Formation of a Hydrophobic Microenvironment in Aqueous PEO−PPO−PEO Block Copolymer Solutions Investigated by Fourier Transform Infrared Spectroscopy

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The application of Fourier transform infrared (FTIR) spectroscopy to the study of poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) block copolymer is shown to give valuable information concerning the formation of a hydrophobic microenvironment in aqueous solutions. FTIR spectra of Pluronic P103 in H_2O and D_2O solutions were measured as a function of temperature. The temperature dependence of FTIR spectral data indicates that the methyl groups in PPO blocks of the polymer are experiencing a progressively less polar environment with an increase of temperature, and the strength of hydrogen bonds formed by the ether oxygen in PO groups with water is reduced by heat. The dehydration of PO segments favors the formation of a hydrophobic microenvironment in aqueous solutions. At higher temperatures, the appearance of the band of the dehydrated methyl groups in the FTIR spectra of aqueous Pluronic P103 solutions is related directly to the aggregation of PEO−PPO−PEO block copolymer and the formation of a hydrophobic microenvironment. The proportion of the dehydrated methyl groups increases with an increase of temperature; Pluronic P103 would form a micelle with a denser PPO core in aqueous solutions at higher temperatures.

Introduction

A great deal of effort has been devoted to understanding the formation of the hydrophobic microenvironment in aqueous surfactant solutions. These systems consist of two components, water and surfactant, the latter molecule comprising hydrophilic and hydrophobic parts. The hydrophilic part of the surfactant has a tendency to solvation, whereas the hydrophobic part of the surfactant adopts its lowest free energy state outside the solvent. The compromise between these conflicting requirements of surfactant is adsorption at the water/air interface and self-association in aqueous solutions. One of the famous macromolecular surfactants is poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) block copolymers, which are commercially available as Poloxamers or Pluronics. The characteristic features of these types of surfactants are their temperature-dependent self-association in aqueous solutions and their rich phase behavior. The process of self-association can be induced by increasing the block copolymer concentration to above the critical micellization concentration (CMC) and/or adjusting the temperature to exceed the critical micellization temperature (CMT). The structure of PEO−PPO−PEO block copolymer micelles is well described by the core−corona model, in which a spherical core composed of PPO is surrounded by a corona composed of the strongly hydrated PEO.[1−10] Because the hydrophilic/hydrophobic property of PEO−PPO−PEO block copolymers can be altered in the synthesis, they are widely used in detergency, wetting, foaming/defoaming, emulsification, lubrication, and solubilization, as well as in cosmetics, bioprocessing, and pharmaceutical applications.[11,12]

Hurter[13,14] and Linse[15,16] have modeled PEO−PPO−PEO block copolymer micellization with a mean-field lattice theory. In this theory, the polymer segments are allowed to have both polar and nonpolar conformations, corresponding to the gauche conformer of the C−C skeleton, which is favored in a polar environment, and the trans conformer, which dominates in a nonpolar environment. The segment density profiles of the predicted micelles indicate that there is a finite concentration of water in the micellar core and a diffuse interface between the core and the corona. Recently, the small-angle neutron scattering (SANS) technique has been used to study the temperature dependence of the structure of PEO−PPO−PEO block copolymer micelles.[17−20] It showed that the micellar core cannot be composed of PPO only but must contain significant quantities of water. The water content in the micellar core decreases with an increase of temperature.

Three different models have been proposed to interpret the solubility of PEO in water. The first mechanistic model is based on the assumption that the rotational conformation around the C−C bonds of the ethylene groups is of importance for the interaction with water. The second model is explained as a consequence of hydrogen bonds between the oxyethylene groups and water.[21] The third water structure model is based on PEO being accommodated with an ice-like structure of water.[22] Despite PPO having the same backbone structure as PEO, an optimal water structure cannot be formed in the PPO hydration shell, because the methyl groups of PPO constitute a sterical hindrance.[22] However, the molecular events of the formation of the hydrophobic microenvironment in aqueous PEO−PPO−PEO block copolymer solutions have not been fully examined.

Vibrational spectroscopy is a quite suitable method to observe the self-association of surfactants[23−26] and the coil−globule transition of water soluble polymers.[27−30] Many spectral features

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are sensitive not only to conformational changes of molecules but also to the local environment and the inter- and intramolecular interactions. In previous work,[31-33] we have reported that FT-Raman and FTIR spectra of PEO—PPO—PEO block copolymers in aqueous solutions are sensitive to the local polarity and conformation of block copolymer chains, and their variations with temperature are indicators of micellization. As an extension of the previous study, we have compared FTIR spectra for the PEO—PPO—PEO block copolymer in H_2O and D_2O solutions. Our aim is to provide important information concerning the formation of the hydrophobic microenvironment in aqueous PEO—PPO—PEO block copolymer solutions.

Materials and Methods

Materials. A PEO—PPO—PEO block copolymer, Pluronic P103, was obtained from BASF Corp. and used as received. Pluronic P103 can be represented by the general formula EO_{17}-$PO_{60}EO_{17}$, based on its molecular weight of 4950 and 30% PEO content. Poly(propylene oxide), PPO1000 ($M_W = 1000$), and poly(ethylene oxide), PEO400 ($M_W = 400$), were kindly donated by Shanghai Surfactant Factory (China). Poly(ethylene glycol), PEG4000 ($M_W = 4000$), was purchased from Beijing Chemical Reagent Corp. (China). These homopolymers were also used as received. D_2O ($\geq$99.8%) was purchased from Beijing Chemical Factory (China). Pluronic P103 solutions (15 wt %) were prepared individually by weighing appropriate amounts of the polymer and H_2O or D_2O. The solutions were facilitated by mixing with gentle agitation and then used in 24 h.

Methods. FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer with a resolution of 2 cm^{-1} using a DTGS (deuteriotriglycine sulfate) detector. The temperature of the sample was measured by a thermocouple inserted into a stainless steel block containing the sample cell. This system was composed of a Graseby-Specac temperature cell (P/N 21525), and temperature measurement was accurate to 0.1 °C. FTIR spectra were recorded by scanning 32 times and the equilibration time for each measurement was 2 min. For FTIR measurement, PPO1000, PEO400, Pluronic P103, and aqueous polymer solutions were sandwiched between two BaF_2 windows of an IR cell; a spacer was also nipped to prevent evaporation during the measurement. The FTIR spectrum of PEG4000 was obtained using the KBr pellet method. In the measurement of FTIR spectra as a function of temperature in the range from 0 to 50 °C, the samples were first cooled to 0 °C by liquid nitrogen and then heated stepwise with a 2 deg temperature interval. All spectroscopic data were further analyzed using Bruker OPUS software.

Results and Discussion

FTIR Spectroscopy of Pure Polymers. FTIR spectra of PPO1000, PEO400, PEG4000, and Pluronic P103 were recorded; the frequencies and assignments of the FTIR absorption bands are summarized in Table 1. These materials have the same skeleton. PPO1000 and PEO400 are liquid at room temperature, but PEG4000 is solid. The band positions of PEG4000 are in a very good agreement with those reported in the literature for the PEO crystalline phase.[34-37] The difference in FTIR spectral profiles between PEG4000 and PEO400 is obvious, because PEO400 is amorphous.

The characteristic bands of the PEO crystalline phase do not appear in the spectral profile of Pluronic P103; it means that the PEO blocks in Pluronic P103 are amorphous. The existence of methyl groups in Pluronic P103 is confirmed by observing the bands at 2970 and 1373 cm^{-1}. The 2970 cm^{-1} band is

TABLE 1: Assignments of FTIR Bands (cm^{-1}) of PPO1000, PEO400, PEG4000, and Pluronic P103 at 20 °C

PPO1000	PEO400	PEG4000	Pluronic P103	assignment[a]
2970			2971	antisymm C—H str of CH_3
2933	2948	2945	2930	antisymm C—H str of CH_2
2900				symm C—H str of CH_3
2868	2866	2885	2871	symm C—H str of CH_2
1374			1373	CH_3 symm deformation
		1360		CH_2 wag, C—C str
	1350			
1345		1343	1345	CH_2 wag
	1325			
1298	1297		1297	
		1280	1280	CH_2 twist
	1249		1250	
		1242		CH_2 twist
		1149		C—O—C str, C—C str
1108	1108	1108	1110	C—O—C str
		1060		C—O—C str, CH_2 rock
1014			1014	
	962			CH_2 rock
942	949	946	934	CH_2 rock, C—O—C str

[a] Assignment based on refs 36 and 37.
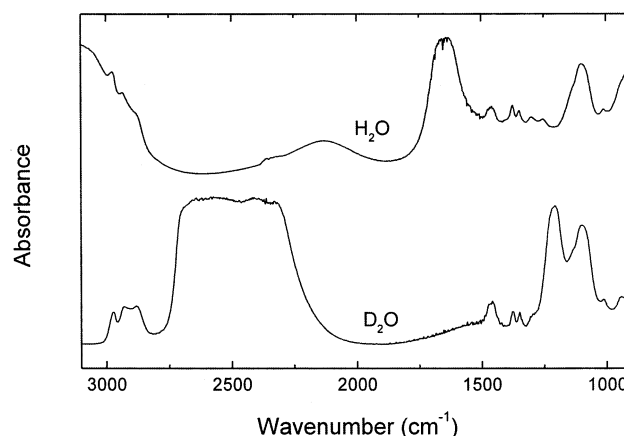
Figure 1. FTIR spectra of 15 wt % Pluronic P103 in D_2O and H_2O solutions at 20 °C.
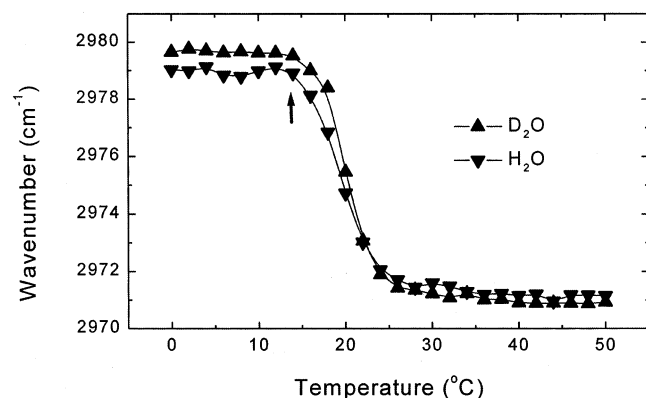
assigned to the antisymmetric C—H stretching vibration of methyl groups in the PPO blocks, and the 1373 cm^{-1} band is assigned to the symmetric deformation band of methyl groups. The weak band at 1014 cm^{-1} of amorphous PPO1000 also appears in the spectrum of Pluronic P103.

Temperature-Induced Micellization of Pluronic P103 in Aqueous Solutions. FTIR spectral profiles of 15 wt % Pluronic P103 in H_2O and D_2O solutions in the range from 3100 to 900 cm^{-1} at 20 °C are presented in Figure 1. The strong IR absorption by H_2O exists in the spectral regions above 2800 cm^{-1}, from 1700 to 1600 cm^{-1}, and below 1000 cm^{-1}. The O—H stretching band of H_2O conceals the C—H stretching vibration of Pluronic P103. The weak shoulder at 2979 cm^{-1}, which is assigned to the antisymmetric C—H stretching band of methyl groups, can be observed in the spectrum of Pluronic P103 in H_2O solution. The major advantage of D_2O as a solvent is a shift in the stretching band of water to the range from 2750 to 2200 cm^{-1}, which prevents the band from overlapping the C—H stretching bands of Pluronic P103. The strong IR absorption by D_2O at 1200 cm^{-1} partially overlaps with the C—O—C stretching vibration of Pluronic P103. However, the C—O—C stretching band of Pluronic P103 in D_2O solution can be assigned clearly, whose position is essentially identical with that in H_2O solution.

An increase of temperature provides the thermodynamic driving force for the transfer of PO groups in PEO—PPO—PEO

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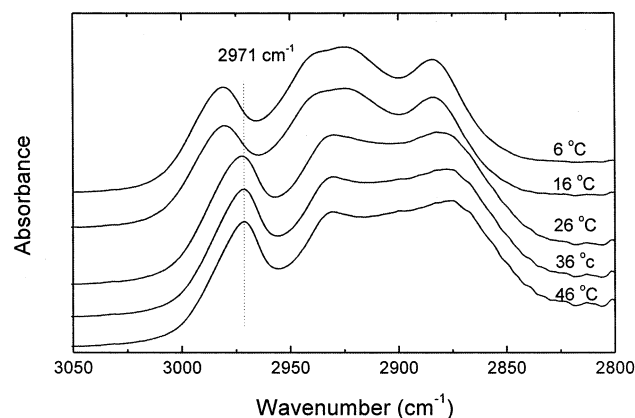
Figure 2. FTIR spectra of 15 wt % Pluronic P103 in D_2O solution at various temperatures in the range from 3050 to 2800 cm^{-1}. The band at 2971 cm^{-1} is denoted.

Figure 4. Temperature dependence of the wavenumber of the C−O−C stretching bands of 15 wt % Pluronic P103 in D_2O and H_2O solutions. The arrow denotes the CMT.
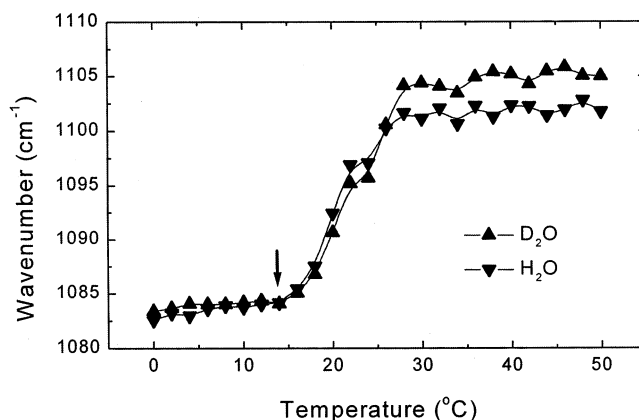

Figure 3. Temperature dependence of the wavenumber of the antisymmetric C−H stretching band of methyl groups of 15 wt % Pluronic P103 in D_2O and H_2O solutions. The arrow denotes the CMT.

block copolymer from the aqueous medium into the hydrophobic microenvironment (micellar core). For characterizing the effect of temperature on the properties of PEO−PPO−PEO block copolymer in H_2O and D_2O solutions, FTIR spectra of aqueous Pluronic P103 solutions at various temperatures were measured. The changes of FTIR absorption intensities, band shapes, and band positions reflect directly the influence of temperature on the properties of Pluronic P103 in aqueous solutions. The temperature-induced changes in the spectral regions of the C−H stretching vibration of methyl groups, the C−O−C stretching vibration, and the deformation vibration of methyl groups are discussed respectively in the following sections.

C−H Stretching Vibration. The temperature dependence of FTIR spectral profiles of 15 wt % Pluroic P103 in D_2O solution in the wavenumber range from 3050 to 2800 cm^{-1} is presented in Figure 2. At lower temperatures, the antisymmetric C−H stretching vibration of Pluronic P103 in D_2O solution is at 2980 cm^{-1}. The remarkable changes in the spectral profiles with an increase of temperature are that the C−H stretching bands undergo a red shift and the valley between the peaks at 2925 and 2880 cm^{-1} is gradually filled.

Figure 3 shows the temperature dependence of the wavenumber of the antisymmetric C−H stretching vibration of methyl groups in Pluronic P103 in D_2O and H_2O solutions. At lower temperatures, the frequency of the antisymmetric C−H stretching band of methyl groups changes slightly with an increase of temperature. When the temperature is above 14 °C, a change occurs, leading to a shift of wavenumber abruptly toward lower frequency. A number of experimental studies have shown that the C−H stretching band of an alkyl group undergoes

a blue shift when the alkyl group interacts with water.[27−33] Because the temperature-induced red shift of the C−H stretching band of methyl groups of Pluronic P103 causes the band to be closer to that of the neat sample, it is indicative of a reduction in the interaction of the methyl groups with water molecules and a decrease in the polarity of the microenvironment around PO segments, which is related to the dehydration of methyl groups and the formation of a hydrophobic microenvironment in aqueous solutions.[31−33]

The frequency changes in methyl groups indicate that the dehydration process accompanies electronic redistribution in the C−H bonds. Gu has suggested that C−H···OH$_2$ interaction appears to be very similar to conventional hydrogen bond in most respects.[38] Ab initio calculations have shown that the exchange force, which tends to contract the C−H bonds, is slightly stronger than the forces pushing toward elongation (electrostatic, polarization, charge transfer, and dispersion) in the C−H···OH$_2$ interaction. A part of electron about the C−H proton is pushed out into the C−H bond due to a repulsive interaction between the C−H hydrogen atom and water oxygen atom. Because the C−H bond is contracted,[38] the C−H···OH$_2$ interaction is called an anti-hydrogen bond, in contrast to a conventional hydrogen bond such as O−H···OH$_2$.[39,40] The red shift of the antisymmetric C−H stretching vibration of methyl groups with an increase of temperature means that the interaction of the methyl groups in PPO with water molecules is weakened by heat and PPO is experiencing a progressively less polar environment.

At higher temperatures, the antisymmetric C−H stretching band of methyl groups is at 2971 cm^{-1}, whose position approaches that of a neat sample, which means that the microenvironment around the methyl groups is very similar to that of a neat sample. Therefore, a nonpolar microenvironment would be created in aqueous solutions. The CMT value of Pluronic P103 in aqueous solution can be obtained from the temperature dependence of FTIR data of methyl groups. The CMT is defined as the temperature at which the wavenumber deviates from the baseline contributed only by unimers at lower temperatures. The CMT values of 15 wt % Pluronic P103 in H_2O and D_2O solutions can be determined to be 14 °C (the CMT value is denoted in Figure 3).

C−O−C Stretching Vibration. The influence of temperature on the C−O−C stretching vibration of aqueous Pluronic P103 solutions is plotted in Figure 4. When the temperature is raised from 0 to 50 °C, the wavenumber of the band shifts toward higher wavenumber. This band is a combination of the C−O−C stretching vibrations of both PPO and PEO blocks. It is known

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that the PEO blocks undergo only a small degree of dehydration with increasing temperature, but the hydrophobic PPO blocks apparently reduce contact with water during the micellization process.[1-10] The high-frequency shift of the C—O—C stretching vibration is mainly attributed to the dehydration of the PPO ether backbone. The trend of wavenumber change of the C—O—C stretching vibration with temperature in D_2O is similar to that in H_2O. The CMT values of 15 wt % Pluronic P103 in H_2O and D_2O solutions can also be obtained from the temperature dependence of the C—O—C stretching vibration, which are 14 °C corresponding to the onset of the significant changes with temperature. The dehydration of methyl groups and ether oxygen in PPO proceeds simultaneously in the course of micellization (see Figures 3 and 4). The frequency of the C—O—C stretching vibration in D_2O solution at higher temperatures is slightly higher than that in H_2O solution.

The hydrogen bond model has been extensively used to interpret the mechanism of the solubility of PEO in water.[21,25,26] Upon the formation of a hydrogen bond, lone pair electrons on the oxygen atom are withdrawn by the hydrogen atom of water, and therefore, a reduction of electron density on the C—O bond takes place, which induces a red shift of the C—O—C stretching band. The breakdown of hydrogen bonds between the ether oxygen and water would induce a blue shift of the C—O—C stretching band. In the case of PEO—PPO—PEO block copolymer dissolved in water, the ether oxygen of EO and PO is considered to form hydrogen bonds with the solvent water. During the micellization process, the breakdown of the hydrogen bonding interaction of the ether oxygen in PO groups with water gives rise to higher frequencies of the C—O—C stretching vibration.

The FTIR data lend support that the temperature-dependent solute—solvent interaction plays an important role in leading PEO—PPO—PEO block copolymer micellization in aqueous solutions.[1] At lower temperatures, a hydration shell with an enhanced structure of water is developed around the polymer. PPO blocks would repel each other becasue PPO is in the hydrated state. An increase of temperature would render the solute—solvent interaction less favorable. At higher temperature, the dehydration of PPO takes place (the dehydration of methyl groups in PPO and the breakage of hydrogen bonds between the ether oxygen and water are confirmed by FTIR spectroscopy). The removal of solvent from the PPO hydration shell would result in effective PO—PO attraction (hydrophobic interaction) dominating over the repulsion, so that Pluronic P103 would self-associate and form a hydrophobic microenvironment in aqueous solutions.

Deformation Vibration of Methyl Groups. FTIR spectral profiles of 15 wt % Pluronic P103 in D_2O solution in the range from 1400 to 1320 cm^{-1} at various temperatures are presented in Figure 5. The symmetric deformation band of methyl groups of 15 wt % Pluronic P103 in D_2O solution is at 1381 cm^{-1} at lower temperatures. With an increase of temperature, the band moves toward lower wavenumber at 1378 cm^{-1} for Pluronic P103 at 20 °C (the band at 1378 cm^{-1} is denoted in Figure 5); the weak shoulder at 1373 cm^{-1} can be found in the low-frequency region of the 1378 cm^{-1} band. The relative peak intensity of the 1378 cm^{-1} band decreases whereas the shoulder at 1373 cm^{-1} increases with an increase of temperature. At higher temperatures, the band at 1373 cm^{-1} dominates over the symmetric deformation band of methyl groups, and the band at 1378 cm^{-1} becomes a weak shoulder.

FTIR spectral profiles of 15 wt % Pluronic P103 in H_2O solution in the range from 1400 to 1320 cm^{-1} at various
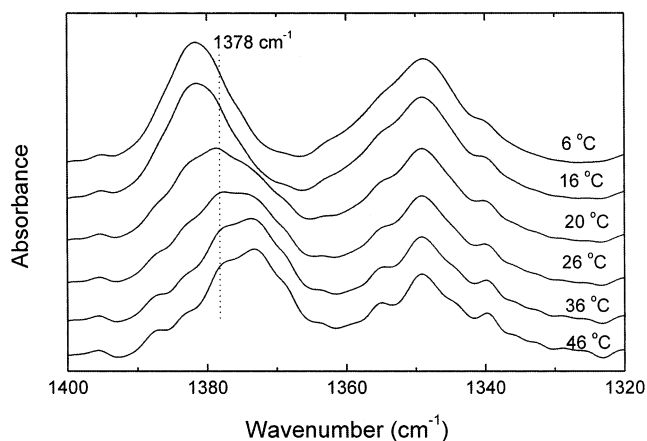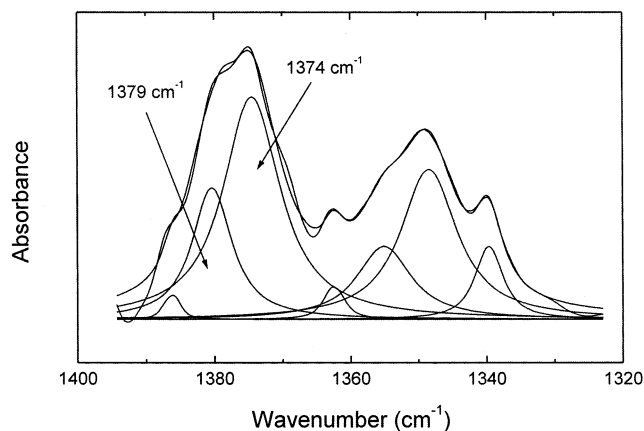
Figure 5. FTIR spectra of 15 wt % Pluronic P103 in D_2O solution at various temperatures in the range from 1400 to 1320 cm^{-1}. The band at 1378 cm^{-1} is denoted.
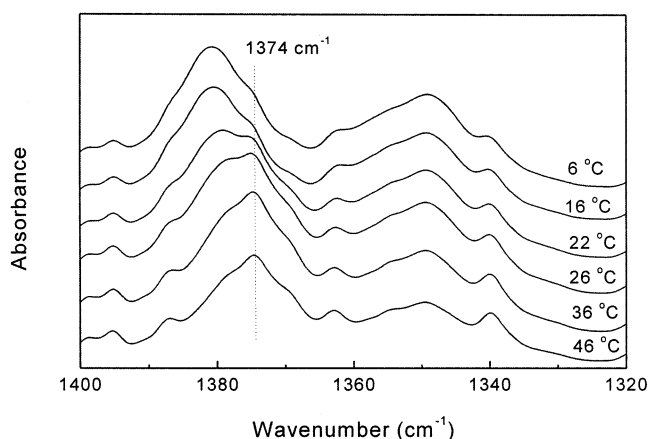
Figure 6. FTIR spectra of 15 wt % Pluronic P103 in H_2O solution at various temperatures in the range from 1400 to 1320 cm^{-1}. The band at 1374 cm^{-1} is denoted.

temperatures are presented in Figure 6. It can be seen clearly in the spectral profiles of Pluronic P103 in H_2O solution at 22 and 26 °C that the bands at 1379 and 1374 cm^{-1} appear simultaneously (the band at 1374 cm^{-1} is denoted in Figure 6). At higher temperatures, the band at 1374 cm^{-1} dominates over the symmetric deformation band of methyl groups. We deduced that the methyl groups of Pluronic P103 in aqueous solutions are composed of two components: one is a hydrated state corresponding to the band around 1379 cm^{-1} (surrounded by water), and the other is a dehydrated state associated with the band at 1374 cm^{-1} (the symmetric deformation vibration of methyl groups of neat Pluronic P103 is at 1373 cm^{-1}). A similar phenomenon that the symmetric C—H stretching of methyl groups of poly(vinyl methyl ether) in water is composed of two components, which are assignable to hydrated and dehydrated methyl species, has been observed by Maeda.[28] The microenvironment around the hydrated methyl groups is polar and around the dehydrated methyl groups is nonpolar.

The shifts of the symmetric deformation vibrations of methyl groups from 1381 cm^{-1} toward lower wavenumbers (1378 cm^{-1} in D_2O and 1379 cm^{-1} in H_2O) means that the interaction of the methyl groups with water are first reduced gradually in the dehydration process. When the temperature is above the CMT, the relative peak intensity associated with the dehydrated methyl groups (1373 cm^{-1} in D_2O and 1374 cm^{-1} in H_2O) increases, whereas the relative peak intensity associated with the hydrated methyl groups decreases. This phenomenon is explained as a

Figure 7. Representative baseline-subtracted FTIR spectrum of 15 wt % Pluronic P103 in H$_2$O solution at 26 °C in the range from 1400 to 1320 cm^{-1} and a best curving-fitting result. The fitting peaks at 1379 and 1374 cm^{-1} are denoted.

part of the methyl groups dehydrating and altering in the local polarity (from polar to nonpolar environment). A significantly nonpolar environment would be created by the dehydrated methyl groups in aqueous solutions, which is located in the micellar interior.

Effect of Temperature on the Structural Properties of Pluronic P103 Micelles. A PEO−PPO−PEO block copolymer micelle is composed of a hydrophobic PPO core surrounded by a hydrated PEO corona. To obtain more quantitative information on the temperature-dependent structural properties of PEO−PPO−PEO block copolymer micelles, the spectral pattern in the symmetric deformation vibration of methyl groups is resolved into two band components: one is associated with the dehydrated methyl groups and the other is associated with the hydrated methyl groups. Because of the overlap of FTIR adsorption bands, the curve-fitting method was used to fit the peaks in the range from 1400 to 1320 cm^{-1}. One representative result is presented in Figure 7, which is the spectral profile of 15 wt % Pluronic P103 in H$_2$O solution at 26 °C. In the curve-fitting procedure, the peak frequency values determined by the fittings are the same as those obtained from the observed spectral profile. On the basis of the fitting results, the integrated peak areas of dehydrated (peak at 1374 cm^{-1}) and hydrated methyl groups (peak at 1379 cm^{-1}) were calculated. The total integrated peak area of dehydrated and hydrated methyl groups was normalized to 1; the normalized integrated peak area of each component corresponds to the fraction of methyl groups in the dehydrated and hydrated state. Of course, the relative peak area fraction is not the exact proportion of dehydrated or hydrated methyl groups. Nevertheless, it can be used as a criterion as far as its increase or decrease unambiguously shows an increase or decrease of the proportion of the dehydrated or hydrated methyl groups.

Figure 8 shows the plots of the relative peak area fractions of the dehydrated methyl groups of 15 wt % Pluronic P103 in aqueous solutions estimated in this way as a function of temperature. A similar trend of the changes of relative peak area fractions with temperature is observed in both D$_2$O and H$_2$O solutions. The relative peak area fraction associated with the dehydrated methyl groups of Pluronic P103 increases with increasing temperature. It illustrates that the proportion of the dehydrated methyl groups increases with an increase of temperature. As the methyl groups are confined to the micellar interior, the decrease of the proportion of the hydrated methyl groups means that water is excluded gradually from micellar
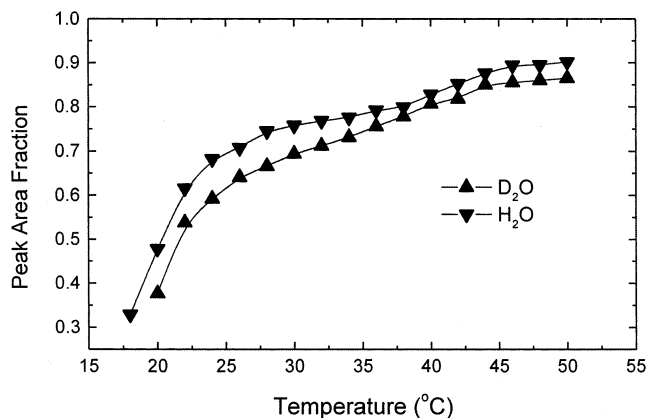
Figure 8. Temperature dependence of the relative peak area fractions of the dehydrated methyl groups of 15 wt % Pluronic P103 in D$_2$O and H$_2$O solutions.

core with an increase of temperature ([the relative peak area fraction of hydrated methyl groups] = 1 − [the relative peak area fraction of dehydrated methyl groups]). Pluronic P103 would form a micelle with a denser PPO core and a lower water content in the micellar core at higher temperatures. This result by FTIR data about the effect of temperature on the structural properties of PEO−PPO−PEO block copolymer micelles is consistent with that obtained by using SANS.[17−19] An increase of temperature would increase the hydrophobicity of the Pluronic polymer micellar core.

Even at the highest temperature of this study, a part of the methyl groups is in the hydrated state. The relative peak area fraction of the hydrated methyl groups of Pluronic P103 is about 0.13 in D$_2$O solution at 50 °C and about 0.10 in H$_2$O solution at 50 °C. This means that PPO blocks are probably dehydrated incompletely and some water may be contained in the micellar core. The segregation between PPO and PEO blocks is not sufficiently strong to cause a sharp boundary between the micellar core and corona even at higher temperature. A diffuse interface between the core and the corona has been used to describe the micellar structure.[13,14] Methyl groups at the core and corona interface may be in the hydrated state where water is retained due to the interaction of PEO with water; EO as a hydrophilic group is stronger than PO.

The solvent effect on the properties of Pluronic P103 micelles in aqueous solutions can be observed from Figure 8. At the same temperature, the relative peak area fraction of the dehydrated methyl groups of Pluronic P103 in D$_2$O solution is smaller than that in H$_2$O solution. This means that the water content in the micellar core in H$_2$O solution is smaller than that in D$_2$O solution. It is known that the hydrogen bonding interaction between D$_2$O molecules is stronger than that between H$_2$O molecules;[28,41] therefore, the ether oxygen of the block polymer forms stronger hydrogen bonds with D$_2$O than that with H$_2$O. More D$_2$O molecules would be retained by the polymer ether backbone in the micellar core.

Conclusions

In this work, we have explored using FTIR spectroscopy to study the formation of a hydrophobic microenvironment in aqueous Pluronic P103 solutions. Analysis of the FTIR spectral profiles of Pluronic P103 in D$_2$O and H$_2$O solutions outlined that the interaction of PPO with water is influenced significantly by temperature. At low temperature, the methyl groups in PPO are hydrated and the ether oxygen atoms of PPO are considered to form hydrogen bonds with water molecules. With an increase

of temperature, the shift of the bands of methyl groups in PPO toward lower frequencies means that the interaction of methyl groups with water is weakened by heat. The move of the C−O−C stretching vibration toward higher frequency indicates that the hydrogen bonding interaction of the ether oxygen in PPO with water is broken gradually by heat. Therefore, when the temperature is above the CMT, the hydrophobic interaction among PPO blocks dominates over the repulsion, Pluronic P103 would self-associate and form a hydrophobic microenvironment in aqueous solutions.

The band of the symmetric deformation vibration of methyl groups of Pluronic P103 in aqueous solutions splits into two bands; one is associated with the hydrated methyl groups, and the other is associated with the dehydrated methyl groups. It is deduced from the FTIR spectral data that the proportion of the dehydrated methyl groups increases and water is excluded gradually from the micellar interior with an increase of temperature. Pluronic P103 would form a micelle with a denser PPO core in aqueous solutions at higher temperatures. The water content in the micellar core in H_2O solution is smaller than that in D_2O solution.

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