SHORT COMMUNICATIONS

**Interaction between Poly(vinyl alcohol) and Poly(ethylene glycol)
in Water Studied by Viscosity and Density**

Isamu INAMURA and Yuji JINBO

*Department of Chemistry, Faculty of Science,
Shimane University, Matsue 690, Japan*

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One of the authors has investigated a liquid–liquid phase separation in a poly(vinyl alcohol) (PVA)–poly(ethylene glycol) (PEG)–water system.^{1,2} We are interested in an interaction between PVA and PEG in water in connection with the phase separation. To evaluate it, viscosity and density in the ternary system were measured over a range of polymer concentration up to high concentration, where a liquid–liquid phase separation sometimes occurred. We clarified the effects of the occurring of the phase separation on the concentration dependences of viscosity and density. To evaluate the interaction between PVA and PEG, we obtained the interaction parameter, Δb_{23} , by the method of Krigbaum and Wall.³ The specific viscosity and partial specific volume of polymer mixtures were also studied on the basis of additivity.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA), PVA-105 and PVA-117 with 98.5 mol% saponification, were kindly donated by Kuraray Co., Ltd. Poly(ethylene glycol) (PEG) manufactured by Kishida Chemical Co., Ltd., was used. PVA and PEG were purified and then PVA was fractionated by the method described previous-

ly.¹ The weight and number average molecular weights (M_w and M_n) of PVA and PEG samples were estimated by gel permeation chromatography (GPC). The ratio M_w/M_n is from 1.10 to 1.57. Thus, the molecular weight distributions of polymers used are moderately narrow. The characteristics of the polymer samples are given in Table I. PVA-1 sample was used for measurements to obtain the data in Figures 1, 2, 6, and 7, while PVA-2 sample used for measurements to get the data in Figures 3–5.

Measurements of Viscosity and Density

Ubbelohde and Ostwald viscometers were used to obtain viscosity, and a Lipkin–Davison pycnometer used to get density. The measurements of viscosity and density were performed at $30 \pm 0.01^\circ\text{C}$ over a range of polymer concentration up to $3\text{--}4\text{ g dl}^{-1}$, where a liquid–liquid phase separation sometimes occurred in the solution. The marks ■ and ▲ in Figure 1 and the mark ● in Figures 2 and 6 represent the phase separation. The aqueous

Table I. Characteristics of the polymer samples

Sample code	$M_w \times 10^{-4}$	M_w/M_n
PVA-1	23.7	1.57
PVA-2	3.94	1.37
PEG	2.10	1.10

polymer solutions were filtered through a membrane filter (pore size $0.45\ \mu\text{m}$) to separate dust and undissolved gels. The solutions of polymer mixtures were prepared by mixing a PVA solution and a PEG solution. The weight ratio PVA/PEG in the solutions were 1/3, 1 and 3.

Calculation of Specific Viscosity Based on Additivity

The calculated curves of specific viscosity η_{sp} for polymer mixtures (in Figure 1) were based on additivity of specific viscosity with respect to the polymer composition. That is, the specific viscosity, $\eta_{sp,m}$ for a polymer mixture (weight fractions of PVA and PEG were w_2 and w_3 , respectively; ($w_2 + w_3 = 1$)) at polymer concentration C_m was calculated from the observed values of specific viscosities, $\eta_{sp,PVA}$ and $\eta_{sp,PEG}$ of single polymer solutions as follows;

$$\eta_{sp,m} \text{ (at } C_m) = \eta_{sp,PVA} \text{ (at } w_2 C_m) + \eta_{sp,PEG} \text{ (at } w_3 C_m)$$

The calculated curves in Figure 1 were drawn by plotting $\eta_{sp,m}$ against C_m .

RESULTS AND DISCUSSION

Viscosity

Figures 1 and 2 shows the specific viscosity η_{sp} vs. polymer concentration C and the reduced viscosity η_{sp}/C vs. C , respectively, for PVA-PEG-water system. As is seen from these figures, the shapes of observed curves of η_{sp} and η_{sp}/C for polymer mixtures changed continuously in order of the weight ratio PVA/PEG.

The observed curves of η_{sp} vs. C plot for all polymer mixtures in Figure 1 positively deviated from the calculated ones at concentrations above $1.2\ \text{gdl}^{-1}$. Williamson and Wright⁴ described that the positive deviation of η_{sp} from additivity may be regarded as good compatibility of the polymer pair, while the negative deviation shows that compatibility is poor.

Figure 1. Specific viscosity vs. polymer concentration for PVA-PEG-water system. The marks ■ and ▲ indicate that a liquid-liquid phase separation occurred in the solution.

Figure 2. Reduced viscosity vs. polymer concentration for PVA-PEG-water system. ●, liquid-liquid phase separation.

Quadrat,⁵ however, claimed that the additivity of η_{sp} cannot become the property to judge a compatibility of polymers. Therefore, the

origin of the positive deviation of η_{sp} from additivity, observed in this work, for PVA-PEG-water system should be elucidated in future. However, it can be inferred that an increase in the number of entanglements of polymer chains by mixing two kinds of polymers may be responsible for the positive deviation.

As seen from Figures 1 and 2, on occurring of a liquid-liquid phase separation at high concentrations, both η_{sp} and η_{sp}/C decreased, and η_{sp} negatively deviated from additivity. We have ascertained from the phase diagram of PVA-PEG-water system¹ that a polymer mixture solution separates into a concentrated PVA-rich and a dilute PEG-rich phase. Therefore, the existence of dilute PEG-rich phase is considered to cause the decrease in η_{sp} and η_{sp}/C .

Figure 3 shows η_{sp}/C vs. C for dilute PVA-PEG-water system. All Huggins plots gave a straight line. The intrinsic viscosity $[\eta]$ and Huggins constant k' were evaluated from the intercept and slope of the plots, respectively.

Figure 4 shows the polymer composition dependences of $[\eta]$ and k' . A plot of $[\eta]$ vs. PVA content was found to be linear. Such linear relationship was also observed for $[\eta]$ obtained from Figure 2 (data not shown). This suggests the additivity of $[\eta]$ with respect to polymer composition. Though additivity of $[\eta]$ is generally observed in polymer-polymer-solvent systems,⁶ it is noted that it is also observed in PVA-PEG-water system showing a liquid-liquid phase separation at high concentration. The Huggins constant k' increased from 0.182 to 0.643 with increasing PVA content. It is well known that k' reflects the solute-solute interactions.⁷

Using the Huggins plots in Figure 3, the polymer 2(PVA)-polymer 3(PEG) interaction parameter, Δb_{23} , was calculated by the method of Krigbaum and Wall.³ Figure 5 shows Δb_{23} against PVA content. The Δb_{23} values are negative, though the absolute values are small.

Figure 3. Reduced viscosity vs. polymer concentration for dilute PVA-PEG-water system.

Figure 4. Polymer composition dependence of intrinsic viscosity and Huggins constant obtained from Figure 3.

Figure 5. Polymer composition dependence of interaction parameter between PVA and PEG.

Further it is noted that Δb_{23} decreased with increasing PEG content and reached to the minimum value at 25 wt% of PVA. According to Krigbaum and Wall,³ positive Δb_{23} values indicate attractive interactions and compatibility, whereas negative values do repulsive interactions and incompatibility. Therefore, it can be inferred that a weak repulsive interaction exists between PVA and PEG in PVA-PEG-water system. Recently, Suto *et al.*⁸ investigated the viscometric behavior of aqueous solutions of polymer mixtures involving a liquid crystalline polymer, and reported that there exist repulsive interactions between hydroxypropyl cellulose (liquid crystalline polymer) and hydroxyethyl cellulose.

Density

Figure 6 shows the density ρ vs. polymer concentration for PVA-PEG-water system. The density increased linearly with increasing concentration in all cases. It is very interesting that the linear relationship is retained even at high concentrations where a liquid-liquid phase separation occurred. This result means that the overall density of a polymer mixture solution is not affected by the separation of solution into two phases with different densities. We will examine in the near future whether this behavior of density can be observed or not in other polymer-polymer-solvent systems.

The partial specific volumes $\bar{v}$ were calculated from the slopes of the straight lines of density in Figure 6, and these values are also noted in this figure. Figure 7 shows $\bar{v}$ vs. PVA content. The $\bar{v}$ values upward deviated from the straight lines which corresponded to additivity. It is noted that the $\bar{v}$ value of the polymer mixture with PVA content equal to 50 wt% was extraordinarily high, being higher than that of PEG. Such a positive deviation of $\bar{v}$ seems to imply that there exists a repulsive interaction between PVA and PEG. This is in good agreement with the suggestion derived from the interaction parameter Δb_{23} . The difference in

Figure 6. Density vs. polymer concentration for PVA-PEG-water system. ●, liquid-liquid phase separation.

Figure 7. Polymer composition dependence of partial specific volume.

PVA content giving the maximum $\bar{v}$ value (50 wt% PVA) and the minimum Δb_{23} value (25 wt% PVA) may be partly due to the difference in M_w of PVA samples used.

CONCLUSION

The occurring of a liquid-liquid phase separation decreased the slopes of η_{sp} vs. C and η_{sp}/C vs. C plot. However, it did not change the slope of density ρ vs. C plot. Both η_{sp} and $\bar{v}$ values positively deviated from additivity, whereas additivity of $[\eta]$ was observed. The interaction parameter Δb_{23} was found to be negative, which suggests that a weak repulsive interaction exists between PVA and PEG.

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