Effects of Solvent Adsorption on Solution Properties of Poly(vinyl alcohol)/Dimethylsulfoxide/Water Ternary Systems

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ABSTRACT: In this study, the solvent adsorption phenomena of poly(vinyl alcohol) (PVA) in cosolvent mixtures of dimethylsulfoxide (DMSO; solvent 1) and water (solvent 2) were investigated. Typically, this cosolvent mixture could form hydrogen-bonded $DMSO/(water)_2$ complexes, involving one DMSO and two water molecules. Because of the complex formation in the cosolvent mixtures, PVA chains preferentially adsorb water molecules at DMSO mole fraction $X_1 < 0.33$, but preferentially adsorb DMSO molecules at $X_1 > 0.33$. The preferential adsorption of DMSO (a good solvent for PVA) could cause the relatively extended conformation of PVA chains in solutions because of the increase in excluded volume effect. Because of various interactions between PVA chains and cosolvent mixtures, the aggregation and gelation behaviors of PVA solutions were significantly affected by the composition of cosolvent mixture. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3211–3217, 2004

Key words: poly(vinyl alcohol); cosolvent mixture; adsorption; solution properties; gelation

INTRODUCTION

It is well known that the degree of polymer–solvent interaction significantly affects the properties of polymer solutions. To clarify these molecular interactions, it has been effective to focus on the chemical structure of each component. Various chemical structures could induce different donor–acceptor electron properties and charge–density rearrangements between polymer and solvent, resulting in the change of molecular interaction.[1,2] Compared with the polymer–solvent interaction in the binary system, it undoubtedly becomes more complicated in the ternary system. For example, the composition of cosolvent, with respect to the polarity of the solvent medium, plays a significant role in the change of the affinity between polymer and cosolvent. In this work, the apparent affinity between poly(vinyl alcohol) (PVA) and dimethylsulfoxide (DMSO)/water mixture at a particular cosolvent composition is quite different from the average affinity of two pure solvent components. This may be considered to be attributed to the formation of a third component (cosolvent complex), resulting in various phenomena of preferential adsorption for PVA chains. Generally, the preferential adsorption coefficient α_a of the solvent on the polymer chain could be evaluated from Read's formalisms.[3–5] However, the application of Read's formalisms still has a restriction; that is, the experimental

systems must contain only weak interactions between each component. Under this circumstance, we modified Read's formalisms, considering the complex formation of cosolvent in a PVA/*N*-methyl-2-pyrrolidone/water system,[6] providing a clear insight into and verification of the change of interactions between polymer chain and cosolvent.

It has been well established that the composition of a DMSO/water mixture deeply affects the phase separation behavior and the gel structure in PVA systems.[7–14] Matsuo et al.[7,8] reported that the phase separation of PVA solution with 50/50 (v/v) DMSO/water composition is more significant than that with a composition of 70/30 (v/v), at the same PVA concentration, through light scattering analyses. Moreover, a series of studies by Kaji and coworkers[9–13] on PVA gels formed in DMSO/water mixtures were reported in detail through various scattering techniques. They found that PVA gel from the solution of 60/40 (v/v) DMSO/water mixture is opaque, whereas the gel becomes translucent with increasing DMSO content in the cosolvent and then is almost transparent for 80/20 (v/v) DMSO/water mixture. Besides, a recent result reported by Takahashi et al.[13] showed that the fastest gelation rate of PVA/DMSO/water solution appears at a volume fraction of DMSO $\varphi = 0.6$, and proposed that the cononsolvency effect, attributed to the formation of $DMSO/(water)_2$ complex, is a main cause that dominates the gelation and phase separation behaviors. Although the structure of PVA gel and the mechanism of phase separation of PVA solu-

tions are discussed explicitly, the effects of cosolvent composition on the solution properties of PVA remain unclear.

In this work, the solution properties of PVA/DMSO/water systems were investigated in a wide range of cosolvent compositions. First, preferential adsorption was discussed to clarify the change of molecular interactions in PVA ternary systems; their effects on the phase separation and gelation behaviors of PVA solutions were investigated as well. Typically, all of these solution properties are significantly influenced by the formation of DMSO/(water)$_2$ complexes.

EXPERIMENTAL

The PVA powder (Aldrich Chemical Co. Ltd., Dorset, UK), of high degree of hydrolysis ($\sim$ 99.8%) and degree of polymerization (P_n) of 2840, was used in this work. Distilled water and analytical-grade solvent [dimethylsulfoxide (DMSO)] were used to prepare the cosolvent mixtures with various DMSO mole fractions, X_1. The PVA solutions were prepared in a wide-mouth bottle, with stirring at 95°C for 3 h until they dissolved into homogeneous solutions.

The viscosities of the cosolvents and the polymer solutions were determined by using a Ubbelohde viscometer (Cannon–Ubbelohde, State College, PA) immersed in a thermostatic water bath maintained at 25°C. The intrinsic viscosity [η] was obtained through the classical Huggins equation,[15] where η_{sp}/C is reduced viscosity:

$$\lim_{c \to 0} (\eta_{sp}/C) = [\eta] \qquad (1)$$

The densities of the cosolvent mixtures (ρ_s) and the PVA/cosolvent solutions (ρ) were determined using a digital precision density meter at 25°C. The values of ρ_s and ρ are listed in Table I. The excess volumes $\Delta \bar{V}^E$ in the cosolvent mixtures could consequently be computed using eq. (2), where M_1 and M_2 are the molecular weights, ρ_1 and ρ_2 are the densities, and X_1 and X_2 are the mole fractions of solvent 1 (DMSO) and solvent 2 (water), respectively. The partial specific volume of PVA $\bar{v}_3$ could be obtained from eq. (3). The values of $\Delta \bar{V}^E$ and $\bar{v}_3$ at a given X_1 are also listed in Table I.

$$\Delta \bar{V}^E = \frac{X_1 M_1 + X_2 M_2}{\rho_s} - \frac{X_1 M_1}{\rho_1} - \frac{X_2 M_2}{\rho_2} \qquad (2)$$

$$\bar{v}_3 = [1 - (\rho - \rho_s)/C]/\rho_s \qquad (3)$$

The gelation time (t_{gel}) was measured using a gelation timer (Techne Co., Poole, UK) operating at 25°C. The determination of gelation time was carried out using a flat weight disc connected by a link with a synchronous motor falling under gravity in the poly-

TABLE I
Densities of the Solvent Mixtures ρ_s, Densities of the PVA Solutions ρ, Excess Volumes $\Delta \bar{V}^E$, Partial Specific Volumes of PVA $\bar{v}_3$ in PVA/DMSO/Water Solutions

X_1	ρ_s	ρ	$\Delta \bar{V}^E$	$\bar{v}_3$
0	0.9998	1.0010	—	0.8802
0.0274	1.0142	1.0154	-0.0846	0.8677
0.0596	1.0295	1.0306	-0.1998	0.8645
0.0980	1.0445	1.0458	-0.3271	0.8329
0.1446	1.0598	1.0612	-0.4851	0.8115
0.2023	1.0750	1.0767	-0.6743	0.7721
0.2756	1.0877	1.0897	-0.8374	0.7355
0.3202	1.0921	1.0943	-0.8752	0.7142
0.3299	1.0935	1.0952	-0.9000	0.7590
0.3502	1.0950	1.0963	-0.9092	0.7945
0.3717	1.0974	1.0984	-0.9493	0.8201
0.5035	1.1019	1.1028	-0.8973	0.8258
0.6953	1.1023	1.1032	-0.6227	0.8255
1	1.0998	1.1005	—	0.8456

mer solutions. At the gelation point the rigidity of the polymer solution is sufficient to support the weight of the disc and causes the link to be compressed and to stop the synchronous motor. The time at which the synchronous motor stopped was defined as gelation time.

Light scattering measurements were carried out with a Malvern series 4700 apparatus (UK) using a He–Ne laser (λ = 632.8 nm, 25 mW) as a light source. The scattering vector $Q = (4\pi n/\lambda)\sin(\theta/2)$ is in the range 0.35–2.71 $\times$ 10^{-3} Å^{-1}, where n is the reflective index. The absolute intensity [Rayleigh ratio (R_θ)] was calculated using toluene as a standard: $R_{90,\text{toluene}} = 13.59 \times 10^{-6}$ cm^{-1}. To reduce the effect of inhomogeneity of samples, the light scattering measurement was performed by rotating the sample cell at 10 rpm.

RESULTS AND DISCUSSION

Figure 1 shows the excess volumes $\Delta \bar{V}^E$ [from eq. (2)], excess enthalpies of mixing $\Delta \bar{H}^E$ (from results reported by Fox et al.[16]), and the relative viscosities η_s/η_2 of the DMSO/water mixtures at various DMSO mole fractions X_1, at 25°C. All of these experimental results present a maximum or minimum value at $X_1 \sim 0.33$. This cosolvent composition is quite particular where the mole ratio of DMSO to water is about 1 : 2. The experimental results in Figure 1 indicate that the strong hydrogen-bonded DMSO/(water)$_2$ complexes may exist in the solutions. Two protons of two water molecules could be strongly bonded with the nonbonding electron pairs of DMSO oxygen by hydrogen bonds. Fuchs et al.[17] reported that the hydrogen bond between water and DMSO molecules is much stronger than that between water molecules themselves in the water/DMSO mixture. On the other hand, Luzar et al.[18] also suggested that the DMSO hydrogen bonding
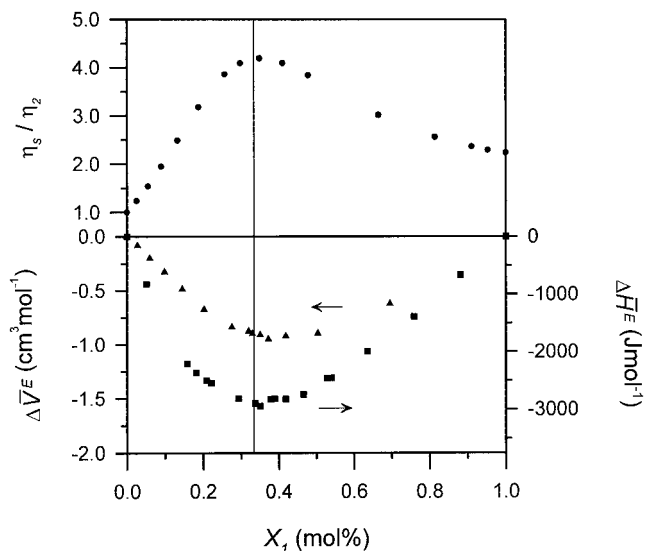
Figure 1 Plots of excess volumes $\Delta \bar{V}^E$ [from eq. (2)], excess enthalpies of mixing $\Delta \bar{H}^E$, and relative viscosities η_s/η_2 as a function of X_1, where η_s and η_2 are the viscosities of mixed solvent and water, respectively.

to water shows a preference compared with the water molecules themselves through computer simulation. A decrease of water–water hydrogen bonds was found as the DMSO concentration was increased. If the DMSO/(water)$_2$ complexes could be formed, it would induce an exothermic mixing process (i.e., negative $\Delta \bar{H}^E$) and increase both the packing density of solvent molecules (i.e., negative $\Delta \bar{V}^E$) and the friction force of flowing (i.e., increasing solution viscosity). From the results of computer simulation reported by Vaisman and Berkowitz,[19] one unambiguously confirmed the formation of DMSO/(water)$_2$ complexes at all compositions of DMSO–water mixtures. At lower DMSO fraction ($X_1 < 0.33$) the solution mainly consists of both DMSO/(water)$_2$ complexes and free water molecules. At higher DMSO fraction ($X_1 > 0.33$), it mainly consists of both DMSO/(water)$_2$ complexes and free DMSO molecules. At $X_1 \sim 0.33$, a large amount of DMSO/(water)$_2$ complexes could be created, and thus the physicochemical properties of the cosolvent mixtures would be significantly changed.

Figure 2 shows the intrinsic viscosity [η] as a function of X_1 at 25°C. The [η] values are 0.93 and 3.25 dL/g, respectively, for the PVA/water and PVA/DMSO solutions. This result directly verifies that DMSO is a good solvent for PVA. The formation of stronger PVA–DMSO hydrogen bonds and large molecular size of DMSO (molar volume $V_1 \cong 71.313$ cm^3/mol) could induce a higher excluded-volume effect, resulting in a PVA coil that extends further in solution. On the other hand, the PVA chains exhibit only a conformation of contracted coil in the aqueous PVA solution, for water with less affinity to PVA and small molecular size (molar volume $V_2 \cong$

18.083 cm^3/mol). The higher attractive interaction between PVA and DMSO than that between PVA and water could be also confirmed from the second virial coefficient A_2, through static light scattering measurements.[6,20,21] In particular, we found other extremes at X_1 values of 0.07 and 0.28 (Fig. 2). Because the minimum [η] was found at $X_1 \sim 0.28$, the PVA chain should exhibit a much contracted coil at this cosolvent composition. The water and DMSO molecules adsorbed on the PVA chains may tend to leave PVA coils for forming stable DMSO/(water)$_2$ complexes. The decreasing numbers of adsorbed solvent molecules in the polymer coils directly cause a more contracted conformation, which may be attributed to the reduction in the excluded volume. Finally, dialysis equilibrium (i.e., the solvent molecules are in and out of polymer coil domain with a similar rate) could be achieved. Then the PVA coils are no longer contracted. At another specific composition of $X_1 = 0.07$, the dimension of the PVA coil in this solution was slightly larger than that in the PVA aqueous solution. Two possible reasons may be considered to cause this particular phenomenon: (1) the intramolecular long-range hydrogen bonds created from the –OH groups of PVA are broken by the addition of DMSO, even in very small amounts, to aqueous PVA solution,[22] and (2) the tetrahedral structures of water molecules are easily broken at the position close to the polar sites (i.e., the S=O group of DMSO), as shown in the following scheme, which may result in more free water molecules to slightly increase PVA–solvent affinity:
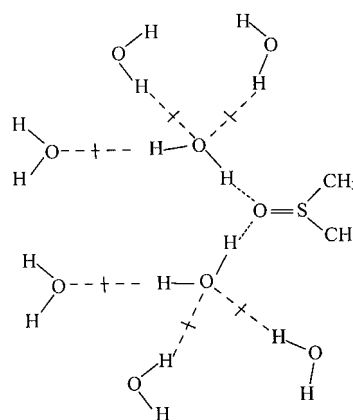
As stated earlier, the preferential adsorption of solvent on polymer chain should affect the solution properties in the ternary system; in particular, it is very sophisticated when a strong interaction exists in the cosolvent mixture (i.e., the complex formation). From the results in Figure 1 the DMSO/(water)$_2$ complex is considered to be formed, the preferential adsorption of the solvent likely explains the molecular interactions in the PVA/DMSO/water ternary solutions. Regarding the ternary system, it is well known that the Gibbs free energy of mixing in a polymer/cosolvent
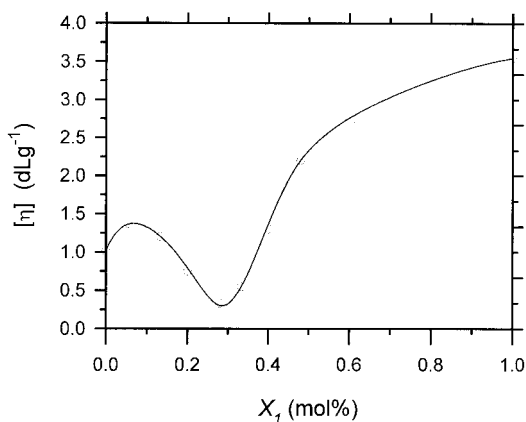
Figure 2 Plot of intrinsic viscosity $[\eta]$ as a function of X_1.

ternary system (ΔG_T^M) could be expressed as eq. (4), where n_i and ϕ_i represent the mole number and the volume fraction of the ith component, respectively; g_{ij} is the binary interaction potentials; g_T is the ternary interaction potential; and $u_1 = \phi_i/(\phi_i + \phi_2)$, respectively.

$$\Delta G_T^M/RT = n_1\ln\phi_1 + n_2\ln\phi_2 + n_3\ln\phi_3 + g_{12}(u_1)n_1\phi_2$$
$$+ g_{13}(\phi_3)n_1\phi_3 + g_{23}(\phi_3)n_2\phi_3 + g_T n_1\phi_2\phi_3 \quad (4)$$

Then, the preferential adsorption coefficient α_a could be derived from the second derivation of ΔG_T^M, $(\partial\mu_i/\partial\mu_j)_{P,T,m_{k\neq j}}$, as eq. (5),[23] where $\bar{v}_3$ is the partial specific volume of polymer, V_i is the molar volume of the ith component, μ_i is the chemical potential of the ith component, and m_i is the molality of the ith component. The second derivation of ΔG_T^M, $(\partial\mu_i/\partial\mu_j)_{P,T,m_{k\neq j}} = a_{ij}$, could be derived from eq. (6), where V_m is the total volume and l is the ratio of solvent molar volume V_1/V_2.

$$\alpha_a = \frac{V_2\bar{v}_3\phi_1}{V_3}\frac{(\partial\mu_2/\partial m_3)_{m_2,m_3\to 0}}{(\partial\mu_2/\partial m_2)_{m_3\to 0}} \quad (5)$$

$$a_{22} = \frac{n_1}{n_2}\frac{V_2 RT}{V_m}b_{22} \quad \text{or} \quad a_{23} = \frac{n_1 V_2 V_3 RT}{V_m^2}b_{23} \quad (6)$$

$$b_{22} = \phi_1 l + \phi_2 - \phi_1\phi_2$$
$$\times\left\{2\left[g_{12} + (\phi_1 - \phi_2)\frac{\partial g_{12}}{\partial u_1}\right] - \phi_1\phi_2\frac{\partial^2 g_{12}}{\partial u_1^2}\right\} \quad (7)$$

$$b_{23} = g_{23}l - g_{13} + 1 - l - (\phi_1 - \phi_2)(g_{12} - g_T)$$
$$+ \phi_1\phi_2\left(\frac{\partial g_{12}}{\partial u_1} - \frac{\partial g_T}{\partial u_1}\right) \quad (8)$$

The binary interaction parameters χ_{i3} and the ternary interaction parameter χ_T, respectively, relate to the g_{i3} and g_T values, as given in eqs. (9) and (10):

$$\chi_{i3} = g_{i3} - (\partial g_{i3}/\partial\phi_3) \quad (9)$$

$$\chi_T = g_T - (\partial g_T/\partial\phi_3) \quad (10)$$

Read[3] derived a formalism, as shown in eq. (11), to determine the theoretical α_a value for a special case in eq. (4), where all g_{ij} values are independent of composition (i.e., $g_{ij} = \chi_{ij}$) and the g_T value is equal to zero.

$$\alpha_a = -\bar{v}_3\phi_1\phi_2\frac{l - 1 + \chi_{13} - l\chi_{23} + \chi_{12}(\phi_1 - \phi_2)}{l\phi_1 + \phi_2 - 2\chi_{12}\phi_1\phi_2} \quad (11)$$

On the other hand, a relatively complete formalism[4,5] was developed, as presented in eq. (12), to calculate α_a with respect to the χ_T parameter.

$$\alpha_a = -\bar{v}_3\phi_1\phi_2\frac{l - 1 + \chi_{13} - l\chi_{23} + (\chi_{12} - \chi_T)(\phi_1 - \phi_2)}{l\phi_1 + \phi_2 - 2\chi_{12}\phi_1\phi_2}$$
$$(12)$$

These two formalisms remain usable only when the system contains weak interactions between each component. In our previous study,[6] we reported that the formation of cosolvent complex would affect the rationality of Read's formalism. Therefore, the formation of the DMSO/(water)$_2$ complex may change the composition of the cosolvent mixture. At $X_1 < 0.33$ the cosolvent mixtures consist mainly of free water molecules and the DMSO/(water)$_2$ complexes; on the other hand, there are only free DMSO molecules and DMSO/(water)$_2$ complexes at $X_1 > 0.33$. Accordingly, the formalism for evaluating α_a value should be concerned with not only the interaction parameters χ_{13} and χ_{23}, but also the interaction parameter χ_{c3} (i.e., the interaction between the complex and polymer chain). Under this circumstance, the complex-free DMSO (χ_{c1}) and the complex-free water (χ_{c2}) interaction parameters must substitute, respectively, for the χ_{12} parameter (the interaction between free DMSO and water molecules) at $X_1 > 0.33$ and $X_1 < 0.33$. Therefore, we provided a more precise operation as eq. (13) to calculate preferential adsorption coefficients α_a, when the solvent complexes are comparatively stable in solution, as follows:

$$\alpha_a = -\bar{v}_3\phi_c\left[\phi_1\frac{l_1 - 1 + \chi_{13} - l_1\chi_{c3} + \chi_{c1}(\phi_1 - \phi_c)}{l_1\phi_1 + \phi_c - 2\chi_{c1}\phi_1\phi_c}\right.$$
$$\left. + \phi_2\frac{l_c - 1 + \chi_{c3} - l_c\chi_{23} + \chi_{c2}(\phi_c - \phi_2)}{l_c\phi_c + \phi_2 - 2\chi_{c2}\phi_c\phi_2}\right] \quad (13)$$

where ϕ_c is the volume fraction of the DMSO/(water)$_2$ complex, $l_c = V_c/V_2$, and $l_1 = V_1/V_c$. The V_1, V_2, and V_c parameters are the molar volumes of DMSO (solvent 1), water (solvent 2), and DMSO/(water)$_2$ complex, respectively. The χ_{13} and χ_{23} values are, respec-
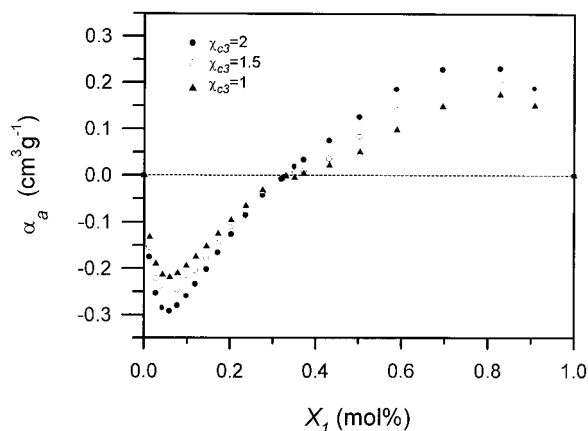
Figure 3 Plots of theoretical α_a value [from eq. (4)] as a function of X_1.

tively, 0.4202 (PVA/DMSO) and 0.4953 (PVA/water), which could be actually calculated from the second virial coefficients (A_{2i}) of PVA binary solutions, as given in eq. (14). The A_2 values are about 8×10^{-4} and 2×10^{-4} mL mol g^{-2}, respectively, for the PVA/DMSO[20] and PVA/water[6,21] systems.

$$\chi_{i3} = \frac{1}{2} - \frac{A_{2i}V_i}{\bar{v}_3^2} \qquad (14)$$

The χ_{c1} and χ_{c2} values might be consequently obtained by consideration of the complex formation through the ΔG^M values from the result reported by Luzar.[24]

$$\chi_{ci} = \frac{\Delta G^M/RT - X_i \ln \phi_i - X_c \ln \phi_c}{X_i \phi_c} \qquad (15)$$

The V_c value is about 106.5 cm^3/mol for deducting the excess volume at $X_1 = 0.33$. The donor–acceptor electron property of the DMSO/(water)$_2$ complex to PVA should be significantly reduced, given that the S=O group of DMSO has been strongly bonded with two water molecules. Therefore, the weaker PVA–complex interaction should be presented. In fact, it is very difficult to obtain the precise χ_{c3} value in the present study. For only the qualitative discussion, the χ_{c3} values of 1, 1.5, and 2 are assumed for the calculations in the present work. The ϕ_1, ϕ_2, and ϕ_c values could be obtained with the same operation reported in our previous study.[6]

It should be mentioned first that a positive α_a value virtually means the preferential adsorption of the better solvent (DMSO), but a negative α_a value means the preferential adsorption of another solvent (water). Figure 3 shows the α_a value as a function of X_1. The result for χ_{c3} values of 1, 1.5, and 2 exhibits a similar tendency. At lower X_1, the water molecules are preferentially adsorbed by PVA chains. At higher X_1, DMSO

molecules are preferentially adsorbed. An inversion of the preferential adsorption phenomenon appears at $X_1 \sim 0.33$, implying that the PVA chains have no preferential adsorption of solvents at this cosolvent composition. At lower DMSO fractions, most DMSO molecules should associate with water molecules to form DMSO/(water)$_2$ complexes; more free water remains to be adsorbed. At this condition, the polymer coil domain should contain only a few DMSO molecules but a large amount of water molecules. Therefore, the slight [η] increase at $X_1 = 0.07$, as shown in Figure 2, may be considered to be attributable to fact that the preferential adsorption of most water molecules would break the tetrahedral structure of water, thus improving the affinity to PVA. At higher DMSO fractions, on the other hand, most DMSO molecules could be adsorbed and then the PVA chains would become extended further because of the increase in the excluded volume effect. At $X_1 \sim 0.33$, the solution contains only a slight amount of free water and free DMSO molecules, thus inducing no preferential adsorption of solvent ($\alpha_a = 0$); in other words, most of the DMSO and water molecules form DMSO/(water)$_2$ complexes. In Figure 2, however, it should be mentioned that the minimum [η] (i.e., the poorest affinity of cosolvent) appears at $X_1 = 0.28$, but not at $X_1 = 0.33$, which is explained by the fact that all DMSO molecules are theoretically considered not to be adsorbed by PVA chains at $X_1 = 0.33$.

In fact, preferential adsorption in the cosolvent system is comparatively suitable to be discussed with respect to diluted polymer solutions. In the present study we also set out to investigate the cosolvent effect on the properties of semidiluted solutions through light scattering measurement. Figure 4 shows the Rayleigh ratio R_θ versus scattering vector Q at ageing times of 5, 10, 20, and 30 h for PVA 1 g/dL solution at 25°C. Ohkura et al.[12] reported that the critical gelation concentration C_{gel}^* is close to 1.2 g/dL for $X_1 \sim 0.28$ PVA ($P_n \cong 2840$) solution at 25°C, indicating that the solutions with a PVA concentration < 1.2 g/dL could not form macroscopic gels but could form sols. The liquid–liquid phase separation or spinodal decomposition should be processed first, to separate the solution into concentrated (polymer-rich) and diluted (polymer-poor) phases. During the spinodal decomposition process, the polymer concentration in the concentrated phase gradually increases, after which crystallization occurs in the concentrated phase of solution. The existence of crystallites, even in the PVA sol state, was confirmed through the neutron scattering experiment.[10,11] In the sol state ($C < 1.2$ g/dL), the infinite network of the concentrated phase could be not formed, but the concentrated phases or microphase domains in the solution were separately dispersed, after which the solution became turbid. For the PVA solution with $X_1 \sim 0.28$, the scattering profile
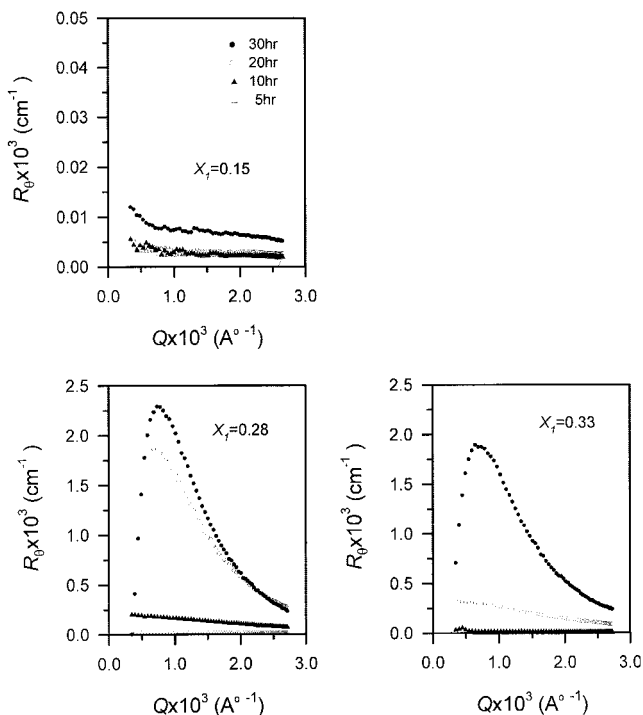
Figure 4 Plots of Rayleigh ratio R_θ versus scattering vector Q for 1 g/dL PVA solution with various ageing times at 25°C.

increased quickly for 20 h ageing and then a strong scattering peak could be found at $Q \cong 0.8 \times 10^{-3}$ Å^{-1}. This result means that the microphase separation of the solution may induce a characteristic wavelength of about 785 nm, obtained from $2\pi/Q$. Compared with X_1 values of 0.28 and 0.33 solutions, the scattering intensity of $X_1 = 0.15$ solution is very weak and no scattering peak was found, even for the solution aged for 30 h at 25°C. These phenomena directly indicate that the large amount of DMSO/(water)$_2$ complexes would decrease the affinity of cosolvent mixture to PVA, resulting in faster microphase separation.

On the other hand, the solvent desorption phenomenon may directly induce spinodal decomposition or crystallite formation. Because formation of the DMSO/(water)$_2$ complex is thermodynamically stable,[17–19] the solvent molecules would leave the PVA coil domain to move into the outside bulk solvent phase to form stable complexes. The hydrogen-bond lifetime[18,25] for PVA–solvent (~ 0.2 ps) is shorter than that for the water–DMSO (~ 0.8 ps) pair, implying that the desorption of solvent molecules could proceed step by step. Consequently, the phase separation induced by solvent desorption may proceed in accordance with the following processes. (1) Many solvent molecules are still adsorbed on polymer chains at the initial stage of spinodal decomposition; therefore, the occurrence of crystallization at this moment is difficult. (2) Then, a quasi-spinodal decomposition oc-

curs,[10,11] that is, the simultaneous occurrence of spinodal decomposition and crystallization. In this stage the solvent desorption becomes observable. (3) Finally, it rapidly forms crystallites in the polymer concentrated phase as the solvent desorption proceeds further. At solvent compositions with lower DMSO fractions, the DMSO molecules in the PVA coil domain (or concentrated phase) tend to move into the bulk solvent domain (or diluted phase) to form DMSO/(water)$_2$ complexes with outside free water molecules. In contrast, the movement of water molecules to the diluted phase becomes difficult because there is no redundancy of free DMSO molecules, which could be used to form cosolvent complexes. Therefore, a greater degree of solvent desorption cannot occur. At higher DMSO fractions, most water molecules exhibit a greater tendency to leave the concentrated phase and then form a complex with free DMSO molecules in the diluted phase. At the same time, the amount of moving DMSO molecules is considerably less because many free DMSO molecules already exist in the diluted phase. At $X_1 \sim 0.33$, both DMSO and water molecules should leave the concentrated phase to form more cosolvent complexes. The spinodal decomposition or crystallization would proceed further near this cosolvent composition.

Figure 5 shows the maximum Rayleigh ratio of the scattering peak R_{max} as a function of the X_1 value for PVA solutions (0.4 g/dL) aged 3 days. The higher R_{max} values are found in X_1 values ranging from 0.20 to 0.33. This is because the larger amount of DMSO/(water)$_2$ complexes are formed in this X_1 range, resulting in the poorer affinity of cosolvent mixture to PVA. The poorer affinity should allow phase separation of the solution to proceed easily, thus increasing the degree of heterogeneity. In particular, the maximum R_{max} value appears at $X_1 \cong 0.28$. This result corresponds well to those results for diluted solution, as discussed earlier. Regarding the cosolvent effect on
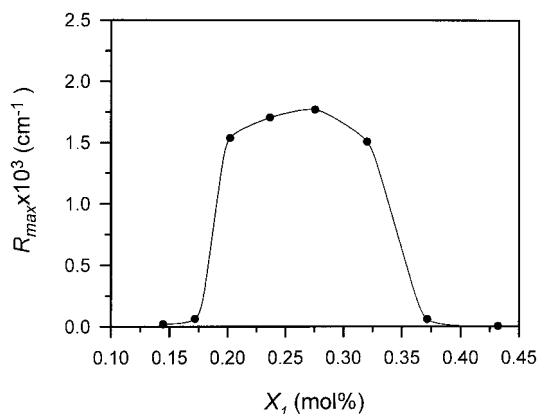

Figure 5 Plot of maximum Rayleigh ratio R_{max} as a function of X_1 for 0.4 g/dL PVA solution after 3 days' ageing.
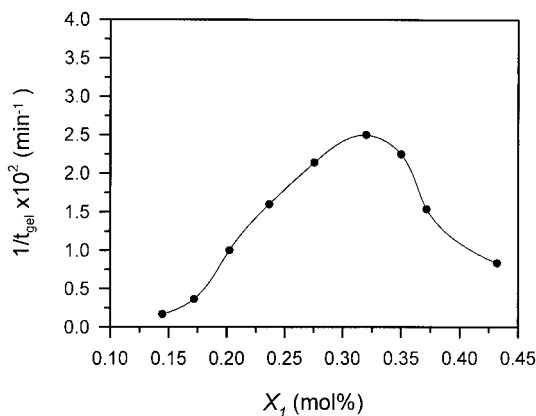
Figure 6 Plot of gelation rate $1/t_{gel}$ as a function of X_1 for 10 g/dL PVA solution.

the rather concentrated solutions (i.e., $C \gg C_{gel}^*$), the connection in the concentrated phases with crystallites/junction points could form an infinite three-dimensional network structure. Figure 6 shows the gelation rate $1/t_{gel}$ as a function of X_1 for 10 g/dL PVA solution at 25°C, where t_{gel} denotes the gelation time. When the amount of desorbed solvents reaches a critical point, numbers of crystallites/junction points are sufficiently formed for connecting PVA chains to create an infinite three-dimensional network structure after which the gelation of the solution occurs. In Figure 6 the gelation rate of concentrated PVA solution changes significantly with various X_1 values. Moreover, it typically presents a higher gelation rate at an X_1 value of about 0.33, where the rate of solvent desorption is considered to be faster than that of other solvent compositions. Even though the fastest rate of solvent desorption inducing the rapid gelation occurs at $X_1 \sim 0.33$, the equilibrium structure containing greater PVA chain aggregation still appears at $X_1 \sim 0.28$, as shown in Figure 5. This is considered mainly attributed to the greater amount of DMSO desorption at $X_1 \sim 0.28$, as discussed earlier.

CONCLUSIONS

In the PVA/DMSO/water ternary solutions, the strong DMSO/(water)$_2$ hydrogen-bonded complexes could be formed in solution, with the result that PVA chains preferentially adsorb water molecules at lower DMSO fractions but preferentially adsorb DMSO molecules at higher DMSO fractions. Because the formation of DMSO/(water)$_2$ complexes give rise to the poorer affinity of DMSO/water mixture to PVA, the

solvent desorption from the concentrated phase to the diluted phase allows the microphase separation of PVA solutions to proceed further. The phase separation induced by solvent desorption may occur in accordance with the following processes. (1) Many solvent molecules are still adsorbed on polymer chains at the initial stage of spinodal decomposition. (2) Then, a quasi-spinodal decomposition occurs. In this stage the solvent desorption becomes observable. (3) Finally, it rapidly forms microcrystallites in the polymer concentrated phase as the solvents are further desorbed, although the solvent desorption phenomenon is considered to directly affect the aggregation behavior of PVA chains in solutions. A number of details associated with the investigation should be studied further to clarify these effects of cosolvent complex on the solution properties of PVA. For example, how the desorption rate of solvents affects the phase separation behavior will be investigated through a computer simulation and other experimental methods in the future.

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