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MODELING VAPOR LIQUID EQUILIBRIUM OF IONIC LIQUIDS + GAS BINARY SYSTEMS AT HIGH PRESSURE WITH CUBIC EQUATIONS OF STATE

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Abstract - Ionic liquids (IL) have been described as novel environmentally benign solvents because of their remarkable characteristics. Numerous applications of these solvents continue to grow at an exponential rate. In this work, high pressure vapor liquid equilibria for 17 different IL + gas binary systems were modeled at different temperatures with Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) equations of state, combined with the van der Waals mixing rule with two binary interaction parameters (vdW-2). The experimental data were taken from the literature. The optimum binary interaction parameters were estimated by minimization of an objective function based on the average absolute relative deviation of liquid and vapor phases, using the modified Simplex algorithm. The solubilities of all gases studied in this work decrease as the temperature increases and increase with increasing pressure. The correlated results were highly satisfactory, with average absolute relative deviations of 2.10% and 2.25% for PR-vdW-2 and SRK-vdW-2, respectively.

Keywords: Ionic liquids; Vapor-liquid equilibria; PR and SRK Eos.

INTRODUCTION

Ionic liquids are organic salts that are liquid at room temperature and consist of a small organic or inorganic anion and a large asymmetric organic cation. Ionic liquids have negligible vapor pressure and a stable and wide liquid range of over 300 K. These fluids have been proposed as attractive alternatives to volatile organic compounds for green processes (Blanchard and Brennecke, 2001).

Ionic liquids have been described as novel environmentally benign solvents because of their remarkable characteristics, such as non-volatility, high thermal stability, non-flammability and high polarity (Anthony *et al.*, 2001; Fadeev *et al.*, 2001). Numerous applications of these solvents continue to grow at an exponential rate; the most common applications found in the literature are in gas and liquid separation processes (Blanchard and Brennecke, 2001; Anthony *et al.*, 2001; Fadeev *et al.*, 2001;Visser *et al.*, 2000); as solvents in various reactions systems, such as hydrogenation, hydroformylations, isomerizations, dimerizations, alkylations, among others (Welton, 1999; Hermann *et al.*, 1999; Seddon, 1995; Blanchard *et al.*, 2001); in electrolytes/fuel cells (Souza *et al.*, 2003); as CO_2 selective separation media (Anthony *et al.*, 2002; Zhang *et al.*, 2006); in the capture or sequestration of

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various gases such as CO_2, H_2S and SO_2 (Anderson *et al*., 2007); and as lubricants in different systems (Bermudez *et al*., 2009).

The use of carbon dioxide (CO_2) as a green reaction media has gained more and more research interest due to its environmental and nontoxic properties. Carbon dioxide is nonflammable, nontoxic and inexpensive. The most important aspect of CO_2 is its tunable properties, which can change significantly with temperature and pressure. CO_2 has a relatively low critical temperature (31.1 °C) and moderate critical pressure (73.8 bar) (Jessop and Leitner, 1999). Wu and coworkers (Wu *et al*., 2005) and Zhou and coworkers (Zhou *et al*., 2006) investigated the use of compressed and supercritical CO_2 as an environmentally benign alternative in ionic liquid synthesis.

The phase behavior of ionic liquids with CO_2 is unique. CO_2 is very soluble in ionic liquids, but, in contrast, ionic liquids are insoluble in the pure CO_2 phase. Therefore, the ionic liquid + CO_2 mixture does not become miscible (critical) even at elevated pressures, which makes them advantageous as biphasic reaction media. Moreover, compressed CO_2 can increase the solubility of reactive gases (H_2 and O_2) in ionic liquids (Solinas *et al*., 2004; Hert *et al*., 2005), and dramatically decreases the melting point of many ionic solids, even inducing melting over 100 °C below the normal melting points of some ionic solids (Scurto and Leitner, 2006; Scurto *et al*., 2008).

Phase equilibria in systems composed of ionic liquids + CO_2 were studied by several authors (Blanchard *et al*., 2001; Ren *et al*., 2010; Nwosu *et al*., 2009; Carvalho *et al*., 2009a, 2009b; Kroon *et al*., 2005; Liu *et al*., 2003; Blanchard *et al*., 1999), but few of them have assessed the solubility in ionic liquids of other gases. The phase equilibria of different imidazolium ionic liquids with 1,1,1,2-tetrafluoroethane (R-134a) were studied by Ren and Scurto (2009a, 2009b); the authors emphasize the importance of understanding these systems for the separation of hydrofluorocarbon refrigerant gases and in other engineering applications.

In this work, isothermal vapor-liquid equilibrium data for 17 binary mixtures composed of ionic liquids and different gases (CO_2, C_2H_6, CHF_3 and R-134a) were analyzed, totalizing 390 experimental data points distributed in 50 isotherms. Pressure and temperature ranges vary between 1-620 bar and 298.15-363.15 K, respectively. The systems were modeled with the Peng-Robinson (Peng and Robinson, 1976) and Soave-Redlich-Kwong (Soave, 1972) equations of state using the van der Waals mixing rule with two adjustable parameters (k_{ij} and l_{ij}). These thermodynamic models were implemented in the PE 2000 software (Pfohl *et al*., 2000).

THERMODYNAMIC MODELING

The Soave–Redlich–Kwong equation of state is (Soave, 1972):

$$P = \frac{RT}{V-b} - \frac{\alpha(T)}{V(V+b)} \quad (1)$$

Here, P is the pressure, V the molar volume, T the temperature, α(T) the temperature-dependent attractive parameter, b the co-volume and R the ideal gas constant. The co-volume is temperature independent and is calculated using the critical properties as follows:

$$b = 0.08664\frac{RT_C}{P_C} \quad (2)$$

The attractive parameter, α(T), is calculated by a Soave-type expression:

$$\alpha = a(T_C, P_C).[1 + m.(1 - T_r^{0.5})]^2 \quad (3)$$

where:

$$a(T_C, P_C) = 0.42748\frac{(RT_C)^2}{P_C} \quad (4)$$

Here, T_r is the reduced temperature. The parameter m is correlated to the acentric factor ω for light non-polar compounds, through the following expression:

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \quad (5)$$

The expression for the Peng-Robinson equation of state is (Peng and Robinson, 1976):

$$P = \frac{RT}{V-b} - \frac{\alpha(T)}{V(V+b) + b(V-b)} \quad (6)$$

The variables are the same explained above. Again, the co-volume is temperature independent and is calculated using the critical properties, as follows:

$$b = 0.0778\frac{RT_C}{P_C} \tag{7}$$

The attractive parameter, α(T), is calculated by:

$$\alpha = a(T_C, P_C).[1 + m.(1 - T_r^{0.5})]^2 \tag{8}$$

where:

$$a(T_C, P_C) = 0.45724\frac{(RT_C)^2}{P_C} \tag{9}$$

Here, the parameter m is also correlated to the acentric factor, ω, for light non-polar compounds through:

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{10}$$

The Peng–Robinson equation is widely used in modeling the solubility of substances in supercritical fluids. For mixtures, cubic EoS like PR and SRK are widely applied utilizing the van der Waals-2-parameter (vdW-2) mixing rules:

$$\alpha_{mix} = \sum_i \sum_j x_i x_j \alpha_{ij} \quad \text{and}$$
$$b_{mix} = \sum_i \sum_j x_i x_j b_{ij} \tag{11}$$

where the cross energy, α_{ij}, and cross co-volume b_{ij} are calculated by combining rules:

$$\alpha_{ij} = (\alpha_i \alpha_j)^{0.5}(1 - k_{ij}) \quad \text{and}$$
$$b_{ij} = \frac{1}{2}(b_i + b_j).(1 - l_{ij}) \tag{12}$$
$$\text{with } k_{ij} = k_{ji} \text{ and } l_{ij} = l_{ji}$$

Here, k_{ij} and l_{ij} are adjustable parameters, determined by fitting binary phase equilibrium data. The combination of van der Waals mixing rules with the PR-EoS and SRK-EoS provides a good compromise between simplicity and accuracy of the modeling algorithm for representing a large variety of systems (Florusse *et al.*, 2008). Modeling high pressure phase equilibria with this combination showed good correspondence with experimental data in previous work (Gamse and Marr, 2000, 2001).

The software Phase Equilibrium 2000 (PE2000), chosen here to calculate the phase equilibria, was developed by Brunner and coworkers (Pfohl *et al*, 2000). The software was used by several other researchers (Petkov *et al.*, 2000; Schwarz and Nieuwoudt, 2003a, 2003b; Teodorescu *et al.*, 2003) with excellent results to correlate and predict phase equilibria. PE2000 uses the modified Simplex algorithm (Nelder and Mead, 1965) for parameter regression of the binary interaction parameters, k_{ij} and l_{ij}, minimizing the objective function of the average absolute relative deviation ($\%AARD$) for liquid and vapor phase mole fractions:

$$\%AARD = \frac{100}{NP}\left(\sum_{i=1}^{N}\left|\frac{x_i^{exp} - x_i^{pred}}{x_i^{exp}}\right| + \sum_{i=1}^{N}\left|\frac{y_i^{exp} - y_i^{pred}}{y_i^{exp}}\right|\right) \tag{13}$$

Here, x_i^{exp} is the experimental liquid mole fraction data; x_i^{pred} is the predicted value; y_i^{exp} is the experimental vapor mole fraction data; y_i^{pred} is the predicted value and NP is the number of experimental data points. This objective function was used in similar works in the literature with good results (Nwosu *et al.*, 2009; Ren and Scurto, 2009; Ren *et al.*, 2010). Several initial guesses were utilized to avoid the local minima in the regression in order to obtain final values for k_{ij} and l_{ij}.

RESULTS AND DISCUSSION

The critical properties of ionic liquids were taken from Valderrama *et al.* (2007, 2008a, 2009), Ren *et al.* (2010) and Nwosu *et al.* (2009). For CO_2, C_2H_6 and CHF_3, the properties were taken from the DIPPR data base (DIADEM, 2000). For R-134a, the critical properties are given by Ren and Scurto (2009a). All critical properties used in this work are given in Table 1.

The solubility of CO_2, CHF_3 and R-134a in various ionic liquids was modeled with the PR-EoS and SRK-EoS with the vdW-2 mixing rule, at different temperatures for each case. The experimental data were taken from the literature (Blanchard and Brennecke, 2001; Ren *et al.*, 2010; Nwosu *et al.*, 2009; Carvalho *et al.*, 2009a, 2009b; Kroon *et al.*, 2005; Liu *et al.*, 2003; Ren and Scurto, 2009a; Shariati and Peters, 2003; Florusse *et al.*, 2008) and the characteristics of these systems are shown in Table 2.

Table 1: Critical properties of pure components.

Compound	Formula	MW (g/mol)	T_C (K)	P_C (bar)	ω
Carbon dioxide	CO_2	44.0	304.2	73.8	0.228
Trifluoromethane	CHF_3	70.0	299.3	48.2	0.264
1,1,1,2-tetrafluoroethane	R-134a	102.0	374.3	40.6	0.327
Ethane	C_2H_6	30.1	305.4	48.8	0.099
1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide	[emim][Tf_2N]	391.3	1244.9	32.6	0.182
1-n-hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide	[C_6mim][Tf_2N]	447.4	1287.3	23.9	0.354
1-n-decyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide	[dmim][Tf_2N]	504.0	1345.1	18.7	0.574
1-n-exyl-3-methyl-imidazolium bromide	[C_6mim][Br]	247.2	841.1	26.7	0.607
1-methylimidazole	1-methylimidazole	82.1	742.4	55.6	0.279
1-n-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide	[bmim][Tf_2N]	419.4	826.3	27.6	0.300
1-n-pentyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide	[pmim][Tf_2N]	433.0	1249.43	26.3	0.412
1-n-octyl-3-methylimidazolium tetrafluoroborate	[omin][BF_4]	282.1	737.0	16.0	1.029
1-n-butyl-3-methylimidazolium tetrafluoroborate	[bmin][BF_4]	226.0	643.2	20.4	0.888
1-ethyl-3-methylimidazolium hexafluorophosphate	[emin][PF_6]	256.2	663.5	19.5	0.671
1-n-butyl-3-methylimidazolium hexafluorophosphate	[bmim][PF_6]	284.2	708.9	17.3	0.755
1-n-butyl-3-methylimidazolium nitrate	[bmim][NO_3]	201.1	946.3	27.3	0.604
1-n-hexyl-3-methylimidazolium tetrafluoroborate	[C_6mim][BF_4]	254.1	679.1	17.9	0.926
1-n-hexyl-3-methylimidazolium hexafluorophosphate	[C_6mim][PF_6]	312.2	754.3	15.5	0.835

Table 2: Physical characteristics of the binary systems studied in this work.

System	Solvent	Ionic liquid	NP[1]	Range of data			References
				T (K)	P (bar)	x_{CO2}	
1	CO_2	[emim][Tf_2N]	14	323.15-343.15	20-150	0.25-0.75	Ren *et al.* (2010)
2	CO_2	[C_6mim][Tf_2N]	18	323.15-343.15	20-250	0.23-0.78	Ren *et al.* (2010)
3	CO_2	[dmim][Tf_2N]	14	323.15-343.15	15-150	0.26-0.82	Ren *et al.* (2010)
4	CO_2	[C_6mim][Br]	11	313.15-333.15	30-150	0.09-0.49	Nwosu *et al.* (2009)
5	CO_2	1-methylimidazole	16	313.15-333.15	12-125	0.07-0.95	Nwosu *et al.* (2009)
6	CO_2	[emim][Tf_2N]	64	298.15-363.15	7-310	0.22-0.70	Carvalho *et al.* (2009b)
7	CO_2	[bmim][Tf_2N]	32	303.15-363.15	7-460	0.23-0.77	Carvalho *et al.* (2009b)
8	CO_2	[pmim][Tf_2N]	63	298.15-353.15	7-570	0.21-0.80	Carvalho *et al.* (2009a)
9	CO_2	[omim][BF_4]	24	313.15-333.15	1-94	0.00-0.71	Blanchard and Brennecke (2001)
10	CO_2	[bmim][BF_4]	20	313.15-353.15	9-620	0.10-0.60	Kroon *et al.* (2005)
11	CHF_3	[emim][PF_6]	20	333.15-352.15	17- 470	0.10-0.93	Shariati and Peters (2003)
12	CO_2	[bmim][PF_6]	43	313.15 - 333.15	1-30	0.00-0.73	Blanchard and Brennecke (2001), Liu *et al.* (2003)
13	CO_2	[bmim][NO_3]	8	333.15	1-93	0.00-0.52	Blanchard and Brennecke (2001)
14	R-134a	[C_6mim][Tf_2N]	14	323.15	1-12	0.07-0.76	Ren and Scurto (2009a)
15	R-134a	[C_6mim][BF_4]	7	323.15	1-12	0.08-0.71	Ren and Scurto (2009a)
16	R-134a	[C_6mim][PF_6]	10	323.15	1-13	0.07-0.77	Ren and Scurto (2009a)
17	C_2H_6	[C_6mim][Tf_2N]	28	313.15-353.15	4-130	0.05-0.40	Florusse *et al.* (2008)

[1]NP Number of experimental points utilized in this work.

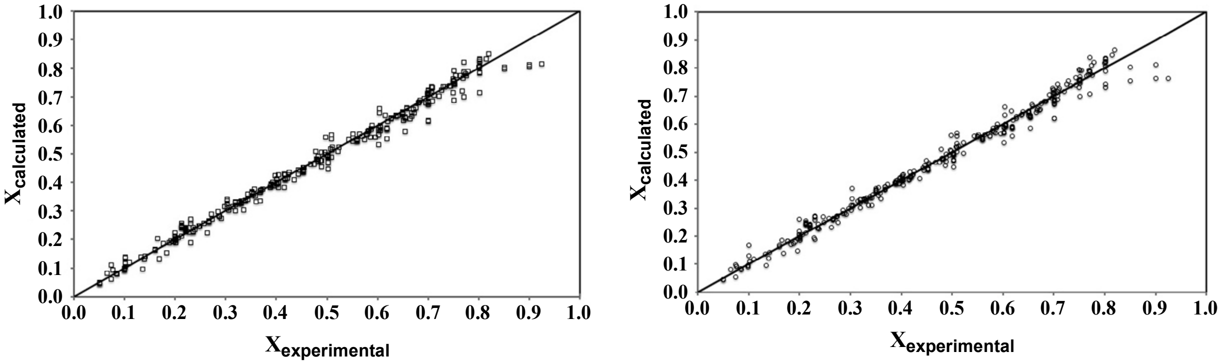
The adjustable parameters, k_{ij} and l_{ij}, the %AARD and the range of experimental data utilized (expressed in pressure and liquid phase molar composition) are shown in Table 3 for all 17 binary systems analyzed here.

Figure 1 shows the comparison between calculated and experimental data for the mole fraction of liquid phase for all 17 systems at all temperatures, for both EoS analyzed. Analyzing Figure 1 and Table 3, it can be verified that a good correlation between experimental and calculated data was obtained for most of the systems analyzed, with low computing time for all cases. Larger deviations were observed for the SRK equation, as shown in Table 3.

We can see that the solubility of CO_2, CHF_3 and C_2H_6 increases when the pressure increases and the solubility decreases with the increase of the temperature of the system. This behavior was observed for the two thermodynamics models studied here and also in the experimental data for all systems studied. This behavior is common in VLE. Another important point is that all systems studied here are at elevated pressures, up to 100 bars. In this condition, we can note the upward curvature in the isotherms, i.e., the elevation of the pressure entails very little increase in the gas solubility.

Table 3: Binary interaction parameters and deviation at different temperatures.

System	PR				SRK			
	T (K)	k_{ij}	l_{ij}	%AARD	T (K)	k_{ij}	l_{ij}	%AARD
1	323.15	0.045	0.048	0.91	323.15	0.026	0.029	1.33
	343.45	0.017	0.025	1.27	343.15	0.024	0.037	1.31
2	323.15	0.010	0.000	0.32	323.15	0.015	0.015	1.61
	343.15	0.026	0.002	2.13	343.15	0.021	-0.001	2.46
3	323.15	0.007	0.016	1.21	323.15	0.001	0.017	1.50
	343.15	-0.008	0.025	0.47	343.15	-0.007	0.026	0.51
4	313.15	0.040	-0.068	4.77	313.15	0.042	-0.066	4.71
	333.15	0.040	-0.068	1.29	333.15	0.043	-0.066	1.25
5	313.15	0.036	-0.014	1.29	313.15	0.021	-0.015	2.68
	333.15	0.037	-0.005	2.80	333.15	0.024	-0.015	3.65
6	298.15	0.051	0.049	0.68	298.15	0.047	0.047	0.68
	303.15	0.053	0.048	0.82	303.15	0.050	0.048	0.84
	313.15	0.059	0.049	1.10	313.15	0.057	0.048	1.22
	323.15	0.061	0.048	1.27	323.15	0.059	0.048	1.30
	333.15	0.063	0.047	1.35	333.15	0.062	0.047	1.38
	343.15	0.063	0.047	1.40	343.15	0.063	0.047	1.44
	353.15	0.065	0.046	1.50	353.15	0.064	0.047	1.50
	363.15	0.066	0.047	1.52	363.15	0.066	0.047	1.50
7	303.15	0.166	0.139	4.07	303.15	0.172	0.136	3.82
	323.15	0.134	0.117	2.63	323.15	0.137	0.117	2.65
	343.15	0.144	0.118	2.74	343.15	0.148	0.118	2.72
	363.15	0.155	0.120	2.68	363.15	0.160	0.120	2.62
8	298.15	0.098	0.064	4.69	298.15	0.094	0.061	4.42
	303.15	0.051	0.043	2.34	303.15	0.051	0.043	2.40
	313.15	0.051	0.043	2.16	313.15	0.050	0.043	2.23
	323.15	0.050	0.042	2.15	323.15	0.047	0.041	2.10
	333.15	0.049	0.041	2.14	333.15	0.047	0.041	2.15
	343.15	0.049	0.042	2.17	343.15	0.048	0.042	2.17
	353.15	0.049	0.043	2.22	353.15	0.048	0.043	2.20
9	313.15	0.087	0.002	1.35	313.15	0.091	0.002	1.35
	323.15	0.092	0.021	1.78	323.15	0.094	0.013	1.12
	333.15	0.086	0.014	1.47	333.15	0.085	0.013	1.57
10	313.15	0.203	0.059	2.09	313.15	0.199	0.050	1.11
	333.15	0.211	0.047	0.84	333.15	0.229	0.053	1.24
	353.15	0.234	0.044	0.85	353.15	0.253	0.052	1.46
11	333	0.079	-0.016	6.58	333	0.098	0.003	10.44
	352	0.090	-0.018	6.85	352	0.090	-0.002	6.01
12	313.15	0.098	0.010	2.46	313.15	0.101	0.008	3.01
	323.15	0.118	0.037	0.75	323.15	0.121	0.036	0.97
	333.15	0.119	0.059	0.84	333.15	0.110	0.032	2.28
13	313.15	0.096	0.016	2.71	313.15	0.087	0.010	3.46
	323.15	0.061	-0.002	3.67	323.15	0.060	0.001	3.26
	333.15	0.064	0.011	1.84	333.15	0.085	0.025	1.73
14	323.15	0.003	0.007	1.89	323.15	-0.007	0.006	1.57
15	323.15	0.090	0.019	2.85	323.15	0.081	0.015	2.60
16	323.15	0.095	0.026	5.45	323.15	0.081	0.011	2.81
17	313.15	0.083	-0.002	1.22	313.15	0.077	0.001	1.42
	323.15	0.082	-0.001	1.52	323.15	0.079	-0.001	1.27
	333.15	0.082	-0.001	1.26	333.15	0.077	0.001	1.64
	353.15	0.101	0.007	0.45	353.15	0.079	-0.001	1.97
Mean deviation	-	-	-	**2.10**	-	-	-	**2.25**



(a) (b)

Figure 1: Comparison of calculated and experimental data for the mole fraction of liquid phase using PR-vdW-2 (a) and SRK-vdW-2 (b).

This behavior was observed in others works in the literature (Shariati and Peters, 2003, 2004; Arce *et al*., 2010). The solubility of CO_2 in ionic liquids follows a linear relationship with the length of alkyl chain. This relationship directly influences the prediction of data across equations of state, since the greater the solubility, the lower the error displayed, as seen for the systems studied (Shariati *et al*., 2005).

Overall, both EoS tested provided a good correlation for the bubble point data in the pressure range of the experimental data utilized, but the correlation was poor in the high pressure region for most systems. This behavior can be seen in Figure 1 in the high gas concentration ($x_{experimental}$) region of the graph. The high concentration of the gas coincides with the high pressure conditions for all systems.

Larger deviations in the regions of high pressure were described in other works in the literature (Carvalho *et al*., 2009a; Nwosu *et al*., 2009; Ren *et al*., 2010) and, because of this behavior, the extrapolation of the model much beyond the data pressure region in which the interaction parameters were fit is not recommended.

For some systems, the combination of the vdW-2 mixing rule with the PR and SRK Eos did not provide a good correlation between experimental and calculated data, mainly to represent the liquid phase. This behavior was expected due to the high complexity of the systems reviewed here. A possible solution to this problem would be to use more elaborate mixing rules, such as the Wong-Sandler (WS) type mixing rules (Wong and Sandler, 1992).

Some papers present the modeling of systems composed of ionic liquid and gas, principally CO_2, using the combination of PR and WS mixing rules with good representation of the thermodynamic behavior, such as Alvarez *et al*. (2008) (PR+WS combined with NRTL model); Valderrama *et al*. (2008b) (PR+WS combined with the Van Laar model); Arce *et al*. (2010) (PRSV-Peng Robinson+ Stryjek-Vera EoS combined with the WS mixing rule and the Van Laar model) and Chilla *et al*. (2011) (PR+WS combined with the Van Laar model).

In Table 4, the deviations presented in different papers and the deviations observed in this paper for the liquid phase (%AARDL, given by Equation (14)) are compared. The deviations were presented only for the liquid phase because in these papers the calculations were performed only for the mole fraction of the liquid phase.

Table 4: Average absolute deviation in the liquid molar fraction and for the pressure in the present work and in some works in the literature.

Reference	Thermodynamic model	Parameters	Observed deviation (%)	Mixtures studied
Alvarez *et al*. (2008)	PR/WS/NRTL	3	3.3[1]	1
Valderrama *et al*. (2008)	PR/WS/VL	3	3.0[1]	8
Valderrama *et al*. (2012)	PR/WS/VL	3	5.3[1]	6
	PR/WS/NRTL	3	7.3[1]	6
Arce *et al*. (2010)	PRSV/WS/VL	6	3.6[1]	17
	PRSV-vdW1	2	2.6[1]	17
Chilla *et al*. (2011)	PR/WS/VL	3	1.5[2]	5
Ren and Scurto (2009)	PR-vdW-2	2	4.0[2]	4
Ren *et al*. (2010)	PR-vdW-2	2	2.9[2]	3
Jang *et al*. (2010)	PR-vdW-2	2	6.4[2]	1
This work	PR-vdW-2	2	4.0[2]	17
	SRK-vdW-2	2	4.4[2]	17

[1]pressure deviations (ΔP%); [2]liquid mole fraction deviations (Δx%).

$$\%\mathrm{AARDL} = \frac{100}{\mathrm{NP}}\left(\sum_{i=1}^{N}\left|\frac{x_i^{\mathrm{exp}} - x_i^{\mathrm{pred}}}{x_i^{\mathrm{exp}}}\right|\right) \tag{14}$$

Most of the papers that used the combination of PR EoS combined with the WS mixing rule showed minor deviations when compared with those that used the PR EoS combined with the vdW-2 mixing rule (see Table 4). In papers that used the same combination used in this paper (PR-vdW2), similar deviations were observed. Works that used the SRK Eos for this type of system were not found in the literature and the comparison was not possible.

Effect of Gas on [C_6mim][Tf_2N] Phase Behavior at 323.15 K

The solubility of three different gases (R-134a, CO_2 and C_2H_6) was analyzed in [C_6mim][Tf_2N] ionic liquid. The solubility of R-134a is greater than that of the other gases at 323.15 K (lower pressure results in higher solubility when compared with the other gases). The results can be seen in Figure 2. This behavior can be explained by the similarity between the molecules of [C_6mim][Tf_2N] and R-134a in terms of polarity.

Effect of Anion Modification on CO_2 and R-134a Solubility

The anion effect on CO_2 and R-134a solubility can be seen in Figures 3 (a) and (b), respectively. For CO_2 solubility, the anion effect is analyzed at 333.15 K for the cation 1-butyl-3-methylimidazolium ([bmim]) with the following anions: hexafluorophosphate ([PF_6]), tetrafluoroborate ([BF_4]) and nitrate ([NO_3]).

As can be seen in Figure 3 (a), CO_2 is more soluble in [PF_6] than in [BF_4] and [NO_3], but the solubility in [NO_3] is approximately equal to the solubility in [BF_4] at pressures up to 80 bar.

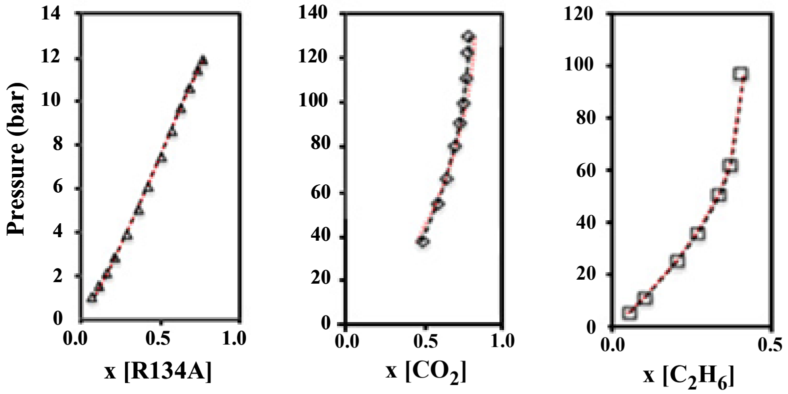
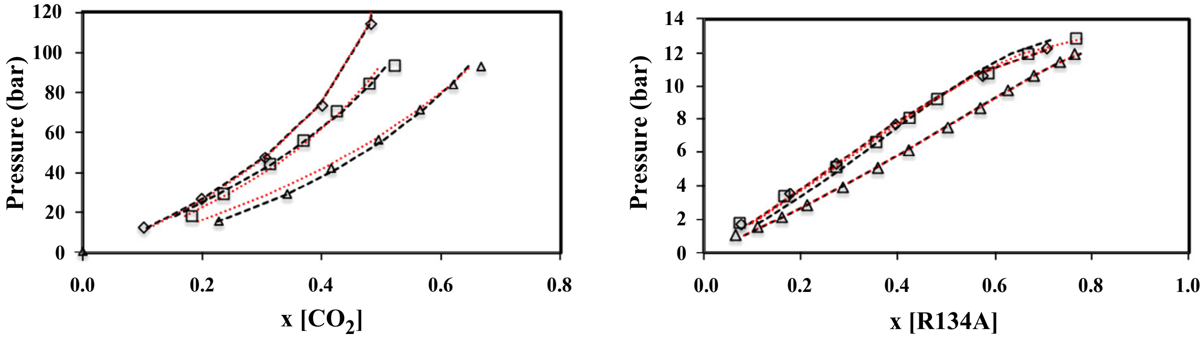


Figure 2: VLE correlation results for systems [C_6mim][Tf_2N] + R-134a, CO_2 and C_2H_6 at 323.15 K. Symbols: (Δ) R-134a, (◊) CO_2, (□) C_2H_6. Experimental data were taken from Ren *et al.* (2010); Ren and Scurto (2009a); and Florusse *et al.* (2008),(---) PR-EoS + vdW2, (···) SRK-EoS + vdW-2.



(a) (b)

Figure 3: (a) VLE correlation results for the systems CO_2 + [bmim][PF_6], [bmim][BF_4] and [bmim][NO_3]. Symbols: (Δ) [bmim][PF_6], (◊) [bmim][BF_4], (□) [bmim][NO_3] at 333.15 K, (--) PR-EoS + vdW2, (···) SRK-EoS + vdW-2.(b)VLE correlation results for the systems R-134a + [C_6mim][Tf_2N], [C_6mim][BF_4], and [C_6mim][PF_6]. Symbols: (Δ) [C_6mim][Tf_2N], (◊) [C_6mim][BF_4], (□) [C_6mim][PF_6] at 323.15 K. (---) PR-EoS + vdW2,(···) SRK-EoS + vdW-2.

For R-134a solubility, the anion effect is analyzed at 323.15 K for the cation 1-hexyl-3-methyl-imidazolium with the following anions: bis(trifluoromethylsulfonyl) imide ([Tf_2N]), [BF_4] and [PF_6].

As can be seen in Figure 3 (b), R-134a is more soluble in [Tf_2N] than in [BF_4] and [PF_6]. The anions [BF_4] and [PF_6] have a very similar solubility for this gas for the whole range of pressure studied here.

The solubility parameter depends on the energy of vaporization and molar volume. Generally, the energy of vaporization is high for all IL, so because the [Tf_2N] anion is larger than other anions, such as ([PF_6] or [BF_4]) its molar volume is significantly larger and therefore [Tf_2N] dissolves CO_2 to a greater degree.

Effect of Cation Modification on CO_2 Solubility

Figure 4 shows the effect of the cation modification on the CO_2 solubility for the following1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids: [dmim][Tf_2N], [C_6mim][Tf_2N], [C_2mim] [Tf_2N], [pmim][Tf_2N] and [bmim][Tf_2N].

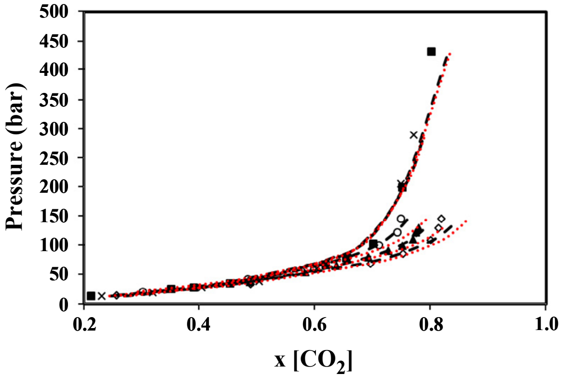


Figure 4: VLE correlation results for the systems CO_2 + [dmim][Tf_2N], CO_2 + [C_6mim][Tf_2N], CO_2 + [C_2mim][Tf_2N], CO_2 + [pmim][Tf_2N] and CO_2 + [bmim][Tf_2N]. Symbols: (◊) [dmim][Tf_2N], (▲) [C_6mim][Tf_2N], (○) [C_2mim][Tf_2N], (▪) [pmim][Tf_2N] and (**x**) [bmim][Tf_2N] at 323.15 K. (--) PR-EoS + vdW2, (···)SRK-EoS + vdW-2.

Furthermore, the solubility of CO_2 is also strongly dependent on the alkyl chain length of the ionic liquid; similar results were observed in the works of Shariati and Peters (2005) and Shin *et al.* (2008). In general, the solubility in IL increases with the increase of the length of the alkyl chain of the IL.

Additionally, the dramatic difference in size between CO_2 and an IL emphasizes the influence of the entropic effect on the solubility. The large entropic effect led to a negative deviation from the ideal solubility that might explain why CO_2 is more soluble in the larger 1-decyl- than in the smaller 1-ethyl-3-methylimidazolium IL`s (Cadena *et al.*, 2004; Anthony *et al.*, 2005).

CONCLUSION

Pressure–composition diagrams for 17 different binary systems of ionic liquids + CHF_3, C_2H_6, CO_2 and R-134a at high pressure were modeled at different temperatures with the PR and SRK equations of state and the vdW-2 mixing rule. Solubilities of all gases studied in this work decrease with an increase in the temperature of the system, and increase with increasing pressure. Predicted results were highly satisfactory for both EoS analyzed, with AARD% between experimental and calculated data of 2.10% and 2.25% for PR-vdW-2 and SRK-vdW-2, respectively.

NOMENCLATURE

List of Symbols

a	EoS attractive parameter
%AARD	average absolute relative deviation
%AARDL	average absolute relative deviation for the liquid phase
b	EoS co-volume parameter
EoS	equation of state
IL	ionic liquid
k_{ij}	binary interaction parameter for the attractive parameter
l_{ij}	binary interaction parameter for the co-volume parameter
m	parameter defined in the function α
MW	molecular weight
NP	number of experimental data points
NRTL	Non Random Two Liquid model
P_C	critical pressure
PR	Peng-Robinson EoS
PRSV	Peng-Robinson Stryjek-Vera EoS
R	universal gas constant
SRK	Soave-Redlich-Kwong EoS
T_C	critical temperature

T_R	reduced temperature
vdW - 1	classic van der Waals mixing rule with 1 adjustable parameter
vdW – 2	classic van der Waals mixing rule with 2 adjustable parameters
VL	Van Laar model
VLE	vapor liquid equilibria
WS	Wong Sandler
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Superscripts

exp	experimental
pred	predicted

Subscripts

i, j	component
mix	mixture
C	critical

Greek Letters

α	auxiliary parameter
ω	acentric factor

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