Non-ideality of Solutions of NH_3, SO_2, and H_2S in Ionic Liquids and the Prediction of Their Solubilities Using the Flory−Huggins Model

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The non-ideality of solutions of light compounds, such as SO_2, NH_3, and H_2S, in ionic liquids (ILs) is studied here using experimental vapor−liquid equilibrium (VLE) data previously published. The data available for systems of ILs with SO_2, NH_3, and H_2S show that these systems present negative deviations to the ideality in the liquid phase and that these deviations are dominated by entropic effects. It is shown here that, for the solutions of SO_2 and NH_3 in ILs, the deviations from ideality and the gas solubility can be predicted using the Flory−Huggins model. For H_2S, a positive deviation to the non-ideality that arises from the enthalpic effects somewhat decreases the quality of the description of the experimental data by the Flory−Huggins model predictions.

Introduction

Sulfur compounds, including hydrogen sulfide (H_2S) and sulfur dioxide (SO_2), frequently appear as contaminants in process streams in the production, processing, and refining of fossil fuels.[1,2] Gasification of heavy residual oil, petroleum coke, coal feedstocks, and hydrocarbons is increasing in importance, and the key gas separation is the selective removal of contaminants, such as H_2S, COS, NH_3, and SO_2, from the synthesis gas. In addition, the presence of acid gases (COS, H_2S, and CO_2) and other impurities require the syngas to undergo a gas treatment process to make it suitable for downstream use. The solubility of gases, such as SO_2, NH_3, and H_2S, in solvents of low volatility or non-volatile is thus highly relevant for many technological applications.

Ammonia is widely used in many industrial sectors, such as fertilizer, explosive, and chemical productions, being one of the most highly produced chemicals in the world. Because of its interesting thermodynamic properties, industrial refrigeration systems are one of the most important industrial applications for NH_3. Moreover, contrary to what is observed for most refrigerants, ammonia is considered to be efficient, economical, and environmental friendly, because it does not deplete the ozone layer or contribute to global warming.

Composed of large organic cations and organic or inorganic anions, ionic liquids (ILs) became one of the fastest growing areas of research for chemists and engineers. The possibility of tuning the IL properties make these compounds viable candidates for a wide range of processes and products. Among the foreseeable applications in multiple fields, their use in oil and fuel desulfurization processes[3−5] and separation and capture of sour gases[6−8] are some of the most interesting.

The large solubility of gases in ILs has been the object, for the past decade, of discussion among the scientific community, concerning the solvation mechanism. Several authors have rationalized that the high gas solubility in ILs was due to specific solute−solvent interactions, and some have even evidenced chemical absorption.[6,9−20] Nonetheless, the information currently available is not enough to support the

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(1) Bashkova, S.; Baker, F. S.; Wu, X.; Armstrong, T. R.; Schwartz, V. Activated carbon catalyst for selective oxidation of hydrogen sulphide: On the influence of pore structure, surface characteristics, and catalytically active nitrogen. *Carbon* **2007**, *45*, 1354–1363.
(2) Mochida, I.; Choi, K. An overview of hydrodesulfurization and hydrodenitrogenation. *J. Jpn. Pet. Inst.* **2004**, *47*, 145–163.
(3) Zhao, D.; Liu, R.; Wang, J.; Liu, B. Photochemical oxidation−ionic liquid extraction coupling technique in deep desulfurization of light oil. *Energy Fuels* **2008**, *22*, 1100–1103.

(4) Wang, J.; Zhao, D.; Li, K. Oxidative desulfurization of dibenzothiophene catalyzed by Brönsted acid ionic liquid. *Energy Fuels* **2009**, *23*, 3831–3834.
(5) Schmidt, R. [bmim]AlCl₄ ionic liquid for deep desulfurization of real fuels. *Energy Fuels* **2008**, *22*, 1774–1778.
(6) Shiflett, M. B.; Yokozeki, A. Separation of carbon dioxide and sulfur dioxide using room-temperature ionic liquid [bmim][MeSO₄]. *Energy Fuels* **2010**, *24*, 1001–1008.
(7) Yokozeki, A.; Shiflett, M. B. Separation of carbon dioxide and sulfur dioxide gases using room-temperature ionic liquid [hmim][Tf₂N]. *Energy Fuels* **2009**, *23*, 4701–4708.
(8) Heintz, Y. J.; Sehabiague, L.; Morsi, B. I.; Jones, K. L.; Luebke, D. R.; Pennline, H. W. Hydrogen sulfide and carbon dioxide removal from dry fuel gas streams using an ionic liquid as a physical solvent. *Energy Fuels* **2009**, *23*, 4822–4830.
(9) Andanson, J.; Jutz, F.; Baiker, A. Supercritical CO₂/ionic liquid systems: What can we extract from infrared and raman spectra? *J. Phys. Chem. B* **2009**, *113*, 10249–10254.
(10) Ando, R. A.; Siqueira, L. J. A.; Bazito, F. C.; Torresi, R. M.; Santos, P. S. The sulfur dioxide-1-butyl-3-methylimidazolium bromide interaction: Drastic changes in structural and physical properties. *J. Phys. Chem. B* **2007**, *111*, 8717–8719.
(11) Siqueira, L. J. A.; Ando, R. A.; Bazito, F. F. C.; Torresi, R. M.; Santos, P. S.; Ribeiro, M. C. C. Shielding of ionic interactions by sulfur dioxide in an ionic liquid. *J. Phys. Chem. B* **2008**, *112*, 6430–6435.
(12) Huang, J.; Riisager, A.; Berg, R. W.; Fehrmann, R. Tuning ionic liquids for high gas solubility and reversible gas sorption. *J. Mol. Catal. A: Chem.* **2008**, *279*, 170–176.
(13) Anthony, J.; Maginn, E.; Brennecke, J. Solubilities and thermodynamic properties of gases in the ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate. *J. Phys. Chem. B* **2002**, *106*, 7315–7320.
(14) Bhargava, B. L.; Balasubramanian, S. Insights into the structure and dynamics of a room-temperature ionic liquid: *Ab initio* molecular dynamics simulation studies of 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) and the [bmim][PF₆]−CO₂ mixture. *J. Phys. Chem. B* **2007**, *111*, 4477–4487.

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proposed mechanisms. Ando et al.[10] and Siqueira et al.[11] have shown no evidence of any interaction between the IL and the SO_2 molecule, by Raman spectroscopy and molecular dynamics simulations, apart from the shift to low wave numbers of the Raman band corresponding to S–O symmetric stretching in comparison to pure SO_2. Huang et al.[12] reported weak interactions or no chemical bonding at all between the solvent and the solute SO_2 molecule in the SO_2-saturated ILs, no significant change of the frequencies of the bands originating from the pure ILs, and no significant proton shift in the ^{1}H nuclear magnetic resonance (NMR) spectra of the SO_2-saturated ILs. Andanson et al.,[9] using infrared (IR) and Raman spectra, showed that, despite the shift of the PF_6^- anion because of stretching, the structure of the ILs does not change significantly. This evidence suggest that, similar to what was found for the solvation of CO_2 in ILs,[21] the mechanism responsible for the solvation of these gases in ILs is essentially physical. Very few cases of chemical complexation of gases with ILs have been reported until now. The most important are 1-butyl-3-methylimidazolium acetate[15,22] and the ILs used for storage of BF_3 and PH_3 reported by Tempel et al.[23]

In the following of a previous work,[21] the mechanism behind the solubility of light compounds, such as NH_3, SO_2, and H_2S, in ILs, is investigated here by analyzing their deviations to ideality in the liquid phase. This approach allows us not only to achieve a deeper understanding of the mechanism behind the solvation of these gases in ILs but also to establish models that can be used to predict the solubility of gases in ILs.

Non-ideality of NH_3 and SO_2 Solutions in ILs

Experimental vapor–liquid equilibrium (VLE) data for systems of ILs with SO_2 and NH_3 are scarce, and high discrepancies (up to 35%) between authors are observed. For IL + NH_3 systems, only data by Yokozeki et al.[24] and Li et al.[25] are available for a handful of ILs, while for IL + SO_2, only data by Anderson et al.,[26] Shiflett et al.,[27] and Yuan et al.[28] are available.

Table 1. SO_2, NH_3, and H_2S Properties Needed for the PR EoS[29]

gas	T_c (K)	P_c (MPa)	ω
SO_2	430.75	7.88	0.245
NH_3	405.65	11.28	0.253
H_2S	373.53	8.96	0.094

The VLE at low and moderate pressures for these systems can be described by a $\gamma-\phi$ approach

$$\phi_{gas} y_{gas} p = x_{gas} \gamma_{gas} p_{gas}^{\sigma} \tag{1}$$

where, in the case of a non-volatile solvent, such as the ILs, $y_{gas} = 1$. The vapor pressure of the gas, p_{gas}^{σ}, was estimated using the correlations reported at the Design Institute for Physical Properties (DIPPR) database.[29]

On these systems, the liquid-phase non-ideality results from not only differences in the energetic interactions between the molecules, as described by the residual contribution to the Gibbs free energy, but also entropic effects because of their size and shape differences, the combinatorial contribution, as summarized by

$$G^E = G^E_{comb} + G^E_{residual} \tag{2}$$

The entropic effects will always have a negative contribution to the non-ideality that, in terms of activity coefficients, can be described by the Flory–Huggins model[30–32]

$$\ln(\gamma_{gas}^{comb}) = \ln \frac{\varphi_{gas}}{x_{gas}} + \left(1 - \frac{\varphi_{gas}}{x_{gas}}\right) \tag{3}$$

where

$$\varphi_{gas} = \frac{x_{gas} V_{m_{gas}}}{x_{gas} V_{m_{gas}} x_{IL} V_{m_{IL}}} \tag{4}$$

is the volume fraction of the gas. The molar volumes of the ILs were derived from their densities,[33–38] and those of the gas were obtained from the DIPPR database.[29]

The non-ideality of the vapor phase is described by the fugacity coefficient, ϕ_{gas}, that was estimated here using the Peng–Robinson (PR) equation of state (EoS).[39] The critical properties used for the gaseous compounds are listed in Table 1.

If only the combinatorial contributions to the non-ideality are taken into account, eq 1 will become

$$p = \frac{x_{gas} \exp\left(\ln \frac{\varphi_{gas}}{x_{gas}} + \left(1 - \frac{\varphi_{gas}}{x_{gas}}\right)\right) p_{gas}^{\sigma}}{\phi_{gas}} \tag{5}$$

Figures 1 and 2 show the VLE phase diagrams for the systems of SO_2 and NH_3 with ILs. The full lines were calculated using eq 5, while the dashed lines, corresponding to the behavior of an ideal liquid phase, were estimated using eq 1, with the activity coefficient of the gas in the liquid phase being
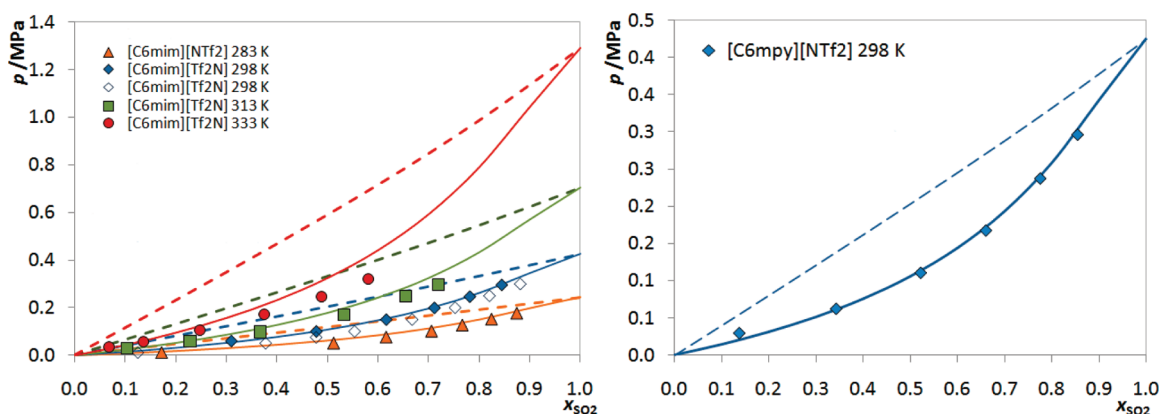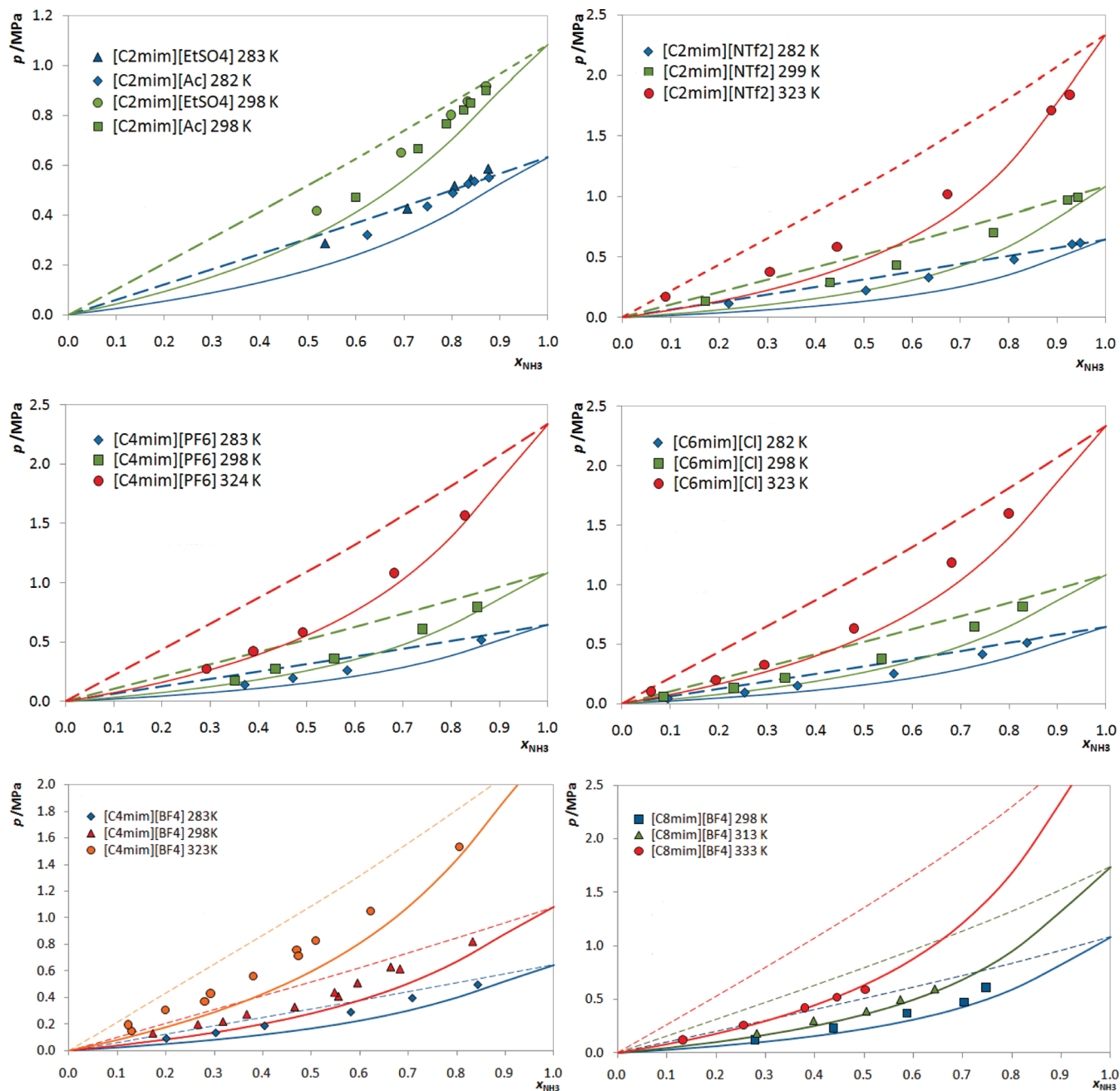

Figure 1. Pressure versus SO_2 molar composition diagram for the systems SO_2 + IL.[7,26,27] The solid lines represent the Flory–Huggins model, and the dashed lines represent the ideal behavior described by Raoult's law.

Figure 2. Pressure versus NH_3 molar composition diagram for the systems NH_3 + IL.[24,25] The solid lines represent the Flory–Huggins model, and the dashed lines represent the ideal behavior described by Raoult's law.

$\gamma_{gas} = 1$. They show the experimental VLE data for these systems as a non-ideal behavior with strong negative deviations that are well-described by the Flory–Huggins model. The average deviations in the equilibrium pressure predicted by the model, presented in Table 2 (extended pressure

deviations as a function of SO_2 and NH_3 mole fractions and temperature are available in the Supporting Information), show that the Flory–Huggins equation is able to describe the

(15) Carvalho, P. J.; Álvarez, V. H.; Schröder, B.; Gil, A. M.; Marrucho, I. M.; Aznar, M.; Santos, L. M. N. B. F.; Coutinho, J. A. P. Specific solvation interactions of CO_2 on acetate and trifluoroacetate imidazolium based ionic liquids at high pressures. *J. Phys. Chem. B* 2009, *113*, 6803–6812.

(16) Deschamps, J.; Costa Gomes, M. F.; Padua, A. A. H. Molecular simulation study of interactions of carbon dioxide and water with ionic liquids. *ChemPhysChem* 2004, *5*, 1049–1052.

(17) Kanakubo, M.; Umecky, T.; Hiejima, Y.; Aizawa, T.; Nanjo, H.; Kameda, Y. Solution structures of 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid saturated with CO_2: Experimental evidence of specific anion–CO_2 interaction. *J. Phys. Chem. B* 2005, *109*, 13847–13850.

(18) Pison, L.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Padua, A. A. H.; Costa Gomes, M. F. Interactions of fluorinated gases with ionic liquids: Solubility of CF_4, C_2F_6, and C_3F_8 in trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide. *J. Phys. Chem. B* 2008, *112*, 12394–12400.

(19) Pomelli, C.; Chiappe, C.; Vidis, A.; Laurenczy, G.; Dyson, P. Influence of the interaction between hydrogen sulfide and ionic liquids on solubility: Experimental and theoretical investigation. *J. Phys. Chem. B* 2007, *111*, 13014–13019.

(20) Ren, S.; Hou, Y.; Wu, W.; Liu, Q.; Xiao, Y.; Chen, X. Properties of ionic liquids absorbing SO_2 and the mechanism of the absorption. *J. Phys. Chem. B* 2010, *114*, 2175–2179.

(21) Carvalho, P. J.; Coutinho, J. A. P. On the non-ideality of CO_2 solutions in ionic liquids and other low volatile solvents. *J. Phys. Chem. Lett.* 2010, *1*, 774–780.
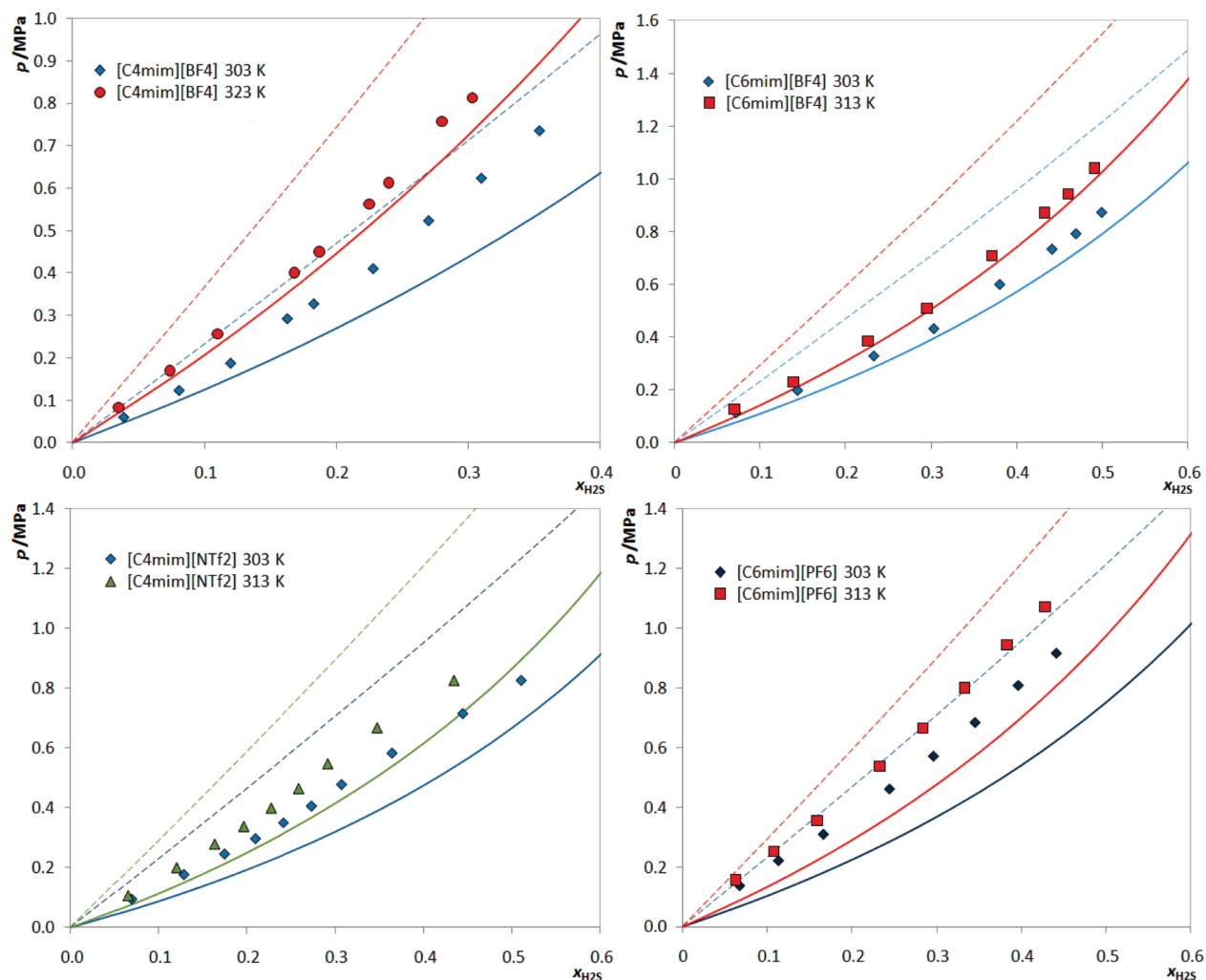
Figure 3. Pressure versus H_2S molar composition diagram for the systems H_2S + IL.[40,41] The solid lines represent the Flory–Huggins model, and the dashed lines represent the ideal behavior described by Raoult's law.

Table 2. Average Pressure Deviations, $AD_{\Delta p}$, between the Available VLE[25−27,40−42] and the Equilibrium Pressure Predicted by the Flory–Huggins Model, as a Function of the Temperature, for the IL + SO_2, IL + NH_3, and IL + H_2S Systems

T (K)	$AD_{\Delta p}$	T (K)	$AD_{\Delta p}$	T (K)	$AD_{\Delta p}$	T (K)	$AD_{\Delta p}$	T (K)	$AD_{\Delta p}$	T (K)	$AD_{\Delta p}$
SO_2 + [C_6mim][NTf_2][26]		NH_3 + [C_8mim][BF_4][25]		NH_3 + [C_2mim][$EtSO_4$][42]		NH_3 + [C_2mim][Ac][42]		NH_3 + [C_4mim][BF_4][42]	
298	−0.032	293	0.03	283	−0.1	283	−0.1	282	−0.06
313	−0.042	298	0.0004	298	−0.1	298	−0.1	298	−0.08
333	0.038	313	0.05	NH_3 + [C_4mim][PF_6][42]		NH_3 + [C_4mim][BF_4][25]		324	−0.15
SO_2 + [C_6mpy][NTf_2][26]		323	0.12	283	−0.05	293	−0.04	NH_3 + [C_2mim][BF_4][25]	
298	0.002	333	0.09	298	−0.05	298	−0.11	293	−0.11
SO_2 + [C_6mim][NTf_2][27]		NH_3 + [C_2mim][NTf_2][42]		325	−0.05	313	−0.06	298	−0.13
283	0.009	283	−0.09	NH_3 + [C_6mim][BF_4][25]		323	−0.15	313	−0.13
298	0.026	299	−0.13	293	−0.06	333	−0.06	323	−0.15
323	0.038	323	−0.08	298	−0.07	NH_3 + [C_6mim][Cl][42]		333	−0.17
348	0.059	H_2S + [C_4mim][BF_4][41]		313	−0.06	283	−0.05	H_2S + [C_4mim][NTf_2][41]	
H_2S + [C_6mim][BF_4][40]		303	−0.09	323	−0.006	298	−0.07	303	−0.13
303	−0.07	313	−0.08	333	0.03	324	−0.11	313	−0.11
313	−0.06	323	−0.06	H_2S + [C_6mim][PF_6][40]					
				303	−0.20				
				313	−0.20				

VLE data. The capacity of the approach proposed here to describe the VLE for these systems suggests that the residual contribution to the excess Gibbs energy is very small, although positive, which implies that there is a small misfit in the

solute–solvent interactions relative to the solute–solute and solvent–solvent interactions that is not enough to energetically compensate for the interactions that are destroyed upon mixing.

(22) Shiflett, M. B.; Kasprzak, D. J.; Junk, C. P.; Yokozeki, A. Phase behavior of {carbon dioxide + [bmim][ac]} mixtures. *J. Chem. Thermodyn.* **2008**, *40*, 25–31.

(23) Tempel, D.; Henderson, P.; Brzozowski, J.; Pearlstein, R.; Cheng, H. High gas storage capacities for ionic liquids through chemical complexation. *J. Am. Chem. Soc.* **2007**, *130*, 400–401.

The most striking result from this analysis is that, despite the major differences in the chemical nature of the solvents studied here and the interactions of their molecules in pure state, the non-ideality of the SO_2 and NH_3 in solution is remarkably low and essentially driven by entropic effects. Analogous to what was previously reported for CO_2,[21] these observations suggest that, by increasing the size difference between SO_2 or NH_3 and the IL solvent, the solubility will increase as the entropic contribution to the solution non-ideality increases. This is in agreement with the results of Huang et al.[12] that have reported weak interactions or no chemical bonding at all between the solvent and the solute SO_2 molecule in the SO_2-saturated ILs.

Non-ideality of H₂S Solutions in ILs

The approach described in the previous section was also applied to IL + H_2S systems. With the exception of some data of questionable quality that are not in agreement with results from other authors, a fair agreement is observed between the experimental and predicted Flory–Huggins equilibrium pressure, with maximum average pressure deviations of 0.2 MPa, as reported in Table 2 (extended pressure deviations as a function of H_2S mole fractions and temperature are available in the Supporting Information). For the H_2S systems, the Flory–Huggins model is no longer able to produce a perfect description of the VLE, and the experimental data reported in Figure 3 fall between the dashed line of an ideal solution and the full line predicted by the Flory–Huggins model. The only exception within the available data is the $[C_6mim][BF_4]$ system,[40] where the model seems to provide a very good description of the system. The results shown in Figure 3 suggest that, although the solubility of H_2S in ILs is still dominated by entropic factors, the residual contributions for the excess Gibbs energy are positive and more important than those observed for SO_2 and NH_3. It clearly shows that the interactions between H_2S and the ILs for which data are available are not favorable. An adequate model to describe these systems must take into account the residual contributions to the liquid-phase non-ideality.

Conclusions

This study shows that the solubility of light compounds, such as SO_2, NH_3, and H_2S, in ILs is driven exclusively or predominantly by entropic effects. For systems where the residual contributions are negligible, such as for NH_3- and SO_2-containing systems, a $\gamma-\phi$ approach using the Flory–Huggins model to describe the liquid-phase non-ideality can provide a very good prediction of the VLE phase diagrams. For acid gases, such as H_2S, the residual contribution to the excess Gibbs energy presents a non-negligible positive contribution that reduces the quality of the predictions by this approach. It is shown that, despite its limitations for some systems, the Flory–Huggins model is a powerful tool to predict the solubility of light compounds in ILs.

Supporting Information Available: Deviations, Δp, between the available VLE and the equilibrium pressure predicted by the Flory–Huggins model, as a function of SO_2 mole fractions and temperature, for the IL + SO_2 systems, (Table S1) as a function of NH_3 mole fractions and temperature, for the IL + NH_3 systems (Table S2), and as a function of H_2S mole fractions and temperature, for the IL + H_2S systems (Table S3). This material is available free of charge via the Internet at http://pubs.acs.org.

(24) Yokozeki, A.; Shiflett, M. B. Ammonia solubilities in room-temperature ionic liquids. *Ind. Eng. Chem. Res.* **2007**, *46*, 1605–1610.

(25) Li, G.; Zhou, Q.; Zhang, X.; Wang, L.; Zhang, S.; Li, J. Solubilities of ammonia in basic imidazolium ionic liquids. *Fluid Phase Equilib.* **2010**, *297*, 34–39.

(26) Anderson, J.; Dixon, J.; Maginn, E.; Brennecke, J. Measurement of SO_2 solubility in ionic liquids. *J. Phys. Chem. B* **2006**, *110*, 15059–15062.

(27) Shiflett, M. B.; Yokozeki, A. Chemical absorption of sulfur dioxide in room-temperature ionic liquids. *Ind. Eng. Chem. Res.* **2010**, *49*, 1370–1377.

(28) Yuan, X.; Zhang, S.; Lu, X. Hydroxyl ammonium ionic liquids: Synthesis, properties, and solubility of SO_2. *J. Chem. Eng. Data* **2007**, *52*, 596–599.

(29) Design Institute for Physical Properties (DIPPR). *DIPPR 801 Database*; Brigham Young University: Provo, UT; 1998.

(30) Flory, P. J. Thermodynamics of high polymer solutions. *J. Chem. Phys.* **1941**, *9*, 660–661.

(31) Prausnitz, J. M.; Lichtenthaler, R. N.; Gomes de Azevedo, E. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice Hall International Series: New York, 1999.

(32) Coutinho, J. A. P.; Andersen, S. I.; Stenby, E. H. Evaluation of activity coefficient models in prediction of alkane solid–liquid equilibria. *Fluid Phase Equilib.* **1995**, *103*, 23–39.

(33) Gardas, R. L.; Freire, M. G.; Carvalho, P. J.; Marrucho, I. M.; Fonseca, I. M. A.; Ferreira, A. G. M.; Coutinho, J. A. P. $P\rho T$ measurements of imidazolium based ionic liquids. *J. Chem. Eng. Data* **2007**, *52*, 1881–1888.

(34) Gomes de Azevedo, R.; Esperanca, J. M. S. S.; Szydlowski, J.; Visak, Z. P.; Pires, P. F.; Guedes, H. J. R.; Rebelo, L. P. N. Thermophysical and thermodynamic properties of ionic liquids over an extended pressure range: [bmim][NTf₂] and [hmim][NTf₂]. *J. Chem. Thermodyn.* **2005**, *37*, 888–899.

(35) Gardas, R. L.; Freire, M. G.; Carvalho, P. J.; Marrucho, I. M.; Fonseca, I. M. A.; Ferreira, A. G. M.; Coutinho, J. A. P. High pressure densities and derived thermodynamic properties of imidazolium based ionic liquids. *J. Chem. Eng. Data* **2007**, *52*, 80–88.

(36) Tomé, L. I. N.; Carvalho, P. J.; Freire, M. G.; Marrucho, I. M.; Fonseca, I. M. A.; Ferreira, A. G. M.; Coutinho, J. A. P.; Gardas, R. L. Measurements and correlation of high-pressure densities of imidazolium-based ionic liquids. *J. Chem. Eng. Data* **2008**, *53*, 1914–1921.

(37) Gómez, E.; González, B.; Domínguez, A.; Tojo, E.; Tojo, J. Dynamic viscosities of a series of 1-alkylimidazolium chloride ionic liquids and their binary mixtures with water at several temperatures. *J. Chem. Eng. Data* **2006**, *51*, 696–701.

(38) Muhammad, A.; Abdul Mutalib, M.; Wilfred, C.; Murugesan, T.; Shafeeq, A. Thermophysical properties of 1-hexyl-3-methyl imidazolium based ionic liquids with tetrafluoroborate, hexafluorophosphate and bis(trifluoromethylsulfonyl)imide anions. *J. Chem. Thermodyn.* **2008**, *40*, 1433–1438.

(39) Peng, D.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.

(40) Rahmati-Rostami, M.; Ghotbi, C.; Hosseini-Jenab, M.; Ahmadi, A. N.; Jalili, A. H. Solubility of H_2S in ionic liquids [hmim][PF₆], [hmim][BF₄], and [hmim][Tf₂N]. *J. Chem. Thermodyn.* **2009**, *41*, 1052–1055.

(41) Jalili, A. H.; Rahmati-Rostami, M.; Ghotbi, C.; Hosseini-Jenab, M.; Ahmadi, A. N. Solubility of H_2S in ionic liquids [bmim][PF₆], [bmim][BF₄], and [bmim][Tf₂N]. *J. Chem. Eng. Data* **2009**, *54*, 1844–1849.

(42) Yokozeki, A.; Shiflett, M. B. Vapor–liquid equilibria of ammonia + ionic liquid mixtures. *Appl. Energy* **2007**, *84*, 1258–1273.