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Spinodal Curve in Highly Asymmetrical Polyelectrolytes

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The study of salt-free polyelectrolytes within the primitive model and with the hypernetted chain integral equation leads to a phase separation at very low concentration. The spinodal line and the critical point are deduced from the compressibility equation and are determined as functions of the polyion charge.

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In a preceding paper[1] (noted here as paper I), the hypernetted-chain integral equation (HNC) has been used to study the structural and equilibrium properties of highly asymmetrical polyelectrolytes in the framework of the primitive model. For a two-component system, polyion+counterion without added salt, an interesting effect was noted: As the concentration is decreased, the osmotic compressibility increases and seems to diverge at a fixed concentration. It is impossible to obtain a HNC solution below this concentration. This problem is not due to a failure of the numerical integration, but is rather an indication of a physical phenomenon: The cut-off concentration is a point of the so-called spinodal line which is the frontier of an unstable region. In this region, the negative compressibility leads to a spinodal decomposition which means a phase separation. In the present Letter, we investigate this effect in a more systematic way by studying the influence of temperature, size, and charge parameters. The spinodal line and the critical point are obtained for different charge dissymmetries. I present here only the most important preliminary results without giving the details of the theory. The latter will be described more precisely in a future paper.[2]

Within the primitive model, the pair potential $v_{ij}(r)$ is given by

$$\begin{aligned} \beta v_{ij}(r) &= +\infty, \quad r < \sigma_{ij} = (\sigma_i + \sigma_j)/2, \\ &= Z_i Z_j L_B / r, \quad r > \sigma_{ij}, \end{aligned} \tag{1}$$

where $\beta = 1/kT$ and $L_B = e^2/4\pi\epsilon_0\epsilon kT$ is the Bjerrum length. ϵ is the dielectric constant of the continuous solvent. The particle i is a charged hard sphere characterized by a diameter σ_i, a charge Z_i, and a concentration ρ_i. It is important to note that the potential is purely hard sphere+Coulombic without specific "van der Waals" attraction. A two-component system corresponds to a mixture of polyions (p) and counterions (c). The electroneutrality condition is $Z_p\rho_p + Z_c\rho_c = 0$. For simplicity, we assume a zero size for the ion, $\sigma_c = 0$. This hypothesis does not restrain the generality of the present model since the size of the ions is always very much smaller than that of the macroparticles (the Coulombic interactions assures a strong short-range repulsion between two counterions). Thus, the present binary mixture is characterized by three independent dimensionless numbers: the volume fraction occupied by the polyions, $\phi = \pi/6\rho_p\sigma_p^3$; the ratio of the charges, $|Z_p/Z_c|$; and the temperature-dependent parameter $|Z_c|L_B/a$ where $a = \sigma_p/2$ is the polyion radius. Without losing generality, we set $Z_c = -1$. The three numbers are then ϕ, $Z = Z_p$, and $t = L_B/a = 1/T^*$, where T^* is the normalized temperature. The problem is now to find the phase diagram (ϕ, t) for different colloidal charges Z.

From the pair potentials, the pair distribution functions and the partial structure factors are calculated with the exact Ornstein-Zernike equation and with the approximation HNC equation.[3] This equation needs an iterative numerical integration which is described in detail in paper I. In general, I have used a real step $P = a/5$ and 256–512 points. The convergence is very slow near the spinodal line, especially in the vicinity of the critical point. The normalized osmotic compressibility $\chi/\chi_0 = kT(\partial\rho/\partial\pi)_T$ is calculated from the infinite-wavelength limit of the structure factors.

The first results correspond to a polyion charge $Z = 20$. In Fig. 1 the normalized compressibility is plotted versus the volume fraction at different values of the parameter T^*. At high temperature, the isothermal curves are obtained in the whole range of concentration. In contrast, at low temperature or high t value, it is impossible to obtain the HNC solution in a part of the concentration range. When the concentration decreases, the compressibility increases and it becomes more and more difficult to get the numerical convergence, which indicates the approach of the spinodal line. The cutoff concentration decreases with increasing temperature until a value T^* near 4.3, above which the whole domain is accessible again. This temperature and the corresponding concentration define the critical point. We note that the locus of the spinodal line cannot be exactly deduced from Fig. 1. In the

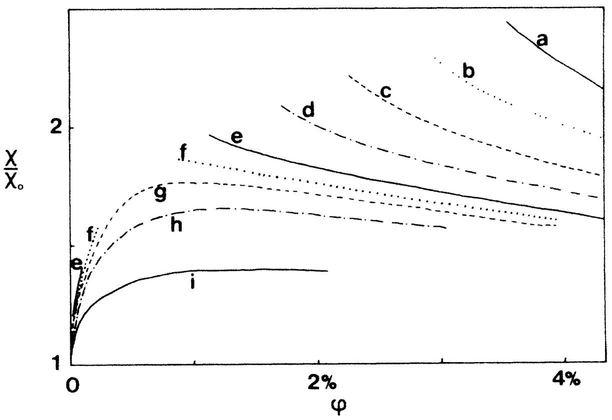

FIG. 1. Normalized compressibility vs volume fraction at different temperatures for $Z=20$. Curve *a*, $T^* = a/L_B = 3.27$; curve *b*, 3.50; curve *c*, 3.73; curve *d*, 3.97; curve *e*, 4.20; curve *f*, 4.32; curve *g*, 4.43; curve *h*, 4.67; curve *i*, 5.83.

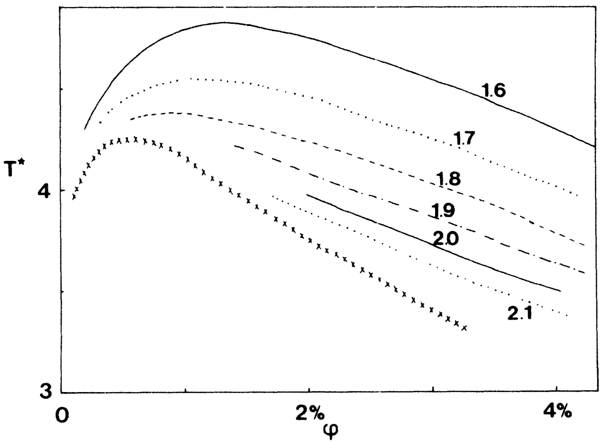

FIG. 2. Phase diagram T^* vs ϕ for $Z=20$. The different curves correspond to different values of the normalized compressibility. The last curve (crosses) represents the spinodal line.

present work I did not try to obtain a more precise evaluation of this curve but it is certainly possible to get it with more numerous numerical points and much patience. I take the opportunity to note that the HNC calculation near the unstable region is more difficult than the corresponding calculation for a classical Lennard-Jones-type potential: First, the ionic mixture needs the treatment of three distribution functions instead of one, then the strong attraction between polyion and counterion needs a small real step while the divergence of the compressibility as the long-range behavior of the Coulombic potential needs a small step in the Fourier space.

The phase diagram T^* vs ϕ is given in Fig. 2. Different curves at constant compressibility are drawn. The special curve $\chi = +\infty$ which defines the spinodal line is obtained by extrapolation. We note that the high-concentration part is obtained in a relative easy manner while the low-concentration part is more imprecise. The reason is that it is difficult to investigate the rare phase below the critical temperature. In the infinite-dilution limit the compressibility differs from the ideal part by a positive term proportional to the square root of the concentration as given by the Debye-Hückel law. Thus, χ/χ_0 increases suddely from 1 at low concentration and diverges rapidly for $T^* < T_c^*$ (see the beginning of the curve *e* in Fig. 1). As a consequence, the rare phase is very dilute and occupies a very narrow part of the phase diagram (Fig. 2). This differs from the results for classical simple liquids for which the compressibility presents a positive or negative linear slope versus ϕ. Another difference is the position of the critical point. Here, we deduce from Fig. 2 $T_c^* \sim 4.25$ or $t_c \sim 0.23$ and $\phi_c \sim 0.6\%$ while the critical volume fraction for a Lennard-Jones potential is about 20 times larger. The coexistence curve which lies outside the spinodal line cannot be calculated from the results of Fig. 1 without numerical integration.

How does the phase diagram depend on the charge dissymmetry? HNC results have been obtained for other charges: $Z=5$, 10, and 100. In a first approximation, the critical volume fraction seems to be nearly independent of the polyion charge and equal to the preceding value. In contrast, the critical temperature is strongly Z dependent. The logarithmic plot of T_c^* vs Z is shown in Fig. 3. The linear behavior of this curve gives

$$T_c^* \sim 0.123 Z^{1.18} \text{ or } t_c \sim 8.14 Z^{-1.18}. \tag{2}$$

The value 1.18 of the exponent is a little larger than one which was expected, since the most important correlations in such systems are the polyion-

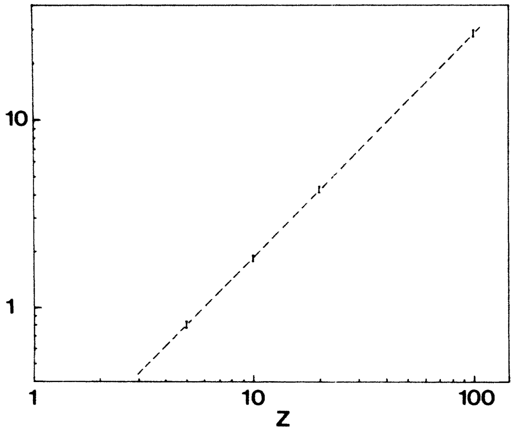

FIG. 3. Log-log plot of the critical reduced temperature vs the polyion charge.

counterion correlations. Indeed, the polyion-counterion potential behaves as $-Zt$, the polyion-polyion potential as $+Z^2t$. The strong attraction between different ions induces large values of the polyion-counterion distribution function at the contact (about 20 for $Z=20$ near the critical point). The expression (2) can be compared to the condensation threshold obtained in the Poisson-Boltzmann-cell theory,[4] $Zt=4$.

What is the physical meaning of such a phenomenon? First, the problem is to know whether the effect is not simply due to an artifact of the HNC approximation. It is known that HNC does not present a self-consistency.[1,3,5] In particular, the virial pressure behaves classically when the compressibility diverges. Stell, Wu, and Larsen[6] have studied the phase separation for the restricted primitive model (symmetrical electrolyte). From fundamentally different equations of state, they obtained various spinodal lines. Their conclusion is that only the precise location of the critical point, rather than its existence, remains in doubt. We have the same opinion in the case of polyelectrolytes: The critical point certainly exists but is not given correctly by the HNC equation. The important difference between electrolytes and polyelectrolytes is that a phase separation can be obtained in aqueous solutions at room temperature in the latter case. The Bjerrum length is about 7 Å under normal conditions. Thus, the critical point given by Eq. (2) can be observed in polyelectrolyte solution if the condition $a \sim 0.9Z^{1.18}$ Å is fulfilled, which corresponds, for example, to $Z=20$, $a=30$ Å (micelle), or $Z=200$, $a=500$ Å (colloid). This result is of interest in the theory of colloidal stability since a phase separation is expected even in absence of a van der Waals attraction. This differs from the classical Derjaguin-Landau-Verwey-Overbeek approach.[7] In fact, the negative Debye-Hückel term plays the role of the attraction in the equation of state.[5]

In the next paper, we will study in a more systematic way the present effect, by comparing the HNC results with some analytical equations of state, by investigating the influence of added salt, and by using the notion of effective polyion-polyion potential as introduced in recent papers.[8-10]

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