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Modeling *pVT* Properties and Vapor-Liquid Equilibrium of Ionic Liquids Using Cubic-plus-association Equation of State*

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Abstract Combining Peng-Robinson (PR) equation of state (EoS) with an association model derived from shield-sticky method (SSM) by Liu *et al.*, a new cubic-plus-association (CPA) EoS is proposed to describe the thermodynamic properties of pure ionic liquids (ILs) and their mixtures. The new molecular parameters for 25 ILs are obtained by fitting the experimental density data over a wide temperature and pressure range, and the overall average deviation is 0.22%. The model parameter b for homologous ILs shows a good linear relationship with their molecular mass, so the number of model parameters is reduced effectively. Using one temperature-independent binary adjustable parameter k_{ij}, satisfactory correlations of vapor-liquid equilibria (VLE) for binary mixtures of ILs + non-associating solvents and + associating solvents are obtained with the overall average deviation of vapor pressure 2.91% and 7.01%, respectively. In addition, VLE results for ILs + non-associating mixtures from CPA, lattice-fluid (LF) and square-well chain fluids with variable range (SWCF-VR) EoSs are compared.

Keywords cubic-plus-association, equation of state, ionic liquids, vapor-liquid equilibrium

1 INTRODUCTION

Thermodynamic properties of ionic liquids (ILs), such as *pVT* and phase equilibrium data, are essential for industrial design and process simulation. Therefore, it is necessary to develop suitable models for correlating and predicting *pVT* and phase equilibrium of ILs. The cubic equation of state (EoS) has been widely used because of its simple form and extensive applicability. Shariati and Peters [1] firstly gave an attempt to describe the high pressure phase behavior of mixtures containing $[C_2mim][PF_6]$ and CHF_3 using the Peng-Robinson equation of state (PR EoS). Soon after, Shiflett *et al.* [2] employed a modified Redlich-Kwong (RK) EoS with a four-parameter mixing rule to calculate vapor-liquid equilibrium (VLE), liquid-liquid equilibrium (LLE), and vapor-liquid-liquid equilibrium (VLLE) of $CO_2 + [C_6mim][Tf_2N]$ mixture using the same binary interaction parameters. Coupling with Wong-Sandler (WS) mixing rule, Carvalho *et al.* [3] reproduced the experimental solubility of CO_2 in $[C_2mim][NTf_2]$ and $[C_5mim][NTf_2]$ at high pressure using PR EoS. Combining PR EoS and the Mathias-Klotz-Prausnitz (MKP) mixing rule, Trindade *et al.* [4] successfully correlated LLE of mixtures of ILs ($[C_nmim][NTf_2]$ ($n = 2$ and $n = 10$) and $[C_2mim][OTf]$) and alkanols (1-propanol, 1,2-propanediol, and glycerol). Arce *et al.* [5] correlated and predicted the VLE of 17 IL + gas binary mixtures with a good precision by the Peng-Robinson/Stryjek-Vera (PRSV) EoS in combination with the van der Waals (VDW) and van Laar (VL) + Wong-Sandler (WS) mixing rules. Although the cubic EoSs have well been extended to mixtures containing ILs, there are usually many binary adjustable parameters contained in complicated mixing rules to obtain good correlations [2–5]. Thus, the application of the cubic EoSs to IL systems is limited.

Moreover, there exist hydrogen bonding interactions in ILs, which have been proved and studied using infrared spectroscopy [6–8]. Since the ILs containing nitrogen, oxygen or fluroine also can form hydrogen bonding with solvents such as water, alcohols, *etc.*, it should be more reasonable if introducing the association interaction of hydrogen bonding into the models of ILs. Andreu and Vega [9, 10] considered ILs as a Lennard-Jones chain with one or three associating site, and an association term was introduced in the soft-statistical associating fluid theory (soft-SAFT) EoS to model the IL systems. Wang *et al.* [11, 12] introduced the associating interaction into the heteronuclear square-well chain fluids (hetero-SWCFs) EoS to correlate imidazolium-based ILs. Ji and Adidharma [13] calculated the solubility of CO_2 in ILs with heterosegmented statistical associating fluid theory (SAFT), in which the associating interaction was also taken into account. However, the hydrogen bonding interaction is usually not considered in the common cubic EoSs, only the CPA EoS proposed by Kontogeorgis *et al.* [14] makes up for this deficiency. Following Kontogeorgis *et al.*'s idea, a CPA EoS derived from PR EoS [15] and an association term [16] based on the sticky-shield method (SSM) (tentatively named

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as CPA-SSM) is presented and extended to IL systems in this work. In the model, ILs are simply considered as neutral molecules composed of ionic pairs with associating interactions. Then, four molecular parameters of pure ILs are obtained by fitting the experimental density data, and the VLE data of the systems containing ILs are calculated.

2 CPA-SSM EOS

The CPA EoS is a combination of a common cubic EoS and the association contribution. The compressibility factor z is usually expressed as

$$z = z_{\text{cubic}} + z_{\text{assoc}} \tag{1}$$

where z_{cubic} and z_{assoc} represent the physical and the association contribution, respectively. In this work, the PR EoS [15] is employed to represent physical contribution, and the corresponding compressibility factor z_{cubic} for a mixture can be written as

$$z_{\text{cubic}} = \frac{V_m}{V_m - b} - \frac{aV_m}{RT\left[V_m\left(V_m + b\right) + b\left(V_m - b\right)\right]} \tag{2}$$

where a and b are characteristic parameters, which can be calculated using the classical van der Waals one-fluid mixing rule

$$a = \sum_i \sum_j x_i x_j a_{ij}\ , \quad b = \sum_i x_i b_i \tag{3}$$

with

$$a_{ij} = \left(1 - k_{ij}\right)\sqrt{a_{ii} a_{jj}} \quad \left(k_{ii} = k_{jj} = 0,\ k_{ij} = k_{ji}\right) \tag{4}$$

$$a_{ii} = a_{0,i}\left[1 + c_{1,i}\left(1 - \sqrt{T_r}\right)\right]^2 \tag{5}$$

where k_{ij} is a temperature-independent binary interaction parameter, $T_r = T/T_c$ represents a reduced temperature, and T_c is the critical temperature. The critical properties of all ILs investigated in this work are from references directly [17–19].

The association contribution to compressibility factor in this model is calculated by Liu and Hu's model [16]

$$z_{\text{assoc}} = \sum_i x_i \left(\frac{1}{X_i} - \frac{1}{2}\right) \rho_0 \left(\frac{\partial X_i}{\partial \rho_0}\right) \tag{6}$$

where X_i represents the mole fraction of molecule i not bonded, x_i is the mole fraction of component i, and ρ_0 is the total molecule number density. In Eq. (6), X_i and $\rho_0\left(\partial X_i / \partial \rho_0\right)$ are calculated by

$$X_i = \left(1 + \sum\nolimits_j X_j \Omega_{ij}\right)^{-1} \tag{7}$$

and

$$\left(\rho_0 \frac{\partial X_i}{\partial \rho_0}\right) = -X_i^2 \sum\nolimits_j \Omega_{ij} \left(\rho_0 \frac{\partial X_j}{\partial \rho_0}\right) - X_i^2 \sum_j \rho_0 \frac{\partial \Omega_{ij}}{\partial \rho_0} X_j \tag{8}$$

where

$$\rho_0 \frac{\partial \Omega_{ij}}{\partial \rho_0} = \Omega_{ij}\left(1 + \eta \frac{\partial \ln y^{\text{ref}}}{\partial \eta}\right) \tag{9}$$

$$\Omega_{ij} = \frac{x_j \Lambda_{ij} b_{ij}}{b} \tag{10}$$

In Eq. (10), the parameter b_{ij} is defined as $b_{ij} = (b_i + b_j)/2$. Λ_{ij} is the association strength between molecules i and j expressed as

$$\Lambda_{ij} = 2\omega_{ij}\left[\exp\left(\delta\varepsilon_{ij}/kT\right) - 1\right] y^{\text{ref}} \eta \tag{11}$$

where ω_{ij} is the surface fraction responsible for the association, and $\delta\varepsilon_{ij}/k$ is the association energy parameter. If $i = j$, ω_{ij} and $\delta\varepsilon_{ij}/k$ are the parameters for pure substances. If $i \neq j$, ω_{ij} and $\delta\varepsilon_{ij}/k$ are the cross-association parameters between molecules i and j. In self-associating systems, the cross-association parameters are equal to zero. Therefore, the combining rules for the association parameters are not needed for the self-associating systems. The cavity-correlation function y^{ref} in Eq. (11) is given by Liu and Hu [16]

$$\ln y^{\text{ref}} = \frac{0.309095\eta + 0.097105}{(1-\eta)} + \frac{0.097105}{(1-\eta)^2} - 2.75503\ln(1-\eta) \tag{12}$$

where the reduced density η is defined as $\eta = b/4V_{\text{m}}$.

So far, the complete expressions of PR EoS and association are given and the final CPA-SSM EoS can be obtained *via* Eqs. (2) and (6). For non-associating fluids, z_{assoc} equals zero, and the CPA-SSM EoS reduces to PR EoS [15]. If $x_i = 1$, the CPA-SSM EoS reduces to the EoS for pure fluids, in which each molecule of pure ILs is characterized by five molecular parameters: two molecular parameters a_0 and c_1 in the physical part as shown in Eq. (5), the surface fraction for association ω and the association energy $\delta\varepsilon/k$ in the association part as shown in Eq. (11), and the size parameter b in both the physical and the association parts. In addition, in this work, the association energy parameter $\delta\varepsilon/k$ of ILs is fixed, thus only four molecular parameters (a_0, c_1, b and ω) in the CPA-SSM EoS are to be determined.

3 RESULTS AND DISCUSSION

3.1 *pVT* of pure ionic liquids

The CPA-SSM EoS is first used to correlate the experimental density data of 25 ILs over a wide temperature and pressure range and model parameters in the CPA-SSM EoS for each IL are obtained. In regression, the following objective function (OF) based on the minimization of calculated errors of the liquid densities is used

$$\text{OF} = \frac{1}{N_{\text{m}}} \sum_{i=1}^{N_{\text{m}}} \left(\frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}}\right)^2 \tag{13}$$

where ρ^{cal} and ρ^{exp} are the calculated and experimental densities of pure IL, respectively, and N_{m} is the number of experimental data point. The obtained molecular parameters (a_0, c_1, b, ω) and the deviation of liquid density for each pure IL are listed in Table 1. The overall average deviation for 25 ILs is only 0.22% by the four-parameter CPA-SSM EoS, which are a little worse than 0.07% for 23 ILs by the SWCF-VR EoS [33] and 0.12% for 48 ILs by the LF EoS [34]. Unlike the LF EoS and SWCF-VR EoS, the CPA-SSM EoS is developed from the empirical PR EoS which is widely applied in engineering areas and extended to ILs and associating fluids. Considering its simple expression, the result of the CPA-SSM EoS is acceptable. In Table 1, the value of the association energy parameter $\delta\varepsilon/k$ is fixed to 3500 K for all ILs investigated since the correlated results using the five-parameter CPA-SSM EoS show that the association energy parameter $\delta\varepsilon/k$ is very close to 3500 K for all systems, which is consistent with the value of association energy parameter (3450 K) reported by Andreu and Vega [10], who correlated the experimental density of some pure ILs containing the group of bis(trifluoromethylsulfonyl)imide anion ($[\mathrm{NTf_2}]^-$) by using the soft-SAFT EoS [35].

For common associating fluids, each molecule in the CPA-SSM EoS is characterized by five molecular parameters. Table 2 lists the molecular parameters and the correlation results of saturated vapor pressures and liquid densities for the interested substances in this work. In the calculation, the temperature range is set from $0.55T_{\mathrm{c}}$ to $90T_{\mathrm{c}}$ for each compound. It should be noted that a suitable associating mechanism for associating component must be selected in advance since different associating mechanisms may result in different results in Kontogeorgis' CPA EoS [14], while the selection of associating mechanism is not needed in the CPA-SSM EoS. The results of the common associating fluids obtained by the CPA-SSM EoS are

Table 1 Molecular parameters and correlated results of pure ionic liquids by CPA-SSM model

ILs	T/K	p/MPa	a_0	c_1	$b\times10^{-3}$/m^3·mol^{-1}	$\omega\times10^5$	ΔV①/%	Ref.
$[\mathrm{C_1mim}][\mathrm{NTf_2}]$	298.15−353.15	0.1	43.326	0.92145	0.21284	206.94	0.03	[20]
$[\mathrm{C_2mim}][\mathrm{NTf_2}]$	293.15−393.15	0.1−30	7.7378	7.0670	0.23976	7.6323	0.36	[21]
$[\mathrm{C_3mim}][\mathrm{NTf_2}]$	298.15−333.15	0.1−59.59	17.294	4.3057	0.25598	12.005	0.33	[22]
$[\mathrm{C_4mim}][\mathrm{NTf_2}]$	298.15−328.2	0.1−59.1	9.8624	6.7146	0.27214	0.90036	0.24	[23]
$[\mathrm{C_5mim}][\mathrm{NTf_2}]$	298.15−333.15	0.1−59.59	8.1477	7.8159	0.28792	1.98486	0.31	[22]
$[\mathrm{C_6mim}][\mathrm{NTf_2}]$	298.15−333.15	0.1−59.59	5.4288	10.586	0.30517	0.52184	0.31	[23]
$[\mathrm{C_7mim}][\mathrm{NTf_2}]$	293.15−393.15	0.1−30	11.430	6.6314	0.31973	0.30314	0.45	[21]
$[\mathrm{C_8mim}][\mathrm{NTf_2}]$	293.15−393.15	0.1−30	4.1183	12.848	0.33674	0.27477	0.46	[21]
$[\mathrm{C_{10}mim}][\mathrm{NTf_2}]$	293.15−393.15	0.1−35	30.756	3.3975	0.36706	1.07406	0.80	[24]
$[\mathrm{C_2mmim}][\mathrm{NTf_2}]$	296.15−333.65	0.1	42.363	1.1799	0.23734	110.26	0.04	[25]
$[\mathrm{C_3mmim}][\mathrm{NTf_2}]$	295.15−344.65	0.1	67.119	0.60645	0.25560	140.31	0.14	[25]
$[\mathrm{N(4)111}][\mathrm{NTf_2}]$	298.15−333.15	0.1	46.090	1.5041	0.26013	116.80	0.01	[26]
$[\mathrm{N(6)111}][\mathrm{NTf_2}]$	298.15−333.15	0.1	72.941	0.75284	0.28853	112.77	0.02	[26]
$[\mathrm{N(6)222}][\mathrm{NTf_2}]$	298.15−333.15	0.1	53.153	1.6882	0.33023	130.57	0.02	[26]
$[\mathrm{C_2mim}][\mathrm{BF_4}]$	293.15−393.15	0.1−30	44.831	1.8539	0.14222	139.40	0.23	[21]
$[\mathrm{C_4mim}][\mathrm{BF_4}]$	293.15−393.15	0.1−10	44.553	2.2801	0.17603	173.49	0.21	[27]
$[\mathrm{C_6mim}][\mathrm{BF_4}]$	288.15−323.15	0.1	51.193	1.2395	0.20020	153.19	0.02	[28]
$[\mathrm{C_8mim}][\mathrm{BF_4}]$	293.15−393.15	0.1−10	55.912	1.8152	0.23690	124.08	0.25	[27]
$[\mathrm{C_2mim}][\mathrm{PF_6}]$	333−500	0.1	75.963	0.59973	0.16650	241.37	0.24	[29]
$[\mathrm{C_4mim}][\mathrm{PF_6}]$	298.15−398.15	0.7−40	13.348	7.3178	0.19677	123.29	0.30	[30]
$[\mathrm{C_6mim}][\mathrm{PF_6}]$	293.15−393.15	0.1−10	30.976	3.5039	0.22561	296.51	0.24	[27]
$[\mathrm{C_8mim}][\mathrm{PF_6}]$	293.15−393.15	0.1−10	25.710	4.5028	0.25787	139.78	0.24	[27]
$[\mathrm{C_4mmim}][\mathrm{PF_6}]$	313.15−393.15	0.1−10	15.877	7.2319	0.21086	139.13	0.18	[27]
$[\mathrm{C1mim}][\mathrm{MeSO_4}]$	313.15−333.15	0.1−25	11.369	4.8598	0.14693	8.0484	0.04	[31]
$[\mathrm{C_4mim}][\mathrm{MeSO_4}]$	293.15−353.15	0.1	45.566	1.0446	0.18780	93.316	0.03	[32]
overall average deviation							0.22	

Note: The value of the association energy parameter $\delta\varepsilon/k$ for all ILs is fixed to 3500 K.

① $\Delta V = (100/N_{\mathrm{m}})\sum\left|\left(V^{\mathrm{exp}} - V^{\mathrm{cal}}\right)/V^{\mathrm{exp}}\right|$.

Table 2 Molecular parameters for pure common fluids in the CPA-SSM model

Name	a_0	c_1	$b\times10^{-3}$/m^3·mol^{-1}	ω	$(\delta\varepsilon/k)$/K	Δp①/%	ΔV②/%
methanol	6.9259	0.4494	0.0327	0.0012757	4463.86	0.39	0.57
ethanol	11.044	0.9607	0.0495	0.0099011	2922.83	0.68	1.12
1-propanol	16.293	0.9848	0.0651	0.0023804	3043.40	0.45	1.17
2-propanol	15.521	1.0485	0.0659	0.0025284	2917.66	0.64	0.87
water	5.3247	0.7559	0.0158	0.00055320	1015.25	0.47	0.39
n-hexane	26.849	0.8073	0.1078	0	0	1.03	2.23
n-octane	40.098	0.9453	0.1433	0	0	1.18	1.44
1-octene	33.617	0.9638	0.1379	0	0	0.32	0.29
n-nonane	47.427	1.0026	0.1619	0	0	0.33	0.84
acetone	16.029	0.7571	0.0621	0	0	0.18	0.93
benzene	20.497	0.7056	0.0751	0	0	1.04	2.37
toluene	26.723	0.7606	0.0923	0	0	0.65	2.01
cyclohexnae	24.236	0.7138	0.0907	0	0	0.91	2.45
cyclohexene	23.366	0.7089	0.0862	0	0	0.62	2.88
tetrahydrofuran	18.009	0.7179	0.0686	0	0	0.68	2.72

Note: Experimental data are from Refs. [36] and [37].

① $\Delta p = (100/N_{\mathrm{m}})\sum\left|\left(p^{\exp}-p^{\mathrm{cal}}\right)/p^{\exp}\right|$.

② $\Delta V = (100/N_{\mathrm{m}})\sum\left|\left(V^{\exp}-V^{\mathrm{cal}}\right)/V^{\exp}\right|$.

comparable to those of Kontogeorgis *et al.*'s model [14].

In Fig. 1, the calculated densities of [C$_1$mim][EtSO$_4$] are compared to the experimental data at temperature ranging from 318 to 333K and pressure up to 25 MPa. The CPA-SSM EoS gives an excellent description of *pVT* for [C$_1$mim][EtSO$_4$] over all pressure ranges except slightly higher deviations in the elevated pressure range.

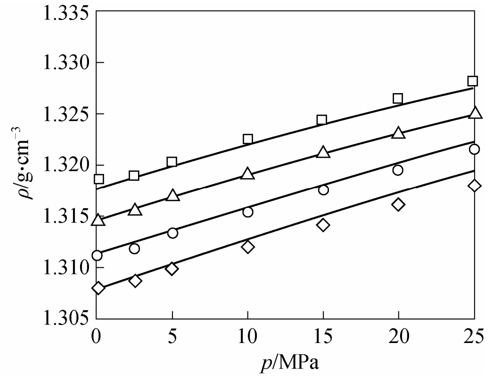

Figure 1 Comparison of theoretical (lines) and experimental [31] (symbols) densities for [C$_1$mim][MeSO$_4$]
T/K: □318.15; △323.15; ○328.15; ◇333.15

Parameter *b* in the CPA-SSM EoS represents the contribution of molecular size. The larger the molecular size, the larger the value of parameter *b*. One can see from Table 1 that parameter *b* increases with molecular mass indeed and has a good linear relation with the molecular mass for different pure homologous ILs, as shown in Fig. 2. However, the other three molecular parameters (a_0, c_1, ω) do not present evident regularity, which is consistent with the results of Kontogeorgis' CPA EoS [14]. The molecular parameter *b* of [C$_x$mim][NTf$_2$], [C$_x$mim][BF$_4$] and [C$_x$mim][PF$_6$], composed of homologous organic cations and the same anions, can be well described *via* linear function of their molecular mass. These relationships can be effectively used to predict parameter *b* of other homologous ILs and further reduce the number of model parameters of the CPA-SSM EoS.

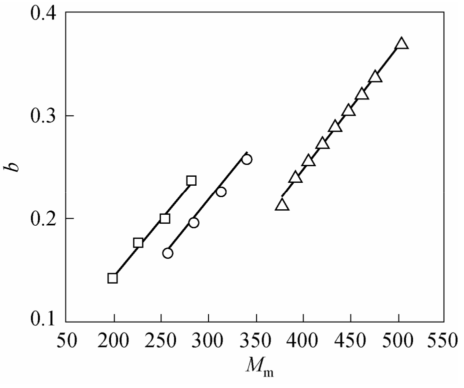

Figure 2 Linear relationships between molecular parameter b and molecular mass for homologous ILs
△[$C_x$mim][NTf$_2$]; □[C$_x$mim][BF$_4$]; ○[C$_x$mim][PF$_6$]

3.2 Vapor-liquid equilibria of binary systems

Due to the extremely low vapor pressure of ILs, their solubilities in vapor phase are usually negligible [38]. Thus, the equilibrium equation for binary IL mixtures at a given temperature can be written as

$$\varphi_1^{\mathrm{V}} = x_1^{\mathrm{L}} \varphi_1^{\mathrm{L}} \tag{14}$$

where x_1^{L} and φ_1^{L} are the solubility (molar fraction) and the fugacity coefficient of the solvent or gas in liquid phase, respectively, and φ_1^{V} is the fugacity coefficient of the pure solvent/gas in vapor phase at the same temperature and pressure.

To obtain satisfactory calculation of phase behavior for IL mixtures by the CPA-SSM EoS, the binary interaction parameter k_{ij} in Eq. (4) is determined from experimental VLE data by minimizing the objection function OF

$$\mathrm{OF} = \frac{1}{N_{\mathrm{m}}} \sum_{i=1}^{N_{\mathrm{m}}} \left(\varphi_{1,i}^{\mathrm{V}} - x_{1,i}^{\mathrm{L}} \varphi_{1,i}^{\mathrm{L}} \right)^2 \tag{15}$$

where N_{m} is the number of experimental data points.

The application of the CPA-SSM EoS in the systems of ILs + non-associating solvents is first carried out. In these systems, only the self-association interaction between ILs exists. Thus, for such systems, no combining rule for cross-association parameters is needed. In the calculation, the molecular parameters of ILs and solvents are directly from Table 1 and Table 2, respectively.

Figure 3 shows a graphical comparison between calculated and experimental results [39] of benzene in [C$_8$mim][BF$_4$] at different temperatures and pressures. The CPA-SSM EoS can satisfactorily reproduce the experimental data, and the overall AADs of pressures is 2.85% with $k_{ij} = 0.03220$.

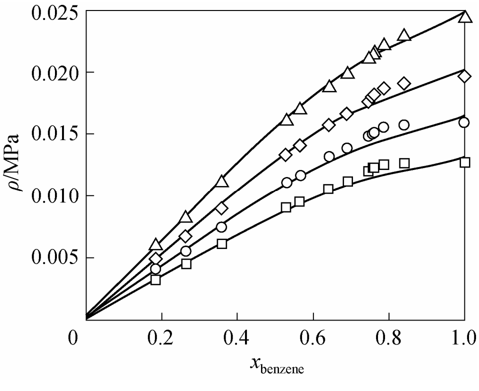

Figure 3 Comparison between theoretical (lines) and experimental [39] (symbols) VLE of benzene + [C$_8$mim][BF$_4$]
T/K: □ 298.15; ○ 303.15; ◇ 308.15; △ 313.15

Figure 4 gives a comparison between the correlated and experimental [40, 41] VLE of cyclohexane in homologous ILs [C$_x$mim][NTf$_2$](x = 1,2,4,6). The CPA-SSM EoS gives satisfactory results in all cases when the mole fraction of cyclohexane is low. However, the results become worse when the mole fraction of cyclohexane increases, especially for cyclohexane + [C$_6$mim][NTf$_2$], in which the contents of solvent in the mixture has a greater influence on the correlated results, although the calculated results are in the same trend as the experimental results.

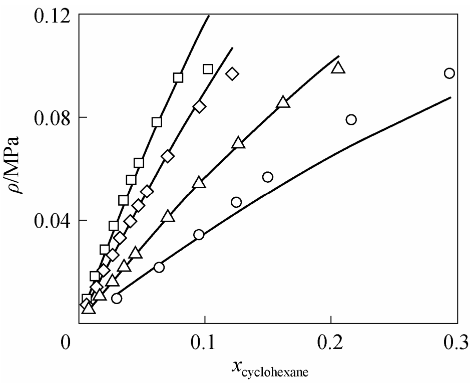

Figure 4 Comparison between theoretical (lines) and experimental [40, 41] (symbols) VLE of cyclohexane + [C$_x$mim][NTf$_2$] at 353.15 K
□ [C$_1$mim][NTf$_2$]; ◇ [C$_2$mim][NTf$_2$]; △ [C$_4$mim][NTf$_2$]; ○ [C$_6$mim][NTf$_2$]

The correlated results from the CPA-SSM EoS and the adjustable parameter k_{ij} for all investigated systems with self-association in this work are listed in Table 3. The results from the SWCF-VR EoS [33] and LF EoS [34] are also given. In the LF EoS and SWCF-VR EoS, ILs are treated as neutral chainlike molecules and no association is considered. As seen in Table 3, the overall AAD of equilibrium pressures for 20 ILs + non-associating solvents is 2.91% from the CPA-SSM EoS. Under the same conditions, the overall AAD of equilibrium pressure for 19 binary systems is 3.96% from the LF EoS [34], and that for 13 binary systems is 4.08% from the SWCF-VR EoS [33] indicating that the CPA-SSM EoS gives better results than the other two EoS.

For systems with ILs + associating solvents, both self- and cross-associating effects exist, the cross-association parameters ω_{ij} and $\delta\varepsilon_{ij}/k$ in the CPA-SSM EoS are required and calculated by the following combining rules:

$$\delta\varepsilon_{ij}/k = \left(\delta\varepsilon_{ii}/k + \delta\varepsilon_{jj}/k\right)/2, \quad \omega_{ij} = \left(\omega_{ii}\omega_{jj}\right)^{1/2} \tag{16}$$

Table 4 gives the calculated results for ILs + associating solvents systems from the CPA-SSM EoS and the overall AAD equilibrium pressure for 13 systems is 7.01%. The adjustable parameter k_{ij} equals zero for systems of [C$_2$mmim][NTf$_2$] + ethanol and [C$_4$mim][NTf$_2$] + 1-propanol, indicating that the calculated accuracy can not be improved by introducing adjustable parameter in such systems and the VLE can be well predicted by using the molecular parameter of pure substances. It is also found that the adjustable parameter k_{ij} of the systems containing water or methanol is larger than those for other systems, and the reason may be from the fact that the hydrogen bonding interactions of water/methanol with ILs are stronger than others.

Table 3 Correlated results of VLE of binary self-associating systems containing ILs using CPA-SSM model

System	T/K	k_{ij}	Δp①/%			N_m	Ref.
			CPA-SSM	LF EoS	SWCF-VR		
[C_1mim][NTf_2] + benzene	353.15	0.04049	4.70	7.73	7.74	35	[40]
[C_1mim][NTf_2] + cyclohexane	353.15	0.29474	4.04	3.40	3.48	10	[40]
[C_2mim][NTf_2] + benzene	353.15	0.03342	6.62	8.86	8.89	20	[40]
[C_2mim][NTf_2] + hexane	353.15	0.26506	1.16	3.27	—	8	[40]
[C_2mim][NTf_2] + cyclohexane	353.15	0.22856	2.44	3.65	4.46	11	[40]
[C_2mim][NTf_2] + cyclohexene	353.15	0.18412	1.37	1.79	—	12	[40]
[C_2mim][NTf_2] + acetone	353.15	−0.09471	0.65	1.86	2.69	29	[42]
[C_2mim][NTf_2] + tetrahydrofuran	353.15	−0.00684	2.14	—	—	37	[42]
[C_2mim][$EtSO_4$] + benzene	303.15	0.10045	3.53	6.76	6.12	22	[40]
[C_4mim][NTf_2] + toluene	363.15	0.01822	4.58	5.20	—	14	[43]
[C_4mim][NTf_2] + cyclohexane	353.15	0.17407	1.43	1.75	1.16	10	[40]
[C_4mim][NTf_2] + acetone	353.15	−0.12900	1.38	1.68	2.07	31	[42]
[C_4mim][NTf_2] + *n*-octane	353.15	0.21453	1.58	2.00	1.59	6	[43]
[C_4mim][NTf_2] + 1-octene	363.15	0.13809	1.93	0.96	—	6	[43]
[C_4mim][NTf_2] + *n*-nonane	353.15	0.21693	2.74	2.56	—	5	[43]
[C_6mim][NTf_2] + *n*-hexane	353.15	0.17493	2.31	1.86	0.50	7	[43]
[C_6mim][NTf_2] + cyclohexane	353.23	0.12387	7.64	9.92	9.60	12	[41]
[C_6mim][NTf_2] + cyclohexene	353.41	0.09798	3.25	4.48	—	27	[41]
[C_8mim][BF_4] + benzene	298.15−313.15	0.03220	2.85	5.67	3.93	52	[39]
[C_8mim][NTf_2] + *n*-hexane	353.15	0.14763	1.86	1.92	0.81	8	[43]
overall average deviation			2.91	3.96	4.08		

Note: The results of SWCF-VR and LF EoS are from Refs. [33] and [34], respectively.

① $\Delta p = (100/N_m)\sum\left|\left(p^{exp} - p^{cal}\right)/p^{exp}\right|$.

Table 4 Correlated results of VLE of binary cross-associating systems containing ILs using CPA-SSM model

System	T/K	k_{ij}	Δp①/%	N	Ref.
[C_2mim][NTf_2] + water	353.15	−0.3662	7.39	6	[40]
[C_2mim][NTf_2] + 2-propanol	353.15	0.0279	4.41	34	[40]
[C_2mmim][NTf_2] + methanol	353.1	−0.0798	8.38	17	[41]
[C_2mmim][NTf_2] + ethanol	353.11	0	4.48	28	[41]
[C_4mim][NTf_2] + water	353.15	−0.4416	7.33	5	[40]
[C_4mim][NTf_2] + methanol	298.15	−0.1137	7.66	12	[44]
[C_4mim][NTf_2] + ethanol	298.15−313.15	−0.0498	9.92	52	[44]
[C_4mim][NTf_2] + 1-propanol	298.15−313.15	0	6.34	48	[44]
[C_4mim][NTf_2] + 2-propanol	353.15	−0.0440	7.37	32	[40]
[C_6mim][NTf_2] + water	353.15	−0.4669	8.72	5	[43]
[C_6mim][NTf_2] + methanol	353.11	−0.2203	10.14	30	[41]
[C_6mim][NTf_2] + ethanol	353.16	−0.1019	4.89	28	[41]
[C_8mim][BF_4] + ethanol	298.15−313.15	0.0047	5.28	52	[39]
[C_8mim][BF_4] + 1-propanol	298.15−313.15	0.0243	7.02	44	[39]
overall average deviation			7.10		

① $\Delta p = (100/N_m)\sum\left|\left(p^{exp} - p^{cal}\right)/p^{exp}\right|$.

A graphical comparison of *p*-*x* diagram between theoretical and experimental results for 1-propanol + [C_4mim][NTf_2] system at different temperatures is illustrated in Fig. 5. The CPA-SSM EoS can well predict the experimental results over the full concentration range of 1-propanol, though some deviations can

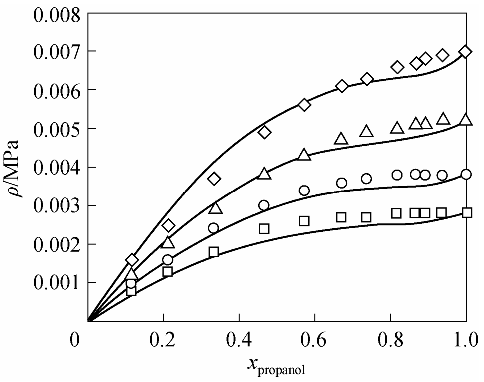

Figure 5 Comparison between predicted (lines) and experimental [44] (symbols) VLE of 1-propanol + $[C_4mim][NTf_2]$ system
T/K: □298.15; ○303.15; △308.15; ◇313.15

be observed in some special conditions.

4 CONCLUSIONS

In this work, a CPA-SSM EoS was presented by combining the cubic PR EoS and the association expression derived from shield-sticky model by Liu *et al.*, and applied to model the phase behavior of IL related systems. Four molecular parameters in CPA-SSM EoS were obtained by fitting the experimental pressure-volume-temperature (*pVT*) data over wide temperature and pressure ranges. The overall average deviation of liquid densities for 25 ILs is 0.22%. The molecular parameter *b* of homologous ILs shows good linear relations with their molecular masses. Coupling with classical van der Waals one-fluid mixing rule, the VLE data of ILs mixtures were calculated with one temperature-independent interaction parameter, and satisfactory results were obtained. For ILs + non-associating solvents mixtures, the results from the CPA-SSM EoS are better than those from the LF and SWCF-VR EoSs. In summary, the CPA-SSM EoS can be applied for the representation of thermodynamic properties for systems containing ILs at low pressures.

NOMENCLATURE

a_0, c_1, b	pure compound parameters from the physical part
k_{ij}	adjustable parameter of physical part
N_m	number of experimental data points
p_c	critical pressure, MPa
R	gas constant
T	temperature, K
T_c	critical temperature, K
T_r	reduced temperature ($T_r = T/T_c$)
V_m	molar volume
X_i	mole fraction of the molecule i not bonded
x_i	mole fraction of component i
y^{ref}	cavity-correlation function
z	compressibility factor
$\delta\varepsilon/k$	association energy parameter, K
η	reduced density
Λ_{ij}	interaction association strength between molecule i and j
ρ	density, $g\cdot cm^{-3}$
ρ_0	number density
φ	fugacity coefficient
ω	acentric factor (degree of association area)

Superscripts

cal	calculated results
exp	experimental results
L	liquid phase
ref	formula of reference expression
V	vapor phase

Subscripts

assoc	contributions due to association
cubic	contributions due to cubic EoS
i, j	different composition

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