Phase Behavior of Mixture of Supercritical CO_2 + Ionic Liquid: Thermodynamic Consistency Test of Experimental Data

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Various models have been applied composed of the Peng-Robinson equation of state (PR-EoS) and the Soave-Redlich-Kwong equation of state (SRK-EoS) associated with three mixing rules including the following: Wong-Sandler (WS), van der Waals one (vdW1), and van der Waals two (vdW2) for phase behavior modeling of mixtures of supercritical CO_2 + different ionic liquids in vapor–liquid equilibrium (VLE) region. It has been found that the PR EoS implying the WS mixing rule can be used as a reliable thermodynamic model to perform a thermodynamic consistency test on the experimental data of phase behaviors of the supercritical CO_2 + ionic liquid systems (19 commonly-used ionic liquids have been studied). The results show that 40% of the experimental data seem to be thermodynamically consistent, 55.5% seem to be thermodynamically inconsistent, and 4.5% seem to be not fully consistent. © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 3892–3913, 2013
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Introduction

Ionic liquids are organic salts, generally liquid at room temperatures.[1,2] They are normally composed of a large organic cation and organic or inorganic anions.[2] The applications of ionic liquids have generated number of discussions in the past decade. This is mainly because of their physicochemical properties, which are able to be adjusted through combination of cations and anions.[2] This phenomenon allows the researchers to design specific solvents for the development of more efficient processes and products.[1–3] No flammability, high-thermal stability, a wide liquid range, electric conductivity, and very low-vapor pressure are among the other elements that make ionic liquids become more and more interesting.[1–3]

So far, several industrial applications of ionic liquids have been proposed including using as solvents in organic synthesis,[4,5] homogeneous and biphasic transfer catalysis,[6–8] for electrical deposition,[9,10] and applications in membrane-based systems for separation.[11] However, their applications in supercritical processes have been more focused by the researchers.[1] Blanchard and coworkers were the first[12–14] to state that the problem of the recovery of the compounds from the ionic liquid media can be solved through using supercritical CO_2 that removes a desired solute from an ionic liquid solvent without contamination.[1] Carbon dioxide as an inexpensive, nonexplosive, available, and easy to remove from the extracted products,[15–19] is considered to be the most suitable fluid in supercritical processes, e.g., (1)

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for extraction of fatty acid esters, vegetable oils, and antioxidants in food engineering industry, and (2) for solving solid phenazopyridine, propranolol, and methyl salicylate in pharmaceutical industries.[18,19]

In this context, application of supercritical CO_2 for separation of ionic liquids from their organic solvents or extraction of various solutes from ionic liquid solvents has found great interest during the recent years. Therefore, accurate knowledge of phase behaviors of the mixtures of supercritical CO_2 + ionic liquids is drastic in order to efficiently design such separation processes. However, the difficulties in experimental measurements may bring about obtaining some unreliable or thermodynamically inconsistent data. Due to these experimental difficulties and also time-consuming and costly nature of such techniques, it is desirable to develop predictive methods for evaluating the phase behavior of these kinds of systems.

During recent years, several attempts have been done concerning this concept. The Peng-Robinson (PR)[20] cubic equation of state (CEoS) was applied by Shariati and Peters[21] to model the solubility of CHF_3 in $[C_2mim][PF_6]$ from 309.3 to 367.5 K and 1.6 to 51.6 $\times$ 10^6 Pa. Breure et al.[22] used the group contribution (GC) equation of state (EoS) to model the phase behavior of binary systems of ionic liquids and supercritical carbon dioxide. In addition, Yokozeki and Shiflett[23] used successfully a generic Redlich-Kwong (RK)[24] EoS in order to understand the global phase behavior of trifluoromethane and room-temperature ionic liquid $[bmim][PF_6]$ mixtures. They gained satisfactory results for vapor–liquid-equilibria (VLE) and vapor–liquid-liquid-equilibria (VLLE) in such systems at wide ranges of pressures.

The truncated perturbed chain polar statistical associating fluid theory tPC—PSAFT[25] has been applied by Kroon et al.[26] to calculate the solubility of CO_2 in several ionic liquids at high pressures. Wang et al.[27] have investigated the solubility of several gas samples in classical ionic liquids by the square well chain fluid (SWCF)[28–30] EoS. Alvarez and coworkers[31] used the PR EoS[20] and G^{ex} mixing rule with different activity coefficient models including the NRTL,[32] UNIQUAC[33] and COSMO—SAC[34] to accurately predict the VLE of some binary mixtures. Recently, Eslamimanesh and coworkers[35] have applied a novel mathematical approach. They investigated the capabilities of the feed forward artificial neural network in prediction of the solubilities of 24 classical ionic liquids in supercritical carbon dioxide. However, extrapolations of the developed model to the systems including other ionic liquids are not recommended. More theoretical and experimental studies on phase behavior of such mixtures and physical properties of ionic liquids can be found elsewhere.[36–46]

However, because ionic liquid molecules are highly asymmetric[26] and also the fact that CO_2 molecules have a quadruple moment,[26] the applied thermodynamic relations, thus, should be able to take these strong interactions into account. Besides, the effects of high pressures generally encountered in supercritical operations have to be considered. All of the aforementioned thermodynamic models have been developed especially for a desired system mainly because of these two reasons and not for a set of systems as we are interested in. Therefore, there is a need to apply more general models capable of calculations of phase behaviors of such systems for many kinds of ionic liquids that are considered now to be alternative of conventional industrial solvents. For this purpose, reliable experimental data are required.

The "Gibbs-Duhem equation"[47–49] is generally applied to analyze thermodynamic consistency of experimental phase equilibrium data. As a matter of fact, if the values of the activity/fugacity coefficients of all of the components in the mixture do not satisfy this relation within an acceptable deviation, the experimental data are suspected to be thermodynamically inconsistent. This is mainly because of various probable errors during experimental works especially those dealing with high pressure, low temperature, and low concentrations of particular species in the mixtures.[50–54] The consistency (or data assessment) tests generally include the following methods: the "Slope Test", the "Integral Test", the "Differential Test" and the "Tangent-Intercept Test".[47–49,55–57] Good reviews of these methods can be found elsewhere.[55]

Bertucco et al.[58] and Valderrama and coworkers[57,59–62] have performed several thermodynamic consistency tests on experimental phase equilibrium data of various systems. Thermodynamic consistency was also performed on VLE of some binary mixtures containing ionic liquids by Àlvarez and Aznar.[63] Very recently, our group[50–54] has applied almost the same method on important systems for petroleum industry including water content of methane in equilibrium with gas hydrate, liquid water or ice,[50] sulfur content of hydrogen sulfide vapor,[51] solubility data of carbon dioxide and methane with water inside and outside gas hydrate formation region,[52] solubility of waxy compounds in natural gas systems,[53] and glycol loss in gaseous systems.[54]

In this article, we focus on applying a thermodynamic model, which leads to an acceptable average absolute relative deviations of the results from existing experimental phase equilibrium data of the supercritical CO_2 plus ionic liquid systems in vapor–liquid equilibrium (VLE) region. Later, a thermodynamic consistency test is performed using the applied model for investigating the reliability of the studied experimental data.

Theory

Equilibrium criteria

The phase behavior calculations are performed using the general equilibrium criterion of fugacity equalities of each component in these phases. Considering the point that ionic liquids are generally nonvolatile at relatively low pressures (especially for pressure lower than 10^7 Pa),[12,26,27] the solubility of the ionic liquids in the gas phase is assumed to be negligible. Therefore, the equilibrium equation is written as follows

$$f_2^L = f_2^V \tag{1}$$

where f is the fugacity, subscript 2 refers to carbon dioxide, and superscripts L and V stand for liquid and vapor phases, respectively.

Equations of state and mixing rules

Reliable equations of state are needed to evaluate the fugacities of the species in a mixture. The CEoSs have been widely used in phase equilibrium calculations due to their simplicity. In addition, the effects of high pressure on phase behavior of the mixtures can be taken into account using tuning the alpha function parameters against vapor pressures of pure components. In this work, two equations of state (the PR[20] and the SRK[64]) are applied to evaluate the fugacities of the investigated components. Previous calculations[65–67]

showed that using a proper alpha function contributes to accurate phase behavior correlation results especially in supercritical fluid region. It is mainly because of the special shape of the alpha function vs. critical temperature.[65–68] In this study, the alpha function proposed by Coquelet et al.[65] is used for the PR EoS[20] and the one presented by Twu et al.[69,70] is applied for the SRK EoS.[64] Details of these equations are given in Appendix A.

Advanced mixing rules are required to extend the use of cubic equations of state for modeling the complex phase behavior of highly nonideal mixtures.[48] In 1992, Wong and Sandler[68] proposed a new mixing rule (WS mixing rule) based on equality of the excess Helmholtz energy of a mixture at infinite pressure from an equation of state to that of a liquid solution model. This rule evades the inconsistencies of different models for the vapor and the liquid phases, while maintaining the flexibility of the excess Gibbs energy models.[71] The WS mixing rule,[68] which was later reformulated by Orbey and Sandler,[72] has been argued to show accurate correlation of different complex systems phase equilibria.[73–75] In this study, the Van Laar activity model[47] is used for evaluating the activity coefficients of the components. Details of the mentioned equations are given in Appendix B.

It should be pointed out that other thermodynamic models (perhaps more accurate ones)[25–30] can be applied for modeling the corresponding phase equilibria. However, we need a thermodynamic model, which is able to represent the experimental data within an acceptable deviation range and at the same time provide us with the required parameters for the consistency test.

Equations

The "Gibbs-Duhem"[47–49] equation for a binary mixture at constant temperature can be rewritten in terms of the fugacity coefficients as follows[50–54,58,60–63]

$$\left[\frac{Z-1}{p}\right]dp = y_1 d(\ln\varphi_1) + y_2 d(\ln\varphi_2) \tag{2}$$

and rewritten as[50–54,58,60–63]

$$\frac{1}{p}\frac{dp}{dy_2} = \frac{y_2}{(Z-1)}\frac{d(\ln\varphi_2)}{dy_2} + \frac{(1-y_2)}{(Z-1)}\frac{d(\ln\varphi_1)}{dy_2} \tag{3}$$

or in integral form as follows[50–54,58,60–63]

$$\int_{p(1)}^{p(2)} \frac{1}{py_2}dp = \int_{\varphi_2(1)}^{\varphi_2(2)} \frac{1}{(Z-1)\varphi_2}d\varphi_2 + \int_{\varphi_1(1)}^{\varphi_1(2)} \frac{(1-y_2)}{y_2(Z-1)\varphi_1}d\varphi_1 \tag{4}$$

In the preceding equations, p is pressure, y is the mole fraction of the species, d is the derivative operator, Z stands for the compressibility factor, φ denotes the fugacity coefficient, subscript 2 refers to carbon dioxide, and indices 1 and 2 stand for the first and second states at which the integrals are evaluated. The properties φ_1, φ_2, and Z are calculated using the thermodynamic model.

In Eq. 4, the lefthand side is designated by A_p, and the righthand side by A_φ, as follows[50–54,58,60–63]

$$A_p = \int_{p(1)}^{p(2)} \frac{1}{py_2}dp \tag{5}$$

$$A_\varphi = A_{\varphi 1} + A_{\varphi 2} \tag{6}$$

$$A_{\varphi 1} = \int_{\varphi_1(1)}^{\varphi_1(2)} \frac{(1-y_2)}{y_2(Z-1)\varphi_1}d\varphi_1 \tag{7}$$

$$A_{\varphi 2} = \int_{\varphi_2(1)}^{\varphi_2(2)} \frac{1}{(Z-1)\varphi_2}d\varphi_2 \tag{8}$$

Consistency criteria

First and perhaps most important is that the thermodynamic model should lead the average absolute deviations of the results from experimental values to be within an acceptable range. Generally, the accepted deviations in equilibrium pressure results for these kinds of systems (defined by the following equation), lie between 0 and 10% for the proposed system[62]

$$ARD_i\% = 100\frac{|p_i^{\text{cal.}} - p_i^{\text{Exp.}}|}{p_i^{\text{Exp.}}} \tag{9}$$

where superscripts Cal. and Exp. refer to calculated and experimental values, respectively. ARD represents absolute relative deviation. The bubble point calculation algorithm has been used to evaluate the equilibrium pressure values ($p_i^{\text{Cal.}}$). If a set of data is considered to be consistent, a percent area deviation (ΔA_i %) between experimental and calculated parameter values[50–54,58,60–63] (defined by Eq. 10) must be within the acceptable range[50–54,58,60–63]

$$\Delta A_i\% = 100\left[\frac{|A_{\varphi i} - A_{pi}|}{A_{pi}}\right] \tag{10}$$

where subscripts φ and p refer to the areas based on calculated and experimental parameter values, respectively, and i refers to the data set number. For determination of the acceptable percentages of the two evaluated areas deviations from each other, the error propagation is performed on the existing experimental data. This is normally done using the method of error propagation,[76] considering the temperature and equilibrium pressure as the independent measured variables.[62] The calculated individual area (A_φ) is treated as the dependent variable. The error in the calculated areas, E_A and the percent error % E_A are calculated as follows[50–54,58,60–63]

$$E_A = \left[\frac{\partial A_{\varphi j}}{\partial T}\right]\Delta T + \left[\frac{\partial A_{\varphi j}}{\partial P}\right]\Delta P \tag{11}$$

$$E_A\% = 100\left[\left|\frac{E_A}{A_{\varphi j}}\right|\right] \tag{12}$$

where subscript j refers to j^{th} calculated area. We assumed maximum uncertainties of 0.1 K for the experimental temperature and 0.01×10^6 Pa for the experimental pressure. However, these uncertainties depend on the method of experimental measurements.

The partial derivatives of the two preceding equations have been evaluated using the central finite difference[77] method. It results in ΔA_i to lie in the range of 0 to about 24%. Therefore, the range [0,24] % is established as the maximum acceptable error (regarding also the inevitable errors in calculation by numerical methods) for the areas (A_i]) below the curves of plotting the experimental and calculated values to conclude about the data consistency.

Regarding these facts, the thermodynamic consistency test criteria are pursued through the following instructions:[50–54,58,60–63]

1. Check the *ARD* % not to be outside of the margins of errors [0,10] %. If it is so, eliminate the weak calculations until the absolute relative deviations of the results from experimental values would be within the acceptable range.
2. If the model correlates the data within the acceptable error ranges of the equilibrium pressure results and the area test is fulfilled for all points in the data set, the proposed model is reliable and the data seem to be thermodynamically consistent.
3. In the case that the model correlates the data acceptably and the area test is not accomplished for most of the data set (more than 75% of the areas), the applied model is reliable but the experimental data are suspected to be thermodynamically inconsistent.
4. In the case that the model acceptably correlates the data and some of the area deviations (equal or less than 25% of the areas) are outside of the error range [0,24] %, the applied method declares the experimental values as suspected to be not fully consistent.

Formulation of the objective function

The optimum values of mathematical model parameters are generally obtained by appropriate optimization methods.[78] The true global optimum values of the model parameters including the binary interaction parameters (k_{ij}) in case of applying vdW1 mixing rule,[47–49,68] k_{ij} and l_{ij} in using vdW2[47–49,68] mixing rule, and A_{ij} and k_{ij} in calculations by WS mixing rule[68] method have been evaluated by the genetic algorithm (GA)[79,80] optimization strategy.

The model parameters have been treated to be the decision variables of the optimization algorithm. Consequently, the following objective function is to be minimized

$$\text{function}\,(p)=\frac{100}{N}\sum_{i}^{N}\frac{|p_i^{\text{cal.}}-p_i^{\text{Exp.}}|}{p_i^{\text{Exp.}}} \tag{13}$$

where N is the number of data points used in the optimization procedure. The aforementioned objective function is subjected to the following constraints

$$(Z-B)>0 \tag{14}$$

$$\left(\frac{Z+\sigma B}{Z+\varepsilon B}\right)>0 \tag{15}$$

where Z is the compressibility factor, B, σ, and ε are parameters of the applied equations of state defined in the Appendix B. The aforementioned constraints are selected to avoid trivial results from the exponential terms of the fugacity expressions because the GA[79,80] is based on random search method and may result in negative values of these parameters.[51,78,81,82] This maybe also the case for other phase behavior calculations using cubic equations of state, in which the optimal values of the corresponding parameters are supposed to be determined by population-based optimization strategies.

The concept of the penalty functions are considered to deal with the optimization problems subjected to several constraints which penalize infeasible solutions (i.e., eliminate the unexpected results).[78,83] Based on this method, the penalty function takes a finite value when a constraint is violated and a value of zero when constraint is satisfied. The penalized function is generally written as[78,81–85]

$$\text{OF}\,(p)=\textit{function}\;(p)+PN\left[\sum_{l=1}^{L}\langle g_l(p)\rangle+\sum_{m=1}^{M}|h_m(p)|\right] \tag{16}$$

where $g_l\,(p)$ is the inequality constraint, $h_m(p)$ is the equality constraint, L and M refer to the number of inequality and equality constraints, respectively, and PN denotes the penalty parameter, which is defined by the user.[34,83] The value of this parameter depends on the order of magnitude of the function values of the problem and usually lies between 1 and 10^6. The[78,81–83] higher selected values for PN, the more effects of constraints on computations would be expected.[78,81–83] In this study, the penalty parameter is set to 10^4. The bracket-operator $\langle\rangle$ denotes the absolute value of the operand, if operand is negative. Therefore, the final formulation of the objective function is given by the following equation (there is no equality constraint in this work)

$$\text{OF}\,(p)=\text{function}\,(p)+10^4\sum_{l=1}^{2}\langle g_l(p)\rangle \tag{17}$$

where

$$g_1(p)=\min\{0,(Z-B)\} \tag{18}$$

$$g_2(p)=\min\left\{0,\left(\frac{Z+\sigma B}{Z+\varepsilon B}\right)\right\} \tag{19}$$

Results and Discussion

As can be seen in the available corresponding experimental works in the literature, there are generally rapid evolutions of equilibrium pressures vs. solubilities of carbon dioxide in high mole fractions of this component. Although it seems to suggest diphasic liquid-liquid equilibria in the system, in this work, we assumed vapor–liquid equilibria for all of the investigated experimental data in the whole pressure-composition ranges (This is also in accordance with the assumptions reported in the literature[86,87] for these data). Table 1 shows the physical properties values of these compounds accompanied with the references. A group contribution method[88,89] is applied to generate the physical properties when the experimental values are not available.

The results of comparison between the different combinations of the PR[20] and the SRK[64] equations of state with three aforementioned mixing rules along with the tuned interaction parameters are reported in Table 2. The interaction parameters are reported for each investigated temperature to deal with the temperature dependency of these parameters.

As can be seen, the optimal values of some of the interaction parameters have not been detected in the range of the considered tolerance of the optimization (tuning) procedure. This may be due to the drawback of the vdW1 mixing rule in phase behavior modeling of complex mixtures. It should be noted that to present general and comprehensive interaction parameters and compare the capabilities of different sets of equations, the tolerance of the GA[79,80] optimization strategy should be kept constant during the minimization of the

Table 1. Physical Properties of the Investigated Ionic Liquids

IUPAC name	Abbreviation	T_c/K	P_c/Pa × 10^{-6}	ω	Ref.[a]
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[C_2-mim][Tf_2N]	788.05	3.31	1.225	86
1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[C4-mim][Tf2N]	831.39	2.69	1.289	86
1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[C6-mim][Tf2N]	876.24	2.22	1.327	86
1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide	[C8-mim][Tf2N]	923.02	1.87	1.331	86
1-ethyl-3-methylimidazolium trifluoromethane sulfonate	[C2-mim][TfO]	756.89	3.48	0.783	87
1-butyl-3-methylimidazolium trifluoromethansulphonate	[C4-mim][TfO]	796.73	2.81	0.879	87
1-hexyl-3-methylimidazolium trifluoromethansulphonate	[C6-mim][TfO]	837.5	2.31	0.963	87
1-methyl-3-octylimidazolium trifluoromethansulphonate	[C8-mim][TfO]	879.6	1.94	1.031	87
N-butyl-N-methylpiperidinium trifluoromethansulphonate	[BMP][TfO]	933.39	2.586	0.61	2
1-octyl-3-methylimidazoliumtetrafluoroborate	[C8-mim][BF4]	726.1	1.6	0.995	35
1-butyl-3-methylimidazolium tetrafluoroborate	[bmim][BF4]	632.3	2.04	0.849	35
N-butylpyridinium tetrafluoroborate	[N-bupy][BF4]	597.6	2.03	0.831	35
1-butyl-3-methylimidazolium dicyanamide	[C4-mim][DCA]	782.96	2.44	0.842	34
1-hexyl-3-methylimidazolium	[HEA]	710.66	4.636	0.809	GC*
2-hydroxyethyl ammonium lactate	[HEL]	821.61	4.354	1.229	GC
bis(2-hydroxyethyl)ammonium acetate	[BHEAA]	836.38	3.485	1.288	GC
bis(2-hydroxyethyl)ammonium lactate	[BHEAL]	950.45	3.321	1.666	GC
2-hydroxyethyl methacrylate	[HEMA]	853.92	2.928	1.331	GC
2-hydroxy-N-(2-hydroxyethyl)-N-methylethanaminium lactate	[HHEMEL]	970.51	2.824	1.672	GC

[a]References of experimental data.
GC: Properties generated using group contribution method.[88,89]

Table 2. Optimum Values of the Applied Thermodynamic Models Parameters for Investigated Binary Mixtures of Ionic Liquids with Supercritical CO_2: These values are also valid for obtaining the results presented in Tables 3 and 4.

				Optimum values of the model parameters							
				PR[20]				SRK[64]			
Set No.	Compound	T/K	Mixing rule	k_{12}	l_{12}	A_{12}	A_{21}	k_{12}	l_{12}	A_{12}	A_{21}
1	[C_2-mim][Tf_2N]	314.05	vdW1	0.398				0.300			
			vdW2	0.194	0.031			0.088	0.034		
			WS	0.268		0.290	0.694	0.098		0.023	0.120
2		324.15	vdW1	0.291				0.300			
			vdW2	0.195	0.019			0.199	0.073		
			WS	0.239		0.932	1.906	0.286		0.484	1.583
3		334.35	vdW1	0.300				0.300			
			vdW2	0.198	0.019			0.195	0.007		
			WS	0.276		0.189	1.287	0.290		0.270	1.809
4		344.55	vdW1	0.300				0.300			
			vdW2	0.199	0.006			0.197	0.017		
			WS	0.288		0.416	1.273	0.286		0.475	1.987
5	[C_4-mim][Tf_2N]	314.05	vdW1	0.300				0.300			
			vdW2	0.183	0.032			0.182	0.090		
			WS	0.298		1.556	0.187	0.250		1.563	0.900
6		324.15	vdW1	0.300				0.300			
			vdW2	0.167	0.042			0.182	0.045		
			WS	0.173		0.680	1.946	0.281		1.833	0.948
7		334.35	vdW1	0.299				0.300			
			vdW2	0.194	0.071			0.198	0.029		
			WS	0.283		0.503	0.904	0.287		1.763	1.306
8		344.55	vdW1	0.295				0.300			
			vdW2	0.194	0.106			0.167	0.037		
			WS	0.266		1.587	1.459	0.277		0.510	0.346
9		314.06	vdW1	0.300				0.300			
			vdW2	0.299	0.417			0.195	0.959		
			WS	0.256		0.452	1.973	0.275		0.158	1.271
10		324.19	vdW1	0.298				0.299			
			vdW2	0.275	0.351			0.096	0.999		
			WS	0.282		0.127	1.904	0.275		0.165	1.558
11		334.35	vdW1	0.296				0.300			
			vdW2	0.300	0.233			0.081	0.945		
			WS	0.293		0.231	1.430	0.272		0.504	1.969
12		344.51	vdW1	0.291				0.197			
			vdW2	0.293	0.288			0.199	0.473		
			WS	0.274		0.109	1.645	0.288		0.292	1.911
13		323.08	vdW1	0.299				0.196			
			vdW2	0.255	0.042			0.172	0.002		
			WS	0.019		1.394	0.021	0.008		0.076	0.464

Table 2. *Continued*

				Optimum values of the model parameters							
				PR[20]				SRK[64]			
Set No.	Compound	T/K	Mixing rule	k_{12}	l_{12}	A_{12}	A_{21}	k_{12}	l_{12}	A_{12}	A_{21}
14	[C_6-mim][Tf_2N]	314.05	vdW1	0.299				0.200			
			vdW2	0.297	0.117			0.185	0.474		
			WS	0.279		0.454	1.658	0.252		0.328	1.708
15		324.15	vdW1	0.300				0.196			
			vdW2	0.293	0.199			0.186	0.477		
			WS	0.286		0.388	1.918	0.238		0.327	1.842
16		344.55	vdW1	0.297				0.198			
			vdW2	0.299	0.158			0.197	0.365		
			WS	0.286		0.402	1.383	0.298		1.129	1.615
17		344.55	vdW1	0.294				0.200			
			vdW2	0.297	0.065			0.199	0.481		
			WS	0.292		0.430	1.006	0.240		0.494	1.535
18		323.15	vdW1	0.300				0.195			
			vdW2	0.297	0.124			0.188	0.489		
			WS	0.269		0.163	1.201	0.217		0.344	1.446
19		343.15	vdW1	0.298				0.199			
			vdW2	0.199	0.114			0.193	0.398		
			WS	0.270		0.300	1.294	0.278		0.338	1.662
20	[C_8-mim][Tf_2N]	314.05	vdW1	0.297				0.199			
			vdW2	0.195	0.021			0.176	0.030		
			WS	0.281		0.576	1.385	0.276		0.072	1.231
21		324.15	vdW1	0.297				0.197			
			vdW2	0.194	0.056			0.192	0.038		
			WS	0.252		0.154	1.262	0.266		0.205	1.430
22		334.35	vdW1	0.299				0.195			
			vdW2	0.198	0.095			0.187	0.125		
			WS	0.271		0.413	1.884	0.243		0.390	1.492
23		344.55	vdW1	0.299				0.199			
			vdW2	0.195	0.111			0.199	0.245		
			WS	0.269		0.341	1.935	0.296		0.472	1.843
24	[C_2-mim][TfO]	314.05	vdW1	0.284				0.199			
			vdW2	0.185	0.018			0.182	0.056		
			WS	0.266		0.590	1.280	0.214		1.158	1.567
25		324.15	vdW1	0.297				0.197			
			vdW2	0.187	0.006			0.178	0.095		
			WS	0.206		1.871	1.937	0.284		1.109	1.312
26		334.35	vdW1	0.293				0.195			
			vdW2	0.160	0.001			0.177	0.056		
			WS	0.283		0.956	1.733	0.299		1.842	1.786
27		344.55	vdW1	0.294				0.182			
			vdW2	0.174	0.041			0.135	0.011		
			WS	0.218		1.407	1.674	0.294		0.776	1.758
28	[C_4-mim][TfO]	314.05	vdW1	0.299				0.194			
			vdW2	0.176	0.032			0.156	0.041		
			WS	0.240		1.016	1.706	0.175		0.769	1.935
29		324.15	vdW1	0.292				0.199			
			vdW2	0.179	0.021			0.154	0.084		
			WS	0.271		1.068	1.996	0.235		0.225	1.072
30		334.35	vdW1	0.288				0.191			
			vdW2	0.175	0.018			0.197	0.015		
			WS	0.225		1.375	1.822	0.243		1.257	1.867
31		344.55	vdW1	0.282				0.196			
			vdW2	0.175	0.006			0.198	0.045		
			WS	0.295		0.548	1.705	0.279		1.999	1.962
32	[C_6-mim][TfO]	314.05	vdW1	0.289				0.199			
			vdW2	0.190	0.012			0.172	0.014		
			WS	0.251		0.225	1.032	0.128		1.526	1.004
33		324.15	vdW1	0.293				0.197			
			vdW2	0.173	0.007			0.099	0.031		
			WS	0.299		0.741	1.245	0.161		0.331	0.988
34		334.35	vdW1	0.298				0.196			
			vdW2	0.176	0.027			0.094	0.035		
			WS	0.286		0.696	1.924	0.187		1.664	1.508
35		344.55	vdW1	0.275				0.200			
			vdW2	0.162	0.028			0.087	0.011		
			WS	0.283		1.331	1.920	0.040		1.521	1.827
36	[C_8-mim][TfO]	314.05	vdW1	0.291				0.299			
			vdW2	0.176	0.029			0.082	0.018		
			WS	0.276		0.679	1.903	0.139		0.372	0.583

Table 2. *Continued*

				Optimum values of the model parameters							
				PR[20]				SRK[64]			
Set No.	Compound	T/K	Mixing rule	k_{12}	l_{12}	A_{12}	A_{21}	k_{12}	l_{12}	A_{12}	A_{21}
37		324.15	vdW1	0.297				0.299			
			vdW2	0.200	0.020			0.083	0.019		
			WS	0.291		0.470	1.470	0.286		0.037	1.403
38		334.35	vdW1	0.295				0.295			
			vdW2	0.193	0.009			0.093	0.035		
			WS	0.283		1.195	1.768	0.134		1.958	1.444
39		344.55	vdW1	0.298				0.300			
			vdW2	0.194	0.011			0.094	0.006		
			WS	0.295		0.656	1.956	0.282		1.783	1.172
40	[BMP][TfO]	323.15	vdW1	0.300				0.400			
			vdW2	0.195	0.054			0.002	0.018		
			WS	0.269		0.609	1.935	0.174		0.624	1.946
41		333.15	vdW1	0.283				0.390			
			vdW2	0.192	0.051			−0.038	0.051		
			WS	0.271		1.025	1.666	0.243		0.508	1.557
42		343.15	vdW1	0.299				0.395			
			vdW2	0.190	0.072			−0.090	0.067		
			WS	0.242		0.536	1.528	0.291		0.696	1.504
43		353.15	vdW1	0.278				0.397			
			vdW2	0.199	0.132			0.039	0.044		
			WS	0.295		0.682	1.678	0.235		1.166	1.864
44	[C_8-mim][BF4]	313.15	vdW1	0.271				0.400			
			vdW2	0.195	0.060			0.091	0.031		
			WS	0.298		1.007	1.617	0.258		0.449	1.594
45		323.15	vdW1	0.298				0.396			
			vdW2	0.180	0.044			0.096	0.006		
			WS	0.241		1.319	1.506	0.271		0.386	1.884
46		333.15	vdW1	0.293				0.399			
			vdW2	0.193	0.003			0.096	0.018		
			WS	0.298		0.319	1.997	0.249		1.243	1.930
47	[bmim][BF_4]	323.15	vdW1	0.296				0.098			
			vdW2	0.190	0.020			0.088	0.021		
			WS	0.024		1.910	1.525	0.263		0.869	0.701
48		348.15	vdW1	0.282				0.099			
			vdW2	0.185	0.030			0.097	0.018		
			WS	0.118		1.495	1.664	0.178		0.806	1.261
49	[N-bupy][BF_4]	313.15	vdW1	0.286				0.294			
			vdW2	0.194	0.026			0.083	0.013		
			WS	0.290		0.972	1.723	0.297		1.062	1.848
50		323.15	vdW1	0.294				0.291			
			vdW2	0.188	0.007			0.069	0.007		
			WS	0.244		1.338	1.964	0.295		0.738	0.921
51		333.15	vdW1	0.290				0.299			
			vdW2	0.174	0.013			0.095	0.013		
			WS	0.257		0.922	1.998	0.282		0.863	1.995
52	[C_4-mim][DCA]	313	vdW1	0.274				0.199			
			vdW2	0.199	0.013			0.098	0.041		
			WS	0.260		1.608	1.846	0.244		0.842	1.915
53		323	vdW1	0.299				0.199			
			vdW2	0.199	0.001			0.083	0.020		
			WS	0.245		0.555	1.906	0.268		1.606	1.999
54		333	vdW1	0.291				0.196			
			vdW2	0.196	0.056			0.085	0.004		
			WS	0.243		0.815	1.711	0.294		1.440	1.975
55		343	vdW1	0.299				0.196			
			vdW2	0.181	0.031			0.077	0.009		
			WS	0.274		1.387	1.541	0.156		0.691	1.894
56	[HEA]	313.15	vdW1	0.296				−[a]			
			vdW2	0.172	0.033			0.095	0.006		
			WS	0.241		0.377	0.657	0.125		0.002	1.058
57		328.15	vdW1	0.264				−			
			vdW2	0.143	0.024			0.089	0.006		
			WS	0.262		0.376	1.835	0.285		0.028	0.947
58	[BHEAA]	313.15	vdW1	−				−			
			vdW2	0.179	0.010			0.040	0.005		
			WS	0.266		1.534	0.485	0.203		0.261	1.693
59		328.15	vdW1	−				−			
			vdW2	0.162	0.015			0.076	0.003		
			WS	0.071		1.867	1.015	0.269		1.181	0.084

Table 2. *Continued*

				Optimum values of the model parameters							
				PR[20]				SRK[64]			
Set No.	Compound	T/K	Mixing rule	k_{12}	l_{12}	A_{12}	A_{21}	k_{12}	l_{12}	A_{12}	A_{21}
60	[HHEMEA]	313.15	vdW1	–				–			
			vdW2	0.156	0.008			0.088	0.002		
			WS	0.267		1.586	0.267	0.050		1.424	0.248
61		328.15	vdW1	–				–			
			vdW2	0.165	0.003			0.074	0.007		
			WS	0.221		1.824	1.212	0.110		1.537	1.526
62	[BHEAL]	313.15	vdW1	–				–			
			vdW2	0.137	0.000			0.086	0.002		
			WS	0.152		1.431	1.918	0.247		0.240	1.038
63		328.15	vdW1	–				–			
			vdW2	0.169	0.011			0.030	0.005		
			WS	0.194		1.769	1.707	0.279		0.906	1.622
64	[HHEMEL]	313.15	vdW1	–				–			
			vdW2	0.197	0.040			0.028	0.000		
			WS	0.241		1.908	1.171	0.208		0.507	1.439
65		328.15	vdW1	–				–			
			vdW2	0.198	0.028			0.040	0.001		
			WS	0.166		1.951	1.593	0.057		1.177	1.311
66	[HEL]	313.15	vdW1	–				–			
			vdW2	0.123	0.012			0.069	0.002		
			WS	0.246		0.846	1.830	0.299		0.036	1.498
67		328.15	vdW1	–				–			
			vdW2	0.116	0.016			0.057	0.000		
			WS	0.168		1.736	1.236	0.061		0.792	1.386

[a]No global optimum values have been detected within the defined tolerance of the optimization algorithm.

objective function. Another factor to be mentioned is that due to the population-based nature of the applied optimization algorithm, we generally face with many local optimum values for the binary interaction parameters (especially A_{12} and A_{21}), although the algorithm tries to reach the global optima. This fact contributes the interaction parameters to be very temperature-dependent, i.e., the values of these parameters may change considerably with increasing the temperature. Apparently, one can obtain different values of interaction parameters using different tuning algorithms. However, by definition of a physically logical limitations for the interaction parameters (feasible regions of the decision variables of the optimization algorithm), the interaction parameters can be determined within thermodynamically acceptable domains. Therefore, two significant points must be taken into account about the obtained interaction parameters (1) they should lie within thermodynamically logical range, and (2) they should lead to acceptable model results, which are able to represent the experimental data within acceptable deviation range.

Table 3 indicates the ranges of the absolute relative deviations of the correlated equilibrium pressures at all of the investigated temperatures and CO_2 solubility ranges. The proposed thermodynamic model uses the experimental points excluding those used in optimization procedure to compare the predicted results. Wide ranges of temperatures, CO_2 solubilities, and numerous experimental data applied (578 data points) insure the generality of the presented model. The results indicate that the combination of the PR EoS[20] with the WS[68] mixing rule has resulted in less average absolute relative deviations (AARD) % from experimental values, which is 2.6%, meanwhile this statistical parameter regarding the set of SRK EoS[64] and WS[68] mixing rule has been concluded to be 4.2%. This is in agreement with the similar study,[61,62] which demonstrates the capability of the former set of equations for correlation of complex mixtures phase behaviors. Consequently, this model is generally acceptable for using in thermodynamic consistency test.

The deviations of the CEoS-based models may be mainly due to this fact that cubic equations of state may generally lead to weak representation/prediction in supercritical fluid regions.[66,67,78,85] This is in accordance with previous works applying this equation of state for complex systems such as mixtures of different solids + supercritical carbon dioxide.[78,85,90] However, as previously discussed, the new Mathias-Copeman-like alpha function[65] results in lessening this drawback in the supercritical region. Another element to consider is that the optimal values of the parameters of the current model parameters have been obtained using the GA[79,80] optimization technique, which has several advantageous over the traditional optimization methods.[78,83,85] All of the detailed calculated equilibrium pressures along with experimental data points used in the calculations are available upon request to the authors.

Sixty seven (isothermal) experimental datasets are studied for consistency test. Table 4 illustrates the results of the consistency test for the investigated datasets. It is shown that 40% of the experimental data seem to be thermodynamically consistent while this percentage is 55.5% for thermodynamically inconsistent data, and 4.5% for not fully consistent data.

Another element to consider is that the performed phase equilibrium data assessment test is inevitably model-dependent. If there is a way that we could measure directly the required parameters for consistency test including the fugacity coefficients, we could have employed this method only based on experimental measurements (we are sure at the moment that is it impossible). This conclusion is valid even at very low pressures, when we can assume with high confidence that the fugacity coefficients of the species are unity.

Table 3. Average Relative Deviations of the Calculated Results from Experimental Values

Component	T range/K	Solubility range	N[a]	Reference	EoS	ARD[b] range/%		
						vdW1	vdW2	WS
[C_2-mim][Tf_2N]	314.05−324.15	0.2330−0.6699	34	86	PR	11−12	7.8−9.5	0.1−6.6
					SRK	11−12	6−9.8	0.1−3.8
[C_4-mim][Tf_2N]	314.05−344.55	0.0847−0.8041	95	86	PR	7.6−25	3.3−5.4	0.1−2.5
					SRK	7.5−11	4−7.8	0.1−1.9
[C_6-mim][Tf_2N]	314.05−344.55	0.3019−0.7867	67	86	PR	7.6−12	5.5−11	1.7−19
					SRK	7.6−12	6.2−11	0.1−2
[C_8-mim][Tf_2N]	314.05−344.55	0.3019−0.7867	53	86	PR	7−7.6	5.5−6	1.5−2.2
					SRK	7−7.6	5.7−6.2	1.7−2.5
[C_2-mim][TfO]	314.05−344.55	0.1794−0.5435	29	87	PR	12−14	8.7−11	1.5−4.9
					SRK	12−14	9.3−12	2.8−3.9
[C_4-mim][TfO]	314.05−344.55	0.2182−0.6134	39	87	PR	10−11	7.5−8.4	2.8−4.4
					SRK	10−11	7.7−8.6	2.1−4.2
[C_6-mim][TfO]	314.05−344.55	0.2885−0.6487	43	87	PR	9.1−11	6.8−8.2	4−4.4
					SRK	11−12	5−7.9	0.1−1.6
[C_8-mim][TfO]	314.05−344.55	0.2166−0.6414	34	87	PR	11−12	7.6−8.8	3−4
					SRK	17−20	7.3−24	0.1−3
[BMP][TfO]	323.15−353.15	0.2583−0.7058	32	2	PR	12−12	13−14	8.8−9.5
					SRK	17−17	13−15	5.9−7.2
[C_8-mim][BF4]	313.15−333.15	0.1910−0.6510	21	14	PR	14−14	11	4.8−6.4
					SRK	17−17	10−11	1.5−3.4
[bmim][BF_4]	323.15−348.1	0.0030−0.1820	18	23	PR	11−11	7.3−8	0.3−0.4
					SRK	14−17	8.3−8.4	0.3
[N-bupy][BF_4]	313.15−333.15	0.1440−0.5490	21	16	PR	14−14	11	5.9−7.2
					SRK	14−14	11−12	3.3−5.3
[C_4-mim][DCA]	313.15−343	0.2000−0.6010	20	14	PR	20	18−22	17
					SRK	25	20−22	13−17
[HEA]	313.15−328.15	0.0081−0.1386	12	46	PR	17	9−9.9	0.2
					SRK	−*	4.4−5.8	0.1−0.7
[BHEAA]	313.15−328.15	0.0074−0.0905	12	46	PR	−	11−15	0.4−6.9
					SRK	−	8.9−9.5	0.2−1.5
[HHEMEA]	313.15−328.15	0.0051−0.0253	12	46	PR	−	14−15	0.4−7.8
					SRK	−	11−15	0.2−0.7
[BHEAL]	313.15−328.15	0.0054−0.0738	12	46	PR	−	13−15	0.1−4.8
					SRK	−	4−13	0.1−0.8
[HHEMEL]	313.15−328.15	0.0027−0.0607	12	46	PR	−	15−15	0.3−5.5
					SRK	−	10−13	0.2−0.8
[HEL]	313.15−328.15	0.0034−0.0921	12	46	PR	−	12−14	0.1−0.3
					SRK	−	0.2−9.9	0.4−0.5
Total	313.15−348.1	0.0020−0.8120	578		PR	7−20	3.3−22	0.1−19
					SRK	7−25	0.2−22	0.1−17

[a]Numebr of experiemntal data.

[b]$\%ARD = \frac{|\text{Calc.}(i) - \text{Exp.}(i)|}{\text{Exp.}(i)}$

*No global optimum values have been detected within the defined tolerance of the optimization algorithm.

Table 4. The Results of the Performed Consistency Test

Set No.	Component	T/K	P/Pa $\times 10^{-6}$	Solubility/CO_2 mole fraction	Z	$\varphi_2{}^L$	$\varphi_1{}^L \times 10^7$	Ap	$A\varphi$	ΔA_i %	Test result	Reference
1	[C_2-mim][Tf_2N]	314.05	18.3	0.233	0.1076	3.8864	3.99	3.416	3.661	7.2	TC	86
			29.8	0.3607	0.1536	2.3492	2.67					
			34.6	0.4361	0.1765	1.8564	2.27					
			39	0.4884	0.1907	1.5996	2.06					
			51.5	0.551	0.2061	1.3506	1.88					
			56.5	0.587	0.2144	1.2277	1.80					
			70.5	0.6448	0.2279	1.0507	1.71					
			77	0.6699	0.2346	0.9777	1.67					
			90.5	0.7043	0.2485	0.8698	1.64					
2		324.15	22	0.233	0.1951	3.6341	4.61	3.059	2.855	6.7	TC	86
			36	0.3607	0.2648	2.1321	3.59					
			41.2	0.4361	0.2943	1.6606	3.38					
			48	0.4884	0.3106	1.4182	3.32					
			63.2	0.551	0.3272	1.1844	3.35					
			69	0.587	0.3367	1.0681	3.40					
			89	0.6448	0.3549	0.8982	3.56					
			107	0.6699	0.364	0.8312	3.67					
			130	0.7043	0.3766	0.7476	3.88					

Table 4. *Continued*

Set No.	Component	T/K	P/Pa $\times 10^{-6}$	Solubility/CO_2 mole fraction	Z	φ_2^L	φ_1^L $\times 10^7$	Ap	$A\varphi$	ΔA_i %	Test result	Reference
3		334.35	26.6	0.233	0.1346	3.8574	10.30	4.251	4.703	10.6	TC	86
			42	0.3607	0.1995	2.3056	6.83					
			48.8	0.4361	0.2357	1.8016	5.75					
			57.8	0.4884	0.2606	1.5352	5.22					
			77	0.551	0.2918	1.2711	4.74					
			85.5	0.587	0.3118	1.1363	4.54					
			113	0.6448	0.353	0.9319	4.31					
			133	0.6699	0.3768	0.8462	4.26					
4		344.55	30.6	0.233	0.1789	3.7641	14.00	4.734	4.8	1.4	TC	86
			46	0.3607	0.2616	2.2192	9.84					
			57.5	0.4361	0.3066	1.7199	8.67					
			70.2	0.4884	0.3374	1.4566	8.16					
			91.5	0.551	0.376	1.1970	7.79					
			104	0.587	0.4008	1.0666	7.69					
			142	0.6448	0.4464	0.8814	7.79					
			168	0.6699	0.4681	0.8108	7.95					
							0.00					
5	[C_4-mim][Tf_2N]	314.05	12.9	0.3103	0.1299	2.9077	1.18	3.137	2.92	6.9	TC	86
			21.4	0.397	0.1546	2.194	0.94					
			36.4	0.5012	0.1817	1.6474	0.74					
			34.3	0.5171	0.1856	1.5815	0.71					
			39.5	0.5544	0.1945	1.4395	0.66					
			45.8	0.5942	0.2037	1.3039	0.61					
			50.4	0.621	0.2098	1.2197	0.57					
			55.2	0.6477	0.2159	1.1404	0.55					
			60	0.6642	0.2197	1.0932	0.53					
			66.7	0.6848	0.2247	1.0353	0.51					
			67.4	0.6986	0.2281	0.9975	0.50					
			74.2	0.7208	0.2341	0.9365	0.48					
6		324.15	15.5	0.3103	0.2184	2.7519	1.44	3.066	2.078	32.2	TI	86
			24.5	0.397	0.2569	2.0476	1.25					
			36.4	0.5012	0.2892	1.5227	1.14					
			41.2	0.5171	0.2929	1.4611	1.13					
			48	0.5544	0.3001	1.33	1.13					
			56.3	0.5942	0.3059	1.2076	1.13					
			61.2	0.621	0.3088	1.1336	1.14					
			70.5	0.6477	0.3109	1.0652	1.15					
			75.4	0.6642	0.312	1.0253	1.17					
			84.5	0.6848	0.313	0.9778	1.19					
			89	0.6986	0.3136	0.9467	1.20					
7		334.35	18	0.3103	0.2173	2.7796	2.57	3.634	2.635	27.5	TI	86
			29.2	0.397	0.2574	2.0696	2.19					
			45.8	0.5012	0.2962	1.5317	1.93					
			49	0.5171	0.3014	1.4673	1.90					
			57.8	0.5544	0.3132	1.3287	1.85					
			67.8	0.5942	0.3254	1.1962	1.80					
			73.8	0.621	0.3339	1.1138	1.78					
			85.2	0.6477	0.3428	1.0356	1.77					
			91.3	0.6642	0.3489	0.9886	1.76					
			106.5	0.6848	0.3573	0.9309	1.76					
8		344.55	21.4	0.3103	0.3681	2.565	3.71	3.574	2.234	37.5	TI	86
			36.4	0.397	0.3858	1.9318	3.76					
			54.5	0.5012	0.3925	1.4623	3.99					
			58.2	0.5171	0.393	1.4065	4.03					
			70	0.5544	0.3941	1.2864	4.15					
			81.2	0.5942	0.3957	1.1717	4.28					
			91.6	0.621	0.3973	1.1006	4.38					
			100.8	0.6477	0.3997	1.0335	4.49					
			113	0.6642	0.4017	0.9932	4.57					
9		314.06	8.7	0.2132	0.1252	4.2951	1.23	709.658	739.92	4.3	TC	86
			21.4	0.376	0.1978	2.2413	0.75					
			34	0.4965	0.2379	1.5733	0.61					
			40	0.5413	0.2499	1.3959	0.58					
			52	0.6124	0.2663	1.1603	0.55					
			55.4	0.6409	0.2723	1.0767	0.54					
			64.6	0.6834	0.2821	0.9576	0.53					
			69.5	0.7003	0.2872	0.9092	0.53					
			79.5	0.731	0.3047	0.8071	0.53					
			89.9	0.7542	0.3275	0.7194	0.54					
			150.2	0.7902	0.3688	0.5984	0.57					

Table 4. *Continued*

Set No.	Component	T/K	P/Pa $\times 10^{-6}$	Solubility/CO_2 mole fraction	Z	φ_2^L	φ_1^L $\times 10^7$	Ap	$A\varphi$	ΔA_i %	Test result	Reference
10		324.19	10.1	0.2132	0.1125	4.3569	2.51	8.389	7.244	13.6	TC	86
			25.8	0.376	0.1846	2.2917	1.43					
			41	0.4965	0.231	1.6097	1.09					
			48.1	0.5413	0.2473	1.4254	1.00					
			62.7	0.6124	0.2734	1.1754	0.88					
			67	0.6409	0.2848	1.0844	0.85					
			79.2	0.6834	0.3051	0.9512	0.80					
			86	0.7003	0.3158	0.8962	0.80					
			105.1	0.731	0.3442	0.7869	0.77					
			119.4	0.7542	0.3754	0.7001	0.77					
			162.3	0.7739	0.4071	0.6304	0.78					
			197.5	0.7902	0.4349	0.5791	0.80					
11		334.35	11.5	0.2132	0.1394	4.3093	3.82	8.676	7.686	11.4	Tc	86
			30	0.376	0.2283	2.2427	2.27					
			47.5	0.4965	0.2858	1.5594	1.80					
			55.8	0.5413	0.3063	1.3741	1.69					
			73.8	0.6124	0.3405	1.1209	1.56					
			81.3	0.6409	0.3564	1.0277	1.52					
			98.5	0.6834	0.3862	0.8908	1.50					
			105	0.7003	0.4012	0.8364	1.50					
			133.5	0.731	0.4341	0.7398	1.52					
			154.7	0.7542	0.4625	0.6723	1.58					
			200.1	0.7739	0.4879	0.6201	1.65					
			232.3	0.7902	0.5082	0.5817	1.73					
			276.1	0.8041	0.5247	0.5523	1.82					
12		344.51	12.9	0.2132	0.1702	4.242	5.39	8.744	31.909	264.9	TI	86
			34	0.376	0.2958	2.1226	3.04					
			53.4	0.4965	0.4115	1.3523	2.30					
			64	0.5413	0.4763	1.1119	2.15					
			85.1	0.6124	0.6166	0.7922	2.16					
			94.9	0.6409	0.6763	0.6991	2.28					
			115.5	0.6834	0.7595	0.5936	2.59					
			126.7	0.7003	0.7892	0.5607	2.76					
			164.2	0.731	0.8367	0.5115	3.14					
			184.5	0.7542	0.866	0.4819	3.51					
			242	0.7739	0.886	0.4611	3.87					
			271.4	0.7902	0.8984	0.4465	4.20					
			317.2	0.8041	0.906	0.4356	4.52					
13		323.08	4.88	0.0847	0.0387	11.5493	7.24	13.025	10.007	23.2	TC	86
			11.72	0.1886	0.0805	5.0405	3.36					
			20.24	0.2926	0.1179	3.1467	2.19					
			29.38	0.3818	0.1461	2.338	1.70					
							0.00					
14	$[C_6\text{-mim}][Tf_2N]$	314.05	17.5	0.3221	0.1867	2.7541	0.26	4.841	2.792	42.3		86
			21.8	0.4079	0.2194	2.0908	0.22	2.667	2.447	8.2	NFC	
			26.8	0.4646	0.2371	1.7831	0.20					
		36.5	0.5568	0.2591		1.4095	0.18					
		47	0.6202	0.2698		1.2099	0.17					
		51	0.6457	0.2733		1.1384	0.16					
			55.5	0.6681	0.2761	1.0785	0.16					
			62	0.7043	0.2802	0.9863	0.16					
			67	0.7191	0.282	0.9495	0.16					
			72.5	0.7315	0.2837	0.9187	0.16					
			78	0.7435	0.2855	0.8887	0.16					
			86.2	0.7657	0.2906	0.83	0.16					
			140	0.7985	0.3115	0.72	0.16					
15		324.15	21	0.3221	0.2095	2.7402	0.48	3.647	3.196	12.4	TC	86
			26.5	0.4079	0.2497	2.072	0.39					
			33.2	0.4646	0.2725	1.7609	0.36					
			45.5	0.5568	0.3039	1.3798	0.32					
			57	0.6202	0.3221	1.1731	0.30					
			63	0.6457	0.3291	1.0979	0.30					
			69	0.6681	0.3354	1.0343	0.29					
			79	0.7043	0.3469	0.9335	0.29					
			86	0.7191	0.3527	0.8918	0.29					
			94	0.7315	0.3586	0.856	0.29					
			101	0.7435	0.3656	0.8199	0.30					
			120	0.7657	0.3833	0.7488	0.32					
			184	0.7985	0.4195	0.6426	0.00					
16		334.35	25.2	0.3221	0.236	2.7256	0.84	4.018	3.262	18.8	Tc	86
			32	0.4079	0.2801	2.0596	0.71					

Table 4. *Continued*

Set No.	Component	T/K	P/Pa $\times 10^{-6}$	Solubility/CO_2 mole fraction	Z	φ_2^L	φ_1^L $\times 10^7$	Ap	$A\varphi$	ΔA_i %	Test result	Reference
			39.5	0.4646	0.3049	1.75	0.65					
			55	0.5568	0.3387	1.3715	0.59					
			71.8	0.6202	0.3586	1.1666	0.57					
			77	0.6457	0.3663	1.0922	0.56					
			84.5	0.6681	0.3734	1.0294	0.56					
			99	0.7043	0.3861	0.9308	0.56					
			108	0.7191	0.3924	0.8906	0.56					
			116	0.7315	0.3982	0.857	0.57					
			130	0.7435	0.4046	0.8243	0.57					
			158	0.7657	0.4187	0.7631	0.59					
		344.55	29.6	0.3221	0.2631	2.7145	1.43	4.211	3.294	21.8	TC	86
17			37.2	0.4079	0.3101	2.0517	1.23					
			46	0.4646	0.3362	1.7441	1.15					
			66	0.5568	0.372	1.3684	1.07					
			84.2	0.6202	0.3936	1.1652	1.04					
			90	0.6457	0.4022	1.0916	1.35					
			100	0.6681	0.4102	1.0294	1.03					
			120	0.7043	0.4246	0.9324	1.04					
			132	0.7191	0.4314	0.8936	1.05					
			144.5	0.7315	0.4376	0.8614	1.06					
			160	0.7435	0.4441	0.8303	1.07					
			194	0.7657	0.458	0.7734	1.10					
18		323.15	37.16	0.487	0.2367	1.7114	0.34	1.577	1.496	5.2	TC	86
			54.3	0.583	0.2664	1.3426	0.29					
			65.6	0.637	0.2815	1.1747	0.26					
			80.39	0.692	0.2968	1.0201	0.25					
			90.78	0.726	0.3075	0.9281	0.24					
			99.69	0.751	0.3174	0.859	0.23					
			110.81	0.769	0.3271	0.806	0.23					
			122.24	0.774	0.3305	0.7905	0.23					
			129.59	0.779	0.3342	0.7746	0.23					
19		343.15	17.93	0.14	0.1178	6.8003	2.82	13.676	10.668	22	TC	86
			27.54	0.239	0.1904	3.8295	1.75					
			55.37	0.436	0.3072	1.9047	1.09					
			88.61	0.596	0.3777	1.2432	0.92					
			115.6	0.673	0.4087	1.0159	0.90					
			144.69	0.721	0.4314	0.8866	0.91					
			198.18	0.755	0.4516	0.7974	0.94					
			247.08	0.771	0.4628	0.7563	0.96					
							0.00					
20	[C_8-mim][Tf_2N]	314.05	8.2	0.3019	0.1982	2.9967	0.08	10.842	5.998	44.7	TI	86
			14.8	0.3762	0.2269	2.3405	0.07					
			18.9	0.4386	0.2452	1.9595	0.06					
			23.4	0.4849	0.2557	1.7385	0.06					
			27.2	0.5344	0.2641	1.5429	0.06					
			32.2	0.5722	0.2688	1.4145	0.05					
			36.6	0.6081	0.272	1.3054	0.05					
			46	0.6587	0.2748	1.1681	0.05					
			53	0.6993	0.2759	1.0679	0.05					
			60	0.7151	0.2762	1.0304	0.05					
			63	0.7378	0.2765	0.9781	0.05					
			66.2	0.7536	0.2768	0.942	0.05					
			83	0.7867	0.278	0.8659	0.04					
			116	0.812	0.2805	0.8051	0.04					
21		324.15	9.6	0.3019	0.1747	3.0518	0.17	10.842	3.113	48.1	TI	86
			17.2	0.3762	0.2074	2.3863	0.14					
			22	0.4386	0.2316	1.9966	0.12					
			27.5	0.4849	0.2477	1.7692	0.11					
			32.6	0.5344	0.2631	1.5661	0.10					
			38	0.5722	0.2738	1.4316	0.10					
			44	0.6081	0.283	1.3167	0.09					
			55.4	0.6587	0.2948	1.1707	0.08					
			65	0.6993	0.3036	1.063	0.08					
			75.5	0.7151	0.307	1.0226	0.08					
			78	0.7378	0.3119	0.9655	0.07					
			85	0.7536	0.3156	0.9261	0.07					
			109	0.7867	0.3248	0.8419	0.07					
22		334.35	12.8	0.3019	0.2432	2.9801	0.28	5.994	4.283	28.6		86
			20	0.3762	0.2858	2.3164	0.24		3.794	11.6	NFC	
			24.8	0.4386	0.3162	1.9286	0.22					
			32.2	0.4849	0.3355	1.7027	0.20					

Table 4. *Continued*

Set No.	Component	T/K	P/Pa $\times 10^{-6}$	Solubility/CO_2 mole fraction	Z	φ_2^L	φ_1^L $\times 10^7$	Ap	$A\varphi$	ΔA_i %	Test result	Reference
			38.2	0.5344	0.3532	1.5014	0.19					
			44.8	0.5722	0.3647	1.3687	0.19					
			53.2	0.6081	0.3743	1.2553	0.18					
			67	0.6587	0.3861	1.1116	0.18					
			79	0.6993	0.3948	1.0055	0.18					
			91	0.7151	0.3983	0.9654	0.18					
			93.8	0.7378	0.4037	0.9089	0.18					
			104	0.7536	0.4084	0.8691	0.18					
			141	0.7867	0.4209	0.7846	0.19					
23		344.55	16	0.3019	0.2609	2.9818	0.50	6.24	3.331	46.6	TI	86
			23.4	0.3762	0.3089	2.3162	0.43					
			28.6	0.4386	0.3442	1.9266	0.39					
			38	0.4849	0.3673	1.6992	0.37					
			46.8	0.5344	0.3894	1.4961	0.35					
			53.8	0.5722	0.4045	1.3618	0.34					
			64	0.6081	0.4178	1.2469	0.34					
			79.2	0.6587	0.435	1.1007	0.33					
			96	0.6993	0.4487	0.9927	0.34					
			107.5	0.7151	0.4545	0.9517	0.34					
			113	0.7378	0.4633	0.8941	0.34					
			128	0.7536	0.4703	0.8542	0.35					
			175	0.7867	0.4879	0.7707	0.37					
							0.00					
							0.00					
24	[C_2-mim][TfO]	314.05	10	0.1794	0.1013	5.0674	9.44	7.877	4.499	42.9	TI	87
			18	0.2613	0.1384	3.3185	6.84					
			28	0.3546	0.1736	2.3082	5.41					
			39	0.4141	0.1924	1.8995	4.88					
			48	0.467	0.2068	1.6217	4.55					
			58	0.5078	0.2166	1.4449	4.37					
			72	0.5435	0.2245	1.3098	4.26					
			86	0.5681	0.2297	1.2253	4.20					
25		324.15	11.5	0.1794	0.2529	4.466	8.43	7.045	2.56	63.7	TI	87
			22	0.2613	0.3002	2.8749	7.65					
			32.5	0.3546	0.3186	2.0179	7.75					
			48	0.4141	0.3178	1.6911	8.13					
			60	0.467	0.3126	1.4758	8.63					
			75	0.5078	0.3071	1.3414	9.10					
			96	0.5435	0.302	1.2396	9.58					
26		334.35	13	0.1794	0.1732	4.8446	18.10	8.134	3.842	52.8	TI	87
			25	0.2613	0.234	3.1121	13.90					
			41	0.3546	0.2902	2.1186	11.90					
			58.5	0.4141	0.3199	1.7188	11.30					
			75	0.467	0.3435	1.4466	11.00					
			95	0.5078	0.3609	1.2725	11.00					
			127	0.5435	0.3765	1.1383	11.10					
27		344.55	15.5	0.1794	0.2415	4.6593	23.60	8.787	2.827	67.8	TI	87
			30.5	0.2613	0.3073	2.9907	200.00					
			50	0.3546	0.3542	2.0636	19.00					
			71	0.4141	0.3718	1.7029	19.10					
			92	0.467	0.3815	1.4642	19.70					
			119	0.5078	0.3862	1.3152	20.30					
			165	0.5435	0.3888	1.204	21.10					
							0.00					
28	[C_4-mim][TfO]	314.05	9.5	0.2182	0.1677	4.0327	2.34	14.295	3.698	74.1	TI	87
			14.1	0.2734	0.1945	3.1227	2.03					
			20.7	0.3344	0.2175	2.4719	1.84					
			26.6	0.3786	0.2303	2.1336	1.75					
			32.3	0.414	0.2383	1.916	1.71					
			40.3	0.4574	0.2458	1.6959	1.67					
			48.1	0.4929	0.2502	1.545	1.66					
			59.7	0.5367	0.2538	1.3858	1.66					
			73.1	0.5761	0.2555	1.2628	1.67					
			95.8	0.6134	0.2561	1.1598	1.69					
29		324.15	11.6	0.2182	0.2084	3.9522	3.60	10.552	3.025	71.3	TI	87
			17.3	0.2734	0.2438	3.0411	3.15					
			25.3	0.3344	0.275	2.3893	2.87					
			32.6	0.3786	0.2929	2.0505	2.76					
			39.5	0.414	0.3045	1.8325	2.70					
			49.6	0.4574	0.3158	1.6119	2.67					
			59.6	0.4929	0.3228	1.4605	2.67					

Table 4. *Continued*

Set No.	Component	T/K	P/Pa $\times 10^{-6}$	Solubility/CO_2 mole fraction	Z	φ_2^L	φ_1^L $\times 10^7$	Ap	$A\varphi$	ΔA_i %	Test result	Reference
			75	0.5367	0.3294	1.3006	2.69					
			94.8	0.5761	0.3338	1.1757	2.75					
			133.8	0.6134	0.3373	1.0699	2.83					
30		334.35	13.5	0.2182	0.2668	3.8501	5.46	10.5	2.521	76	TI	87
			23	0.2734	0.3024	2.966	5.02					
			32	0.3344	0.3298	2.3409	4.81					
			39	0.3786	0.3428	2.0198	4.77					
			47.5	0.414	0.3498	1.8147	4.79					
			64	0.4574	0.355	1.6084	4.88					
			76	0.4929	0.357	1.4676	4.98					
			92	0.5367	0.3575	1.3193	5.16					
			114	0.5761	0.3566	1.2044	5.35					
			166	0.6134	0.3552	1.108	5.58					
31		344.55	19	0.2182	0.1917	4.0773	11.10	6.975	3.387	51.4	TI	87
			28	0.2734	0.2326	3.145	9.27					
			37	0.3344	0.2743	2.4691	8.03					
			47.5	0.3786	0.3023	2.1126	7.42					
			55	0.414	0.3234	1.8802	7.06					
			78	0.4574	0.348	1.6418	6.73					
			90	0.4929	0.3674	1.475	6.54					
			112	0.5367	0.3907	1.2965	6.41					
			147	0.5761	0.4118	1.155	6.36					
							0.00					
32	[C_6-mim][TfO]	314.05	16.5	0.2885	0.1368	3.1668	0.90	4.61	2.57	44.2	TI	87
			21	0.3566	0.1617	2.4949	0.73					
			26.5	0.4162	0.1811	2.0832	0.63					
			32	0.4632	0.1949	1.8303	0.57					
			42	0.5329	0.2127	1.5317	0.50					
			50	0.5626	0.2194	1.4249	0.48					
			55	0.5898	0.225	1.3351	0.46					
			62	0.611	0.2292	1.2696	0.44					
			74	0.6236	0.2315	1.2324	0.43					
			92	0.6487	0.2359	1.1615	0.42					
			105	0.6668	0.2389	1.1126	0.41					
33		324.15	20	0.2885	0.2112	3.0447	1.28	5.038	11.029	118.9	TI	87
			27	0.3566	0.2399	2.3871	1.13					
			34	0.4162	0.2596	1.9871	1.04					
			40	0.4632	0.2721	1.7431	1.00					
			52	0.5329	0.2864	1.4569	0.95					
			65	0.5626	0.2913	1.3542	0.93					
			70	0.5898	0.2954	1.268	0.92					
			80	0.611	0.2983	1.2051	0.91					
			94	0.6236	0.3	1.1691	0.91					
			125	0.6487	0.3034	1.1001	0.90					
			143	0.6668	0.3059	1.0522	8.98					
34		334.35	23	0.2885	0.2515	3.0052	2.05	5.374	2.474	54	TI	87
			33	0.3566	0.2917	2.3403	1.81					
			41	0.4162	0.321	1.9353	1.68					
			48.5	0.4632	0.3403	1.6897	1.61					
			65	0.5329	0.3634	1.3977	1.56					
			78	0.5626	0.3716	1.2938	1.55					
			85	0.5898	0.3784	1.2067	1.55					
			98	0.611	0.3833	1.1431	1.56					
			120	0.6236	0.3862	1.1068	1.56					
			158	0.6487	0.3919	1.0372	1.58					
			182	0.6668	0.3962	0.989	1.60					
35		344.55	28	0.2885	0.3804	2.8426	3.02	5.416	2.602	52	TI	87
			39	0.3566	0.4142	2.218	3.94					
			48	0.4162	0.4311	1.8456	2.97					
			58	0.4632	0.438	1.6216	3.04					
			80	0.5329	0.4407	1.3628	3.20					
			95	0.5626	0.4403	1.2707	3.29					
			105	0.5898	0.4394	1.1939	3.39					
			119	0.611	0.4386	1.1378	3.47					
			151	0.6236	0.4381	1.1059	3.52					
			189	0.6487	0.4374	1.045	3.64					
							0.00					
36	[C_8-mim][TfO]	314.05	8	0.2166	0.1613	4.2666	0.30	5.066	3.426	32.4	TI	87
			19	0.3445	0.2239	2.5508	0.21					
			30	0.4377	0.2544	1.93	0.18					
			38	0.4896	0.2662	1.6852	0.18					

Table 4. *Continued*

Set No.	Component	T/K	P/Pa $\times 10^{-6}$	Solubility/CO_2 mole fraction	Z	φ_2^L	φ_1^L $\times 10^7$	Ap	$A\varphi$	ΔA_i %	Test result	Reference
			47.5	0.5508	0.2756	1.4532	0.17					
			53	0.578	0.2785	1.3647	0.16					
			60	0.6105	0.2808	1.2683	0.16					
			69	0.6414	0.2821	1.1842	0.16					
			79	0.6703	0.2826	1.1109	0.16					
37		324.15	10.8	0.2166	0.1595	4.2936	0.59	5.35	3.794	29.1		87
			23.5	0.3445	0.2274	2.5691	0.41	4.307	3.311	23.1	NFC	
			37	0.4377	0.2646	1.9402	0.35					
			47	0.4896	0.281	1.6903	0.32					
			58	0.5508	0.2965	1.4523	0.30					
			65.5	0.578	0.3023	1.3609	0.29					
			75	0.6105	0.3083	1.2605	0.28					
			86	0.6414	0.3134	1.1722	0.28					
			106	0.6703	0.3177	1.0946	0.27					
38		334.35	13.5	0.2166	0.2786	4.1064	0.78	5.486	3.125	43	TI	87
			28.5	0.3445	0.3509	2.4421	0.67					
			44.5	0.4377	0.3733	1.8526	0.66					
			55	0.4896	0.3781	1.6224	0.66					
			69	0.5508	0.3791	1.4048	0.68					
			78.5	0.578	0.3785	1.3217	0.69					
			94	0.6105	0.3772	1.2305	0.70					
			109	0.6414	0.3758	1.1504	0.71					
39		344.55	16.5	0.2166	0.235	4.2116	1.55	5.585	4.247	24	TC	87
			33.5	0.3445	0.3327	2.492	1.15					
			52	0.4377	0.3843	1.8681	1.05					
			64	0.4896	0.4062	1.6209	1.02					
			83	0.5508	0.4262	1.3866	1.01					
			92	0.578	0.4334	1.2969	1.01					
			111	0.6105	0.4408	1.1986	1.02					
			132	0.6414	0.4471	1.1123	1.03					
							0.00					
40	[BMP][TfO]	323.15	27.1	0.2583	0.2157	3.9353	0.12	17.356	4.11	76.3	TI	2
			36.2	0.3118	0.2492	2.7262	0.10					
			53.4	0.3877	0.2901	2.0901	0.09					
			77.9	0.4623	0.3226	1.6637	0.08					
			100	0.5697	0.3583	1.2327	0.08					
			148.7	0.6216	0.3735	1.0666	0.08					
			281.7	0.6651	0.3899	0.934	0.08					
			482.1	0.7058	0.4159	0.8048	0.08					
41		333.15	29.2	0.2583	0.305	3.2583	0.19	16.151	3.156	80.5	TI	2
			44.1	0.3118	0.3412	2.6097	0.18					
			60.8	0.3877	0.3787	2.0018	0.17					
			90	0.4623	0.4024	1.6011	0.17					
			140	0.5697	0.4203	1.2044	0.18					
			192.4	0.6216	0.4262	1.0546	0.18					
			332	0.6651	0.4329	0.9396	0.19					
			529.2	0.7058	0.4433	0.8361	0.21					
42		343.15	31	0.2583	0.2569	3.3851	0.39	16.121	3.663	77.3	TI	2
			50.3	0.3118	0.2981	2.7157	0.35					
			69.5	0.3877	0.3493	2.0796	0.31					
			102.7	0.4623	0.3917	1.653	0.29					
			173	0.5697	0.4414	1.2227	0.28					
			232	0.6216	0.4632	1.0599	0.29					
			378.8	0.6651	0.4826	0.9369	0.30					
			595.3	0.7058	0.5033	0.8304	0.32					
43		353.15	39.1	0.2583	0.3235	3.3079	0.62	14.041	4.476	68.1	TI	2
			59.5	0.3118	0.3744	2.6407	0.56					
			80.6	0.3877	0.4371	2.008	0.52					
			118.4	0.4623	0.4888	1.5847	0.51					
			205	0.5697	0.5505	1.1593	0.53					
			271.1	0.6216	0.5782	1.0004	0.57					
			418	0.6651	0.6017	0.8837	0.62					
			623	0.7058	0.6238	0.7868	0.69					
							0.00					
44	[C_8-mim][BF_4]	313.15	17.26	0.197	0.1424	4.7509	13.70	4.007	3.48	13.1	TC	14
			28.85	0.319	0.1911	2.8271	10.00					
			44.15	0.417	0.2143	2.0991	8.73					
			56.7	0.507	0.2267	1.6758	7.99					
			70.49	0.589	0.2329	1.3964	7.42					
			83.73	0.658	0.2361	1.2073	6.90					
			92.9	0.708	0.2378	1.0867	6.47					

Table 4. *Continued*

Set No.	Component	T/K	P/Pa $\times 10^{-6}$	Solubility/CO_2 mole fraction	Z	φ_2^L	$\varphi_1^L \times 10^7$	Ap	$A\varphi$	ΔA_i %	Test result	Reference
45		323.15	15.61	0.191	0.1761	4.8582	20.10	4.404	3.026	31.3	TI	14
			28.78	0.297	0.2192	3.0308	16.40					
			43.33	0.398	0.24	2.2035	15.10					
			57.18	0.489	0.249	1.7498	14.40					
			70.42	0.551	0.2525	1.5228	14.00					
			83.73	0.627	0.2556	1.2987	13.40					
			92.28	0.671	0.2575	1.187	12.90					
46		333.15	15.61	0.16	0.102	6.0083	50.60	4.88	5.245	7.5	TC	14
			28.43	0.292	0.1731	3.1665	28.50					
			43.46	0.373	0.2109	2.4099	22.60					
			56.15	0.454	0.2442	1.9156	18.80					
			70.49	0.523	0.2694	1.608	16.40					
			84.14	0.605	0.2957	1.3233	14.20					
			93.73	0.651	0.282	1.4675	15.30					
							0.00					
47	[bmim][BF_4]	323.15	0.1015	0.003	0.0047	332.5511	5540.00	3548.509	245.304	93.1	TI	23
			0.5011	0.006	0.0094	165.8931	2810.00					
			1.0014	0.012	0.0183	82.5672	1440.00					
			3.997	0.044	0.0603	22.0331	450.00			93.1		
			6.9962	0.073	0.0906	13.0602	310.00					
			10.002	0.1	0.1132	9.4096	250.00					
			12.9965	0.127	0.1313	7.3267	220.00					
			15.0011	0.143	0.1402	6.4691	210.00					
			20	0.182	0.1572	5.0215	190.00					
48		348.15	0.102	0.002	0.003	499.3767	22700.00	5818.887	402.672	93.1	TI	23
			0.5013	0.003	0.0045	332.7092	15100.00					
			1.0018	0.007	0.0105	142.2386	6560.00					
			4.0018	0.03	0.0429	32.7338	1630.00					
			6.9956	0.051	0.0701	19.0273	1020.00					
			10.0027	0.071	0.0937	13.5216	770.00					
			13	0.089	0.1133	10.6881	650.00					
			15.0024	0.103	0.1275	9.1715	580.00					
			19.999	0.133	0.1547	7.0058	490.00					
							0.00					
49	[N-bupy][BF_4]	313.15	15.47	0.144	0.0869	6.5689	410.00	5.479	5.008	8.6	TC	16
			28.57	0.243	0.1302	3.7514	270.00					
			43.05	0.331	0.159	2.6653	220.00					
			56.43	0.399	0.1758	2.1548	190.00					
			70.91	0.47	0.1892	1.7782	180.00					
			83.8	0.533	0.1981	1.5258	170.00					
			91.59	0.579	0.2032	1.3742	160.00					
50		323.15	16.57	0.142	0.1179	6.572	480.00	5.133	4.058	21	TC	16
			32.36	0.25	0.1735	3.573	330.00					
			41.95	0.306	0.1931	2.8603	300.00					
			56.98	0.392	0.2139	2.1681	280.00					
			71.66	0.466	0.225	1.7791	270.00					
			83.87	0.532	0.2314	1.5224	260.00					
			92.35	0.581	0.2349	1.3677	260.00					
51		333.15	18.65	0.166	0.1203	5.6336	670.00	5.3	5.308	0.2	TC	16
			28.99	0.231	0.157	3.9437	510.00					
			42.85	0.298	0.189	2.9751	430.00					
			56.71	0.372	0.2177	2.312	370.00					
			70.08	0.44	0.2386	1.8993	340.00					
			84.9	0.511	0.2555	1.5844	320.00					
			95.8	0.549	0.2629	1.4485	320.00					
							0.00					
52	[C_4-mim][DCA]	313	17.71	0.2	0.2091	4.3498	2.68	26.496	1.767	93.3	TI	14
			32.3	0.3	0.2457	2.7746	2.37					
			50.88	0.41	0.2575	1.9555	2.35					
			88.56	0.507	0.2552	1.5333	2.44					
			467.49	0.601	0.2485	1.249	2.57					
53		323	22.6	0.2	0.1342	4.6022	6.48	23.536	3.207	86.4	TI	14
			40.05	0.3	0.1871	2.9273	4.61					
			63.95	0.41	0.2337	2.0221	3.66					
			131.84	0.507	0.2647	1.5428	3.23					
			531.74	0.601	0.2863	1.2175	3.02					
54		333	26.4	0.2	0.1774	4.5175	9.03	21.588	2.887	86.6	TI	14
			48.6	0.3	0.2395	2.859	6.87					
			77.43	0.41	0.2881	1.9728	5.90					
			175.66	0.507	0.3156	1.51	5.58					
			590.07	0.601	0.3316	1.1994	5.56					

Table 4. *Continued*

Set No.	Component	T/K	P/Pa $\times 10^{-6}$	Solubility/CO_2 mole fraction	Z	φ_2^L	φ_1^L $\times 10^7$	Ap	$A\varphi$	ΔA_i %	Test result	Reference
55		343	31.08	0.2	0.2622	4.3517	11.60	18.483	2.192	88.8	TI	14
			57.76	0.3	0.3208	2.758	10.20					
			94.52	0.41	0.3517	1.9238	9.92					
			217.5	0.507	0.3626	1.4913	10.20					
			642.17	0.601	0.3679	1.197	10.70					
							0.00					
56	[HEA]	313.15	1.45	0.0135	0.0061	73.5634	450.00	91.63	66.067	27.9	TI	46
			3.48	0.0316	0.0142	31.134	190.00					
			6.79	0.0616	0.0272	15.7213	100.00					
			10.48	0.0957	0.0415	9.9362	70.00					
			13.78	0.1248	0.0532	7.4987	50.00					
			15.42	0.1386	0.0586	6.7001	50.00					
57		328.15	1.24	0.0081	0.0045	122.8952	1310.00	128.81	118.445	8	TC	46
			4.48	0.0315	0.0175	31.1804	340.00					
			7.89	0.0558	0.0308	17.3513	190.00					
			10.78	0.0761	0.0418	12.5672	140.00					
			13.54	0.0948	0.0518	9.9713	110.00					
			15.02	0.1061	0.0578	8.8468	100.00					
							0.00					
58	[BHEAA]	313.15	1.26	0.0074	0.008	134.34	16.80	157.721	123.101	22	TC	46
			3.78	0.0231	0.0245	42.5035	5.50					
			6.15	0.0371	0.0389	26.1727	3.49					
			9.45	0.0572	0.0587	16.7087	2.32					
			12.61	0.0761	0.0767	12.3717	1.79					
			14.94	0.0905	0.0898	10.2859	1.54					
59		328.15	1.78	0.0074	0.0112	134.1407	30.80	166.864	118.223	29.1	TI	46
			3.48	0.0146	0.022	67.4971	15.80					
			5.48	0.0225	0.0336	43.4541	10.40					
			8.94	0.0371	0.0544	25.9746	6.49					
			12.15	0.0502	0.0725	18.948	4.92					
			15.05	0.0626	0.0891	15.0105	4.04					
60	[HHEMEA]	313.15	1.34	0.0051	0.0107	194.8185	8.14	333.679	171.547	48.6	TI	46
			2.18	0.0085	0.0177	116.3837	4.94					
			5.89	0.0226	0.0458	43.0144	1.95					
			10.61	0.0411	0.0801	23.1328	1.14					
			12.87	0.0496	0.0949	18.98	0.97					
			14.1	0.0546	0.1033	17.1436	0.90					
61		328.15	1.56	0.0024	0.0121	413.9363	19.10	584.936	376.413	35.6	TI	46
			2.98	0.0045	0.0226	219.5011	10.30					
			5.48	0.0092	0.0459	105.9971	5.17					
			9.48	0.016	0.0792	59.8214	3.08					
			12.36	0.0206	0.1014	45.8833	2.46					
			15.16	0.0253	0.1239	36.8797	2.05					
62	[BHEAL]	313.15	1.21	0.0054	0.0092	184.1239	0.81	242.082	123.953	48.8	TI	46
			3.48	0.0158	0.0266	62.2333	28.40					
			7.48	0.0342	0.0562	28.2024	0.14					
			10.59	0.0484	0.0799	19.6362	0.10					
			13.15	0.0601	0.095	15.626	0.08					
			15.98	0.0738	0.1143	12.5514	0.07					
63		328.15	1.69	0.0035	0.0127	283.7022	1.81	337.772	247.598	26.7	TI	46
			3.48	0.0071	0.0256	138.8239	0.91					
			7.46	0.015	0.0533	64.6739	0.44					
			10.56	0.0211	0.0741	45.4168	0.33					
			12.12	0.0238	0.0832	40.049	0.29					
			15.06	0.0284	0.0985	33.2583	0.25					
64	[HHEMEL]	313.15	1.86	0.0074	0.0178	133.8775	0.25					46
			4.21	0.0163	0.0386	60.1087	0.12	138.562	114.351	17.5	TC	
			8.15	0.0317	0.0729	30.3341	0.06					
			11.89	0.0464	0.1036	20.3633	0.05					
			13.48	0.0525	0.1158	17.8699	0.04					
			15.62	0.0607	0.1316	15.3111	0.04					
65		328.15	1.58	0.0027	0.0131	368.1277	1.08					
			3.59	0.0062	0.0298	159.0375	0.48	426.449	329.837	22.7	TC	46
			7.98	0.0142	0.0672	68.2119	0.22					
			10.52	0.0182	0.0854	52.7465	0.18					
			13.14	0.023	0.1068	41.3021	0.14					
			15.35	0.0271	0.1248	34.7434	0.12					
66	[HEL]	313.15	1.76	0.0106	0.009	93.5511	21.40					
			3.92	0.0239	0.0202	41.0492	9.61	103.235	83.743	18.9	TC	46
			7.48	0.0445	0.037	21.6838	5.25					
			10.45	0.0621	0.051	15.3166	3.82					

Table 4. *Continued*

Set No.	Component	T/K	P/Pa $\times 10^{-6}$	Solubility/CO_2 mole fraction	Z	φ_2^L	φ_1^L $\times 10^7$	Ap	$A\varphi$	ΔA_i %	Test result	Reference
			12.48	0.0743	0.0606	12.6744	3.23					
			15.56	0.0921	0.0741	10.076	2.65					
67		328.15	1.27	0.0034	0.0065	292.542	75.20					
			3.68	0.0092	0.0174	107.1176	28.20	367.058	267.177	27.2	TI	46
			6.95	0.0181	0.0339	53.685	14.60					
			10.12	0.0264	0.049	36.3249	10.20					
			13.56	0.0352	0.0646	26.8678	7.82					
			15.45	0.0398	0.0727	23.5909	6.99					

A significant point should not be omitted from our discussions. We are well aware that perhaps not all of the experimental data are fully trustable. This may be due to the inaccuracy of the used experimental techniques. For instance, the observation technique for detecting the bubble point of mixtures inside a variable volume cell can be much more inaccurate than the indirect technique relying on pressure-volume dependence which displays a break point.[91] We should point out that that PVT methods may have limitations. Nondestructive methods like RAMAN may contribute to more promising results. However, these kinds' of techniques are expensive. In this study, as we were interested in defining only the data quality, consequently, we have focused on consistency tests, our objective being not a comparison between the different experimental methods. More meticulous investigations should be made on the validity of the applied experimental techniques in future works.

Another conclusion is that the thermodynamic consistency tests may provide only rough information about data quality. The users must be very careful in keeping or removing these treated data from the database merely depending on the consistency test results. We recommend the users to keep all the data defined as fully consistent, with some of the data declared as not fully consistent with the help of their own skills and experiences on the related subject.

Conclusions

In this work, a thermodynamic model based on the well-known PR[20] EoS with the Wong-Sandler[68] mixing rule was applied to correlate the phase behaviors of the supercritical CO_2 + classical ionic liquid at various carbon dioxide solubilities. Nineteen different ionic liquids were studied for this purpose. The obtained results were compared to combination of the PR[20] and the SRK[64] with other mixing rules including the vdW1[47–49,68] and the vdW2.[47–49,68] The results indicate that the proposed model has reasonable capabilities and flexibilities to correlate the accurate equilibrium pressures of mixtures of supercritical carbon dioxide with various ionic liquids (with different chemical structures). Furthermore, the model uses the cubic two-parameter equations of state which are familiar and easy to use for engineers and can be simply adopted in simulation softwares. As the more accuracy of the presented model than other combinations of equations of state and mixing rules was confirmed, it was applied to perform a thermodynamic consistency test on 67 isothermal experimental datasets from the literature. As a result, 40% of the experimental data seem to be thermodynamically consistent, while this percentage is 55.5% for thermodynamically inconsistent data and 4.5% for not fully consistent data. These calculations indicate that selection of the experimental technique and also measuring the equilibrium pressures for such systems should be done very deliberately in order to reduce the error sources in obtaining such data. In addition, the users of the studied experimental data should be careful in keeping or removing these treated data from their database only according to the consistency test results. We generally recommend the researchers to keep the whole data determined as fully consistent and some of the data declared as not fully consistent considering their skills and experiences on the related subject.

Acknowledgment

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Notation

A = area or Van Laar parameter in activity model
a = attractive parameter of the equation of state, Pa.m^6/mol^2
$\hat{a}$ = parameter of equation of state defined by Eq. B2
ARD = absolute relative deviation, %
B = parameter of equation of state
b = repulsive parameter of the equation of state, m^3/mol
c_{1-3} = parameters of Mathias-Copeman[93] alpha function
D = parameter defined by Eq. B23
d = *derivative operator*
E = error
f = fugacity, Pa
function = primary objective function
G = Gibbs energy, Pa.m^3/mol
g = inequality constraint
h = equality constraint
k = binary interaction parameter
L = number of inequality constraint or the parameter of the Twu et al.[69,70] alpha function
l = counter in Eq. 16 or binary interaction parameter
M = number of equality constraints or the parameter of the Twu et al.[69,70] alpha function
M = counter in Eq. 16
N = number of components in the mixture or number of experimental data
n = number of moles
OF = objective function
PR EoS = Peng-Robinson equation of state
p = pressure, Pa
PN = penalty parameter
Q = parameter defined by Eq. B22
SRK EoS = Soave-Redlich-Kwong equation of state
R = universal gas constant, Pa.m^3/mol.K
T = temperature, K
vdW = van-der-Waals mixing rule

v = molar volume, (m^3/mol)
WS = Wong-Sandler mixing rule
y = mole fraction
Z = compressibility factor

Greek letters

α = alpha function in equation of state
∂ = partial derivative operator
ω = acentric factor
γ = activity coefficient
^ = defines the derivative of the parameters of the equations of state
φ = fugacity coefficient
σ = parameter of equation of state
ε = parameter of equation of state
Δ = difference operator
Ω = parameter in Eq. B28

Superscripts

Cal. = calculated values
E = excess property
Exp. = experimental values
L = liquid phase
V = vapor phase
0 = defines a parameter in Twu et al.[69,70] alpha function
1 = defines a parameter in Twu et al.[69,70] alpha function

Subscripts

A = area
c = critical property
i = i^{th} component in the mixture, i^{th} experimental dataset, i^{th} calculated equilibrium pressure, or defines a parameter in Twu et al.[69,70] alpha function
j = j^{th} component in the mixture, or j^{th} experimental dataset
l = l^{th} equality constraint
m = m^{th} inequality constraint or calculated parameters of equations of state for mixtures
r = reduced property
2 = refers to CO_2
(1), (2) = refer to the first and second states for integration
φ = refers to the area calculated using the thermodynamic model
p = refers to the area calculated using the experimental data

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Appendix A

Alpha functions

In 2004, Coquelet and coworkers[65] proposed a new alpha function for the PR EoS[20] for accurate correlation of pure component vapor pressures and saturated vapor and liquid densities.[65] This alpha function combines the advantages of the two alpha functions: Trebble-Bishnoi (TB)[92] and Mathias and Copeman (MC)[93] as follows:[65]

For $T > T_C$

$$\alpha(T)=\exp\left[c_1\left(1-\frac{T}{T_c}\right)\right]\left[1+c_2\left(1-\sqrt{\frac{T}{T_c}}\right)^2+c_3\left(1-\sqrt{\frac{T}{T_c}}\right)^3\right]^2 \tag{A1}$$

For $T > T_C$:

$$\alpha(T)=\exp\left[c_1\left(1-\frac{T}{T_c}\right)\right] \tag{A2}$$

where

$$c_1=-\left(\frac{\partial\alpha}{\partial T_r}\right)_{T_{r=1}} \tag{A3}$$

In the preceding equations

$$c_1=1.3569\omega^2+0.9957\omega+0.4077 \tag{A4}$$

$$c_2=-11.2986\omega^2+3.5590\omega-0.1146 \tag{A5}$$

$$c_3=11.7802\omega^2-3.8901\omega+0.5033 \tag{A6}$$

For the SRK EoS,[64] the alpha function proposed by Twu et al.[69,70] has been applied as follows[69,70]

$$\alpha(T_r)=\alpha^{(0)}(T_r)+\omega\left(\alpha^{(1)}(T_r)-\alpha^{(0)}(T_r)\right) \tag{A7}$$

with

$$\alpha^{(i)}(T_r)=T_r^{N(M-1)}\left[\exp\left(L\left(1-T_r^{NM}\right)\right)\right] \tag{A8}$$

where

Parameters	$Tr \le 1$		$Tr > 1$	
	$\alpha^{(0)}(Tr)$	$\alpha^{(1)}(Tr)$	$\alpha^{(0)}(Tr)$	$\alpha^{(1)}(Tr)$
	For SRK EoS[64]			
L	0.141599	0.500315	0.441411	0.032580
M	0.919422	0.799457	6.500018	1.289098
N	2.496441	3.29179	−0.200000	−8.000000

Appendix B

Fugacity coefficient expression and mixing rules used in this study

The following equation is used to evaluate the fugacity coefficients of species in the mixture

$$\ln\left(\hat{\phi}_i\right)=\frac{\hat{b}_i}{b_m}(Z-1)-\ln(Z-B)-\frac{a_m RT}{b_m(\sigma-\varepsilon)}\left[1+\frac{\hat{a}_i}{a_m}-\frac{\hat{b}_i}{b_m}\right]\ln\left(\frac{Z+\sigma B}{Z+\varepsilon B}\right) \tag{B1}$$

where

$$\hat{a}_i=\left[\frac{\partial(na_m)}{\partial(n_i)}\right]_{T,P,n_{j\neq i}} \tag{B2}$$

$$\hat{b}_i=\left[\frac{\partial(nb_m)}{\partial(n_i)}\right]_{T,P,n_{j\neq i}} \tag{B3}$$

$$B=\frac{b_m P}{RT} \tag{B4}$$

where a and b are the attraction and repulsion parameters of the equations of state, Z is the compressibility factor, and φ is the activity coefficient. For the PR EoS[20]

$$\sigma=1-\sqrt{2} \tag{B5}$$

$$\varepsilon=1+\sqrt{2} \tag{B6}$$

and for the SRK EoS[64]

$$\sigma=0 \tag{B7}$$

$$\varepsilon=1 \tag{B8}$$

Mixing rules

1. vdW1 mixing rule[47–49,68]

$$a_m=\sum_i\sum_j y_i y_j a_{ij} \tag{B9}$$

$$b_m=\sum_j y_j b_j \tag{B10}$$

$$a_{ij}=\sqrt{a_{ii}a_{jj}}\left(1-k_{ij}\right) \tag{B11}$$

where y is the mole fraction in a desired phase, and k is the binary interaction parameter. Therefore, the derivatives related to the attractive and repulsive parameters of the equations of state will be written as follows

$$\hat{a}_i=\left[\frac{\partial(na_m)}{\partial(n_i)}\right]_{T,P,n_{j\neq i}}=2\sum_{j=1}^{N}y_j a_{ij} \tag{B12}$$

$$\hat{b}_i = \left[\frac{\partial(nb_m)}{\partial(n_i)}\right]_{T,P,n_{j\neq i}} = b_i \tag{B13}$$

2. vdW2 mixing rule[47–49,68]

$$a_m = \sum_i \sum_j y_i y_j a_{ij} \tag{B14}$$

$$b_m = \sum_i \sum_j y_i y_j b_{ij} \tag{B15}$$

$$a_{ij} = \sqrt{a_{ii} a_{jj}}\left(1 - k_{ij}\right) \tag{B16}$$

$$b_{ij} = \frac{b_i + b_j}{2}\left(1 - l_{ij}\right) \tag{B17}$$

and

$$\hat{a}_i = \left[\frac{\partial(na_m)}{\partial(n_i)}\right]_{T,P,n_{j\neq i}} = 2\sum_{j=1}^{N} y_j a_{ij} \tag{B18}$$

$$\hat{b}_i = \left[\frac{\partial(nb_m)}{\partial(n_i)}\right]_{T,P,n_{j\neq i}} = 2\sum_{j=1}^{N} y_j b_{ij} \tag{B19}$$

3. WS mixing rule[68]

$$b_m = \frac{Q}{1-D} \tag{B20}$$

$$a_m = RTDb_m \tag{B21}$$

$$Q = \sum_i^N \sum_j^N y_i y_j \left(b - \frac{a}{RT}\right)_{ij} \tag{B22}$$

$$D = \sum_i^N \frac{y_i a_i}{b_i RT} + \frac{G^E}{\Omega RT} \tag{B23}$$

where

$$\left(b - \frac{a}{RT}\right)_{ij} = \left[b_i - {}^{i}\frac{a_i}{RT} + b_j - \frac{a_j}{RT}\right]\left(\frac{1-k_{ij}}{2}\right) \tag{B24}$$

$$\Omega = -0.6232 \tag{B25}$$

where

$$\hat{b}_i = \left[\frac{\partial(nb_m)}{\partial(n_i)}\right]_{T,P,n_{j\neq i}} = \frac{1}{1-D}\left(\frac{\partial(n^2 Q)}{n\partial n_i}\right) - \frac{Q}{(1-D)^2}\left(1 - \frac{\partial(nD)}{\partial n_i}\right) \tag{B26}$$

$$\hat{a}_i = \left[\frac{\partial(na_m)}{\partial(n_i)}\right]_{T,P,n_{j\neq i}} = RT\left[D\frac{\partial(nb)}{\partial n_i} + b\frac{\partial(nD)}{\partial n_i}\right] - a_m \tag{B27}$$

$$\frac{\partial(nD)}{\partial n_i} = \frac{a_i}{b_i RT} + \frac{\ln\gamma_i}{\Omega} \tag{B28}$$

$$\frac{\partial(n^2 Q)}{n\partial n_i} = 2\sum_{j=1}^{N} y_j \left(b - \frac{a}{RT}\right)_{ij} \tag{B29}$$

According to Van-Laar activity model, the excess Gibbs energy is calculated by the following expressions

$$\frac{G^E}{RT} = \frac{A_{12}A_{21}y_1 y_2}{A_{12}y_1 + A_{21}y_2} \tag{B30}$$

$$\ln\gamma_1 = A_{12}\left(1 + \frac{A_{12}y_1}{A_{21}y_2}\right)^{-2} \tag{B31}$$

$$\ln\gamma_2 = A_{21}\left(1 + \frac{A_{21}y_2}{A_{12}y_1}\right)^{-2} \tag{B32}$$

where A is the adjustable parameter of the Van Laar activity model and the subscripts 1 and 2 refer to the first and second compounds in the mixture, respectively.

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