2. The distance between reactants in the precusor state can be used to calculate changes in k_{obsd} attributable to ionic strength effects using the Debye/Hückel/Brönsted relationship. In a similar fashion, the work required to form the precursor state can be calculated, allowing the unimolecular electron-transfer rate constant k_{et} to be extracted from k_{obsd}.

3. Currently, there is considerable interest in discerning if discrepancies between k_{obsd} and k_{calcd} are due to nonunity transmission coefficients induced by poor electronic coupling between reactants in the precursor state. This electronic coupling will be a function of the reaction distance as well as the electronic nature of the medium separating the reactants.

4. Accurate values of diffusion-limited rate constants are important for the analysis and interpretation of rate constants for extremely rapid reactions, such as photoinduced electron transfers.[27] This analysis provides information about how the rate constant varies with reaction distance, which can be compared to the sum of the average radii for the reactants.

If accurate values of λ^0 can be obtained, we suggest that reasonable estimates for $\langle r \rangle$ can be obtained from eq 7, and the values so obtained may be superior to values obtained from SF models. It is difficult to account for several structural features when estimating $\langle r \rangle$ from models, namely how to treat nonspherical molecules, how to account for gaps between the ligands, and how to account for various conformations of the molecule. Values of $\langle r \rangle$ obtained from eq 7 are based on an experimental observable that reflects the average size of the molecule as it exists in solution. The concept of relating the size of a nonspherical molecule to that of a spherical one is inherent in the use of eq 7.

Conclusions

Diffusion-limited currents for the oxidation or reduction of 14 complex ions have been measured at a rotating-disk electrode. A procedure for calculating diffusion coefficients, limiting ionic conductivities, and average radii from these currents is described. In all cases where complex ions have similar structures, larger ligands lead to smaller diffusion coefficients. For complex ions with radii greater than ca. 4 Å, the diffusion coefficient measured at low ionic strength can be used to calculate limiting ionic conductivities that agree well with values obtained by other methods. For smaller complex ions, this procedure yields limiting conductivities that are significantly larger than those obtained by other methods. If accurate ionic conductivities are used, equations derived from Stokes' law yield reasonable values for the average radii of the ions.

Registry No. I, 14403-82-8; II, 14970-14-0; III, 32424-84-3; IV, 30051-70-8; V, 31900-26-2; VI, 30051-71-9; VII, 31900-27-3; VIII, 18581-79-8; IX, 16788-34-4; X, 47872-45-7; XI, 88326-61-8; XII, 18943-33-4; XIII, 19482-30-5; XIV, 14878-41-2.

Photoluminescence Probes for Pressure and Temperature Effects on the Aggregates of Water-Soluble Block Copolymers

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Three kinds of fluorescence probes, an indole detergent, pyrene, and pyrene-3-carboxaldehyde (In, P, and PA), are used to monitor the properties of the aggregates of four poly(ethylene oxide–propylene oxide–ethylene oxide) (EPE) block copolymers in aqueous solution as a function of pressure and temperature. The fluorescence parameters acquired from these three probes are interpreted in terms of micropolarity and microviscosity of the aggregates and are employed to estimate the pressure and temperature effects on the microscopic structure of EPE block copolymers. Also, the pressure and temperature effects on fluorescence parameters for the probes associated with four kinds of EPE block copolymers are compared and related to their composition and their cloud points, and the following conclusions can be drawn: (a) increasing pressure initially increases the hydrophilicity of EPE aggregates, and a maximum increase in hydrophilicity is reached at 1000–1500 bar, the effect being more significant at higher temperatures; (b) increasing temperature decreases the hydrophilicity of EPE aggregates, the effect being more significant at low pressures. The pressure effect is more significant for EPE possessing higher PPO content, and the temperature effect is more significant for EPE having a cloud point closer to the temperature of measurement.

Introduction

Block copolymers ABA of which the A and B parts have very different solubilities in a given solvent have been reported to form aggregates in that solvent.[1] Poly(ethylene oxide–propylene oxide–ethylene oxide) block copolymers (EPE) are composed of low water-soluble poly(propylene oxide) (PPO) and high water-soluble poly(ethylene oxide) (PEO) segments. Due to the ability to design such block polymer structures to obtain optimum properties for specific requirements in diverse fields, EPE block copolymers have attracted considerable attention in both fundamental research and practical applications.[2]

The issue of high pressure is often involved in industrial activities such as lubrication, adhesion, and enhanced oil recovery. The effect of pressure on the solubility of polymers and on the micellar properties such as cmc, solubilization, apparent molal volume, radius, and aggregation number has been studied;[3] however, the effect of pressure on the solution properties of EPE block co-

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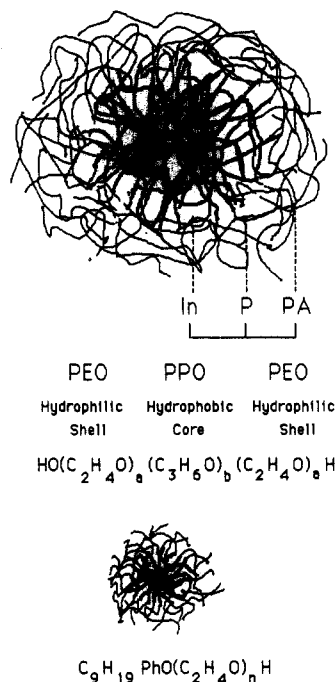
Figure 1. Sketch of the aggregate of EPE block copolymer and of the nonionic surfactant C_9PhE_n and the expected location for In, P, and PA in EPE.

polymers has received much less attention. Our previous work[4] reported that some fluroescence probes in an aqueous solution of EPE showed remarkable changes in photoluminescence phenomena under high pressure (range 1-3000 bar). In this paper, three kinds of probes (In, P, and PA) which are expected to be located
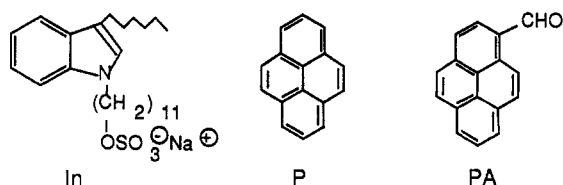
at three different sites in the EPE aggregates were used to monitor the local change in micropolarity so as to investigate the pressure and temperature effects on the EPE aggregates. The correlated information is used to interpret the structural changes of EPE which occur upon pressure and temperature variation.

Aqueous solutions of EPE block copolymers are suggested to form monomolecular micelles at low concentration and polymolecular micelles at high concentration.[5] We report here an investigation of EPE aqueous solutions at high concentration (10%). The EPE aggregates formed at high concentration are conventionally represented (Figure 1) as spherical micelles possessing hydrophobic cores (PPO) surrounded by hydrophilic shells (PEO).[1,5]

Experimental Section

Materials. Pyrene (P) and pyrene-3-carboxaldehyde (PA, Aldrich Chemical Co.) were purified by three recrystallizations from ethanol. The synthesis of sodium 11-(3-hexyl-1-indolyl)-undecyl sulfate (In) is described in the literature.[6] Poly(ethylene oxide–propylene oxide) block copolymers (EPE(r), r = 0.8, 5, 0.3, and 3, the molecular weight ratios of ethylene oxide to propylene oxide; Polysciences Co.) were used as received. Some of their physical properties are shown in Table I. EPE(0.8) was purified by three precipitations from toluene/heptane. The purification procedure did not change the cloud point of the polymer solutions

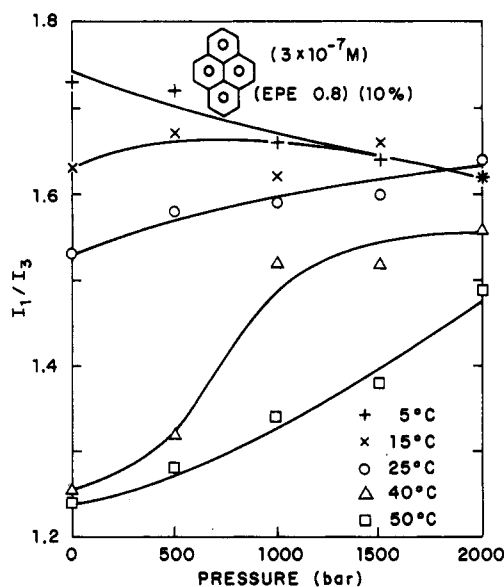(4) Turro, N. J.; Chung, C.-J. *Macromolecules* **1984**, *17*, 2123.
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TABLE I: Physical Properties of EPE Block Copolymers

sample	commercial name	PPO, mol wt	PPO, wt %	mol wt	cloud point, °C
EPE(0.8)	L64	1750	40	2917	61
EPE(5)	F68	1750	20	8750	100
EPE(0.3)	L92	2750	80	3438	16
EPE(3)	F127	4000	30	13333	100

nor the molecule weight distribution as characterized by gel permeation chromatography. The selected poly(ethylene glycol) n-nonylphenyl ethers (C_9PhE_n) (Tokyo Kasei Co.) were employed without further purification.

Measurement. The high-pressure experiments were performed in a stainless steel high-pressure cell[7] (Union Giken Eng.) possessing a sample container of ca. 3 mL. The sample was excited, and the emission was detected by passing light through the quartz (or sapphire) windows of the cell. Temperatures were controlled by an internal circulating water jacket which surrounded the cell. All of the fluorescence spectra were recorded on a Perkin-Elmer MPF-3L spectrometer. The polarization of the emission of In was acquired on a SLM 8000 spectrophotometer employing a two-polarizer system.

Results

The probes In, P, and PA were selected based on previous investigations which suggest that (1) In should be located on a time average near the hydrophobic micellar core,[8] (2) P should be located on a time average near the inner surface of the hydrophilic shell,[9] and (3) PA should be located on a time average near the outer surface of the hydrophilic shell.[9b,10] These expectations are shown pictorially in Figure 1. The maximum wavelength of the emision of In (λ_F^{In}) and of PA (λ_F^{PA}) and the ratio of the intensity of the first peak (373 nm) to the third peak (385 nm) of P emission (termed the I_1/I_3 value) were investigated as a function of pressure and temperature for solutions of the EPE block copolymers. These fluorescence parameters have been shown to be reliable microscopic probes of microheterogeneous environments.

The parameter λ_F^{In} shifts to longer wavelengths as solvent polarity is increasd (372 nm in water and 333 nm in dodecane).[8,11] In an aqueous solution of a nonionic surfactant (C_9PhE_{10}) and of an anionic surfactant (SDS), λ_F^{In} is 330 and 360 nm, respectively. For the four kinds of EPE block copolymers used in this study (Table I), the values of λ_F^{In} are in the range 339-354 nm (Table II). Thus, micropolarity or water content in the hydrophobic core of EPE block copolymers is higher than C_9PhE_{10} but lower than SDS.

The parameter I_1/I_3 is also proportional to microscopic polarity.[12] The I_1/I_3 values for four EPE copolymers are in the range 1.30-1.53 (at 25 or 15 °C), which are similar to those for C_9PhE_n (1.41 for $n = 10$, 1.47 for $n = 20$).

The parameter λ_F^{PA} shifts to longer wavelengths as solvent polarity increases.[11,13] λ_F^{PA} values for these four block copolymers are in the range 450-461 nm, close to those for C_9PhE_n (452 nm for $n = 10$, 20). From the information provided by In, P, and PA, it is clear that, relative to C_9PhE_n, the water content of EPE block copolymers is higher in the hydrophobic core but similar in the hydrophilic shell. Thus, the hydrophobic bonding in the

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TABLE II: Values of λ_F^{In}, I_1/I_3, and λ_F^{PA} in Various Environments at 1 bar, 25 °C

	surfactant						solvent	
probe	EPE(0.8)	EPE(5)	EPE(0.3)	EPE(3)	C_9PhE_{10}	C_9PhE_{20}	H_2O	dodecane
$\lambda_F^{In},{}^a$ nm	354	344	350	339	330	332	372	333
$I_1/I_3{}^b$	1.53	1.36	1.48	1.30	1.41	1.47	1.90	0.60
$\lambda_F^{PA},{}^a$ nm	461	461	459	450	452	452	468	415

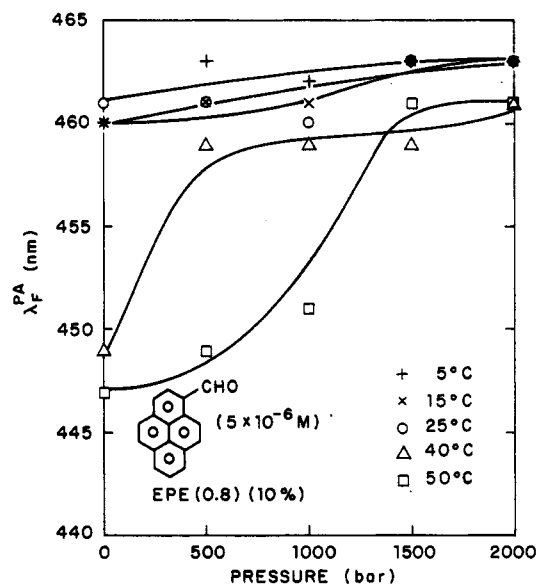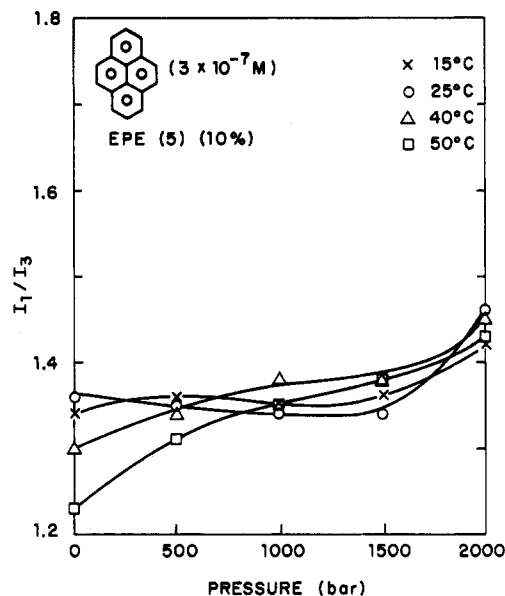^{a} Deviation is ±1 nm. ^{b} Deviation is ±0.02.
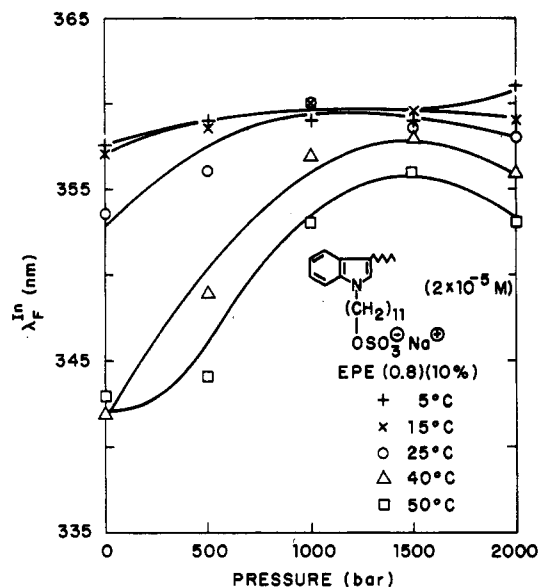
Figure 2. Pressure and temperature effects on parameter λ_F^{In} in EPE(0.8).

Figure 4. Pressure and temperature effects on parameter λ_F^{PA} in EPE-(0.8).

Figure 3. Pressure and temperature effects on parameter I_1/I_3 in EPE-(0.8).

Figure 5. Pressure and temperature effects on parameter I_1/I_3 in EPE-(5).

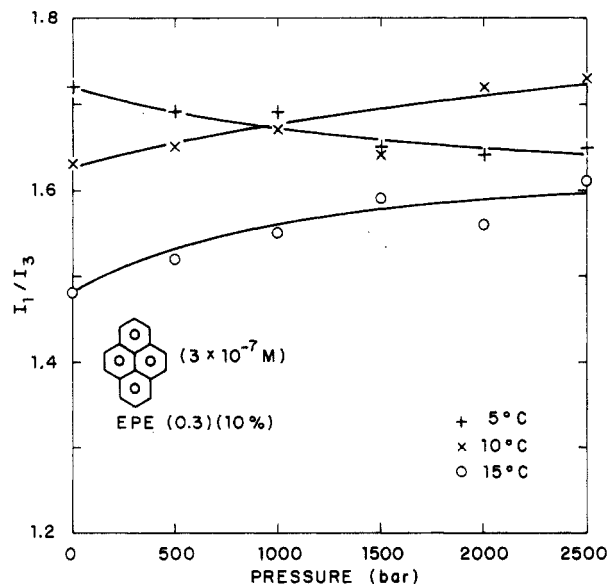hydrophobic core of EPE block copolymers is generally weaker than that of C_9PhE_n.

Pressure and temperature effects on λ_F^{In} for EPE(0.8) are shown in Figure 2. An increase of pressure up to 1000–1500 bar increases λ_F^{In} within the temperature range studied. For pressures greater than 1000–1500 bar, an increasing pressure decreases λ_F^{In}. The increase or decrease of λ_F^{In} on increasing pressure is more significant at higher temperatures. As the temperature is increased from 5 to 50 °C, λ_F^{In} in EPE(0.8) decreases considerably from 358 to 343 nm under 1 bar but decreases only slightly from 361 to 353 nm at 2000 bar. Thus, the temperature effect is much less significant at higher pressures.

The pressure and temperature effects on I_1/I_3 values of P in EPE(0.8) are shown in Figure 3. Above 15 °C, I_1/I_3 values increase with the increasing pressure. The higher the temperature

is, the more pronounced the changes in I_1/I_3 with pressure become. Below 15 °C, I_1/I_3 changes only slightly with increasing pressure. At a given pressure, increasing temperature significantly decreases the I_1/I_3 values. In general, this temperature effect under lower pressure is more significant than under higher pressures.

Pressure and temperature effects on the λ_F^{PA} in EPE(0.8) are shown in Figure 4. Increasing pressure increases λ_F^{PA} significantly from ca. 447 to 461 nm at 40 or 50 °C but does not change λ_F^{PA} significantly at 5, 15, and 25 °C. Again, the increasing temperature decreases λ_F^{PA} values, and this effect is more significant at the lower pressure. The behavior of λ_F^{PA} as a function of pressure and temperature is similar to that of I_1/I_3 with P (Figure 3).

Figure 6. Pressure and temperature effects on parameter I_1/I_3 in EPE-(0.3).

Figure 7. Pressure and temperature effects on parameter I_1/I_3 in EPE-(3).

P was used to investigate the pressure and temperature effects on the aggregates of the other EPE block copolymers. EPE(5) has basically the same hydrophobic core but has a much larger hydrophilic shell than EPE(0.8). The pressure and temperature effects on I_1/I_3 in EPE(5) are shown in Figure 5. In this system, I_1/I_3 increases with increasing pressure at all the temperatures studied, but this pressure effect is smaller than that for EPE(0.8). An increase in temperature of 35 °C decreases I_1/I_3 values by only 8% at 1 bar, and the change of I_1/I_3 is insignificant at 2000 bar.

EPE(0.3) has a similar molecular weight to EPE(0.8), but the PPO weight percent of the former is twice as large as the latter. Due to the low cloud point (16 °C) of EPE(0.3), all of the experiments were conducted below 15 °C. Even for the slight temperature increase from 5 to 15 °C, the I_1/I_3 values decreased remarkably from 1.72 to 1.48 at 1-bar pressure. At 10 and 15 °C, an increase in pressure increased I_1/I_3 values significantly (Figure 6). It is clear that pressure and temperature influence I_1/I_3 values more significantly in EPE(0.3) than in EPE(0.8).
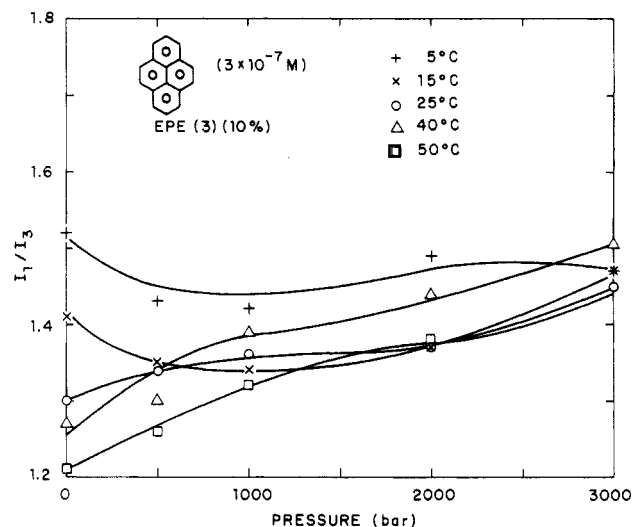
For EPE(3), molecular weights of both PPO cores and PEO shells increase from 1750 and 1167 to 4000 and 9333, respectively. The total PPO weight percent is larger than that of EPE(5) but smaller than that of EPE(0.8). For EPE(3), increasing pressure causes an increase of the I_1/I_3 value above 25 °C, and this effect is more significant at higher temperatures (25, 40, and 50 °C). Increasing temperature decreases the I_1/I_3 value, especially at lower pressures (Figure 7). This temperature effect at 1-bar pressure with EPE(3) is smaller than that with EPE(0.8) but greater than that with EPE(5). The effect of pressure at higher temperatures with EPE(3) is close to that with EPE(5) but smaller than that with EPE(0.8).

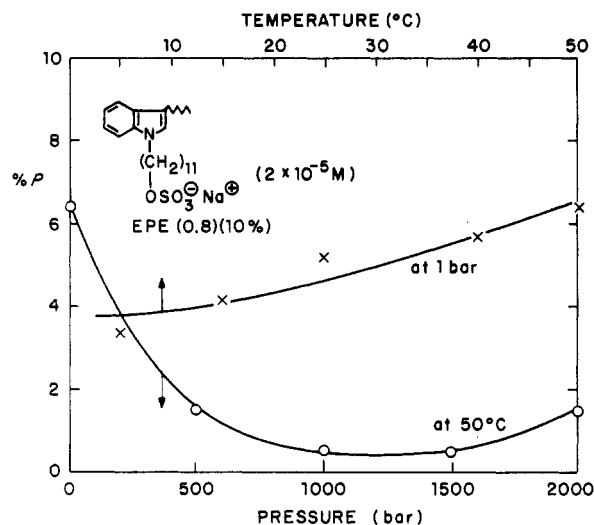The degree of fluorescence polarization, P, is given by[14]

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \quad (1)$$

where $I_{\parallel}$ and $I_{\perp}$ are the intensity of the emission parallel and perpendicular to the incident beam, respectively. From the Perrin equation (eq 2),[14] the microviscosity of the micelle or membrane can be estimated from the value of P,[15] where P_0 is the limiting

$$\frac{1/P - 1/3}{1/P_0 - 1/3} = 1 + \frac{kT\tau}{\eta V} \quad (2)$$

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Figure 8. Pressure and temperature effects on %P of In in EPE(0.8).

value of P, V the effective volume of the probe, τ the lifetime of fluorescence, η the microviscosity, T the temperature, and k the Boltzmann constant. Since P_0 is constant, the microviscosity is proportional to P, assuming V and τ to be constant. For In in EPE(0.8), the value of P increases with the increasing temperature and with the decreasing pressure as shown in Figure 8.

Discussion

We consider three possible mechanisms for pressure to influence the emission of the probes, i.e., by changing (1) the structure of EPE block copolymer aggregates and the corresponding microenvironment viewed by the probe, (2) the location of the probe, and (3) the inherent emission of the probe itself.

Since P is expected to be located in the boundary of the hydrophobic and hydrophilic regions, it is a convenient probe to monitor the overall change in the polymer aggregation and is a useful probe to investigate the effect of pressure on the micelle structure. There exists a similarity in structure between EPE block copolymers and the polyethylenated nonionic surfactants (Figure 1). The location of P in EPE block copolymers is therefore assumed to be similar to that in nonionic micelles. I_1/I_3 values of P in C_9PhE_{10} or C_9PhE_{20} do not change significantly with the increasing pressure (Figure 9), even at high temperatures (40 or 50 °C). For EPE(0.8), however, I_1/I_3 values are significantly increased by the increasing pressure. Thus, we conclude that the change in probe location with increasing pressure cannot account for the significant changes in I_1/I_3 values for EPE block copolymers. Furthermore, the observation of only small changes
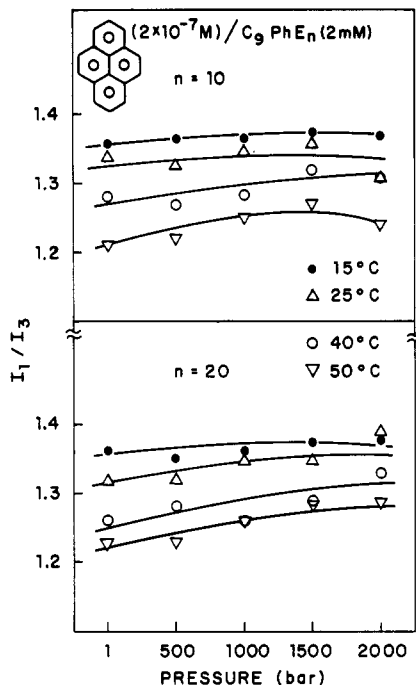
Figure 9. Pressure and temperature effects on parameter I_1/I_3 in C_9PhE_n ($n = 10, 20$).

in I_1/I_3 for C_9PhE_{10} is attributed to the low sensitivity of this micelle structure to high pressure.

The effect of pressure on the emission of P was tested in homogeneous hydrophobic (dodecane) and hydrophilic (water) solvents. Increasing pressure does not change the I_1/I_3 values significantly in dodecane (1 bar, 0.60; 500 bar, 0.60; 1000 bar, 0.59; 1500 bar, 0.59; 2000 bar, 0.60) or in water (1 bar, 1.61; 500 bar, 1.61; 1000 bar, 1.64; 1500 bar, 1.59; 2000 bar, 1.59). The above-mentioned results suggest that high pressure does not change either inherent P emission or P location significantly. Thus, we conclude that the change in I_1/I_3 under high pressure is attributed mainly to the change in the structure of block copolymers.

It has been suggested that hydrophobic bonding is weakened by application of pressure up to 1000–1500 bar but is promoted by the application of pressure greater than 1500 bar;[3,16] as a result, micellar volumes and aggregation numbers are expected to be pressure dependent. In an aqueous solution of EPE(0.8), the pressure effect on the hydrophobic core was investigated by determining the change in the microviscosity, as monitored by the degree of polarization of the emission of In. As shown in Figure 8, increasing the pressure up to 1000–1500 bar decreases the value of P; above that, a slight increase in P values can be observed. The decrease in the value of P indicates a decrease in microviscosity, suggesting that the structure of the PPO segment is loosened. This result corresponds to a maximum in the corresponding pressure region observed in the plot of λ_F^{In} vs. pressure (Figure 2). A significant increase in λ_F^{In} upon increasing pressure up to ca. 1000–1500 bar at the higher temperature (40 and 50 °C) suggests that the hydrophobic bonding in the hydrophobic core of EPE(0.8) aggregates is weakened by pressure, and consequently more water enters the aggregate. Above ca. 1000–1500 bar, the decrease in λ_F^{In} upon increasing pressure is probably due to the hydrophobic bonding promoted by the higher pressure.

The significant increase in λ_F^{In} upon increasing pressure at 40 or 50 °C corresponds to a large increase in I_1/I_3 and λ_F^{PA} under the same conditions (Figures 3 and 4). A weakening of the hydrophobic bonding in the core by pressure simultaneously causes P and PA to encounter a more water-rich environment in the hydrophilic shell. Above the maximum, the increasing pressure promotes hydrophobic bonding, but it also serves to enhance the hydration of EO groups at least up to 4 kbar.[17] As a result, the

net hydrophobic bonding change is small because of these compensating effects.

At lower temperature (15 and 25 °C), the change in λ_F^{In} upon increasing pressure also shows a maximum at 1000–1500 bar, but the changes below and above the maximum are small compared with those at the higher temperature. Because of the concurrent enhanced hydration of PEO segments by the pressure, the small increase or decrease in λ_F^{In} upon increasing pressure corresponds to the small change in I_1/I_3 and λ_F^{PA}.

The significant decrease in λ_F^{In} in EPE(0.8) solution upon increasing temperature indicates a decrease in water content around In. As shown in Figure 8, increasing temperature also increases the microviscosity experienced by In. The decrease in water content in the PPO hydrophobic region is probably due to the more compact arrangement of this section of the micelle upon increasing temperature. Increasing temperature significantly decreases the values of I_1/I_3 and λ_F^{PA}. In addition to the more compact PPO hydrophobic core of the aggregate, the decreased hydration of poly(oxyethylene) upon increasing temperature[18] is a possible cause for the decrease in the polarity of the outer shell of the aggregate.

From the emission parameter of the three probes investigated, it is clear that increasing temperature makes the whole polymer aggregate become more closely packed. Under higher pressures, however, the increasing temperature does not decrease λ_F^{In}, I_1/I_3, and λ_F^{PA} as significantly as much as observed at lower pressures. This can be interpreted as follows: since increasing pressure destroys the hydrophobic bonding of the inner PPO core and increases the hydration of the outer PEO shell, the increasing temperature cannot effectively make the aggregate become more compacted at higher pressures.

The iceberg structure of water is destroyed by high pressure.[19] Thus, increasing pressure favors monomer formation of nonionic surfactant; i.e., hydrophobic bonding is weakened and micellization is disfavored.[3b] Since the increasing pressure enhances the hydration of PEO[17] and weakens hydrophobic bonding, increasing pressure is expected to also enhance the hydration of PPO core of EPE block copolymers. The weakened hydrophobic bonding by increasing pressure can be interpreted in terms of the further expansion of PPO core because either water becomes a "better" solvent for the core (in the sense of polymer solubility) or because of the increased hydration of PPO core.

At low temperature (50 °C) and at high pressure (1 bar), the polymer cores appeared to be "loose" and more hydrated than that at higher temperature and lower pressure. Thus, the parameters λ_F^{In}, I_1/I_3, and λ_F^{PA} all report this loosening of the core, which we attribute to weakening hydrophobic binding. From Figures 2–4, it can be seen that, at high temperatures, an increase in pressure tends to bring the parameters to values similar to those achieved at low temperature at 1 bar.

Using P as a probe, one can draw similar conclusions concerning structural changes for the four EPE polymers from Figures 3 and 5–7: (a) increasing pressure increases the hydrophilicity around P, especially at higher temperatures; (b) increasing temperature decreases the hydrophilicity around P, in particular at low pressures. These phenomena can be interpreted in terms of the change in the PPO hydrophobic core and PEO hydrophilic shell as discussed above.

Correlating the pressure and temperature effects with the properties of these polymers (Figures 3 and 5–7, Table I), one can conclude the following: (1) increasing pressure increases I_1/I_3 values in different polymer solutions with the order of greatest effect corresponding to the respective ratios of PPO in the polymers being EPE(0.3) > EPE(0.8) > EPE(3) > EPE(5), where EPE(0.3) is compared at 15 °C; (2) the effect of temperature is more significant for the polymers having their cloud points closer to the temperature at which the value for I_1/I_3 was measured

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(EPE(0.3); cloud point 16 °C > EPE(0.8); cloud point 61 °C > EPE(3); cloud point > 100 °C ≠ EPE(5); cloud point > 100 °C).

The cloud point is the temperature above which the phase separation of an aqueous solution of a nonionic surfactant occurs due to the sharp increase in micellar size. Below the cloud point, the increase in micellar size with increasing temperature is more significant as the cloud point is approached.[20] Similarly, the temperature effect on the micellar size of EPE aggregates can be expected to be more significant in the same temperature range. Since the change in micellar size is accompanied by a change in hydrophobicity and microviscosity, the changes in the microenvironments monitored by In, P, and PA are also more sensitive to temperature as the temperature of measurement is close to the cloud point.

Summary

The micropolarity of EPE block copolymers in the hydrophobic core, the inner part of hydrophilic, and the outer surface of hydrophilic shells has been investigated by use of the fluorescence probes In, P, and PA respectively. The information obtained indicates that the hydrophobic bonding in the hydrophobic cores

of EPE block copolymers is weaker than that of nonionic surfactants, C_9PhE_n. The hydrophobic bonding of EPE(0.8) is weakened by increasing pressure up to 1000–1500 bar but is strengthened above that pressure. Experimentally, this corresponds to a maximum in λ_F^{In} as a function of pressure. The pressure effects on hydrophilic bonding and on the PEO segment structure also allow an explanation of the increasing value of I_1/I_3 and λ_F^{PA} with increasing pressure. Increasing temperature decreases λ_F^{In}, I_1/I_3, and λ_F^{PA}. These observations are consistent with a more compact structure in EPE aggregates with increasing temperature. The effect of pressure is more significant at higher temperatures, while the effect of temperature is less significant at higher pressures. These conclusions hold for three kinds of microenvironments around probes in four kinds of EPE block copolymers. A comparison of the pressure and temperature effects on different EPE block copolymers leads to two conclusions: (1) pressure affects the block copolymer structure more significantly as the proportion of PPO is increased, and (2) changes in temperature influence this structure to a greater extent as the temperature of the system approaches its cloud point.

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GENERAL PHYSICAL CHEMISTRY

NMR Study of Solid Naphthalene Solubilities in Supercritical Carbon Dioxide near the Upper Critical End Point

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Solid solubilities of naphthalene in supercritical carbon dioxide have been measured near the upper critical end point of the binary mixture by using a novel, in situ NMR technique. Solubility data were obtained at 50.0, 55.0, and 58.5 °C over a pressure range of 120–500 bar. The pressure–temperature trace of the solid–liquid–gas phase line that terminates at the upper critical end point was also determined. The solubility results are discussed in terms of the supercritical solubility theory of Gitterman and Procaccia. This approximative analysis gives the location of the upper critical end point as $T_c = 60.1$ °C and $P_c = 226$ bar.

Introduction

During the past few years there has been an active interest in supercritical fluids and their mixtures due to the recent development of supercritical fluid extraction techniques.[1-3] Supercritical fluid solvents have been used in separation processes ranging from the decaffeination of coffee beans to the extraction of hydrocarbons from coal. Unfortunately, there is a lack of fundamental data on model supercritical fluid systems. In this paper, we present the results of our experiments on the solubility of solid naphthalene in supercritical carbon dioxide.

The particular phase behavior of the naphthalene–CO_2 system makes it a viable choice for studies of solid solubilities in supercritical fluids. The system is known as a class III mixture;[4] its pressure–temperature diagram is depicted in Figure 1. This type of phase behavior occurs for highly asymmetric binary mixtures where the melting point of the heavy component is greater than the critical temperature of the volatile component. Here the three-phase solid–liquid–gas (S–L–G) freezing point depression curve intersects the mixture critical line at two locations: the lower critical end point (LCEP) and the upper critical end point (UCEP). The LCEP is typically very near the critical point of the pure light component; the location of the UCEP must be

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