



# Representation of phase behavior of ionic liquids and their mixtures using various forms of cubic-two-state equation of state



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## ARTICLE INFO

### Article history:

Received 20 October 2016

Received in revised form

5 December 2016

Accepted 7 December 2016

Available online 9 December 2016

### Keywords:

Ionic liquids

Cubic-Two-State equation of state (CTS EoS)

Vapor-liquid equilibrium

Self association

Cross association

## ABSTRACT

In this work, in addition of Soave-Redlich-Kwong (SRK) equation of state, two other alternative cubic models such as Peng-Robinson (PR) and Cubic Square Well (CSW) EoSs are combined with the Two-State Association Model (TSAM) and the new forms of the Cubic-Two-State equation of state (CTS EoS) as PR-TS and CSW-TS are presented. In the beginning, the present models are used to correlate the saturated vapor pressure and liquid density of pure water, alcohols and phenol. The models are also employed to predict vapor molar volume and second virial coefficients of pure compounds to explore the predictability of the different type of the CTS models. Also, the liquid density of different pure ionic liquids (ILs) at various temperatures from 298.15 K up to 500 K and pressure from 0.1 MPa up to 59.59 MPa is correlated and the parameters of the CTS models are obtained. Following successful application of the models for the pure components, using one temperature independent binary interaction parameter, the SRK-TS and PR-TS models are applied to predict the vapor-liquid equilibrium of the several binary mixtures consists of IL with non-association and association components at various temperatures from 298.15 K up to 363.15 K and pressure from 0.09 kPa up to 216 kPa. The results of the SRK-TS and PR-TS models for pure and binary systems containing ILs are in very good agreement with experiments and also are compared with various equations of states that show better results. In overall for the systems that are presented in this work, the PR-TS model shows slightly better results with respect to the SRK-TS model specially in prediction, and PR-TS and SRK-TS models present superiority with respect to the CSW-TS EoS.

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## 1. Introduction

In the past decade, ionic liquids (ILs) as a new class of compounds have been considered by many researchers. Ionic liquids are organic salts that are in liquid form below 100 °C even at the room temperature (RTILs). The unique properties of ionic liquids like negligible vapor pressure, thermal and chemical stability, a wide liquid temperature range, nonflammable, tunable nature and good CO<sub>2</sub> solubility are representing them as green solvents and interesting candidates for a variety of applications. The negligible vapor pressure of ILs presents them desirable as a replacement for volatile organic compounds (VOCs) which introduce several health, environmental, and economic concerns in numerous industrial

applications [1,2].

The knowledge about the thermodynamic properties data such as the phase behavior of pure and mixtures containing ionic liquids is very important for industrial use like extractions and purifications. However, experiments are time-consuming and usually difficult and expensive. Therefore, it is highly desirable to develop predictive methods for estimating the thermodynamic properties at different temperatures and pressures. Equation of state (EoS) is a powerful tool for accurate representation of thermodynamic properties of pure fluids in a wide range of temperature and pressure. It can also be applied for calculation of thermodynamic properties of the mixtures using proper mixing rule. The phase behavior of systems containing ionic liquids is one of the important properties for the design and operation of chemical processes. In the past few years, many researchers are modeling these types of systems using different equations of state.

In an earlier work, Shariati and Peters [3] used the Peng-Robinson (PR) EoS to model the solubility of fluoroform (CF<sub>3</sub>H) in 1-ethyl-3-methylimidazolium hexafluorophosphate, [C<sub>2</sub>mim]

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[PF<sub>6</sub>], at different temperatures and pressures up to 50 MPa. Yang et al. [4] and Xu et al. [5] employed the lattice-fluid equation of state which takes into account the hydrogen bonding through an exchange energy function to describe several thermodynamic properties such as vapor-liquid equilibrium of the [BF<sub>4</sub>], [PF<sub>6</sub>] and [NTf<sub>2</sub>] ILs family mixtures with alcohols and CO<sub>2</sub>. Wang et al., in two separate works [6,7], correlated the *pVT* behavior of different pure ILs and some mixtures with gases, alcohol and water, with only one temperature-independent adjustable parameter, using the homo-nuclear and heteronuclear versions of the square-well chain fluids (SWCF) equation of state. Ji and Adidharma [8] utilized hetero-segmented SAFT to estimate the density of [BF<sub>4</sub>], [PF<sub>6</sub>] and [NTf<sub>2</sub>] imidazolium ionic liquids. Economou and co-workers published several works [9–12] where they applied the truncated perturbed chain polar statistical associating fluid theory (tPC-PSAFT) to calculate thermodynamic properties and phase behavior of several ionic liquids. Andreu and Vega [13,14] used the soft-SAFT equation of state as a simpler model than the other above-mentioned versions of SAFT (SWCF and tPC-PSAFT) for the correlation of solubility data of CO<sub>2</sub>, H<sub>2</sub>, CO and Xe in the alkylimidazolium based ionic liquid family with different fluorinated anions. Vega and co-workers [15] applied the soft-SAFT model for describing the thermodynamic characterization of [C<sub>n</sub>mim] [NTf<sub>2</sub>] family ILs and mixtures with several other associating compounds. Li et al. [16] employed the square-well chain fluids with variable range (SWCF-VR) based on statistical mechanics for chemical association for the calculations of pressure-volume-temperature (*pVT*) and phase equilibrium of 23 pure ionic liquids (ILs) and their mixtures. Xu et al. [17] developed lattice-fluid equation of state (LF EoS) to model the *pVT* properties and phase equilibria of IL systems. They used one adjustable binary parameter for description of the vapor-liquid equilibria (VLE) of binary IL-solvent systems. Also in a recent work, Jun et al. [18] used the cubic plus association shield-sticky method (CPA-SSM) EoS that is combined from the Peng-Robinson equation of state with an associated model derived from the shield-sticky method (SSM) to model the phase behavior of pure and binary IL systems. For pure ILs, four molecular parameters in CPA-SSM model is obtained by fitting and for description of binary systems one interaction parameter is used.

Recently, Medeiros and Tellez-Arredondo [19] developed the cubic-two-state equation of state (CTS EoS) based on cubic plus association (CPA) concept [20] and two state association model (TSAM) as associating contribution [21]. The CTS EoS is applied successfully to represent the phase behavior of self associating [19] and cross associating [22] systems of hydrocarbons, alcohol and water. Also, in a recent work by Medeiros and co-workers [23], an extension of the CTS EoS was employed for modeling CO<sub>2</sub> and H<sub>2</sub>S solubilities in aqueous alkanolamine solutions. In the mentioned work by Medeiros and et al. [19,22,23] the Soave-Redlich-Kwong (SRK) equation of state is applied as the cubic term.

In the present work, two new forms of CTS EoS namely PR-TS and CSW-TS EoSs are presented by combining the Peng-Robinson [24] and cubic-square-well [25] equation of states as cubic models for non-specific energy contribution with two-state association model (TSAM) for association energy contribution. The new models similar to the original forms of CTS EoS namely SRK-TS EoS, have five pure adjustable parameters. For investigation and comparison the ability of the models to describe the phase behavior of the pure association components the present models are applied for representation of the *pVT* behavior of pure water, alcohols, phenol and ionic liquids and the results compared with each other. Also, the present models are used to describe the phase behavior of the binary systems containing ionic liquid with hydrocarbons as self association and with alcohols and water as cross association binary mixtures. It is important to mention that for the first time

the CTS equation of state as various forms are applied to pure and binary systems consist of ionic liquids. Also, another reason that in this work the CTS EoS is chosen for the representation of the phase behavior of association systems is due to the simplicity of the CTS EoS respect to other association models such as CPA or SAFT EoSs. The ionic liquid in the solutions is considered as neutral molecules, due to strong electrostatic interactions [26,27], with possess associating interactions [18].

## 2. Thermodynamic modeling

The cubic-two-state equation of state (CTS EoS) based on cubic plus association (CPA) EoS consists of two individual terms. A cubic equation of state as the non-specific contribution and the association model for association contribution as follows

$$P_{CTS} = P_{cubic} + P_{association} \quad (1)$$

Similar to the work of Medeiros and co-workers [19], in this work, the two-state association model (TSAM) is applied to describe the association energy contribution. The association contribution to the pressure expression of the CTS EoS are

$$P_{association} = -RT \sum_i x_i \frac{\sum_j x_j v_{ij} f_{ij}(T)}{v \left[ v + \sum_j x_j v_{ij} f_{ij}(T) \right]} \quad (2)$$

$$f_{ij}(T) = e^{-E_{ij}/RT} - 1 \quad (3)$$

where  $P$ ,  $v$ ,  $T$  and  $R$  are the pressure, molar volume, absolute temperature and gas constant, respectively. Also,  $E_{ij}$  and  $v_{ij}$  are the association energy and association characteristic volume between species  $i$  and  $j$ , respectively. The association energy ( $E_{ij}$ ) and association characteristic volume ( $v_{ij}$ ) for the cross association mixtures are calculated using the following combining rules

$$E_{ij} = \frac{E_{ii} + E_{jj}}{2} \quad (4)$$

$$v_{ij} = \sqrt{v_{ii} v_{jj}} \quad (5)$$

A cubic equation of state as the non-specific energy contribution is used in CTS model. In this work three different cubic models, SRK, PR and CSW EoSs, are presented as cubic contribution.

The expression of SRK [28] and PR [24] EoSs are described by Eqs. (6) and (7) respectively as following

$$P_{SRK} = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad (6)$$

$$P_{PR}(X, v, T) = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)} \quad (7)$$

For pure compounds in the SRK and PR EoSs,  $b$  is the temperature independent parameter and temperature following of the  $a(T)$  is expressed by

$$a(T) = a_0 \left[ 1 + c_1 \left( 1 - \sqrt{T/T_c} \right) \right]^2 \quad (8)$$

where  $T_c$  is the critical temperature.

The parameters  $a$  and  $b$  for a mixture are calculated by one-fluid van der Waals mixing and combining rules as

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