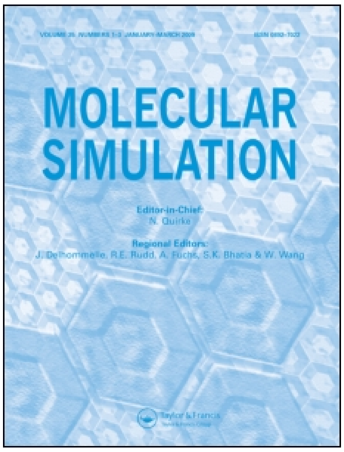

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Thermodynamic analysis of micellization in PEO-PPO-PEO block copolymer solutions from the hydrogen bonding point of view

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Thermodynamic analysis of micellization in PEO–PPO–PEO block copolymer solutions from the hydrogen bonding point of view

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A thermodynamic approach is suggested to study the micellization mechanism of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymers solutions from the hydrogen bonding point of view. Using Flory–Huggins theory, an association model is presented to describe hydrogen bonded (HB) chains, which are bridged by hydrogen bonds between water molecules and segments of the copolymer. The entropic change due to hydrogen bonding is formulated and the individual contribution of EO–water (EO–W) and PO–water (PO–W) hydrogen bonding to the micellization are derived respectively. Fourier transform infrared (FTIR) spectroscopy is applied to obtain the information of hydrogen bonds. During the temperature-dependent micellization of P105 block copolymer solutions, rapid disruption of PO–W hydrogen bonds is observed by FTIR and the calculated entropy relating to PO–W hydrogen bonds increases drastically compared with that of EO–W hydrogen bonds. The results demonstrate that PO–W hydrogen bonds play a dominant role in micellization.

Keywords: Thermodynamic model; Hydrogen bonds; Block copolymers; Micelles; Fourier transform infrared spectroscopy

1. Introduction

Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymers, commercially available as Pluronics or Poloxamers, are high-molecular weight nonionic surfactants. The most characteristic property of PEO–PPO–PEO block copolymers is the inverse temperature dependence of micellization. In dilute solution and at low temperature, the block copolymers dissolve in aqueous solution as unimers. When the temperature approaches the critical micellization temperature (CMT), the copolymers aggregate into micelles. There is a broad temperature range (transition region) above the CMT where micelles coexist in solution with unimers. When the temperature is above the transition region, most copolymers form stable micelles.

Because of the widespread potential industrial applications, the micellization of Pluronic solutions have been investigated both experimentally and theoretically. Alexandridis reviewed the thermodynamics, structure, dynamics and modeling of micellization in detail [1]. Using the association model, which assumed equilibrium between unimer and micelles, a representative thermodynamic work for various PEO–PPO–PEO copolymers was carried out [2]. Effect of copolymer composition and molecular weight on micellization thermodynamics was discussed. The traditional view of the "hydrophobic effect" based on solvent–solvent interactions was employed to explain the calculated thermodynamics.

Solute–solvent or solute–solute interactions have also been proposed in thermodynamic analysis of water-soluble polymers solutions phase behavior including poly(ethylene oxide)(PEO) solutions as well as PEO–PPO–PEO solutions. Karlstrom [3] assumed that the PEO chain can be replaced by a heteropolymer with a temperature-dependent number of monomers of two sorts, denoted as the low- and high-temperature states of a PEO unit. These two monomers can interact with themselves, with each other and with solvent. Hurter and Linse [4–7] developed the self-consistent mean field model (SCMF) for predicting the

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solution behavior of PEO–PPO–PEO block copolymer micelles, which incorporated Karlstrom's ideas to account for the conformational distribution in PEO and PPO. The model predictions agree well with the trends observed experimentally.

Recently, we reported FTIR spectroscopic investigation on the temperature-dependent micellization of PEO–PPO–PEO block copolymer in water [8–12]. Accompanying the transition from unimers to micelles, the frequency of the C–O–C stretching band in FTIR spectra shifted toward a higher wave number, which indicates the break of the hydrogen bonds between ether oxygen atoms in the polymer backbone and the water hydrogen atoms. The micellization of PEO–PPO–PEO block copolymer in water was explained as the conformational change of the polymer induced by the changes in hydrogen bonding during the temperature increase. Hydrogen bonds were shown to play an important role in micellization.

Hydrogen bonding taking place in aqueous solutions of PEO has been well studied both experimentally and theoretically to explain its lower critical solution temperature (LCST) behavior [13–19]. The results indicated that the hydrogen bonding was likely to be the specific interaction controlling the phase behavior. Many theoretical approaches have also been put forward to quantify the contribution of PEO–W hydrogen bonding as driving force for its complex behavior, including lattice model [15], molecular dynamics (MD) simulations [16,17] and mean-field like approach [18,19].

However, few considerations of such hydrogen bonds have been performed when modeling and illustrating the micellization mechanism of Pluronic solutions. How does the solution composition and temperature affect the hydrogen bonding and hence result in micellization? As it is well-known that micellization is an entropicly driven process [1, 2], how much does hydrogen bonding contribute to the change of entropy? Since the role of EO units in micellization remained uncertain, does the hydrogen bonding competition between EO blocks and PO blocks affect the phase behavior? A quantitative thermodynamic analysis of the hydrogen bonding in Pluronic solutions is helpful to clarify these questions.

In the present paper, we will develop a thermodynamic model to describe the hydrogen bonding association in Pluronic solutions and derive the individual entropy contribution of EO–W and PO–W hydrogen bonding to the micellization. FTIR spectroscopy will be employed to obtain the information of hydrogen bonds. The micellization mechanism of PEO–PPO–PEO block copolymer and the role of PO, EO blocks in micellization will be discussed in detail from the hydrogen bonding point of view.

2. Experimental methods

2.1. Materials

PEO–PPO–PEO block copolymer Pluronic P105 is manufactured by BASF and was used without further purification. Pluronic P105 polymer has a nominal molecular weight of 6500 and can be represented by the formula $(EO)_{37}(PO)_{58}(EO)_{37}$. PEO4000 ($M=4000$) and PPO2700 ($M=2700$) were purchased from Sigma and were also used as received. Aqueous solutions of PPO2700, PEO4000 and Pluronic P105 were prepared by dissolving the polymer in distilled water with gentle agitation and then stored in a refrigerator.

2.2. FTIR measurements

FTIR spectra with a resolution of 2 cm^{-1} were recorded on a Bruker Vecter 22 FTIR spectrometer using a deuterotriglycine sulfate detector. The temperature study was carried out in the range of 2–50°C. The temperature of the samples was measured by a thermocouple inserted into a stainless steel block containing the sample cell; equilibration time for each temperature was 2 min. OPUS spectroscopic software was used for data handling and the frequencies of the bands were determined using the peak pick function. For the 1200–1000 cm^{-1} region, the deconvolution of spectra was performed using the OPUS deconvolution function. The deconvoluted spectra were then curve-fitted with Gaussian bands, the frequency and intensity of the subbands were obtained.

3. Model

3.1. Stoichiometry of hydrogen bonding association

MD simulation[16,17] and ^{1}H, ^{2}H-NMR experiments [13] of PEO solutions indicated that in the most concentration and temperature range, water has a strong tendency to form two EO–W hydrogen bonds with different EO blocks, thereby forming hydrogen bonding bridges between EO blocks. These bridges connect both neighbor, next-neighbor EO within the same PEO chain and intermolecular EO on the different chains into several polydisperse hydrogen bonded (HB) chains which can be represented as $(W)_{m1}$–EO–$(W)_n$–EO–$(W)_{m2}$ ($m1$, $m2$ vary from 0 to ∞ and n varies from 1 to ∞). When modeling these HB chains, it is necessary to make a suitable definition of them which can cover the majority of the possible stoichiometries. In this study, we cut off the W–W hydrogen bonds in $(W)_{m1}$–EO–$(W)_n$–EO–$(W)_{m2}$ chains when $n \geq 2$ or $m1$, $m2 \geq 2$, which results in unique stoichiometry of EO–W–EO–W…W–EO–W–EO but with various chain lengths. This simplification is reasonable because W–W hydrogen bonds in $(W)_{m1}$–EO–$(W)_n$–EO–$(W)_{m2}$ chains are the same as hydrogen bonding network of water in the bulk solution when $n \geq 2$ or $m1$, $m2 \geq 2$. The water molecules which were cut from the chains were treated as free waters in bulk solution. Similarly, in PEO–PPO–PEO block copolymer solutions, there are two main sorts of such HB chains twisting together: EO–W–EO–W…W–EO–W–EO and PO–W–PO–W…W–PO–W–PO, which are schematically shown in figure 1. These chains manifest dependence on both

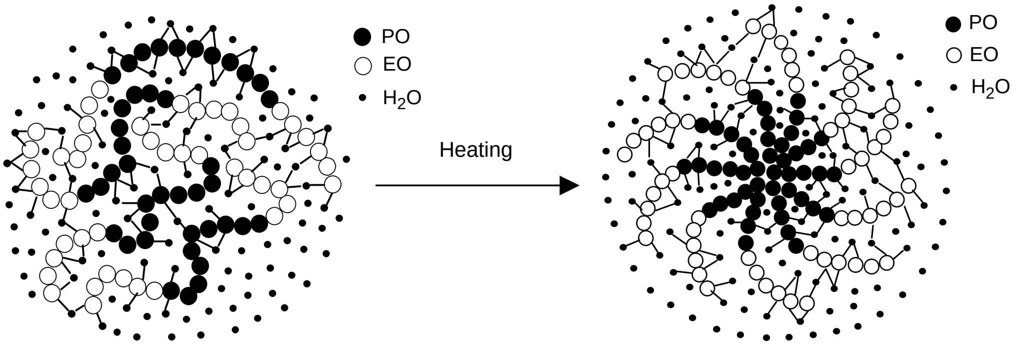

Figure 1. Schematic presentation of hydrogen bonding bridges between the segments and water in PEO–PPO–PEO block copolymer solutions. The corresponding chain conformation of block copolymer at low temperature (a) and high temperature (b) indicates that with increasing the temperature, the disruption of hydrogen bonding leads to the formation of micelle.

composition and temperature accompanying with the breaking and reforming of the hydrogen bonding bridges in micellization process. We defined these chains as h-length HB chains where h functional units were linked by $h-1$ water molecules. If we let S and W represent functional segments of polymer and water, respectively, the h-length HB chains can be represented as S_hW_{h-1}, h varied from 1 to ∞ (in EO–W–EO–W…W–EO–W–EO chains, S should be replaced by "E" which represents EO blocks; in PO–W–PO–W…W–PO–W–PO chains, S should be replaced by 'P' which represents PO blocks). At equilibrium, we can write:

$$S_{h-1}W_{h-2} + W + S_1 \overset{K_S}{\longleftrightarrow} S_hW_{h-1}. \tag{1}$$

Following Flory [20], assuming independent chain length, the dimensionless equilibrium constant (K_S) describing the distribution of HB chains can then be defined in terms of volume fraction (Φ) as follows:

$$K_S = \frac{\Phi_{S_h}}{\Phi_{S_{h-1}}\Phi_{W0}\Phi_{S_1}/\Phi_S}\,\frac{2h-3}{2h-1} \tag{2}$$

where Φ_{S_1}, Φ_{S_h} and Φ_S represent the volume fractions of non-HB segments, h-length HB chains and total segments, respectively. Φ_{W0} is the volume fraction of water uninvolved in the HB chains (free water), precisely it should be

$$\Phi_{W0} = \Phi_W - \frac{\Phi_E}{H_E+1} - \frac{\Phi_P}{H_P+1} \tag{3}$$

where Φ_E and Φ_P is the volume fraction of EO blocks and PO blocks in PEO–PPO–PEO block copolymer solutions respectively. However, the micellar phase of PEO–PPO–PEO copolymer solution occurred almost in dilute solution where Φ_W is much bigger than Φ_E and Φ_P. Consequently, we replace Φ_{W0} with Φ_W for simplicity. The stoichiometric relationships are simply obtained from materials balance considerations,

$$\Phi_S = \sum_{h=1}^{\infty}\frac{h}{2h-1}\Phi_{S_h}. \tag{4}$$

For formation of h-length HB chains, according to equations (1) and (2) we have,

$$\Phi_{S_h} = \frac{2h-1}{2h-3}K_S\Phi_{S_{h-1}}\Phi_W\Phi_{S_1}/\Phi_S \tag{5}$$

$$\Phi_{S_{h-1}} = \frac{2h-3}{2h-5}K_S\Phi_{S_{h-2}}\Phi_W\Phi_{S_1}/\Phi_S \tag{6}$$

$$\cdots$$

$$\Phi_{S_2} = \frac{3}{1}K_S\Phi_W\Phi_{S_1}^2/\Phi_S. \tag{7}$$

By successive substitution of $\Phi_{S_{h-1}}, \Phi_{S_{h-2}}, \ldots \Phi_{S_2}$, we obtain:

$$\Phi_{S_h} = (2h-1)(K_S\Phi_W\Phi_{S_1}/\Phi_S)^{h-1}\Phi_{S_1}. \tag{8}$$

Substituting,

$$\sum_{h=1}^{\infty}\frac{h}{2h-1}\Phi_{S_h} = \sum_{h=1}^{\infty} h(K_S\Phi_W\Phi_{S_1}/\Phi_S)^{h-1}\Phi_{S_1}. \tag{9}$$

For $K_S\Phi_W\Phi_S/\Phi_S < 1$,

$$\sum_{h=1}^{\infty} h(K_S\Phi_{S_1}\Phi_W)^{h-1} = \frac{1}{(1-K_S\Phi_W\Phi_S/\Phi_S)^2}. \tag{10}$$

Substituting into, we obtain

$$\Phi_S = \frac{\Phi_{S_1}}{(1-K_S\Phi_W\Phi_S/\Phi_S)^2}. \tag{11}$$

Then the fraction of non-HB segments ($f_F = \Phi_{S_1}/\Phi_S$) can be shown that

$$f_F = (1-f_FK_S\Phi_W)^2. \tag{12}$$

After some manifestation, we have:

$$f_F = \frac{2K_S\Phi_W + 1 - \sqrt{2K_S\Phi_W + 1}}{2(K_S\Phi_W)^2}. \tag{13}$$

This equation relates the fraction of non-HB segments (f_F) with the volume fraction of water Φ_W. f_F can be obtained from FTIR spectra which will be discussed in the following section and allow the determination of the dimensionless equilibrium constant (K_S) from a least squares fitting method.

3.2. Determination of hydrogen bonding information using FTIR

Figure 2 shows C–O–C stretching regions of the representative FTIR spectra for aqueous PEO4000, PPO2700 and Pluronic P105 solutions (Φ_W is 0.96) in the temperature range of 2–50°C. As the temperature increases, the frequency of the band for Pluronic P105 solutions shifts from 1084 to 1101 cm^{-1} while the band for PPO2700 solutions remains 1108 $\mathrm{cm}^{-1}$and the band for PEO4000 solutions remains 1090 cm^{-1}. When ether groups form hydrogen bonds, 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 C–O–C stretching band shifts to lower wave number [8–12]. Consequently, the FTIR spectra indicate that most of ether groups in PEO solutions keep HB while the majority in PPO solutions retains non-HB (free). In contrast, ether groups in Pluronic solutions undergo a transition from HB status to non-HB status. This change of hydrogen bonding corresponds to the micellization of Pluronic solutions.

The status of the two C–O–C groups are supposed to be reflected as two bands in FTIR spectrum. Therefore, as shown in figure 3, we applied the deconvolution method to obtain the independent information on both HB and free status under a complex band profile in the C–O–C stretching band of PEO4000, PPO2700 and Pluronic P105 solutions. The bands around 1112 and 1090 cm^{-1} were assigned to free PO and HB PO for PPO solutions while the bands around 1104 and 1082 cm^{-1} were assigned to free EO and HB EO for PEO solutions. For Pluronic solutions, there are five bands in the deconvoluted spectra which are in a good agreement with the assignment except that the band around 1082 cm^{-1}(HB EO) is split into two bands around 1083 and 1074 cm^{-1} which may represent two status of HB EO. According to Beer–Lambert law, the relative peak intensity of each band represents the number of the corresponding functional groups. We let the symbol I represents the intensity of each band, the subscripts S1 and SH represent the free segments and HB segments respectively. Then the experimental fraction of non-HB segments, f_F, at any given concentration can then be obtained as follows:

$$f_{\mathrm{F}} = \frac{\Phi_{\mathrm{S}_1}}{\Phi_{\mathrm{S}}} = \frac{I_{\mathrm{S1}}}{I_{\mathrm{S1}} + I_{\mathrm{SH}}} = \frac{H}{H+1} \tag{14}$$

where H is defined as $I_{\mathrm{S1}}/I_{\mathrm{SH}}$.

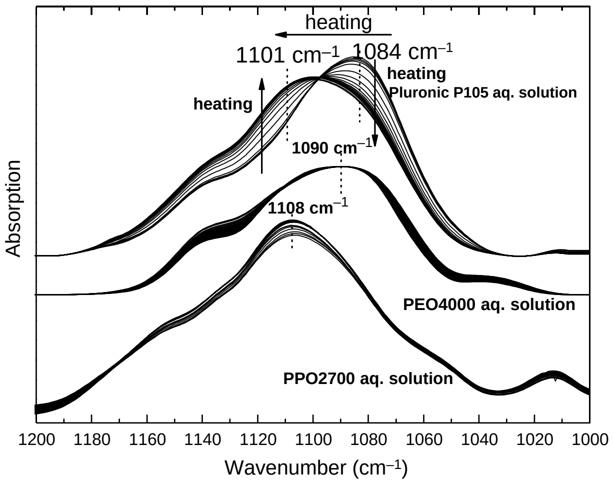

Figure 2. Temperature-dependent FTIR spectra of aqueous PEO4000, PPO2700 and Pluronic P105 solutions ($\Phi_W = 0.96$) in the range from 1200 to 1000 cm^{-1}.

3.3. Entropy change in micellization of Pluronic solutions due to hydrogen bonding

The formation of hydrogen bonds results in a loss of degrees of rotational freedom in the molecules or segments involved and hence induced significant entropic changes [15–19]. Therefore, disruptions of hydrogen bonding during the micellization of PEO–PPO–PEO block copolymer solutions result in an increase of entropy which usually dominates the micellization process. Flory pointed out that the entropy expressions for the thermodynamic properties of heterogeneous polymer solutions derived by lattice model are also suited to describe chemical equilibrium between HB polymer species in terms of statistical mechanics [20]. However, in the case of hydrogen bonding in PEO–PPO–PEO block copolymer solutions, a formal derivation of entropy using florg's lattice filling procedure becomes complicated because we encounter the problem of describing two sets of chains: one covalent the other HB, both of which share the same segments. Based on lattice model, Painter and Coleman [21–24] put forward an association treatment (PCAM) and successfully got over this common problem of hydrogen bonding in polymer blends. Similar to PCAM, we assume that the HB chains in PEO–PPO–PEO copolymer solutions as new, distinguishable and independent species so that thermodynamic contribution related to covalent chains and HB chains can be separated. As a result, the entropy of athermally mixing the HB polymer species is given by the Flory–Huggins expression describing heterogeneous polymers with different molecular weight:

$$\frac{-\Delta S^*}{R} = n_{\mathrm{W0}} \ln \Phi_{\mathrm{W0}} + \sum_{h=1}^{\infty} n_{\mathrm{E}_h} \ln \Phi_{\mathrm{E}_h} + \sum_{h=1}^{\infty} n_{\mathrm{P}_h} \ln \Phi_{\mathrm{P}_h} \tag{15}$$

where n_{W0}, n_{E_h} and n_{P_h} are the mole number of free water, h-length EO HB chains and h-length PO HB chains, respectively. However, it is obvious that this expression is not only algebraically long-winded, but of little use, requiring a knowledge of the entire distribution of species.

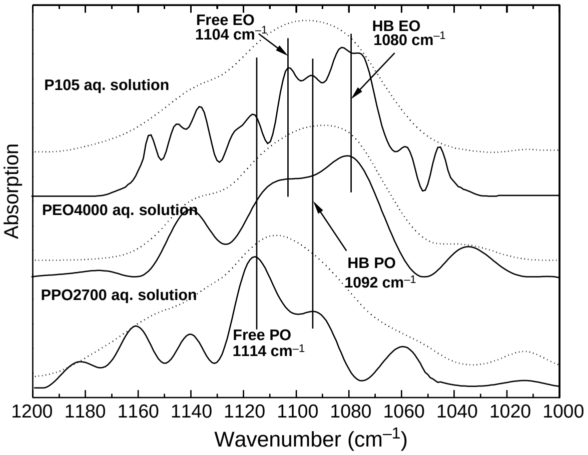

Figure 3. The FTIR spectra (dot line) and deconvolution spectra (solid line) of Pluronic P105, PEO4000 and PPO2700 aqueous solutions ($\Phi_W = 0.96$) in 1200–1000 cm^{-1} range at 20°C.

Fortunately, a solution related to the stoichiometry of hydrogen bonding association and the dimensionless equilibrium constants can be obtained. Prigogine [25] demonstrated that in a system in equilibrium, the macroscopic chemical potentials of components are equal to the chemical potentials of the monomer units. For HB chains in PEO–PPO–PEO block copolymer solutions, non-HB EO, PO and free water can be refered as "monomer units". Consequently, similar results, as presented in appendix A, were derived for HB chains following Prigogine's approach. The chemical potentials of EO, PO and water are equal to the chemical potentials of non-HB EO, PO and free water,

$$\mu_W = \mu_{W0}, \quad \mu_E = \mu_{E_1}, \quad \mu_P = \mu_{P_1}. \tag{16}$$

Based on equations (15) and (16), we finally derived a simple expression for the entropy of mixing the HB polymer species per lattice site after some manifestation presented in appendix B:

$$\begin{aligned} \frac{-\Delta S^*}{R} &= (\Phi_W \ln \Phi_W + 1 - \Phi_W) \\ &\quad + \left(\Phi_E \ln \Phi_{E1} - \frac{\Phi_{E1}}{1 - K_E \Phi_W \Phi_{E1}/\Phi_E}\right) \\ &\quad + \left(\Phi_P \ln \Phi_{P1} - \frac{\Phi_{P1}}{1 - K_P \Phi_W \Phi_{P1}/\Phi_P}\right). \end{aligned} \tag{17}$$

This equation is composed of three parts and the last two components represent the entropy contribution of EO–W and PO–W hydrogen bonds respectively. The entropy change in the micellization of Pluronic solutions (ΔS_H) can be derived by subtracting the entropy of the unimer phase ($\Delta S^*_{\text{unimer}}$) from the entropy of the stable micellar phase ($\Delta S^*_{\text{micellar}}$), that is to say,

$$\Delta S_H = \Delta S^*_{\text{micellar}} - \Delta S^*_{\text{unimer}}. \tag{18}$$

Cooperation of equations (17) and (18) provides us the quantitative expression of entropy attributed to hydrogen bonding in the micellization of PEO–PPO–PEO block copolymer solutions and the individual contribution of PO–W and EO–W hydrogen bonds. The additional advantage of our approach is that the parameters, K_E, K_P, K_E, K_P, Φ_{E_1} and Φ_{P_1} can be determined from the stoichiometry of hydrogen bonding association equation (13) and FTIR measurements mentioned above.

4. Results and discussion

4.1. Effect of temperature on hydrogen bonding in micellization

The information of free and HB EO or PO segments in Pluronic solutions at various temperatures can be obtained from FTIR deconvoluted spectra of C–O–C stretching regions. In addition, the information of PO–W hydrogen bonds can also be obtained directly by investigating methyl groups (–CH$_3$) deformation band of PO blocks in FTIR spectra [9–12]. The two regions in FTIR spectra of Pluronic P105 solutions are presented in figure 4. When the temperature approaches the CMT, the symmetric deformation vibration of methyl groups shift from 1381 toward 1378 cm^{-1}. At higher temperatures, the symmetric deformation mode of the methyl groups is composed of two bands which are assignable to hydrated (the band at 1378 cm^{-1}) and dehydrated states (the band at 1373 cm^{-1}) corresponding to HB and non-HB PO segments.

Figure 5 shows the plot of the fraction of non-HB functional groups f_F as the function of temperature. All curves show a sigmoid shape consisting of three regions: unimer phase, unimer–micellar coexistence and stable micellar phase. At low temperatures, f_F changes slightly with the increase of temperature indicating that the hydrogen bonding remains almost unchanged in unimer phase. When the temperature is above 20 °C, f_F increases abruptly which means the disruption of hydrogen bonds when unimers aggregating into micelles. Even at 50 °C, the fraction of free PO is about 0.6, which implies that PPO blocks are probably dehydrated incompletely and some water may be contained in the micelle core. The results are consistent with SCMF simulation and small angle neutron scattering (SANS) studies [26–28]. Fractions of free PO blocks are much larger than those of free EO blocks because EO blocks are hydrophilic and easier to form hydrogen bonds with water. Also, fractions of free PO blocks exhibit drastic increase while those of the EO blocks show small changes. That is to say, PO–W hydrogen bonds are more sensitive to temperature than EO–W hydrogen bonds and hence break up more rapidly.

4.2. Dimensionless equilibrium constants of hydrogen bonding

The dimensionless equilibrium constant (K_S) represents association degree of the HB chains in polymer solutions and the ability of the functional group to form hydrogen bonds with water molecules at certain temperature.

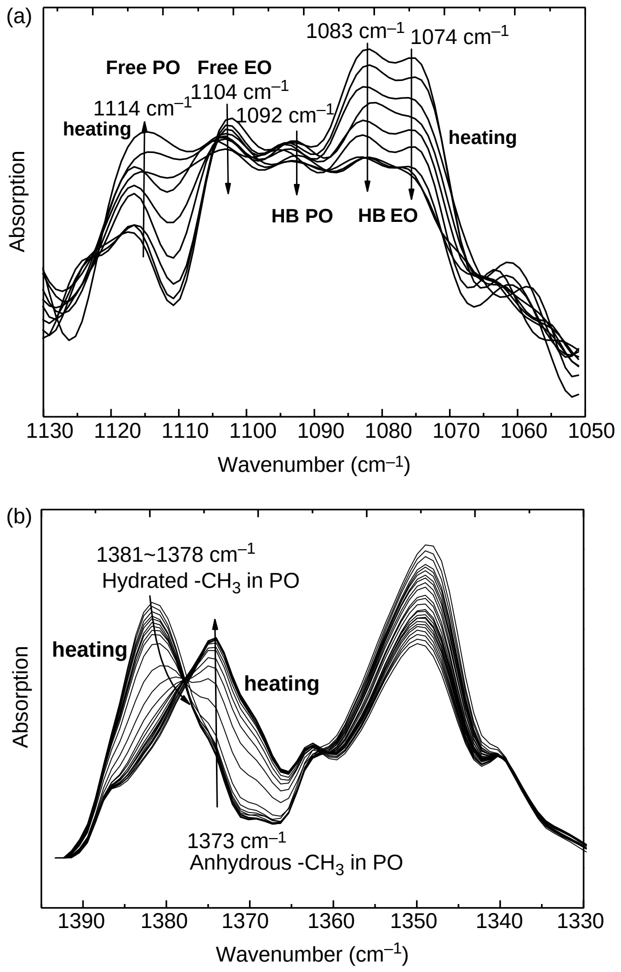

Figure 4. (a) C–O–C band region and (b) –CH_3 deformation band region in FTIR spectra of Pluronic P105 solution ($\Phi_W = 0.96$) at various temperatures.

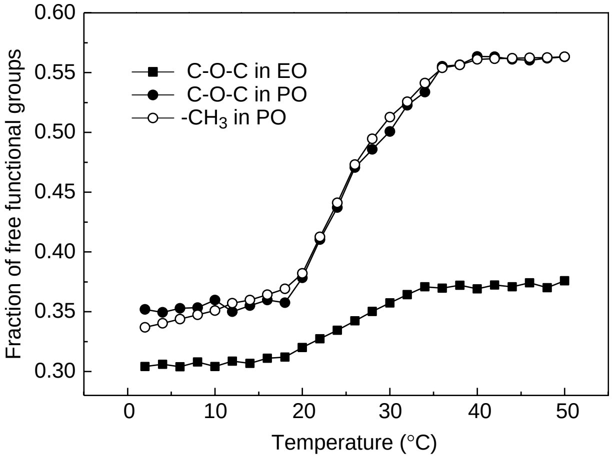

Figure 5. The fractions of free C–O–C in EO segments, free C–O–C and –CH_3 in PO segments of Pluronic P105 solution ($\Phi_W = 0.96$) as the function of temperature.

Figure 6 presents the least squares fitting results of equation (13) for EO blocks and PO blocks of P105 copolymer at various temperatures. The good fit demonstrates that our association model is able to describe the hydrogen bonding association behavior of PEO–PPO–PEO block copolymer solutions.

K_E and K_P of P105 copolymer solutions at a temperature range of 2–50 °C are shown in figure 7. An increase in temperature leads to a decrease in equilibrium constant, which corresponds to the disruption of hydrogen bonds. Both K_E and K_P also show sigmoid shape curves and can be expressed as:

$$K(T) = K_U + \frac{K_M - K_U}{1 + \exp\left(-A\left(\frac{1}{T} - \frac{1}{T_m}\right)\right)} \qquad (19)$$

where K_U, K_M, A and T_m are all constants. In the temperature range 2–20°C, a slight decrease of K_P and K_E indicate that few breaking of hydrogen bonds and the polymer solution remains in stable unimer phase. When temperature increases to the CMT, either K_E or K_P declines rapidly, which can be inferred as significant disruption of hydrogen bonds and hence unimer-to-micelle transition. Both equilibrium constants leveled off at 36°C, which implied that the majority of micelles were stable. Therefore, K_U and K_M are the intrinsic properties of a specific type of PEO–PPO–PEO solutions and essentially represent the equilibrium constants of hydrogen bonding in the unimer phase and the stable micellar phase, respectively. The least square fitting results of equation (19) show that, for PO blocks of Pluronic P105, $K_U = 0.430$, $K_M = 1.197$, while for EO blocks of Pluronic P105, $K_U = 1.061$, $K_M = 1.529$. That is to say, during the aggregation, K_P declined almost two times as fast as K_E. The hydrogen bonding between PO blocks and water undergo a large degree of breaking while most of EO blocks maintain hydrogen bonding connection with each other.

4.3. Entropy change due to hydrogen bonding in micellization

As presented in figure 8, with the solution concentrated or heated, an increase in the entropy of the solution manifests that the disruption of PO–W and EO–W hydrogen bonding leads to the clustering of the blocks and consequently formation of micelle. However, the roles of these two types of hydrogen bonds in micellization are different. In very dilute solution where no micellization occurs in the temperature range of 2–50 °C, both the entropy related to PO–W hydrogen bonding (ΔS^*(PO–W)) and the entropy related to EO–W hydrogen bonding (ΔS^*(EO–W)) increased slightly with an increase of temperature. In the case of concentrated solution where micellization occurs, with temperature increasing, ΔS^*(PO–W) increased with a great degree while ΔS^*(EO–W) almost remained almost unchanged. It is obvious that, for Pluronic P105 solutions, the entropy change of the copolymer due to the break of the PO–W hydrogen bonding is the dominative driving force of the

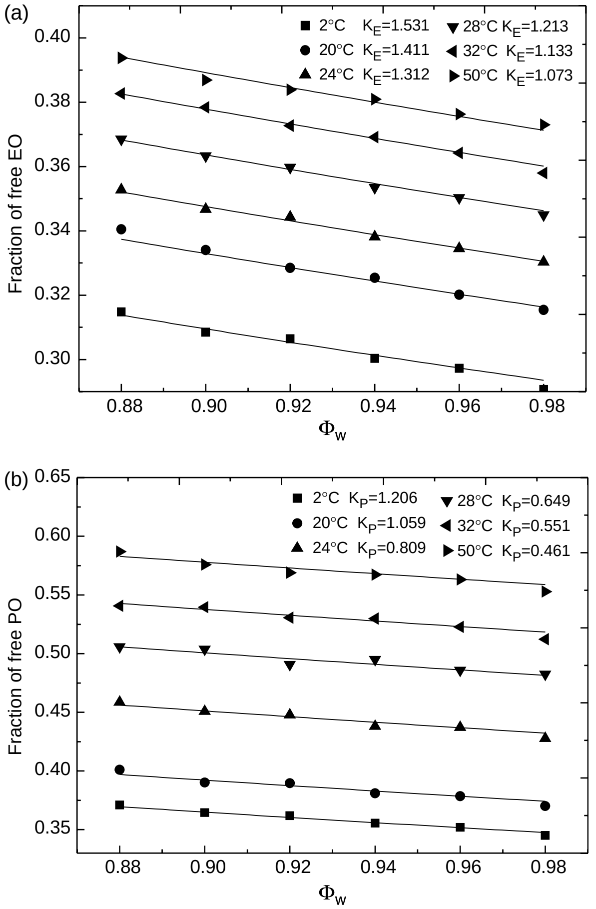

Figure 6. The least squares fitting results of equation (13) to the experimental fraction of free EO blocks (a) and PO blocks (b) of P105 copolymer versus the volume fraction for water (Φ_W) at various temperatures.

micellization. Similar conclusions were derived by Alexandridis [1,2] and Lopes [29], while our results provided a quantitative thermodynamic explanation to their observations from the hydrogen bonding point of view.

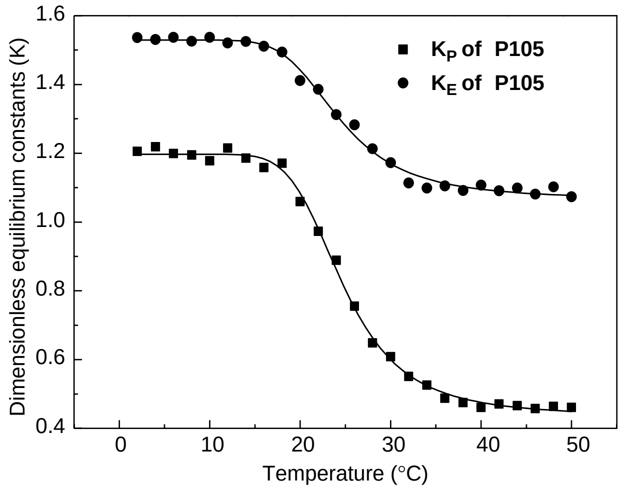

Figure 7. Temperature-dependent equilibrium constants of EO–W hydrogen bonding and PO–W hydrogen bonding in P105 solution. Solid curves are obtained by a least square fit of equation (19).

5. Conclusion

A thermodynamic approach is suggested to explain the micellization mechanism of PEO–PPO–PEO triblock copolymers solutions from the hydrogen bonding point of view. According to Flory–Huggins theory, an association model is presented describing polydisperse HB chains, which are bridged by hydrogen bonds between water molecules and oxygen atoms in the ether backbone of the copolymer. The entropic change due to hydrogen bonding is formulated and the individual contribution of EO–W and PO–W hydrogen bonding to the micellization are derived, respectively. FTIR spectroscopy is applied to detect the information of hydrogen bonds and hence provides parameters for the model.

By investigating the temperature dependent micellization of Pluronic P105 aqueous solutions in the framework of the model, we observed the rapid increase in the fraction of non-HB PO segments (f_F) by FTIR, meanwhile, the drastic decrease in equilibrium constants of PO–W hydrogen bonding (K_P) and sharp change in the calculated entropy relating to PO–W hydrogen bonds (ΔS^*(PO–W)) were obtained from association model. It demonstrates that the disruption of PO–W hydrogen bonding plays a dominative role in micellization. The results are consistent with previous experiments, furthermore our approach presents a quantitative thermodynamic explanation from the hydrogen bonding point of view: heating leads to the disruption of hydrogen bonds between blocks and water. PO–W hydrogen bonding is more sensitive to temperature than EO–W hydrogen bonding. The removal of water from PO blocks results in PO blocks clustering into a nonpolar micellar core region, which leads to sharp increase in entropy, while EO blocks kept in hydrogen bonding with water in corona.

Hydrogen bonds taking place in amphiphilics solutions have attracted much attention recently both experimentally and theoretically, because it has been proven to be of crucial importance on the structural and dynamic properties of micelles [30]. We first presented a useful thermodynamic approach to study the quantitative contribution of polymer–water hydrogen bonds to the micellization and our model can be extended for further studies, however, it has been difficult to use thermodynamic method to disclose the detailed picture of hydrogen bonding in such a complex system. Molecular simulation is a valuable and promising tool in this area. MD simulation will contribute to the molecular lever structural information on both polymer–water and water–water hydrogen bonds [31]. In addition, dissipative particle dynamic simulation (DPD) also proved efficient in providing useful mesoscale information on micellization and polymer–water interactions [32]. We are currently exploring these studies.

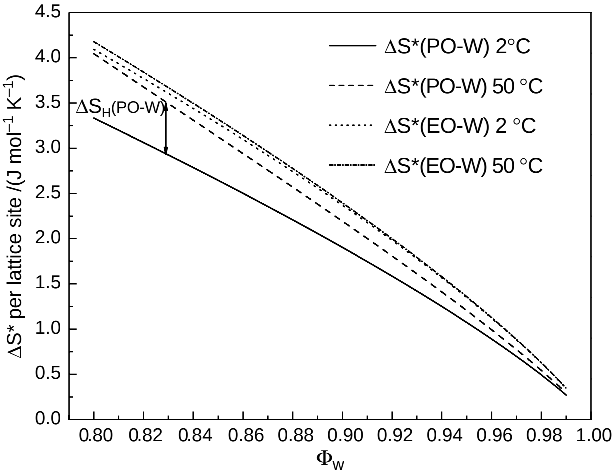

Figure 8. Plot of entropy change due to PO–W hydrogen bonding and EO–W hydrogen bonding in P105 solutions versus the volume fraction of water (Φ_W) at 2 and 50°C.

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Appendix A. Derivation of chemical potentials

We let n_E, n_P and n_W represent the number of EO blocks, PO blocks and water, respectively. μ_x represents the chemical potential of different HB chains. μ_E, μ_P and μ_W are the chemical potentials of EO, PO and water in the HB chains solutions. μ_{E1},μ_{P1} and μ_{W0} are equal to the chemical potentials of non-HB EO, PO and free water. According to stoichometry of hydrogen bonding and materials balance,

$$n_E = \sum_{h=1}^{\infty} h n_{E_h}, \quad n_P = \sum_{h=1}^{\infty} h n_{P_h},$$
$$n_W = n_{W0} + \sum_{h=1}^{\infty}(h-1)n_{E_h} + \sum_{h=1}^{\infty}(h-1)n_{P_h} \tag{A1}$$

$$\mu_{E_h} = h\mu_{E1} + (h-1)\mu_{W0},$$
$$\mu_{P_h} = h\mu_{P1} + (h-1)\mu_{W0} \tag{A2}$$

Gibbs free energy of PEO–PPO–PEO block copolymer solutions is described as follows:

$$\begin{aligned} dG &= \mu_{W0}\, dn_{W0} + \sum_{h=1}^{\infty} \mu_{E_h}\, dn_{E_h} + \sum_{h=1}^{\infty} \mu_{P_h}\, dn_{P_h} \\ &= \mu_{W0}\, dn_{w0} + \sum_{h=1}^{\infty}(h\mu_{E1} + (h-1)\mu_{W0})dn_{E_h} \\ &\quad + \sum_{h=1}^{\infty}(h\mu_{P1} + (h-1)\mu_{W0})dn_{P_h} \\ &= \mu_{W0}\, d\left(n_{w0} + \sum_{h=1}^{\infty}(h-1)n_{E_h} + \sum_{h=1}^{\infty}(h-1)n_{P_h} \right) \\ &\quad + \mu_{E1}\, d\sum_{h=1}^{\infty} h n_{E_h} + \mu_{P1}\, d\sum_{h=1}^{\infty} h n_{P_h} \\ &= \mu_{W0}\, dn_W + \mu_{E1}\, dn_E + \mu_{P1}\, dn_P. \end{aligned} \tag{A3}$$

Gibbs free energy of polymer solutions can also be described as follows:

$$dG = \mu_W\, dn_W + \mu_E\, dn_E + \mu_P\, dn_P. \tag{A4}$$

Hence,

$$\mu_W = \mu_{W0}, \quad \mu_E = \mu_{E1}, \quad \mu_P = \mu_{P1}. \tag{A5}$$

Appendix B. Derivation of mixing entropy from chemical potentials

Equation (15) can also be viewed as ΔG_e^*/RT, free energy accounting for the entropy of the HB polymer species. Consequently, the chemical potential of the species E_h with respect to Flory's reference state ($\mu_{E_h} - \mu_{E_h}^*$) can be found by differentiating ΔG_e^* with respect to n_{E_h} and given by

$$\begin{aligned} \frac{\mu_{E_h} - \mu_{E_h}^*}{RT} &= \ln \Phi_{E_h} + 1 - (2h-1)\Phi_{W0} - (2h-1) \\ &\quad \times \sum_{h=1}^{\infty} \frac{n_{E_h}}{N} - (2h-1) \sum_{h=1}^{\infty} \frac{n_{P_h}}{N}. \end{aligned} \tag{B1}$$

Putting $h = 1$, then;

$$\begin{aligned} \frac{\mu_E - \mu_E^*}{RT} &= \frac{\mu_{E1} - \mu_{E1}^*}{RT} \\ &= \ln \Phi_{E1} + 1 - \Phi_{W0} - \sum_{h=1}^{\infty} \frac{n_{E_h}}{N} - \sum_{h=1}^{\infty} \frac{n_{P_h}}{N}. \end{aligned} \tag{B2}$$

$\sum n_{E_h}/N$ and $\sum n_{P_h}/N$ can be obtained using the stoichiometric relationships given by equation (8)

$$\begin{aligned} \sum_{h=1}^{\infty} \frac{n_{Eh}}{N} &= \sum_{h=1}^{\infty} \frac{\Phi_{E_h}}{2h-1} \\ &= \Phi_{E1} \sum_{h=1}^{\infty} \left(K_E \Phi_W \Phi_{E1} / \Phi_E \right)^{h-1} \end{aligned} \tag{B3}$$

for $K_S\Phi_W\Phi_{S_1}/\Phi_S < 1$,

$$\sum_{h=1}^{\infty}\left(K_E\Phi_W\Phi_{E1}/\Phi_E\right)^{h-1} = \frac{1}{1-K_E\Phi_W\Phi_{E1}/\Phi_E}. \tag{B4}$$

Similarly,

$$\sum_{h=1}^{\infty}\left(K_P\Phi_W\Phi_{P1}/\Phi_P\right)^{h-1} = \frac{1}{1-K_P\Phi_W\Phi_{P1}/\Phi_P}. \tag{B5}$$

Substituting into equation (B2) we obtain,

$$\frac{\mu_E-\mu_E^*}{RT} = \ln\Phi_{E1} + 1 - \Phi_W - \frac{\Phi_{E1}}{1-K_E\Phi_W\Phi_{E1}/\Phi_E} - \frac{\Phi_{P1}}{1-K_P\Phi_W\Phi_{P1}/\Phi_P}. \tag{B6}$$

Similarly, for the species P_h and water molecules,

$$\frac{\mu_P-\mu_P^*}{RT} = \ln\Phi_{P1} + 1 - \Phi_W - \frac{\Phi_{E1}}{1-K_E\Phi_W\Phi_{E1}/\Phi_E} - \frac{\Phi_{P1}}{1-K_P\Phi_W\Phi_{P1}/\Phi_P} \tag{B7}$$

$$\frac{\mu_W-\mu_W^*}{RT} = \ln\Phi_W + 1 - \Phi_W - \frac{\Phi_{E1}}{1-K_E\Phi_W\Phi_{E1}/\Phi_E} - \frac{\Phi_{P1}}{1-K_P\Phi_W\Phi_{P1}/\Phi_P}. \tag{B8}$$

Combining equations (B6)–(B8), we finally derived a simple expression for the entropy of mixing the HB polymer species per lattice site.

$$\frac{-\varDelta S^*}{R} = (\Phi_W\ln\Phi_W + 1 - \Phi_W) + \left(\Phi_E\ln\Phi_{E1} - \frac{\Phi_{E1}}{1-K_E\Phi_W\Phi_{E1}/\Phi_E}\right) + \left(\Phi_P\ln\Phi_{P1} - \frac{\Phi_{P1}}{1-K_P\Phi_W\Phi_{P1}/\Phi_P}\right). \tag{B9}$$

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