PHASE AND CRITICAL BEHAVIOR OF IONIC FLUIDS

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S u m m a r y

It is well known that the electrostatic forces determine the properties of physical, chemical, or biological systems. In particular, the Coulomb interactions are of great importance when dealing with ionic fluids which include molten salts, electrolyte solutions, and ionic liquids. In most cases, the Coulomb interaction is a dominant one and can substantially affect the critical properties and the phase behavior of ionic systems due to its long-range character. Thus, the investigations concerning these issues are of great fundamental interest and of practical importance.

Over the last fifteen years, the phase diagrams and the critical behavior of ionic solutions have been intensively studied using experimental and theoretical methods. These studies were stimulated by controversial experimental results demonstrating the three types of the critical behavior in ionic fluids: classical and Ising-like behaviors, as well as a crossover between the two. Any theoretical model that demonstrates the phase separation driven exclusively by Coulombic forces is a primitive model. In such a model, the ionic fluid is described as an electroneutral mixture of charged hard spheres immersed in a structureless dielectric continuum. A lot of efforts have been made to obtain the phase diagrams and to calculate the locus of the gas-liquid critical point even for the simplest symmetric version of the primitive model – the so-called restricted primitive model (RPM). Recent simulation studies have indicated that the critical behavior of the RPM belongs to the Ising universality class. However, the investigation of more complex models is still very important for understanding the nature of phase and critical behaviors of real ionic fluids demonstrating both charge and size asymmetries, as well as other complexities. The studies of the effects of charge and size asymmetries on the phase diagram have been recently started with the use of the computer-based simulations and theoretical methods.

We present the overview of achievements in studying the phase diagrams and criticality in the systems with dominant Coulomb interactions obtained by experimental and theoretical methods, as well as by computer-based simulations. The main attention is focused on the theoretical results. We present the results of the mean-field theories, in particular, those of the Debye–Hückel theory and the mean spherical approximation, as well as those of their generalizations related to the explicit inclusion of the ion association. We also overview the results of statistical field theories that use functional methods and allow one to go beyond the mean-field approximation. Areas of future research are also discussed.