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Surface thermodynamic properties of ionic liquids from new molecular thermodynamic model and ion-contribution equation of state

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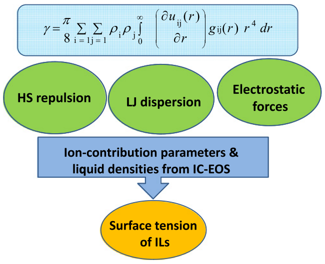
HIGHLIGHTS

- Development of new molecular thermodynamic model for the surface tension correlation of pure ILs.
- Consideration of additive hard-sphere, *LJ* dispersion and columbic interactions in the development.
- Estimation of surface thermodynamic functions.
- Estimation of sound velocities of ILs.

GRAPHICAL ABSTRACT



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ABSTRACT

We aim to develop a new molecular thermodynamic model for predicting the surface thermodynamic properties of pure ionic liquids (ILs) based on the statistical mechanical expression developed by Winterfeld et al. (1978. AIChE. J. 24, 1010). In this respect, contributions to surface tension from the hard-sphere repulsion, Lennard–Jones dispersion force, and electrostatic interactions were considered and assumed to be additive in the development of the model. According to Winterfeld et al. approach, the surface tension of ILs is closely related to their pair potential function, pair radial distribution function and liquid densities. The required densities were predicted from our previous ion-contribution equation of state. The reliability of the proposed model was checked by calculating 464 surface tension data points for 13 different ILs over temperature range within 268.6–393 K. The overall average absolute deviation of the correlated surface tensions from the experimental ones was found to be 1.55%. This result demonstrates the good performance of the proposed model and the rationality of molecular parameters, i.e., the soft-sphere diameter, σ dispersive energy, ε and inverse shielding length parameter, Γ. The uncertainty of the predicted surface tension was of the order of ±8.14%. Finally, our method has also been employed to estimate the sound velocities in ILs. The uncertainty of the calculated sound velocities was equal to ±9.25%.

1. Introduction

The surface tension is an important property in the study of physics and chemistry at free surfaces. It affects the transfer rates of vapor absorption where a vapour–liquid interface exists. Such data are of importance to scientists and engineers.

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The versatility of ILs has driven increasing interest in using them in extraction and multiphase homogeneous catalytic reactions (Welton, 1999; Herrmann and Bohm, 1999; Carmichael et al., 1999; Olivier and Chauvin, 1996; Chauvin and Olivier-Bourbigou, 1995; Cull et al., 2000; Erbeldinger et al., 2000; Lau et al., 2000) where one phase is chosen to dissolve the catalyst and be immiscible, and the second phase contains the reactant and products. Such processes occur at the interface between the IL and the overlying aqueous or organic phase, and are dependent on the access of the material to the surface and the transfer of material across the interface. A clearer understanding of the mechanisms behind these processes requires a more detailed examination of the surface properties of the ionic liquids. Therefore the knowledge of the surface properties of the ILs is highly useful to understand clearly the mechanisms behind such processes.

Since the experimental data for surface tensions of ionic liquids are somewhat scarce compared with their density data and limited mainly to imidazolium based ionic liquids, the development of a theoretical or semi-empirical method can be considerably useful to establish the surface tension data in the design specifications. For this purpose, the correlation/prediction of surface tension of ILs and their surface thermodynamic functions is an important task.

So far, numerous methods have been proposed in literature (Gardas and Coutinho, 2008; Mirkhani et al., 2013; Souckova et al., 2012; Gharagheizi et al., 2012; Wu et al., 2012; Mousazadeh and Faramarzi, 2011; Ghatee et al., 2010; Ghasemian and Zobeydi, 2013) to estimate the surface tension of pure ILs. Further, several researchers have used quantitative structure–property relationship (QSPR) correlations to estimate the surface tension of ILs. Gardas and Coutinho (2008), Mirkhani et al. (2013) and Souckova et al. (2012) proposed the resultant model equations based on the QSPR analysis to predict the surface tensions of ILs. The group contribution (GC) method has also been employed to estimate the surface tension of ionic liquids in literature. For instance, Gharagheizi et al. (2012) developed a reliable group contribution method for this purpose and their results showed an average absolute deviation (AAD) of the predicted surface tension equal to 3.6% from the experimental data. Wu et al. (2012) also developed the corresponding-states group-contribution method to estimate the surface tension of ILs covering wide range of temperature.

Mousazadeh and Faramarzi (2011) also proposed a correlation for surface tension of ILs based on the corresponding states theory. However, the need for the surface tension data of ILs at melting point, for which their values cannot be accurately obtained for most ILs, limits the applicability of their approach. Ghatee et al. (2010) developed a linear correlation between logarithm of surface tension and fluidity involving the characteristic exponent for 20 ILs.

Recently, a simple equation has been employed by Ghasemian and Zobeydi (2013) to predict the surface tensions of pure ILs based on enthalpy of vaporization. However, the input parameters of their equation are the acentric factor, critical temperature, and critical pressure of ILs, for which their values are not accurately determined yet (there are only several methods for estimating these parameters), which limits the performance, applicability and reliability of their approach.

So far, some expressions based on molecular thermodynamic considerations have been developed by Li and Lu (2001) and Mousavi et al. (2007) for predicting the surface tensions of pure polar liquids and their mixtures. In these expressions the contributions to surface tension from hard spheres, dispersion, dipolar interactions have been considered. Also, the required molecular parameters have been taken from the transport properties as well as experimental surface tension data. However, the performance of molecular thermodynamic approaches has not been yet assessed for electrolytes such as ILs.

In this work, for the first time, a molecular thermodynamic model is developed based on the statistical mechanical expression of interfacial tension to predict the interfacial properties of ILs. Another distinctive feature of the proposed molecular model is to utilize the ion-contribution molecular parameters, for which their values were previously determined by Alavianmehr et al. (2014) based on the ion-contribution equation of state (IC-EOS). According to the Alavianmehr et al. model, each IL was divided into two charged hard-spheres representing cation and anion. The ion parameters which reflect the soft-core diameter σ and the dispersive energy ε were optimized by pressure–volume–temperature (PVT) data. The new idea of the present work is considering contributions arising from the columbic interactions as well as the hard-sphere repulsions and Lennard–Jones dispersion forces in surface tension of ILs.

The new molecular thermodynamic model is employed to correlate the surface tensions of 13 ILs including 12 imidazolium-based and 1 phosphonium-based ones. Then the surface thermodynamic properties such as surface entropy and surface enthalpy are estimated using the linear or quasi-linear variation of the surface tensions of studied ILs with temperature. Finally, the sound velocities in some selected ILs are estimated based on the simple equation using the liquid densities and surface tensions. The performance and accuracy of the proposed model are checked against experimental data as well as other models.

2. Theory

Fowler (1937), Kirkwood and Buff (1949) have utilized the statistical mechanical analysis to relate the surface tension to the intermolecular forces acting at an interface between two fluid phases. They considered a step transition from liquid to vapour phases, with no interface zone (and hence with no interface thickness). Generally, the expression for the calculation of the surface tensions of polyatomic fluids according to FKB's approximation, regardless the contribution of the vapour density, is given by Davis (1975):

$$\gamma = \pi\frac{\rho^2}{8}\int_0^\infty \left(\frac{\partial u(r)}{\partial r}\right) g(r)\, r^4\, dr \tag{1}$$

where, r is the intermolecular distance, ρ is the density of liquids, $u(r)$ is the intermolecular pair potential, and $g(r)$ is the radial distribution function (RDF). As it is clear from Eq. (1), based on the FKB's approximation and statistical mechanics method, the surface tension can be obtained from the intermolecular potential and the RDF in terms of bulk properties of fluid, i.e., the density of liquid at vapour–liquid interface.

Davis (1975) and Winterfeld et al. (1978) developed an expression for the surface tension in terms of radial distribution function for non-simple molecules mixtures and at low vapour pressures:

$$\gamma = \frac{\pi}{8}\sum_{i=1}\sum_{j=1}\rho_i\rho_j\int_0^\infty \left(\frac{\partial u_{ij}(r)}{\partial r}\right) g_{ij}(r)\, r^4\, dr \tag{2}$$

where, i and j are the molecular number density of components i and j, respectively, r is the distance between the unlike molecules (pair ions herein). $g_{ij}(r)$ denotes the RDF and $u_{ij}(r)$ is the potential function, both applied to fluid mixtures.

2.1. The new molecular thermodynamic model

We have considered the contributions from hard-sphere repulsion, *LJ* dispersion, and the electrostatic interactions to surface