Phase Diagram of Polyelectrolyte Solutions: Weak Polymer Effect

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Received August 21, 2002

ABSTRACT: We present a mean field theory of phase diagram of solutions of flexible polyelectrolytes with neutralizing counterions. We show that the temperature−concentration curve, corresponding to the coexistence of polymer-rich and polymer-poor solutions, is highly asymmetric, and the degree of polymerization of the polymer has only a weak effect. We have addressed the role of added salt in destabilizing the homogeneous phase of polyelectrolyte solutions, within the framework of quasi-two-component description of the multicomponent system.

Introduction

Theoretical formulations of phase behavior of polyelectrolyte solutions are difficult due to the coupled long-ranged correlations of electrostatic interaction and chain connectivity and due to the multicomponent nature of the system. Although the phase behavior of uncharged polymers has been extensively investigated,[1] there have been only a few attempts[2−4] on polyelectrolyte phase behavior. For two-component solutions of uncharged polymers, the molecular weight M of the polymer dictates the critical point and the coexistence curve is asymmetric in polymer concentration, with the critical polymer concentration being roughly proportional to $1/M$. This asymmetry is due to the long-ranged correlation arising from chain connectivity. Analogously, the coexistence curve for electrolyte solutions of low molar mass ions is asymmetric[5−9] due to the long-range nature of Coulomb interactions, although the molar volumes of ions are comparable. Therefore, the coexistence curve of polyelectrolyte solutions is expected to be strongly asymmetric, arising from contributions of both chain connectivity and electrostatic interactions. Preliminary theoretical attempts[2,3] suggest the opposite to this expectation. In the present paper, we show that the coexistence curve for polyelectrolyte solutions is indeed strongly asymmetric, which is dominated by electrostatic interactions and the molecular weight of the polyelectrolyte playing an insignificant role.

Theory

We consider a solution of n polyelectrolyte chains each of N segments, n_c counterions of valency Z_c, n_+ cations of valency Z_+ from dissolved salt, n_- anions of valency Z_- from dissolved salt, and n_0 solvent molecules in volume Ω. Let α be the degree of ionization of the polymer and Z_p be the effective valency of each segment so that there are $\alpha nNZ_p/Z_c$ counterions. For notational convenience, we assume that all ions and segments have the same volume $\pi\ell^3/6$ as a solvent molecule. In the absence of special effects such as chain bridging by multivalent ions, the Helmholtz free energy F of the present system is given by[10]

$$\frac{\ell^3 F}{\Omega k_B T} = f_S + f_H + f_{fl,i} + f_{fl,p} \qquad (1)$$

where f_S and f_H are respectively contributions from entropy of mixing and enthalpy of mixing. $f_{fl,i}$ is the free energy density from fluctuations in the distribution of dissociated ions, as obtained by a generalization of the Debye−Hückel theory.[11−13] $f_{fl,p}$ is the contribution from fluctuations of polymer configurations. k_BT is the Boltzmann constant times the absolute temperature.

The expressions for the various terms in eq 1 are obtained using the following procedure and assumptions, as explicitly derived in ref 10. There are three steps in the derivation of eq 1. In the first step, the free energy density of the electrically neutral solution of polyelectrolyte molecules, counterions, and dissociated ions of added salt is calculated without fluctuations in concentrations of these ions and by maintaining electroneutrality. This step leads to eq 2 below. Even in this step without consideration of fluctuations, chain connectivity is included. Next, concentration fluctuations are treated in two stages. In the second step (i.e., first stage of treatment of fluctuations), fluctuations of concentrations of counterions and dissociated ions of added salt are considered in the background of neutralizing polymers. This step is carried out using the random phase approximation, and the result is the Debye screening and $f_{fl,i}$ given by eq 7. In the third step, the remaining degrees of freedom are integrated out to consider the fluctuations of conformations of charged polymer molecules in the background of screened electrostatic field of step 2, and the result is $f_{fl,p}$. The contribution of charged monomers to electrostatic screening is contained in $f_{fl,p}$. As derived in ref 10, $f_{fl,p}$ is proportional to ξ^{-3}, where ξ is a complicated function of the polymer volume fraction ϕ, given by a set of coupled integral equations. Asymptotically, ξ is proportional to $\phi^{-3/4}$ for high salt concentrations (corresponding to semidilute solutions of uncharged polymers). For the crossover regime encountered in the present context, ξ is expected to depend on ϕ with an effective exponent η_{eff}, $\xi \sim \phi^{-\eta_{eff}}$, where $1/2 < \eta_{eff} < 3/4$. Therefore, for low polymer concentrations, we expect $f_{fl,p}$ ($\sim\phi^{3\eta_{eff}}$) to contribute less significantly to free energy density than $f_{fl,i}$ (see eq 7 for details). Motivated by this argument and analytical intractability with the inclusion of $f_{fl,p}$, we have ignored $f_{fl,p}$ in the following discussion. It must also be noted that the consequence of $f_{fl,p}$ on the phase behavior has never so far been addressed even for solutions of uncharged polymer ($f_{fl,p} \sim \phi^{9/4}$). The present approximation allows us to derive the equivalent of

10.1021/ma021456z CCC: $22.00

Flory–Huggins theory of uncharged polymer solutions to polyelectrolyte solutions by considering chain connectivity and fluctuations in concentrations of counterions and dissociated salt ions in an electrically neutral solution.

(i) f_S is given by

$$f_S = \frac{\phi}{N}\ln\phi + \alpha_1\phi\ln\phi + \left[1 - (1+\alpha_1)\phi - \left(1 + \frac{Z_+}{Z_-}\right)\phi_+\right]\ln\left[1 - (1+\alpha_1)\phi - \left(1 + \frac{Z_+}{Z_-}\right)\phi_+\right] + \left(1 + \frac{Z_+}{Z_-}\right)\phi_+\ln\phi_+ \quad (2)$$

where $\phi = nN\ell^3/\Omega$, $\phi_+ = n_+\ell^3/\Omega$, and $\alpha_1 = \alpha Z_p/Z_c$. In writing the above expression, we have utilized the incompressibility constraint $\phi + \phi' + \phi_+ + \phi_- + \phi_0 = 1$, where $\phi_0 = n_0 l^3/\Omega$, $\phi' = \alpha_1\phi$, and $\phi_- = n_-\ell^3/\Omega$, and the electroneutrality condition $n_+Z_+ = n_-Z_-$. Also, eq 2 does not contain the unnecessary terms that are independent and linear in the polymer volume fraction ϕ and linear in ϕ_+.

(ii) f_H is given by

$$f_H = -\phi^2\left[\chi(\alpha) - \frac{1}{2}\alpha^2 Z_p^{\,2}\frac{\ell_B}{\ell}\frac{1}{\kappa^2\ell^2}\right] \quad (3)$$

The first term inside the square brackets is the usual Flory–Huggins parameter corresponding to the uncharged part of the polyelectrolyte,

$$\chi(\alpha) = \frac{w_{sp}}{\ell^3}(1-\alpha)(1+\alpha_1) - \frac{1}{2}\left[\frac{w_{ss}}{\ell^3}(1+\alpha_1)^2 + \frac{w_{pp}}{\ell^3}(1-\alpha)^2\right] \quad (4)$$

with w_{ss}, w_{pp}, and w_{sp} being the pseudopotential excluded-volume parameters for solvent–solvent, segment–segment, and solvent–segment pairs, respectively. The second term inside the square brackets of eq 3 is the electrostatic energy contribution to the free energy of polyelectrolyte chains, for sufficiently large concentrations of counterions and salt ions such that the electrostatic interaction is short-ranged. Here ℓ_B is the Bjerrum length,

$$\ell_B = \frac{e^2}{4\pi\epsilon_0\epsilon k_B T} \quad (5)$$

where e is the electronic charge, ϵ_0 is the permittivity of the vacuum, and ϵ is the dielectric constant of the solution. The Debye length κ^{-1} is given by

$$\kappa^2\ell^2 = 4\pi\frac{\ell_B}{\ell}[Z_c^{\,2}\alpha_1\phi + Z_+^{\,2}\phi_+ + Z_-^{\,2}\phi_-] \quad (6)$$

The form of eq 3 was already recognized[14−16] a long time ago. However, the distinction between the present calculation and the pioneering work of Refs 14–16 is in the form of eq 6. It is necessary to include the contribution of dissociated counterions of the polyelectrolyte to κ, which in turn couples κ to ϕ, as derived in ref 10.

(iii) $f_{fl,i}$ is given by

$$f_{fl,i} = -\frac{1}{4\pi}\left[\ln(1+\kappa\ell) - \kappa\ell + \frac{1}{2}(\kappa\ell)^2\right] \quad (7)$$

with κ given by eq 6. This expression arises from charge density fluctuations in the nonneutral plasma consisting of counterions and dissociated salt ions. The contribution from fluctuations of monomer density of neutralizing polymers is contained in $f_{fl,p}$. It must be noted that the form of eq 7 is identical to that of the Debye–Hückel theory[11] for electrolyte solutions with equal number of positively and negatively charged species. In the latter case, polyelectrolyte volume fraction $\phi = 0$ and κ of eq 6 reduces to the Debye–Hückel result. The derivation of eq 7 is illustrated by considering a collection of $n_c = \alpha_1 nN$ counterions (taken as charged hard spheres of diameter ℓ) of charge Z_ce and following the theory of ref 10 as given in section II.B. The counterions constitute a nonneutral plasma.[12,13] Let $\rho(\mathbf{r})$ be the fluctuation of the counterion density from its average $\rho_0 = n_c/\Omega$. The effective electrostatic potential $\psi(\mathbf{r})$ at space location $\mathbf{r}$, solely due to the fluctuation in n_c, surrounding one counterion fixed at the origin of the coordinate system is given by the Poisson equation[12,13]

$$\nabla^2\psi(\mathbf{r}) = -\frac{Z_ce}{\epsilon_0\epsilon}\rho(\mathbf{r}) \quad (8)$$

Although one counterion is fixed, for the thermodynamic limit of $n_c \gg 1$, we assume that the fluctuation in n_c is given by the Boltzmann distribution,[12,13]

$$\rho(\mathbf{r}) = \rho_0 e^{-Z_ce\psi(\mathbf{r})/k_BT} - \rho_0 \quad (9)$$

Linearization of eq 9 and combination with eq 8 yields

$$\nabla^2\psi(\mathbf{r}) = \kappa^2\psi(\mathbf{r}) \quad (10)$$

where

$$\kappa^2 = \frac{Z_c^{\,2}e^2\rho_0}{\epsilon_0\epsilon k_BT} \quad (11)$$

such that

$$\kappa^2 l^2 = \frac{4\pi l_B Z_c^{\,2}\alpha_1\phi}{l} \quad (12)$$

as given in eq 6 (for the salt-free case). Since each counterion is taken as a charged hard sphere of diameter l, eq 10 is valid for $r > l$, with $r = |\mathbf{r}|$. Using $\nabla^2\psi(\mathbf{r}) = 0$ for $0 < r \le l$ and the boundary conditions that $\psi(r) \to 0$ as $r \to \infty$, $\psi(r)$ be continuous at l, and $\partial\psi(r)/\partial r$ be continuous at l, the Debye–Hückel form for $\psi(r)$ is obtained even for the nonneutral system of only counterions,

$$\psi(r) = \begin{cases} \dfrac{Z_ce}{4\pi\epsilon_0\epsilon r} - \dfrac{Z_ce\kappa}{4\pi\epsilon_0\epsilon(1+\kappa l)} & 0 < r < l \\[2ex] \dfrac{Z_ce\,e^{-\kappa(r-l)}}{4\pi\epsilon_0\epsilon r(1+\kappa l)} & r > l \end{cases} \quad (13)$$

The electrostatic potential ψ_i on the ith counterion from all other ions except the ith ion due to counterion density fluctuations follows from eq 13 as

$$\psi_i = -\frac{Z_c e\kappa}{4\pi\epsilon_0\epsilon(1+\kappa l)} \tag{14}$$

The Helmholtz free energy arising from the counterion density fluctuations is given by eq 2.13 of ref 10, and for the limit of $\kappa l \rightarrow 0$, $f_{\mathrm{fl,i}}$ approaches $-\kappa^3/12\pi$. The modification of this limit by the finiteness of counterions (taken as spheres of diameter l) can be derived by adopting the Debye–Hückel argument, as described in ref 11. The change in the Helmholtz free energy $\Delta F_{\mathrm{fl,i}}$, due to counterion density fluctuations, is (see ref 11 for details)

$$\Delta F_{\mathrm{fl,i}} = \sum_{i=1}^{n_c} Z_c e \int_0^1 \mathrm{d}\lambda\, \psi_i(\lambda) \tag{15}$$

where $\psi_i(\lambda)$ is the electrostatic potential acting on the ith ion where each of the counterions has the charge $\lambda Z_c e$. Substituting eq 14 into eq 15, we get

$$f_{\mathrm{fl,i}} = \frac{l^3(\Delta F_{\mathrm{fl,c}})}{\Omega k_B T} = -\frac{1}{4\pi}\left[\ln(1+\kappa l) - \kappa l + \frac{1}{2}(\kappa l)^2\right] \tag{16}$$

This is the same equation as eq 7 for the salt-free case. When salt ions are present, the same assumptions used in deriving eq 16 lead to eq 7. It must be remarked that the free energy density given by eqs 1–7 is different from those of refs 2 and 3 and other previous theories.[17,18] More work is needed to sort out the relative merits of underlying assumptions employed in various theories, including ours.

Results

Salt-Free Case. First, we consider "salt-free" polyelectrolyte solutions, with $\phi_+ = 0 = \phi_-$. By taking the second derivative of F with respect to ϕ, we get the spinodal curve to be

$$\left(\alpha_1 + \frac{1}{N}\right)\frac{1}{\phi} + \frac{(1+\alpha_1)^2}{1-(1+\alpha_1)\phi} - 2\chi - \frac{1}{16\pi}\frac{1}{\sqrt{\phi t}}\frac{1}{(\sqrt{t}+\sqrt{\phi})^2} = 0 \tag{17}$$

where t is the reduced temperature,

$$t = \frac{\ell}{4\pi\ell_B Z_p Z_c \alpha} \tag{18}$$

The coexistence curve is calculated by stipulating the chemical potentials of the components to be the same values in the coexisting phases. The critical point is obtained by solving eq 17, in conjunction with $\partial^3 F/\partial\phi^3 = 0$. The phase diagram is illustrated in Figure 1 for $N = 100$, $Z_p = 1 = Z_c$, $\alpha = 1$, and $\chi = 1/(20\pi t)$ (corresponding roughly to a value of 0.6 at room temperatures). The full curve and the dashed curve correspond respectively to the coexistence and spinodal curves. These curves are asymmetric in ϕ, and the critical polyelectrolyte concentration ϕ_c is very small. The smallness of ϕ_c allows an approximate analytical evaluation of the critical point to be

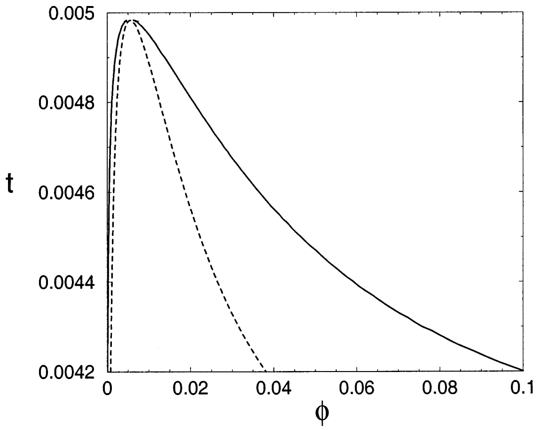

Figure 1. Coexistence and spinodal curves for the salt-free case. t is the reduced temperature as defined in eq 18, and ϕ is the volume fraction of the polyelectrolyte.

$$\phi_c = t_c = \frac{1}{64\pi}\frac{1}{\alpha_1 + \frac{1}{N}}$$
$$\left(\frac{\ell}{\ell_B}\right)_c = \frac{1}{16}\frac{Z_c^{\,2}\alpha_1}{\alpha_1 + \frac{1}{N}} \tag{19}$$

These results reduce to the values of the restricted primitive model[5-9] of electrolytes with $N = 1, \alpha = 1$, and $Z_c = 1 = Z_p$. The most important feature of eq 19 is that polylelectrolyte molecular weight appears only as a small correction to the degree of ionization of the polymer. Numerical solutions of eq 17 for ϕ_c not very small do not remove this weak polymer effect.

Effect of Added Salt. The polyelectrolyte solution is truly a multicomponent system, and the phase diagram needs to be appropriately constructed. It is necessary to compute the chemical potential of each component and maintain the Donnan membrane polyelectrolyte equilibrium. For the nondilute polyelectrolyte solutions of present interest, this computation requires substantial numerical work which is in progress. To gain some insight into the role of added salt on polyelectrolyte phase behavior, we imagine the solution to be a quasi-two-component system. This then demands a choice of distributing the ions of added salt inside the system. We make the particular choice of each polyelectrolyte chain getting the same number of n_+ and n_- ions everywhere in the solution. With this choice, $\phi_+ + \phi_- = \gamma\phi$, where $\gamma = (1 + Z_+/Z_-)\phi_+/\phi$. Taking γ as a fixed parameter (i.e., fixing the ratio of salt concentration to the polymer concentration), we get the same equation as eq 17 for the spinodal curve, with α_1 replaced by $\alpha_1 + \gamma$, and t is now given by

$$t = \frac{\ell}{4\pi\ell_B Z_c^{\,2}}\frac{1}{\alpha_1 + \gamma_1} \tag{20}$$

with $\gamma_1 = Z_+Z_-\gamma/Z_c^{\,2}$. The critical point is now given by

$$\phi_c = t_c = \frac{1}{64\pi}\frac{1}{\alpha_1 + \gamma + \frac{1}{N}}$$

$$\left(\frac{\ell}{\ell_B}\right)_c = \frac{1}{16}\frac{{Z_c}^2(\alpha_1 + \gamma_1)}{\alpha_1 + \gamma + \frac{1}{N}} \tag{21}$$

Again, N does not affect the critical point significantly. As the ratio of salt concentration to polymer concentration increases, ϕ_c decreases and the critical temperature given by $(\ell/\ell_B)_c$ increases. This result captures the enhanced asymmetry of coexistence curves in polyelectrolyte solutions and the diminished stability[19] of the homogeneous phase with added salt.

Conclusions

A simple mean-field theory is presented to address the phase diagram of solutions of flexible polyelectrolytes. We find the role of polymer molecular weight to be very weak in determining the critical point as given by eq 19, and the critical polymer concentration is very small. We have also addressed the role of added salt within the quasi-two-component approximation, and we find the critical polymer concentration to decrease even more and the critical temperature to increase with an increase in the ratio of salt concentration to polymer concentration.

Acknowledgment. Stimulating discussions with Kingshuk Ghosh are gratefully acknowledged. Acknowledgment is made to the National Science Foundation Grant DMR-9970718 and the Materials Research Science and Engineering Center at the University of Massachusetts.

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MA021456Z