SHORT COMMUNICATIONS

Effects of Molecular Weight on the Phase Equilibrium of a Poly(vinyl alcohol)–Poly(ethylene glycol)– Water System

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As far as we know, only Toyoshima *et al.*[1] have reported binodal curves of the system poly(vinyl alcohol) (PVA) + poly(ethylene glycol) (PEG) + water, using a PEG sample of 4000 molecular weight and PVA samples with a low degree of saponification of 88 mol% and various degrees of polymerization of 500 and 1700. However, they found no phase separation for a PVA–PEG–water system with a PVA sample highly saponified.

We recently determined by an optical microscope the composition region where phase separation occurs and also that where gelation occurs for the PVA–PEG–water system with PVA of a high degree of saponification of 98.5 or 99.9 mol%.[2] A comparison of the results obtained for systems with PEG of different molecular weights showed that liquid-liquid phase separation occurred when the molecular weight of PEG was higher than about 6000.

In the present study, the effects of the molecular weights of PVA and PEG on the phase behavior of the system PVA + PEG + water were investigated using polymer samples of narrow molecular weight distribution. The results obtained are discussed in terms of the Flory–Huggins theory[3] and its subsequent developments by Scott,[4] Tompa,[5] and Hsu and Prausnitz.[6]

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA), PVA-117 and PVA-105 with 98.5 mol% saponification, were kindly donated by Kuraray Co., Ltd. Poly(ethylene glycol) (PEG): M_w, 7200 and 20000 manufactured by Kishida Chemical Co., Ltd., and M_w, 160000 and 668000 manufactured by Toyo Soda Manufacturing Co., Ltd. were used. PVA and PEG were purified by reprecipitation in water–methanol and benzene–petroleum ether, respectively. Samples PVA-105 and PVA-117 were separated into 4 and 5 fractions by the addition of 1-propanol into 3 and 1.5% aqueous solutions, respectively. The viscosity average molecular weights (M_v) of the fractionated PVA samples were estimated from intrinsic viscosities in aqueous solution at 25°C.[7] 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 characteristics of the samples used are given in Table I.

Table I. Characteristics of the polymer samples

Sample code	$M_v \times 10^{-5}$ [a]	$M_w \times 10^{-5}$	M_w/M_n
PVA-1	0.37		1.38
PVA-2	0.93		1.44
PVA-3	1.59		1.43
PVA-4	7.30		1.57
PEG-1		0.072	1.08
PEG-2		0.20	1.10
PEG-3		1.60[b]	1.04[b]
PEG-4		6.68[b]	1.04[b]

[a] Calculated from the equation of ref 7: $[\eta] = 67 \times 10^{-5} M^{0.55}$.

[b] Manufacturer's data supplied by Toyo Soda Manufacturing Co., Ltd.

Determination of Binodal Curves

Binodal curves for the PVA–PEG–water system were determined in the following way. Both aqueous solutions of PVA and PEG were combined in a graduated cylinder which was then placed in a water bath kept at $30 \pm 0.02°C$. The mixture with desired composition was vigorously stirred for about 5 min by a glass bar and then allowed to stand for 2—7 days, until it separated clearly into upper and lower phases with a distinct interface intervening. After the volume of each phase was measured by graduation of the cylinder, each phase was placed in a separate beaker using a pipette, and weighed. The phases were then diluted with water to appropriate concentrations of the polymers. This was followed by the addition of methanol in more than 8 times the solution volume so as to precipitate the PVA selectively. The precipitate was separated from the mixture by centrifugation at 4500 rpm, dried and the weight of PVA in each phase was determined. The filtrate was evaporated to dryness and weighed, giving the amount of PEG in each phase. The completion of separation of PVA from PEG by this method was confirmed by IR spectra of the dried materials from the precipitate and filtrate. The volume percents (v/v%) of PVA, PEG and water of the upper and lower phases and the whole system, were

calculated using the following densities: PVA, 1.27; PEG, 1.13; water, 1.00.

THEORETICAL BACKGROUND

Phase relationships of ternary systems consisting of polymer 2, polymer 3, and a solvent (component 1) such as those used here were investigated[4-6] extensively on the basis of the Flory–Huggins theory[3] and expressed in terms of the polymer molecular weights x_2 and x_3 and the interaction parameters χ_{12}, χ_{13}, and χ_{23}. Some of the important observations from these investigations[3-6] are the following:

(1) Polymers with a positive χ_{23} do not mix at all in the solid state. A solution of such polymers separates into two phases even for very small positive values of χ_{23}.

(2) A binodal curve is more or less symmetric when $x_2 \simeq x_3$.

(3) For a system with $x_2 = x_3$, tie lines are parallel to the polymer 2-polymer 3 axis when $\chi_{12} = \chi_{13}$. When $\chi_{12} > \chi_{13}$, they are inclined toward the solvent–polymer 2 axis.

(4) For a given polymer mixture, the binodal moves toward the solvent apex with increasing $\chi(\chi = \chi_{12} = \chi_{13} = \chi_{23})$.

(5) For systems in which x_2 is fixed but x_3 varied, the binodal moves toward the solvent apex and inclines toward the solvent–polymer 2 axis as x_3 increases.

(6) For systems with a definitely negative χ_{23}, the binodal is closed near or on the polymer 2-polymer 3 axis.

RESULTS AND DISCUSSION

Table I gives the molecular weights of the PVA and PEG samples used. The ratio M_w/M_n is from 1.38 to 1.57 for the PVA samples and from 1.04 to 1.10 for the PEG samples. Thus, the molecualr weight distributions of these samples are moderately narrow. We choose water as component 1, and PVA and PEG as components 2 and 3, respectively.

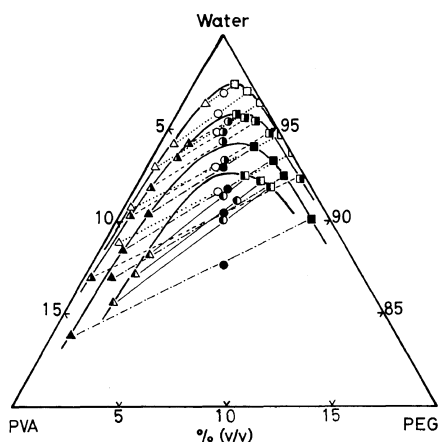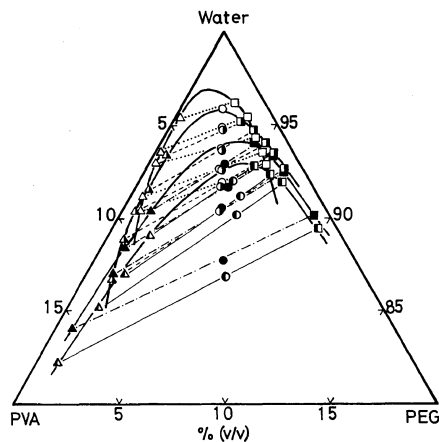Figure 1 shows the effect of PVA molecular

Figure 1. Phase diagram for the PVA–PEG–water system at 30°C and 1 atm. The tie lines connecting the equilibrium compositions of the two conjugate phases (triangles, squares) *via* that of the original mixture (circles) are shown. △---○---□, PVA-4–PEG-2; ▲---◑---◨, PVA-3–PEG-2; ▲---●---■, PVA-2–PEG-2; ▲—◐—◫, PVA-1–PEG-2.

Figure 2. Phase diagram for the PVA–PEG–water system at 30°C and 1 atm. The tie lines connecting the equilibrium compositions of the two conjugate phases (triangles, squares) *via* that of the original mixture (circles) are shown. △---○---□, PVA-2–PEG-4; ▲---◑---◨, PVA-2–PEG-3; ▲---●---■, PVA-2–PEG-2; ▲—◐—◫, PVA-2–PEG-1.

weight on the binodal curves for the system PVA–PEG–water with a PEG sample of 20,000 M_w. As seen from the tie lines on the binodal curves, each mixture separates into a concentrated PVA-rich and a dilute PEG-rich phase. As the PVA molecular weight increases, the binodal curve moves toward the water apex of the triangular diagram, indicating that miscibility of the system decreases with increasing PVA molecular weight. This trend is consistent with (5) mentioned above. In the limit of very large PVA molecular weight, the binodal curve becomes similar to that of a polymer–solvent–nonsolvent system, which is compatible with theoretical analyses by Scott,[4] Tompa,[5] and Hsu and Prausnitz.[6]

Figure 2 shows the effect of PEG molecular weight on the binodal curves for the PVA–PEG–water system with the PVA M_v fixed at 93000. Each mixture separates into a concentrated PVA-rich phase and a dilute PEG-rich phase. As the M_w of PEG increases, the binodal moves upward almost parallel to the water–PEG axis and is inclined toward the water–PVA axis. This trend is essentially the

same as that in Figure 1, where the molecular weight of PVA changes. It can be seen that the binodal curve is almost symmetric if PVA and PEG have the same molecular weight. This conforms to (2).

It is interesting to note that the binodal curves for PEG-3 and PEG-4 intersect each other and cross those for PEG-1 and PEG-2. They tend to become almost vertical at high polymer concentration. Thus, these binodal curves may become closed or nearly so at high polymer concentration. No such behavior was observed when the molecular weight of PVA changed, as evident from Figure 1.

In the light of the Flory–Huggins theory, a closed binodal may be expected for a system with a negative χ_{23} as mentioned in (6). Thus, the data shown in Figure 2 suggest that χ_{23} decreases with increasing PEG molecular weight. The system PVA–PEG is a typical incompatible system,[8] and χ_{23} is probably positive in the solid state (1). Thus, χ_{23} should show complicated dependence on PEG molecular weight and polymer concentration.

In either Figure 1 or 2, the tie lines incline

toward the PVA–water axis, indicating the PEG-rich phase to be more dilute than the PVA-rich phase irrespective of molecular weight. According to (3), due to Hsu and Prausnitz,[6] this behavior is expected if $\chi_{12} > \chi_{13}$; that is, water is a better solvent for PEG than for PVA.

In conclusion, the important observations based on the Flory–Huggins theory on ternary phase diagrams have been experimentally substantiated by our phase separation data for the system PVA–PEG–water. It was found that the polymer-polymer interaction parameter χ_{23} is a complicated function of PEG molecular weight and that water is a better solvent for PEG than for PVA at polymer concentrations where phase separation occurs.

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