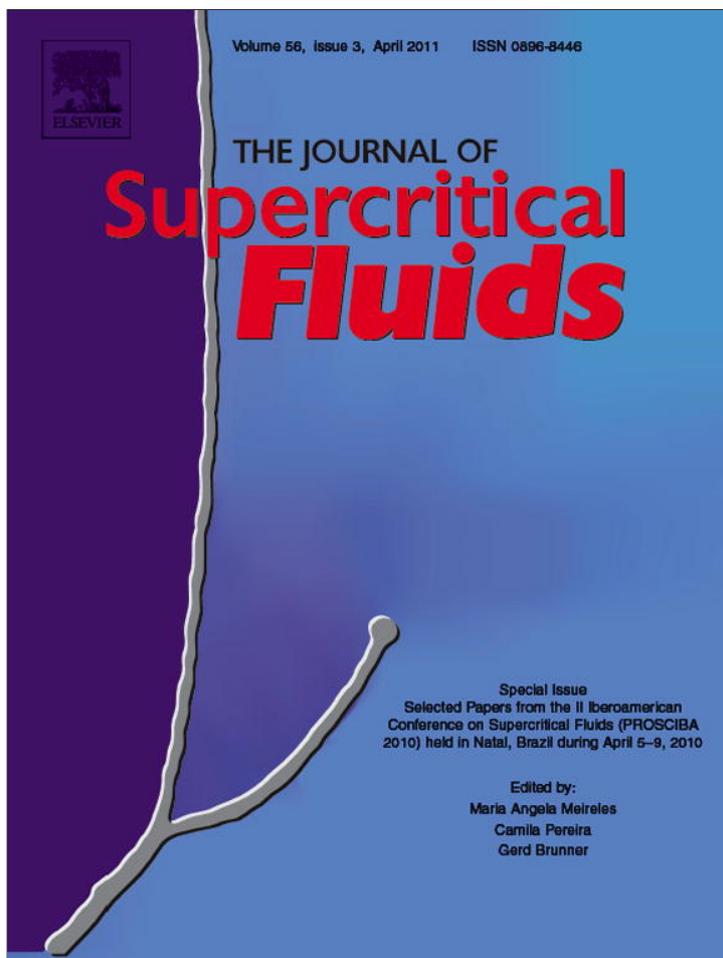


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The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supfluHigh pressure CO₂ solubility in N-methyl-2-hydroxyethylammonium protic ionic liquidsSilvana Mattedi^{a,*}, Pedro J. Carvalho^b, João A.P. Coutinho^b, Víctor H. Alvarez^c, Miguel Iglesias^{a,d}^a Programa de Pós Graduação em Engenharia Química, Escola Politécnica, Universidade Federal da Bahia (UFBA), R. Aristides Novis 2 Federação 40210-630 Salvador-Bahia, Brazil^b Departamento de Química, CICECO, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal^c Faculdade de Engenharia Química, Universidade Estadual de Campinas (UNICAMP), Cidade Universitária "Zeferino Vaz" Av. Albert Einstein, 500, CEP 13083-852, Campinas, SP, Brazil^d Departamento de Ingeniería Química – ETSE, Universidade de Santiago de Compostela (USC), Rúa Lope Gómez de Marzoa s/n, Campus Sur, 15782 Santiago de Compostela, Spain

ARTICLE INFO

Article history:

Received 31 May 2010

Received in revised form

24 September 2010

Accepted 20 October 2010

Keywords:

Brønsted ionic liquids

Protic ionic liquids

Carbon dioxide

Supercritical

N-methyl-2-hydroxyethylammonium acetate

N-methyl-2-hydroxyethylammonium formate

Solubility

ABSTRACT

The use of ionic liquids for CO₂ capture and natural gas sweetening is being object of intense research. Within the enormous group of existing ionic liquids, those based on conjugate bases of carboxylic acids seem to be particularly promising. This work addresses the study of the high pressure CO₂ solubility (up to 80 MPa) in two protic ionic liquids, N-methyl-2-hydroxyethylammonium formate and N-methyl-2-hydroxyethylammonium acetate, in a wide range of temperatures (293–353 K). A thermodynamic model based on the Peng–Robinson equation of state with the Wong–Sandler mixing rule, using the NRTL model for the activity coefficients, was here adopted to describe and evaluate the thermodynamic consistency of the experimental data. Furthermore, the study of a ternary mixture of CO₂ + CH₄ + N-methyl-2-hydroxyethylammonium acetate was investigated showing a high selectivity from the IL towards these solutes.

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1. Introduction

Ionic liquids (ILs) are a new class of solvents composed only of ions but whose size and shape differences allow them to remain liquid at temperatures below 100 °C. Among other interesting properties they present negligible vapor pressures, high thermal stabilities, large liquid phase range, no flammability and high solvation capacity. The possibilities of fine tune the ILs properties, through an endless combination of cations and anions, allow the design of solvents for task specific applications leading to more efficient and sustainable processes and products.

Until now, studies concerning ionic liquids have been based on the imidazolium cation and, to a lesser extent, on the alkyl pyridiniums and trialkylamines [1]. Protic ionic liquids (PILs) have, however, received limited attention from the academia. The first PIL reported, ethanolanionium nitrate, was reported by Gabriel and Weiner in 1888 [2], followed by ethylammonium nitrate (EAN), in 1914, synthesized by Walden [3]. These PILs were produced by

a stoichiometric acid–base Brønsted reaction and their main difference, compared to aprotic ILs (AILs), is the presence of at least a proton, which is/are able to promote extensive hydrogen bonding [4]. These liquids present some characteristics, such as a slightly lower conductivity and stability, which may reduce, at first, their interest for a number of applications. However, their low cost, simple synthesis and purification methods, low toxicity and high biodegradation character, among other set of appealing characteristics, overcomes those limitations for many different purposes.

Recently, some work has been reported on the synthesis, physicochemical and structural characterization of PILs. Bicak [5] synthesized the 2-hydroxyethylammonium formate (2-HEAF), an ionic liquid formed by the neutralization of monoethanolamine with formic acid. Greaves et al. [6] proposed different protic ionic liquids from primary amines and organic and inorganic acids. Cota et al. [7], Kurnia et al. [8] and Alvarez et al. [9] synthesized a family of these ILs by modifying the aliphatic chain of the organic acid and/or using secondary and tertiary hydroxyamines. There were also studies that use PILs in catalytic reactions [7] and on the interaction with hydroxylic solvents (like water and alcohols), showing that 2-HEAF is soluble in water, ethanol and methanol in all the concentration range [10]. Moreover, a relevant aspect, considering the interest in

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these substances as more environmentally sustainable solvents, is their potential toxicity. This issue has not been sufficiently studied until now, especially taking into account the need of this information to fulfill the REACH (Registration, Evaluation, Authorization and Restriction of Chemical Substances) requirements (UE) and so, allowing the assessment of hygiene and safety issues derived from their manufacture, use, and transport in the industrial sectors in which these substances will be applied. In what is referred to PIL's, the first results highlight that total biodegradation and low toxicity are intrinsic characteristics of these kind of ionic liquids [11,12].

The presence of an anion with a strong basic character suggests that PILs could be an interesting alternative to be applied to processes with supercritical gases for capture of acid gases, such as CO₂, H₂S and SO₂ [13–15]. In order to study the viability of such alternative, vapor–liquid equilibria data at high and moderate pressures are necessary. Thus, in the wake of previous studies [16–19], this work investigates gas–liquid equilibrium of binary CO₂ + N-methyl-2-hydroxy ethylammonium-based ILs systems, in temperatures up to 363.15 K and pressures up to 80 MPa. Furthermore, the study of a ternary mixture of CO₂ + CH₄ + N-methyl-2-hydroxyethylammonium acetate was also investigated, showing a high selectivity from the IL towards these solutes.

The Peng–Robinson equation of state with the Wong–Sandler/NRTL mixing rule, using the NRTL model for the activity coefficients, was used to model the experimental data measured in this work.

2. Experimental

2.1. Materials

Two protic ionic liquids, N-methyl-2-hydroxy ethylammonium acetate, m-2-HEAA, and N-methyl-2-hydroxy ethylammonium formate, m-2-HEAF, were used in this study. Both ionic liquids were synthesized, at our laboratories, by reacting equimolar amounts of amine and organic acid. The amine was placed in a three necked glass flask, mounted in a thermal bath at 283.15 K, equipped with a reflux condenser, a PT-100 temperature probe for controlling temperature and a dropping funnel. Strong agitation (ca. 450 rpm) was applied in order to improve the contact between the reactants allowing the reaction to be completed. The organic acid was added drop wise to the flask under stirring with a magnetic bar. Stirring was continued for 24 h at laboratory temperature, in order to obtain a final viscous liquid. Then, agitation, slight heating (temperature up to 293.15 K for m-2-HEAF and up to 323.15 K for m-2-HEAA) and moderate vacuum (20 kPa) for the vaporization of residual non reactants were applied for at least 48 h. During the purification step and storage the m-2-HEAF was light protected in order to prevent any degradation. More details about the synthesis can be found in Alvarez et al. [9]. The ionic liquids were dried under high vacuum (10⁻⁴ Pa), for a period never smaller than 48 h, and the structure and purity checked by ¹H NMR and ¹³C NMR both before and after the measurements. These spectra have shown purity better than 95% (w/w). The adopted purification procedure assures that water and volatile compounds are removed and consequently the influence of these impurities on the thermophysical properties of ILs minimized [20–22].

The final water content was determined with a Metrohm 831 Karl Fischer coulometer, indicating a water mass fraction of (184 and 60) × 10⁻⁶ for m-2-HEAA and m-2-HEAF, respectively.

The carbon dioxide (CO₂) and methane (CH₄) were acquired from Air Liquide. The CO₂ presents a purity of ≥99.998% and H₂O, O₂, C_nH_m, N₂ and H₂ impurities volume fractions lower than (3, 2, 2, 8 and 0.5) × 10⁻⁶, respectively, while the methane presents a purity of ≥99.9% and H₂O, O₂, CO₂, C_nH_m, N₂, H₂ and C₂H₆ impurities vol-

ume fractions lower than (20, 50, 10, 80, 500, 40 and 400) × 10⁻⁶, respectively.

2.2. Experimental equipment

The high pressure equilibrium cell used in this work is based on a cell designed by Daridon et al. [23–27] using the synthetic method. Both the apparatus and the methodology here followed were fully described in previous works [16–19], and shown to be adequate to accurately measure vapor–liquid phase equilibrium in a wide range of pressures and temperatures. The temperature is measured with a high precision thermometer, model PN 5207 with an accuracy of 0.01 K, connected to a calibrated platinum resistance inserted inside the cell close to the sample. The pressure is measured by a piezoresistive silicon pressure transducer (Kulite) fixed directly inside the cell to reduce dead volumes, that was previously calibrated and certified by an independent laboratory with IPAC accreditation, following the EN 837-1 standard and with accuracy better than 0.2%. The accuracy for the measured mole fraction of gas dissolved in the liquid phase was better than 0.003.

The purity of the IL is checked again by NMR at the end of the study to confirm that no degradation takes place during the measurements.

2.3. Thermodynamic modeling

The well known Peng–Robinson equation of state [28],

$$p = \frac{RT}{V - b_m} - \frac{a_m}{V(V + b_m) + b(V - b_m)} \quad (1)$$

where the constants a_m and b_m are expressed as functions of concentration of the different components in the mixture through the Wong and Sandler mixing rule [29] using the NRTL model [30] for the activity coefficient was applied to the modeling of the experimental data and the thermodynamic consistency was studied with the method of Alvarez and Aznar [31,32].

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - (a/RT))_{ij}}{1 - \sum_i (x_i a_{ii} / b_{ii} RT) - (A_\infty^E / \Omega RT)} \quad (2)$$

$$a_m = b_m \left[\sum_i \frac{x_i a_{ii}}{b_{ii}} + \frac{A_\infty^E}{\Omega} \right] \quad (3)$$

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{b_{ii} + b_{jj}}{2} - \frac{(1 - k_{ij}) \sqrt{a_{ii} a_{jj}}}{RT} \quad (4)$$

in these equations, a_m and b_m are the EoS constants, $\Omega = 0.34657$, and A_∞^E , the excess Helmholtz free energy at the limit of infinite pressure, that is calculated assuming that $A_\infty^E \approx A_0^E \approx G_0^E$ where G_0^E is the excess Gibbs free energy at the limit of zero pressure here calculated using the NRTL model [30]. The equations for the NRTL model to calculate the activity coefficient in multicomponent systems are:

$$\frac{G^E}{RT} = \sum_i x_i \ln \frac{\sum_j G_{ji} \tau_{ji} x_j}{\sum_k G_{ki} x_k} \quad (5)$$

$$\tau_{ij} = \frac{A_{ij}}{RT}, \quad G_{ij} = \exp(-\alpha_{ij} \tau_{ij}), \quad \alpha_{ij} = \alpha_{ji} \quad (6)$$

where A_{ij} and A_{ji} represent the interaction energy between molecules i and j , R is the universal constant of gases, T is the temperature, and α_{ij} is the non-randomness parameter.

Furthermore, the proposed model was applied, in the diluted region limit, to determine the Henry's constant, Table 4, for the studied systems. The Henry's law relates the amount of a given gas dissolved in a given type and volume of liquid, at a constant

Table 1
Bubble point data of the system CO₂ (1) + m-2-HEAF (2).

x ₁	T/K	p/MPa												
0.057	293.22	0.494	0.119	293.21	1.194	0.172	293.30	1.835	0.231	293.26	2.482	0.281	293.37	3.108
0.057	303.07	0.666	0.119	303.12	1.563	0.172	303.22	2.317	0.231	303.15	3.155	0.281	303.27	3.959
0.057	313.25	0.889	0.119	313.16	1.912	0.172	313.16	2.843	0.231	313.26	3.895	0.281	313.33	4.940
0.057	323.28	1.105	0.119	323.28	2.284	0.172	323.18	3.435	0.231	323.22	4.746	0.281	323.13	5.985
0.057	333.31	1.354	0.119	333.30	2.710	0.172	333.25	4.078	0.231	333.21	5.622	0.281	333.15	7.176
0.057	343.42	1.662	0.119	343.18	3.133	0.172	343.27	4.742	0.231	343.29	6.576	0.281	343.19	8.456
0.057	353.26	1.950	0.119	353.19	3.612	0.172	353.18	5.414	0.231	353.20	7.572	0.281	353.24	9.764
0.057	363.21	2.280	0.119	363.27	4.071	0.172	363.23	6.112	0.231	363.31	8.549	0.281	363.42	11.138
0.336	293.27	3.808	0.381	293.30	4.417	0.429	293.32	5.116	0.483	293.29	12.094	0.534	293.32	26.849
0.336	303.18	4.885	0.381	303.23	5.746	0.429	303.14	6.950	0.483	303.20	17.625	0.534	303.37	32.578
0.336	313.12	6.150	0.381	313.10	7.366	0.429	313.31	11.215	0.483	313.30	22.384	0.534	313.32	37.662
0.336	323.23	7.632	0.381	323.11	9.467	0.429	323.28	15.098	0.483	323.29	26.654	0.534	323.17	42.016
0.336	333.17	9.293	0.381	333.25	12.078	0.429	333.33	18.618	0.483	333.25	30.414	0.534	333.27	45.617
0.336	343.23	11.098	0.381	343.23	14.687	0.429	343.21	21.819	0.483	343.23	33.635	0.534	343.28	48.511
0.336	353.28	12.966	0.381	353.50	17.347	0.429	353.23	24.718	0.483	353.21	36.359	0.534	353.22	50.852
0.336	363.17	14.818	0.381	363.31	19.623	0.429	363.15	27.090	0.483	363.25	38.678	0.534	363.28	52.910

Table 2
Bubble point data of the system CO₂ (1) + m-2-HEAA (2).

x ₁	T/K	p/MPa									
0.157	313.27	0.840	0.208	313.12	1.732	0.249	312.93	2.790	0.299	313.28	3.903
0.157	323.40	1.230	0.208	323.33	2.194	0.249	323.22	3.571	0.299	323.37	4.865
0.157	333.60	1.680	0.208	333.36	2.774	0.249	333.16	4.225	0.299	333.59	6.070
0.157	343.42	2.151	0.208	343.37	3.438	0.249	343.06	5.027	0.299	343.37	7.421
0.157	353.25	2.682	0.208	353.28	4.187	0.249	353.31	6.235	0.299	353.44	8.923
0.157	363.20	3.357	0.208	362.62	4.910	0.249	363.48	7.794	0.299	363.27	10.516
0.402	313.26	7.498	0.452	313.02	19.475	0.500	313.09	46.587			
0.402	323.21	10.590	0.452	323.16	26.393	0.500	323.23	55.198			
0.402	333.23	14.872	0.452	333.33	33.002	0.500	333.33	62.754			
0.402	343.25	19.405	0.452	343.31	38.887	0.500	343.36	69.597			
0.402	353.19	24.254	0.452	353.48	44.317	0.500	353.38	75.591			
0.402	363.25	28.545	0.452	363.61	49.244	0.500	363.35	80.500			

temperature, to the fugacity of that gas in equilibrium with that liquid and can be described as

$$H_{12}(T, p) = \lim_{x_1 \rightarrow 0} \frac{f_1^L}{x_1} \quad (7)$$

where $H_{12}(T, p)$ is the Henry's constant, x_1 is the mole fraction of gas dissolved in the liquid phase, and f_1^L is the fugacity of the gas in the liquid phase.

The results for the Henry's constant of CO₂ in m-2-HEAF and in m-2-HEAA were correlated as a function of temperature by an empirical equation of the type:

$$\ln(H_{12}) = A \left(\frac{1}{T} \right) + B \quad (8)$$

where, the coefficients A and B obtained are listed in Table 4 together with the Henry's constant average absolute deviations, $|\Delta H_{12}|$, obtained for each ionic liquid.

The correlation of the experimental data was carried by the minimization of the objective function, OF , for

$$OF = \sum_{i=1}^N \left[\frac{p^{cal} - p^{exp}}{\sigma_p} \right]_i^2 \quad (9)$$

where N is the number of data points, p is the pressure, the superscripts “exp” and “cal” refers to the experimental and calculated values respectively, and σ_p is the standard deviation of pressure. The experimental uncertainties in the pressure data were used for σ_p . The minimization method was performed using a genetic algorithm code, implemented and fully explained in Alvarez et al. [33]. The difference between experimental and calculated values was calculated as the average percent deviation, expressed in absolute

form, as follows:

$$|\Delta p| = \frac{100}{N} \sum_{i=1}^N \left[\frac{|p_i^{cal} - p_i^{exp}|}{p_i^{exp}} \right] \quad (10)$$

3. Results and discussion

The solubility of carbon dioxide and methane in the studied ILs, was measured for concentrations from (0.2 to 0.9), in the temperature range (293 to 363) K and pressures from (0.1 to 80) MPa. The solubility data is reported in Tables 1 through 3 and plotted in Figs. 1a, b and 2. It follows the typical solubility behavior decreasing with temperature and increasing with pressure as observed previously for other ILs [16–19].

The carbon dioxide solubility in the m-2-HEAF and m-2-HEAA ILs, at 313 K, is compared with the CO₂ solubility in the 2-HEAF and 2-hydroxy ethylammonium acetate (2-HEAA) reported by Yuan et al. [14] as depicted in Fig. 3. The inclusion of a methyl group on the cation leads to an increase of the CO₂ solubility which is in agreement with the conclusions of our previous work showing that the physical sorption of CO₂ increases with the molecular weight of the

Table 3
Bubble point data of the system CO₂ (1) + CH₄ (2) + m-2-HEAA (3).

x ₁	x ₂	T/K	p/MPa
0.236	0.052	313.13	32.85
0.236	0.052	323.30	33.29
0.236	0.052	333.11	34.02
0.236	0.052	343.23	34.96
0.236	0.052	353.25	35.95
0.236	0.052	363.37	36.92

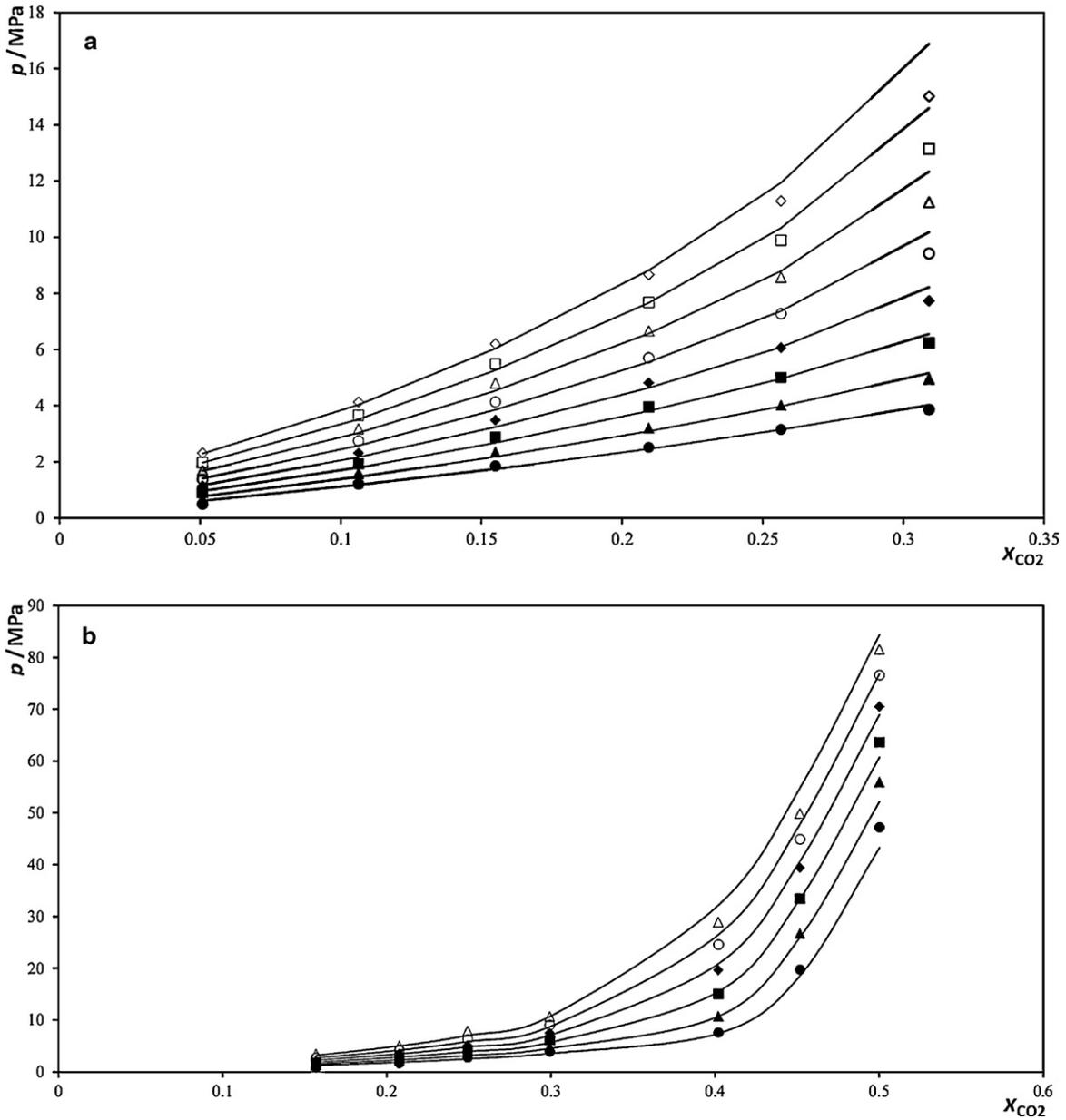


Fig. 1. PTx diagram and modeling for the systems CO₂ + m-2-HEAF, 293.15 (●), 303.15 (▲), 313.15 (■), 323.15 (◆), 333.15 (○), 343.15 (△), 353.15 (□), 363.15 (◇) (a) and CO₂ + m-2-HEAA, 313.15 (●), 323.15 (▲), 333.15 (■), 343.15 (◆), 353.15 (○), 363.15 (△), (b). The solid line represents the calculations from PR-VS/NRTL EoS.

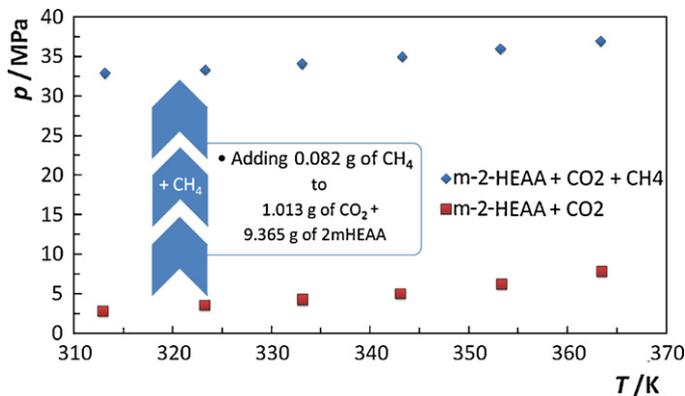


Fig. 2. Pressure–temperature diagram of the systems CO₂ ($x_{CO_2} = 0.25$) + m-2-HEAA ($x_{IL} = 0.75$) and CO₂ ($x_{CO_2} = 0.24$) + CH₄ ($x_{CH_4} = 0.05$) + m-2-HEAA ($x_{IL} = 0.71$).

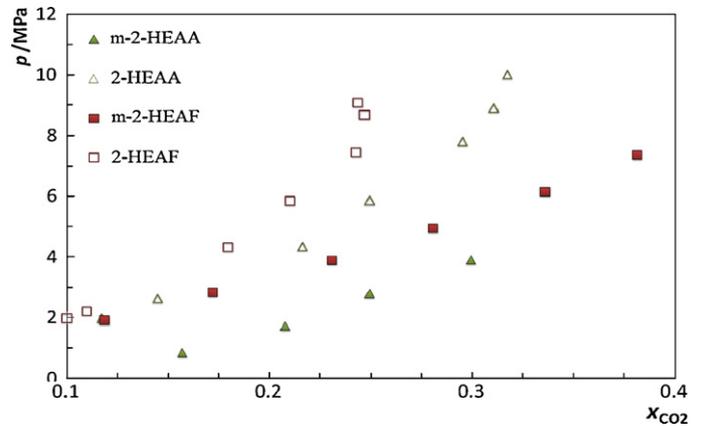


Fig. 3. Comparison between the CO₂ solubility, at 313 K, in m-2-HEAF and m-2-HEAA and that in 2-HEAF and 2-HEAA previously reported by Yuan et al. [12].

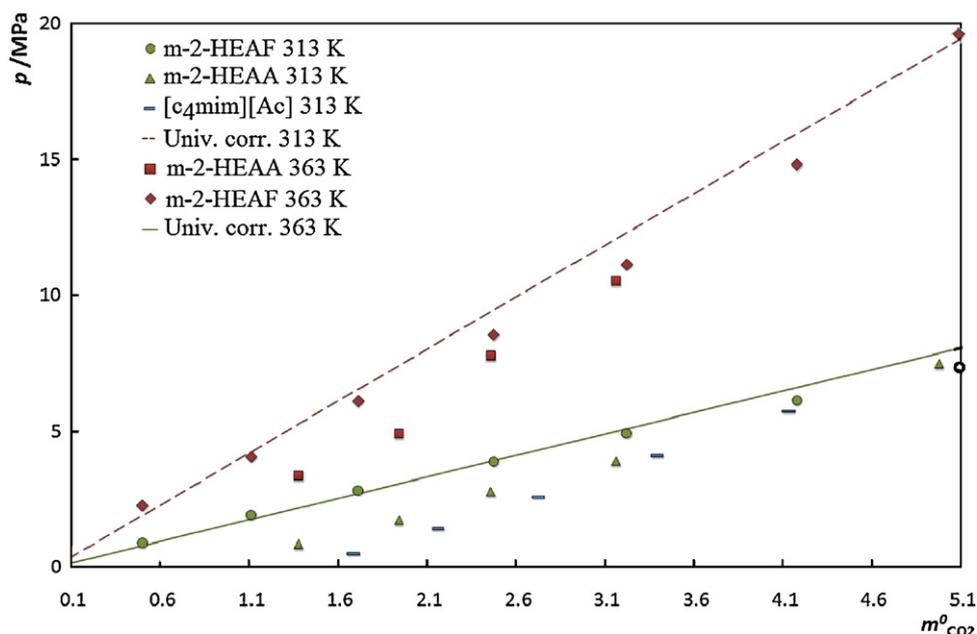


Fig. 4. Pressure–molality diagram of the systems CO₂ + m-2-HEAF and CO₂ + m-2-HEAA. The solid and dashed line represents the universal correlation for 313 K and 363 K, respectively [34].

Table 4

Results of the consistency test using PR + WS/NRTL, with estimated k_{ij} , α , A_{12} and A_{21} parameters, and Henry constant predicted.

NP	T (K)	k_{ij}	α	A_{12} (kJ/kmol)	A_{21} (kJ/kmol)	$ \Delta P $ (%)	Result	H_{12} (MPa)
CO ₂ + m-2-HEAF, $\ln H_{12} = -2163.8783/T + 9.7305$, $ \Delta H_{12} = 2.2$								
6	293.15	-0.9995	0.5500	-41071.4023	18683.8926	5.5	TC	9.91
6	303.15	-0.0852	0.4706	7901.9165	56426.9609	1.9	TC	13.95
6	313.15	-0.2812	0.3850	9843.7500	-65.5746	0.3	TC	17.06
6	323.15	-0.1106	0.4493	7648.2334	33752.0586	0.2	TC	20.96
6	333.15	0.4536	0.3253	1926.8668	46596.8359	0.3	TC	25.55
6	343.15	0.4073	0.5391	2646.3318	24960.9375	0.4	TC	31.17
6	353.15	0.5625	0.3613	1859.4362	39505.7617	0.4	TC	36.42
6	363.15	0.6750	0.4489	1569.2855	30238.8379	0.4	TC	42.42
CO ₂ + m-2-HEAA, $\ln H_{12} = -3304.5677/T + 12.2156$, $ \Delta H_{12} = 2.6$								
7	313.15	-0.9980	0.2527	-71728.2344	-3126.9836	9.6	NFC/TC	5.12
7	323.15	0.1860	0.3805	-49838.1055	-3911.3367	11.1	NFC/TC	7.52
7	333.15	-0.9780	0.2724	-78574.2422	-3889.1602	1.9	NFC/TC	10.15
7	343.15	1.0000	0.3721	-89949.1953	-8085.9268	7.6	NFC/TC	12.85
7	353.15	0.1937	0.2000	31291.0371	-3864.1941	6.6	NFC/TC	18.21
7	363.15	0.2360	0.2000	29020.3438	-4191.6221	5.4	NFC/TC	21.86

TC: thermodynamically consistent; NFC: not fully consistent.

compound when the concentration is expressed in mole fractions [34]. Furthermore, while the addition of a methyl group produces a slight increase of the CO₂ solubility in the formate-based ionic liquid (m-2-HEAF and 2-HEAF have similar solubility values at ca. 2 MPa) for the acetate-based ILs it leads to a higher increase. The m-2-HEAA phase behavior suggests that, for low CO₂ mole fractions exists chemical interaction between the CO₂ and the IL. The formation of electron donor acceptor (EDA) complexes between CO₂ and acetate anions was previously observed by ¹³C HRMAS NMR spectra for the CO₂ + 1-butyl-3-methylimidazolium acetate, [C₄mim][Ac], system [17]. The formation of the EDA complex is here confirmed since, as previously observed [34] for the CO₂ + [C₄mim][Ac] system, the CO₂ + m-2-HEAA system, unlike CO₂ + m-2-HEAF system, does not follow the universal correlation previously proposed [34], as depicted in Fig. 4. Moreover, the chemisorption present at low CO₂ mole fractions, leads in the m-2-HEAA system to solubilities higher than those observed for ammonium-based ILs with similar molecular weight [14] for pressures up to ca. 4 MPa. For higher pressures the solubility becomes slightly lower and the equilibria pressure increases exponentially. This can be explained consider-

ing that m-2-HEAA forms the EDA complexes with carbon dioxide in the low pressure region where the chemical absorption is the predominant phenomena. Upon saturation the physical dissolution becomes predominant with small solubility changes induced by large pressure variations. This trend was also observed with another acetate based IL where chemical followed by physical absorption takes place [17].

The results of the application of the thermodynamic consistency test to the binary systems are presented in Table 4, the properties of the substances used in the modeling in Table 5. They show that the data from CO₂ + m-2-HEAF binary system is thermodynamically consistent (TC), while the CO₂ + m-2-HEAA binary system is not fully consistent (NFC). Nonetheless, the elimination of the data points with individual area deviations greater than 20% leads to consistent data for the remaining points. The CO₂ + m-2-HEAA system presents high deviations for the isopleths at $x_1 = 0.5$, for temperatures lower than 343 K, and $x_1 = 0.157$, for temperatures over 343 K. Therefore, the isotherms with these compositions are not fully consistent. Nonetheless, the model provides a very good description of the experimental data, as depicted in Fig. 1a and b.

Table 5
Properties of the substances used in the modeling.

Compound	T_b /K	T_c /K	P_c /MPa	ω
CO ₂		304.21 ^a	7.38 ^a	0.2236 ^a
m-2-HEAF	514.55 ^b	698.95 ^c	4.14 ^c	0.9359 ^d
m-2-HEAA	538.13 ^b	715.66 ^c	3.33 ^c	0.9836 ^d

^a Ref. [35].

^b Calculated with [37].

^c Calculated with [36].

^d Calculated with [38].

The introduction of methane, CH₄ ($m_{\text{CH}_4} = 0.082$ g), in the binary system m-2-HEAA + CO₂ ($x_{\text{CO}_2} = 0.249$) leads to a strong increase on the equilibrium pressure as shown in Fig. 2. This indicates that methane, unlike the carbon dioxide, is poorly soluble on this PIL and suggests that the 2mHEAA could be used to selectively separate the carbon dioxide from methane.

4. Conclusions

Gas solubilities of carbon dioxide in two protic ionic liquids, namely N-methyl-2-hydroxy ethylammonium acetate and N-methyl-2-hydroxy ethylammonium formate, was presented for temperatures from (293 to 353) K and pressures up to 80 MPa.

Comparison with other similar fluids indicates that while the m-2-HEAF presents no specific interaction towards the CO₂ whereas the m-2-HEAA asymmetric and nonideal phase diagram suggests that this ionic liquid interact chemically with the carbon dioxide at low CO₂ molar concentrations.

The data here reported were well correlated by the PR EoS and found to be thermodynamically consistent for the m-2-HEAF + CO₂ system and not fully consistent for the m-2-HEAA + CO₂ system.

The high solubility pressures exhibited by the ternary mixture CO₂ + CH₄ + m-2-HEAA indicate the m-2-HEAA could be used to selectively separate carbon dioxide from methane mixture.

Acknowledgments

The authors are thankful for financial support from Fundação para a Ciência e a Tecnologia (Project PTDC/EQU-FTT/102166/2008) and Ph.D. grant (SFRH/BD/41562/2007) of Pedro J. Carvalho. The authors would like to acknowledge FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo), for a D.Sc. grant (process #2006/03711-1) of Victor H. Alvarez. Silvana Mattedi would like to thank the support of Universidad de Santiago de Compostela, during her stay in Santiago de Compostela, Spain. Additionally financial support from CNPq [Process PDE 201764/2008-3] is gratefully acknowledged. Miguel Iglesias would like to acknowledge to the Fundación Ibercaja (Programa de Excelencia en Investigación 2009) for its support in developing this research.

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