# Phase Equilibria of Size-Asymmetric Primitive Model Electrolytes

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The low-temperature phase coexistence of size-asymmetric primitive model electrolyte solutions has been investigated by means of Monte Carlo simulations. Binodal curves and critical parameters are reported as a function of size ratio $\lambda = \sigma_+/\sigma_-$ in the range 0.05 to 1. Both the critical temperature and the critical density are found to decrease as $\lambda$ decreases. These trends are in conflict with available theoretical predictions. For highly asymmetric systems, the depression of the critical parameters is accompanied by the formation of large chainlike and ringlike structures, thereby giving rise to considerable finite-size effects.

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The so-called primitive models (PM) provide the simplest representation of electrolyte solutions. In these models, the system is represented by a binary mixture of charged hard spheres immersed in a dielectric continuum. Many well-known theories, including that of Debye and Hückel [1], are based on such models [2–5]. The special case in which both anions and cations are constrained to have the same charge and size (the restricted primitive model, RPM), is now believed to exhibit vapor-liquid coexistence at low temperatures. However, in spite of its importance, only recently has some consensus emerged regarding the nature of the coexistence curve and the precise location of the critical temperature $T_c$ and the critical density $\rho_c$ [6–8].

Most theoretical work to date and all published simulation studies have been limited to the restricted primitive model. Both from the practical and fundamental points of view, however, asymmetric electrolytes are considerably more important than perfectly symmetric systems. The lack of theoretical and numerical work on asymmetric systems is therefore witness to the difficulties associated with calculations of the vapor-liquid coexistence curve of primitive models.

This work provides a molecular simulation study of the effects of size asymmetry on the phase behavior and critical properties of primitive models. The calculations presented here have been possible through the advent of recently proposed hyperparallel tempering Monte Carlo techniques [6]. The simulated trends for $T_c$ and $\rho_c$ are compared to available theoretical predictions [9].

In our simulations we consider a system consisting of $2N$ hard spheres, half of them carrying a positive charge and the other half carrying a negative charge. The charge numbers $z_i$ for all ions are the same. The diameters of cations and anions are denoted by $\sigma_+$ and $\sigma_-$, respectively. Ions interact via a hard-core and a Coulombic potential energy functions given by

$$U_{ij} = \begin{cases} +\infty & r_{ij} \le \sigma_{ij}\,, \\ \frac{e^2}{4\pi D D_0}\frac{z_i z_j}{r_{ij}} & r_{ij} > \sigma_{ij}\,, \end{cases} \qquad (1)$$

where $\sigma_{ij}$ is the collision diameter between ions $i$ and $j$, given by $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, $e$ is the charge of the electron ($e = 1.602 \times 10^{-19}$ C), and $D_0$ is the dielectric permeability of vacuum ($D_0 = 8.85 \times 10^{-12}\ \mathrm{C^2\,N^{-1}\,m^{-2}}$).

The parameter of central interest to this paper is the ratio of diameters of cations and anions, denoted by $\lambda = \sigma_+/\sigma_-$. Throughout this Letter, results are reported in reduced units. The quantity $\sigma_\pm = (\sigma_+ + \sigma_-)/2$ is introduced, and the reduced temperature is defined as $T^* = 4\pi D D_0 \sigma_\pm k_B T/e^2$. The reduced density is given by $\rho^* = 2N\sigma_\pm^3/V$, and the reduced box size is defined as $L^* = L/\sigma_\pm$.

The low temperatures at which the liquid-vapor coexistence occurs in the RPM pose considerable challenges for traditional simulation methods, and a number of biased sampling techniques have been experimented with in attempts to overcome them. Recently, Panagiotopoulos and Kumar [10] proposed a departure from a continuum by discretizing the RPM model into a finely spaced grid, thereby reducing the calculation of interaction energies to the handling of a look-up table. In this work, as in our recent study of the RPM, we have opted to avoid such approximations, and simulations have been conducted in a continuum using the hyperparallel tempering Monte Carlo method (HPTMC) [6]. Recent studies have shown that, for complex fluids, HPTMC can improve considerably the sampling of phase space [11]. In HPTMC, simulations are conducted simultaneously on several boxes; in the particular implementation employed here, each box represents a grand canonical ensemble at specified values of $\mu$, $V$, and $T$. During a simulation, trial attempts are made to exchange configurations between different boxes. These are accepted according to probability criteria that ensure proper sampling of the relevant ensembles corresponding to the specified set of chemical potentials, volumes, and temperatures of the various simulation boxes. For details of the method, readers are referred to the original publications [6,11]. As in our previous work, long-range interactions are calculated by the Ewald-sum method, with conducting boundary conditions.

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Joint histograms are collected for the distribution of a number of particles and total potential energy of each simulation box. Histogram reweighting techniques [12,13] are then used to combine these histograms and to calculate binodal curves. Apparent critical parameters for a given box size are estimated by means of mixed-field finite-size scaling techniques [14,15], assuming that the criticality of PM belongs to the Ising universality class.

Figure 1 shows simulated binodal curves for asymmetric ionic systems. For clarity, coexistence curves are shown only for $\lambda = 1$ , 0.75, 0.50, and 0.25. The corresponding critical temperatures and critical densities are reported in Table I, together with the sizes of the simulation boxes employed in our work. As the size disparity between positive and negative ions increases, both $T_c^*$ and $\rho_c^*$ decrease. These effects become increasingly pronounced as $\lambda$ becomes smaller. In the near-symmetric region (e.g., $\lambda = 0.75$), the effect of $\lambda$ is small. In fact, the binodals for $\lambda = 1$ and $\lambda = 0.75$ are nearly identical. In contrast, in the highly asymmetric region, the effect of $\lambda$ is much stronger.

These marked decreasing trends of $T_c^*$ and $\rho_c^*$ with size asymmetry are in conflict with the predictions of integral equation calculations using the mean spherical approximation (MSA). Figure 2 shows MSA results generated by both the virial and the energy routes [9]. As expected from a mean-field calculation, the MSA critical-point predictions are not quantitative. What is perhaps more surprising, is that the trends observed in the simulations and the theory are not the same; MSA predicts that both the critical temperature and density *increase* as $\lambda$ decreases. One possible reason for this conflict is that the MSA theory does not satisfy the Debye-Hückel limiting law. A recent binding mean spherical approximation (BIMSA) theory [16], which takes three-body hard-core exclusion into account, does satisfy this limiting law, and might prove to be consistent with our simulation data. Unfortunately, theoretical critical predictions using BIMSA are not available.

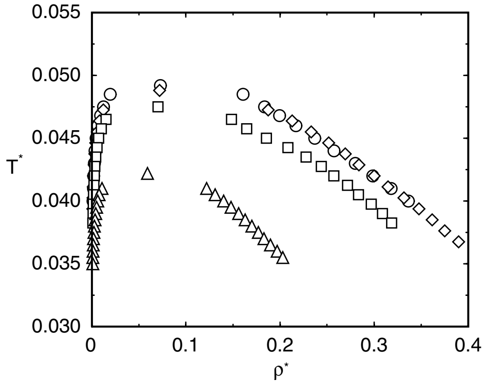

FIG. 1. Simulated binodal curves for size-asymmetric electrolyte systems with different $\lambda$. Circles: $\lambda = 1$; diamonds: $\lambda = 0.75$; squares: $\lambda = 0.5$; triangles: $\lambda = 0.25$.

TABLE I. Effect of $\lambda$ on apparent critical parameters for size-asymmetric electrolytes.

| $\lambda$ | $L^*$ | $T_c^*$ | $\rho_c^*$ |
|---|---|---|---|
| 1 | 17 | 0.0492(2) | 0.073(2) |
| 0.75 | 17 | 0.0488(2) | 0.072(2) |
| 0.50 | 18 | 0.0475(3) | 0.070(2) |
| 0.25 | 18 | 0.0422(3) | 0.059(3) |
| 0.20 | 20 | 0.0386(4) | 0.051(3) |
| 0.10 | 22 | 0.0297(5) | 0.033(4) |
| 0.05 | 28 | 0.0263(6) | 0.022(3) |

Previous authors, most notably Caillol and Weis [17], have described the formation of ionic clusters in the RPM. Furthermore, the concentration fluctuations that arise near a critical point are likely to give rise to the formation of clusters in the critical region of ionic fluids. It turns out that asymmetric systems exhibit a much more pronounced tendency to form clusters than symmetric systems. Ions segregate into polymerlike clusters. The shapes observed in our simulations include chains, rings, and branched chains. In fact, at higher densities, these clusters eventually merge into a networklike structure that percolates throughout the whole system. To explain these shapes,

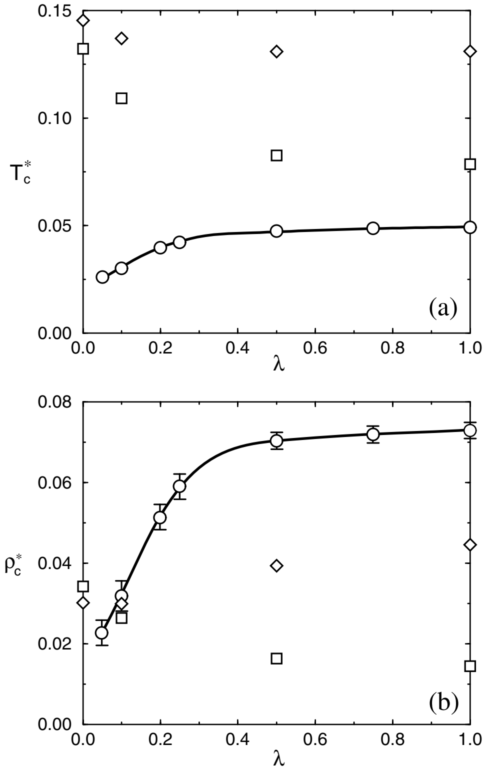

FIG. 2. Critical parameters for size-asymmetric PM electrolytes. (a) Critical temperature as a function of asymmetry. Circles correspond to results of simulations; squares are MSA results via the energy route, and diamonds are MSA results via the viral route. (b) Critical density as a function of asymmetry. The meaning of the symbols is the same as in (a).

it is instructive to consider a simple cluster of only four ions. For a symmetric electrolyte the potential energy of a tight four-ion cluster is lower than that of a linear tetramer. For highly asymmetric systems (e.g., $\lambda < 0.12$), however, linear tetramers have lower potential energy than any other cluster shape. This lower energy, plus a higher entropy, help explain why chains and large rings occur. It is also interesting to point out that, for $\lambda > 0.4$, the energy of linear tetramers or clusters is independent of $\lambda$. For $\lambda < 0.4$, however, the energy of clusters increases markedly as $\lambda$ decreases, while that of linear tetramers remains unchanged. Interestingly, $\lambda \approx 0.4$ is also the point at which the critical temperature and density appear to take a sharp turn towards smaller values.

To quantify the formation of clusters, we follow Gillan's definition [18], i.e., an ion belongs to a cluster if the smallest distance between the ion and the other members of the cluster is less than some critical distance $R_c$. Three critical distances are defined in this work; more specifically, for particle pair $ij$ the critical distance is chosen as $R_{ij,c} = 1.5\sigma_{ij}$. Figure 3 shows the fraction of ions involved in clusters of a given size $n$, for $\lambda = 0.05$, at $T^* = 0.0289$ and $\langle \rho^* \rangle = 0.0016$. We find that most clusters are neutral, and the probability of finding ions in even-sized clusters is much larger than in odd-sized clusters. Most of the clusters are chainlike structures. The largest clusters encountered in this case have more than 100 ions. In contrast, at approximately the same density, most of the ions in RPM systems form simple dimers. This strong proclivity of asymmetric systems to associate may play an important role in the properties of electrolytes solutions, and is likely to have important consequences in the development of models for polyelectrolyte solutions, where, in the interest of simplicity, counterions have often been assumed to have the same size as charged polymer segments.

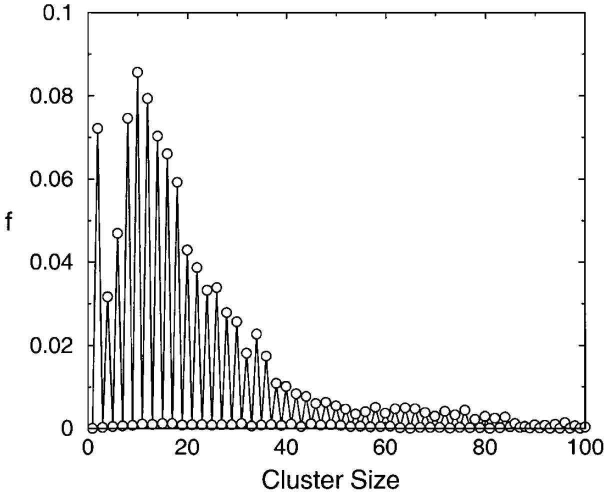

FIG. 3. Probability of finding an ion involved in a cluster of size $n$ at $T^* = 0.0289$ and $\rho^* = 0.0016$ for a $\lambda = 0.05$ system of size $L^* = 76$.

The depression of the critical point, or the smaller region of coexistence observed for highly asymmetric systems, can be attributed to the formation of large clusters. In the fluid phase (above the critical point), these large structures would have a tendency to stabilize the system by leading to considerably lower chemical potentials than a system of simple dimers, thereby preventing the onset of a phase separation.

The formation of large clusters in highly asymmetric electrolytes suggests that finite-size effects, analogous to those encountered in simulations of polymers, are likely to be large. These effects have been considered in detail in our calculations, where we have conducted a considerable number of simulations in boxes of different sizes, some as large as $L^* = 90$. While we have verified that our systems and calculations are large enough not to be adversely affected by finite-size effects, it is important to emphasize that, at low temperatures and concentrations (i.e., for highly asymmetric systems), finite-size effects become increasingly pronounced. It would therefore be difficult to conduct simulations of coexistence below the range of $\lambda$ considered in this work (that is $\lambda < 0.05$). Also note that, to the best of our knowledge, the simulations reported here have been conducted on systems larger than those considered by previous simulation studies [7,8,17,19].

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*Note added.*—Romero-Enrique *et al.* [20] recently completed a study of coexistence for size-asymmetric primitive electrolytes. The results presented in that work are consistent with those presented here. We are grateful to Professor Fisher and Professor Panagiotopoulos for providing us with a preprint of that work.

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