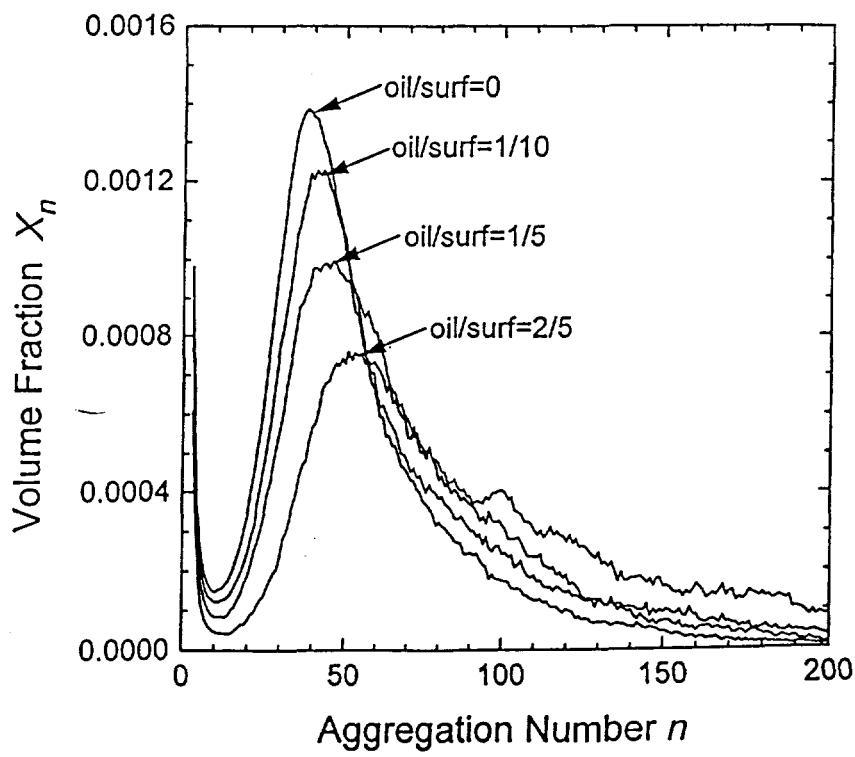


Figure 19. Typical aggregate morphologies of short diblock copolymer micelles laden with solubilized oil as determined by Monte Carlo simulations

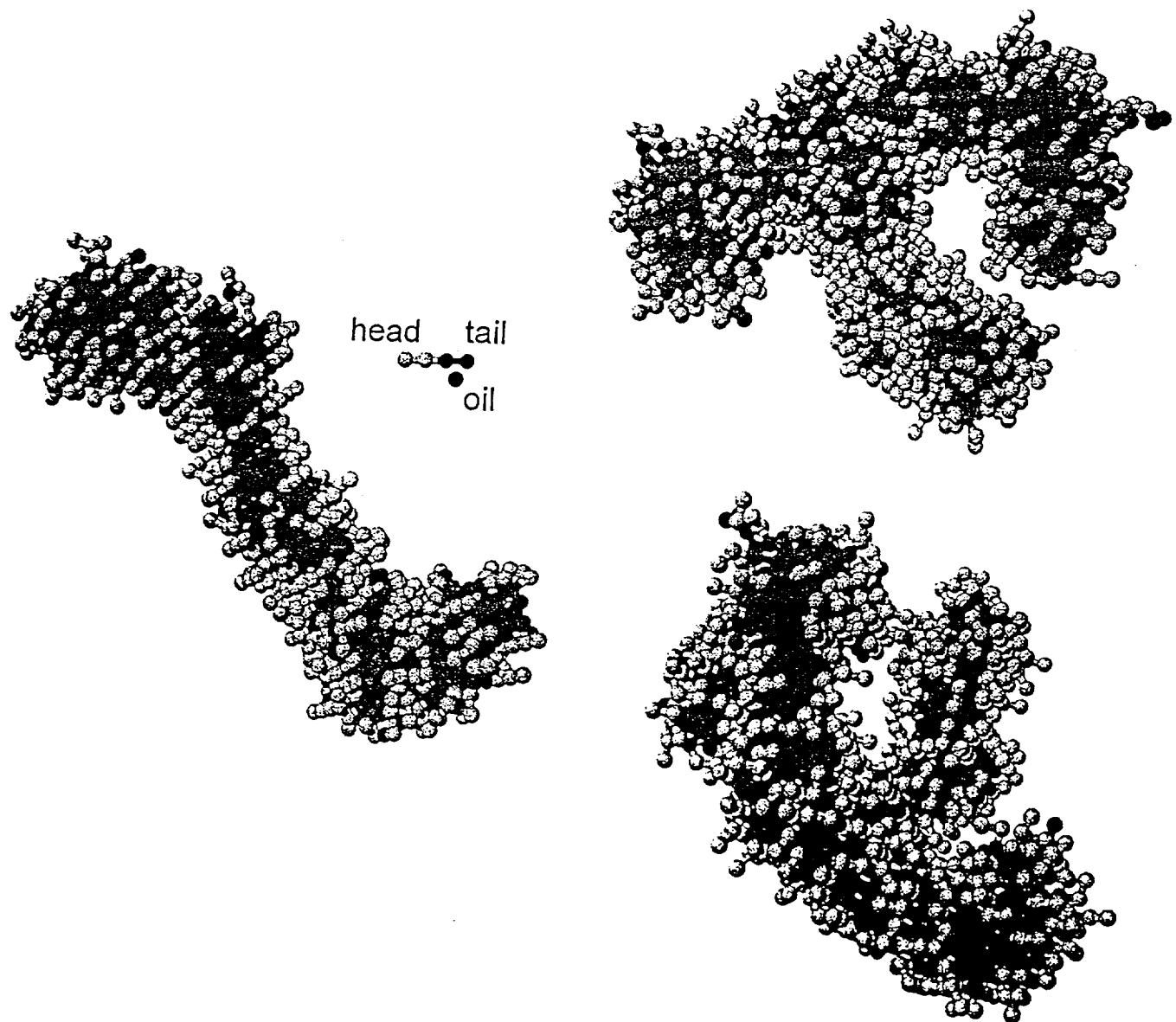


Figure 20. The effect of oil concentration on the solubility enhancement factor in short diblock copolymer micelles as determined by Monte Carlo simulations

