

# Phase separation of polyelectrolyte/nonionic polymer systems in aqueous solution: effects of salt and charge density

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Aqueous systems of two soluble polymers often phase separate. The phase separation and the composition of each phase strongly depend on the nature of polymers and the existence of specific interactions between them. In this work we study the phase separation of poly(sodium acrylate)/nonionic polymer systems in aqueous solution. It is found that the phase diagrams are very asymmetrical, phase separation occurs mainly for mixtures of high polyelectrolyte concentration. The asymmetry and the position of the cloud point curve in the ternary diagram highly depends on the salt concentration (NaCl) in the mixture. This behaviour is ascribed to the presence of polyelectrolyte counterions. The phase diagram also depends on the neutralization degree ( $\alpha$ ) of poly(sodium acrylate). The compatibility of the mixture increases when the neutralization degree decreases and for values of  $\alpha < 20\%$  complex coacervation occurs.

(Keywords: phase separation; water soluble polymers; polyelectrolyte; salt effect)

## INTRODUCTION

The phase separation of two polymers (poly-A and poly-B) in organic solvents has been largely studied from both the experimental and theoretical points of view and is relatively well understood<sup>1-3</sup>. Polymer/polymer phase separation in aqueous solutions is less well understood because of the complexity of such systems in which features such as the structure of water and the presence of polar, ionic and hydrophobic groups in the chains of the water soluble polymers must be considered<sup>4-6</sup>. Nevertheless, polymer two-phase aqueous systems are used successfully for separation of biological macromolecules and particles<sup>7,8</sup>. The knowledge of the factors which control polymer mixing in water is very important for practical separation purposes.

Two important parameters, among others, are ionic strength and specific interactions between macromolecular chains (electrostatic, H-bond, etc.). The effect of salts on phase separation of systems containing two neutral polymers has been presented in many papers<sup>8-11</sup>. For instance, great attention has been paid to the system poly(ethylene glycol)/dextran<sup>10,11</sup>. However, the salt effect on mixtures of a polyelectrolyte with a non-ionic polymer is less well studied and understood<sup>6,8</sup>. On the other hand, only a few studies have been devoted to originally incompatible systems for which compatibility can be substantially enhanced by adjustable increase in polymer interactions<sup>12,13</sup>. As reported by Albertsson<sup>8</sup> and suggested by Molyneux<sup>14</sup>, such systems may present three types of behaviour: phase separation, miscibility, and complex coacervation.

In this paper the phase separation in a system containing simple synthetic polymers is studied by determination of phase diagrams using the cloud point

method. The mixtures contain a polyelectrolyte-poly-(acrylic acid sodium salt) (PAA<sub>Na</sub>), and a neutral polymer-poly(ethylene glycol) (PEG) or polyvinylpyrrolidone (PVP) or polyacrylamide (PAM). The effect of a salt (NaCl) and of the extent of poly(acrylic acid) ionization on the compatibility and the shape of binodals is discussed. Comparison with a system of two neutral polymers (PEG/PAM) is also presented.

## EXPERIMENTAL

### Materials and apparatus

Poly(acrylic acid) (PAA) in concentrated aqueous solution was supplied by Polysciences (25% solids in water). In order to obtain pure PAA in the acid form, commercial solution was ultrafiltered, first with an aqueous HCl solution ( $10^{-2}$  mol l<sup>-1</sup>), then with a large excess of pure water and finally freeze-dried.

Polyvinylpyrrolidone-K60 (PVP) concentrated solution (45% solids in water) was supplied by Fluka. It was ultrafiltered with a large excess of pure water and freeze-dried.

Poly(ethylene glycol) (PEG), from Fluka, was used without further purification.

Polyacrylamide (PAM) was obtained by radical polymerization of acrylamide (Merck-Schuchardt, synthesis grade) in water using a redox initiator:  $(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_5$ . The following concentration was used: [acrylamide] =  $1.25$  mol l<sup>-1</sup>;  $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 7.16 \times 10^{-3}$  mol l<sup>-1</sup>;  $[\text{Na}_2\text{S}_2\text{O}_5] = 5.37 \times 10^{-3}$  mol l<sup>-1</sup>. For more details about polymerization conditions see reference 15.

All these water soluble polymers contain small amounts of moisture which were estimated by comparison of experimental and theoretical values of carbon, oxygen, hydrogen and nitrogen (for PVP and PAM) content. Experimental values were obtained by elemental analysis.

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The calculated moisture content is taken into account in the preparation of the polymer stock solutions.

Water was purified by a Milli-Q system (Millipore). All other reagents were of analytical grade. Ultrafiltration was performed in an Amicon Ultrafiltration Cell-2000, using Diaflo PM 10 (Amicon) membranes of 10 000 nominal molecular weight cut-off. Because the molecular weight of ultrafiltered polymers (PAA and PVP) is much higher than 10 000 (see Table 1), in practice only the low molecular weight impurities are removed during this treatment.

The molecular weights ( $\bar{M}_v$ ) of polymers were estimated by viscometry, in water (PEG, PVP, PAM) or in 0.5 M NaBr (fully neutralized PAA) at  $25.0 \pm 0.1^\circ\text{C}$ , using Mark-Houwink-Sakurada (MHS) laws given in Table 1.

### Phase diagrams

Phase diagrams were determined at  $22 \pm 1^\circ\text{C}$ . Stock solutions of the polymers were prepared at 15% (g/g) in the suitable solvent (pure water or aqueous salt solution). For each couple of polymers several phase separated samples (15% in polymers) were obtained by mixing the appropriate stock solutions and then diluted until the one phase region was reached. In the case of complex coacervation (see Figure 8) some of the concentrated mixtures were homogeneous and phase separation occurred with dilution. The horizontal dashed line in all the figures corresponds to the experimental limit of polymer concentrations, i.e. 15%.

## RESULTS AND DISCUSSION

### Influence of ionic strength

Figure 1 displays the ternary diagram for three systems in pure water: PEG ( $\bar{M}_v = 36\,000$ )/PAM ( $\bar{M}_v = 110\,000$ ); PEG ( $\bar{M}_v = 36\,000$ )/PAANa ( $\bar{M}_v = 185\,000$ ); and PVP ( $\bar{M}_v = 210\,000$ )/PAANa ( $\bar{M}_v = 185\,000$ ).

For the first couple, PEG/PAM, a typical behaviour is observed (upper curve in Figure 1). Phase separation occurs for relatively low polymer concentrations and the top of the cloud point curve is reached when polymer concentration exceeds 4.5%. In addition, the curve is asymmetrical and displaced towards the low molecular weight polymer as generally expected for polymer mixtures of very different molecular weights<sup>20,21</sup>. On the contrary, the couple PEG/PAANa presents a quite unusual cloud point curve. Although PAANa has a much higher molecular weight than PEG which is even higher than that of PAM, its cloud point curve is far lower than the PEG/PAM curve and clearly displaced to the side of the high molecular weight polymer (lowest curve in Figure 1).

A similar behaviour is obtained with the system PVP/PAANa. In spite of the high molecular weight of

PVP ( $\bar{M}_v = 210\,000$ ) the cloud point curve is obtained for relatively high polymer concentrations (>9%). The curve asymmetry is found again.

The couple PAM/PAANa is entirely compatible, at least in the range of concentrations used.

A similar behaviour has been previously reported by other authors<sup>6,13</sup>. In an interesting paper<sup>6</sup> Helford ascribed the asymmetry of the cloud point curve to the large difference between the second virial coefficient values of the ionic and nonionic species. We think that this unusual behaviour is very general and is correlated to the polyelectrolyte nature of one of the polymers.

Figure 2 presents the cloud point curves for the system PEG/PAANa in pure water, in 0.1 M NaCl and in 1 M NaCl aqueous solution. Even at the lower salt concentration (0.1 M NaCl) the cloud point curve clearly shifts to lower polymer concentration (enhanced incompatibility). Its general shape remains unchanged and it is displaced to the side of high polyelectrolyte concentration. The situation completely changes when the more concentrated salt solution (1 M NaCl) is used as solvent (upper curve in Figure 2). The phase separation is obtained for very low polymer concentrations. The top of the cloud point curve is reached when the polymer concentration exceeds 1.4% and a conventional asymmetry is found again so that there is displacement of the top of the curve towards the low molecular weight polymer, as in the case of nonionic polymer couples (upper curve in Figure 1).

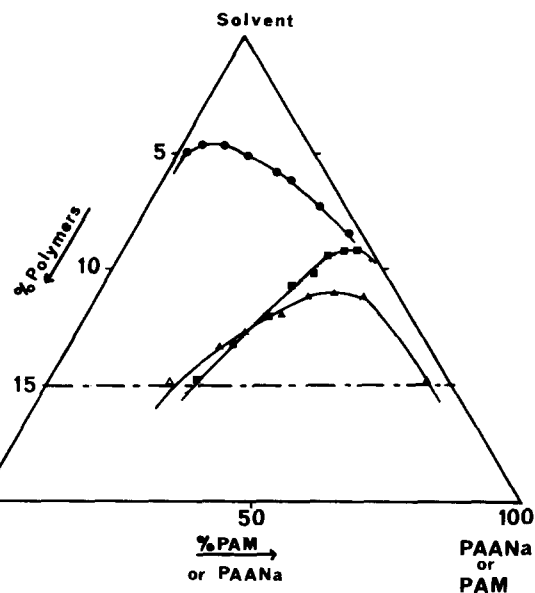


Figure 1 Ternary phase diagram of two polymers in water: (●) PEG ( $\bar{M}_v = 36\,000$ )/PAM ( $\bar{M}_v = 110\,000$ ); (■) PVP ( $\bar{M}_v = 210\,000$ )/PAANa ( $\bar{M}_v = 185\,000$ ); (▲) PEG ( $\bar{M}_v = 36\,000$ )/PAANa ( $\bar{M}_v = 185\,000$ ). Open symbols indicate compatible mixtures. The dashed line is the experimental limit of polymer concentration

Table 1 Polymer species used in this study

Sample	Origin	$\bar{M}$ given by the supplier	$[\eta]$ (ml/g)	MHS laws		Calculated $\bar{M}_v$	Ref.
				$K \times 10^2$	$\alpha$		
PAA	Polysciences	150 000	145	5.06	0.656	185 000	16
PVP	Fluka	160 000	48	5.65	0.55	210 000	17
PEG	Fluka	35 000	53	2.4	0.73	36 000*	18
PAM	—	—	63	1.0	0.755	110 000	19

\* This value was obtained by using the complete law given by Ring *et al.*:  $[\eta] = 2 + 2.4 \times 10^{-2} \bar{M}_v^{0.73}$

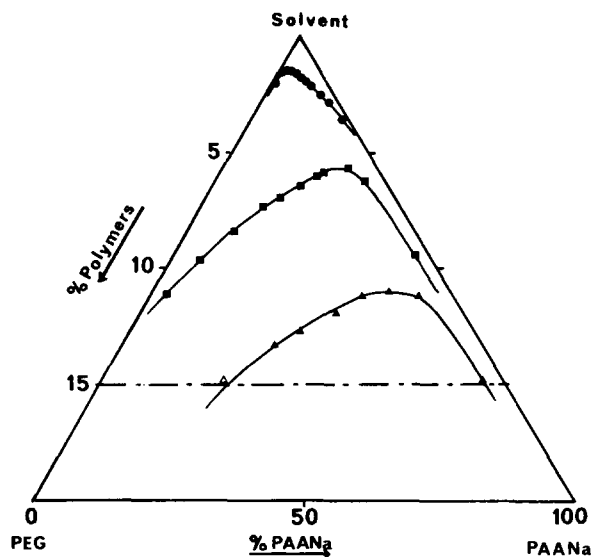


Figure 2 Phase diagram of the system PEG/PAANa/solvent: (▲) pure water; (■) 0.1 M NaCl; (●) 1 M NaCl. Open symbols indicate compatible mixtures

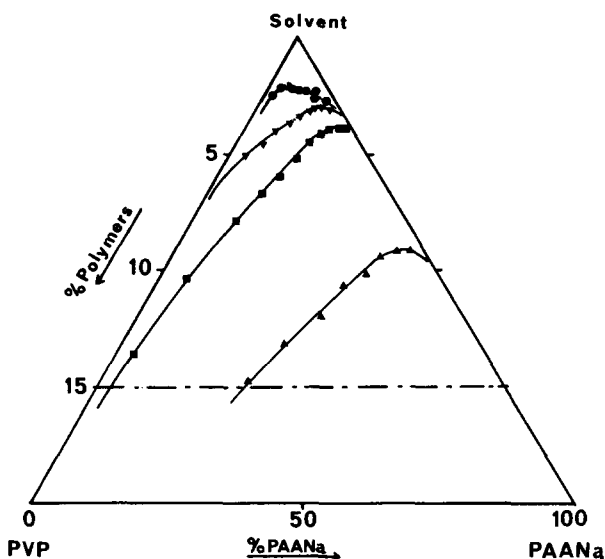


Figure 3 Phase diagram of the system PVP/PAANa/solvent: (▲) pure water; (■) 0.1 M NaCl; (▼) 0.2 M NaCl; (●) 1 M NaCl

This behaviour, in the presence of salts, is very general for the system polyelectrolyte/nonionic polymer. In Figure 3 four cloud point curves for the system PVP/PAANa at various concentrations of NaCl (0, 0.1, 0.2 and 1 M NaCl) are shown. Addition of NaCl brings the curve up towards the solvent vertex in the same way as for the PEG/PAANa system. Even the PAM/PAANa couple, which was compatible in pure water (at least for polymer concentrations <15%), exhibits phase separation after addition of 0.1 M NaCl and behaves like the other systems when the salt concentration reaches 1 M (Figure 4). Similar results were obtained when mixtures of PVP with half-neutralized poly(acrylic acid) (PAANa-50) were used. The phase separation curves in aqueous NaCl solutions (0.2 and 1 M) are given in the Figure 5.

In order to clearly point out the difference in the behaviour of ionic/nonionic and nonionic/nonionic polymer systems in the presence of salts, the cloud points for the system PEG/PAM in pure water, in 0.1 M NaCl and in 1 M NaCl are shown in Figure 6. It is obvious

that all experimental points lie almost on the same curve. A similar insensibility to the presence of salt was reported for the system PEG/dextran<sup>9,11</sup> and for other nonionic polymer systems<sup>9</sup>.

The above results seem to confirm the idea that the peculiar behaviour of polyelectrolyte/nonionic polymer system is due to the ionic nature of one of the macromolecular species. This implies that the polyelectrolyte counterions are at least partially free in solution and, from a thermodynamic point of view, they must be taken into account as a complementary constituent of the system.

Qualitatively our results can be interpreted on the basis of the model proposed by Albertsson for the partition of charged particles between two aqueous phases (ref. 8, p. 50). Let us consider a mixture of a nonionic polymer (e.g. PEG) with a polyelectrolyte (e.g. PAANa) in pure water and assume a total condensation of the counterions on the polyelectrolyte chain. In this case phase separation

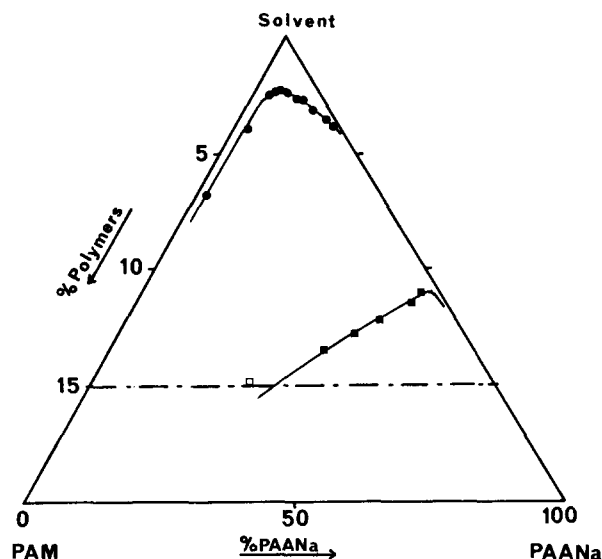


Figure 4 Phase diagram of the system PAM/PAANa/solvent: (■) 0.1 M NaCl; (●) 1 M NaCl. Open symbols indicate compatible mixtures. The system is compatible in pure water, at least for polymer concentrations <15%

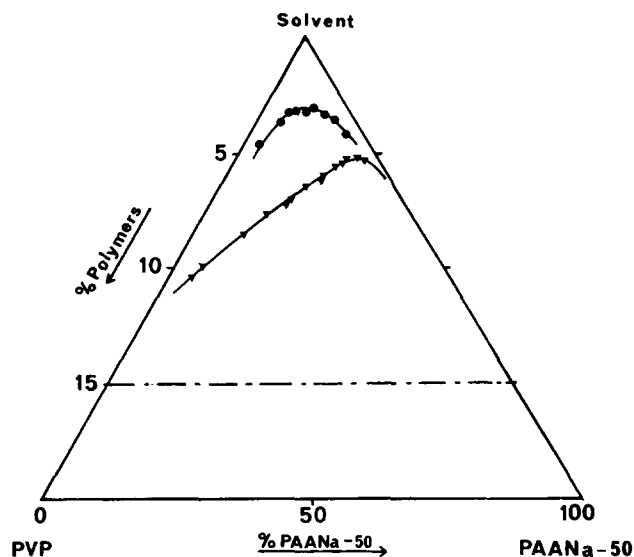


Figure 5 Phase diagram of the system PVP/PAANa-50/solvent: (▼) 0.2 M NaCl; (●) 1 M NaCl

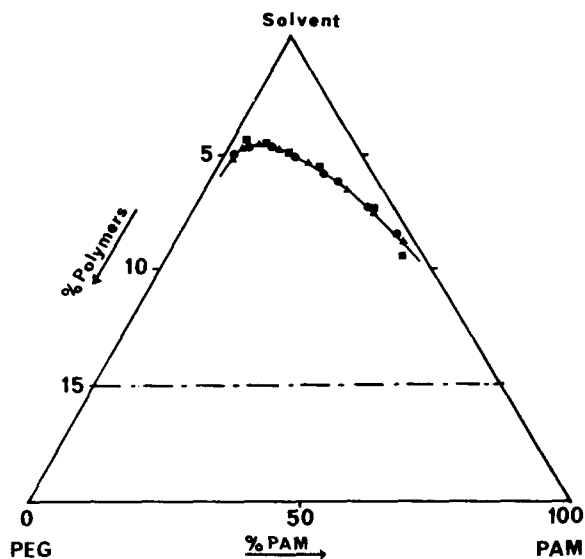


Figure 6 Phase diagram of the system PEG/PAM/solvent. Symbols as in Figure 2

would occur in the same way as in a mixture of nonionic polymers, that is a rather symmetrical diagram (Figure 6) with a large diphasic region where each of two phases contains predominantly one of the polymeric species would result. In fact, dissociation of the polyelectrolyte occurs and the small counterions tend to migrate in the whole system and carry polyacrylate chains along by electrostatic interaction. Consequently, the solubility of polyelectrolyte in the PEG phase is increased. Because a similar phenomenon does not exist for the nonionic polymer (PEG), its solubility in the PAANa phase remains low and the phase diagram is asymmetrical as observed in Figure 2.

If a salt (e.g. NaCl) is added in the system, the charge of sodium ions present in the PEG phase could be balanced by chlorine ions and not necessarily by poly-anions. Therefore, the solubility of PAA<sup>-</sup> in the nonionic polymer phase decreases as the salt concentration increases and we find again the typical features of mixtures of nonionic polymers. There is a high incompatibility and a displacement of the cloud point curve towards the side of low molecular weight polymer (Figures 2-4, upper curves).

In other words, for neutral polymers the phase equilibrium is expressed simply by the equality of the chemical potentials of each constituent in the two phases, while for ionic species electrochemical potentials must be considered.

#### Influence of neutralization degree of PAA

The compatibilization of polymers in solution through specific interactions was first studied for polymers soluble in organic solvents<sup>22-25</sup>. In a pioneering work Djadoun, Goldberg and Morawetz<sup>22</sup> showed that the miscibility in a ternary system containing two incompatible polymers is enhanced as they introduce increasing densities of strongly interacting groups into the polymeric chains. When the density of interacting groups is high enough, complex coacervation occurs and the phase diagram contains a closed loop such that a solution containing both polymers is in equilibrium with a nearly pure solvent. If the two kinds of macromolecules have the

same density of interacting groups, the closed diagram seems to be a symmetrical loop<sup>22,23</sup>.

Minh and Nose<sup>12,13,26</sup> studied systems of water soluble polymers, especially the effect of neutralization degree of PAA,  $\alpha$ , on the phase diagram of poly(vinyl alcohol)/PAANa system in pure water<sup>13</sup>. They investigated the range of neutralization degrees between 100% and 40% and showed that the compatibility increases when the neutralization degree decreases. This compatibility enhancement is ascribed to the formation of hydrogen bonds between the acid groups (COOH) of PAA and the hydroxyl groups of PVA. Unfortunately, they do not give any phase diagram for neutralization degrees lower than 30% for which polymer complex formation is well known<sup>27,28</sup>. Recently, Eustace, Siano and Drake<sup>29</sup> published phase diagrams for the system PAM/PAA under conditions of complexation ( $\alpha \leq 5\%$ ).

In this study we investigate the changes in phase diagram of the couple PVP/PAANa- $\alpha$ , which can be presented as an incompatible system ( $\alpha = 100\%$ , Figure 3) or as a polymer complex ( $\alpha = 0\%$ )<sup>27,28,30,31</sup>. In the light of results presented above which are related to the salt effect on the phase separation, it seems suitable to work under high ionic strength conditions (e.g. 1 M NaCl) to completely screen the polyelectrolyte effects. Nevertheless, the salt concentration is limited to  $0.2 \text{ mol l}^{-1}$  because of the poor solubility of partially neutralized PAA in more concentrated salt solutions (for  $\alpha = 0\%$ , PAA precipitates when the concentration of NaCl is higher than about  $0.3 \text{ mol l}^{-1}$  (Refs 32, 33)).

Figures 7 and 8 display the phase diagrams for the couple PVP/PAANa- $\alpha$  in 0.2 M NaCl and for various neutralization degrees,  $\alpha$ , of PAA. When the degree of neutralization decreases from 100% to 50% the compatibility is slightly enhanced and the maximum of the cloud point curve is lowered from 3% to 5% in polymer. With further decrease in  $\alpha$  the system becomes rapidly compatible. For  $\alpha = 25\%$  all mixtures are homogeneous, at least if the polymer concentration is lower than 15%. The system remains homogeneous when  $\alpha = 20\%$ , but for lower  $\alpha$  values an abrupt complex coacervation appears. Under these conditions the phase

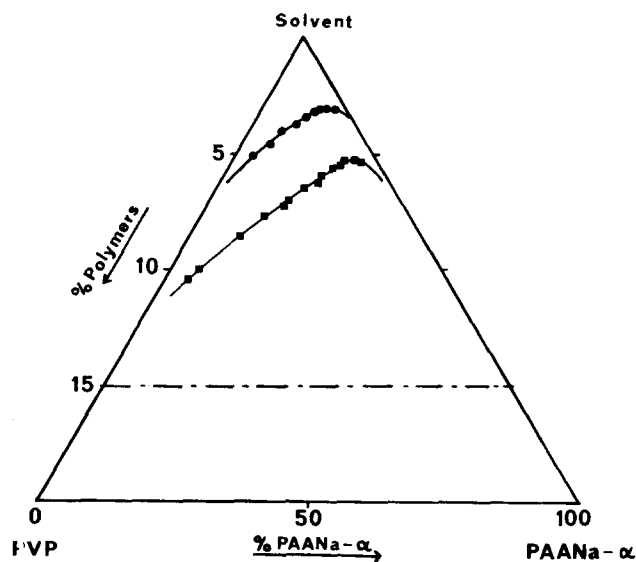


Figure 7 Phase diagram of the system PVP/PAANa- $\alpha$ /solvent for two degrees of neutralization of PAA: (●)  $\alpha = 100\%$ ; (■)  $\alpha = 50\%$ . Solvent: 0.2 M NaCl. For  $\alpha = 25\%$  and  $20\%$  the mixtures are homogeneous

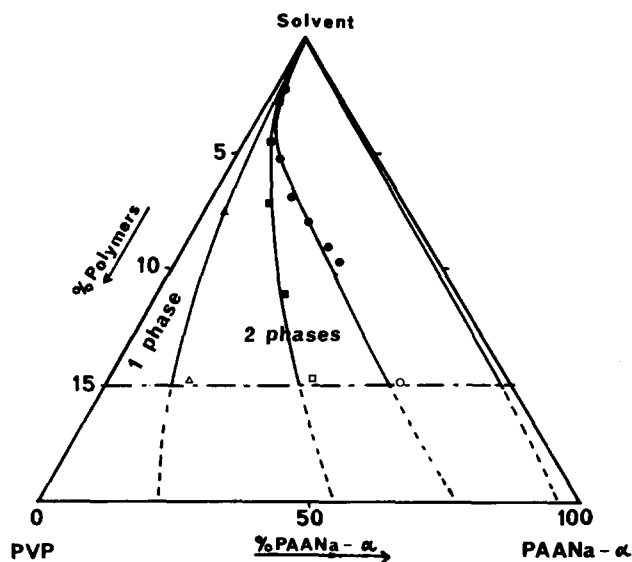


Figure 8 System as in Figure 7. (●)  $\alpha=18\%$ ; (■)  $\alpha=15\%$ ; (▲)  $\alpha=10\%$ . Open symbols indicate compatible mixtures. When  $\alpha=0\%$  the biphasic region practically takes up the whole diagram

diagrams are asymmetrical. The cloud point curve constitutes the upper part of an asymmetrical closed loop which divides the ternary diagram almost in two parts: a monophasic (PVP side) and a biphasic (near to the PAANa- $\alpha$  side). The lower the  $\alpha$  value the larger the biphasic region (Figure 8). At the limit of  $\alpha=0\%$  the biphasic region nearly takes up the whole diagram. These biphasic mixtures are constituted of a concentrated phase (coacervate), corresponding to a polymer complex swollen by the solvent, in equilibrium with a dilute phase (supernatant).

The influence of neutralization degree of PAA on the phase separation behaviour of PVP/PAANa- $\alpha$  system is attributed to the formation of H-bonds between the acid groups of PAA and the carbonyl groups of PVP<sup>27,28,34,35</sup>. This hydrogen bonding is very important for values of  $\alpha$  lower than 25% and leads to polymer complex formation<sup>30,31</sup>. The drastic extension of the biphasic region when  $\alpha$  becomes small enough can be explained by the cooperativity of polymer complexation mechanism<sup>36,37</sup>.

The great asymmetry of coacervation ternary diagrams presented in Figure 8 is probably due either to a polyelectrolyte effect, similar to that of incompatible systems (Figures 2–4), or to the difference in density of interacting groups, respectively, along the PAANa- $\alpha$  and PVP chains. This last effect was already observed with polymer mixtures in organic solvents<sup>23</sup> and in aqueous solution<sup>29,38</sup>. However, it is very difficult to estimate the importance of each of the above effects on the cloud point curve asymmetry. Further experiments with symmetrical systems are required.

Therefore, an adequate choice of water-soluble polymers leads to ternary systems ranging from high incompatibility to total miscibility and finally to complex coacervation. This behaviour is reversible (depending on the pH and the ionic strength) and can be worthwhile if used to the partition and purification processes of such things as biopolymers and cell organelles.

## CONCLUSIONS

Mixtures of poly(sodium acrylate) with nonionic polymers

in pure water phase-separate at polymer concentrations much higher than those expected for equivalent mixtures of nonionic polymers. Moreover, the phase diagrams are asymmetrical and displaced towards the poly(sodium acrylate) side. Addition of a salt (NaCl), even in small amounts, brings up the cloud point curve rapidly. When the salt concentration is high enough the system behaves as a mixture of nonionic polymers. In fact, the polyelectrolyte counterions increase the solubility of PAANa in the phase of nonionic polymer. Another factor influencing the phase separation of these systems is the neutralization degree of PAANa. A decrease in neutralization degree, at first compatibilizes the system and finally leads to complex coacervation. The control of both neutralization degree and ionic strength is of the first importance when aqueous biphasic systems are to be used for purification of biopolymers.

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