



# Modeling of ionic liquid + polar solvent mixture molar volumes using a generalized volume translation on the Peng–Robinson equation of state



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## ARTICLE INFO

### Article history:

Received 22 November 2014

Received in revised form 26 February 2015

Accepted 2 March 2015

Available online 5 March 2015

### Keywords:

Phase behavior

Modeling

Volume translation

Ionic liquids

Density

## ABSTRACT

In this study, a volume-translated version of the Peng–Robinson equation of state (PR EoS) is developed for ionic liquid + polar solvent mixtures to estimate molar volumes within a range of compositions and temperatures. The ionic liquids investigated consisted of various combinations of either the 2-hydroxyethylammonium or the alkyl-methylimidazolium cation with various alkyl chain lengths, with the anions methyl-sulfate, ethyl-sulfate, hydrogen-sulfate, dicyanamide, acetate, bis(trifluoromethyl-sulfonyl)imide, and tetrafluoroborate. The polar solvents consisted of water, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, acetone, nitromethane and dichloromethane. The volume shift parameter,  $c$ , was first optimized for all of the systems investigated at each composition and temperature. Based on the values obtained, it was observed that temperature-dependency is negligible. Therefore, a generalized equation was presented for the  $c$  parameter as a function of the molar composition of the polar solvent and the molecular weight of the ionic liquid. This relation, which contains a combination of exponential, logarithmic and polynomial terms, was able to improve the predictions of the PR EoS and reduce the errors with respect to experimental data. The average errors of the conventional PR EoS and the volume-translated PR EoS (both without using any binary interaction parameters) were equal to 14.92% and 5.91%, respectively. The added advantage of using this correlation is that it omits the need to optimize any binary interaction coefficients in such highly nonideal systems, making it a very simple and practical engineering tool for the industries, while at the same time increasing predictive accuracy.

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## 1. Introduction

The chemical industries play a very significant role in daily life, however, at the same time, they have negative impacts on the environment and human health. Therefore, the reduction of the negative effects of chemical processes has become a concern for scientists [1–3]. Researchers are trying to reduce the undesirable effects of chemicals by replacing them with less polluting materials or materials that are easily recycled [4–8]. Ionic liquids (ILs), with their unique properties, are a rather new group of chemical compounds which can be used to carry out chemical processes with minimal air pollution. Because of this, they have been considered as a revolution in the chemical industries since they can potentially be used in place of the prevalent polluting, or even dangerous, solvents [9–11].

An ionic liquid, which is actually a salt, usually comprises a large asymmetrical organic cation and an organic or mineral anion. Ionic liquids have low melting points due to their asymmetrical molecular structure, being liquid at ambient temperatures [12–14]. For this reason, these compounds are also called “room-temperature ionic liquids.” Ionic liquids have special chemical and physical properties which make them useful for different processes. For example, ionic liquids could be used as absorbents for acidic gases, as substitutes for organic solvents in chemical processes, as catalysts in the petrochemical industries, and as green solvents in reactions requiring a polarized environment [8,9–16]. To modify current industries with the aid of ionic liquids and to produce new chemicals, it is very important to develop precise models for predicting thermodynamic properties and phase equilibria of the specific ionic liquids and their various mixtures over a vast range of temperatures and pressures [17–19].

Equations of state (EoS) are among the models that are able to predict the phase equilibria of various mixtures of ionic liquids. A number of researchers have investigated the ability of equations of state in predicting the molar volumes of pure ionic liquids and their

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mixtures with other substances. Arce et al. [20] examined vapor–liquid equilibria in some ionic liquid+gas systems at high temperatures using the Peng–Robinson/Stryjek–Vera (PRSV) equation of state and a number of mixing rules. Yokozeki and Shiflett [21] used the original van der Waals equation of state to study the solubility of different gases in ionic liquids. In a study by Valderrama et al. [22], gas–liquid equilibria in mixtures of supercritical carbon dioxide and ionic liquids were investigated using the gamma–phi model (with either the Peng–Robinson/Kwak–Mansoori mixing rules or the Peng–Robinson/Wong–Sandler mixing rules and the NRTL and van Laar models for the activity coefficient) and the results were compared with experimental data. González et al. [23] studied liquid–liquid equilibria of binary systems of benzene+ionic liquid at atmospheric pressure using the group contribution equation of state. In 2013, using the electrolyte cubic square well equation of state, Zare et al. [24] studied the vapor–liquid equilibria of ionic liquid solutions with methane hydrate. Some of these studies indicated that equations of state can have large errors in predicting the phase equilibria of such mixtures, especially for the liquid phase. Therefore, modifications aimed at improving EoS predictions of ionic liquid mixtures are called for.

Accurate mixture densities are particularly important in designing and optimizing chemical processes. In general, applying a volume-translation technique to an equation of state can increase the accuracy of liquid phase density predictions [25–27]. For example, Tsai and Chen [17] reported that the results of a volume-translated Peng–Robinson (VTPR) equation of state are better than the conventional cubic EoS for predicting the liquid molar volume of pure components, as well as mixtures. Laugier et al. [28] applied the cubic equation of state and a neural network-based volume translation method to model the vapor–liquid equilibria of pure and mixed systems, and compared the results with the Lee–Kessler–Plöcker equation, as well as the SRK and BWRS EoS. They reported lower average relative deviations for their model. Using a volume-translated Peng–Robinson equation of state, Abudour et al. [29] studied the densities of diverse binary liquid mixtures over large ranges of pressures and temperatures. Using a

volume-translated method with the SRK EoS, Frey et al. [30] also studied the densities of various liquid mixtures over large ranges of pressures and temperatures and obtained satisfactory results. Nazarzadeh and Moshfeghian [31] modeled pure compounds, as well as gas condensate systems, by using the PR EoS and a new temperature-dependent volume-translation.

Therefore, although the volume-translation method has been used for some pure and mixed systems, such as hydrocarbons and noble gases, it has not yet been investigated to predict the behavior of ionic liquid systems. Considering the strong intermolecular interactions prevailing in mixtures containing ionic liquid, making them rather challenging to model accurately, a volume-translation method coupled with the Peng–Robinson equation of state is used in this study in an attempt to better correlate the density of mixtures of ionic liquids and polar solvents over a range of temperatures.

## 2. Theoretical background

After the introduction of the first cubic equation of state by van der Waals, other scholars also proposed different cubic equations of state. The cubic equation of state is one of the simplest equations of state for modeling and simulating processes since it does not demand large amounts of data and does not require very complicated mathematical calculations [17–19]. However, one of the major problems of these equations is that they cannot predict the density of liquids accurately. A comparison of predicted molar masses of liquids by cubic equations of state and the experimental values indicated systematic deviations [26,27] which could be decreased by adding a constant to the predicted molar mass as follows [17].

$$C = v_{\text{EoS}} - v_{\text{exp}} \quad (1)$$

in which, the  $c$  parameter represents a systematic deviation [17].

This concept was used for the first time by Peneloux et al. [32] for the Soave–Redlich–Kwong (SRK) equation of state. They used the correction of the liquid molar mass as a function of the Rackett compressibility factor. In other words, they used the  $c$  parameter as

**Table 1**  
The ionic liquid + polar solvent mixtures investigated in this study.

System I.D.	System	Number of experimental data	Temperature range (K)	Ref.	Error of PR EoS (%)	Error of modified model (%)
1	bmimMeSO <sub>4</sub> + 2-propanol	40	298.15–313.15	[35]	1.45	–
2	bmimMeSO <sub>4</sub> + ethanol	14	298.15–313.15	[35]	2.50	–
3	emimDCA + ethanol	40	298.15–343.15	[36]	31.63	2.10
4	hmimNTf <sub>2</sub> + dichloromethane	33	288.15–298.15	[37]	9.98	2.73
5	emimOAC + water	40	298.15–343.15	[36]	28.03	2.44
6	emimDCA + water	40	298.15–343.15	[36]	40.8	3.55
7	emimOAC + ethanol	40	298.15–343.15	[36]	19.78	2.98
8	bmimBF <sub>4</sub> + ethanol	11	298.15	[38]	16.20	9.46
9	bmimBF <sub>4</sub> + nitromethane	13	298.15	[38]	23.20	16.06
10	hmimBF <sub>4</sub> + ethanol	9	298.15	[39]	18.40	9.24
11	hmimBF <sub>4</sub> + water	7	298.15	[39]	22.86	11.45
12	moimBF <sub>4</sub> + ethanol	9	298.15	[40]	21.35	24.06
13	hmimBF <sub>4</sub> + 1-propanol	35	293.15–333.15	[40]	16.74	3.01
14	hmimNTf <sub>2</sub> + acetone	33	288.15–298.15	[37]	13.76	2.56
15	hmimNTf <sub>2</sub> + 1-propanol	33	298.15–328.15	[37]	8.79	2.71
16	hmimBF <sub>4</sub> + 2-propanol	45	293.15–333.15	[41]	17.54	3.67
17	2 + heaa + ethanol	55	288.15–323.15	[42]	10.08	2.34
18	hmimNTf <sub>2</sub> + ethanol	36	298.15–328.15	[37]	10.66	3.21
19	hmimNTf <sub>2</sub> + methanol	24	298.15–313.15	[37]	14.16	2.63
20	hmimNTf <sub>2</sub> + 1-propanol	33	298.15–328.15	[37]	9.10	2.12
21	bmimMeSO <sub>4</sub> + 1-butanol	32	298.15–313.15	[35]	0.80	–
22	bmimMeSO <sub>4</sub> + nitromethane	12	298.15	[38]	9.76	–
23	emimc <sub>2</sub> SO <sub>4</sub> + water	49	283.15–343.15	[43]	4.94	–
24	bmimHSO <sub>4</sub> + water	35	303.15–343.15	[43]	5.58	–
	All systems	719			14.92	5.91

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