



Modeling the volumetric properties of some imidazolium and phosphonium based ionic liquids from surface tension



Farkhondeh Mozaffari

Department of Chemistry, College of Sciences, Persian Gulf University, Bushehr 75168, Iran

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ABSTRACT

In this work, we have extended Song and Mason equation of state with a simple modification to imidazolium and phosphonium based ionic liquids. Four temperature-dependent parameters in the equation of state have been calculated as functions of reduced temperature with the use of the law of corresponding states. It is shown that the knowledge of surface tension, liquid density at the room temperature and two other constants that are obtained by fitting against experimental data is sufficient to predict the *PVT* properties of these ILs. Predicted densities are in good agreement with experimental literature data in a wide range of temperatures, 273.15–472.6 K, and pressures, 0.1–200.0 MPa. The overall average absolute deviation of calculated densities from literature values for 3302 data points of 17 ionic liquids was found to be 0.89%. Moreover, we indicate that the Zeno line regularity can well be predicted by proposed model for ILs. Also, we have demonstrated the density behavior of studied imidazolium based ILs in terms of the chain length of alkyl group of cation using modified SM EOS.

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1. Introduction

Ionic liquids (ILs) are one of rapidly developing areas and the most interesting of modern physical chemistry, technologies and engineering. The unique properties of these liquids include negligible vapor pressure [1,2], low melting temperature, nonflammability, electric conductivity, thermal stability, and high heat capacity, a broad liquid range [3], and a very rich and complex behavior as solvents [4–7] that can be modified by changing the nature of the anion or cation. These unique properties make them very interesting, especially for applications in the field of green chemistry.

For the successful use of ILs and efficient design of chemical products and processes, an intensive and systematic investigation of their physicochemical properties is required. These properties are of interest from the point of view of both fundamental and applied research. On the other hand, a comprehensive knowledge of the thermophysical properties of ILs is important in relating microscopic and macroscopic behavior [8–11]. Therefore, precise knowledge of the pressure–volume–temperature (*PVT*) properties of ILs is worth as it is necessary to determine whether the use of ILs could be extended from the laboratory level to large scale industrial applications. The equation of state (EOS) and *PVT* correlations are two most commonly used methods of calculating *PVT* properties.

The present work is a continuation of our study on modeling of the volumetric properties of imidazolium ionic liquids [12] using Song and Mason (SM) EOS [13]. The second virial coefficient, which specifies binary interactions between atoms and molecules, plays an important role in the proposed EOS. By knowing the second virial coefficient, the prediction of the entire *PVT* surface of fluids can be attained. Therefore, the knowledge of the binary intermolecular potential energy between atomic and molecular constituents of that system is maximum information for predicting thermodynamic properties of systems by EOS [14, 15]. Unfortunately, except for some simple gases, there are no exact intermolecular potential energies for real fluids. Of course, the experimental second virial coefficient is another good source for using the EOS [14], but the experimental second virial coefficients have not been measured in a wide range of temperature for all systems. The most generally useful method of prediction of *PVT* properties of the fluids is the use of the hypothesis of corresponding states, which came originally from well-known van der Waals EOS. A macroscopic theory of corresponding states was derived by van der Waals based on his EOS. It can be shown, however, that van der Waals' derivation is not tied to a particular equation but can be applied to any EOS containing two arbitrary constants. Several correlation procedures for the second virial coefficient have been proposed in the literature via, the heat of vaporization and the liquid density at the freezing points [16], the critical constants [17], the normal boiling point constants [18], boiling point [19] and the surface tension and the liquid density at the freezing point [20]. It should be mentioned that the microscopic theory of corresponding states, which is based on mathematical properties of the potential energy function, has also been applied to thermodynamic properties. [21–23].

E-mail address: mozaffarif@pgu.ac.ir.

In this work, the proposed equation of state consists of four temperature dependent parameters. In the previous study, we used liquid density at the normal boiling point and normal boiling temperature as two scaling parameters to determine temperature dependent parameters in SM EOS. In this study, we predict the equation of state for imidazolium and phosphonium ILs from surface tension and liquid density at room temperature as two scaling parameters which, as we will show, can correlate and predict the thermophysical behavior of ILs over a wide range of temperatures and pressures. Moreover, we compare the predictive power of SM EOS and modified SM EOS [24] together as well as with experimental data. The ILs studied in this work have been listed in Table 1.

Moreover, we indicate that the Zeno line regularity can well be predicted by proposed model for ILs. This paper also deals with the consideration of density behavior of ILs with respect to the chain length of alkyl group of cation. Generally, density of ILs shows that it can be described by variations in the cation and anion size. From the experimental data, a regular decrease in the molar density with the addition of $-CH_2$ to the alkyl chain of imidazolium cation of the corresponding ILs and a molar density decrease of ILs with increasing anion size were observed [25].

2. Theoretical equation of state

The general frame of the SM EOS for convex-molecular fluids based on statistical-mechanical perturbation theory can be expressed as [13]:

$$\frac{P}{\rho kT} = 1 + B_2(T)\rho + \alpha(T)\rho[G(\eta) - 1] \quad (1)$$

where P is the pressure, ρ is the molar (number) density, $B_2(T)$ is the second virial coefficient, $\alpha(T)$ is the contribution of repulsive branch of pair potential function according to Weeks–Chandler–Anderson approach in perturbation theory of liquids [26]. $G(\eta)$ is the average pair distribution function at contact for equivalent hard convex bodies, η is the packing fraction, and kT is the thermal energy per one molecule. Song and Mason [13] adopted the following form for $G(\eta)$, which is shown to be accurate for hard convex bodies [13,27].

$$G(\eta) = \frac{1 - \gamma_1\eta + \gamma_2\eta^2}{(1 - \eta)^3} \quad (2)$$

where γ_1 and γ_2 are chosen to reproduce the correct third and fourth virial coefficients. In practice γ_1 and γ_2 can be approximated in terms of

a single nonsphericity parameter γ . The parameters γ_1 and γ_2 have been defined in terms of γ as [13]:

$$\gamma_1 = 3 - \frac{1 + 6\gamma + 3\gamma^2}{1 + 3\gamma} \quad (3)$$

and

$$\gamma_2 = 3 - \frac{2 + 2.64\gamma + 7\gamma^2}{1 + 3\gamma} \quad (4)$$

The packing fraction, η , is given by

$$\eta = \frac{b(T)\rho}{1 + 3\gamma} \quad (5)$$

where b is the van der Waals covolume and can be defined in terms of α as [13]:

$$b(T) = \alpha(T) + T \frac{d\alpha(T)}{dT} \quad (6)$$

In this section, the temperature-dependent parameters $B_2(T)$, $\alpha(T)$ and $b(T)$ must be evaluated. Once the intermolecular potential energy function is known, these parameters can be found by three integrations. The second virial coefficient $B_2(T)$ is used both directly and as the source of a scaling constant for calculation of $\alpha(T)$ and $b(T)$ [13]. In fact, $B_2(T)$ is used to determine the Boyle parameters, the Boyle volume and the Boyle temperature, and it is shown that when reduced in terms of the Boyle volume $\alpha(T)$ and $b(T)$ are universal functions of the reduced temperature [28]. This means that one can also use experimental values of $B_2(T)$ over a wide range of temperatures to determine the Boyle parameters, and hence $\alpha(T)$ and $b(T)$. But accurate potential energy function for the calculation of $B_2(T)$ are scarce. In absence potential energy function and experimental values of $B_2(T)$, the most generally useful method to predict these parameters is the use of the hypothesis of corresponding states. In these methods, we need two scaling constants, one to reduce the temperature-dependent parameters and one to reduce the temperature. [16–20,29–31].

In this study, we aim to parameterize preceding corresponding states correlations [20] together with alternative scaling constants; i.e. surface tension and liquid density at room temperature of some ILs have been taken as two available scaling constants into account. These correlations can be defined as:

$$B_2(T)\rho^* = 0.0804 - 2.1288T_r^{-1} + 8.5597T_r^{-2} + 7.4294T_r^{-3} - 3.3494T_r^{-4} \quad (7)$$

Table 1
Molecular weight, surface energy constants (σ^* and ρ^*), adjustable parameter (γ) of SM EOS for ionic liquids and the value of coefficients b_1 – b_2 used in Eq. (12) for modified SM EOS.

ILs	M (g/mol)	σ^* (mN/m)	ρ^* (mol/m ³)	γ	b_1	b_2
[C ₄ mim][PF ₆]	284.18	47.92	4783.34	0.533	0.620	−0.564
[C ₂ mim][NTf ₂]	391.32	35.71	3881.16	0.531	0.626	−0.553
[C ₃ mim][NTf ₂]	405.34	34.22	3629.40	0.545	0.663	0.689
[C ₄ mim][NTf ₂]	419.20	32.80	3427.00	0.543	0.661	−0.676
[C ₅ mim][NTf ₂]	433.39	32.41	3230.03	0.546	0.663	−0.682
[C ₆ mim][NTf ₂]	447.42	32.31	3079.14	0.539	0.639	−0.592
[C ₇ mim][NTf ₂]	461.45	31.36	2909.31	0.536	0.639	−0.604
[C ₈ mim][NTf ₂]	475.50	30.63	2778.12	0.533	0.637	−0.611
[C ₁₀ mim][NTf ₂]	503.53	31.34	2529.82	0.541	0.653	−0.703
[C ₂ mim][EtOSO ₃]	236.3	45.43	5252.22	0.535	0.604	−0.396
[C ₂ mim][CF ₃ SO ₃]	260.2	44.40	5302.84	0.530	0.621	−0.514
[C ₄ mim][MeSO ₄]	250.31	47.92	4810.44	0.531	0.618	−0.531
[C ₄ mim][OcSO ₄]	349.00	26.71	3052.51	0.573	0.545	0.106
[C ₄ mim][BF ₄]	226.02	40.56	5327.65	0.560	0.565	−0.025
[C ₆ mim][BF ₄]	282.13	32.70	3949.95	0.531	0.593	−0.292
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)] [Cl]	519.30	33.40	1716.92	0.543	0.677	−0.925
[(C ₆ H ₁₃) ₃ P(C ₁₄ H ₂₉)] [NTf ₂]	764.00	33.00	1396.07	0.546	0.700	−1.26

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