J. Chem. Eng. Data **2009,** *54,* 2005–2022

Evaluation of Gas Solubility Prediction in Ionic Liquids using COSMOthermX

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As the range of available ionic liquids increases, methods by which important engineering parameters such as gas solubilities can be estimated from simple structural information become ever more desirable. COSMO-based thermodynamic models, such as that used by COSMOthermX, allow the determination of such data for pure and mixed component systems. Herein, we evaluate the predictive capability of COSMOthermX through a comparison with literature data obtained from the IUPAC database which contains data for 15 gases in 27 ionic liquids. To determine any effect inherent to ionic liquids, gas solubility predictions were first performed for selected molecular solvents at constant temperature and pressure. Further estimations of gas solubility at temperatures ranging from (278 to 368) K at 0.1 MPa in water were performed for 14 gases. The study has demonstrated that COSMOthermX is capable of predicting, qualitatively, gas solubilities in ionic liquids and, hence, reducing the amount of unnecessary experimental measurements prior to specific applications using ionic liquids.

Introduction

Ionic liquids (ILs) are molten salts which have melting points commonly below 100 °C and have been considered as potential "green" solvents by researchers due to their negligible vapor pressures.[1] One of the most appealing features of ILs is their potential to be custom designed with preselected characteristics by varying the constituents of the cation and anion. This unique property has allowed ILs to be studied as reaction media,[2−9] catalysts,[10−16] and novel solvents[17−22] in several potential applications such as gas separations,[23,24] liquid separations,[25,26] media for cleaning operations,[27] electrolytes/fuel cells,[28−30] and heat-transfer fluids.[31−33]

To design IL processes which involve volatile components, such as gas−liquid reactions or gas separation processes, methods by physical properties of pure or mixed solvents containing at least one IL component that may be estimated are highly desirable, particularly given the large number of possible IL modifications[34,35] available and large range of combinations when binary or ternary mixtures are included. Recently, several methods have been reported which have developed correlations to predict key IL properties. These can generally be categorized into three main methods: Equation of States (EOS);[36−44] Molecular Simulation;[45−53] Group Contribution Models (GCM);[54−56] or Correlation Models.[57,58] Examples of the EOS method include those proposed by Camper et al.,[36] using Regular Solution Theory (RTS) for low pressure conditions, and that of Ally et al.,[41] which used an Irregular Ionic Lattice model to predict CO_2 solubility at temperatures ranging from (298.15 to 333.15) K. However, this EOS model was unable to accurately predict the solubility for systems at high concentrations of CO_2. Molecular simulations, which require the determination of the pair potential parameters between each molecule, have been shown to produce reasonable agreement with experimental values.[53] Furthermore, group contribution models, reported by Kim et al.[54] for the calculation of CO_2 solubility in 1-alkyl-3-methylimidazolium-based ILs as a function of the temperature and the pressure, predicted solubilities with an average absolute deviation of approximately (0.23 to 5.11) %. However, in this study no anion dependence was determined which limits the general applicability of the model. In addition to the above-mentioned estimation methods, Qin and Prausnitz[59] used perturbed-hard-sphere theory adapted from molecular physics where the solution is considered as "electrolyte-like" to predict the solubility of a number of gases in several ILs. Therein, estimated solubility values within ± 70 % of experimental values were found. Freire et al.[60] also reported the prediction of liquid−liquid equilibrium and vapor−liquid equilibrium of alcohols and ILs. Therein, activity models such as Wilson,[61] UNIQUAC (UNIversal QUAsi-Chemical),[62−65] original and modified UNIFAC (UNIversal quasi-chemical Functional group Activity Coefficients),[66−68] and NRTL (Non-Random, Two-Liquids)[69] which have been applied previously were compared together with a discussion of their limitations.[60] The limitations were mainly associated with the limited IL group parameters available for the group contribution method which reduced the capability of the other approach.

Herein, we discuss the extent to which COSMOthermX (version 2.1, release 01.06),[70] which is an advanced software tool based on Electron Density Functional Theory (DFT), has been evaluated for the prediction of gas solubilities in ILs. The underlying theory of COSMOthermX software is a COSMO-RS (Conductor-like Screening Model for Real Solvents) method which describes the interactions in a fluid as local contact interactions of molecular surfaces with the interaction energies being quantified using values of the two screening charge densities σ and σ' which form a molecular contact.[71,72] To date, a number of studies have examined the use of the COSMO-RS methodology as a descriptor of the Henry Law coefficients for

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10.1021/je800857x CCC: $40.75

Table 1. Ionic Liquid Abbreviations List

cations	abbreviations
1-ethyl-3-methylimidazolium	$[C_2mim]^+$
1-butyl-3-methylimidazolium	$[C_4mim]^+$
1-hexyl-3-methylimidazolium	$[C_6mim]^+$
1-alkyl-3-methylimidazolium	$[C_nmim]^+$
1-alkyl-2,3-methylimidazolium	$[C_nmmim]^+$
1-butyl-3-methylpyrrolidinium	$[C_4mPyrro]^+$
trimethyl-butylammonium	$[N_{1114}]^+$
methyl-tributylammonium	$[N_{4441}]^+$
1-butyl-pyridinium	$[C_4Py]^+$
1-hexyl −3-methylpyridinium	$[C_6mPy]$
tri-isobutyl-methylphosphonium	$[P_{1(4i)3}]^+$

anions	abbreviations
bis{(trifluoromethylsulfonyl)imide}	$[NTf_2]^-$
trifluoromethanesulfonate (triflate)	$[OTf]^-$
tris(trifluoromethylsulfonyl)methide	$[(CF_3SO_2)_3C]^-$
methylsulfate	$[C_1SO_4]^-$
ethylsulphate	$[C_2SO_4]^-$
dicyanamide	$[N(CN)_2]^-$
hexafluorophosphate	$[PF_6]^-$
tetrafluoroborate	$[BF_4]^-$
nitrate	$[NO_3]^-$
p-toluenesulfonate	$[Tos]^-$

the gas solubility of several gases in traditional solvents[73] or, very recently, for the determination of CO_2 solubility in several ionic liquids.[74] However, in each case, no comparisons were reported between the Henry Law coefficient calculations using COSMOthermX and the mole fraction of the gas in the liquid phase calculated directly by using the Gas−Liquid-Equilibrium protocol with the software. In this paper, these comparisons are made systematically for 15 gases in three different classes of solvent (organic, water, and ionic liquids) increasing the statistical evaluation of this program.

COSMOthermX Calculations of Gas Solubility in Ionic Liquids

COSMO-RS combines the electrostatic theory of locally interacting molecular surface descriptors, which are calculated from a quantum chemistry method known as COSMO (Conductor-like Screening Model), with a statistical thermodynamics methodology.[75] To examine the predictive capability of COSMOthermX, a comparison of gas solubilities in methanol, ethanol, acetone, hexane, heptane, cyclohexane, benzene, toluene, and water was calculated and compared with previously reported data.[76−80] From these calculations, the order of gas solubility and the solvation process of the respective gases were determined so that comparisons could be made with those determined for ILs.

Prior to performing the gas solubility calculations in COSMOthermX, the structure of each species was optimized using DFT within Gaussian Version 3.0[81] utilizing the B3LYP method and the DGTZVP basis set. The resultant optimized structure of each molecule was used as an input for the generation of the COSMO file within the Turbomole program,[82] in this case, using the BP-DFT method and the Ahlrichs-TZVP basis set[83] for each cation, anion, and gas species.

In COSMOthermX, the calculation of the partial vapor pressure uses the equation

$$p_{(i)} = p_{\mathrm{o}}{}^{\mathrm{vap}}{}_{(i)}x_{(i)}\gamma_{(i)} \tag{1}$$

where $p_{(i)}$, $p_{\mathrm{o}}{}^{\mathrm{vap}}{}_{(i)}$, $x_{(i)}$, and $\gamma_{(i)}$ are the partial and pure vapor pressures, mole fraction, and activity coefficient of a selected gaseous species *i* in a particular solvent. For each compound, *i*, the mole fraction $x_{(i)}$ was varied until its partial pressure $p_{(i)}$ was equal to the given reference pressure, *p*. Hence, the calculation of the gas solubility requires the pure compound vapor pressure $p_{\mathrm{o}}{}^{\mathrm{vap}}{}_{(i)}$. This value can either be estimated by COSMOthermX using gas-phase energy information (held in an *.energy file and produced via Turbomole) or by using experimental data (through correlations, such as the Antoine equation or directly from experimental data sets).[84] In the case of the energy file, the following empirical equation was used to determine the pure compound gas-phase chemical potential and, hence, to determine the vapor pressure

$$\mu_{\mathrm{Gas}}^{X_i} = E_{\mathrm{Gas}}^{X_i} + E_{\mathrm{COSMO}}^{X_i} - E_{\mathrm{vDw}}^{X_i} + \omega_{\mathrm{Ring}}n_{\mathrm{Ring}}^{X_i} + \eta_{\mathrm{Gas}}RT \tag{2}$$

where $E_{\mathrm{Gas}}^{X_i}$, $E_{COSMO}^{X_i}$, and $E_{\mathrm{vDw}}^{X_i}$ are the quantum chemical total energies of the molecule in the gas phase, the COSMO conductor, and the van der Waals energy of species X_i, respectively. The other terms are the correction term for ring-shaped molecules with $n_{\mathrm{Ring}}^{X_i}$ denoting the number of ring atoms in the molecule; ω_{Ring} denoting an adjustable parameter; and η_{Gas} representing a link between the reference states of the system's free energy in the gas and liquid phase.[71]

Within this methodology, experimental values for $p_{\mathrm{o}}{}^{\mathrm{vap}}{}_{(i)}$ are preferred compared with estimated values when available, and therefore, the experimental $p_{\mathrm{o}}{}^{\mathrm{vap}}{}_{(i)}$ values of the gases were calculated using the semiempirical Antoine[84] and Wagner[85] equations.[86] The constants within the Antoine and Wagner equations were taken from the NIST[87] and Korean KDB[88] database Web sites, respectively. These constants were utilized within COSMOthermX through the generation of a *.vap file. Theoretically, these correlations should only be used for temperatures defined within and below the critical value of each gas. However, since many of the studied gases have a significantly lower critical value compared with the temperatures at which the data are reported, for example 33 K, 151 K, and 155 K for hydrogen, oxygen, and argon, respectively, the temperature limits were removed to allow the Antoine equation to be extrapolated. This allowed a comparison of the calculated gas solubilities to be made using both methods. Herein, the energy file was used to predict the vapor pressure and hence gas solubility, for gases where the system temperature (*T*) was much greater than the critical temperatures (T_c). The Antoine/Wagner vapor pressure correlation was used where the system temperature was below or approximately equal to the critical temperature, unless otherwise stated.

To estimate the gas solubility in ILs, the ionic liquid may be treated as either an ion pair or discrete cations and anions. While the use of separate ions has the advantage of reducing the number of overall calculations, the ion pair description may be more realistic to describe the local potential. For binary systems of gas and IL using separated ions, the system was treated as a ternary mixture of cation, anion, and gas, with the boundary condition that the cation and anion are equimolar ($n_{\mathrm{ion}} = n_{\mathrm{anion}} = n_{\mathrm{cation}}$). Therefore, the mole fraction of the gas was calculated as

$$x_{\mathrm{gas}}^{\mathrm{T}} = \frac{n_{\mathrm{gas}}}{n_{\mathrm{gas}} + 2 \cdot n_{\mathrm{ion}}} \tag{3}$$

where n_{gas} is the amount in moles of solute dissolved. However, the experimental determination of IL thermodynamic properties is based on the assumption of a binary system consisting of the IL and the solute, i.e.

$$x_{\mathrm{gas}}^{\mathrm{B}} = \frac{n_{\mathrm{gas}}}{n_{\mathrm{gas}} + n_{\mathrm{IL}}} \tag{4}$$

Combining eqs 3 and 4, the corrected mole fraction (x^{B}) from the COSMOthermX (x^{T} value) calculation was determined, as follows

$$x_{\mathrm{gas}}^{\mathrm{B}} = \frac{2x_{\mathrm{gas}}^{\mathrm{T}}}{1 + x_{\mathrm{gas}}^{\mathrm{T}}} \tag{5}$$

It should be noted that all gas solubilities calculated/reported herein are in mole fraction.

The uncertainties in the gas solubility estimated using COSMOthermX were determined by calculating the relative deviation (RD) and relative absolute deviation (RAD), as defined by eqs 6 and 7

$$\mathrm{RD} = \frac{1}{N}\sum\left(\frac{X_{\mathrm{calcd}} - X_{\mathrm{exptl}}}{X_{\mathrm{exptl}}}\right) \tag{6}$$

$$\mathrm{RAD} = \frac{1}{N}\sum\left|\frac{X_{\mathrm{calcd}} - X_{\mathrm{exptl}}}{X_{\mathrm{exptl}}}\right| \tag{7}$$

where N is the total number of data used; X_{calcd} is the desired property calculated for a given ionic liquid at a given temperature; and X_{exptl} is the corresponding value obtained from experimental work reported previously.

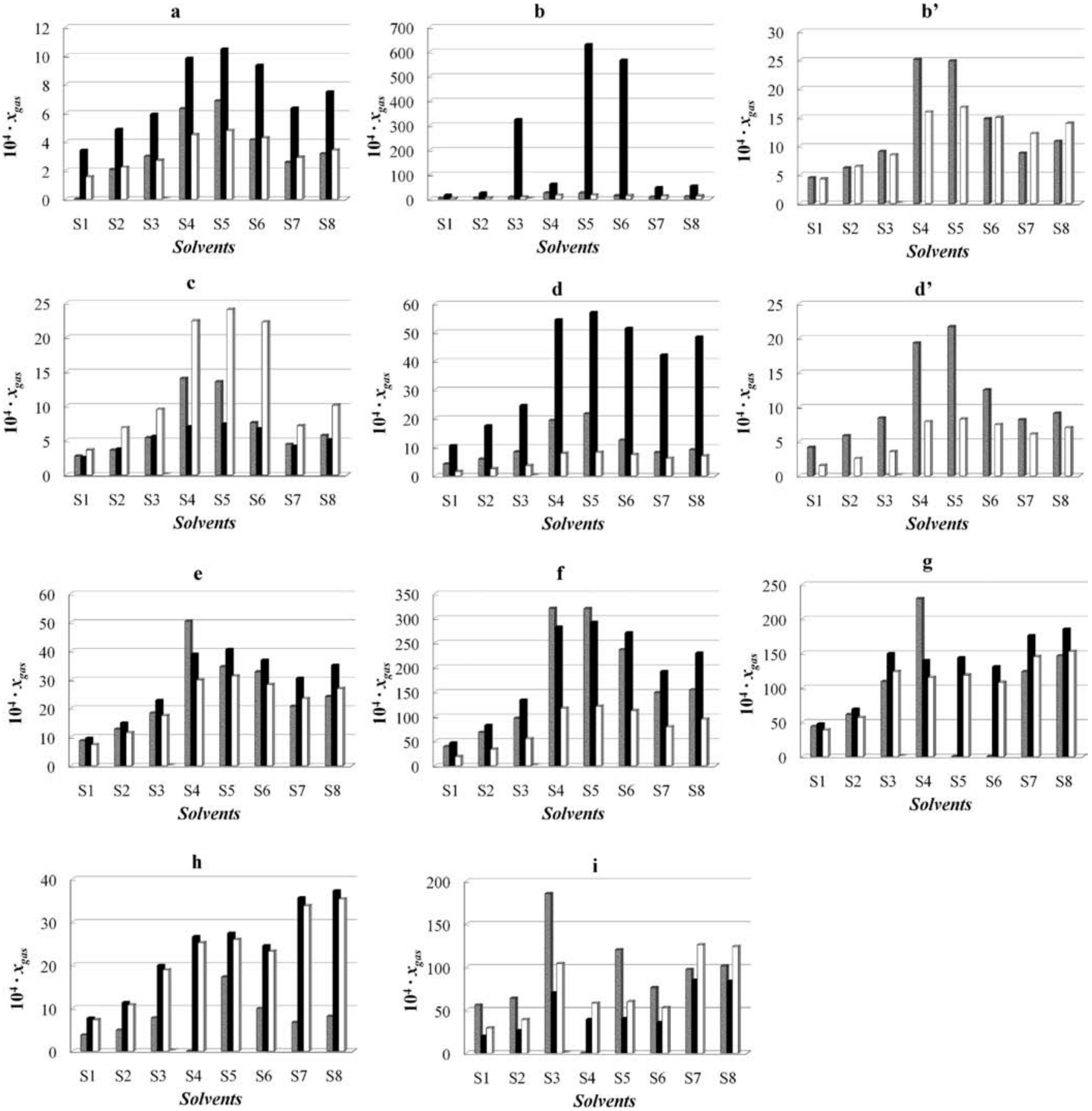

Figure 1. Gas solubility of a, hydrogen; b, argon; c, nitrogen; d, oxygen; e, methane; f, ethane; g, ethylene; h, carbon monoxide; and i, carbon dioxide in S1, methanol; S2, ethanol; S3, acetone; S4, hexane; S5, heptane; S6, cyclohexane; S7, benzene; and S8, toluene at 298.15 K and 0.1 MPa partial gas pressure. Gray bars from Wilhelm and Battino;[76] black bars from COSMOthermX calculations by using *.vap file to describe the gas phase; white bars from COSMOthermX calculations by using *.energy file to describe the gas phase. Where the values from the calculations and the experimental data are significantly different in magnitude, an expanded scale figure has also been included in the cases of argon and oxygen b' and d', respectively.

Table 2. Ratio (R) between Calculated Vapor Pressures of Carbon Monoxide from *.vap File (Defined by the Carbon Monoxide Wagner Equation[88]) and *.energy File on the Temperature Range Definition of its Antoine Equation

	p_o^{vap}/mbar		
T/K	*.energy file	*.vap file[88]	R
73.00	0.004698	333.3	70954
79.67	0.03670	806.6	21978
86.33	0.2075	1678	8089
93.00	0.9108	3117	3422
99.67	3.269	5306	1623
106.33	9.963	8438	847
113.00	26.56	12719	479
119.67	63.37	18379	290
126.33	137.7	25701	187
132.91	273.9	34974	128

[a] $R = [(p_o^{vap}$ *.vap file$)/(p_o^{vap}$ *.energy file$)]$.

Table 3. New Antoine Coefficients Calculated from Equation 5 and Relative Absolute Deviation (RAD) Obtained by Comparison with the Carbon Monoxide Wagner Equation[88] to Define Hypothetical Values of Carbon Monoxide Vapor Pressure for a Temperature Range from (73 to 413) K

New Antoine Coefficients			
A	B	C	100·RAD
15.7265	681.6394	− 4.2511	0.78

Table 4. Relative Deviation (RD) between Experimental Carbon Monoxide Vapor Pressure Calculated Using the Wagner Equation[88] and that Calculated from *.energy and *.vap Files Defined by the New Antoine Coefficients Presented in Table 3 as a Function of Temperature from (73 to 413) K

	p_o^{vap}/mbar			
T/K	Wagner equation[88]	*.energy file	*.vap file (new coefficients)	[a]100·RD
73.00	333.3	0.004698	334.1	0.25
79.67	806.6	0.03670	802.8	−0.48
86.33	1678	0.2075	1673	−0.34
93.00	3117	0.9108	3121	0.13
99.67	5306	3.269	5338	0.60
106.33	8438	9.963	8511	0.87
113.00	12719	26.56	12816	0.77
119.67	18379	63.37	18408	0.16
126.33	25701	137.7	25414	−1.11
132.91	34974	273.9	33809	−3.33
298.15	-	349686	664773	-
334.15	-	618528	856229	-
413.55	-	1448731	1278396	-

[a] RD $= [(p_o^{vap}$ Wagner eq $- p_o^{vap}$ *.vap file$)/(p_o^{vap}$ Wagner eq$)]$.

Gas Solubility in the IL Experimental Database

A wide range of experimental values of gas solubility in ILs have been collated within the IUPAC database.[89] To compare the prediction from COSMOthermX, the data Ar, H_2, O_2, N_2, N_2O, CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_2H_4, C_3H_6, C_4H_8, CO, SO_2, and CO_2 were used.[43,46,50,54,55,90−122] In addition, recent data reported by Jiang et al.[123] for SO_2 solubility in ILs were also included. The list and the abbreviations for each IL used herein are summarized in Table 1.

Results and Discussions

To validate the capability of COSMOthermX to predict gas solubilities, selected organic solvents and water, for which data are readily available within the literature, were examined in detail.[76,77]

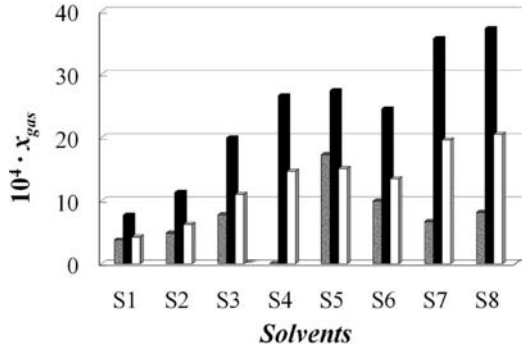

Figure 2. Carbon monoxide solubility in S1, methanol; S2, ethanol; S3, acetone; S4, hexane; S5, heptane; S6, cyclohexane; S7, benzene; and S8, toluene, at 298.15 K and 0.1 MPa partial gas pressure. Gray bars from Wilhelm and Battino;[76] black bars from COSMOthermX calculations by using *.energy file to describe the gas phase; white bars from COSMOthermX calculations by using *.vap file using new Antoine coefficients given in Table 2 to describe the gas phase.

Table 5. Relative Deviation (RD) between Carbon Monoxide Solubility in Methanol Calculated by COSMOThermX Using *.energy File and *.vap File Defined by New Antoine Coefficients Presented in Table 3 with Literature Data[80] as a Function of Temperature from (300 to 413) K and Pressure up to 1.8 MPa

		literature[80]	*.energy file		*.vap file (new coefficients)	
T/K	p/MPa	$10^4 \cdot x_{CO}$	$10^4 \cdot x_{CO}$	[a]100·RD	$10^4 \cdot x_{CO}$	[a]100·RD
300.45	0.5038	19.30	38.5	99.41	20.7	7.3
315.85	0.5288	20.70	32.4	56.65	20.2	2.6
322.65	0.5348	21.00	30.1	43.13	19.8	5.7
334.25	0.5626	22.20	27.6	24.33	20.0	10.1
342.45	0.5763	23.00	25.9	12.64	19.9	13.5
353.55	0.5948	24.50	24.0	2.00	19.9	18.8
362.35	0.6023	26.40	22.5	14.77	19.7	25.4
373.05	0.5846	31.80	20.0	36.98	18.7	41.3
303.55	0.8963	35.40	66.0	86.34	36.2	2.4
313.35	0.9237	36.30	59.1	62.72	35.6	1.9
323.45	0.9655	37.90	54.1	42.86	35.7	5.9
334.05	1.0002	39.10	49.2	25.77	35.5	9.2
343.75	1.0243	41.30	45.4	10.03	35.2	14.7
353.85	1.0499	43.60	42.3	3.06	35.1	19.6
365.65	1.0913	44.70	39.7	11.27	35.4	20.8
374.65	1.1114	48.00	37.6	21.58	35.4	26.3
384.35	1.131	51.00	35.7	29.94	35.4	30.6
393.95	1.1017	61.00	32.7	46.43	33.9	44.4
402.95	1.13	63.60	31.7	50.08	34.4	46.0
413.55	1.0786	75.60	28.6	62.20	32.4	57.2
303.95	1.331	48.80	97.8	100.47	54.1	10.9
315.05	1.3882	49.10	87.1	77.43	53.5	9.0
322.95	1.4404	50.10	81.6	62.86	53.7	7.2
332.75	1.4897	51.60	75.1	45.54	53.5	3.7
344.15	1.54	55.10	68.7	24.66	53.3	3.3
353.25	1.5929	55.70	65.0	16.78	53.7	3.6
364.95	1.6457	58.80	60.6	3.13	53.9	8.4
373.55	1.6693	63.90	57.4	10.12	53.6	16.0
393.55	1.7493	72.20	52.4	27.49	54.3	24.8
410.75	1.5918	107.0	42.8	59.99	48.0	55.2
303.15	0.0735	3.13	5.4	72.21	2.98	4.8
303.15	0.1459	6.03	10.7	77.43	5.91	1.9
303.15	0.3383	13.17	24.8	88.36	13.7	4.1
303.15	0.4021	15.50	29.5	90.23	16.3	5.1
303.15	0.4653	17.86	34.1	91.04	18.9	5.6
303.15	0.6312	23.97	46.6	94.42	25.6	6.7
303.15	0.8685	32.87	64.3	95.60	35.2	7.1
303.15	1.0535	39.13	78.1	99.71	42.7	9.1
303.15	1.2564	46.67	93.4	100.14	51.3	9.9

[a] RD $= [(x_{CO}$ literature $- x_{CO}$ *.i file$)/(x_{CO}$ literature$)]$.

Evaluation of the COSMOthermX Predictability of the Gas Solubility in Organic Solvents. The solubility of nine gases (hydrogen, argon, nitrogen, oxygen, methane, ethane, ethene, carbon monoxide, and carbon dioxide) was estimated using COSMOthermX in a range of organic solvents (methanol, ethanol, acetone, benzene, toluene, heptane, hexane, and

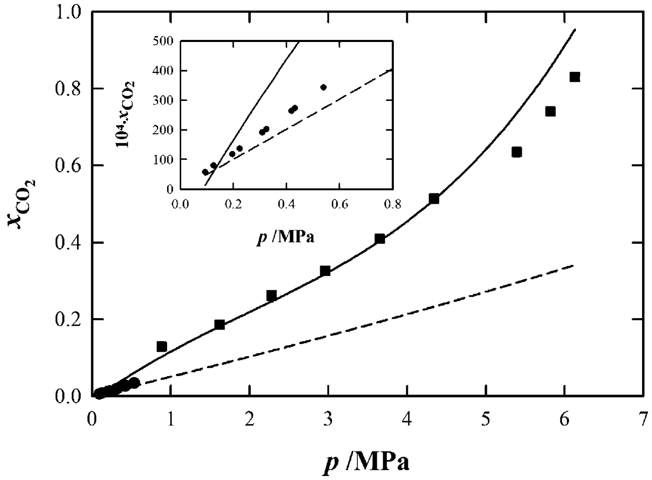

Figure 3. Carbon dioxide solubility in ethanol as a function of pressure up to 7 MPa at 298.15 K. ●, Dalmolin et al.;[78] ■, Day et al.;[79] the lines represent COSMOthermX calculations by using *.vap file (solid line) and *.energy file (dashed line).

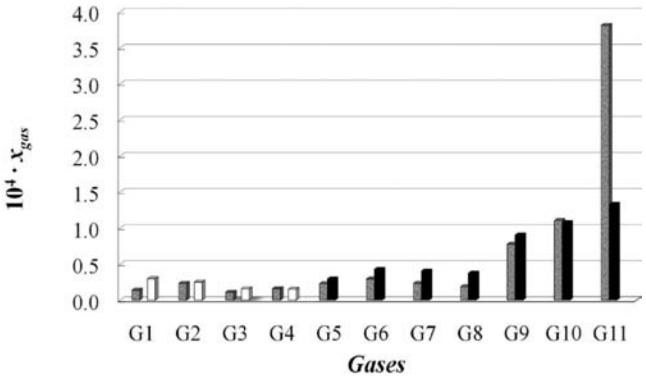

Figure 4. Comparison between literature data from Wilhelm et al.[77] and COSMOthermX calculations of the gas solubility in water at 303.15 K and 0.1 MPa. Gray bars from Wilhelm et al.;[77] black bars from COSMOthermX calculations by using *.vap file to describe the gas phase; white bars from COSMOthermX calculations by using *.energy file to describe the gas phase. G1, H_2; G2, Ar; G3, N_2; G4, CO; G5, CH_4; G6, C_2H_6; G7, C_3H_8; G8, C_4H_{10}; G9, C_2H_4; G10, C_3H_6; G11, N_2O.

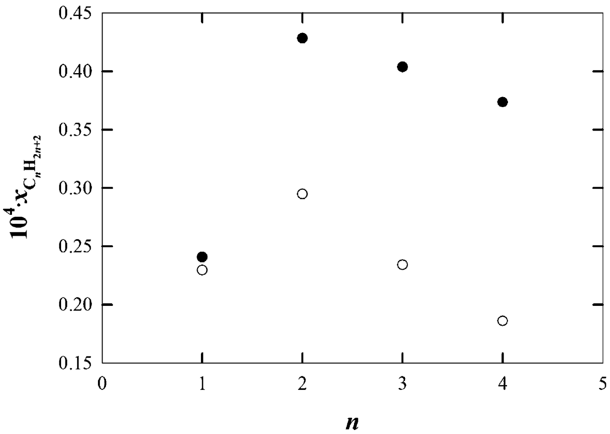

Figure 5. Alkane gas solubility in water at 303.15 K and 0.1 MPa as a function alkyl chain length, *n*, of the alkane at 298.15 K and 0.1 MPa. ○,Wilhelm et al.;[77] ●, COSMOthermX calculations.

cyclohexane) covering a range of solvent classes. The predictions were compared with the experimental values reported by Wilhelm and Battino.[76] Figure 1 summarizes the results[76] for two different types of COSMOthermX calculations, i.e., using either the Antoine equation or energy file to describe the vapor pressure of the solutes according to eq 1.

From Figure 1, it can be observed that, whenever the studied temperature (298 K) is significantly higher than the critical temperature or maximum limit defined for the Antoine equation, the estimation of the gas solubility is, in general, more accurate when the energy value is used in the case of, for example, hydrogen, argon, oxygen, and methane. It is expected that this is due to errors associated with the vapor pressure calculated using the Antoine equation when extrapolated well beyond the proposed temperature limits. However, this is not the case for nitrogen and carbon monoxide. For gases with vapor pressures within the range of the correlations used or which only require slight extrapolation, the predictions are better when using the available vapor pressure data, as shown for ethane and ethene. However, in this case, carbon dioxide is an exception.

In the case of nitrogen, the prediction of gas solubility in selected organic solvents is not well described using the energy data in comparison with similar gases having a very low critical temperature. In this case, the solubility is better defined when using an extrapolated Antoine equation (defined below 126 K) at 298 K. Despite this large extrapolation, the predicted solubility in the majority of solvents is very close to the experimentally determined values, with the notable exceptions of hexane or heptane which show a relative deviation, in both cases, of ≈50 %. Overall, the Relative Absolute Deviation (RAD) of the nitrogen in all eight solvents at 298 K and 1 atm when using the extrapolated Antoine equation (*.vap file) and estimated value (*.energy file) is ≈18 % and 68 %, respectively.

In the case of carbon monoxide, the predicted values using either the vapor pressure data or the energy file are grossly overestimated with an RAD of 185 % and 200 %, respectively. In both cases, the vapor pressures calculated using the energy data (34.97 MPa) and extrapolated Antoine equation (36.07 MPa) at 298 K are similar. By fitting the temperature and the pure vapor pressure of the gas (T, p_o^{vap}) using both the data estimated from the energy data and the experimental values calculated by available correlations (Table 2), it is possible to determine new empirical constants (A, B, C) for the Antoine equation

$$\ln(p_o^{vap}) = A - \frac{B}{(T + C)} \tag{8}$$

These fitted parameters are a blend of both models, and the new Antoine constants are shown in Table 3.

As can be seen in Table 4, these constants have been validated by comparison with the calculated vapor pressure using the alternative Wagner equation.[88] Using the newly calculated Antoine constants, the carbon monoxide solubility in selected organic solvents was recalculated and compared with the experimental values and those predicted from the energy data (Figure 2). This development of the vapor pressure constants resulted in a decrease in the RAD to below 68 % with the highest errors associated with benzene and toluene. To verify this methodology as a function of temperature and pressure, the carbon monoxide solubility in methanol was calculated and compared with available data over a temperature range of (303 to 413) K and for pressures of between (0.073 and 1.8) MPa[80] as shown in Table 5. In this case, the RAD of the predicted carbon monoxide solubility in methanol improved from 50 % to 15 % using the new Antoine constants.

Despite the fact that the estimates for carbon dioxide are made within the vapor pressure calculation limits, the gas solubility predictions are more accurate using the energy data. At 298 K,

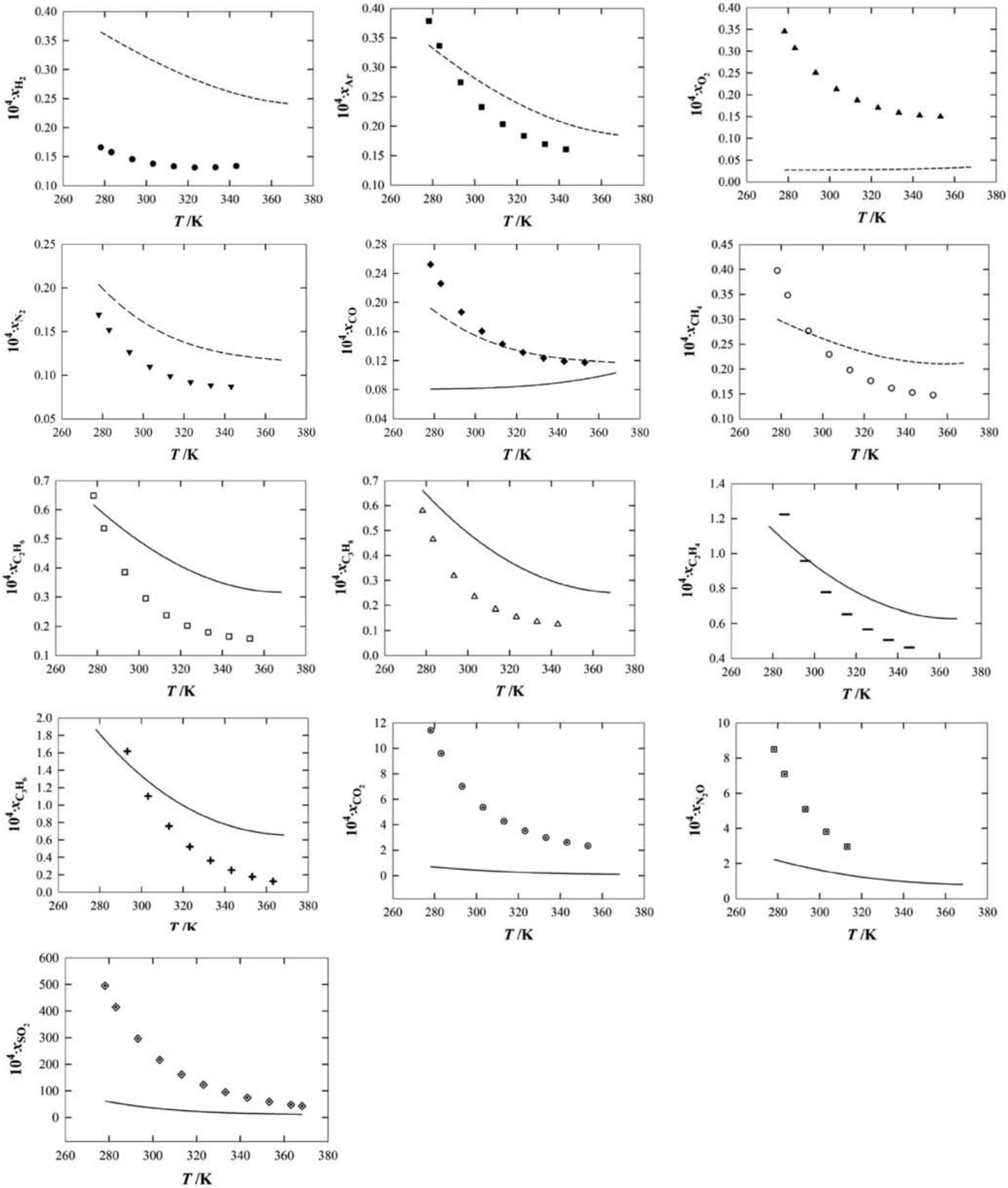

Figure 6. Comparison between literature data from Wilhelm et al.[77] and COSMOthermX calculations of the gas solubility in water as a function of temperature from (278 to 363) K at 0.1 MPa., ●, H_2; ■, Ar; ▲, O_2; ▼, N_2; ♦, CO; ○, CH_4; □, C_2H_6; Δ, C_3H_8; ▽, C_4H_{10}; −, C_2H_4; +, C_3H_6; ⊙, CO_2; ⊡, N_2O; ◇ with a dot in the middle, SO_2; the lines represent COSMOthermX calculations by using *.vap file (solid line) and *.energy file (dashed line).

the difference between the p_o^{vap} estimated by COSMOthermX (12.91 MPa) and that calculated using the Antoine equation (6.43 MPa) is significant. This indicates that the value of the activity coefficient, γ, is incorrectly calculated but is compensated by the overestimation of p_o^{vap}. Thus, the $p_o^{vap}\gamma$ term generates a more accurate estimation for carbon dioxide solubility at 298 K and 1 atm when using the energy data. However, for pressures higher than atmospheric pressure, Figure 3 shows that carbon dioxide solubility calculated using the available vapor pressure data (*.vap file) does lead to a better prediction of the gas solubility behavior at 298 K for ethanol.[78,79] This suggests that overall the carbon dioxide solubility in organic solvents as a function of pressure should use the vapor pressure data.

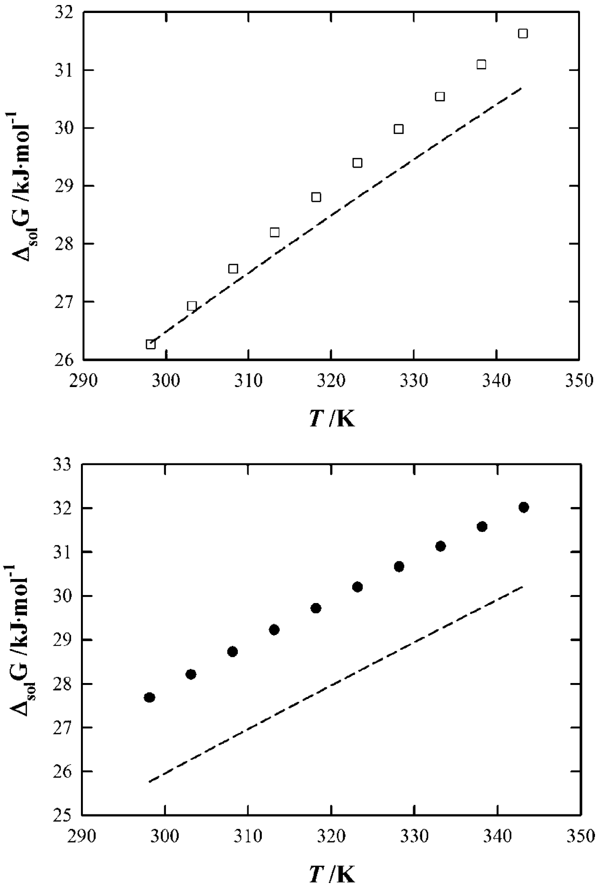

Figure 7. Partial molar Gibbs energy of solution of the gases in water as a function of temperature: □, methane from Wilhelm et al.;[77] ●, hydrogen from Wilhelm et al.;[77] the dashed lines represent COSMOthermX calculations.

Henry's Law constants can be determined from the solubility data or directly using the COSMOthermX program and is defined as

$$K_H = \frac{p}{x_{(i)}} \tag{9}$$

where K_H, p, and $x_{(i)}$ are the Henry's Law constant, the studied pressure, and the solubility of the gaseous solute in the solvent expressed in mole fraction, respectively. For carbon dioxide in ethanol at 298 K, this was determined as (38.2 and 19.9) MPa using solubility data calculated from the vapor pressure equation (*.vap file) and the estimated value (*.energy file), respectively. Comparing these values with the Henry's Law constant directly calculated by COSMOthermX indicates that only the energy data are used to calculate Henry's Law constant. From Wilhelm and Battino,[76] the Henry's Law constant was experimentally determined as 15.7 MPa at 298 K, i.e., a 26 % deviation from the calculated value using COSMOthermX. Therefore, for those gases where the predicted solubilities are better described when using the available vapor pressure data (*.vap file), a more accurate value for the Henry's Law constant would have to be determined manually from eq 8 using the calculated solubility data determined by vapor pressure data (*.vap file) as opposed to the direct option within the program. Nevertheless, the use of the energy data to calculate the Henry's Law constant in the COSMOthermX program from the direct option is defended by COSMOlogic as it is believed to be more consistent from a physical point of view.[124] This is due to the fact that since the Henry's Law constant is a property that is extrapolated from a (virtual) ideal gas reference state it should be predicted using the ideal gas reference state, i.e.

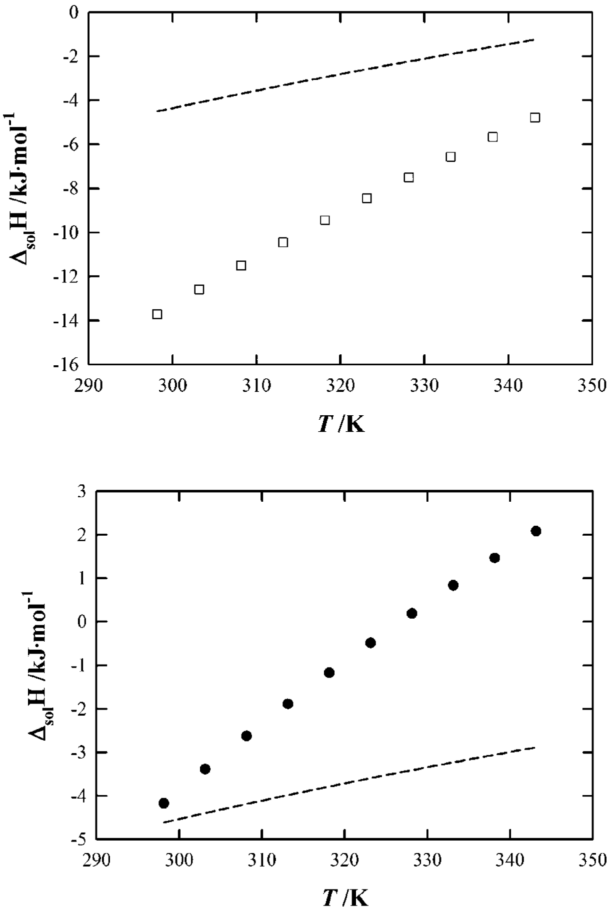

Figure 8. Partial molar enthalpy of solution of the gases in water as a function of temperature: □, methane from Wilhelm et al.;[77] ●, hydrogen from Wilhelm et al.;[77] the dashed lines represent COSMOthermX calculations.

$$K_H = \gamma_i^{\infty} p_o^{\text{vap}} \tag{10}$$

where K_H, γ_i^{∞}, and p_o^{vap} are the Henry's Law constant, the activity coefficient at infinite dilution, and the vapor pressure of the pure gas, respectively. However, it should be noted that the determination of p_o^{vap} is extremely sensitive to the value of energy data. For example, the calculated vapor pressure for *n*-butane at 298 K is 0.6091 MPa when using an energy value of −158.5089 hartree as determined using the Turbomole calculation. Calculations using available data for the Antoine equation produce a value of 0.2429 MPa thus indicating a significant overprediction in the vapor pressure when using the energy file. However, by changing the energy value to −158.5080 hartree the calculated vapor pressures when using the Antoine and energy value are the same and, in general, lead to a better prediction of the vapor pressure−temperature relationship. Currently, no DFT method can predict the energy to such an accuracy, and this would suggest a particular sensitivity of COSMOthemX to the small differences in energy. As the method compares this externally calculated energy file to the internally calculated values, such large differences in the vapor pressure can result showing that it is important to have consistency in the DFT method used.

The above results show that the predictive capability of COSMOthermX is clearly dependent on the correct determination of both the vapor pressure and the activity coefficient.

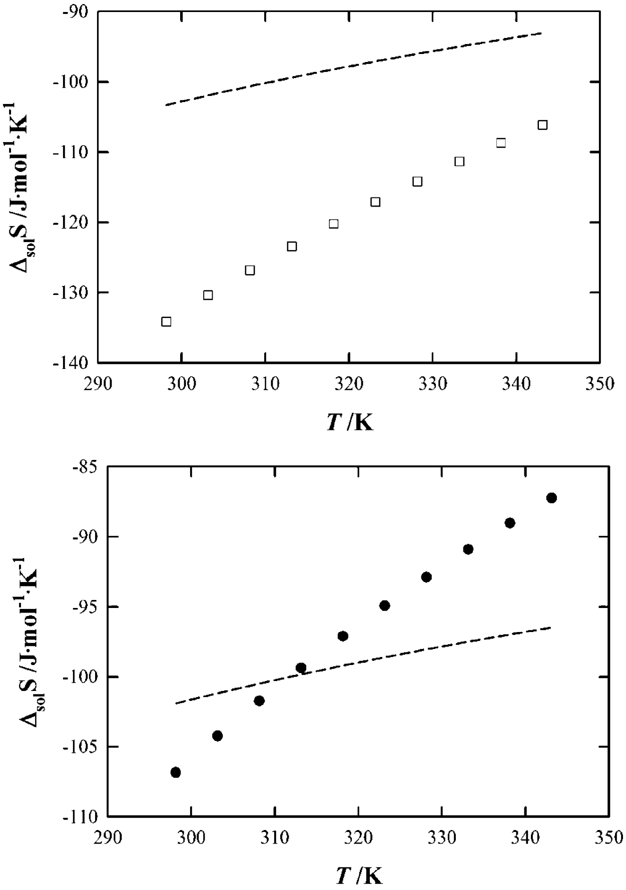

Figure 9. Partial molar entropy of solution of the gases in water as a function of temperature: □, methane from Wilhelm et al.;[77] ●, hydrogen from Wilhelm et al.;[77] the dashed lines represent COSMOthermX calculations.

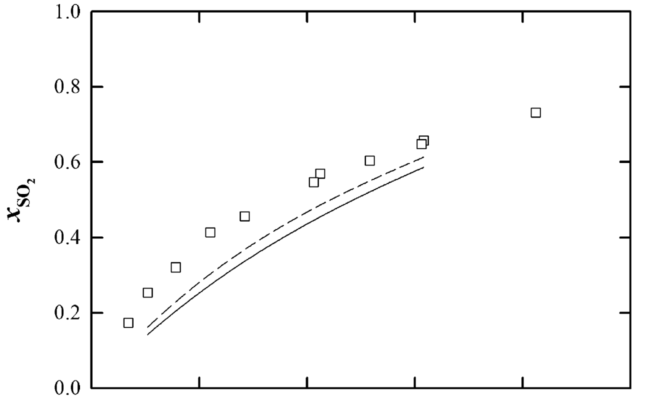

Figure 10. SO_2 solubility in [C_2mim][BF_4]. □, experimental data from Jiang et al.;[123] the dashed and solid lines represent the COSMOthermX prediction calculations with the lowest and highest energy conformers, respectively.

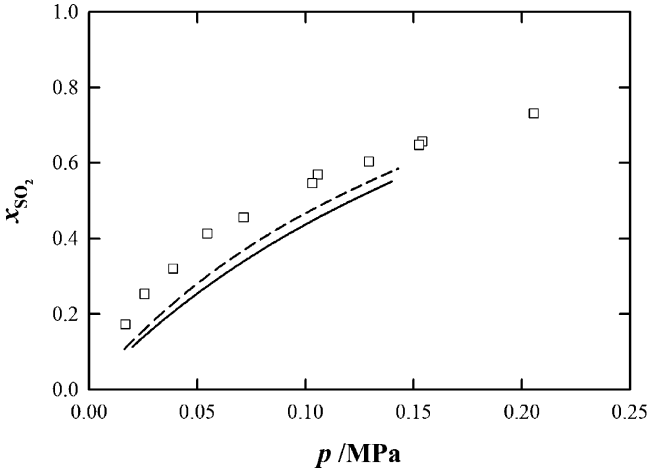

Figure 11. SO_2 solubility in [C_2mim][NTf_2]. □, experimental data from Jiang et al.;[123] the dashed and solid lines represent the COSMOthermX prediction calculations with the lowest and highest energy conformers, respectively.

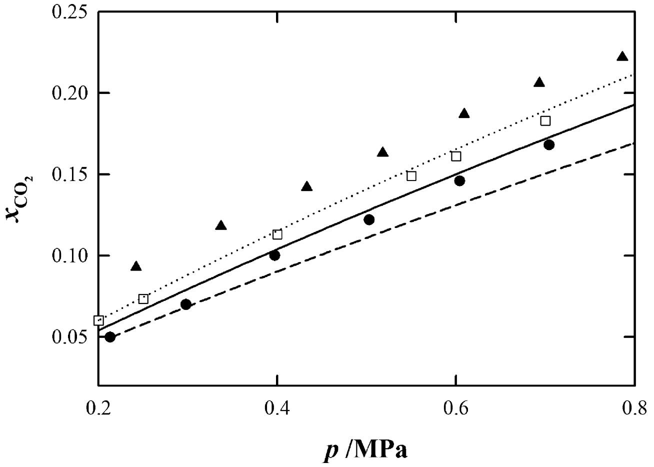

Figure 12. COSMOthermX predictive capability of the alkyl chain length effect on the gas solubility in [$C_n$mim][NTf_2] reported at 298.15 K as a function of pressure in the case of the CO_2 solubility. Experimental data for the CO_2 solubility in: ●, [C_2mim][NTf_2] from Kim et al.;[54] □, [C_4mim][NTf_2] from Anthony et al.;[54] ▲, [C_6mim][NTf_2] from Kim et al.[54] The dashed, solid, and dotted lines represent the COSMOthermX calculations by using the *.energy file of the CO_2 solubility in [C_2mim][NTf_2], in [C_4mim][NTf_2], and in [C_6mim][NTf_2], respectively.

In general, when the vapor pressure is known the prediction is reasonable indicating that the activity is correctly described. Moreover, even when the vapor pressure is estimated, the results are qualitatively correct (Figure 1) and predict the trends for the solubility for gases in one organic solvent and the solubility of one gas in a range of organic solvents.

Evaluation of the COSMOthermX Predictability of the Gas Solubility in Water. The solubility of 14 gases (Ar, H_2, O_2, N_2, N_2O, CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_2H_4, C_3H_6, CO_2, CO, and SO_2) was investigated in water, and comparisons were made with experimental data.[77] Within these calculations, the same protocol was used as that for the organic solvents; namely, the energy file was used when the $T \gg T_c$ and the vapor pressure data were used when $T_c > T$ or $T \approx T_c$.

A comparison of the gas solubility in water at constant temperature calculated using COSMOthermX and the experimental data showed good agreement for each gas with the exception of O_2, CO_2, and SO_2 (Figure 4). For these three gases, the predicted gas solubilities in water are 1 order of magnitude lower than the reported experimental data.[77] Figure 5 shows that for alkanes the correct trend with increasing alkyl chain length is found. In general, as shown for organic solvents, the correct order of gas solubility in water is obtained. However, in water the gas solubility is very small, and therefore, any small variation of solubility will generate large deviations. For example, at 303 K, the overall RAD is 53 % for the 14 gases studied by COSMOthermX, with the lowest deviation found for C_3H_6 (3 %) and the highest for H_2 (116 %).

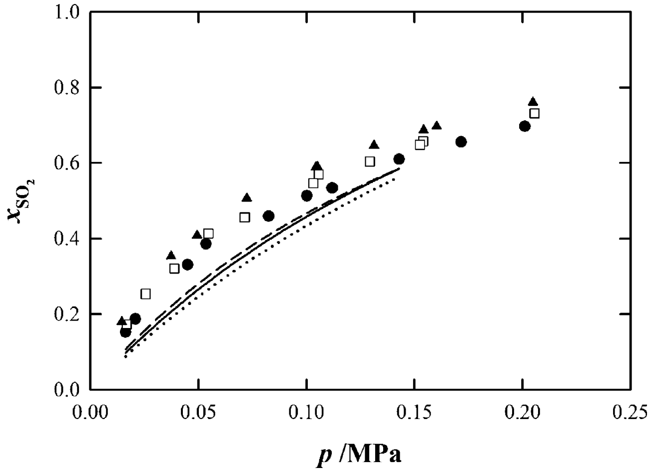

Figure 13. Gas solubility of the SO_2 in □ and dashed line, $[C_2mim][NTf_2]$; ●, and solid line, $[C_4mim][NTf_2]$; ▲, and dotted line, $[C_6mim][NTf_2]$ as a function of pressure at 298.15 K. The single symbols and lines represent, respectively, the experimental data from Jiang et al.[123] and the COSMOthermX prediction calculations.

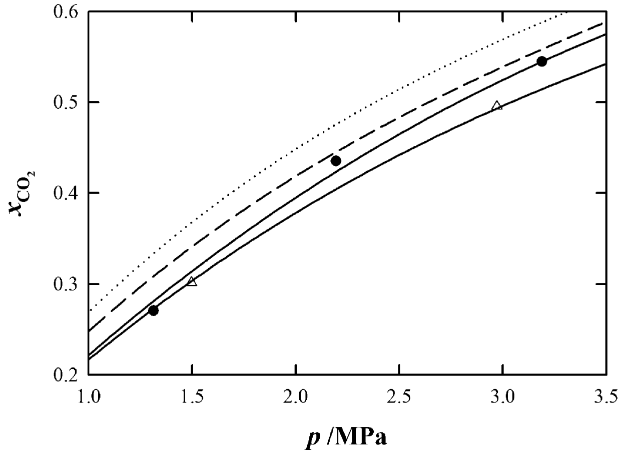

Figure 14. COSMOthermX predictive capability of substitution at the C(2) position by a methyl group on the 1-alkyl-3-methyl imidazolium ring. Experimental data from Aki et al.[54] for the CO_2 solubility in: ●, $[C_6mim][NTf_2]$; Δ, $[C_6mmim][NTf_2]$; the solid lines represent their correlations as a function of pressure as a guide. The dotted and the dashed lines represent the COSMOthermX calculations by using the *.energy file of the CO_2 solubility in $[C_6mmim][NTf_2]$ and in $[C_6mim][NTf_2]$, respectively.

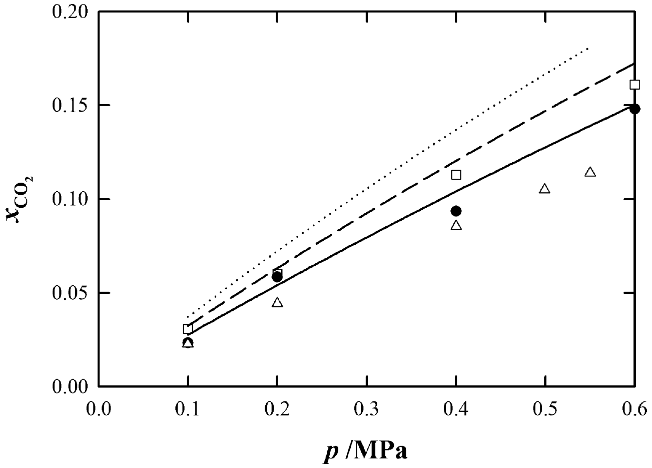

Figure 15. COSMOthermX predictive capability of the cation family changed on the gas solubility in $[NTf_2]^-$ based ILs, reported at 298.15 K as a function of pressure in the case of the CO_2 solubility. Experimental data from Anthony et al.[54] for the CO_2 solubility in: □, $[C_4mim][NTf_2]$; ●, $[C_4mPyrro][NTf_2]$; Δ, $[N_{4441}][NTf_2]$. The solid, dashed, and dotted lines represent the COSMOthermX calculations of the CO_2 solubility in $[C_4mim][NTf_2]$, in $[C_4mPyrro][NTf_2]$, and in $[N_{4441}][NTf_2]$, respectively.

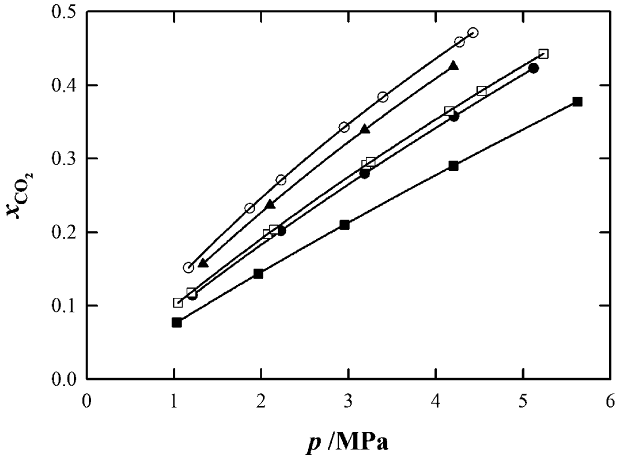

Figure 16. COSMOthermX predictive capability of anion change effect on the CO_2 solubility in the $[C_4mim]^+$ based ILs investigated at 298.15 K and as a function of pressure with counteranion based on the ■, $[NO_3]^-$; ●, $[BF_4]^-$; ▲, $[PF_6]^-$; □, $[OTf]^-$; ○, $[NTf_2]^-$.

With the exception of H_2, the solubility as a function of temperature shows a decrease as the temperature increases over the range studied.[77] Figure 6 shows that COSMOthermX is able to predict this trend for almost all gases except O_2, where the opposite was obtained.

In the case of the CO, the energy file and the extended vapor pressure data presented in Table 3 were used. In contrast with the organic solvents, better agreement is found between the predicted and experimental data for water[77] by using the energy file than with the vapor pressure data. Over the temperature range from (278 to 368) K, RAD of 8 % and 42 % were obtained by defining the gas phase by the energy file and by the vapor pressure data, respectively. Furthermore, using the vapor pressure data (Table 3), the opposite trend in the calculated solubility as a function of temperature is found compared with the experiment indicating that the CO solubility in water increases with the temperature.

Overall, while the correct trends in solubility are found, COSMOthermX is unable to predict that H_2 has the lowest solubility among the studied gases in water or predict a good variation of H_2 solubility in water as a function of temperature indicating a minimum solubility at a temperature in the region of 323 K.

To analyze the ability of COSMOthermX to predict the gas solubility as a function of temperature in greater detail, the Henry's Law constants and solvation properties were calculated for each gas in water at a function of temperature at a fixed pressure of 0.1 MPa. The variation of solubility with temperature for all gases studied expressed in the form of the Henry's Law constant is directly related to the thermodynamic properties of solvation through eqs 11 to 13. For gaseous solutes at low pressure, the Gibbs energy of solvation can be described by the following equation[125]

$$\Delta_{sol}G^{\infty} = RT\ln(K_H/p^0) \tag{11}$$

where p^0 is the standard state pressure. For gaseous solutes at low pressure, this free energy of solvation can be regarded as a good approximation for the Gibbs energy of solution.

The partial molar differences in enthalpy and entropy between the two states can be obtained by calculating the corresponding

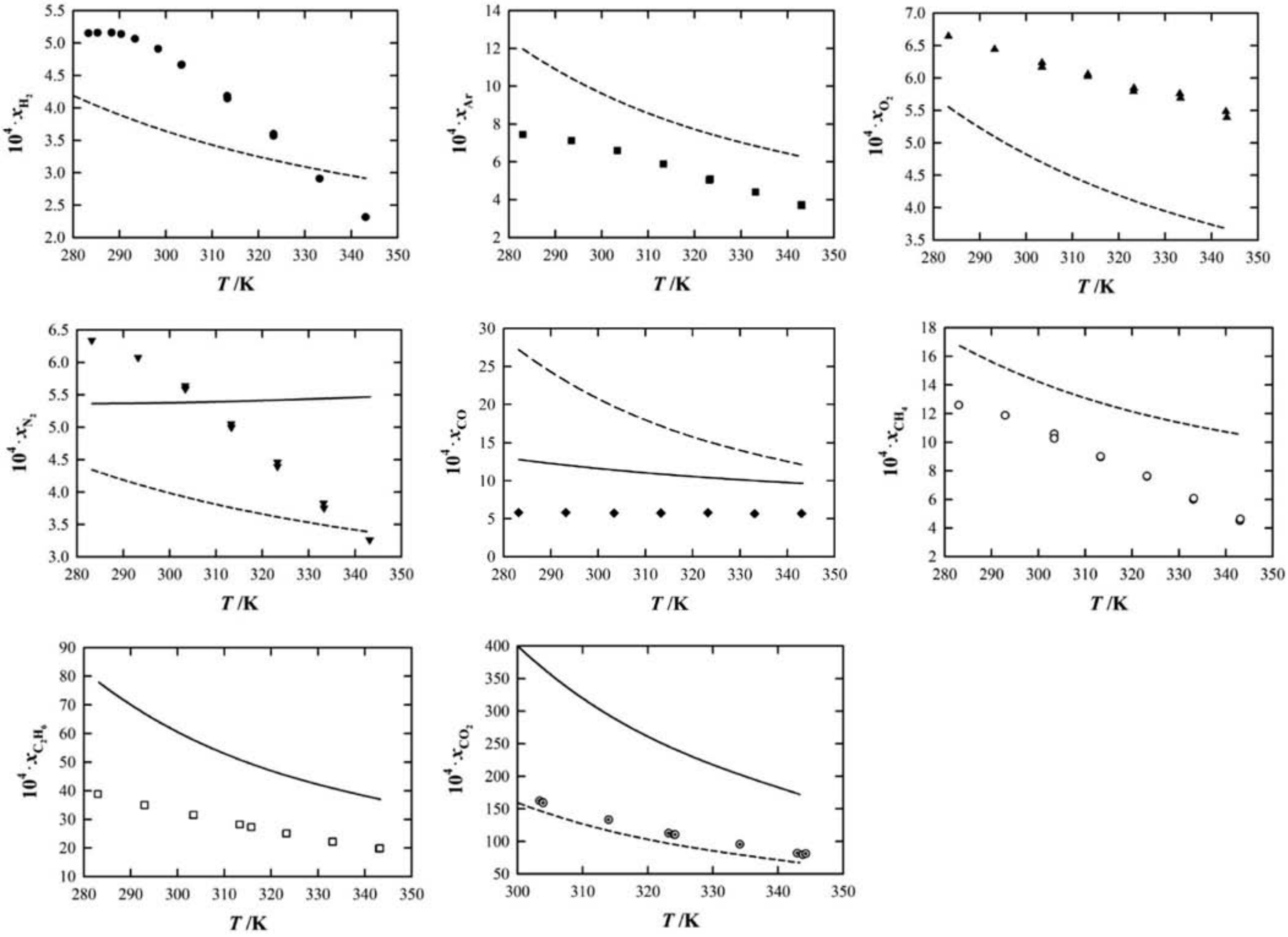

Figure 17. Comparison between literature data from Jacquemin et al.[91] and COSMOthermX calculations of the gas solubility in [C_4mim][BF_4] as a function of temperature from (278 to 363) K at 0.1 MPa. ●, H_2; ■, Ar; ▲, O_2; ▼, N_2; ◆, CO; ○, CH_4; □, C_2H_6; ⊙, CO_2; the lines represent COSMOthermX calculations by using *.vap file (solid line) and *.energy file (dashed line).

partial derivatives of the Gibbs energy with respect to temperature as follows

$$\Delta_{\text{sol}}H^{\infty} = -T^2\partial/\partial T(\Delta_{\text{sol}}G^{\infty}/T) = -RT^2\partial/\partial T[\ln(K_H/p^0)] \quad (12)$$

$$\Delta_{\text{sol}}S^{\infty} = (\Delta_{\text{sol}}H^{\infty} - \Delta_{\text{sol}}G^{\infty})/T = -RT\partial/\partial T[\ln(K_H/p^0)] - R\ln(K_H/p^0) \quad (13)$$

The values for the partial molar Gibbs energy, enthalpy, and entropy of solvation determined from the COSMOthermX calculations were then compared with the reported values by Wilhelm et al.[77] and are exemplified for the cases of H_2 and CH_4 in Figures 7 to 9 over the temperature range from (278 to 368) K.

From Figure 7, the partial molar Gibbs energy of solvation is found to have a similar variation with temperature for all the gases studied and is found to be directly proportional to the logarithm of the Henry's Law constants. A comparison of the COSMOthermX calculations using the energy file with the experimental values[77] shows that for CH_4, C_2H_4, CO, and Ar an RAD of < 2 % is obtained over the studied temperature range. This may be compared with an RAD of 6 % by using the extended vapor pressure data. The COSMOthermX calculated partial molar Gibbs energy of solvation for the cases of H_2, O_2, CO, C_2H_6, C_3H_8, C_3H_6, and C_4H_{10} were obtained with slightly higher deviations but all of which are < 6 %. However, for all the other studied gases, higher deviations (up to 46 % in the case of the SO_2) were obtained for the Gibbs energy of solvation compared with the experimental data.[77]

The effect of temperature on the enthalpy and entropy of solution is illustrated in Figures 8 and 9. On the basis of the COSMOthermX calculations, all studied gases exhibit negative enthalpies of solution corresponding to an exothermic solvation with the exception of O_2 which shows an endothermic process, as expected from Figure 6. A comparison with the experimental data[77] indicates that COSMOthermX is unable to predict the correct trend of the enthalpy of solvation for H_2 as a function of the temperature or the existence of an *extremum* at temperatures close to 323 K. Furthermore, incorrect solvation energetics are predicted for O_2, which limits its use to predict the thermodynamic properties of these gases. On the basis of these 14 gases, the lowest RAD was obtained for CO_2, which resulted in a RAD of 13 % when compared with experimental solvation data,[77] and the highest deviation was found for O_2 (≈160 %). In the case of CO, RADs of 40 % and 180 % were obtained compared with the experimental data[77] using the energy file and the extended vapor pressure data, respectively. A comparison of the calculated enthalpies of solvation with the solvation data from Wilhelm et al.[77] shows that COSMOthermX can describe this solvation property with an overall RAD of 61 % for the 14 gases studied.

In the case of the entropy of solvation, COSMOthermX calculations showed qualitative agreement with the experimental data.[77] In each case, the values are negative and increase with

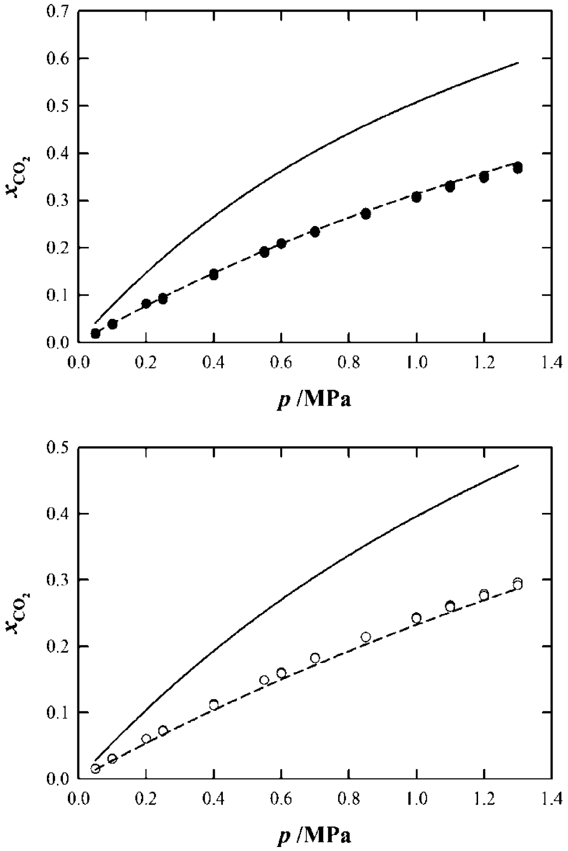

Figure 18. Comparison between literature data from Anthony et al.[94] and COSMOthermX calculations of the CO_2 solubility in [C_4mim][NTf_2] as a function of pressure up to 1.3 MPa. ●, 283.15 K; ○, 298.15 K; the lines represent COSMOthermX calculations by using *.vap file (solid line) and *.energy file (dashed line).

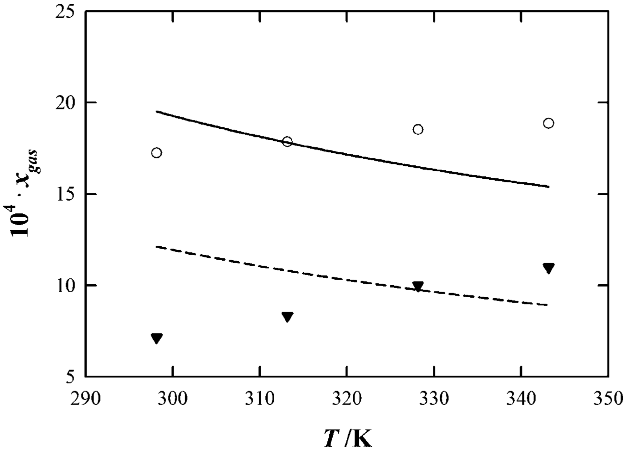

Figure 19. Comparison between literature data from Finotello et al.[91] and COSMOthermX calculations of the gas solubility in [C_2mim][NTf_2] as a function of temperature from (298 to 343) K at 0.1 MPa. ▼ and dashed line, H_2; ○ and solid line, N_2; the symbols and the lines represent literature data from Finotello et al.[91] and COSMOthermX calculations using *.energy file, respectively.

temperature; however, all the calculated entropies of solvation increase more slowly with the temperature than expected.[77] For the 14 gases studied, COSMOthermX calculations predict the entropy of solvation as an overall RAD of 20 %.

Evaluation of the COSMOthermX Predictability of the Gas Solubility in IL. Due to the very low vapor pressures of ionic liquids, any errors associated from neglecting the fugacity and nonideality can be eliminated by replacing the volatile solvent with an IL. A priori, COSMOthermX predictions of gas solubility in IL may, therefore, be expected to give better predictions than for molecular solvents. On the basis of this hypothesis, different systems have been investigated to evaluate the COSMOthermX predictability of the gas solubility in IL by changing the cation and the anion constituting the IL, the gas, temperature, and pressure. Again the rules with regard to selection of the vapor pressure model were employed; i.e., the energy file was used when the $T \gg T_c$, and the vapor pressure data were used when $T_c > T$ or $T \approx T_c$.

Effect of IL Conformers. Molecule conformers represent different energy states of the molecule which result from torsional rotations of the bonds within it. To examine the effect of these conformers on gas solubility, the solubility of SO_2 in [C_2mim][BF_4] was used. In this case, three different energy states for the cation exist and only one for the anion and the gas, and the results are shown in Figure 10. From these data, conformers with the lowest state of energy were found to give the best prediction of the solubility of SO_2 in [C_2mim][BF_4]. Similar observations were also reported by Freire et al.[60] for VLE and LLE when using ionic liquids with alcohols. However, unlike the prediction of LLE, the effect of conformers on gas solubility is very small. The effect of other conformers, for example, those of the [NTf_2]$^-$ anions, has also been studied, and a similar trend was observed as shown in Figure 11.

Effect of the Alkyl Chain Length on the Cation. The effect of alkyl chain length on the gas solubility in [NTf_2]$^-$ based ILs was analyzed using ILs based on the 1-alkyl, 3-methylimidazolium cation, as shown in Figure 12. Experimentally, the CO_2 gas solubility is found to increase with increasing alkyl chain length at all pressures and constant temperature,[98,101,112,120] and similarly, for the CO_2 solubility in [$C_n$mim][NTf_2] between n = 2 and 6 at 298 K, the calculated values from COSMOthermX show the correct trend (Figure 12). In addition, the apparent increase in solubility at higher pressure is predicted. In general, this trend was also observed with all other gases studied with the exception of SO_2. On the basis of calculations shown in Figure 13, SO_2 solubility in [$C_n$mim][NTf_2] decreased slowly with the increase of the alkyl chain length which has also been reported experimentally.[123]

Effect of the Methyl Substitution on C(2) Position. The effect of substitution at the C(2) position on the imidazolium ring was also investigated, and Figure 14 shows a comparison of the solubility of CO_2 in [C_6mim][NTf_2] and [C_6mmim][NTf_2]. In this case, COSMOthermX predicts that the inclusion of the methyl group at the C(2) position should increase the gas solubility in ionic liquid, whereas experimentally the opposite trend is observed.[50,101] This may be due to the fact that little change in polarity is found on the replacement of the acidic hydrogen by a methyl group in the C(2) position of the imidazolium cation in the profile of the charge density, as also reported by Freire et al.[60] for the liquid−liquid equilibrium.

Effect of the Cation Family. The effect of changing the IL cation was examined by calculating the solubility of carbon dioxide in [C_4mim][NTf_2] and in [C_4mPyrro][NTf_2], i.e., for ILs with an aromatic and a nonaromatic cation but with the same alkyl chain lengths at the nitrogen center as well as in [N_{4441}][NTf_2]. Figure 15 shows that the solubility of carbon dioxide in [C_4mim][NTf_2] and [C_4mPyrro][NTf_2] is comparable at low pressure, but as the pressure increases, the difference in solubility for the different cations increases. This phenomenon has been observed experimentally.[92,94,112,113] However, COSMOthermX was unable to predict the correct trend in the order of solubility when compared with experimental observations.[94,112]

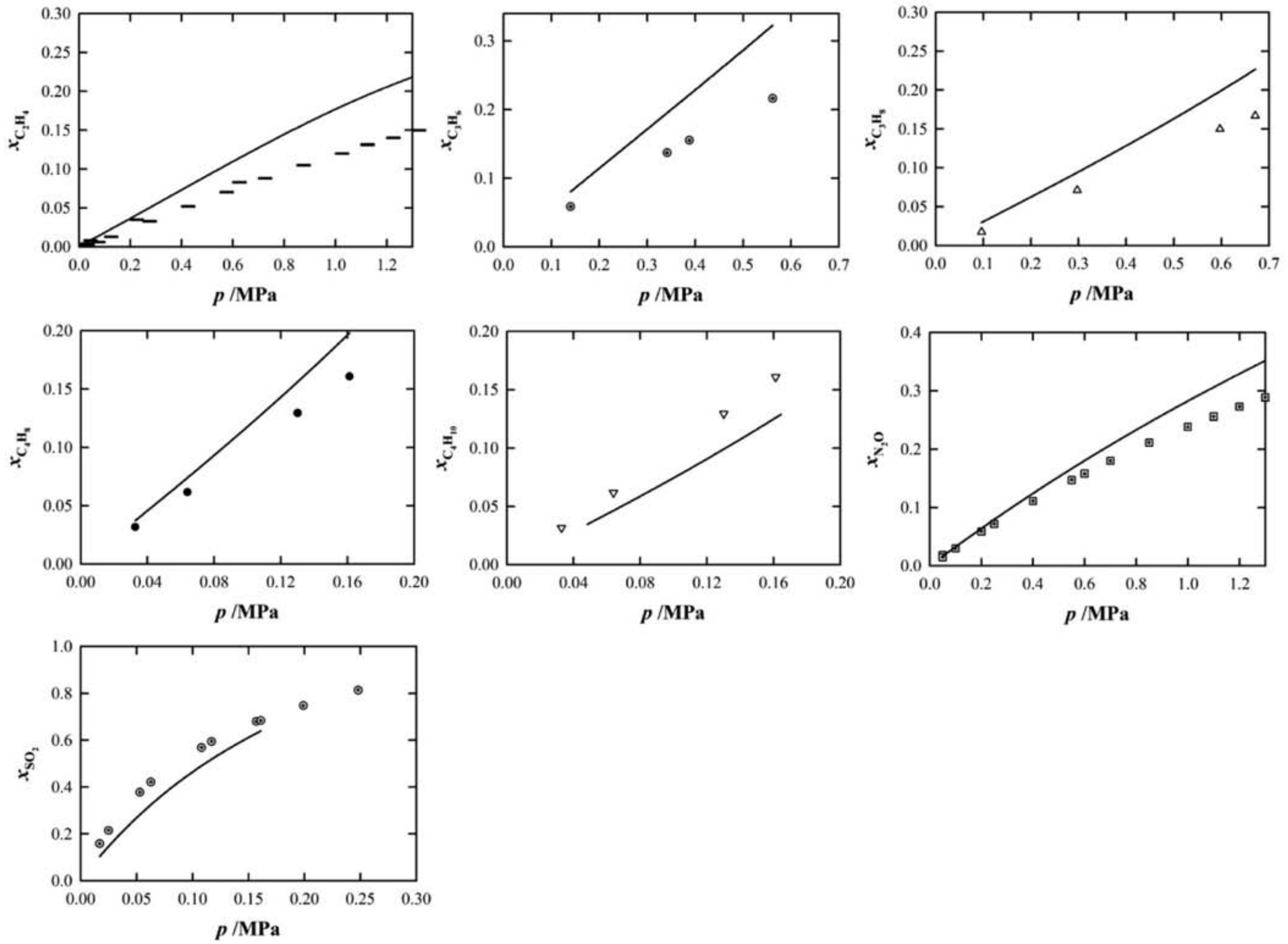

Figure 20. Comparison between literature data and COSMOthermX calculations of the gas solubility in [C_2mim][NTf_2] as a function of pressure. −, C_2H_4 at 298.15 K from Anthony et al.;[94] ⊙, C_3H_6 at 299.98 K from Lee and Outcalt;[106] Δ, C_3H_8 at 299.98 K from Lee and Outcalt;[106] ●, C_4H_8 at 300.00 K from Lee and Outcalt;[106] ▽, C_4H_{10} at 300.00 K from Lee and Outcalt;[106] ⊡, N_2O at 298.15 K from Anthony et al.;[94] ◇ with a dot in the center, SO_2 at 298.15 K from Jiang et al.;[123] the solid lines represent COSMOthermX calculations by using *.vap file.

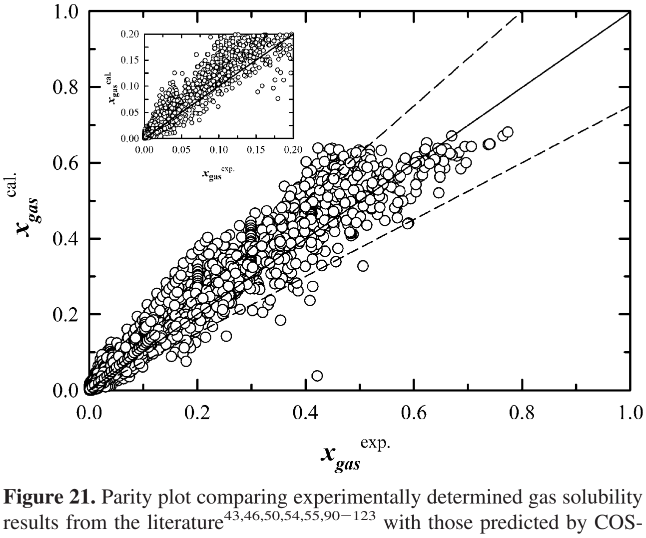

Figure 21. Parity plot comparing experimentally determined gas solubility results from the literature[43,46,50,54,55,90−123] with those predicted by COSMOthermX. The dashed lines represent deviations of ± 25 % with the literature data.

Effect of Anion. The effect of changing the anion of the IL was examined for CO_2 solubility data calculated by COSMOthermX in 1-butyl, 3-methylimidazolium-based ILs. Five anions were examined, namely, $[NO_3]^-$, $[BF_4]^-$, $[OTf]^-$, $[PF_6]^-$, and $[NTf_2]^-$, and the results are reported in Figure 16. It can be seen that with the exception of the order of the $[PF_6]^-$ and $[OTf]^-$ based ILs,[94] COSMOthermX predicts the correct order for the CO_2 solubility, i.e., $[NO_3]^- < [BF_4]^- < [OTf]^- < [PF_6]^- < [NTf_2]^-$.

Effect of Different Gases on the COSMOthermX Gas Solubility Calculations in IL. Figure 17 compares the experimentally determined solubility data[91] for eight gases in [C_4mim][BF_4] with those calculated by COSMOthermX. In general, the calculations are found to reflect the effect of the solute on the solubility in the IL as well as the fact that the solubility decreases as the temperature increases at 0.1 MPa using the vapor pressure model protocols stated. However, for N_2 and CO_2, better predictions were obtained using the energy data compared with the vapor pressure correlations. For the case of CO_2, the deviation for the calculated solubility in [C_4mim][BF_4] by comparison with experimental data was 11 % and 125 % when using energy and vapor pressure data, respectively. As observed for organic solvents, a better description of CO_2 solubility is given by using the energy data (Figure 18).

From an overall comparison of the eight gases, the calculated solubilities in [C_4mim][BF_4] had an RAD of 44 % deviation from those reported by Jacquemin et al.[91] No agreed trend of the effect of temperature on gas solubility in IL has been reported to date.[39,46−50,91−98,101−117] For example, Finotello et

Table 6. Uncertainty, Ordered with Respect to the Gas, of the COSMOthermX Model for the Prediction of Gas Solubilities in Ionic Liquids

gas	temperature range K	pressure range MPa	number of data	100·RAD	ref
all gases	279.9 to 413.2	0.02 to 10.0	2998 [c]	36.9[c]	43, 46, 50, 54, 55, 90−123
argon	283.0 to 343.2	0.02 to 1.3	126 (35)[c]	904[b] (31.0)[b−c]	91−94
but-1-ene	280.0 to 340.0	0.02 to 0.4	16	24.3[a]	106
n-butane	280.0 to 340.0	0.03 to 0.3	16	18.2[a]	106
carbon dioxide	280.0 to 413.2	0.02 to 10.0	1931	32.4[b] (145.4)[a]	43, 50, 54, 90−94, 98−115, 118−122
carbon monoxide	283.2 to 373.2	0.02 to 9.2	78	153.9[a] (302.9)[b]	91, 92, 97, 115
ethane	283.1 to 344.7	0.02 to 1.3	236 (131)[c]	*55.9*[a] (35.9)[a−c]	91−94, 98, 114
ethene	283.1 to 323.2	0.02 to 1.3	180	40.9[a]	93, 94
hydrogen	283.4 to 413.2	0.04 to 9.8	125	36.8[b]	91, 92, 95, 96, 98, 115
methane	283.1 to 413.2	0.02 to 8.9	126 (44)[c]	*86.3*[b] (29.2)[b−c]	91−93, 116
nitrogen	283.2 to 343.2	0.04 to 0.9	25	57.8[b]	91, 92
nitrous oxide	283.1 to 323.1	0.02 to 1.3	120	15.7[a]	94
oxygen	283.1 to 373.1	0.02 to 9.2	424 (159)[c]	*12521*[b] (38.0)[b−c]	46, 90−94
propane	279.9 to 340.0	0.08 to 1.1	26	38.8[a]	55, 106
propene	279.9 to 340.0	0.09 to 1.2	23	43.8[a]	106
sulfur dioxide	298.2 to 333.2	0.02 to 0.2	92	22.8[a]	111, 123

[a] Uncertainty reported was calculated by using the *.vap file. [b] Uncertainty reported was calculated by using the *.energy file. [c] Values reported under brackets were reported without accounting calculated deviations with the refs 93 and/or 94 (see Supporting Information).

Table 7. Uncertainty, Ordered with Respect to the Ionic Liquid, of the COSMOthermX Model for the Prediction of Gas Solubilities in Ionic Liquids

ionic liquid	gas	number of data	100·RAD	ref
all ILs	all 15 selected gases	2998[a]	36.9[a]	43, 46, 50, 54, 55, 90−123
[C_2mim][BF_4]	SO_2, CO_2	21	26.0	54, 123
[C_2mim][C_2SO_4]	CO_2	21	36.8	102
[C_2mim][NTf_2]	CO_2, C_2H_6	62	15.5	50, 54, 113, 114
[C_2mmim][NTf_2]	CO_2	50	23.1	50
[C_2mim][PF_6]	CO_2	27	20.1	109
[C_4mim][$(CF_3SO_2)_3C$]	CO_2	21	10.4	101
[C_4mim][BF_4]	SO_2, CO_2, CO, O_2, N_2, H_2, Ar, CH_4, C_2H_6	401	29.2	43, 50, 90, 91, 94, 100, 101, 123
[C_4mim][C_1SO_4]	CO_2, CO, CH_4, H_2	128	76.7	107, 115, 116
[C_4mim][$N(CN)_2$]	CO_2	19	9.4	101
[C_4mim][NO_3]	CO_2	38	20.0	101, 102
[C_4mim][NTf_2]	SO_2, CO_2, N_2O, O_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8, C_4H_{10}	518	38.4	94, 106, 123
[C_4mim][OTf]	CO_2	28	15.9	101
[C_4mim][PF_6]	SO_2, CO_2, CO, O_2, N_2, H_2, Ar, CH_4, C_2H_4, C_2H_6	766[D]	45.3[a]	43, 54, 92, 94, 95, 97, 101−105, 123
[C_4mmim][BF_4]	CO_2	98	61.5	50
[C_4mmim][PF_6]	CO_2	124	73.1	50
[C_4mPyrro][NTf_2]	CO_2, C_2H_6	152	30.1	50, 114
[C_4Py][BF_4]	CO_2	21	10.7	102
[C_6mim][BF_4]	SO_2, CO_2	72	42.4	54, 100, 108, 123
[C_6mim][PF_6]	CO_2	76	11.8	54, 109
[C_6mim][NTf_2]	SO_2, CO_2, H_2, C_2H_6, C_3H_8	155	20.0	54, 55, 96, 98, 101, 111, 115
[C_6mmim][NTf_2]	CO_2	14	8.1	101
[C_6mpy][NTf_2]	SO_2	11	14.6	111
[C_8mim][BF_4]	CO_2	32	16.4	100, 102
[C_8mim][PF_6]	CO_2	11	12.5	102
[C_8mim][NTf_2]	CO_2	11	6.4	101
[N_{4441}][NTf_2]	CO_2, O_2	55	70.1	94
[$P_{1(4i)3}$][Tos]	CO_2, O_2	66	28.1	94

[a] Values were reported without accounting data from the references[93] (see Supporting Information).

al.[39] reported that hydrogen and nitrogen solubility in ILs increases with temperature, which is contrary to that reported previously.[91,98] COSMOthermX did not predict the trend reported by Finotello as shown in Figure 19; however, the nitrogen and hydrogen gas solubility in [C_2mim][NTf_2] was found to be within 20 % of the experimental data.

The calculated gas solubility of C_2H_4, C_3H_6, C_3H_8, C_4H_8, C_4H_{10}, N_2O, and SO_2 in [C_4mim][NTf_2] was also investigated as a function of pressure and compared with the available experimental data. The vapor pressures for each of these gases were determined using the Antoine/Wagner correlations, and thus this group of gases serves to determine the accuracy of the activity calculation. Figure 20 shows that COSMOthermX provides the correct trend for the effect of the solute on gas solubility in ILs as a function of pressure, with the solubility increasing with pressure, as expected. A comparison of COSMOthermX gas solubility calculations with the data from Lee and Outcalt[106] provides a RAD of 44 %, 38 %, 25 %, and 19 % for C_3H_6, C_3H_8, C_4H_8, and C_4H_{10} in [C_4mim][NTf_2], respectively. Similar RADs were obtained for C_2H_4 (45 %) and

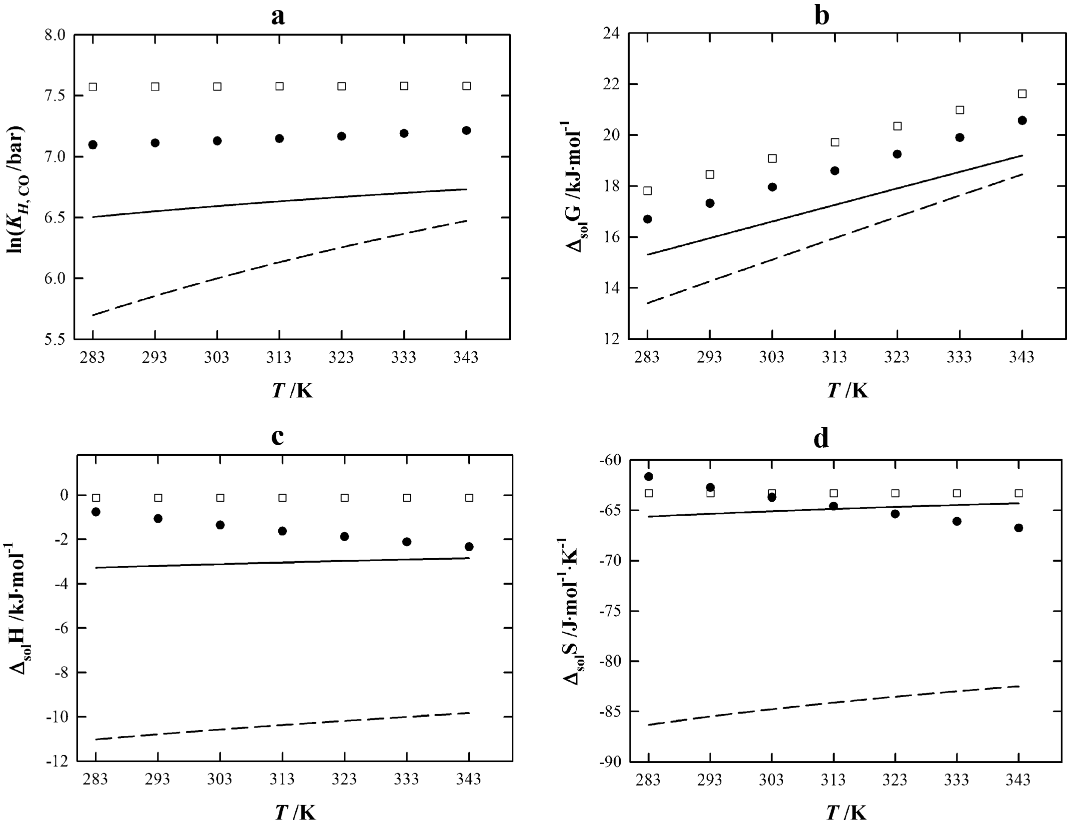

Figure 22. Henry's constant of CO in [C_4mim][PF_6]: a, their thermodynamic properties of solution; b, the partial molar Gibbs energy of solution; c, the partial molar enthalpy of solution; d, the partial molar entropy of solution - of the CO in [C_4mim][PF_6] as a function of temperature: □, from Kumelan et al.;[46] ●, from Jacquemin et al.;[92] the solid and the dashed lines represent COSMOthermX calculations by using the *.vap file by using the new Antoine coefficients reported in Table 3 and the *.energy file (equivalent to data calculated by using the COSMOthermX Henry's Law coefficients option), respectively.

N_2O (18 %) in [C_4mim][NTf_2] when compared with data reported by Anthony et al.[94] In these cases, the largest deviations were obtained at high pressure for C_2H_4, C_3H_6, and N_2O.

Overview of the COSMOthermX Gas Solubility Calculations in IL. With the exception of the incorrect description of the effect of methyl substitution at the C(2) position of the 1-alkyl-3-methylimidazolium cations on the gas solubility in IL, the incorrect trend for ammonium and triflate based ILs, and the utilization of the energy data to obtain a more accurate result regarding the literature for CO_2, COSMOthermX has been shown to obtain qualitative gas solubility data in ILs without prior knowledge of any of the ILs physical properties as shown in the parity plot in Figure 21. Tables 6 and 7 summarize the calculated uncertainties for the gases and ionic liquids studied, respectively, with the overall uncertainty calculated between the calculated and experimental data found to be 43 %. As found for the solubility in water, the utilization of the new Antoine coefficients (described in Table 3) for the solubility of CO in [C_4mim][PF_6][46,92] leads to better results than those calculated using the energy value, as shown in Figure 22. Figure 22 also shows that the calculation predicts an exothermic solvation process ($\Delta H_{\mathrm{sol}} = -3.2\ \mathrm{kJ \cdot mol^{-1}}$ at 298.15 K) which is in qualitative agreement with the reported experimental values as is described in the ($\Delta H_{\mathrm{sol}} = -0.11\ \mathrm{kJ \cdot mol^{-1}}$)[46] and ($\Delta H_{\mathrm{sol}} = -1.2\ \mathrm{kJ \cdot mol^{-1}}$)[92] at 298.15 K. As described for water, the COSMOthermX Henry's Law coefficient option gives exactly the same results as those calculated by using the energy value. However, since this value results in poor predictions, the use of the new Antoine constants discussed above was used to improve the estimation of this coefficient.

The solvation properties from the CO_2 solubility in the [C_4mim][PF_6] are shown in Figure 23. As found for the case of molecular solvents, the COSMOthermX prediction of the CO_2 solubility in ILs and, vide supra, their solvation properties/Henry's Law coefficients are improved by using the energy value rather than the vapor pressure data (by comparison of these absolute average deviations described in the Table 6). However, despite the improvement, as found for water, it must be noted that COSMOthermX was found to be unable to predict quantitative solvation properties.

The lack of predictability obtained for the triflate and ammonium based ILs as well as the effect of the methyl substitution at the C(2) position in imidazolium based ionic liquids could evolve from the σ-profile definitions of these ions. Recently, Palomar et al.[126] suggested that the effect of counterion interactions on the σ-profile of IL compounds may not adequately describe an IL by defining the ionic medium with two separate COSMO files, i.e., separate cation and anion. In this case, the gas solubility calculation may be improved by defining an IL with only one COSMO file based on the ion pair. This will be influenced by the choice of IL conformer within the ion pairs. A preliminary investigation into the effect of different ion pair conformers within the same IL, as determined from molecular dynamics simulations, on the σ-profiles indicates that COSMOthermX predicts a wide range of gas solubility values which spans the experimental values. However, by using a population weighted average based on the relative energies of each ion pair conformer and a Boltzmann distribution, it is possible to get a close prediction of the experimental data from the COSMOthermX calculation. This

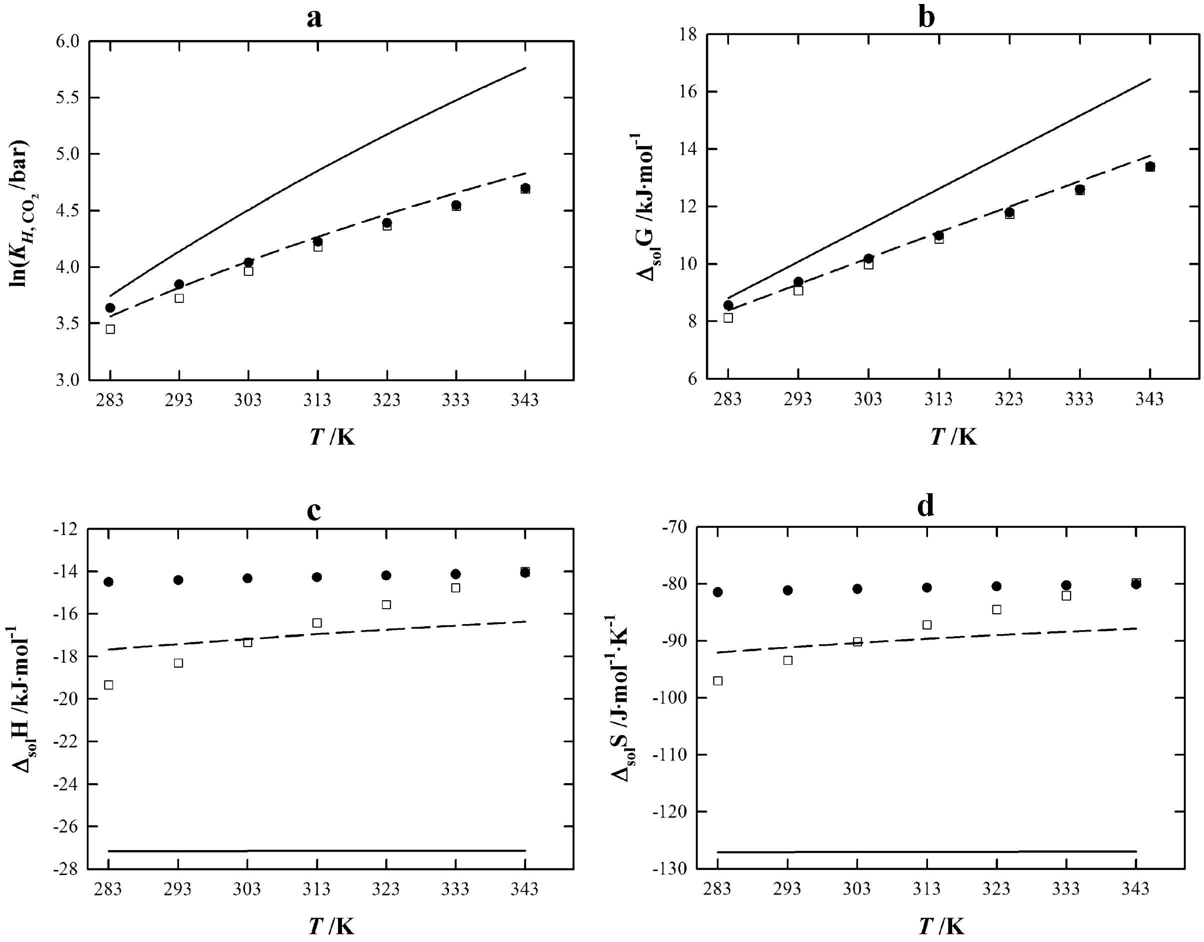

Figure 23. Henry's constant of CO_2 in [C_4mim][PF_6]: a, their thermodynamic properties of solution; b, the partial molar Gibbs energy of solution; c, the partial molar enthalpy of solution; d, the partial molar entropy of solution - of the CO in [C_4mim][PF_6] as a function of temperature: □, from Kamps et al.;[103] ●, from Jacquemin et al.;[92] the solid and the dashed lines represent COSMOthermX calculations by using the *.vap file by using the new Antoine coefficients reported in Table 3 and the *.energy file (equivalent to data calculated by using the COSMOthermX Henry's Law coefficients option), respectively.

requires further investigation to understand the generality of this approach for improving the current gas solubility prediction in COSMOthermX.

Comparing this work with previous studies using the COSMO-RS method to predict properties of ionic liquids[60,74,127,128] shows that there is a general agreement that it has the potential to be used as a priori qualitative prediction in selecting and refining suitable ionic liquids for specific tasks. However, there are still some significant limitations which are predominantly due to the definition of the gas phase (solute) and the descriptors used to define the solvent phase. Nevertheless, by neglecting the presence of the solvent in the gas phase due to the very low vapor pressure of the IL, the description of the solvent and solute phases should provide an opportunity for better predictability than for the case of volatile molecular solvents.

Conclusions

Ionic liquids have significant potential to be developed as "green" solvents for chemical processes as well as being employed in gas separations, and therefore, the need for the development of preliminary selection tools capable of assessing or scanning suitable ionic liquids for specific applications with minimal information available has increased. Using theoretical prediction capabilities of COSMOthermX which are based on the COSMO-RS thermodynamic model, the solubility of several gases in ionic liquids were evaluated. A systematic assessment of the predictive capability of COSMOthermX for calculating gas solubility was performed in stages, initially predicting several gas solubilities in selected organic solvents and further evaluating COSMOthermX for the calculation of the solvation properties of several gases in water as a function of temperature. Using these tools, it was possible to predict the gas solubility in ionic liquids and compare these with reported experimental data collected from the IUPAC database. Of the two components required for a gas solubility prediction (vapor pressure and activity), accurate vapor pressure determination would appear to be the most difficult to obtain. When the system temperature (T) is below the critical temperature (T_c), the general trend is that better predictions are obtained for gases when using experimental correlations such as the Antoine or Wagner equation, while the energy value is preferred when $T \gg T_c$. As with many rules, a number of exceptions were found, for example, the case of CO_2 and more strikingly for CO where new correlations were found to be necessary. Without accurate values for pseudovapor pressures at $T \gg T_c$, it is impossible to state, at this stage, the accuracy of the activity model for any system be it ionic liquid or not. However, it has been demonstrated that COSMOthermX is able to qualitatively predict the gas solubility in ionic liquids by describing the correct gas solubility order of magnitude when compared with the experimental data.

From a chemical engineering perspective, this information is practical in terms of understanding the trend of gas solubility in ionic liquid as a function of anion and cation, as well as the choice of gases with ionic liquids and its solubility. Furthermore, the qualitative prediction of COSMOthermX may be used to reduce the range of preliminary experimental measurements necessary to examine suitable ionic liquids prior to detailed experimental measurements of a specific task of the ionic liquid.

Acknowledgment

P. Nancarrow (QUB) and F. Eckert (COSMOlogic) are acknowledged for useful discussions.

Supporting Information Available:

Additional Supporting Information includes spreadsheets of the reported gas solubility data in molecular solvents and ILs, used as a comparison with the predicted values, as well as the corresponding solvation property information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review November 13, 2008. Accepted March 17, 2009. The authors would like to thank the UK EPSRC under a portfolio partnership for financially supporting this work. N.A.M. acknowledges studentship funding from Petronas.

JE800857X