

# Effect of co-solvent complex on preferential adsorption phenomenon in polyvinyl alcohol ternary solutions

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## Abstract

In this work, the effect of co-solvent complex on preferential adsorption phenomenon in polyvinyl alcohol (PVA)/*N*-methyl-2-pyrrolidone (NMP)/water ternary solutions was studied. It should be noticed that in this system one NMP molecule could bind with two water molecules to form NMP(water)<sub>2</sub> ter-solvency complex. The formation of the NMP(water)<sub>2</sub> complex is found to significantly affect the preferential adsorption phenomenon. At the NMP volume fraction of  $\phi_1 < 0.73$  in co-solvent mixture, the PVA chains preferentially adsorb the water molecule. Owing to the poorer affinity of water compared with that of NMP to PVA, contracted PVA coils are formed at this condition. At  $\phi_1 > 0.73$ , the PVA chains preferentially adsorb the NMP molecule, which is a better solvent for PVA, inducing an  $A_2$  value that rapidly increases. The PVA coil exhibits a much-extended conformation. Moreover, the theoretical values of preferential adsorption coefficient,  $\alpha_a$ , obtained from two Read formalisms are in poor agreement with the experimental results. This is due, considerably, to the effect of the NMP(water)<sub>2</sub> complex formation in this co-solvent system. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Polyvinyl alcohol; Co-solvent mixture; Dilute solution

## 1. Introduction

In polymer/co-solvent ternary solutions, the affinity between the polymer and co-solvent must directly affect the concentration and density fluctuations of the solutions. Generally, the enhancement of the polymer–solvent affinity directly reflects on the reduction of the free volume available for fluctuations and the diminishing of the Rayleigh scattering [1]. On the other hand, the chemical structures, the dipole moments and the donor–acceptor electron properties of each component should be primarily considered to affect the affinity. In our previous study [2,3], the interaction between polyvinyl chloride and organic solvents has been discussed, indicating that the increment of the donor–acceptor electron property and the charge-density rearrangement directly generate the attractive interaction between PVC and the solvent. The effect of polymer–solvent interaction on the conformational change and the aggregation behavior of PVC chains were investigated from dilute solution to semi-dilute solution.

Compared with the polymer–solvent interaction in the binary system, the interactions undoubtedly become more

complicated in the ternary system. For example, the composition of co-solvent, concerned with the polarity of the solvent medium, plays a significant role in changing the degree of the affinity between polymer and co-solvent. In this study, the apparent affinity between polyvinyl alcohol (PVA) and co-solvent *N*-methyl-2-pyrrolidone (NMP)/water at a particular co-solvent composition is quite different from the average affinity of the two pure solvent components. This fact may be mainly because of the formation of a third component (co-solvent complex), resulting in the various phenomena of preferential adsorption for PVA chains.

It is well known that the insight into the preferential adsorption phenomenon is very sophisticated. Many parameters [4–15], such as the binary interaction parameters  $\chi_{ij}$ , the ternary interaction parameter  $\chi_T$ , the molar volumes of two solvents [4,5], the molar volume of the side group of polymer [5], the molecular weight of polymer [6] and temperature [7–9], fundamentally dominate the preferential adsorption of solvents on polymer chains in solution state. Katime et al. [6] have already verified that the increase in the molecular weight of polymer causes the lowering of the preferential adsorption coefficient. Horta et al. [10] also pointed out that the solvent with small molecular volume is preferentially adsorbed because the combinatorial entropy is favourable to the entrance of small molecules into the

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Table 1

The refractive index increment,  $dn/dC$ , the densities of the solvent mixtures,  $\rho_s$ , the densities of the PVA solutions,  $\rho$ , the excess volumes,  $\Delta\bar{V}^E$  and the partial specific volumes of PVA,  $\bar{v}_3$ , in the PVA/NMP/water solutions

$\phi_1$	$dn/dC$ (cm <sup>3</sup> g <sup>-1</sup> )	$\rho_s$ (g cm <sup>-3</sup> )	$\rho$ (g cm <sup>-3</sup> )	$\Delta\bar{V}^E$ (cm <sup>-3</sup> mol <sup>-1</sup> )	$\bar{v}_3$ (cm <sup>3</sup> g <sup>-1</sup> )
0	0.162	0.9954	0.9971	–	0.835
0.2	0.141	1.0121	1.0139	–0.211	0.815
0.4	0.119	1.0268	1.0287	–0.470	0.789
0.6	0.098	1.0386	1.0404	–0.790	0.785
0.7	0.087	1.0404	1.0422	–0.877	0.790
0.8	0.077	1.0403	1.0420	–0.913	0.798
0.9	0.065	1.0349	1.0365	–0.630	0.815
1.0	0.055	1.0285	1.0298	–	0.845

polymer domain. Generally, the theoretical  $\alpha_a$  values could be evaluated from Read formalisms, considering  $\chi_{ij}$ ,  $\chi_T$  and the effect of solvent volume [11–13]. Unfortunately, the application of these formalisms has a restriction, i.e. the experimental systems must only contain weak interactions between each component. For example, the CCl<sub>4</sub>/MeOH mixture is a weak co-solvent for PMMA; then, the preferential adsorption phenomenon could be interpreted perfectly using the Read formalisms [14,15]. In this study, the co-solvents from the NMP (component 1) and water (component 2) mixtures were used to dissolve PVA (component 3). In this ternary system, the NMP molecule, which is a typical dipolar aprotic solvent, could particularly bind with two water molecules to form a NMP(water)<sub>2</sub> complex (1–2–2 contact). Therefore, the formation of NMP(water)<sub>2</sub> complex may affect the preferential adsorption phenomenon and the thermodynamic properties of PVA solutions. In addition, the discrepancy between the experimental and the theoretical preferential adsorption coefficients are also discussed in this work.

## 2. Experimental

### 2.1. Sample preparation

A PVA powder (Aldrich Chemical Co. Ltd, USA) with a high degree of hydrolysis (about 99.8%) was used in this work. The distilled water and analytical grade solvent NMP were repeatedly filtered using a 0.02  $\mu\text{m}$  Teflon filter for removing dust. The PVA solutions were prepared in a pre-cleaned wide mouth bottle, with stirring at 95°C for 2 h until they dissolved into homogeneous solutions. The PVA solutions with concentrations 0.1–1 g l<sup>-1</sup>, were filtered using a 0.45  $\mu\text{m}$  Teflon filter, then cooled into a thermostat oven at constant temperature 30°C for one day to stabilize the solutions before the measurements.

### 2.2. Measurements

Light scattering measurements were carried out using a Malvern series 4700 apparatus with an argon ion laser of vertical light 100 : 1 (LiCONiX 5302AH) operating at wavelength 514.5 nm. The reciprocal reduced scattering

intensity,  $KC/\Delta R_\theta$ , was derived, where  $C$  is the concentration of polymer and  $\Delta R_\theta$  is the difference of the Rayleigh ratio of the solution to the solvent obtained through the calibration of toluene,  $R_{90,\text{toluene}} = 18 \times 10^{-6} \text{ cm}^{-1}$ . The optical constant for vertically polarized light  $K = 4\pi^2 n_0^2 (dn/dC)^2 / N_A \lambda^4$  was derived, where  $n_0$  is the refractive index of solvent,  $dn/dC$ , the refractive index increment,  $\lambda_0$ , the wavelength of light in vacuum,  $N_A$ , the Avogadro's constant and  $\theta$ , the scattering angle. Thereafter, the second virial coefficient,  $A_2$ , the  $z$ -average radius of gyration,  $R_G$  and the weight-average molecular weight,  $\bar{M}_w$ , could be directly achieved using the well-known Zimm equation.

$$\frac{KC}{\Delta R_\theta} = \frac{1}{\bar{M}_w} \left[ 1 + \frac{16}{3} \pi^2 \frac{R_G^2}{\lambda_0^2} \sin^2 \frac{\theta}{2} + \dots \right] + 2A_2C + \dots \quad (1)$$

The values of the refractive index increment,  $dn/dC$ , for the PVA solutions at 30°C were obtained by operating the Optilab DSP interferometric refractometer with wavelength 514.5 nm (Wyatt Tech. Co.). The  $(dn/dC)_{\phi_1}$  values, as given in Table 1, decrease with increasing volume fraction of NMP,  $\phi_1$ .

The viscosities of the co-solvents and the polymer solutions were determined using an Ubbelohde viscometer immersed in a thermostatic water bath held at 30°C. The intrinsic viscosity  $[\eta]$  and the Huggins constant  $k$  were obtained through the classical Huggins equation, where  $t$  is the flowing time of polymer solution;  $t_0$  the flowing time of solvent and  $\eta_{sp}$  is the specific viscosity [16].

$$\frac{(t - t_0)/t_0}{C} = (\eta_{sp}/C) = [\eta] + k[\eta]^2 C \quad (2)$$

The densities of the co-solvent mixtures,  $\rho_s$ , and the PVA/co-solvent solutions,  $\rho$ , with concentration 0.01 g cm<sup>-3</sup> were measured using a digital precision density meter at 30°C. The values of  $\rho_s$  and  $\rho$  are also listed in Table 1. The excess volumes,  $\Delta\bar{V}^E$ , in the solvent mixtures could, consequently, be computed using Eq. (3), where  $M_1$  and  $M_2$  are the molecular weights,  $\rho_1$  and  $\rho_2$ , the densities and  $x_1$  and  $x_2$ , the mole fractions of solvent 1 and solvent 2, respectively. The partial specific volume of PVA,  $\bar{v}_3$ , at PVA concentration 0.01 g cm<sup>-3</sup> also could be computed using

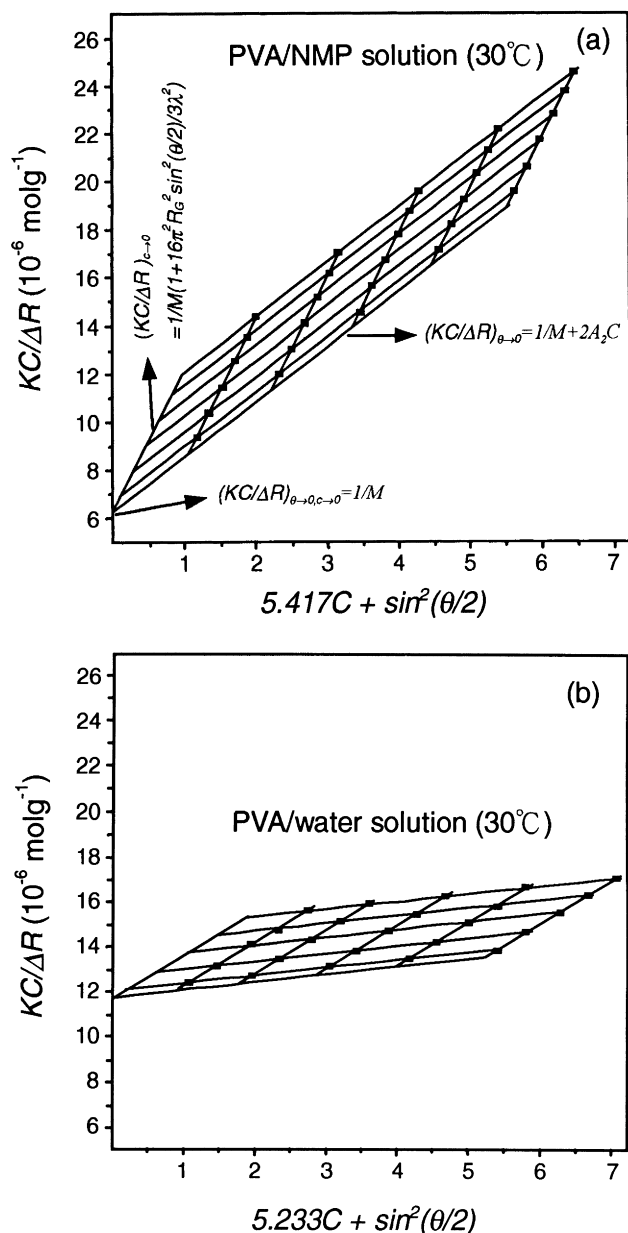


Fig. 1. The Zimm plots of: (a) PVA/NMP; and (b) PVA/water dilute solutions at 30°C.

Eq. (4) [17]. The values of  $\Delta\bar{V}^E$  and  $\bar{v}_3$  at a given  $\phi_1$  are also presented in Table 1.

$$\Delta\bar{V}^E = \frac{x_1M_1 + x_2M_2}{\rho_s} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \quad (3)$$

$$\bar{v}_3 = \frac{[1 - (\rho - \rho_s)/C]}{\rho_s} \quad (4)$$

### 3. Results and discussion

The  $A_2$  values obtained from the Zimm double-extrapolation method could be regarded as the degree of the

polymer–solvent interaction. The Zimm plots of PVA/NMP and PVA/water solutions at 30°C are shown in Fig. 1(a) and (b), respectively. In PVA/NMP, a large  $A_2$  value (ca.  $A_2 = 23.3 \times 10^{-4} \text{ ml mol g}^{-2}$ ) indicates that there exists a strongly attractive force between PVA chains and NMP molecules. On the other hand, a small  $A_2$  value (ca.  $A_2 = 1.8 \times 10^{-4} \text{ ml mol g}^{-2}$ ) in the PVA/water solution illustrates that the interaction between PVA and water is much lower than the PVA/NMP solution. The results from Zimm plots also show larger  $R_G$  value (ca. 47.8 nm) in PVA/NMP solution as comparison to that (ca. 21.3 nm) in PVA/water solution. When PVA chains associate with a good solvent, NMP, the intramolecular segments of PVA exclude one another to extend the PVA chain, and reduce the frequency of collision of the intramolecular segments. On the other hand, comparatively contracted PVA coils are formed in the PVA/water solution because of stronger intramolecular segment–segment interaction within the PVA chains.

Fig. 2 shows the reduced viscosity,  $\eta_{sp}/C$ , as a function of the PVA concentration,  $C$ , consequently obtaining  $k = 0.23$  and  $[\eta] = 2.40 \text{ dl g}^{-1}$  in PVA/NMP solution and  $k = 0.53$  and  $[\eta] = 1.01 \text{ dl g}^{-1}$  in PVA/water solution. It is well known that the Huggins constant,  $k$  value, could also be used for predicting the degree of polymer–solvent interaction in the polymer/single solvent solution. In  $\theta$  solvent ( $k = 0.52$ ), the polymer chains exhibit unperturbed coils. In a good solvent ( $k < 0.52$ ), the polymer chains should exhibit relatively extended conformations, and in a poor solvent ( $0.8 < k < 1.3$ ) the polymer chains are collapsed and the intramolecular aggregation occurs easily. Therefore, final interpretations simultaneously manifest that NMP is a good solvent ( $k = 0.23$ ;  $A_2 = 23.3 \times 10^{-4} \text{ ml mol g}^{-2}$ ) for PVA and that water is quite close to a  $\theta$  solvent ( $k = 0.53$ ;  $A_2 = 1.8 \times 10^{-4} \text{ ml mol g}^{-2}$ ) for PVA, at 30°C. The interaction between PVA and NMP (or water) can be understood by the donor–acceptor electron properties. NMP, a typical dipolar aprotic solvent, could be either a strong electron donor or a hydrogen acceptor for enhancing the affinity between PVA and NMP. The doubly bound oxygen of NMP could form more stable H-bonding with the hydroxyl groups of PVA, and break the H-bonding within the PVA hydroxyl groups. Therefore, the “C=O” group of NMP is a “strong site” for PVA. On the other hand, the “O–H” group of water is only a “weak site” for PVA, producing only weak H-bonding between PVA and water.

In the PVA/NMP/water ternary solution, we should not only consider the properties of PVA/NMP and PVA/water solutions but also the property between NMP and water. Fig. 3 shows the excess volumes,  $\Delta\bar{V}^E$  (from Eq. (3)), excess enthalpies of mixing,  $\Delta\bar{H}^E$  (from the results of Ryabtseva et al. [18]) and the viscometric values,  $\eta_s$  for the NMP/water co-solvents at various NMP volume fractions,  $\phi_1$ , at 30°C. The values  $\Delta\bar{V}^E \neq 0$  and  $\Delta\bar{H}^E \neq 0$  indicate that this co-solvent system is a non-ideal system. From Fig. 3,

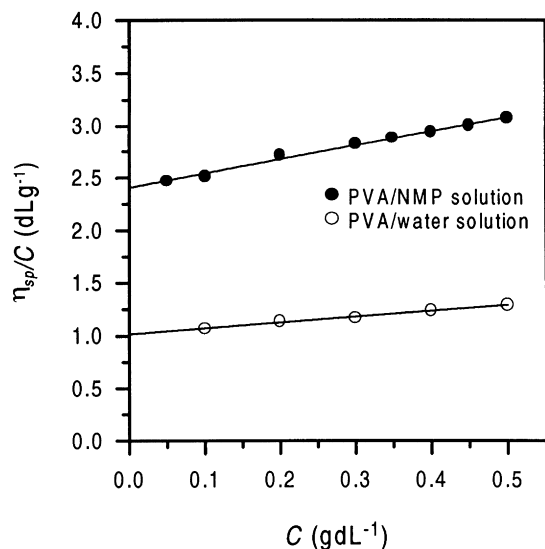
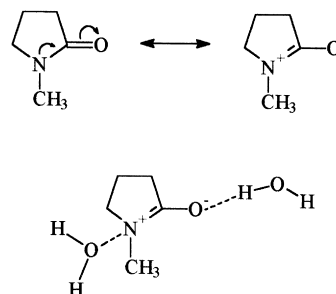


Fig. 2. The reduced viscosity,  $\eta_{sp}/C$ , as a function of  $C$  at 30°C.

minimum  $\Delta\bar{V}^E$  (ca.  $\Delta\bar{V}^E = -0.91 \text{ cm}^3 \text{ mol}^{-1}$ ), minimum  $\Delta\bar{H}^E$  (ca.  $\Delta\bar{H}^E = -2740 \text{ J mol}^{-1}$ ) and maximum  $\eta_s$  (ca.  $\eta_s/\eta_2 = 3.52$ ) values appeared at around  $\phi_1 = 0.7-0.8$ . A co-solvent composition ( $\phi_1 = 0.73$ ) is quite particular where the mole ratio of NMP to water is about 1 : 2, indicating that one NMP molecule could directly bind with two water molecules to the build NMP(water)<sub>2</sub> ter-solvency complex. Complex formation, therefore, understandably induces the exothermic mixing process, increases the packing density of the solvent molecules, reduces the movement of the solvent molecules and increases the friction force of flowing. Typically at  $\phi_1 = 0.7-0.8$ , large amount of NMP(water)<sub>2</sub> complexes could be formed to change remarkably the physicochemical properties of the co-solvent

mixtures. From the viewpoint of the molecular structures, the oxygen atom is more electronegative than nitrogen atom and it could be expected that the negative charge on NMP prefers to reside on oxygen atom. This resonance structure contains about 40% double bond character for the C–N bond of the amide group in NMP, evidenced by the <sup>13</sup>C–H coupling constant for the *N*-methyl group in NMR [19]. The partial positive charge on the nitrogen atom and the partial negative charge on the oxygen atom could be an electron acceptor and a donor, respectively [19,20]. Hence, this resonance property gives rise to the enhanced stability of the NMP(water)<sub>2</sub> complex as shown in the following scheme. Assarsson et al. [21] have also confirmed this ter-solvency complex formation through the freezing-point depression method.



Subsequently, we explored the physicochemical properties of PVA chains in NMP/water co-solvent by light scattering measurement. Two experimental procedures, including constant solvent composition and constant chemical potential of the solvents, could be generally selected to operate. The refractive index increment at constant chemical potential,  $(dn/dC)_{\mu}$ , could be measured through a semi-permeable membrane, where the co-solvent

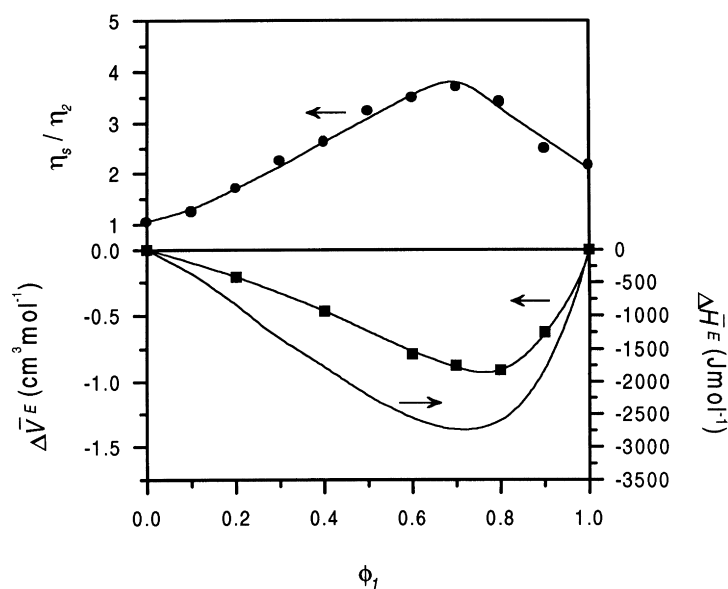


Fig. 3. The excess enthalpies,  $\Delta\bar{H}^E$ , the excess volumes,  $\Delta\bar{V}^E$  and the relative viscosity values,  $\eta_s/\eta_2$ , as a function of  $\phi_1$  at 30°C, where  $\eta_2$  is the viscosity of water.

Table 2

The  $\bar{M}_a/\bar{M}_w$  values, the preferential adsorption coefficients,  $\alpha_a$ , the excess number of water or NMP molecules,  $n_{\text{water}}^E$  or  $n_{\text{NMP}}^E$  and the excess number per repeat unit of PVA,  $n_{\text{water,unit}}^E$  and  $n_{\text{NMP,unit}}^E$ , in the PVA/NMP/water solutions

$\phi_1$	$\bar{M}_a/\bar{M}_w$	$\alpha_a$ ( $\text{cm}^3 \text{g}^{-1}$ )	$n_{\text{water}}^E$ ( $n_{\text{water,unit}}^E$ )	$n_{\text{NMP}}^E$ ( $n_{\text{NMP,unit}}^E$ )
0.2	0.697	-0.151	712 (0.37)	-
0.4	0.631	-0.159	751 (0.39)	-
0.6	0.709	-0.101	472 (0.24)	-
0.7	0.915	-0.025	116 (0.06)	-
0.8	1.124	0.030	-	26 (0.01)
0.9	1.421	0.081	-	72 (0.04)

mixture and the polymer solution must be at dialysis equilibrium. The chemical potential of either solvent component (solvent 1 or solvent 2) in solution and co-solvent must be equal, i.e.  $\mu_{1,\text{solution}} = \mu_{1,\text{solvent}}$  and  $\mu_{2,\text{solution}} = \mu_{2,\text{solvent}}$ . When the  $dn/dC$  factor in Eq. (1) is substituted by  $(dn/dC)_\mu$ , the formula of Eq. (1) remains applicable, and the true molecular weight,  $\bar{M}_w$ , could still be achieved. On the other hand, if we select the refractive index increment at a constant solvent composition,  $(dn/dC)_{\phi_1}$ , the Zimm equation must be altered to Eq. (5) because the polymer chains preferentially adsorb one of the two solvents. Thereafter, only the apparent molecular weight  $\bar{M}_a$  can be achieved.

$$\frac{KC}{\Delta R_\theta} = \frac{1}{\bar{M}_a} \left[ 1 + \frac{16}{3} \pi^2 \frac{R_G^2}{\lambda_0^2} \sin^2 \frac{\theta}{2} + \dots \right] + 2 \left( \frac{\bar{M}_w}{\bar{M}_a} \right) A_2 C + \dots \quad (5)$$

Generally, the apparent molecular weight never shifts when the refractive indices,  $n$ , of two solvents are identical ( $\Delta n < 0.025$ ), whether or not the preferential adsorption phenomenon

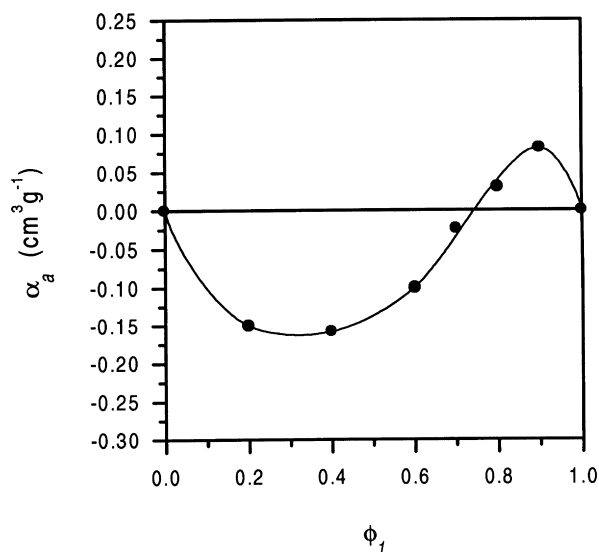


Fig. 4. The preferential adsorption coefficients as a function of  $\phi_1$ .

exists. In this system, the difference in the refractive index between the two solvents  $\Delta n = n_{\text{NMP}} - n_{\text{water}} = 0.152 \gg 0.025$  indicates that this system is a non-isorefractive system. Moreover, the apparent molecular weight in this system is far from the true molecular weight  $0.63 < \bar{M}_a/\bar{M}_w < 1.42$  (listed in Table 2), where  $\bar{M}_w$  of PVA approximates to  $85470.8 \text{ g mol}^{-1}$ , which was obtained from the Zimm plot in the PVA/water solution at  $30^\circ\text{C}$  (close to  $\theta$ -condition). This result indicates that the preferential adsorption phenomenon in this system is, in fact, very remarkable. Therefore, the preferential adsorption coefficient,  $\alpha_a$ , obtained through the Strazielle–Benoit equation [22], could be used to understand the preferential adsorption property in this system:

$$\alpha_a = \left[ \left( \frac{\bar{M}_a}{\bar{M}_w} \right)^{1/2} - 1 \right] \frac{(dn/dC)_{\phi_1}}{dn_0/d\phi_1} \quad (6)$$

where, the refractive index increments of the solution,  $(dn/dC)_{\phi_1}$ , at various  $\phi_1$  are obtained easily using a refractometer, as shown in Table 1. The variations of the solvent refractive index with various co-solvent compositions,  $dn_0/d\phi_1$ , could be obtained using the Gladstone–Dale equation [23] where  $\rho_1$  ( $\rho_2$ ),  $n_1$  ( $n_2$ ) and  $w_1$  ( $w_2$ ) denote the densities, the refractive indices and the weight fractions of component 1 and 2, respectively. The  $dn_0/d\phi_1$  factor in this system is 0.154.

$$\frac{1}{\rho} (n_0 - 1) = \left( \frac{w_1}{\rho_1} \right) (n_1 - 1) + \left( \frac{w_2}{\rho_2} \right) (n_2 - 1) \quad (7)$$

According to Eq. (6), the  $\alpha_a$  values could be calculated without any difficulty. We must first mention that the positive  $\alpha_a$  values in this system virtually indicate the preferential adsorption of the better solvent, NMP and negative  $\alpha_a$  values indicate the preferential adsorption of solvent 2, water.

Fig. 4 shows a continuous curve of  $\alpha_a$  against  $\phi_1$ , representing the negative  $\alpha_a$  values at  $\phi_1 < 0.73$ , the positive  $\alpha_a$  values at  $\phi_1 > 0.73$  and  $\alpha_a = 0$  at  $\phi_1 \cong 0.73$ . These results illustrate that the water molecules are adsorbed preferentially by PVA chains at  $\phi_1 < 0.73$  and that the NMP molecules are adsorbed preferentially by PVA chains at  $\phi_1 > 0.73$ . Particularly, we could observe an inversion of the preferential adsorption coefficient at  $\phi_1 = 0.73$ , while the mole ratio of NMP to water at this co-solvent composition is exactly equal to 1 : 2. This composition,  $\phi_1 = 0.73$ , could be painstakingly selected to carry out the static light scattering measurement for obtaining the true molecular weight of polymer. Actually, the  $\alpha_a$  values mainly depend on the excess numbers of bonding solvents, NMP (or water),  $n_1^E$  and  $n_2^E$  (Eq. (8)), and on the arbitrary volume surrounding the PVA chains compared with the solvent composition in the bulk solvent [24]. Here,  $\alpha_{a1}$  (and  $\alpha_{a2}$ ) and  $\bar{V}_1$  (and  $\bar{V}_2$ ) denote, respectively, the preferential adsorption coefficients and the partial molar volumes

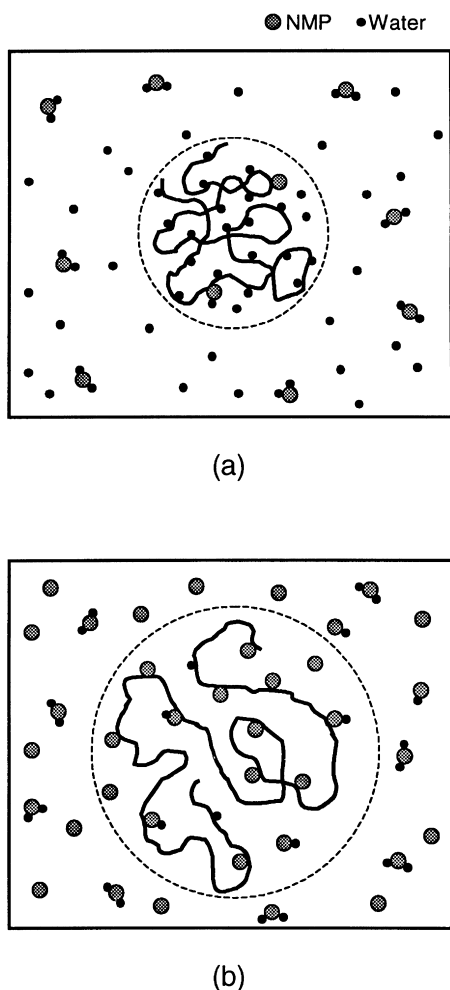


Fig. 5. Microphase equilibrium models in PVA/NMP/water solutions at: (a)  $\phi_1 < 0.73$ ; and (b) at  $\phi_1 > 0.73$ , the dashed lines represent a fictitious phase-boundary that delimits the dilute PVA solution into two phases.

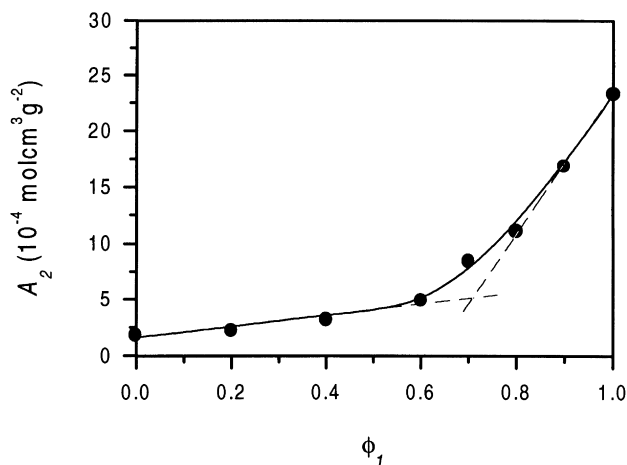


Fig. 6. The second virial coefficients,  $A_2$ , as a function of  $\phi_1$ .

of the two solvents.

$$n_1^E = \frac{\alpha_{a1} \bar{M}_w}{\bar{V}_1} \left( n_2^E = \frac{\alpha_{a2} \bar{M}_w}{\bar{V}_2} \right) \quad (8)$$

Table 2 lists the numbers of excess NMP or water molecules,  $n_{\text{NMP}}^E$  and  $n_{\text{water}}^E$ , and the numbers of excess NMP or water molecules per repeat unit of PVA,  $n_{\text{NMP,unit}}^E$  and  $n_{\text{water,unit}}^E$ , at various co-solvent compositions. At lower  $\phi_1$ , one repeat unit of PVA preferentially adsorbs an average of 0.06–0.39 excess water molecules, but only an average of 0.01–0.04 excess NMP molecules is preferentially adsorbed by one repeat unit of PVA at higher  $\phi_1$ . It might be due to the fact that in the limited space of the solvation shell of PVA chain, it is harder to pack a solvent like NMP that has a larger size, but water molecules with smaller molar volume are possibly packed more in the limited space.

In fact, the preferential adsorption phenomenon in this system is very special and very dissimilar to other systems. In several polymer/solvent/non-solvent systems, one of the solvents can break down the association (clustering) of another solvent and the polymer chains preferentially adsorb the broken solvents in order to make better affinity properties. The maximum  $A_2$  value was found at the co-solvent composition with an inversion of the preferential adsorption coefficient [25–28]. Besides, in polystyrene/benzene (good solvent)/alcohol or paraffin (precipitant) systems, a good solvent is always preferentially adsorbed as the precipitant is added [7,29]. In the polyvinyl pyrrolidone (PVP)/water/THF and PVP/ethanol/*n*-hexane systems, water and ethanol (good solvents) are always preferentially adsorbed, when THF and *n*-hexane are precipitants for PVP [30]. However, in this PVA/NMP/water system, the formation of the NMP(water)<sub>2</sub> complex significantly affects the preferential adsorption phenomenon of PVA chains. At  $\phi_1 < 0.73$ , it could be considered that almost whole NMP molecules should be associated with water molecules to form NMP(water)<sub>2</sub> complexes, then the free water molecules in co-solvent are adsorbed preferentially onto the PVA chains. On the other hand, almost whole water molecules are supposed to form NMP(water)<sub>2</sub> complexes at  $\phi_1 > 0.73$ , then the free NMP molecules are preferentially adsorbed. At  $\phi_1 = 0.73$ , almost whole solvent molecules form NMP(water)<sub>2</sub> complexes, inducing PVA chains without preferential adsorption phenomenon at this co-solvent composition. Fig. 5(a) and (b) describes the outcome of the preferential adsorption phenomena in this system. The dashed lines in Fig. 5 represent a fictitious phase-boundary that delimits the diluted polymer solution into two-phase systems, one phase is the swollen polymer coil and the other phase is the bulk solvent. As PVA chains preferentially adsorb water molecules (Fig. 5(a)), the phase in the inner boundary domain has a higher water fraction as compared with that in the bulk solvent. On the other hand, when the NMP molecules are preferentially adsorbed onto

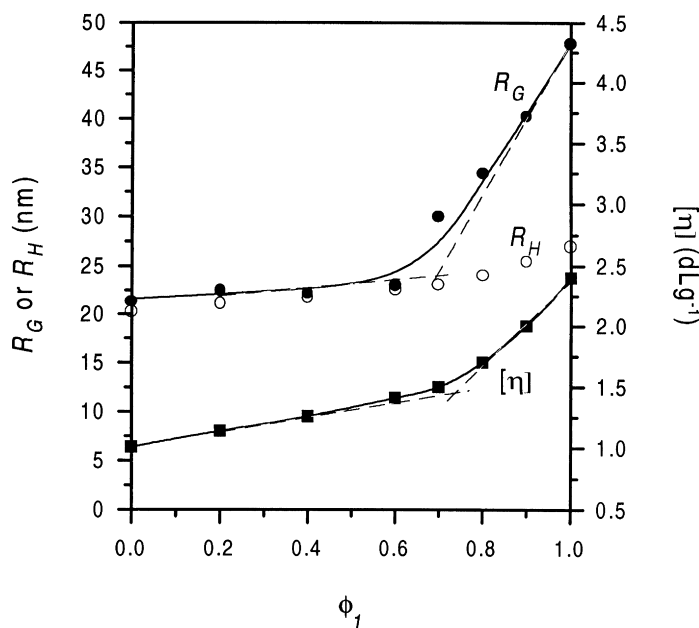


Fig. 7. The  $z$ -average radius of gyration  $R_G$ , the intrinsic viscosity  $[\eta]$  and the equivalent hydrodynamic radius,  $R_H$ , in the PVA/NMP/water solutions.

the PVA chains (Fig. 5(b)), the solvent composition contains less NMP fraction in the bulk solvent phase.

The interaction between PVA and co-solvent could be better discussed as soon as the preferential adsorption phenomena have definite outcomes. Fig. 6 shows the  $A_2$  values as a function of  $\phi_1$ . The  $A_2$  values only slightly increase at  $\phi_1 < 0.73$  but rapidly increase at  $\phi_1 > 0.73$ . The  $A_2$  values at  $\phi_1 > 0.73$  (ca.  $10\text{--}25 \times 10^{-4} \text{ ml mol g}^{-2}$ ) are several times larger than those (ca.  $1\text{--}5 \times 10^{-4} \text{ ml mol g}^{-2}$ ) at  $\phi_1 < 0.73$ , implying that the affinity between PVA and co-solvent is hard to increase at lower NMP content. At  $\phi_1 < 0.73$  the PVA chains preferentially adsorb water molecules ( $n_{\text{water,unit}}^E =$

0.06–0.39), only a “weak site” exists for PVA. It is of no value to enhance the affinity between PVA and co-solvent. On the other hand, although the PVA chain preferentially adsorb few “strong site” NMP molecules ( $n_{\text{NMP,unit}}^E = 0.01\text{--}0.04$ ), it is sufficient to increase the affinity.

Moreover, the  $z$ -average radius of gyration  $R_G$  and the intrinsic viscosity  $[\eta]$ , also concern with the preferential adsorption phenomena, as presented in Fig. 7. Focus on the viewpoint of  $R_G$ , a contracted coil-to-coil transition was found at the critical solvent composition  $\phi_1 \approx 0.73$ . At  $\phi_1 < 0.73$ , the PVA chains exhibit a conformation of contracted coil, since the PVA chains preferentially adsorb the “weak site” water molecule that has smaller molecular size (the molar volume  $V_2 \approx 18.1 \text{ cm}^3 \text{ mol}$ ), to induce lower excluded-volume effect. On the other hand, immediately, the PVA chains preferentially adsorb the “strong site” NMP molecule that has large molecular size (the molar volume  $V_1 \approx 96.3 \text{ cm}^3 \text{ mol}$ ), at  $\phi_1 > 0.73$ . The excluded-volume effect is increased to exhibit more extended PVA coils. The corresponding conformations and the dimensions of PVA chains can be seen in Fig. 5(a) and (b). In addition, the equivalent hydrodynamic radius of PVA chain,  $R_H$ , could be generally calculated from the  $[\eta]$  values using the Debye–Bueche equation [31], considering the mutual interaction among the spheres, where  $M$  is the molecular weight of polymer:

$$R_H = \left( \frac{2}{5} \frac{3}{4\pi} M[\eta] \right)^{1/3} \quad (9)$$

The  $R_H$  value, as shown in Fig. 7, only slightly increases with  $\phi_1$ , and  $R_G > R_H$  is always observed for the whole

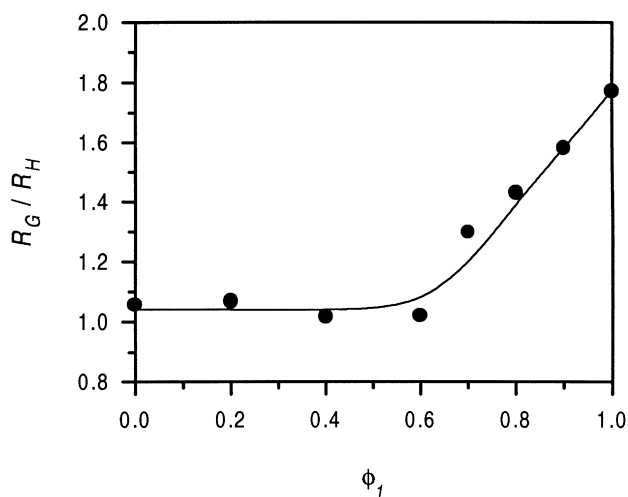


Fig. 8. The  $R_G/R_H$  values as a function of  $\phi_1$ .

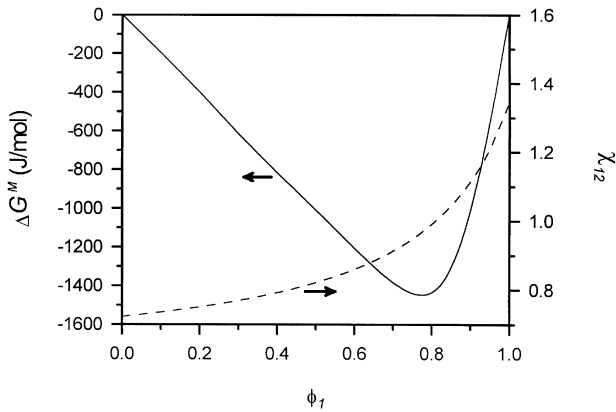


Fig. 9. The  $\Delta G^M$  and  $\chi_{12}$  values as a function of  $\phi_1$ .

range of  $\phi_1$ . Actually, the  $R_G$  and  $R_H$  values correspond, respectively, to the radius of the actual space of PVA chains and the radius of an equivalent hard sphere in solution. The PVA chains are contracted at  $\phi_1 < 0.73$  and the solvent molecules become less draining, inducing an  $R_H$  that is very close to  $R_G$ . At  $\phi_1 > 0.73$ , the much extended PVA coils induce the free draining of solvent molecules, resulting in larger values of  $R_G$ . Furthermore, the conformations of PVA chains depend much on the molecular interaction that could be better viewed through the  $R_G/R_H$  values, as shown in Fig. 8. At  $\phi_1 = 1$ , the  $R_G/R_H \sim 1.8$  corresponds to the conformation of the polymer chains in the good solvent. This result is in good agreement with the  $R_G/R_H (= 1.86)$  value derived by Akcasu [32] from the Kirkwood–Riseman theory and the theoretical prediction of molecular motion in the good solvent. At  $0 < \phi_1 < 0.6$ , the  $R_G/R_H \sim 1.05$  means that the conformation of the polymer chain is close to that of the  $\theta$ -condition and the polymer conformation within this composition should have no remarkable change [33].

The Gibbs free energy of mixing in the ternary system,  $\Delta G_T^M$ , could be generally expressed as Eq. (10), where  $n_i$  is the number of moles of the  $i$ th component,  $g_{ij}$  the binary interaction potentials,  $g_T$  the ternary interaction potential and  $u_1 = \phi_1/(\phi_1 + \phi_2)$ .

$$\begin{aligned} \Delta G_T^M/RT = & n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + g_{12}(u_1)n_1\phi_2 \\ & + g_{13}(\phi_3)n_1\phi_3 + g_{23}(\phi_3)n_2\phi_3 + g_T n_1\phi_2\phi_3 \end{aligned} \quad (10)$$

Then, the preferential adsorption coefficient  $\alpha_a$  was derived from the second derivation of  $\Delta G_T^M$ ,  $(\partial^2 \mu_i / \partial m_j)_{P,T,m_{k \neq j}}$ , as Eq. (11), where  $\bar{v}_3$  is the partial specific volume of polymer,  $V_i$  the molar volume of the  $i$ th component,  $\mu_i$  the chemical potential of the  $i$ th component and  $m_i$  the molality of the  $i$ th component [34]. The second derivations of  $\Delta G_T^M$ ,  $(\partial^2 \mu_i / \partial m_j)_{P,T,m_{k \neq j}} = a_{ij}$  could be derived as given in

Eq. (12), where  $V_m$  is total volume and  $l$  is the ratio of molar volumes  $V_1/V_2$ .

$$\alpha_a = \frac{V_2 \bar{v}_3 \phi_1}{V_3} \frac{(\partial \mu_2 / \partial m_3)_{m_2, m_3 \rightarrow 0}}{(\partial \mu_2 / \partial m_2)_{m_3 \rightarrow 0}} \quad (11)$$

$$a_{22} = \frac{n_1}{n_2} \frac{V_2 RT}{V_m} b_{22} \quad \left( \text{or } a_{23} = \frac{n_1 V_2 V_3 RT}{V_m^2} b_{23} \right) \quad (12)$$

Here

$$\begin{aligned} b_{22} = & \phi_1 l + \phi_2 \\ & - \phi_1 \phi_2 \left\{ 2 \left[ g_{12} + (\phi_1 - \phi_2) \frac{\partial g_{12}}{\partial u_1} \right] - \phi_1 \phi_2 \frac{\partial^2 g_{12}}{\partial u_1^2} \right\} \end{aligned} \quad (13)$$

$$\begin{aligned} b_{23} = & g_{23} l - g_{13} + 1 - l - (\phi_1 - \phi_2)(g_{12} - g_T) \\ & + \phi_1 \phi_2 \left( \frac{\partial g_{12}}{\partial u_1} - \frac{\partial g_T}{\partial u_1} \right) \end{aligned} \quad (14)$$

The binary interaction parameters  $\chi_{i3}$  and the ternary interaction parameter  $\chi_T$ , respectively, relate to the  $g_{i3}$  and  $g_T$  values, as given in Eqs. (15) and (16).

$$\chi_{i3} = g_{i3} - (\partial g_{i3} / \partial \phi_3) \quad (15)$$

$$\chi_T = g_T - (\partial g_T / \partial \phi_3) \quad (16)$$

Read [11] has derived a formalism for determining the theoretical  $\alpha_a$  value for a special case in Eq. (10), where all  $g_{ij}$  values are independent of composition (i.e.  $g_{ij} = \chi_{ij}$ ) and the  $g_T$  value is equal to zero, as shown in Eq. (17):

$$\alpha_a = -\bar{v}_3 \phi_1 \phi_2 \frac{l - 1 + \chi_{13} - l\chi_{23} + \chi_{12}(\phi_1 - \phi_2)}{l\phi_1 + \phi_2 - 2\chi_{12}\phi_1\phi_2} \quad (17)$$

On the other hand, Read [35,36] also developed a more complete formalism as presented in Eq. (18) to derive  $\alpha_a$  by considering the  $\chi_T$  parameter that could be calculated through Eqs. (19) and (20).

$$\alpha_a = -\bar{v}_3 \phi_1 \phi_2 \frac{l - 1 + \chi_{13} - l\chi_{23} + (\chi_{12} - \chi_T)(\phi_1 - \phi_2)}{l\phi_1 + \phi_2 - 2\chi_{12}\phi_1\phi_2} \quad (18)$$

$$\begin{aligned} \chi_T(\phi_1) = & -\frac{1}{\phi_2} \int_{\phi_1}^1 L(\phi_1) b_{22} d\phi_1 + \frac{1}{\phi_1} \int_0^{\phi_1} L(\phi_1) b_{22} d\phi_1 \\ & + \frac{0.5 - \chi_{13}}{\phi_2} + \frac{l(0.5 - \chi_{23})}{\phi_1} - \frac{V_1 A_2}{\bar{v}_3 \phi_1 \phi_2} - \frac{L^2 b_{22}}{2} \end{aligned} \quad (19)$$

$$L(\phi_1) = \frac{\alpha_a}{\phi_1 \phi_2 \bar{v}_3} \quad (20)$$

The  $\chi_{13}$  and  $\chi_{23}$  values in this system, which are 0.186 and 0.495, respectively, could be actually calculated from the



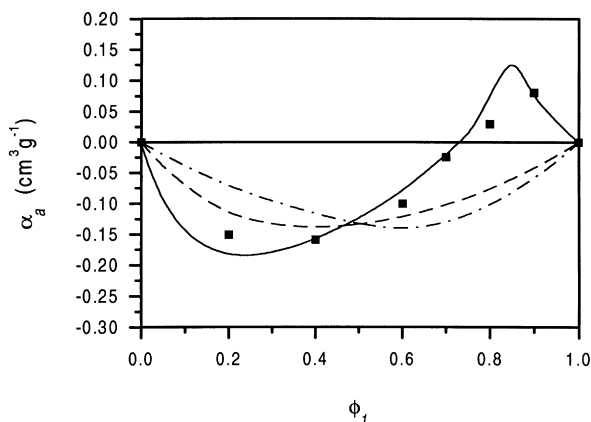


Fig. 10. The experimental  $\alpha_a$  values (■) and the theoretical  $\alpha_a$  values calculated, respectively, from Eq. (17) (---), Eq. (18) (-·-·-) and Eq. (24) (—).

$A_{2i}$  values.

$$\chi_{i3} = \frac{1}{2} - \frac{A_{2i}V_i}{\bar{v}_3^2} \quad (21)$$

Regarding the thermodynamic properties of the NMP/water co-solvent mixtures, Pavlov et al. [37,38] obtained the activity coefficients of NMP and water,  $\gamma_1$  and  $\gamma_2$ , for NMP/water mixtures through the vapor–liquid phase equilibrium method at various pressures and temperatures, indicating  $\gamma_1 = P_1/P_1^0$  and  $\gamma_2 = P_2/P_2^0$ . Here, the  $P_i^0$  is the equilibrium vapor pressure of pure solvent. Using a well-known equation,  $(d \ln \gamma_i/d(1/T)) = \text{constant}$ , the  $\gamma_1$  and  $\gamma_2$  values at 30°C could be achieved by extrapolating from the results. Then, the Gibbs free energy of mixing of the co-solvents,  $\Delta G^M$ , directly relates to the activity coefficients of two solvents,  $\gamma_1$  and  $\gamma_2$ , as represented in Eq. (22). The NMP/water interaction parameter,  $\chi_{12}$ , could be subsequently obtained using Eq. (23).

$$\Delta G^M = RT(x_1 \ln x_1 \gamma_1 + x_2 \ln x_2 \gamma_2) \quad (22)$$

$$\chi_{12} = \frac{\Delta G^M/RT - x_1 \ln \phi_1 - x_2 \ln \phi_2}{x_1 \phi_2} \quad (23)$$

Fig. 9 shows the calculated values of  $\Delta G^M$  and  $\chi_{12}$  for the NMP/water mixtures as a function of  $\phi_1$ . The  $\Delta G^M$  values are negative, as expected, for a good miscibility between NMP and water at all co-solvent compositions. Minimum  $\Delta G^M$  value is found at around  $\phi_1 = 0.80$ . Although, this composition is slightly higher than that of the co-solvent complex formation ( $\phi_1 = 0.73$ ), it could be considered that the NMP/water mixture becomes further miscible because of the formation of the NMP(water)<sub>2</sub> complex. On the other hand, the  $\chi_{12}$  value varies from 0.75 at  $\phi_1 = 0.1$  to 1.13 at  $\phi_1 = 0.9$ . Zeman and Tkacik [38] have reported a similar result for NMP/water co-solvent system and taken a constant value ( $\chi_{12} = 1.0$ ) for NMP/water pair for calculating some physical parameters in the formation of

polyethersulfone (PES) membrane from PES/NMP/water ternary solution.

The theoretical  $\alpha_a$  values from the two Read formalisms could be obtained using the above calculations, as shown in Fig. 10. Unfortunately, the negative  $\alpha_a$  values in the entire  $\phi_1$  range are in poor agreement with the experimental values. This fact may be the reason that the Read formalisms remain usable when the system contains only weak interactions between each component. Owing to the strong intermolecular H-bonding between NMP and water molecules, the formation of NMP(water)<sub>2</sub> complex could affect the rationality of the two Read formalisms. It could be established that NMP(water)<sub>2</sub> complexes are comparatively stable in the solutions, resulting in a large value of negative excess enthalpies  $\Delta \bar{H}^E$  during the mixing process at the co-solvent composition close to  $\phi_1 = 0.73$  (Fig. 3). Therefore, the formation of the NMP(water)<sub>2</sub> complex should change the composition of the co-solvent mixture. At  $\phi_1 < 0.73$  the co-solvent mixtures consist mainly of free water molecules and the NMP(water)<sub>2</sub> complexes, while there are only free NMP molecules and the NMP(water)<sub>2</sub> complexes for the co-solvent mixtures at  $\phi_1 > 0.73$ . Accordingly, the formalism for evaluating the  $\alpha_a$  coefficient should be concerned with not only the interaction parameters,  $\chi_{13}$  and  $\chi_{23}$ , but also the interaction parameter  $\chi_{c3}$ , i.e. the interaction between polymer chains and the co-solvent complex. Under this circumstance, the complex-free NMP ( $\chi_{c1}$ ) and the complex-free water ( $\chi_{c2}$ ) interaction parameters must substitute, respectively, for the  $\chi_{12}$  parameter (the interaction between free NMP and water molecules) at  $\phi_1 > 0.73$  and  $\phi_1 < 0.73$ .

From the considerations stated above, we try to expand the Read formalism by considering the formation of the NMP(water)<sub>2</sub> complex, involving the  $\chi_{c1}$ ,  $\chi_{c2}$ ,  $\chi_{c3}$  parameters and the volume fraction of the complex,  $\phi_c$ :

$$\alpha_a = -\bar{v}_3 \phi_c \left[ \phi_1 \frac{l_1 - 1 + \chi_{13} - l_1 \chi_{c3} + \chi_{c1}(\phi_1 - \phi_c)}{l_1 \phi_1 + \phi_c - 2\chi_{c1} \phi_1 \phi_c} + \phi_2 \frac{l_c - 1 + \chi_{c3} - l_c \chi_{23} + \chi_{c2}(\phi_c - \phi_2)}{l_c \phi_c + \phi_2 - 2\chi_{c2} \phi_c \phi_2} \right] \quad (24)$$

The  $l_c$  and  $l_1$  factors denote the ratio of molar volumes  $V_c/V_2$  and  $V_1/V_c$ , respectively, where  $V_c$  is the partial molar volume of the complex and about  $131.5 \text{ cm}^3 \text{ mol}^{-1}$  for deducting the excess volume at  $\phi_1 = 0.73$ . The  $\chi_{c3}$  factor, the interaction parameter between PVA chain and the NMP(water)<sub>2</sub> complex, could be directly calculated from the  $A_2$  value at  $\phi_1 = 0.73$  ( $\chi_{c3} = 0.387$  obtained from Eq. (18)). The  $\phi_c$  values could be roughly estimated from the viscometric results of the co-solvent mixtures as shown in Fig. 3. As stated earlier, one NMP molecule could bind with two water molecules to form the maximum amount of NMP(water)<sub>2</sub> complexes ( $\phi_c = 1.0$ ) at  $\phi_1 = 0.73$ , where the maximum viscosity of the NMP/water mixture is completely related to the co-solvent complexes.

Table 3

The volume fraction of the complex,  $\phi_c$ , the complex-free NMP interaction parameter,  $\chi_{c1}$  and the complex-free water interaction parameter,  $\chi_{c2}$ , in the PVA/NMP/water solutions

$\phi_1$	$\phi_c$	$\chi_{c1}$	$\chi_{c2}$
0.2	0.28	–	0.88
0.4	0.55	–	1.05
0.6	0.83	–	1.42
0.7	0.96	–	1.17
0.8	0.73	0.12	–
0.9	0.37	0.33	–

At  $\phi_1 = 1.0$  or  $\phi_1 = 0$ , the  $\phi_c$  value is zero. Conveniently, the viscosities of the co-solvent mixtures at  $\phi_1 < 0.73$  could be considered to be contributed from the viscosities of the free water molecules and the NMP(water)<sub>2</sub> complexes. The calculated result of the viscosity of the co-solvent mixture from the above procedure is in good agreement with the experimental result in Fig. 3. The  $\phi_c$  values could then be easily obtained. Besides, the exact evaluation of the  $\chi_{c1}$  and  $\chi_{c2}$  interaction parameters is another operational problem. If we assume that the  $\Delta G^M$  values from Eq. (22) is still reliable because they are indeed derived from the experimental results of Pavlov et al. [37,38] as stated earlier, then the  $\chi_{c1}$  and  $\chi_{c2}$  values, as listed in Table 3, might be consequently obtained by considering the complex formation through the  $\Delta G^M$  values from Eq. (25).

$$\chi_{ci} = \frac{\Delta G^M/RT - x_i \ln \phi_i - x_c \ln \phi_c}{x_i \phi_c} \quad (25)$$

More precise operations may be required to evaluate these interaction parameters for the quantitative calculations. For the qualitative discussion in this work, Eq. (24) may be used to calculate the  $\alpha_a$  values in PVA/NMP/water ternary solutions, considering the effect of the co-solvent complex. Fortunately, these calculated  $\alpha_a$  values, as also shown in Fig. 10, provide a good fit for the experimental ones. Although, Eq. (24) is derived from the Read formalisms, it seems to be more applicable for describing the preferential adsorption phenomenon in the PVA/NMP/water ternary solution.

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