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Average intermolecular interaction in ionic liquids and a new equation of state

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ABSTRACT

In this work an equation of state was presented for ionic liquids that can be derived using the average intermolecular potential (6, 3). This equation of state predicts the linear behavior of $(Z-1)\upsilon^2$ versus ρ. It was shown that two types of temperature dependency relations for the equation of state parameters are applicable. The superiority of the temperature dependency relations for the proposed equation of state parameters respect to the corresponding relations for Farzi et al. and Tait equations of state parameters was investigated. The density, the isothermal compressibility, and the isobaric expansivity of ionic liquids were calculated using the presented equation of state. The percentage of the average absolute relative deviation for density prediction was 0.05% and for the isothermal compressibility and the isobaric expansivity was in the limit of the reported values in literatures.

1. Introduction

Ionic liquids (ILs), are designable solvents which have at least one organic cation, such as imidazolium, pyridinium and one anion such as halogen and fluorinated [1]. They have major application in industry and attract the researcher attention due to their unique properties. Low vapor pressure, low flammability, high thermal stability and high electrochemical stability, are some examples of a broad range of physico-chemical properties of ILs [2–4]. ILs are known as environmentally friendly solvents [5,6] and have extensive applications in catalysis [7], biocatalysis [8], separation, extraction [9], biodiesel production [10,11], electrochemical systems [12,13], nanosystems [14–16], pharmaceuticals, therapeutics [17], and biotechnology [18].

Due to the unique physico-chemical properties of ILs and their extensive applications in green chemistry, measuring and predicting the thermodynamic properties of ILs are very important. Actually, the knowledge of thermophysical properties [19] of ILs is a fundamental pillar in the design of industrial processes and new products which are based on ILs. The thermophysical properties data of materials can be obtained from the experiment [20,21] or modeling [22,23].

Equations of state (EOSs) were employed as a useful tool for modeling of P-υ-T data and consequently the thermophysical properties of ILs. Karakatsani et al. [24] used the truncated perturbed chain polar statistical associating fluid theory (tPC-PSAFT) for investigation of the phase behavior of binary and ternary IL mixtures in polar and nonpolar solvent. Shariati and Peters [25] modeled the solubility of fluoroform in 1-ethyl-3-methyl imidazolium hexafluoro phosphate, [C2mim][PF6], using the two parameters EOS of Peng–Robinson (PR). Shiflett and Yokozeki [26,27] used Redlich–Kwong (RK) EOS to model the solubility of CO_2 in ILs. Shen et al. [28] estimated the density of ILs using the three parameters EOS of Patel-Teja and determined their critical properties from group contribution method. Hosseini [29] presented a perturbed hard sphere EOS for phosphonium-, pyridinium-, and pyrrolidinium-based ILs. Then this EOS extended to another class of ILs in compressed states [30]. Maia et al. [31] applied the cubic plus association (CPA) EOS to describe the phase behavior of two ILs, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, ($[C_2mim][NTf_2]$), and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, ($[C_4mim][NTf_2]$). Li et al. [32] used a thermodynamic model based on an EOS for square-well chain fluid with variable range (SWCF-VR) to describe the thermodynamic properties of aqueous solutions of ILs. Nobandegani et al. [33] used the perturbed hard-sphere EOS for modeling vapor-liquid equilibria of some binary mixtures consisting of ILs, refrigerants, hydrocarbons, and monatomic fluids. Hosseini et al. [34] used a modified perturbed hard-sphere EOS for modeling the volumetric properties of ILs and their mixtures. Yousefi and Karimi [35] modified the cubic EOS of Tao–Mason for predicting the density of some ILs at any temperature and pressure. Joshipura [36] predicted the properties of ILs using the cubic EOS of Patel-Teja (CEOS). Wang et al. [37] were developed a two parameter EOS on the basis of hard sphere perturbation theory for investigation of the electrostatic contribution in the thermodynamic property of ILs.

Furthermore, there is another class of EOSs which were derived by considering the average intermolecular potentials between the molecules of fluids. These EOSs can be used for prediction of ILs properties. In Section 2, some EOSs which were obtained using the average

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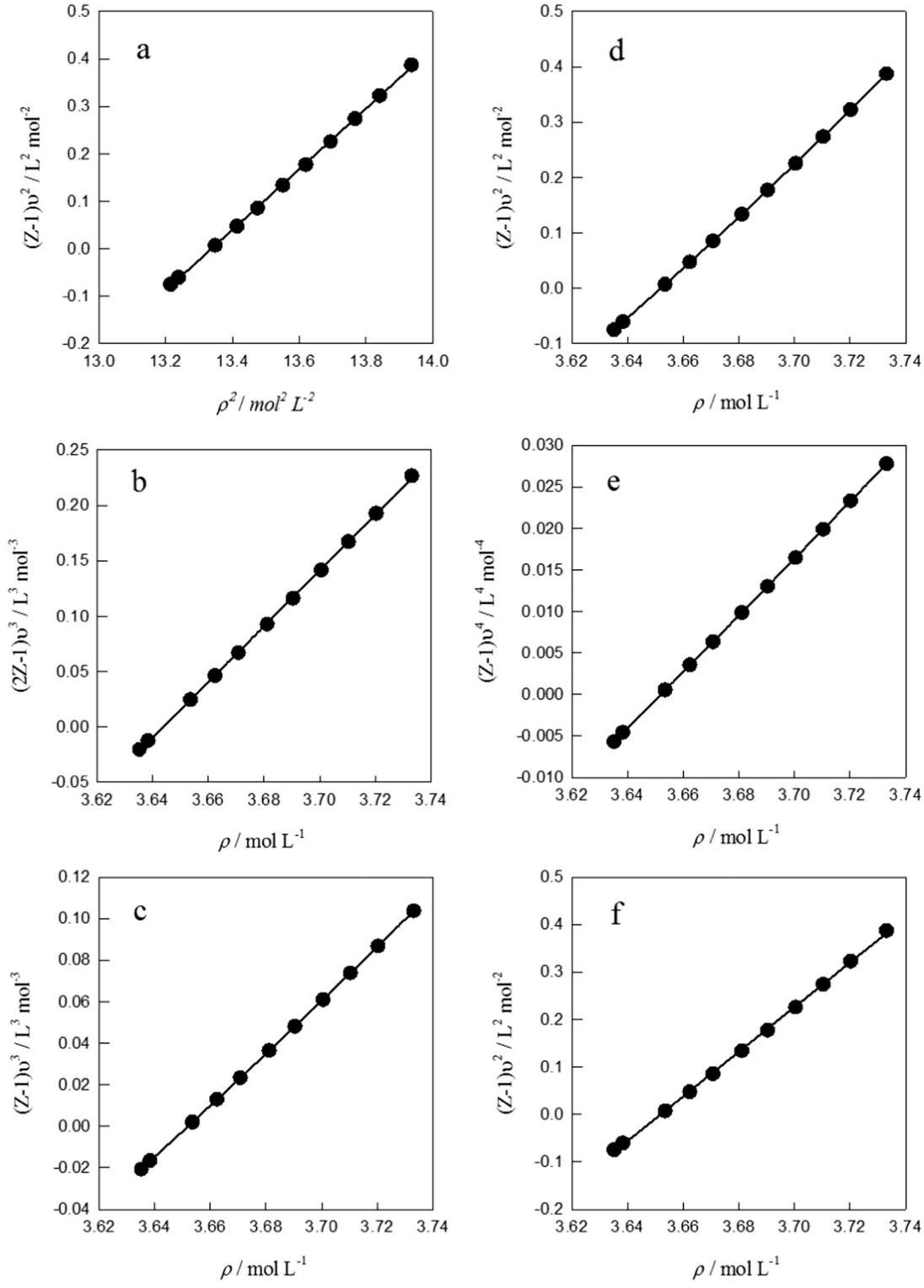

Fig. 1. Comparison of a) the LIR, b) the GMA, c) the MGMA, d) the PSP, e) the FH and f) the new EOSs in description of the experimental behavior of $[C_3mim][NTf_2]$ in 300.15 K.

intermolecular interaction between the components of fluids have been introduced.

A new EOS was presented by comparing the intermolecular potentials which were used in derivation of such EOSs and considering the least interactions that can exist between ILs components. The temperature dependencies of the new equation of state parameters have been investigated. The volumetric properties of ILs like as the density, the isothermal compressibility, and the isobaric expansivity were predicted by the new EOS and compared in Section 3 with the experimental values and other EOSs that was obtained in the same manner. The conclusion of this work has been given in Section 4.

2. Average intermolecular potential and equations of state

2.1. A new equation of state for ionic liquids

Recently, several EOSs have been derived for fluids using the thermodynamic equation of state for internal pressure and the average