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Cosolvent Effects on Thermally-Induced Transitions of a Block Copolymer: Poly(ethylene oxide)–Poly(propylene oxide) in Aqueous Solutions

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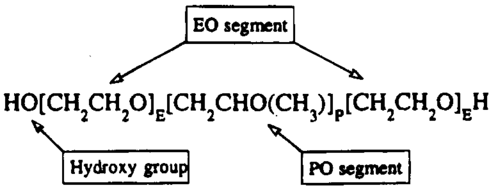
ABSTRACT: The thermally-induced transitions of a water-soluble block copolymer, poly(ethylene oxide)–poly(propylene oxide) (MW 12 000, PO/EO ratio 3.46:1), were investigated in mixed aqueous–organic solvents using a high-sensitivity differential scanning calorimeter (DSC). The endothermic transitions of the block copolymer are markedly influenced by the addition of various organic cosolvents, ethylene glycol (EG), enthanolamine (EA), ethylenediamine (ED), 2-methoxyethanol (2-ME), and 1-propanol (1-PrOH). The transition temperatures, T_m, are lowered from ~30 °C in water to ~10 °C in the mixed solvents at relatively low cosolvent mole fraction ($X \leq 0.15$);. the transition enthalpies, ΔH_m, are simultaneously decreased. Among the five cosolvents, 1-PrOH exhibits the largest effect on T_m and ΔH_m, whereas ED displays an effect on T_m similar to that of 1-PrOH but the weakest effect on ΔH_m. T_m versus ΔH_m may be described by a second-order polynomial with a linear term (ϱ_1) and a nonlinear term (ϱ_2). Since T_m variations relate to solvent composition changes, ϱ_1 and ϱ_2 may be viewed as reflecting respectively the cosolvent/water interactions or affinities and changes in these interactions in the presence of the copolymer (ternary cosolvent/water/copolymer interactions). Attempts to correlate the ϱ_1 values with various parameters of the cosolvents show a qualitative relationship between ϱ_1 and a solvent hydrophobic parameter (θ) derived from the binary water/cosolvent mixture using the Kirkwood–Buff theory. The trends observed in the transition enthalpies (ΔH_m) and entropies (ΔS_m) are consistent with the view that the transition is initially of the type sol–micelle and that the hydrophobic effects associated with the PO segment of the copolymer, or with the cosolvent, largely dominate this process.

Introduction

The physico-chemical properties of block copolymer so-called "Pluronic" or "Poloxamer" in aqueous solutions have been extensively studied in terms of hydrophobicity.[1] The molecular associations of these surfactants have been the central interests of many researchers. The early investigations were largely concerned with the widely differing values of "critical micelle concentration" and aimed to know the exact nature of the colloidal behaviors of these surfactants, in particular whether or not micelles are formed.[2–10] The surface-tension measurements on a series of Poloxamers in aqueous solutions[8] and photon correlation spectroscopy results[9] have resolved some of the issues. At low concentrations, the Poloxamer monomers are thought to form monomolecular micelles by a change in configuration in solutions. At higher concentrations, these monomolecular micelles associate to form aggregates of varying size. Such complex patterns might befit Poloxamer structure in which the propylene oxide (PO) segments behave as "nonsoluble" or hydrophobic portions and ethylene oxide (EO) segments as "soluble" or hydrophilic portions in an aqueous solution, as illustrated in Figure 1. More recent work has mostly dealt with the temperature-dependent phase behaviors of Poloxamers.[11–26] Some anomalous temperature-dependent properties were observed: with elevated temperature, the critical micelle concentrations are decreased; the average aggregation number, micellar size, and fraction of polymer molecules in micellar form are increased.[27] However, the molecular effects responsible for these observations remain unclear.



$$HO[CH_2CH_2O]_E[CH_2CHO(CH_3)]_P[CH_2CH_2O]_EH$$

Figure 1. Constituent of Poloxamer, PEO–PPO–PEO.

Poloxamers' complex phase behaviors involve rather complicated intra- and intermolecular effects. PO and EO segments interact differently with solvent, and the temperature-dependent conformations of the block copolymer will depend on the hydration of these segments. However, the solvent effect on the phase behavior of the block copolymers has been rather poorly studied, compared to the tremendous number of studies on block copolymers with different block sequences. One may also expect that any change in the solvent compositions will affect the phase behavior of the block copolymer. Indeed, varying transitions of Poloxamers have been observed under several solvent conditions.[28] An anomalous phase behavior of a PO–EO copolymer was reported; the cloud point in the mixed solvent water–*N*-methylacetamide is decreased at cosolvent contents lower than 70% but is rapidly increased at higher cosolvent contents, which is relevant to the formation of a two-phase region of the copolymer in this mixed solvent.[29] It appears, however, that additional systematic studies on the phase transition behaviors of Poloxamers in mixed solvent systems are required in order to better understand the role of the cosolvents in the dehydration of these polymers in an aqueous solution. The knowledge gained from such investigations would be of interest to many applications of these block copolymers, including pharmaceutical applications.[13,14,18]

In this paper, we report results on the thermal transitions of a triblock copolymer, poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–

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Table 1. Physical Properties of Water and Cosolvents at 25 °C[a]

solvent	water	EG	EA	ED	2-ME	1-PrOH
MW	18.01	62.07	61.08	60.10	76.10	60.09
d (g/cm^3)	0.99705	1.11083	1.01239	0.89283	0.96034	0.79935
V_m (cm^3/mol)	18.07	55.92	60.34	67.31	73.24	75.18
$\epsilon_r{}^b$	78.30	37.7	37.72	3.78	16.93	20.45
μ^c	5.9	7.7	7.6	4.0	6.8	5.5
f^d	4.62	2.90	2.86	0.15	1.15	1.12
$D_{ce}{}^e$	2410	1006	829	642	502	590
$P_i{}^f$	162	510	638	648	488	550
Δ^g	2248	496	191	−6	14	40
θ^h		−28.12	−35.05	−223.52	−77.28	1083.3

[a] Data refs 36 and 41−45. [b] Relative permittivity (dielectric constant). [c] Dipole moment in Coulombmeter (10^{-30} cm). [d] Electrostatic factor, $f = \epsilon_r\mu$ (10^{-28} cm). [e] Cohension energy density (J/cm^3). [f] Internal pressure (J/cm^3). [g] Hydrogen-bonding contribution, $\Delta = D_{ce} - P_i$ (J/cm^3). [h] Hydrophobic effect (cm^3/mol).

PPO−PEO), in pure water and in mixtures of water with cosolvents, ethylene glycol (EG), enthanolamine (EA), ethylenediamine (ED), 2-methoxyethanol (2-ME), and 1-propanol (1-PrOH) using a high-sensitivity differential scanning calorimeter (DSC). The cosolvents selected include monofunctional and bifunctional organic compounds. The physico-chemical properties of these cosolvents were well-studied previously,[30,36,39,42,47] and some of those relevant to the current work are listed in Table 1.

Experimental Section

Materials. A triblock copolymer, poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO), with molecular mass 12 000 and PO/EO ratio 3.46:1 (Polyscience Inc.) was used without further purification. The cosolvents EG (Fisher), EA, ED, 2-ME (Fluka Chemie), and 1-PrOH (Anachemia) were used as received. Deionized (Millipore) water was used through the entire experiment.

Preparation. Mixed aqueous−organic solvents were prepared by weight. The mixed solvents prepared were stored in a refrigerator. The block copolymer was dissolved in the mixed solvents; the concentration of PEO−PPO−PEO in the solutions was kept at 1.0% (w/w). Dissolution was carried out in a water bath (about 50 °C); in some cases, a shaken bath (Precision Scientific Co.) was needed to achieve better dissolution. All samples were degassed immediately before each injection.

DSC Measurements. Thermograms of the samples were obtained with a microcalorimeter (MC-2, Microcal Inc.). Routine DSC operation followed the procedures described in the manual.[31a] The scanning rate (60 °C/h), scanning temperature range (5−90 °C), and filter constant (15) were fixed through all measurements. Reversibility of the thermal transitions was checked by rescanning each sample (cooling down and then heating up). Data acquisition and analysis were performed by DA-2 data acquisition software.[31b]

Results

Thermograms of PEO−PPO−PEO Transitions. The thermally-induced phase transitions of PEO−PPO−PEO were measured in five mixed solvents at a constant block copolymer concentration (1.0% w/w) and different cosolvent mole fractions. The trends of the cosolvent effects on the transition are similar for each solvent mixture; parts a−e of Figure 2 present the thermograms for the five solvent systems investigated. The transition baselines were processed by use of a spline method, which determines a baseline of the transition area by fitting the pre- and posttransition heat capacity data. The thermal transitions were found fully reversible in the mixed solvents.

As seen from Figure 2, upon increasing the cosolvent concentration, the transition temperatures, T_m, are, in general, lowered from ~30 °C in pure water to ~10 °C in the mixed solvents; the transition enthalpies (area under each curve), ΔH_m, are also decreased. The "sharpness" of the endothermic profiles is reduced with increasing cosolvent concentration and appears in the order of 1-PrOH > 2-ME > EG > EA > ED; this suggests a change in the phase transition cooperativity (see discussion later in this paper). The thermal transitions involving ED, EA, and EG are different from those with 1-PrOH and 2-ME as judged by their effects on the transition enthalpy. In addition, the maximum cosolvent concentrations up to which the transitions were recordable are different: $X \leq 0.15$ for EG, EA, and 2-ME, $X < 0.1$ for ED, and $X < 0.05$ for 1-PrOH.

Transition Parameters. The transition parameters, temperature and enthalpy, were obtained by analysis of the DSC thermograms as outlined earlier. Both ΔH_m and T_m are found to decrease with increasing cosolvent concentrations. The correlations between the transition temperatures and the solvent compositions are shown in Figure 3. With increased cosolvent concentration, the cosolvents ED and 1-PrOH have an apparently similar effect on T_m; the cosolvents EG, EA, and 2-ME exhibit a similarity in their T_m versus X relations at $X < 0.1$. Figure 4 shows the transition enthalpy versus solvent composition. In comparison with Figure 3, several features of Figure 4 are noteworthy. First, the ΔH_m versus X relation discriminates ED and 1-PrOH by their obviously different effects on transition enthalpy; second, Figure 4 also discriminates 2-ME out of the group of EG and EA; finally, the influence of the cosolvents EG, EA, and ED on ΔH_m is remarkably similar in contrast to their relative effects on T_m.

The correlations of ΔH_m versus T_m should be highly informative in the understanding of the cosolvent effects on the thermal transition, as shown in Figure 5, where the data were fitted to a second-order polynomial:

$$\Delta H_m = \Delta H_m{}^{X=0} + \varrho_1(T_m - T_m{}^{X=0}) + \varrho_2(T_m - T_m{}^{X=0})^2 \quad (1)$$

ΔH_m = 387.6 kJ/mol, $T_m{}^{X=0}$ = 302.5 K, and ϱ_1 and ϱ_2 are linear and nonlinear coefficients to be determined and their numerical values are listed in Table 2. As seen from Figure 5, the cosolvent 1-PrOH is obviously different from others by its strong effect in changing both ΔH_m and T_m. The cosolvent effect of 2-ME is found to be next to 1-PrOH but shows a curvature with increasing concentration. The cosolvents ED, EA, and EG demonstrate their relatively weak effect on transition enthalpy in spite of the large decrement in the transition temperature. Since the slopes of the linear term in the above equation decrease in the order 1-PrOH > 2-ME > EG > EA > ED and the linear

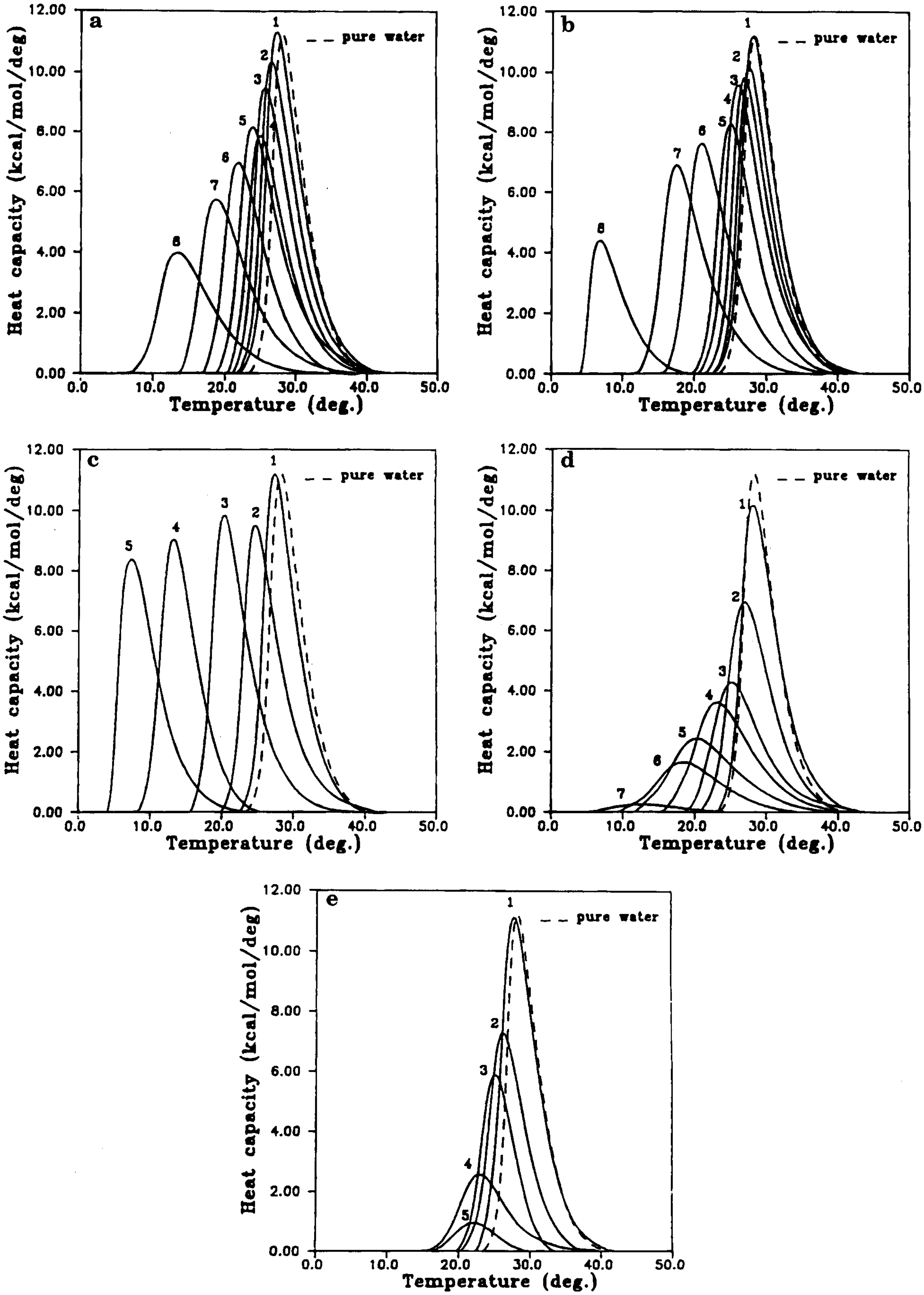

Figure 2. (a) Thermograms of transition in a water/EG/PEO−PPO−PEO system [X_{EG}: (1) 0.051 32; (2) 0.020 02; (3) 0.029 93; (4) 0.040 02; (5) 0.051 32; (6) 0.070 06; (7) 0.1000; (8) 0.1501]. (b) Thermograms of transition in a water/EA/PEO−PPO−PEO system [X_{EA}: (1) 0.010 02; (2) 0.020 46; (3) 0.030 04; (4) 0.050 02; (5) 0.060 03; (6) 0.080 02; (7) 0.010 04; (8) 0.1500]. (c) Thermograms of transition in a water/ED/PEO−PPO−PEO system [X_{ED}: (1) 0.010 20; (2) 0.030 48; (3) 0.050 76; (4) 0.074 93; (5) 0.091 32]. (d) Thermograms of transition in a water/2-ME/PEO−PPO−PEO system [$X_{\text{2-ME}}$: (1) 0.010 03; (2) 0.030 02; (3) 0.050 03; (4) 0.067 77; (5) 0.090 05; (6) 0.1017; (7) 0.1501]. (e) Thermograms of transition in a water/1-PrOH/PEO−PPO−PEO system [$X_{\text{1-PrOH}}$: (1) 0.010 04; (2) 0.020 29; (3) 0.030 05; (4) 0.040 12; (5) 0.045 03].

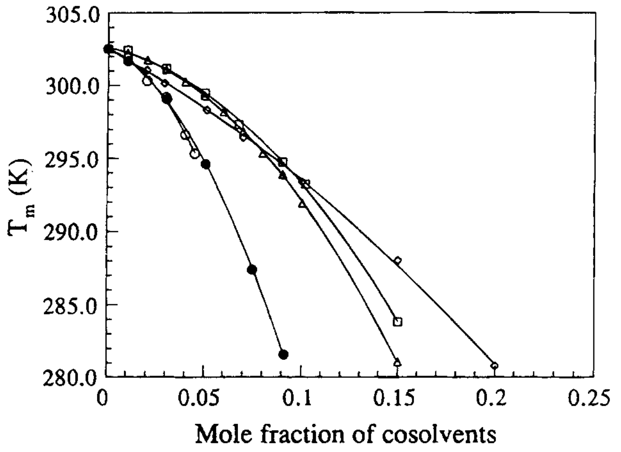

Figure 3. Transition temperature (T_m) as a function of cosolvent mole fraction (the lines are plotted for guidance; (○) water/1-PrOH; (□) water/2-ME; (◇) water/EG; (△) water/EA; (●) water/ED).

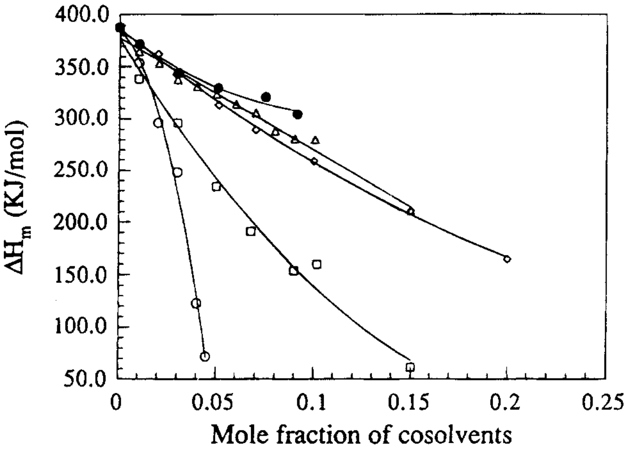

Figure 4. Transition enthalpy (ΔH_m) as a function of cosolvent mole fraction (the lines are plotted for guidance; for legends, see Figure 3).

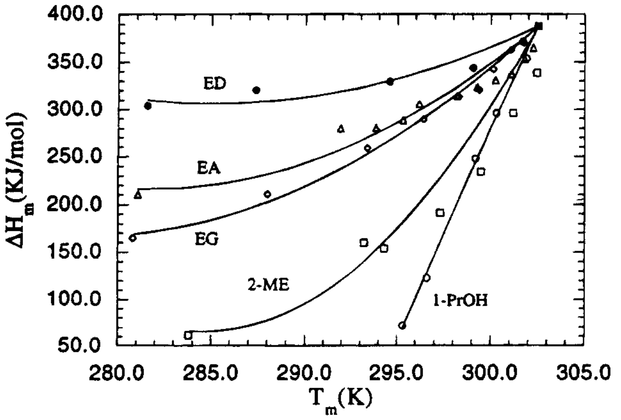

Figure 5. Transition enthalpy (ΔH_m) in relation to transition temperature (T_m) (for legends, see Figure 3).

correlations appear at low cosolvent concentrations (except for 1-PrOH), it is then believed that the slopes of the linear terms may represent the magnitude of the cosolvent/water interactions (i.e., the water affinities). The coefficients of the second-order terms in the above equation show a sequence of 1-PrOH < EG ~ EA ~ ED < 2-ME and are likely related to ternary water/cosolvent/copolymer interactions.

Discussion

Upon addition of the cosolvents, both transition temperatures and enthalpies are decreased to a large extent. This suggests that the hydrophobic interactions of the block copolymer are facilitated in the mixed solvents. Since the monofunctional and bifunctional cosolvents differ largely in their water affinities in aqueous solutions,[36] their influence in changing the transition behaviors of the block copolymer may be expected to be different. Such water affinities are generally attributed to those noncovalent interactions like the hydrophobic effect, van der Waals interactions, and hydrogen bonding and should be meaningful to the understanding of the role of the cosolvents in the dehydration of the block copolymer.

Table 2. Coefficients of ϱ_1 and ϱ_2 in Equation 1

mixed solvent	ϱ_1 (kJ/mol/K)	σ_{ϱ_1}[a]	ϱ_2 (kJ/mol/K^2)	σ_{ϱ_1}[a]
W/1-PrOH	42.1	±1.5	−0.2978	±0.2951
W/2-ME	35.9	±6.3	0.9998	±0.5305
W/EG	18.1	±1.0	0.3709	±0.07856
W/EA	16.5	±3.0	0.3964	±0.2540
W/ED	9.4	±1.2	0.2696	±0.07868

[a] The error of the coefficient: $\sigma_{\varrho_1} = [\Sigma(\Delta H_m^{exp} - \Delta H_m^{cal})^2/(n - 1)]^{1/2}/(T_m - T_m^{x=0})$ and $\sigma_{\varrho_1} = [\Sigma(\Delta H_m^{exp} - \Delta H_m^{cal})^2/(n - 1)]^{1/2}/(T_m - T_m^{x=0})^2$.

Physical Basis of Cosolvent Effects. The cosolvents affect the transition of the block copolymer through their interaction with the solvent (water) and with the copolymer itself. Liquid water bears various molecular and structural features different from those of most cosolvents: (1) intramolecular [water molecule has a small size but a large dipole moment (see Table 1)]; (2) intermolecular [its quadrupolar charge distribution and parity of proton donor and acceptor sites facilitate the formation of hydrogen-bonding networks]; (3) uniqueness [differing from other hydrogen-bonding solvents, water possesses cooperative fluctuation domains dynamically embedded in the network structure[32,33]]. Upon addition of a cosolvent, the water structure is changed to an extent dependent on the properties of the cosolvent, the water/copolymer interactions are altered, and new cosolvent/copolymer interactions are established. To elucidate the type of interactions responsible for changes in T_m or ΔH_m in the presence of the cosolvents, one may examine the correlation between the cosolvent effects (the linear term of the curves presented in Figure 5) and their water affinities in terms of various physico-chemical properties such as (1) the electrostatic factor (f), (2) hydrogen-bonding contribution (Δ), and (3) hydrophobic effect (θ). Their significance is described as follows.

The electrostatic factor is defined by[34]

$$f = \epsilon_r \mu \tag{2}$$

where ϵ_r is the relative permittivity (dielectric constant) and μ the dipole moment. The electrostatic factor takes into account both properties and could be reasonably related to the van der Waals interactions in which polar and/or nonpolar groups attract each other and induce the polarization effect.

The hydrogen-bonding contribution is defined by

$$\Delta = D_{ce} - P_i \tag{3}$$

where D_{ce} is the cohesive energy density, given by

$$D_{ce} = \frac{\Delta H_v - RT}{V_m} \tag{4}$$

and P_i is the internal pressure, given by

$$P_{\mathrm{i}} = T\left(\frac{\partial P}{\partial T}\right) - P = T\left(\frac{\alpha}{\beta}\right) \tag{5}$$

It has been proposed[35] that P_i is mainly a reflection of dispersion and dipole–dipole interactions within the solvent, whereas D_{ce} additionally includes the specific intermolecular contribution from hydrogen bonding. Therefore, Δ values reflect the hydrogen-bonding contribution.

The hydrophobic effect, θ, is defined by[36]

$$\theta = G_{11} + G_{22} - 2G_{12} \tag{6}$$

The G_{ij} $(i,j = 1,2)$ is called the Kirkwood–Buff integral and is given by[37]

$$G_{ij} = \int_0^{\infty}[g_{ij}(\mathrm{r}) - 1]4\pi r^2\,\mathrm{d}r \tag{7}$$

The Kirkwood–Buff integrals can be calculated from a set of thermodynamic properties and represent an overall affinity between solvent–solvent (G_{11}), solute–solute (G_{22}), and solvent–solute (G_{12}).[38] θ is zero when $G_{11} + G_{22} = 2G_{12}$, the net resulting affinity between various molecules cancels out, and the distribution of molecular species in the mixture approaches a complete randomness. The nonzero θ is then attributed to various molecular correlations. The stronger the correlation, the larger the value of θ. The strong hydrophobic correlation is featured by the large positive θ; the small positive or negative θ arises from the weak hydrophobic effect. The θ values employed here are those averaged over the range of the cosolvent concentration where the transitions of the block copolymer were observed and from our previous calculations.[46]

Table 1 lists the numerical values of the three parameters f, Δ, and θ. The affinities of the cosolvents and water in terms of the f and Δ values show the order: ED < 1-PrOH < 2-ME < EA < EG. It is somewhat surprising that the cosolvent ED exhibits the smallest f and Δ values. On the one hand, compared to EG and EA, ED has considerably lower association energy[47] since it retains highly repulsive interactions from its diamine groups;[48] on the other hand, ED has a dipole moment comparable to EA and EG, and, consequently, it should be highly solvated in an aqueous solution. The θ values indicate that ED has the weakest hydrophobicity among the five cosolvents (see Table 1): ED < 2-ME < EA < EG < 1-PrOH. In the case of 2-ME, the large negative value of θ can be partially attributed to the excluded volume of the methoxyl group, which has a negative contribution to the Kirkwood–Buff integral.[36] However, as will be seen later, in the presence of the block copolymer, the methoxyl group makes 2-ME apparently more hydrophobic, and thus more analogous to 1-PrOH.

In Figures 6 and 7, the cosolvent effect represented by the slope of the linear term of eq 1, is plotted against the f and Δ parameters. The data show that the cosolvent 1-PrOH with a low water affinity induces a high effect on ΔH_m of the block copolymer. Such a correlation is obviously different for the cosolvents ED, EA, and EG, which have higher affinities with water but weak effects on ΔH_m. 1-PrOH carries one polar functional group, $-OH$, whereas ED, EA, EG, and 2-ME bear two functional groups (ED with two $-NH_2$, EA with one $-NH_2$ and one $-OH$, EG with two $-OH$, and 2-ME with one $-OH$ and one $-OCH_3$). In an aqueous solution, the monofunctional and bifunctional cosolvents differ largely in their water affinities, as reelected by their different intermolecular correlations,[36,47,48] as shown in Table 1. There is no apparent correlation between f or Δ and ϱ_1, the linear term in ΔH_m versus T_m. 1-PrOH and 2-ME stand out with comparable and relatively low water affinities and similarly high ϱ_1 values. These two cosolvents, however, show very different ϱ_2 values, i.e., curvature of the ΔH_m versus T_m plot (see also Table 2). If, as mentioned earlier, the ϱ_2 coefficients reflect the importance of the ternary water/cosolvent/copolymer interactions, the relative behavior of EG, 2-ME, and 1-PrOH may be understood: in spite of widely varying f and Δ values, the curvature of the ΔH_m versus T_m plot for 2-ME is intermediate between those of EG and 1-PrOH. It may thus be suggested, at this point, that the marked effect of 2-ME and 1-PrOH on ΔH_m is due to (hydrophobic) preferential interactions with the (hydrophobic) PO segments of the block copolymer. This type of interaction would induce dehydration of the hydrophobic PO groups (decreasing the enthalpy) and facilitate the transition (at lower T_m). This explains the strong ΔH_m versus T_m correlations in the mixed solvents with 1-PrOH and 2-ME. On the other hand, the bifunctional cosolvents having higher water affinities would tend to preferentially interact with the EO segments and the local solvent in the vicinity of the block copolymer. In this situation, the transition enthalpy would not be decreased as strongly as in the case of 1-PrOH and 2-ME, leading to relatively weak ΔH_m versus T_m correlations.

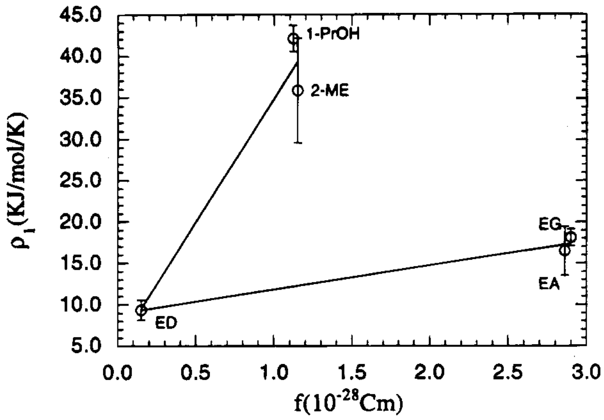

Figure 6. Correlation between the cosolvent effect, ϱ_1, and cosolvents' electrostatic factor, f.

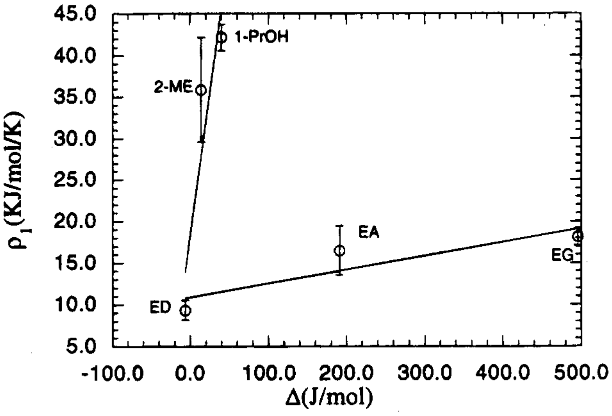

Figure 7. Correlation between the cosolvent effect, ϱ_1, and cosolvents' hydrogen-bonding contribution, Δ.

The electrostatic factor (f) and the hydrogen-bonding contribution (Δ) are mostly indicative of short-range molecular effects (van der Waals and hydrogen-bonding interactions). Although correlations of these parameters to the cosolvent effect (ϱ_1) yield valuable insight into the enthalpic effects of the transition process, they do not explain the cosolvent sequence: 1-PrOH > 2-ME

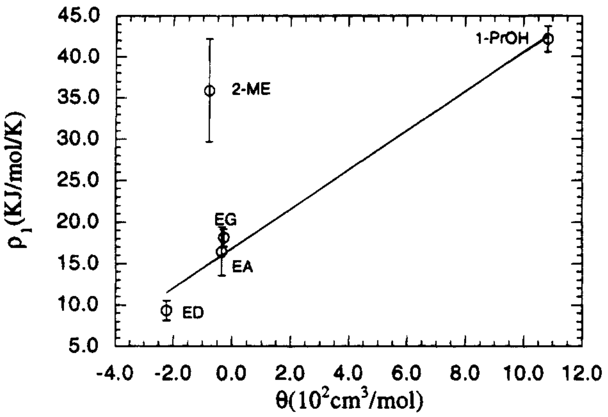

Figure 8. Correlation between the cosolvent effect, ϱ_1, and cosolvents' hydrophobic effect, θ.

> EG > EA > ED found in Figure 5. On the other hand, the cosolvent effect (again, represented by ϱ_1) and their hydrophobic effects (θ) appear better related as can be seen in Figure 8. 1-PrOH, with the largest hydrophobic effect among the five cosolvents, has the largest effect on both the transition temperature and enthalpy. Those cosolvents with negative values of θ (weak hydrophobicities) exhibit weaker effects on the transitions. Again, 2-ME stands out of the bifunctional cosolvents, with a relatively low θ value but strong effect on ΔH_m. This irregularity may be, again, attributed to the interaction of the methoxyl group with the PO segment. The correlation shown in Figure 8 is strongly indicative that the cosolvent effects on the transitions are closely related to their hydrophobic effect in aqueous solutions. Moreover, it is also indicative of the molecular interaction predominant to the phase transition of the block copolymer in the mixed solvents. On the basis of the polymer molecular weight, monomer molecular weight, and PO/EO ratio, the block copolymer studied contains 169 PO segments and 49 EO segments, i.e., $PPO_{169}-PEO_{49}$. The transition of the block copolymer in an aqueous solution ($X = 0$) generates an enthalpy change (ΔH_m) of 387.6 kJ/mol. If this enthalpy is attributed to the various molecular interactions of the block copolymer upon transition, each segment has a contribution of only 1.78 kJ/mol. Comparing to, for instance, the hydrogen-bond strength in a range of 8–40 kJ/mol,[40] this enthalpy change is a relatively small value and becomes even lower in the mixed solvents. Therefore, the thermally-induced phase transition of the block copolymer is dominated by low-energy effects, which may be mainly attributed to hydrophobic interaction involving the PO segments. The cosolvents (1-PrOH and 2-ME) preferentially interacting with PO segments play a more important role in the dehydration of the block copolymer than the other cosolvents (ED, etc.) which are more involved in the interactions with EO segments and with the solvent (water).

Phase Behaviors of Block Copolymer in Mixed Solvents. The block copolymer may form micelles and/or gels in an aqueous solution. In the mixed solvents, the phase behaviors of the block copolymer are closely related to the enthalpic or entropic contribution of the cosolvent to the transition. At a transition temperature, the Gibbs free energy, ΔG, equals zero. From the equation

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

the transition entropy may be obtained by

$$\Delta S_m = \Delta H_m / T_m \tag{9}$$

The plot of ΔS_m versus ΔH_m data for all systems studied here is found to be linear, suggesting a general enthalpy–entropy compensation, with a compensation temperature of ~360 K (Figure 9). Given the fact that the transition is endothermic in all the solvent mixtures investigated, the transition must be driven by an overall enthalpy. However, it is interesting to speculate on the origin of the enthalpic effects and the contribution of the cosolvent to these effects.

As expected from Figures 4 and 9, plots of ΔS_m versus X exhibit a behavior similar to those of ΔH_m versus X, as shown in Figure 10. In all cases, the addition of a cosolvent reduces ΔS_m and the effect is again in the order 1-PrOH > 2-ME > EG > EA > ED. The entropy change during the transition process includes two main contributions: the configurational entropy of the polymer and the entropy changes in the solvent (hydration effects). The configurational entropy change upon polymer aggregation (and partial dehydration) may be expected to be negative. The solvent contribution to ΔS_m resulting from dehydration of the hydrophobic PO segments will be positive (the latter frequently dominates the aggregation process of hydrophobic solutes). While both the initial and final states (before and after transition) will be influenced by the cosolvent, it seems reasonable to assume that the entropy of the aggregated state will be less influenced by changes in the composition of the surrounding solvent. In this case, the significant reduction in ΔS_m induced by 1-PrOH is likely due to the dehydration of the PO groups (in the initial state) as suggested earlier from ΔH_m data. In the other extreme, the weak influence of ED on the transition entropy may then be assigned to ED interactions with the EO segments and the influence of ED on the water–water interactions (hydrogen-bonding, structural networks). These qualitative considerations are consistent with the view that the transition features of the copolymer are dominated by the hydrophobic effects associated with the PO segments of the polymer and with the cosolvent. Recalling, however, that ED has a strong influence on T_m, i.e., comparable to that of 1-PrOH (Figure 3), additional effects must be involved which may lead to canceling contributions to ΔS_m and ΔH_m but leaving large effects on T_m.

As implied above, the phase transitions of the block copolymer observed by DSC in aqueous solutions may be generally regarded as a two-state process (sol–micelles); the gelation is only slightly endothermic.[49,50] From Figure 2, it is readily seen that the endothermic profile and the cooperativity (sharpness of peak) of the transition are more rapidly lost in the presence of 1-PrOH than of the other cosolvents. This suggests that the sol/micelle transition could be progressively replaced by a sol/gel transition with increasing cosolvent concentration in the mixed solvents. As noted earlier, the cosolvent 1-PrOH promotes the phase transition at a lower T_m than other cosolvents (except ED) at the same cosolvent concentrations, the sol/gel transition thus takes place more early in the mixed solvent with 1-PrOH. In fact, the endothermic profile of the transition disappears (and gelation takes place) with 1-PrOH at a relatively low cosolvent concentration ($X > 0.045$) (see Figure 2e). In contrast, the thermal transition of the block copolymer in the mixed solvent with ED has little change in both the endothermic profile and cooperativity in the entire range of the solvent composition. This suggests that the phase transition remains a two-state process of sol/micelle when the cosolvent has a

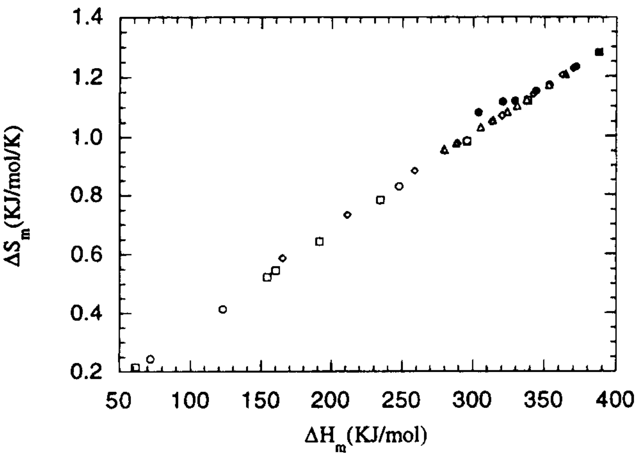

Figure 9. Enthalpy–entropy compensation for the transitions of the PEO–PPO–PEO block copolymer in the mixed solvents (for legends, see Figure 3).

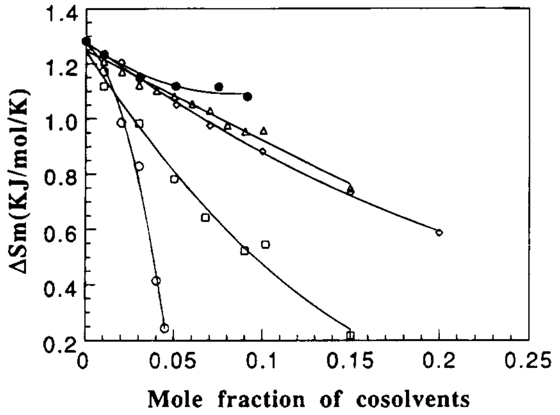

Figure 10. Transition entropy (ΔS_m) as a function of cosolvent mole fractions (for legends, see Figure 3).

strong interaction with water. The phase behaviors of the block copolymer in the mixed solvents with EA or EG are similar to that of ED. Finally, compared to 1-PrOH, the phase transition of the block copolymer can tolerate a much higher cosolvent concentration in the mixed solvent with 2-ME. This suggests that sol/gel transition is less significant and the sol/micelle transition remains dominant for the copolymer in the mixed solvent with 2-ME.

Conclusion

The addition of various organic cosolvents to aqueous solutions of PEO–PPO–PEO block copolymer causes a simultaneous decrease in the transition temperature and enthalpy, both varying markedly as a function of the cosolvent concentration. The influence of cosolvents on the transition may be partly understood in terms of their relative affinities for water. Differences in the water/cosolvent interactions for monofunctional and bifunctional cosolvents play an important role in differentiating their effects on the phase transition processes. The enthalpy and entropy associated with this transition appear largely dominated by hydrophobic effects involving PO segments and the hydrophobic character of the cosolvent as defined from a method using Kirkwood–Buff integrals. The cosolvent 2-ME often exhibits distinctive behavior, intermediate between a bifunctional cosolvent (such as EG) and a hydrophobic cosolvent (1-PrOH). ED also exhibits irregular behavior, with a pronounced effect on T_m but little influence on ΔH_m or ΔS_m.

The transition, as observed by DSC, is considered to be a two-state process of the sol → micelle type. In attempts to understand the molecular effects associated with the cosolvents, their influence on both the sol and the micellar states must be considered. The cosolvent may also induce the sol/gel transition (the latter having very low enthalpies), with a concomitant disappearance of the sol → micelle transition. Judging from the cosolvent effect on ΔH_m (or ΔS_m) and on the sharpness (cooperativity) of the transition, it might be suggested that hydrophobic cosolvents promote the sol/gel transition, whereas very hydrophilic cosolvents, such as ED, maintain the sol/micelle transition.

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