Thermophysical properties of alkyl-imidazolium based ionic liquids through the heterosegmented SAFT-BACK equation of state

Ali Maghari *, Fatemeh ZiaMajidi, Elham Pashaei

Department of Physical Chemistry, School of Chemistry, College of Science, University of Tehran, Tehran, Iran

ARTICLE INFO

ABSTRACT

Heterosegmented molecular model combined with SAFT-BACK EOS was developed to predict the *pVT* and second derivative properties including speed-of-sound, isothermal compressibility and isobaric thermal expansivity of some alkyl-imidazolium ionic liquids (ILs) with $[PF_6]^-$, $[BF_4]^-$ and $[NTf_2]$ anions. In this work, an IL was considered as two components, a cation and an anion. The cation of IL is treated as chain-like entity and was divided into several kinds of segments including cation head (imidazolium ring) and several segments of $-CH_2$ (including $-CH_3$) in the alkyl tails of the IL molecule, while the anion is not divided into segments and treated as a whole. The segment shape is described by a non-spherical parameter with using a hard convex body term as the reference. To account for the association scheme, the cation head and the anion of ILs each was considered one association site, which can only cross-associate. Moreover, we have considered a dipolar interaction between anion and cation head where the effective dipole moment is approximated as a linear function of density. The heterosegmented SAFT-BACK model was found to be able to correctly describe the second-order thermodynamic derivative properties as well as *pVT* properties of ILs studied in this work.

1. Introduction

Ionic liquids (ILs) are organic molten salts with extremely low volatility, nonflammable, non-explosive and relative thermal stability which makes them good candidates for alternative solvents. ILs are generally constituted by an asymmetric organic cation and a weakly coordinating organic or inorganic anion that cannot form an ordered crystal and thus remain liquid at room temperature. The organic cation consists of a cation head and several alkyl groups, whereas the anion with smaller size and more symmetrical shape can be inorganic anion, i.e. tetrafluoroborate $[BF_4]^-$, hexafluorophosphate $[PF_6]^-$ or organic anion, such as nitrate $[NO_3]^-$ and bis (trifluoromethylsulfonyl) imide $[NTf_2]^-$. Asymmetry of the cation is responsible for the low melting points of ILs, while the nature of the anion is usually assumed to be responsible

for many of the physical properties of ILs [1]. For example IL with $[C_4mim]$ cation and PF_6 anion is immiscible with water, whereas IL with same cation and BF_4 anion is water soluble.

The alkyl-chain length of the cations has been known to significantly influence the physical and chemical properties of ILs, especially liquid crystal formation [2]. The flexibility of molecular tuning by ability to vary different cations and anions allows for synthesis of numerous ILs for many specific applications. Properties such as density, heat capacities, surface tension and viscosity are affected. Motivated by these interesting properties, some experimental and theoretical studies on ILs have been investigated by several groups in the last two decades and have still been the subject of many academic and industrial researches, since the study of the molecular ILs is still in its early stages.

In recent years, many theoretical approaches have been proposed for the representation of the thermodynamic characteristics and phase behavior of systems containing ILs. The group contribution methods [3–8], activity coefficient models [9–11] and cubic equations of state [12–17] have been applied to calculate the thermodynamic properties of ILs. Moreover, the statistical associating fluid theory (SAFT) provides an excellent model for the estimation and prediction of the thermophysical properties and phase behavior of ILs and their mixtures. SAFT is based on the first-order perturbation theory of Wertheim [18–21], and is first proposed by Chapman et al. [22] and have been converted into a very useful engineering equation [23,24]. An important feature of the SAFT theory is that it explicitly takes into account nonsphericity and association interactions and has since been used to predict the phase equilibria behavior of a wide variety of pure components and their mixtures. It is considered one of the most powerful predictive tools for the study

of fluid phase equilibria. In SAFT a molecule is composed of m segments correspond to atoms, functional groups, or complete molecules. Each segment has the same volume and interaction energy parameters. Molecules are represented as covalently bonded chains of segments that may contain sites capable of forming associative complexes. Several versions of SAFT have been developed by different methods to calculate the free energy of monomers (segments). Although SAFT approach has been widely used to predict the thermophysical properties of real fluids, there has been relatively small work about the ability of SAFT in predicting thermodynamic properties of ionic fluids, such as ILs. Blas and Vega [25] have predicted the thermophysical properties of ILs using the soft-SAFT equation of state (EOS). Moreover, the soft-SAFT EOS has been used to study the solubility of carbon dioxide, hydrogen, carbon monoxide and xenon in the alkylimidazolium $[C_nmim]^+$ with some fluorinated anions $[BF_4]^-$, $[PF_6]^-$ and $[NTf_2]^-$, achieving quantitative agreement with experimental data [26,27]. Rahmati and co-workers have used the SAFT-VR and PC-SAFT to predict the solubility of hydrogen sulfide in six imidazolium-based ILs [28]. Domańska et al. [29–33] have recently used the PC-SAFT EOS to reproduce diverse thermophysical data, such as phase diagrams and excess enthalpies for pure ILs as well as their mixtures with organic or inorganic solvents. Polishuk [34] has also provided an estimate of the second derivatives of ILs using the PC-SAFT, generalized (G) SAFT-plus-Cubic and Cubic-Plus-Associating (CPA) models. It showed that the PC-SAFT substantially overestimates heat capacities and underestimates the temperature and pressure dependencies of sound velocities and compressibilities, whereas the GSAFT + Cubic model can predict these more reliably. The ability of the PC-SAFT equation to represent the solubility of carbon dioxide in ionic liquids has been investigated by Chen et al. [35]. Ji et al. [36] have applied the ePC-SAFT with six strategies to model the density of imidazolium-based ILs and the solubility of CO_2 and CH_4 in these ILs. It was shown that all strategies can be used to accurately represent the density of pure ILs, but only the ion-based model accounting for Coulomb interactions provides reliable prediction results with respect to the CO_2 solubility in ILs. Llovell et al. [37] have recently studied the solubility of three common pollutants, SO_2, NH_3 and H_2S, in three types of ILs using the soft-SAFT EOS. Ji and Adidharma have developed a new version of SAFT, called heterosegmented SAFT model to predict the densities of pure ILs [38] and molar volumes of CO_2/IL mixtures [39,40]. They have divided the IL in four different parts, including the anion, the cation head, the methyl group and the alkyl chain as independent components with their molecular parameters.

In our recent work [41], we have extended the SAFT-BACK model to predict the pressure–volume–temperature (pVT) and second-order thermodynamic properties of pure alkyl-imidazolium ionic liquids (ILs) with $[PF_6]^-$ and $[BF_4]^-$ anions. In our previous work, we assumed that the IL is modeled as a chain-like dipolar ion-pairs composed of non-spherical molecules, which interact with other dipolar ion-pairs. We achieved very good results for densities and speed of sound of ILs over a wide range of temperature and pressure, whereas the extended SAFT-BACK EOS overestimates the isobaric thermal expansion coefficients of $[C_nmim][BF_4]$ with respect to experimental data. In the present work, a heterosegmented SAFT-BACK model (hetero-SAFT-BACK for short) is developed to describe the first and second derivative properties of ILs. In this study, twelve kinds of ILs including $[C_nmim][PF_6]$, $[C_nmim][BF_4]$ with $n = 2, 4, 6, 8$ and $[C_nmim][NTf_2]$ with $n = 3, 4, 5$ and 6 in a wide range of temperatures and pressures have been extensively evaluated.

2. Theory and thermodynamic modeling

Based on statistical mechanical description for systems composed of non-spherical molecules, an EOS for hard convex body (hcb) fluids was proposed by Boublik [42] from the scaled particle theory. Chen and Kreglewski [43] used this equation combined with the equation of Alder et al. [44] to establish an EOS called Boublik–Alder–Chen–

Kreglewski (BACK). Chen and co-workers combined BACK with SAFT and proposed two modifications for a better description of the properties of chain fluids [45] as well as polar [46] and association [47] fluids in the whole region: (i) the chain formation term is modified for a more accurate description of the long chain fluids; (ii) the effect of chain formation on the dispersion term is included. This new version of SAFT, the so-called modified SAFT-BACK EOS has been recently developed by Maghari et al. [48–51] to determine the thermodynamic derivative properties of some pure fluids and their mixtures in the wide density and temperature ranges including critical temperature.

The SAFT type equations of state are usually written in terms of the residual Helmholtz energy as

$$A^{res} \equiv A - A^{id} = A^{ref} + A^{dis} + A^{chain} + A^{polar} + A^{assoc} \tag{1}$$

where the superscripts "id", "ref", "dis", "chain", "polar" and "assoc" stand for ideal, reference, dispersion, chain, polar, and association terms, respectively.

In this work, we assume that a pure IL is composed of two components, which are designated by i, where $i = 1, 2$ represent the anion and cation, respectively. Each component may be divided into several segments, which are designated by a ($a = 1, 2, \cdots s$). Since the anion (as component 1) is not divided into segments, we have $s_1 = 1$, and there is no chain term for anion component. The cation of IL (component 2) is divided into s_2 segments including cation head (imidazolium ring) and several segments of $-CH_2$ (including $-CH_3$) in the alkyl tails of the IL molecule. Clearly, these alkyl segments are not chained as a straight line, but are zigzag or crooked ones, so that we consider a shape parameter for the alkyl segments. The number of segment a of component i ($= 1, 2$) is designated by $m_{a,i}$ and $m_i = \sum_{a=1}^{s_i} m_{a,i}$ is the total number of segments in component i. For example, the IL $[C_4mim]$ $[PF_6]$ is composed two components: (i) component 1 is the anion $[PF_6]$; (ii) component 2 is cation $[C_4mim]$. The anion is treated as one segment and the cation $[C_4mim]$ is composed of 5 segments of $-CH_2$ (including $-CH_3$) and one segment of imidazolium ring (cation head). In our model, the cation head and the anion have one association site, which can only cross-associate.

The detailed expressions required for the individual terms in Eq. (1) are briefly described below.

2.1. Reference term

The reference term in the hetero-SAFT-BACK version has been chosen as hard convex body (hcb) proposed by Boublik [42] given by

$$\frac{A^{hcb}}{Nk_BT} = m\left[\frac{\alpha^2}{(1-\eta)^2} - \frac{\alpha^2-3\alpha}{1-\eta} - (1-\alpha^2)\ln(1-\eta) - 3\alpha\right] \tag{2}$$

where $m = m_1 + m_2$ is the total segment number and α is a parameter which is related directly to the geometry of the hard-convex body. The average non-spherical parameter α can be obtained from the following mixing rules:

$$\alpha = \frac{1}{2}(\alpha_1 + \alpha_2) \tag{3}$$

where α_1 and α_2 $\left(\equiv \alpha_{CH_2} + \alpha_{cation\ head}\right)$ are the shape parameters of anion and cation, respectively. The packing factor η, appeared in Eq. (2) is defined as:

$$\eta \equiv \frac{\pi}{6} N_{Av} \rho_s \sum_{i=1}^{2} x_i m_i d_i^3 \tag{4}$$

where x_i and m_i are mole fraction and the total segment number of component i, respectively, N_{Av} is the Avogadro's number, $\rho_s \equiv c\rho$ in which ρ