

Phase Equilibrium of Poly(acrylic acid) Partially Neutralized by NaOH–Poly(vinyl alcohol)–Water System

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ABSTRACT: The phase diagram of a system consisting of poly(acrylic acid) partially neutralized by NaOH (PAA-Na), poly(vinyl alcohol) (PVA), and water was determined as a function of molecular weight and carboxyl group content of PAA-Na. As in the case of poly(acrylamide) with carboxyl groups–PVA–water system studied previously, incorporation of carboxyl (COOH) groups into the polyelectrolyte caused anomalous behavior in the phase diagrams. Thus, an increase in the molecular weight of PAA-Na at a fixed COOH content enhanced the miscibility of the mixture. A simple theoretical model based on the Voorn–Veis theory was applied to the phase behavior of the present system. It was found that the theory can qualitatively explain the COOH content dependence of the miscibility, but fails to predict the experimental dependence of the phase diagram on the molecular weight of the polyelectrolyte.

KEY WORDS Phase Equilibrium / Polyelectrolyte / Cloud Point / Coexistence Curve / Molecular Weight Dependence / Aqueous Solution /

In our previous study,¹ we determined the phase diagram of a system consisting of poly(acrylamide) containing a small number of carboxyl groups (PAAm-A), poly(vinyl alcohol) (PVA), and water as a function of molecular weight and carboxyl (COOH) group content of PAAm-A. The molecular weight dependence of the phase diagram was anomalous since an increase in the molecular weight of PAAm-A enhanced the miscibility of the mixture. When the COOH group was replaced by the COONa group, the molecular weight dependence of the phase diagram became normal. This fact suggests that the factor primarily responsible for the anomalous behavior is the presence of a small number of COOH groups in PAAm-A. It should be worthwhile to investigate whether this anomaly is peculiar to the PAAm-A–PVA–water system or a common property of any polyelectrolyte containing a COOH group–nonelectrolytic polymer–water system. Thus, in the present work, we investigated a system consisting of poly(sodium acrylate) containing COOH groups (PAA-Na), PVA, and water to determine the dependence of the phase diagram on molecular weight and COOH content of PAA-Na. PAA-Na is a strongly charged polyelectrolyte with

ionic COONa groups resulting from the partial neutralization of the COOH groups. On the other hand, PAAm-A is a weakly charged polyelectrolyte in which nonionic CONH₂ groups are partly replaced by COOH groups. Although it has not as yet been established whether the distribution of COOH groups on PAAm-A chains is uniform, the distribution of COOH groups on PAA-Na chains must be statistically uniform. We also examined the applicability of a simple model based on the Voorn–Veis theory^{2–5} to the present system to find what should be taken into account to explain the anomalous phase behavior.

EXPERIMENTAL

Sample Preparations

A poly(acrylic acid) (PAA) (WAKO Chem. Co.) sample was separated into 11 fractions by successive solution fractionation using a mixture of diethyl ether, methyl alcohol, and water. Each fraction was purified by repeated precipitation from a methyl alcohol solution with acetone and passing the solution through an ion exchanger. The viscosity average molecular weights M_v of the purified PAA

samples were estimated from the intrinsic viscosities in 1,4-dioxan at 30°C.⁶ The degrees of polymerization \bar{P} calculated from M_v were 1290, 2560, 4060, 7460, and 11000 for the five samples used here. The ratios of weight average molecular weight M_w to the number-average molecular weight, M_n , M_w/M_n , were found to be approximately 1.2–1.3 by gel permeation chromatography.

Poly(sodium acrylate) containing COOH groups (PAA-Na) was prepared by partial neutralization of a PAA with 0.1 *N* aqueous NaOH.

Poly(vinyl alcohol) (PVA) was the same fractionated sample as used in the previous study,¹ and had a degree of polymerization, $\bar{P}=1650$ and $M_w/M_n=1.5$.

Methods

Cloud points and coexistence curves were determined at 53.7°C by the same methods used in the previous study.¹ The relative concentration of PVA to PAA-Na was determined by elemental analysis.

RESULTS AND DISCUSSION

Coexistence Curves of PAA-Na–PVA–H₂O Systems

Figure 1 shows the coexistence curves of the PAA-Na–PVA–H₂O systems, in which the COOH content of PAA-Na sample is expressed as, $\rho_{\text{COOH}} = (\text{the number of COOH group})/(\text{the number of monomer unit})$. The incorporation of COOH

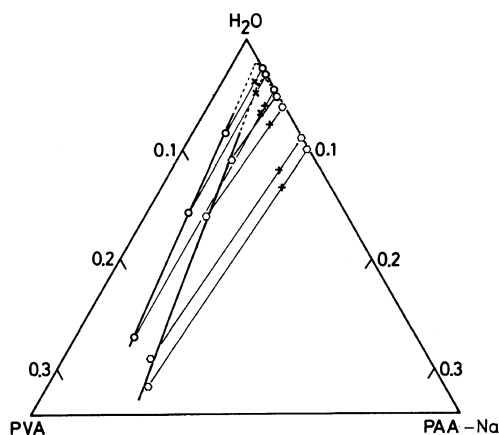


Figure 1. Coexistence curves of PAA-Na–PVA–H₂O system with \bar{P} (PAA-Na) = 4060 at 53.7°C: (○), $\rho_{\text{COOH}}=0$; (◐), $\rho_{\text{COOH}}=0.2198$. The initial mixture compositions are indicated on the tie lines: (×), $\rho_{\text{COOH}}=0$; (+), $\rho_{\text{COOH}}=0.2198$.

groups enhanced the miscibility of the mixture. As with the PAAM-A–PVA–H₂O system,¹ the present system was asymmetrical, since the mixture separated into a PAA-Na-rich phase with lower polymer concentration and a PVA-rich phase with higher polymer concentration. The tie lines had larger slopes against the PAA-Na–PVA axis than those of the PAAM-A system.

Cloud Point Curves of PAA-Na–PVA–H₂O Systems

Figure 2 shows the cloud point curves of the PAA-Na ($\bar{P}=11000$)–PVA–H₂O system for dif-

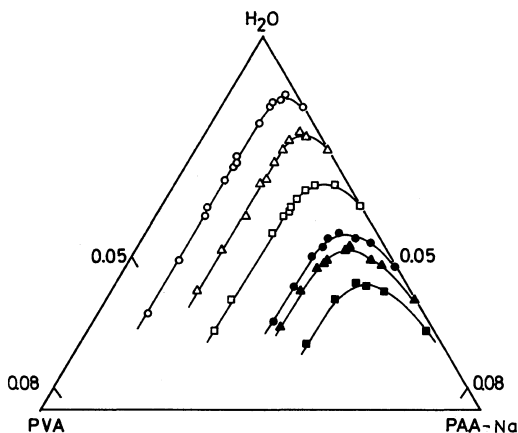


Figure 2. Cloud point curves of PAA-Na–PVA–H₂O system with \bar{P} (PAA-Na) = 11000 at 53.7°C for various COOH contents: (○), $\rho_{\text{COOH}}=0$; (△), $\rho_{\text{COOH}}=0.0202$; (◻), $\rho_{\text{COOH}}=0.0442$; (●), $\rho_{\text{COOH}}=0.1008$; (▲), $\rho_{\text{COOH}}=0.2063$; (■), $\rho_{\text{COOH}}=0.4584$.

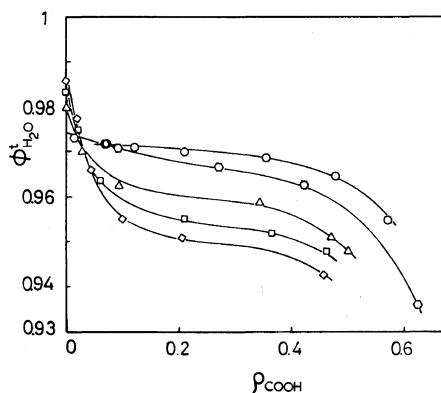


Figure 3. Dependence of miscibility indicated by $\Phi_{\text{H}_2\text{O}}$ on the COOH content for various degrees of polymerization of PAA-Na (○), $\bar{P}=1290$; (◐), $\bar{P}=2560$; (△), $\bar{P}=4060$; (◻), $\bar{P}=7460$; (◊), $\bar{P}=11000$.

ferent COOH content. The two-phase region inclines toward the PAA-Na-rich side for any COOH content and shifts to higher polymer concentration as the COOH content increases. Figure 3 shows the water concentration at the top of the cloud point curve, $\Phi_{\text{H}_2\text{O}}^i$, as a function of the COOH content for various molecular weights. The miscibility of the mixture increases (*i.e.*, $\Phi_{\text{H}_2\text{O}}^i$ decreases) with increasing COOH content, and the higher the molecular weight of PAA-Na, the more remarkably the miscibility increases at small COOH content. This behavior is quite similar to that of the PAAm-A-PVA-water system.¹

It should be noted that an increase in COOH content in the present system implies a decrease in COONa content. Hence, there is a decrease in charge density of the polyelectrolyte, since the degree of dissociation of COOH groups is very small compared with that of COONa groups. In the case of PAAm-A, the increase in COOH content increases the charge density. Therefore, the phase equilibrium in the present system did not depend simply on the charge density of the polyelectrolyte.

As can be seen from Figure 3, the miscibility of the mixture increases remarkably in the region of a COOH content larger than 40%. A strong interaction of the COOH groups of PAA-Na with the OH groups of PVA may be responsible for this remarkable increase in miscibility, since poly(acrylic acid) forms a complex with a water-soluble nonelectrolytic polymer such as poly(ethylene oxide) and PVA through hydrogen bonding of the oxygen atoms of the nonelectrolytic polymer and the car-

boxyl groups of the polyelectrolyte.⁷

Figure 4 shows the dependence of $\Phi_{\text{H}_2\text{O}}^i$ on the molecular weight of PAA-Na for various COOH content. The increase in molecular weight depresses the miscibility at a COOH content less than 3%, but the reverse occurs at a COOH content exceeding 3%, as was also found in the PAAm-A-PVA-water system. Thus, the phase equilibrium of the PAAm-A-PVA-water system is also anomalous with respect to the molecular weight dependence. (It should be noted here that the molecular weight distribution of PAA-Na used was much narrower than that of PAAm-A in the previous system.) Therefore, it may be concluded that regardless of whether the polyelectrolyte is weakly or strongly charged, the incorporation of COOH groups results in an anomalous molecular weight dependence of phase equilibrium behavior.

Theoretical Consideration

Theoretical Model. The theoretical model used below was first proposed by Voorn and later modified by Veis.²⁻⁵ It is assumed that the total free energy of mixing, ΔF_T , of a polyelectrolyte solution is the sum of the electrostatic free energy ΔF_E due to polyions and counter-ions and the nonelectrolytic free energy of mixing, ΔF_M , of the polymer solution:

$$\Delta F_T = \Delta F_E + \Delta F_M \quad (1)$$

According to Voorn's theory,² ΔF_E is assumed to be given by the Debye-Hückel equation, *i.e.*,

$$(\Delta F_E/N_r kT) = -\beta(\sum_i \sigma_i \Phi_i)^{3/2} \quad (2)$$

where N_r is the total number of lattice sites in the system, β the electrostatic interaction constant, σ_i the fraction of charged lattice sites (charge density) in the i -component lattice sites, and Φ_i the volume fraction of the i -component. The Flory-Huggins equation is adopted for ΔF_M , *i.e.*,

$$\Delta F_M = kT \sum_i n_i \ln \Phi_i + kT N_r \sum_{i,j} \chi_{i,j} \Phi_i \Phi_j \quad (3)$$

with n_i being the number of i -component molecules and $\chi_{i,j}$ the interaction parameter between segments of i - and j -components. Using the electro neutrality condition

$$\Phi_3 \sigma_3 = \Phi_1 \sigma_1 \quad (4)$$

ΔF_T for the present system is obtained from eq 1-3 as

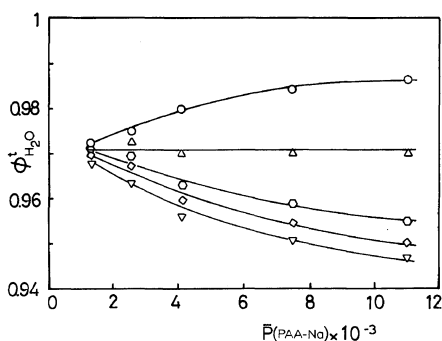


Figure 4. Dependence of the miscibility indicated by $\Phi_{\text{H}_2\text{O}}^i$ on the molecular weight of PAA-Na: (○) $\rho_{\text{COOH}} = 0$; (△), $\rho_{\text{COOH}} = 0.03$; (□), $\rho_{\text{COOH}} = 0.10$; (◇), $\rho_{\text{COOH}} = 0.20$; (▽), $\rho_{\text{COOH}} = 0.40$.

$$\begin{aligned} \frac{\Delta F_T}{N_r kT} = & -\beta(2\sigma_1\Phi_1)^{3/2} + \frac{\sigma_1\Phi_1}{\sigma_3} \ln\left(\frac{\sigma_1}{\sigma_3}\right) \\ & + \left(\frac{1}{P_1} + \frac{\sigma_1}{\sigma_3}\right)\Phi_1 \ln \Phi_1 + \frac{\Phi_2}{P_2} \ln \Phi_2 + \Phi_0 \ln \Phi_0 \\ & + \chi_{0,1}\Phi_0\Phi_1 + \chi_{1,2}\Phi_1\Phi_2 + \chi_{0,2}\Phi_0\Phi_2 \quad (5) \end{aligned}$$

where the subscripts 0, 1, 2, and 3 indicate the solvent (water), the polyelectrolyte, the nonelectrolytic polymer, and the counter-ion, respectively, and P is the number of segments in a polymer molecule. The counter-ion interaction terms $\chi_{0,3}$ and $\chi_{2,3}$ have been eliminated in eq 5 by allowing these terms to be absorbed in the terms $\chi_{0,1}$ and $\chi_{1,2}$.⁸

The polyelectrolyte considered is a copolymer consisting of two kinds of repeating unit; one (a) is $[-\text{CH}_2-\text{CH}(\text{COOH})-]$ and the other (b) is $[\text{CH}_2-\text{CH}(\text{CONH}_2)-]$ for PAAM-A, or $[-\text{CH}_2-\text{CH}(\text{COONa})-]$ for PAA-Na. Thus, the terms $\chi_{0,1}\Phi_0\Phi_1$ and $\chi_{1,2}\Phi_1\Phi_2$ in eq 5 may be written as

$$\chi_{0,1}\Phi_0\Phi_1 = \chi_{0,1a}\Phi_0\Phi_{1a} + \chi_{0,1b}\Phi_0\Phi_{1b}$$

$$\chi_{1,2}\Phi_1\Phi_2 = \chi_{1a,2}\Phi_{1a}\Phi_2 + \chi_{1b,2}\Phi_{1b}\Phi_2$$

i.e.,

$$\chi_{0,1} = \chi_{0,1a}\rho + \chi_{0,1b}(1-\rho)$$

$$\chi_{1,2} = \chi_{1a,2}\rho + \chi_{1b,2}(1-\rho)$$

where Φ_{1a} and Φ_{1b} are the volume fractions of repeating units a and b in the polyelectrolyte (1), respectively, and $\rho = \Phi_{1a}/\Phi_1$.

The charge density of a counter-ion σ_3 is unity in any cases. The expression of σ_1 , however, depends on the system. In the case of PAAM-A (or sodium salt of PAAM-A, *i.e.*, PAAM-ANa), the charge of the polyion arises from the dissociation of COOH groups (or COONa groups). Therefore, σ_1 is equal to $\lambda\rho_{\text{COOH}}$ for PAAM-A and ρ_{COONa} for PAAM-ANa, where λ is the degree of dissociation of COOH groups, being assumed to be independent of ρ_{COOH} . In the case of PAA-Na, the charge arises from dissociation of both COOH and COONa groups. Since the degree of dissociation of COONa is very close to unity, σ_1 may be expressed by

$$\sigma_1 = 1 - \rho_{\text{COOH}}(1 - \lambda) \quad (6)$$

which is the analytical charge density. When σ_1 is not much smaller than unity, we must consider the

counter-ion condensation⁹⁻¹² which reduces the effective charge density to a value lower than the analytical one. Therefore, the charge density σ_1 in eq 5 must be replaced by $f\sigma_1$ in the case of Na-salt of PAA, where f is the ratio of the effective charges (structural charges uncompensated by bound counter-ions) to the analytical charges (total structural charges) and is expressed by

$$f = 1 - N\theta_N$$

Here, θ_N is the number of bound counter-ions per charged group of polyions, and N is the counter-ion valence.

Expressions for the spinodal and critical points are derived from eq 5 in the Appendix. The electrostatic interaction constant β was taken as 3.655, according to the calculation of Voorn.² We chose the values of the χ -parameters in such a way that phase separation would occur at a concentration comparable to that observed, considering that the values of $\chi_{0,1a}$ and $\chi_{1a,2}$ are negative because of strong interactions between 0- and 1a-components and 1a- and 2-components. Figure 5 shows an example of a calculated phase diagram (spinodal curve and critical point). As an indicator for the miscibility of the mixture, we used the volume fraction of water Φ_c at the critical point. In the present systems, Φ_c is very close to $\Phi_{\text{H}_2\text{O}}^I$, as can be seen from Figures 1 and 5 (and Figure 2 in the

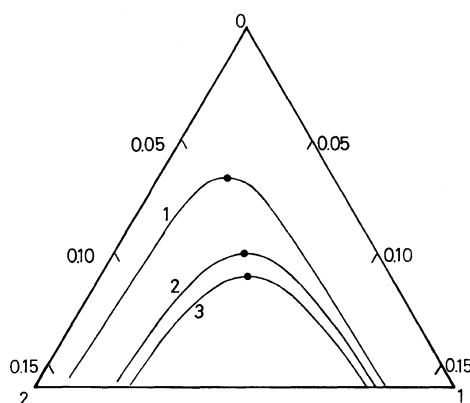


Figure 5. Spinodal lines and critical points calculated from eq 5 for different degrees of polymerization and COOH content with $\chi_{0,1a} = -0.3$, $\chi_{0,1b} = 0.2$, $\chi_{1a,2} = -0.3$, $\chi_{1b,2} = 0.2$, $\chi_{0,2} = 0.2$, $\lambda = 0.05$ and $P_2 = 100$: (1) $P_1 = 400$ and $\rho_{\text{COOH}} = 0.02$; (2) $P_1 = 100$ and $\rho_{\text{COOH}} = 0$; (3) $P_1 = 100$ and $\rho_{\text{COOH}} = 0.02$. The filled circles show the critical points.

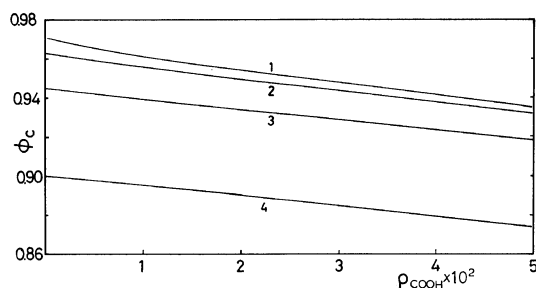


Figure 6. Dependence of miscibility indicated by Φ_c on the COOH content for the PPAm-A-PVA-H₂O system: (1), $P_1 = 6400$; (2), $P_1 = 1600$; (3), $P_1 = 400$; (4), $P_1 = 100$. The values of χ -parameters, λ and P_2 are the same as those in Figure 5.

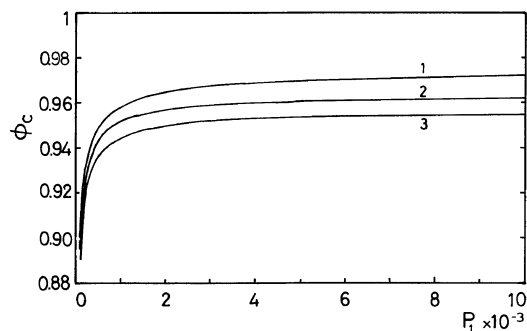


Figure 7. Miscibility indicated by Φ_c against the molecular weight of polyelectrolyte for the PAAM-A-PVA-H₂O: (1), $\rho_{\text{COOH}} = 0$; (2), $\rho_{\text{COOH}} = 0.01$; (3), $\rho_{\text{COOH}} = 0.02$. The values of χ -parameters, λ and P_2 are the same as those in Figure 5.

previous paper¹).

PAAM-A (or PAAM-ANa)-PVA-H₂O System. Figure 6 shows the calculated values of Φ_c as a function of the COOH content for various molecular weights of the polyelectrolyte. The increase in COOH content enhances the miscibility, which is consistent with the observed results. However, increase in miscibility with increasing COOH content varies only slightly with molecular weight, while the observed increase depends strongly on the molecular weight, particularly at small COOH content.

Figure 7 shows the calculated molecular weight dependence of Φ_c for various charge densities. The increase in molecular weight depresses the miscibility at any COOH content. The same trend was found for other χ -parameters. Therefore, the theory fails to predict the experimental results for the dependence of a phase diagram on the molecular-

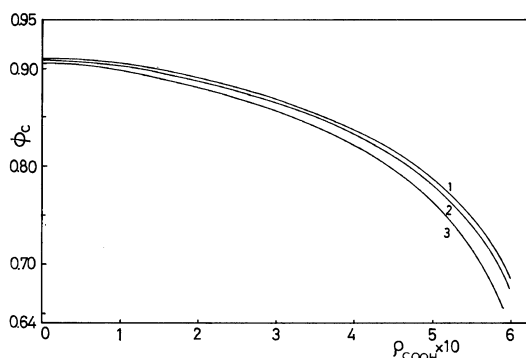


Figure 8. Dependence of miscibility indicated by Φ_c on the COOH content for the PAA-Na-PVA-H₂O system with $\chi_{0,1a} = -0.2$, $\chi_{0,1b} = 0.3$, $\chi_{1a,2} = -0.2$, $\chi_{1b,2} = 0.3$, $\chi_{0,2} = 0.3$, $\lambda = 0.01$ and $P_2 = 100$: (1), $P_1 = 6400$; (2), $P_1 = 1600$; (3), $P_1 = 100$.

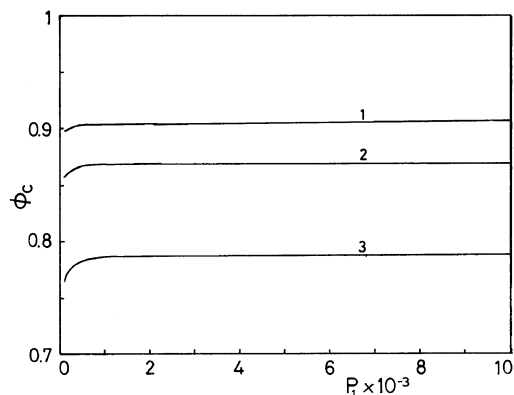


Figure 9. Dependence of miscibility indicated by Φ_c on the molecular weight of polyelectrolyte for the PAA-Na-PVA-H₂O system: (1), $\rho_{\text{COOH}} = 0.1$; (2), $\rho_{\text{COOH}} = 0.3$; (3), $\rho_{\text{COOH}} = 0.5$. The values of χ -parameters, λ and P_2 are the same as those in Figure 8.

weight in the range of $\rho_{\text{COOH}} > 0.5\%$ where $\Phi_{\text{H}_2\text{O}}^t$ decreases with increasing molecular weight.¹ However, when the COOH group is replaced by COONa, the experimental value of $\Phi_{\text{H}_2\text{O}}^t$ increases with increasing molecular weight, as predicted by the theory.

PAA-Na-PVA-H₂O System. The value of θ_N was taken to be 0.76 for the present case where $N = 1$.¹² Figure 8 shows the dependence of miscibility on ρ_{COOH} for various molecular weights of the polyelectrolyte. Because of negative values of $\chi_{0,1a}$ and $\chi_{1a,2}$ for the COOH group, the increase in COOH content increases the miscibility of the mixture, although the charge density of the polyelec-

trolyte decreases with increasing COOH content. The calculated curves predict well the remarkable decrease in $\Phi_{H_2O}^t$ at large COOH content (see Figure 3), but not the sharp decrease near $\rho_{COOH}=0$ for the higher molecular weight samples.

Figure 9 shows the calculated values of Φ_c plotted against PAA-Na molecular weight for various COOH content. As with the PAAm-A-PVA-H₂O system, the miscibility decreases with an increase in molecular weight at any COOH content, in contradiction to the observed molecular weight dependence of miscibility at $\rho_{COOH} > 4\%$ (Figure 4).

In conclusion, the theory treated in this paper can quantitatively explain the COOH content dependence of miscibility in both PAAm-A-PVA-H₂O and PAA-Na-PVA-H₂O systems if negative values are assigned to χ -parameters associated with the COOH group, but fails to describe the remarkable decrease in $\Phi_{H_2O}^t$ for higher molecular weight samples near $\rho_{COOH}=0$. In other words, this theory cannot explain the anomalous molecular weight dependence of miscibility at $\rho_{COOH} > 0.5\%$ in the PAAm-A system and at $\rho_{COOH} > 4\%$ in the PAA-Na system.

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APPENDIX

Spinodal Curve

The spinodal point satisfies the condition

$$Sp(\Phi_1, \Phi_2) = \begin{vmatrix} \frac{\partial^2 \Delta F_T}{\partial \Phi_1^2} & \frac{\partial^2 \Delta F_T}{\partial \Phi_2 \partial \Phi_1} \\ \frac{\partial^2 \Delta F_T}{\partial \Phi_1 \partial \Phi_2} & \frac{\partial^2 \Delta F_T}{\partial \Phi_2^2} \end{vmatrix} = 0 \quad (A-1)$$

Inserting eq 5 into eq A-1, we obtain

$$\begin{aligned} \frac{Sp(\Phi_1, \Phi_2)}{N_r kT} = & \left[-\frac{3\beta\sigma_1^2}{\sqrt{2\sigma_1\Phi_1}} \right. \\ & \left. + (1/P_1 + \sigma_1) \frac{1}{\Phi_1} + \frac{1}{\Phi_0} - 2\chi_{0,1} \right] \\ & \times \left[\frac{1}{P_2\Phi_2} + \frac{1}{\Phi_0} - 2\chi_{2,0} \right] \end{aligned}$$

$$-\left(\frac{1}{\Phi_0} - \chi_{0,1} + \chi_{1,2} - \chi_{2,0} \right)^2 = 0 \quad (A-2)$$

which gives the spinodal curve.

Critical Point

At the critical point, the spinodal and binodal curves touch each other with an equal slope, *i.e.*,

$$\left(\frac{d\Phi_1}{d\Phi_2} \right)_{sp} = \left(\frac{d\Phi_1}{d\Phi_2} \right)_c \quad (A-3)$$

where the subscripts sp and c, respectively, indicate that the derivatives are to be evaluated along the spinodal curve and the curve c, the latter being defined by

$$\left(\frac{\partial \Delta F_T}{\partial \Phi_1} \right)_{\Phi_2} = 0$$

The explicit expression for the derivatives in eq A-3 are

$$\begin{aligned} \left(\frac{d\Phi_1}{d\Phi_2} \right)_c = & \left[\frac{1/\Phi_0 - \chi_{0,1} + \chi_{1,2} - \chi_{2,0}}{(-3\beta\sigma_1^2)/(\sqrt{2\sigma_1\Phi_1}) + (1/P_1 + \sigma_1) \frac{1}{\Phi_1} + \frac{1}{\Phi_0} - 2\chi_{0,1}} \right] \quad (A-4) \end{aligned}$$

and

$$\begin{aligned} \left(\frac{d\Phi_1}{d\Phi_2} \right)_{sp} = & [(-3\beta\sigma_1^2)(1/\Phi_0^2 - 1/P_2\Phi_2^2)/(\sqrt{2\sigma_1\Phi_1}) \\ & + (1/\Phi_1)(1/P_1 + \sigma_1)(1/\Phi_0^2 - 1/P_2\Phi_2^2) \\ & + (1/P_2\Phi_0\Phi_2)(1/\Phi_0 - 1/\Phi_2) \\ & + 2\chi_{0,1}/P_2\Phi_2^2 - 2\chi_{1,2}/\Phi_0^2] / \\ & [(3\sqrt{2}/4)\beta(\sigma_1/\Phi_1)^{3/2}(1/P_2\Phi_2 + 1/\Phi_0 - 2\chi_{2,0}) \\ & - (3\beta\sigma_1^2)/(\Phi_0^2\sqrt{2\sigma_1\Phi_1}) \\ & + (1/\Phi_1)(1/P_1 + \sigma_1)(1/\Phi_0^2 - 1/\Phi_1\Phi_0 \\ & - 1/P_2\Phi_1\Phi_2) + (1/P_2\Phi_2\Phi_0^2) \\ & + (2\chi_{2,0}/\Phi_1^2)(1/P_1 + \sigma_1) - (2\chi_{1,2}/\Phi_0^2)] \end{aligned}$$

Equation A-3 along with eq A-4 and A-5 determines the critical point.

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