Non-ideality of Solutions of NH\textsubscript{3}, SO\textsubscript{2}, and H\textsubscript{2}S in Ionic Liquids and the Prediction of Their Solubilities Using the Flory–Huggins Model

Pedro J. Carvalho and João A. P. Coutinho*  
Departamento de Química, Centro de Investigação em Materiais Cerâmicos e Compositos (CICECO), Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

Received July 29, 2010. Revised Manuscript Received October 25, 2010

The non-ideality of solutions of light compounds, such as SO\textsubscript{2}, NH\textsubscript{3}, and H\textsubscript{2}S, 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\textsubscript{2}, NH\textsubscript{3}, and H\textsubscript{2}S 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\textsubscript{2} and NH\textsubscript{3} in ILs, the deviations from ideality and the gas solubility can be predicted using the Flory–Huggins model. For H\textsubscript{2}S, 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\textsubscript{2}S) and sulfur dioxide (SO\textsubscript{2}), frequently appear as contaminants in process streams in the production, processing, and refining of fossil fuels.\textsuperscript{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\textsubscript{2}S, COS, NH\textsubscript{3}, and SO\textsubscript{2}, from the synthesis gas. In addition, the presence of acid gases (COS, H\textsubscript{2}S, and CO\textsubscript{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\textsubscript{2}, NH\textsubscript{3}, and H\textsubscript{2}S, 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\textsubscript{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\textsuperscript{3–5} and separation and capture of sour gases\textsuperscript{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.\textsuperscript{6,9} Nonetheless, the information currently available is not enough to support the

(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][PF\textsubscript{6}]) and the [bmim][PF\textsubscript{6}]/CO\textsubscript{2} mixture. J. Phys. Chem. B 2007, 111, 4477–4487.
proposed mechanisms. Ando et al.\textsuperscript{10} and Siqueira et al.\textsuperscript{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.\textsuperscript{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.,\textsuperscript{9} using infrared (IR) and Raman spectra, showed that, despite the shift of the PF$_6$-

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

$$\phi_{\text{gas}} = y_{\text{gas}} p = x_{\text{gas}} y_{\text{gas}} p'_{\text{gas}}$$

where, in the case of a non-volatile solvent, such as the ILs, $y_{\text{gas}} = 1$. The vapor pressure of the gas, $p'_{\text{gas}}$, was estimated using the correlations reported at the Design Institute for Physical Properties (DIPPR) database.\textsuperscript{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

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

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\textsuperscript{30–32}

$$\ln y_{\text{comb}} = \ln \frac{\phi_{\text{gas}}}{x_{\text{gas}}} + \left(1 - \frac{\phi_{\text{gas}}}{x_{\text{gas}}} \right)$$

where

$$\phi_{\text{gas}} = \frac{x_{\text{gas}} V_{m_{\text{gas}}}}{x_{\text{gas}} V_{m_{\text{gas}}} + V_{m_{\text{IL}}}}$$

is the volume fraction of the gas. The molar volumes of the gases were derived from their densities,\textsuperscript{33–38} and those of the ILs were obtained from the DIPPR database.\textsuperscript{29}

The non-ideality of the vapor phase is described by the fugacity coefficient, $\phi_{\text{gas}}$, that was estimated here using the Peng–Robinson (PR) equation of state (EoS).\textsuperscript{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

$$p = \frac{x_{\text{gas}} \exp \left( \ln \frac{\phi_{\text{gas}}}{x_{\text{gas}}} + \left(1 - \frac{\phi_{\text{gas}}}{x_{\text{gas}}} \right) \right) p'_{\text{gas}}}{\phi_{\text{gas}}}$$

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

<table>
<thead>
<tr>
<th>gas</th>
<th>$T_c$ (K)</th>
<th>$P_c$ (MPa)</th>
<th>$\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>430.75</td>
<td>7.88</td>
<td>0.245</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>405.65</td>
<td>11.28</td>
<td>0.253</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>373.53</td>
<td>8.96</td>
<td>0.094</td>
</tr>
</tbody>
</table>

The VLE diagram for the systems SO$_2$ + IL.\textsuperscript{7,26,27} The solid lines represent the Flory–Huggins model, and the dashed lines represent the ideal behavior described by Raoult’s law.
\[ \gamma_{\text{gas}} = 1 \]. 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\textsubscript{2} and NH\textsubscript{3} mole fractions and temperature are available in the Supporting Information), show that the Flory–Huggins equation is able to describe the

Figure 2. Pressure versus NH\textsubscript{3} molar composition diagram for the systems NH\textsubscript{3} + IL.\textsuperscript{24,25} The solid lines represent the Flory–Huggins model, and the dashed lines represent the ideal behavior described by Raoult’s law.


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–solute 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.


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 SO₂ and NH₃ in solution is remarkably low and essentially driven by entropic effects. Analogous to what was previously reported for CO₂, these observations suggest that, by increasing the size difference between SO₂ or NH₃ 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. that have reported weak interactions or no chemical bonding at all between the solvent and the solute SO₂ molecule in the SO₂-saturated ILs.

**Non-ideality of H₂S Solutions in ILs**

The approach described in the previous section was also applied to IL + H₂S 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 H₂S mole fractions and temperature are available in the Supporting Information). For the H₂S 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 [C₅mim][BF₄] system, 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 H₂S 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 SO₂ and NH₃. It clearly shows that the interactions between H₂S 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 SO₂, NH₃, and H₂S, in ILs is driven exclusively or predominantly by entropic effects. For systems where the residual contributions are negligible, such as for NH₃- and SO₂-containing systems, a γ–φ 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 H₂S, 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.

**Acknowledgment**

The authors are thankful for financial support from Fundação para a Ciência e a Tecnologia (Project PTDC/EQU-FTT/102166/2008). Pedro J. Carvalho acknowledges the financial support from Fundação para a Ciência e a Tecnologia through his Ph.D. scholarship (SFRH/BD/41562/2007).

**Supporting Information Available:** Deviations, Ap, between the available VLE and the equilibrium pressure predicted by the Flory–Huggins model, as a function of SO₂ mole fractions and temperature, for the IL + SO₂ systems, Table S1) as a function of NH₃ mole fractions and temperature, for the IL + NH₃ systems (Table S2), and as a function of H₂S mole fractions and temperature, for the IL + H₂S systems (Table S3). This material is available free of charge via the Internet at http://pubs.acs.org.