SHORT COMMUNICATION

Phase Equilibrium of Poly(acrylamide)– Poly(vinyl alcohol)–Water System

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Phase equilibria in aqueous solutions of oppositely charged polyelectrolytes and those of two nonelectrolytic polymers have been investigated in detail.¹⁻³ To our knowledge, however, no research on the phase separation of a polyelectrolyte-nonelectrolyte polymer-water system has yet been reported. In this paper, a system consisting of poly(acrylamide) containing a small amount of carboxyl group (PAAm-A), poly(vinyl alcohol), and water is investigated in regard to the dependence of the phase diagram on molecular weight and charge density of the polyelectrolyte (PAAm-A). The dependence of the phase diagram on the molecular weight of this system was found to be anomalous, since an increase in the molecular weight of PAAm-A enhanced the miscibility of the mixture. This anomaly led us to carry out a more detailed investigation of the phase equilibrium of this system.

EXPERIMENTAL

Materials

Poly(acrylamide) (PAAm). Five samples of PAAm of varying molecular weight were supplied by NITTO Chemical Co. These samples were purified by repeatedly pouring their aqueous solutions into ethyl alcohol. The viscosity average molecular weights M_v of the purified samples estimated from intrinsic viscosities in 0.2 *N*-NaCl aqueous solution⁴ were 6.0×10^4 , 1.8×10^5 , 2.5×10^5 , 3.0×10^5 , and 5.2×10^5 . According to GPC (gel permeation chromatography) measurements, all the samples had nearly the same molecular weight distribution and

each a single peak. The ratios of weight-average molecular weight M_w to number-average molecular weight M_n , M_w/M_n , were approximately 2.2–2.3.

Poly(acrylamide) Containing a Small Amount of Carboxyl group (PAAm-A). Except for PAAm of $M_v = 6.0 \times 10^4$, the original polymer samples contained detectable amounts of carboxyl (COOH) groups. Further incorporation of COOH groups into the polymer chain was made by hydrolysis of the amide groups with ammonia. The amount of incorporated COOH was controlled by adjusting the concentration of ammonia, the temperature and the time of reaction. The resulting polymers were purified by evaporating unreacted ammonia into a vacuum and passing their solutions through an ion exchanger followed by repeated precipitation with ethyl alcohol. The intrinsic viscosities of the PAAm-A samples so treated were measured to ascertain whether the polymer chains not degraded during the hydrolysis reaction. The COOH content ρ (COOH) defined as (number of COOH)/(number of monomer unit) was determined within an accuracy of $\pm 0.02\%$ by potentiometric titration⁵ with a CORNING pH meter 125. The measured COOH content was of the order of a few percent.

Sodium salts of PAAm-A (PAAm-ANa) were prepared by neutralization with dilute aqueous solutions of NaOH.

Poly(vinyl alcohol)(PVA). Two samples of PVA (IWAI Chemical Co.) with degrees of polymerization $\bar{P}=1700$ and 500 were purified by repeated precipitation from an aqueous solution into methyl alcohol. The values of M_w/M_n estimated by GPC were about 2.2 for both samples. The sample of $\bar{P} = 1700$ was separated into 6 fractions by the addition of methyl alcohol into a 2% aqueous solution. The third fraction with $M_v = 7.25 \times 10^4$ ($\bar{P} = 1650$) (calculated by the equation of ref 6) and $M_w/M_n = 1.5$ (estimated by GPC) was used for cloud point measurements except for the two cases in Figure 1.

Measurements of Cloud-Point and Coexistence Curves

Cloud points were measured by the gradual addition of a solution of a given sample to a solution of another sample in a thin glass tube equipped with a magnetic stirrer at a constant temperature controlled to $\pm 0.02^{\circ}$ C.

Coexistence curves were determined in the following way. An aqueous solution of PAAm-A and PVA with a desired composition was made in a sample tube. After stirring it for about 1 h in a water bath kept at a desired temperature within ± 0.02 °C, the sample tube was transferred into a centrifuge having the same temperature as the water bath. The solution separated clearly into two phases, each of which was analyzed by the drying method for the total polymer concentration and by the IR method for the relative concentration of PVA to PAAm-A using absorption peaks at 1640 cm⁻¹ and 1070 cm⁻¹.

RESULTS AND DISCUSSION

$PAAm-A-PVA-H_2O$ Systems

Figure 1 shows the cloud-point curves for two



Figure 1. Cloud-point curves for different molecular weights of PVA at 40.2°C with PAAm-A ($M_v = 1.8 \times 10^5$; $\rho = 1.2\%$): (\bigcirc), $\bar{P} = 1700$; (\bigcirc), $\bar{P} = 500$.

unfractionated PVA. The cloud-point curve for the PVA sample of higher molecular weight appears at a lower polymer concentration, indicating that an increase in molecular weight of PVA decreases the miscibility of the mixture. This molecular weight dependence is normal since it can be expected from Flory–Huggins type theories of polymers solutions.^{1,7}

Figure 2 shows the coexistence curves for different samples of PAAm-A. The mixture separates into a PAAm-A-rich phase with a lower polymer



Figure 2. Coexistence curves for various molecular weights of PAAm-A at 53.7°C with PVA (\bar{P} =1700): (\triangle), M_v =1.8×10⁵ (ρ =1.2%); (\bigcirc), M_v =2.5×10⁵ (ρ =1.3%); (\bigcirc), M_v =5.2×10⁵ (ρ =4%). The filled circles indicate the critical points estimated from the tie lines. The initial concentrations are indicated on the tie lins: (\perp), M_v =1.8×10⁵; (+), M_v =2.5×10⁵; (×), M_v =5.2×10⁵.



Figure 3. Cloud-point curves for various molecular weights of PAAm-A at 53.7°C with PVA (\bar{P} =1650): (\bigcirc), M_v =6.0×10⁴ (ρ =1.2%); (\triangle), M_v =1.8×10⁵ (ρ =1.2%); (\bigcirc), M_v =2.5×10⁵ (ρ =1.3%); (\square), M_v =3.0×10⁵ (ρ =1.2%).

concentration and a PVA-rich phase with a higher polymer concentration, and the coexistence curve for the higher molecular weight appears at the higher polymer concentration.

Figure 3 shows the cloud-point curves for PAAm-A samples with the same COOH content. The cloud-point curve for higher molecular weight appears at a higher polymer concentration, which is consistent with the coexistence curve. Thus, contrary to the dependence on the molecular weight of PVA, the increase in the molecular weight of PAAm-A brings about an increase in the miscibility of the mixture. This behavior is quite unexpected in consideration of the usual theories of polymer solutions.



Figure 4. Cloud-point curves for various COOH contents at 53.7°C with PVA (\bar{P} =1650) and PAAm-A (M_v =6.0×10⁴): (\bigcirc), ρ =0%; (\triangle), ρ =0.8%; (\bigcirc), ρ =1.2%; (\bigcirc), ρ =2.8%.

In Figure 4 are shown the cloud-point curves for PAAm-A samples of $M_v = 6.0 \times 10^4$ with different COOH content. Figure 5 shows the water concentration at the top of the cloud-point curve, $\Phi_{\rm H_2O}^t$, plotted against the COOH content ρ for various molecular weights. $\Phi_{H_2O}^t$ decreases with increasing ρ , *i.e.*, the miscibility increases with an increase in the COOH content at a rate depending considerably on the molecular weight. The higher the molecular weight of PAAm-A, the more remarkably the introduction of COOH group increases the miscibility of the mixture, especially, at a small COOH content. Thus, when ρ is greater than about 0.5%, we find anomalous behavior such that the miscibility of the mixture increases with an increase in the molecular weight of PAAm-A.

PAAm-ANa-PVA-H₂O systems

The cloud-point curves of PAAm-ANa–PVA– H₂O systems have shapes substantially similar to those of the PAAm-A–PVA–H₂O systems. In Figure 5, the filled circles indicate the water concentrations at the top of cloud point curves $\Phi_{H_{2O}}^t$ for three molecular weights of PAAm-A as a function of COONa content, ρ (COONa). As in the case of COOH, the increase in COONa content increases the miscibility of the mixture. However, in contrast to the case of COOH, the rate of increase in the miscibility with ρ (COONa) is nearly independent of molecular weight. Thus, the molecular weight dependence of the miscibility is normal at any COONa content, *i.e.*, the increase in the molecular



Figure 5. Dependence of miscibility indicated by $\Phi_{\rm H_{2O}}^t$ on COOH (or COONa) content ρ for various molecualr weights of PAAm-A with PVA ($\bar{P}=1650$): For COONa content, (\odot), $M_v=3.0 \times 10^5$; (\odot), $M_v=1.8 \times 10^5$; (Δ), $M_v=6.0 \times 10^4$. For COOH content, (\Box), $M_v=5.2 \times 10^5$; (\bigcirc), $M_v=3.0 \times 10^5$; (\diamond), $M_v=2.5 \times 10^5$; (\bigcirc), $M_v=1.8 \times 10^5$; (\triangle), $M_v=6.0 \times 10^4$.

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Figure 6. Dependence of miscibility indicated by $\Phi_{H_{2O}}^t$ on molecular weight for PAAm, PAAm-A and PAAm-ANa: (\bigcirc), $\rho(COOH) = \rho(COONa) = 0\%$; (\diamondsuit), $\rho(COONa) = 1.2\%$; (\bigtriangleup), $\rho(COOH) = 1.2\%$.

weight of PAAm-ANa decreases the miscibility at any fixed COONa content. Extrapolation of $\Phi_{H_{2O}}^{t}$ to $\rho = 0$ for both PAAm-A and PAAm-ANa solutions gives a consistent value of $\Phi_{H_{2O}}^{t}$, *i.e.*, $\Phi_{H_{2O}}^{t}$ for PAAm ($\rho = 0$)-PVA-H₂O, as can be seen from Figure 5. Figure 6 compares the molecular weight dependence of miscibility for three cases, $\rho = 0\%$, ρ (COONa)=1.2%, and ρ (COOH)=1.2%. For the former two ρ , the miscibility of the mixture decreases with increasing molecular weight, while the reverse is the case with the last ρ . Therefore, the factor directly responsible for the anomalous behavior is not the incorporation of ions but the presence of a small amount of COOH groups in PAAm-A.

The molecular weight distributions (MWD) of the PAAm-A samples used are relatively broad, but their effects on the phase diagram have not yet been investigated. However, we note that 1) the MWD was almost the same for all the PAAm-A samples used; 2) the dependence of the cloud-point curve on the molecular weight of PAAm-A was qualitatively consistent with that of the coexistence curve; 3) when the COOH groups were removed or replaced by COONa groups without changing the MWD, the molecular weight dependence normal; and 4) although the spread of MWD of the unfractionated PVA is comparable to that of PAAm-A, the dependence of the cloud-point curve on the molecular weight of PVA was normal. From these facts, we conclude that MWD is *not* responsible for the unexpected phase separation phenomenon observed in the present study.

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