Effects of disordered porous media on the vapour-liquid phase equilibrium in ionic fluids: application of the association concept

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ABSTRACT

We study the vapour-liquid phase diagram of a model ionic fluid, the so-called restricted primitive model, confined in a disordered porous medium formed by the matrix of hard sphere (HS) or overlapping hard sphere (OHS) particles. Our theoretical approach is based on a combination of the scaled-particle theory and the associative mean-spherical approximation incorporating the concept of ion association. It is shown that the HS and OHS matrices have a similar effect on the phase diagrams of an ionic fluid: the critical temperature T_c and the critical density ρ_c lower with a decrease of the matrix porosity and the coexistence region gets narrower. However, quantitatively both T_c and ρ_c are higher in the case of OHS matrix than in the HS matrix. It is also observed that the presence of disordered porous media leads to a decrease of the degree of dissociation in comparison with the bulk case.

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1. Introduction

It is a great honor and pleasure for us to contribute this paper to the festschrift dedicated to professor Vojko Vlachy, one of the leaders in physical chemistry of electrolyte and polyelectrolyte solutions.

Ionic liquids confined in porous materials are of great interest from both academic and practical points of view. First of all, it is motivated by a number of special properties of ionic liquids themselves, such as their high chemical and thermal stability, negligible volatility, non-flammability, high ionic conductivity, good electrolytic and solvation abilities [1,2]. On the other hand, ionic liquids confined in nanoporous materials present a new class of hybrid materials, the so-called ionogels which find a large variety of applications in the production of lithium batteries, sensors, fuel cells, supercapacitors, dye-sensitized solar cells, light emitting devices and others [3,4]. Host solid materials incorporating ionic liquids are used in supported catalysis [5] and gas separation processes [6]. At the same time, ionic liquids as solvents are suitable candidates for preparation of nanoporous materials with particular structures [7,8]. Taking into account all of these attractive possibilities, an understanding and prediction of the properties of confined ionic liquids are highly required. Moreover, it is known that a porous medium affects strongly the properties of the guest liquid. Thus, the role of confinement in such systems is crucial and in most cases the confined liquid cannot be considered in the same way as in the bulk phase. It is mainly related to the excluded volume effect appearing due to solid material presence and a large specific area of pore surface formed by this material. Furthermore, the pore structure (e.g. ordered or disordered), sizes and shapes of pores are important. An interaction between the guest liquid and the host material can essentially modify properties of the confined liquid as well.

One of the most intriguing aspects related to the properties of confined ionic liquids consists in changes in their vapour-liquid phase transition. In experimental and theoretical studies of simple and some complex fluids in different types of confinements it has been shown that the vapour-liquid phase diagram of such systems can be drastically different from that observed in the bulk (see Ref. [9] and references therein). It especially concerns fluids in gel-like porous structures which have large specific area of pore surface, complex topology of pores and high dispersity of pore sizes. In our study we consider an ionic liquid in gel-like porous material with a disordered structure presenting a model of ionogel material. Within this model, the porous structure is formed by a matrix of

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spherical obstacles randomly distributed in the volume. It should be noted that although great attention has been paid to such systems for the last three decades, phase transitions of ionic fluids in disordered confinements are not studied well. It mostly relates to the fact that it still remains a challenge to provide a good quantitative and in some cases even a qualitative theoretical description of the vapour-liquid behaviour of ionic fluids not only in a porous medium, but also in the bulk. Therefore, in the present study we start from the simplest model of ionic liquids, the so-called restricted primitive model (RPM). In accordance with this model, an electrolyte is considered as a fluid of charged hard spheres of equal diameter σ half of which carry charge $+e$ while the other half carry charge $-e$ (e is the elementary charge). The fluid is immersed in a solvent dielectric continuum characterized by dielectric permittivity ε. The reduced thermodynamic quantities, temperature and density, appropriate to this model, are defined as $T^* = k_B T \varepsilon \sigma / e^2$ and $\rho^* = \rho \sigma^3$, where k_B is Boltzmann's constant, T is the temperature, $\rho = (N_+ + N_-)/V$ is the total number density, $N_+ = N_-$ is the number of positive and negative particles, and V is the volume of the system. The specific feature of the RPM is the existence of the vapour-liquid-like phase transition at low temperature and low density (for a detailed historical review see, for example, [10–13]). The RPM became a key model for the study of the critical and phase behaviour of the ionic fluids with dominant Coulomb interactions. Significant progress in the description of the phase behaviour of ionic fluids was made within the framework of the associative approach [14–16].

This paper is devoted to application of the associative approach to the study of the vapour-liquid phase behaviour of the RPM confined in a disordered porous matrix. In order to distinguish a pure geometrical effect of confinement, we restrict the model only to a hard-core interaction between the fluid and matrix particles which are considered as uncharged. Therefore, we neglect any possible Coulomb or van der Waals types of interactions of the RPM fluid with a pore surface.

The existing theoretical approaches consider a fluid confined in a disordered matrix as a partly-quenched system in which some of the degrees of freedom are quenched while others are annealed [17]. In this case, statistical-mechanical averages used for the calculation of thermodynamic properties become double ensemble averages: the first average is taken over all degrees of freedom of annealed particles keeping the quenched particles fixed, and the other average is performed over all realizations of a matrix. The application of the replica method made it possible to relate the matrix averaged quantities to thermodynamic quantities of the corresponding fully equilibrated model [18,19]. The major part of theoretical studies of partly-quenched systems containing charges was mainly focused on structural and thermodynamic properties within the framework of the replica Ornstein-Zernike (ROZ) theory. Pioneering studies in this field are related to the works of V. Vlachy and his co-workers [20–25]. The studies of the phase behaviour of partly-quenched models using the ROZ were concerned with systems characterized only by short-range interactions [26–28].

It is also worth noting the works [29–31] in which the vapour-liquid phase behaviour of the RPM confined in slit-like pores with uncharged walls was studied within the framework of the density functional theory. It was shown that due to confinement the critical temperature of the model decreases with a decrease of the pore width. The effect becomes more pronounced when the ion association is taken into account [31]. However, the behaviour of ionic fluids in a disordered porous matrix is more complicated: one should take into account the effects of separate pores as well as the effects of correlations between the ions confined into different pores.

In our recent paper [32], combining the collective variable (CV) method [33–35] with a new extension of the scaled particle theory (SPT) [36–40], we developed a theoretical approach which allowed us to formulate the perturbation theory treating the model of an uncharged hard-sphere fluid in an uncharged hard-sphere matrix as a reference system. Using this approach we derived an explicit equation for the vapour-liquid spinodal of the RPM which takes into account the effects of the third- and forth-order correlations. It was shown that with a decrease of porosity the critical point obtained from this equation shifted towards lower fluid densities and lower temperatures and the coexistence region got narrower.

In the present paper, extending our previous study we take into account the effects of ion association within the framework of the associative mean spherical approximation (AMSA) theory [41]. We focus on the vapour-liquid phase equilibrium of the model ionic fluid confined in disordered matrices of different morphologies and porosities. In particular, two matrices formed by an equilibrium system of neutral hard spheres and overlapping hard spheres are considered. An ionic fluid is modelled as a mixture of free ions and ion pairs which are in chemical equilibrium according to the mass action law (MAL). We study the way the matrix characteristics affect the phase diagram and the degree of ion dissociation along the coexistence curve. As in [32], we use the extended SPT theory for the description of thermodynamic and structural properties of the reference system.

The layout of the paper is as follows. In Section 2, for the convenience of the reader we give a brief review of the application of the association concept in the theory of ionic fluids. We present a development of the theoretical formalism for the description of the RPM in the disordered porous matrices with a use of the association concept in Section 3. In Section 4, vapour-liquid phase diagrams of an ionic model confined in disordered hard sphere matrices of two morphologies are calculated. A detailed discussion of the results is presented here. We conclude in Section 5.

2. The association concept in the theory of ionic fluids

In this section we present a brief review of the application of the association concept in the theory of ionic fluids.

The first successful statistical-mechanical description of electrolyte solutions is connected with the Debye-Hückel (DH) theory proposed over ninety years ago [42]. In this theory, the simplest model of electrolyte solutions, the RPM, was introduced. The idea of ionic screening was originally quantitatively formulated within the framework of the DH theory. However, this idea and the corresponding results were obtained for the fluid of point ions. The attempts to take the ion size into account were not consistent enough. A more consistent description of ionic systems taking into account the ion sizes was proposed within the framework of the mean spherical (MSA) approximation [43–46]. It should be noted that a finite size of ions was consistently taken into consideration for the first time in [47], where the results obtained for thermodynamic functions closely resemble the MSA results [48].

Both the MSA approach and the DH theory are linear (in charge) theories. The concept of ionic association was introduced to include nonlinear effects into the theory. First, this concept was introduced by Bjerrum [49] in order to improve the DH theory. In accordance with the ionic association concept, an electrolyte solution is considered to be a mixture of free ions and ion clusters [50] (usually ion pairs but sometimes also trimers, tetramers and larger clusters) which are assumed to take part in chemical equilibrium according to the mass action law (MAL). Since in the DH theory the ions are treated as point particles, the point ion pairs make no electrostatic contribution to thermodynamic properties in the original Bjerrum approach. Hence, the DH theory was modified by correcting the ion concentration in the electrostatic contribution using the concentration of free ions obtained from the MAL. The second modification