



Prediction of phase behaviors of ionic liquids over a wide range of conditions



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ABSTRACT

We propose a new predictive approach for the calculation of properties and phase behavior of mixtures containing ionic liquids (ILs). In this method the Pitzer–Debye–Hückel (PDH) model for the long-range electrostatic interactions is combined with the COSMO-SAC model for the short-range interactions between contacting molecules. While the COSMO-SAC model alone has been shown to be accurate for vapor–liquid equilibrium (VLE) and infinite dilution activity coefficient (IDAC) of solvents in ILs, it is inaccurate for dilute IL solution properties such as the osmotic coefficient (OC) and mean ionic activity coefficient (MIAC), where long-range interactions are important. The PDH model alone is accurate for dilute IL solutions; however, it is not applicable at high IL concentrations. Here we propose a novel method for attenuating the long-range effects from the PDH model at high IL concentrations. The resultant model is found to be accurate over the whole concentration ranges of the IL solutions. We have examined this method for three versions of the COSMO-SAC model, denoted as COSMO-SAC(2007) + PDH(α), COSMO-SAC(2010) + PDH(α), and COSMO-SAC(ion, α), for mixtures involving 73 ILs formed from the combination of 20 cations and 15 anions. The absolute relative deviations (ARD) from the three models for IDAC (3552 points) are 107.89%, 165.37%, and 116.94%, respectively. The errors for VLE (1626 points) are 23.98%, 28.88%, and 22.02%, respectively. The prediction accuracy for OC (1348 points) are 40.86%, 48.10% and 24.09%, and the predicted MIAC (484 points) of ionic liquid showed a similar accuracy of about 48%. The proposed COSMO-SAC models provide prediction of properties of IL fluids with consistent accuracy over the full range of concentrations.

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1. Introduction

Ionic liquids (ILs) have attracted much attention recently because of their unique properties such as nonflammability, negligible vapor pressure, broad liquid state temperature ranges with a melting point near or below 373.15 K, high thermal and chemical stability, and high ionic conductivity. Ionic liquids are also referred to as green and designable solvents because a wide spectrum of properties can be obtained from the nearly unlimited combinations of anions and cations [1]. The utilization of ionic liquids have been investigated in various applications, including replacement of volatile organic solvents, solvents for organic synthesis (both catalytic and non-catalytic) [2], reaction media for biopolymer fiber formation [3] or biocatalysis [4], extraction solvent for the removal of sulfur compounds [5], entrainer for separation of azeotropic mixtures [6,7] and for liquid–liquid extraction [8], novel processing media in combination with supercritical carbon dioxide

(CO₂) [9,10], and electrolytes in electrochemical devices such as batteries [11].

Since the thermodynamic properties and phase behaviors of ILs are fundamental to the application of ILs, many experimental measurements have been conducted and models developed for correlation or prediction of the data. For example, quantitative structure property relationship (QSPR) models were developed for making quantitative predictions of the physical properties of ionic liquids [12–14]. Equations of state (EOS), such as PR and tPC-SAFT, are shown to provide the phase behavior of mixtures IL + CO₂ and of pure ionic liquids [15–19]. The excess Gibbs energy models, such as the UNIQUAC [20,21], UNIFAC [22,23], and NRTL [24,25] models, are commonly used to correlate experimental data of vapor–liquid and liquid–liquid equilibria of IL mixtures. More recently, models based on results of quantum mechanical calculations, such as COSMO-RS [26–28] and COSMO-SAC [29,30] have been shown to provide reliable predictions for a variety of thermodynamic properties of ILs, including the infinite dilution activity coefficient (IDAC), vapor–liquid (VLE), and liquid–liquid equilibrium (LLE). The success of COSMO-type models opens up the possibility of fast screening of ILs for desired properties [31–33].

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Nomenclature

The list of symbols

A_i	cavity surface area
A_ϕ	Debye–Hückel constant
d_s	density of solvent
G^{ex}	excess Gibbs energy
I_x	ionic strength
k	Boltzmann constant
M_s	molecular weight of solvent
N_a	Avogadro's number
p_i	probability of finding a small surface segment with a certain charge density
q_i	surface area parameters
Q_e	charge of an electron
r_i	volume parameters
\bar{r}	mean radius of cation and anion
R	gas constant
T	temperature
V_i	cavity volume
w_i	weight fraction of species i
ΔW	energy of interaction between two surface segments
x_i	mole fraction of species i
z	electrovalence

Greek letters

α	fraction of electrolyte species that do not form ion pairs
ϵ_s	dielectric of solvent
θ_i	surface-area fraction
ν_i	valence of ion i
ρ	closest approach parameter
σ_m	charge density
ϕ	osmotic coefficient
ϕ_{ii}	volume fraction
Γ^t	segment activity coefficient of a segment of type t

Superscript

b	binary system
$comb$	combinatorial term
ex	excess
o	initial state
res	residual term
t	surface types

Subscript

i	species i
s	solvent
$+$	cation of ionic liquid
$-$	anion of ionic liquid
\pm	IL-pair

The success of COSMO-type models for ILs is quite surprising considering the fact that the model was developed based only on short-ranged interactions [34], while long-range columbic interactions should not be negligible in ILs. In our recent work [35], we show that the COSMO-SAC model without long-range interaction contribution term fails to describe the property (e.g., osmotic coefficient) of dilute IL solutions, where the IL may fully dissociate and long-range interactions are the dominating forces. In fact, there are many efforts made to incorporate long-range effects by combining the short-range model with either the Pitzer–Debye–Hückel (PDH) model [36,37] or the mean spherical approximation (MSA) model [38]. However, limited by the need for

binary interaction parameters, such models may not be applicable for systems containing new ILs whose parameters are not available.

The purpose of the present work is to develop a predictive model that is applicable for ILs at all concentrations. Hsieh and Lin [39] have recently developed a version of COSMO-SAC model, COSMO-SAC(ion), which is compatible with long-range effects from the Pitzer–Debye–Hückel model [40]. This model has been shown to provide accurate predictions of mean activity coefficient for strong electrolytes in various types of solvents. While IL solutions should obey the PDH theory at low IL concentrations, the long-range effects should be completely screened at high IL concentrations [35]. In this work, we applied this model to various solutions containing ILs and propose a simple treatment for the dissociation of IL in order to attenuate long-range electrostatic interactions in the PDH model such that the composite model (COSMO-SAC+PDH) can be used for ILs mixed with different types of solvents. The resultant model does not require any parameter fitting for new ILs, and therefore can provide a priori predictions of properties and phase behaviors of mixtures containing ILs. We believe that new model can serve as a powerful tool in the design of processes involving ILs.

2. Theory and model

2.1. The COSMO-SAC models

One important feature of ILs that distinguishes them from most other solvents is the existence of charged species in the fluid where the long-range electrostatic interaction may be important. Therefore, we model the excess Gibbs energy (G^{ex}) of a fluid containing IL to be the sum of two contributions: a long-range term, modeled by the Pitzer–Debye–Hückel (PDH) model, and a short-range term, modeled by the COSMO-SAC model,

$$G^{ex} = G^{ex,PDH} + G^{ex,COSMO-SAC} \quad (1)$$

The activity coefficient derived from Eq. (1) thus contains two terms,

$$\ln \gamma_i^* = \ln \gamma_i^{*PDH} + \ln \gamma_i^{*COSMO-SAC} \quad (2)$$

The asterisks in Eq. (2) indicate the use of unsymmetric reference states for the activity coefficient: pure liquid for uncharged species, and infinite dilution for charged species (i.e., the cation and anion of ILs). The long-range electrostatic contribution to the activity coefficient from the PDH theory is [41]

$$\ln \gamma_i^{*PDH} = -\sqrt{\frac{1000}{M_s}} A_\phi \left[\frac{2z_i^2}{\rho} \ln \left(1 + \rho \sqrt{I_x} \right) + \frac{z_i^2 \sqrt{I_x} - 2I_x^{3/2} x}{1 + \rho \sqrt{I_x}} \right] \quad (3)$$

where M_s is the molecular weight of solvent, ρ is the closest approach parameter, I_x is the ionic strength ($I_x = 1/2 \sum_i x_i z_i^2$, where z is the electrovalence) and A_ϕ is the Debye–Hückel constant ($A_f = 1/3(2pN_a d_s/1000)^{1/2} (Q_e^2/e_s kT)^{3/2}$, with d_s being the density of solvent, N_a the Avogadro's number, Q_e the charge of an electron, ϵ_s the average dielectric of solvent, and k the Boltzmann constant).

The COSMO-SAC model describes the activity coefficient due to interactions between molecules in contact via a combinatorial term ($comb$) and a residual term (res),

$$\ln \gamma_i^{COSMO-SAC} = \ln \gamma_i^{res} + \ln \gamma_i^{comb} \quad (4)$$

The combinatorial term considers the non-ideality resulting from the repulsive interactions between species, with consideration of size and shape differences between molecules. In the

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