Phase behaviour of aqueous solutions of neutral and charged polymer mixtures

M. Yu* and J. de Swaan Arons
Faculty of Chemical Technology and Materials Science, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands
(Received 24 August 1993)

A model for the Gibbs energy of mixing for the systems composed of water, neutral polymer and polyelectrolyte is established by combining the theories of Flory–Huggins and Manning, and by treating the free counterions as complementary species. The phase behaviour of two model systems and its dependence on the salt concentration are studied by using the model. The basic features of the phase behaviour of the systems can be captured, and the calculated results are in good agreement with the experimental data.

(Keywords: polyelectrolyte; phase behaviour; salt-effect)

INTRODUCTION

It is often found that aqueous solutions of binary neutral polymer mixtures may phase-separate into two isotropic solutions, each enriched in one of the polymer components, even when the polymer concentrations are relatively low[1]. Such 'polymer incompatibility' is due to the large number of segments in the polymer molecules and the small gain in the entropy of mixing of unlike polymers. The higher the molecular weights of the polymeric components, then the more immiscible the two polymers will be; similarly, the larger the difference between the molecular weights of the polymers, the more asymmetric will be the tie lines and binodal curves. Curve 1 in *Figure 1* shows the cloud point curve of water/poly(ethylene glycol) (PEG)/polyacrylamide (PAM) mixtures[2]. It can be seen that the curve is asymmetrical and displaced towards the *low*-molecular-weight polymer, as predicted theoretically[3]. The situation is quite different, however, for water/neutral polymer/polyelectrolyte mixtures. Such systems may form homogeneous mixtures even when the polymer concentrations are relatively high. It is the charge density of the polyelectrolyte, rather than the molecular weights of the polymeric components, which dominates the asymmetry of the phase diagram. As an example, curve 2 in *Figure 1* shows the cloud point curve of water/PEG/Na salt of poly(acrylic acid) (PAANa) mixtures[2]. Although the molecular weight of the PAANa is much larger than that of the PEG, the cloud point curve of the water/PEG/PAANa mixtures is clearly displaced to the side of the PAANa, although the PAANa has a higher molecular weight than the PAM, the cloud point curve of the water/PEG/PAANa system is much higher than that of the water/PEG/PAM system, thus indicating that PAANa is more miscible with PEG in water than PAM. However, the high miscibility can be reduced significantly and the unusual asymmetry of the cloud point curves can be made less pronounced by adding a small amount of low-molecular-weight (LMW) salt to the aqueous solutions of neutral and charged polymer mixtures. If enough salt is added, the phase behaviour will be quite similar to that shown by aqueous solutions of binary neutral polymer mixtures, and the binodal (and also the cloud point) curves will be displaced towards the *low*-molecular-weight polymer.

Although thermodynamic theories for aqueous solutions of neutral polymer mixtures have become so sophisticated that the experimental data of such systems can be correlated within experimental accuracy, the thermodynamic study of aqueous solutions of polyelectrolytes is very scant[4–9]. To our knowledge, no model has yet been shown which is able to describe quantitatively the phase behaviour of aqueous solutions of binary charged and neutral polymer mixtures and its dependence on the salt concentration. It is the objective of this work to propose an approach, which should be valid for both with and even without salt, to model the phase behaviour of such systems and its dependence on salt. Our approach is similar to that of Minh and Nose[6,7] and also that of Khokhlov and coworkers[8,9], in the sense that we use the Flory–Huggins theory and treat the free counterion as a complementary constituent of the system. The differences between our approach and those of these other workers is twofold. First, the electrostatic interactions are modelled by using Manning's theory[10], which is believed to be more realistic for polyelectrolyte solutions. Secondly, we accept the ideas of Manning on counterion-condensation and suggest that only free counterions contribute to the enhanced miscibility, which makes this approach useful for both weakly charged and strongly charged polyelectrolyte solutions.

THERMODYNAMIC MODEL

Consider a mixture of a neutral polymer A of volume fraction ϕ_A, a charged polymer B of volume fraction ϕ_B, and a solvent S of volume fraction ϕ_S ($\phi_A + \phi_B + \phi_S = 1$).

---

*To whom correspondence should be addressed

0032-3861/94/16/3499–04

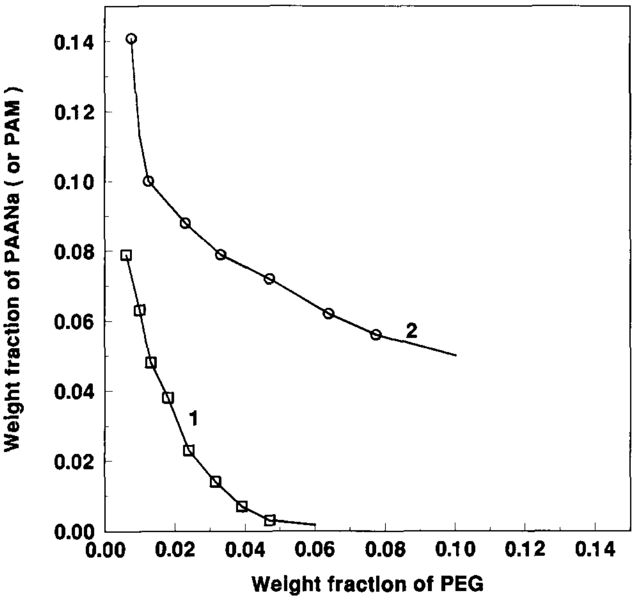

Figure 1 Phase diagram of aqueous solutions of binary polymer mixtures: (1) PEG ($M=36\,000$)/PAM ($M=110\,000$); (2) PEG ($M=36\,000$)/PAANa ($M=150\,000$). Experimental data from ref. 2

In addition, many small ions are present in the system, including counterions which appear as a result of the dissociation of polymer B and the LMW salt, and co-ions which are derived solely from the salt. In our analysis, the following species are defined: solvent, co-ions, free counterions, neutral polymer, and 'net polyions', i.e. the polyion together with the counterions bound to it. For the sake of simplicity, we assume that both the salt and the charged groups of polymer B are univalent (extension to multivalent cases is straightforward). In addition, we neglect the self-volume of the small co-ions and counterions, and we assume that all interactions involving the small ions are of the nature of Coulomb interactions. Therefore, in the framework of the Flory–Huggins lattice theory, the expression for the Gibbs energy of mixing may be written in the following form:

$$\frac{\Delta G}{VRT}=\frac{1}{b^3}\left(\frac{\phi_A}{N_A}\ln\phi_A+\frac{\phi_B}{N_B}\ln\phi_B+\phi_s\ln\phi_s+\chi_{AS}\phi_A\phi_S+\chi_{BS}\phi_B\phi_S+\chi_{AB}\phi_A\phi_B\right)+\frac{1}{b^3}[c_sb^3+(1-\theta)\phi_B]\ln[c_sb^3+(1-\theta)\phi_B]-\frac{\xi}{2}(1-\theta)^2\frac{\phi_B}{b^3}\ln[2c_sb^3+(1-\theta)\phi_B] \quad (1)$$

where χ_{ij} is the interaction parameter between the i and j components (i, j = A, B, or S), N_i is the number of segments in polymer i, V is the volume of the system ($V=n_tb^3$, where n_t is the total number of lattice sites in the Flory model and b^3 is the characteristic spacing of the lattice), c_s is the molarity of the LMW salt, $(1-\theta)$ is the fraction of free counterions from polymer B, and ξ is the charge parameter of polymer B.

The terms contained within the first brackets are from the Flory–Huggins theory. The first three terms represent the contributions to the Gibbs energy from the translational motion entropies of the polymer chains and the solvent molecules, respectively. The next three terms describe the non-electrostatic interaction of the components. The assumption involved in these terms is that the segments of both charged and neutral polymers are distributed uniformly in the system. This assumption should be quite acceptable providing that the polymer concentration is not too low.

The seventh term in equation (1) is the contribution to the Gibbs energy arising from the mixing of free counterions, which is simply the product of the mole number n and the chemical potential μ of the free counterions, i.e.

$$\Delta G_{\mathrm{free}}=n_{\mathrm{free}}\,\Delta\mu_{\mathrm{free}} \quad (2)$$

Because of the high electrostatic potential around the polyion and possibly the presence of some short-range interactions, a fraction of the counterions is bound to the polyion. However, the LMW salt is assumed to be completely dissociated. Therefore, the total number of free counterions should be the sum of the counterions dissociated from the LMW salt and those from the polyelectrolyte, minus the fraction of counterions that are bound to polyions, i.e.

$$n_{\mathrm{free}}=\left[c_s+(1-\theta)\frac{\phi_B}{b^3}\right]V \quad (3)$$

In evaluating the chemical potential of the free counterions, it is assumed that all short-range interactions involving the free counterions may be neglected. Therefore, without including the long-range interactions, which will be discussed separately below, the chemical potential of the free counterions may be written as

$$\Delta\mu_{\mathrm{free}}=RT\ln\left[c_s+(1-\theta)\frac{\phi_B}{b^3}\right] \quad (4)$$

The last term in equation (1) is the contribution associated with the electrostatic free energy of interaction, ΔG_{el}. According to Manning[10,11]:

$$\frac{\Delta G_{\mathrm{el}}}{VRT}=-\xi\frac{\phi_B}{b^3}(1-\theta)^2\ln[1-\exp(-\kappa a)]\approx\xi\frac{\phi_B}{b^3}(1-\theta)^2\ln\kappa \quad (5)$$

In this equation, a is the axial charge spacing on the charged polymer, and the Debye screening parameter κ, including all free small ions, is given by

$$\kappa^2=(4\pi)10^3N_{\mathrm{av}}\xi a\left[2c_s+(1-\theta)\frac{\phi_B}{b^3}\right] \quad (6)$$

where N_{av} is the Avogadro constant. Because the contributions from the electrostatic interactions between the small ions are of a higher order in κ and are negligible when compared to those involving the polyions, equation (5) includes only interactions between the net polyion charge and its ion atmosphere, plus the self-energy of the net charge. The assumptions involved in equation (5) are as follows[12]:

(i) the real polyelectrolyte can be replaced by a line of length L with a continuous charge distribution;
(ii) at low ionic strengths counterion-condensation limits the charge density such that $\xi_{\mathrm{eff}}\leqslant 1$;
(iii) the linearized Poisson–Boltzman equation adequately describes the behaviour of the uncondensed small free ions;
(iv) the effective Debye length given in equation (6) adequately accounts for interactions between polyions in concentrated solution.

In equation (1), several terms that are proportional to ϕ_B have been omitted because they do not contribute to the phase equilibrium calculation.

RESULTS

From equation (1) it is possible to find the corresponding equation for the spinodal curve:

$$\left(\frac{1}{\phi_B N_B}+\frac{1}{\phi_S}-2\chi_{BS}+\frac{(1-\theta)^2}{c_s b^3+(1-\theta)\phi_B}-\frac{\xi(1-\theta)^3}{2c_s b^3+(1-\theta)\phi_B}+\frac{\xi(1-\theta)^4\phi_B}{2(2c_s b^3+(1-\theta)\phi_B)^2}\right)\times\left(\frac{1}{\phi_A N_A}+\frac{1}{\phi_s}-2\chi_{AS}\right)=\left(\frac{1}{\phi_S}+\chi_{AB}-\chi_{AS}-\chi_{BS}\right)^2 \tag{7}$$

The corresponding equations for the critical point can also be calculated by using equation (1).

In order to calculate the binodal curve, the expressions for the chemical potentials of each component are needed. These can also be obtained from equation (1), as shown below:

$$\begin{aligned}\frac{(\mu_S-\mu_S^\circ)b^3}{RT}&=\ln\phi_S+\left(1-\frac{1}{N_A}\right)\phi_A+\left(1-\frac{1}{N_B}\right)\phi_B+\chi_{AS}\phi_A^2\\&+\chi_{BS}\phi_B^2+(\chi_{AS}+\chi_{BS}-\chi_{AB})\phi_A\phi_B\\&+c_s b^3\ln[c_S b^3+(1-\theta)\phi_B]\\&-(1-\theta)\phi_B+\frac{\xi(1-\theta)^3\phi_B^2}{4c_s b^3+2(1-\theta)\phi_B}\end{aligned} \tag{8}$$

$$\begin{aligned}\frac{(\mu_A-\mu_A^\circ)b^3}{RT}&=\ln\phi_A+(1-N_A)\phi_S+\left(1-\frac{N_A}{N_B}\right)\phi_B\\&+N_A[\chi_{AS}\phi_S^2+\chi_{AB}\phi_B^2+(\chi_{AS}+\chi_{AB}-\chi_{BS})\phi_S\phi_B]\\&+N_A c_s b^3\ln[c_s b^3+(1-\theta)\phi_B]\\&-N_A(1-\theta)\phi_B+N_A\frac{\xi(1-\theta)^3\phi_B^2}{4c_s b^3+2(1-\theta)\phi_B}\end{aligned} \tag{9}$$

$$\begin{aligned}\frac{(\mu_B-\mu_B^\circ)b^3}{RT}&=\ln\phi_B+(1-N_B)\phi_S+\left(1-\frac{N_B}{N_A}\right)\phi_A\\&+N_B[\chi_{BS}\phi_S^2+\chi_{AB}\phi_A^2+(\chi_{BS}+\chi_{AB}-\chi_{AS})\phi_S\phi_A]\\&+N_B(c_s b^3+(1-\theta))\ln[c_s b^3+(1-\theta)\phi_B]\\&+N_B(1-\theta)(1-\phi_B)\\&-N_B\frac{\xi}{2}(1-\theta)^2\ln[2c_s b^3+(1-\theta)\phi_B]\\&-N_B\frac{\xi}{2}(1-\theta)^3\frac{\phi_B(1-\phi_B)}{2c_s b^3+(1-\theta)\phi_B}\end{aligned} \tag{10}$$

In this model, there are several parameters for each system. The pure component parameters include N_A, N_B, and ξ. The number of segments of the polymer molecules, N_A and N_B, may be calculated as the degrees of polymerization. The charge parameter ξ can be simply determined as $\xi=\tau d_B/l_B$ (where τ is the fraction of charged segments, l_B is the monomer contour length of the polyelectrolyte, and d_B is the Bjerrum length, equal to ~ 7.18 Å at 25°C)[13]. The pure component parameters that were used in our calculations are given in *Table 1*.

The binary parameters in the model are the Flory–Huggins parameters χ_{AS}, χ_{BS}, and χ_{AB}, which characterize the short-range interactions between the different components. Although the change in concentration of the LMW salt changes the quality of the solvent and also the solvent-related short-range interaction parameters, it is believed that the influence of the salt concentration on χ_{AS} and χ_{BS} is not significant. Evidently, the very weak dependence of χ_{AS} and χ_{BS} on the salt concentration cannot be responsible for the high sensitivity of the phase behaviour of such mixtures on the ionic strength. Therefore, these short-range interaction parameters are treated as being salt-independent parameters. In solutions with very high salt concentrations, polyelectrolytes behave like neutral polymers and our model then simplifies to the Flory–Huggins theory. Therefore, the value of these binary parameters can be estimated by fitting the Flory–Huggins theory to the cloud-point data of the mixtures at very high salt concentrations. The short-range interaction parameters of our model systems are given in *Table 2* and will be used in calculations for solutions with different salt concentrations.

Another very important parameter in our model is the fraction of the free counterions of the polyelectrolyte. In Manning's limiting law, this parameter is treated as a constant, which is dependent only on the charge density of the charged polymer. He suggests that $(1-\theta)=1$ if $\xi<1$, and $(1-\theta)=1/\xi$ if $\xi\geqslant 1$. However, for polyelectrolyte solutions of finite concentration, recent experimental results show that this parameter depends on many factors, including salt concentration and polyelectrolyte concentration. It seems to us that the quantitative estimation of the fraction of free counterions as a function of both salt and polyelectrolyte concentrations is still an open question. Therefore, we regard this parameter as being an adjusted parameter. Our other parameter is the lattice spacing parameter, b^3, which is an empirical one. Although this parameter is very important for modelling the salt-effect on the phase behaviour, it is irrelevant for modelling the phase behaviour of salt-free solutions.

Figures 2 and *3* show the calculated spinodal curves, binodal curves and critical points which were obtained by using the model, together with the experimental cloud

Table 1 Pure component parameters used in calculations

Polymer	Molecular weight	Degree of polymerization	Charge parameter
Poly(ethylene glycol) (PEG)	36000	795	–
Poly(vinylpyrrolidone) (PVP)	160000	1441	–
Na salt of poly(acrylic acid) (PAANa)	150000	2113	2.8
Polyacrylamide (PAM)	110000	1571	–

Table 2 Estimated parameters used in calculations of the model systems examined in this work

System	χ_{AS}	χ_{BS}	χ_{AB}	$1-\theta$	b^3
PEG/PAANa	0.436	0.35	0.40	0.031	0.0045
PVP/PAANa	0.40	0.35	0.5	0.031	0.004

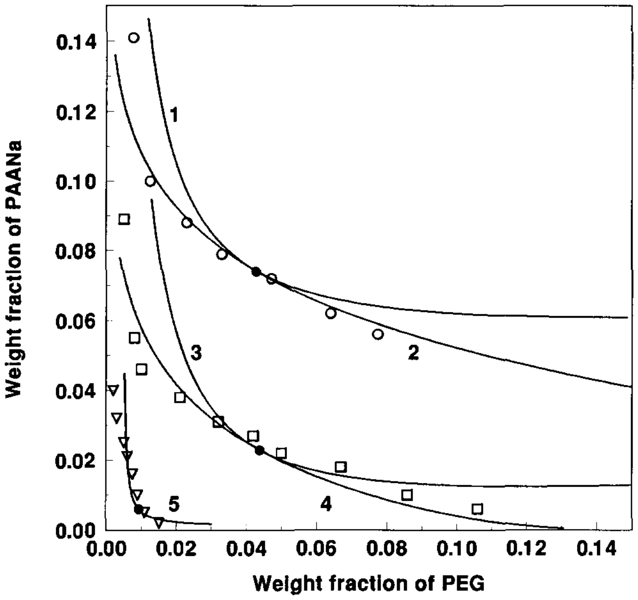

Figure 2 Phase diagram of the PEG/PAANa/brine system with cloud points at $C_s=0$ (○), 0.1 M (□) and 1.0 M (▽), using experimental data from ref. 2. Results from this work: (1) spinodal curve at $C_s=0$; (2) binodal curve at $C_s=0$; (3) spinodal curve at $C_s=0.1$ M; (4) binodal curve at $C_s=0.1$ M; (5) spinodal curve at $C_s=1.0$ M; (●) critical points

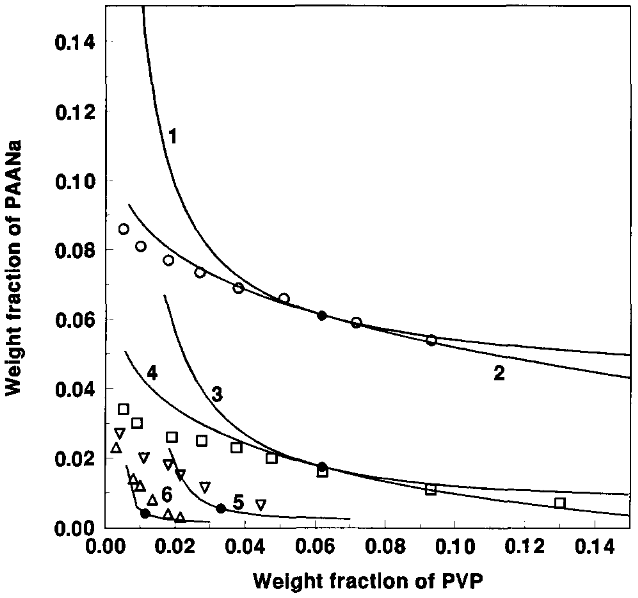

Figure 3 Phase diagram of the PVP/PAANa/brine system, with cloud points at $C_s=0$ (○), 0.1 M (□), 0.2 M (▽) and 1.0 M (△), using experimental data from ref. 2. Results from this work: (1) spinodal curve at $C_s=0$; (2) binodal curve at $C_s=0$; (3) spinodal curve at $C_s=0.1$ M; (4) binodal curve at $C_s=0.1$ M; (5) spinodal curve at $C_s=0.2$ M; (6) spinodal curve at $C_s=1.0$ M; (●) critical points

points, for two model systems. In spite of polydispersity in the molecular weights of the polymers, the two model systems are assumed to be strictly ternary mixtures composed of a neutral polymer A, a charged polymer B, and solvent, together with LMW salt. The values of the fraction of the free counterions and those of the lattice spacing parameters used in the calculations are also listed in *Table 2*. It can be seen from the two figures that the calculated results fit the experimental data reasonably well. This model can encompass all of the basic features of the phase behaviour of aqueous solutions of binary charged and neutral polymer mixtures. In salt-free solutions, the miscibility between the neutral polymer and the polyelectrolyte is very high and the asymmetry of the binodal curve is unusual, because it is displaced to the side of the high-molecular-weight polymer. By adding a small amount of salt to the system, the very high miscibility can be reduced significantly and the unusual asymmetry of the binodal curve can be made less pronounced.

CONCLUSION

An expression for the Gibbs energy of mixing for aqueous solutions of charged and neutral polymer mixtures is established by combining the theories of Flory–Huggins and Manning, and by treating the free counterion as a complementary component. This model should be valid for polyelectrolyte solutions, with or even without salt, when the concentrations are not very low. Although the model may be very crude, as a result of the fact that all short-range interactions involving small ions and the long-range interactions between small ions have been neglected, all of the basic features of the phase behaviour of such systems can be captured by using the model. The spinodal and binodal curves, and the critical points of two model systems at different salt concentrations have been calculated by using the model. The calculated binodal curves fit the experimental cloud point data quite well, and the salt-effect on the phase behaviour can also be accounted for.

ACKNOWLEDGEMENT

The authors thank STN (Netherlands) and Unilever Research Laboratorium (Vlaardingen) for financial support.

REFERENCES

1 Albertsson, P. A. 'Partition of Cells, Particles, and Macromolecules', Wiley, New York, 1986
2 Perrau, M. B., Iliopoulos, I. and Audebert, R. *Polymer* 1989, **30**, 2112
3 Scott, R. L. *J. Chem. Phys.* 1949, **17**, 279
4 Voorn, M. J. and Overbeek, J. Th. G. *J. Cell. Comp. Physiol.* 1957, **49**, Suppl. 1, 7
5 Veis, A. and Aranyi, C. *J. Phys. Chem.* 1961, **65**, 1798
6 Minh, L. V. and Nose, T. *Polym. J.* 1983, **15**, 145
7 Minh, L. V. and Nose, T. *Polym. J.* 1983, **15**, 159
8 Nyrkova, I. A., Khokhlov, A. R. and Kramarenko, Ye. Yu. *Polym. Sci. USSR (Engl. Transl.)* 1990, **32**, 852
9 Khokhlov, A. R. and Nyrkova, I. A. *Macromolecules* 1992, **25**, 1493
10 Manning, G. S. *J. Chem. Phys.* 1969, **51**, 924
11 Manning, G. S. *Acc. Chem. Res.* 1979, **12**, 443
12 Russel, W. B. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 1233
13 Reed, W. F., Ghosh, S., Medjahdi, G. and Francois, J. *Macromolecules* 1991, **24**, 6189