

Comment on “Solubility of CO₂, H₂S, and Their Mixture in the Ionic Liquid 1-Octyl-3-methylimidazolium Bis(trifluoromethyl)sulfonylimide”

Álvaro Pérez-Salado Kamps and Gerd Maurer*

Department of Mechanical and Process Engineering, University of Kaiserslautern, D-67653 Kaiserslautern, Germany

J. Phys. Chem. B **2012**, *116* (9), 2758–2774. DOI: 10.1021/jp2075572

■ INTRODUCTION

This Comment deals with a correlation presented in ref 1. That particular correlation is revised, resulting in a more reasonable set of model parameters and better predictions for the simultaneous solubility of both gases in the investigated ionic liquid.

Besides new experimental results, Jalili et al.¹ also report correlations for their gas solubility data. One of the correlation methods describes the Gibbs excess energy of the liquid phase with a model that was successfully applied in various publications from our group on the solubility of single gases and gas mixtures in ionic liquids. However, the parameters reported by Jalili et al. are—at least in some cases—without a physical meaning. For example, in the section on the simultaneous solubility of CO₂ and H₂S in 1-octyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide ([C₈mim][Tf₂N]), the authors use two different binary parameters for interactions between CO₂ on one side and H₂S on the other side (cf. eq 8 of the paper by Jalili et al.: $\beta_{2,\text{CO}_2,\text{H}_2\text{S}}$ and $\beta_{2,\text{H}_2\text{S},\text{CO}_2}$) which are different—according to Table 7: $\beta_{2,\text{CO}_2,\text{H}_2\text{S}} \neq \beta_{2,\text{H}_2\text{S},\text{CO}_2}$. Furthermore, the equation given for the influence of temperature on the parameter $\beta_{2,\text{CO}_2,\text{H}_2\text{S}}$ results in unreasonably large numbers for that parameter (for example, $\beta_{2,\text{CO}_2,\text{H}_2\text{S}}(303.15 \text{ K}) = -1.564$, whereas the order of magnitude of such interaction parameters should be around 0.01–0.1). These large numerical values yield strange results when the mutual influence of one of the dissolved gases on the solubility of the other gas is calculated from the model (cf. Kumelan et al.² and Tuma and Maurer³). Therefore, all experimental results reported by Jalili et al. were reevaluated and the resulting correlation is reported. All parameters of the new correlation have the correct order of magnitude. Furthermore, in comparison with the correlation reported by Jalili et al., less parameters are required to reproduce the experimental data.

The correlation was performed for the solubility of the single gases as well as of the gas mixture in [C₈mim][Tf₂N]. Only an outline of the correlation is given here. The nomenclature is adopted from Kumelan et al.² to enable an easy comparison with previous publications from our group.

■ MODELING OF GAS SOLUBILITY

In the correlation, the partial pressure of the ionic liquid in the vapor phase is neglected. Furthermore, the solubility of a gas in an ionic liquid is expressed by the extended Henry's law on the molality scale for any dissolved gas:

$$\begin{aligned} f_G^L(T, p, m_{\text{H}_2\text{S}}, m_{\text{CO}_2}) \\ &= k_{\text{H},\text{G,IL}}^{(m)}(T, p) \cdot a_G(T, m_{\text{H}_2\text{S}}, m_{\text{CO}_2}) \\ &= f_G^V(T, p, y_{\text{H}_2\text{S}}) \end{aligned} \quad (1)$$

where G = CO₂ and H₂S and f_G^L and f_G^V are the fugacities of gas G in the liquid and vapor phases, respectively. $k_{\text{H},\text{G,IL}}^{(m)}(T, p)$ is Henry's constant for the solubility of gas G in the ionic liquid IL on the molality scale at temperature T and pressure p , $a_G(T, m_{\text{H}_2\text{S}}, m_{\text{CO}_2})$ is the activity of gas G in the liquid phase whose composition is expressed via the molalities $m_{\text{H}_2\text{S}}$ and m_{CO_2} (i.e., the number of moles per kilogram of ionic liquid) of the dissolved gases. The composition of the vapor phase is expressed via the mole fraction of H₂S, $y_{\text{H}_2\text{S}}$. When a single gas is dissolved in [C₈mim][Tf₂N], the vapor phase is the corresponding pure gas and its fugacity is calculated from an appropriate equation of state for the pure substance employing the software package *ThermoFluids*.⁴ For H₂S, that software package is based on a publication by Lemmon and Span⁵ and for CO₂ it is based on a publication by Span and Wagner.⁶ When both gases are simultaneously dissolved in the ionic liquid, the fugacities in the vapor phase are calculated from the virial equation of state that was truncated after the second virial coefficient. This is a reasonable approximation, as in the experiments by Jalili et al. the highest total pressure is only slightly above 1 MPa. Pure component second virial coefficients ($B_{\text{H}_2\text{S},\text{H}_2\text{S}}$ and $B_{\text{CO}_2,\text{CO}_2}$) were also calculated with *ThermoFluids*, while the mixed second virial coefficient $B_{\text{H}_2\text{S},\text{CO}_2}$ was calculated from the procedure described by Hayden and O'Connell.⁷ All required second virial coefficients are given in Table 1.

Both Henry's constants at zero pressure were evaluated in the common way from the experimental data of Jalili et al. for the solubility of the single gases in the ionic liquid [C₈mim][Tf₂N]. For carbon dioxide, the newly determined

Table 1. Second Virial Coefficients B_{ij} (cm³·mol^{−1})

T (K)	$B_{\text{H}_2\text{S},\text{H}_2\text{S}}$	$B_{\text{CO}_2,\text{CO}_2}$	$B_{\text{CO}_2,\text{H}_2\text{S}}$
303	−179	−118	−153
323	−156	−102	−135
343	−137	−88.5	−121

Received: June 12, 2012

Revised: November 6, 2012

Published: November 14, 2012

numerical values for Henry's constant agree with the data reported by Jalili et al. within the uncertainty that was estimated by those authors. For hydrogen sulfide, the deviations are larger. Therefore, the newly evaluated results are given together with their estimated uncertainty in Table 2. The absolute

Table 2. Henry's Constant on the Molality Scale for the Solubility of H₂S in [C₈mim][Tf₂N]

T (K)	$k_{\text{H}_2\text{S}}^{(\text{m})}[\text{C}_8\text{mim}][\text{Tf}_2\text{N}](T, p = 0)$ (MPa)	estimated uncertainty (MPa)
303.15	0.533	0.011
313.15	0.610	0.013
323.15	0.708	0.014
333.15	0.810	0.014
343.15	0.878	0.016
353.15	0.976	0.016

uncertainty was estimated to twice the standard deviation of the evaluation results (from various evaluations with different numbers of experimental data on an isotherm) from the average value. The relative uncertainty of the Henry's constants at zero pressure is roughly 2%. The influence of temperature on Henry's constant was described by

$$\ln k_{\text{H}_2\text{S}}^{(\text{m})}(T, p = 0)/\text{MPa} = A_{\text{G,IL}} + B_{\text{G,IL}}/(T/\text{K}) + C_{\text{G,IL}} \ln(T/\text{K}) \quad (2)$$

The resulting parameters ($A_{\text{G,IL}}$, $B_{\text{G,IL}}$, and $C_{\text{G,IL}}$) are given in Table 3. Calculation results from eq 2 agree with the directly determined Henry's constants with an average absolute deviation of 0.8% (for H₂S) and 0.2% (for CO₂), respectively.

Table 3. Parameters of eq 2 for the Correlation for Henry's Constants

G	$A_{\text{G,IL}}$	$B_{\text{G,IL}}$	$C_{\text{G,IL}}$
H ₂ S	53.0595	−3682.4	−7.2708
CO ₂	55.8219	−3640.1	−7.6306

As in all experiments by Jalili et al., the highest solubility pressure only slightly surmounted 2 MPa, the influence of pressure on Henry's constant was neglected; i.e., $k_{\text{H}_2\text{S}}^{(\text{m})}(T, p)$ was approximated by $k_{\text{H}_2\text{S}}^{(\text{m})}(T, p = 0)$.

The activity of a gas G in the ionic liquid is expressed on the molality scale:

$$a_{\text{G}}(T, m_{\text{H}_2\text{S}}, m_{\text{CO}_2}) = \frac{m_{\text{G}}}{m^{\circ}} \gamma_{\text{G}}(T, m_{\text{H}_2\text{S}}, m_{\text{CO}_2}) \quad (3)$$

where $m^{\circ} = 1 \text{ mol} \cdot \text{kg}^{-1}$. The activity coefficient γ_{G} is calculated employing the virial expansion for the excess Gibbs energy (also on the molality scale):

$$\ln \gamma_{\text{G}} = 2 \sum_J \left(\frac{m_J}{m^{\circ}} \right) \cdot \beta_{\text{G},J} + 3 \sum_J \sum_K \left(\frac{m_J}{m^{\circ}} \right) \cdot \left(\frac{m_K}{m^{\circ}} \right) \cdot \mu_{\text{G},J,K} \quad (4)$$

where $J, K = \text{H}_2\text{S}$ and CO_2

$\beta_{\text{G},J}$ and $\mu_{\text{G},J,K}$ are parameters that describe the strength of binary and ternary interactions, respectively, between gas molecules in the liquid phase. These parameters depend on temperature and are symmetric: $\beta_{\text{G},J} = \beta_{J,\text{G}}$ and $\mu_{\text{G},J,K} = \mu_{J,\text{G},K} = \mu_{J,K,\text{G}}$. The influence of temperature on such a parameter PAR is here approximated by

$$\text{PAR} = A_{\text{PAR}} + B_{\text{PAR}}/(T/\text{K}) \quad (5)$$

Interaction parameters between the pure solutes were determined by minimizing the differences between the experimental data and the correlation results for the fugacity of the dissolved gas (for preset temperature and liquid phase composition). The quality of the correlation was assessed by comparing (now for preset temperature and vapor phase fugacity) the differences between the calculation results for the mole fraction of gas G in the liquid phase $x_{\text{G,calc}}$ and the experimental results $x_{\text{G,exp}}$:

$$\Delta x_{\text{G}} = \text{abs}(x_{\text{G,exp}} - x_{\text{G,calc}}) T f_{\text{G}}^{\text{V}} \quad (6)$$

where the experimental uncertainty $\Delta x_{\text{G,exp}}$ for that mole fraction was reported by Jalili et al.

The correlation results revealed that for the solubility of H₂S in [C₈mim][Tf₂N] the influence of temperature on the binary parameter $\beta_{\text{H}_2\text{S},\text{H}_2\text{S}}$ can be neglected, whereas it has to be taken into account for the ternary interaction parameter $\mu_{\text{H}_2\text{S},\text{H}_2\text{S},\text{H}_2\text{S}}$. The resulting parameters are given in Table 4.

Table 4. Solubility of the Single Gases CO₂ and H₂S in [C₈mim][Tf₂N]: Parameters of eq 5

PAR	A_{PAR}	B_{PAR}
$\beta_{\text{CO}_2,\text{CO}_2}$	−0.1902	39.8723
$\mu_{\text{CO}_2,\text{CO}_2,\text{CO}_2}$	0	0
$\beta_{\text{H}_2\text{S},\text{H}_2\text{S}}$	−0.1339	0
$\mu_{\text{H}_2\text{S},\text{H}_2\text{S},\text{H}_2\text{S}}$	0.063031	−16.8744

$\Delta x_{\text{G}} < \Delta x_{\text{G,exp}}$ for 35 out of 47 data points reported by Jalili et al. for the solubility of H₂S in [C₈mim][Tf₂N]. The arithmetic average of Δx_{G} for the remaining 12 data points is 0.007, while the corresponding arithmetic average of the experimental data is $\Delta x_{\text{G,exp}} = 0.004$.

For the solubility of CO₂ in [C₈mim][Tf₂N], the correlation results revealed that no ternary interaction parameter is required (i.e., $\mu_{\text{CO}_2,\text{CO}_2,\text{CO}_2} = 0$), but the influence of temperature on the binary parameter $\beta_{\text{CO}_2,\text{CO}_2}$ has to be taken into account. The resulting parameters are given in Table 4. For all 42 experimental data points reported by Jalili et al. for the solubility of CO₂ in [C₈mim][Tf₂N], Δx_{G} is smaller than $\Delta x_{\text{G,exp}}$; i.e., for all experimental data points the correlation results agree with the experimental results within experimental uncertainty.

When all mixed interaction parameters in the model for the liquid phase (as, for example, $\beta_{\text{H}_2\text{S},\text{CO}_2}$) are neglected, the model allows the simultaneous solubility of H₂S and CO₂ in [C₈mim][Tf₂N] to be predicted. In such predictions, the fugacities of both gases in the liquid (vapor) phase were calculated from the experimental results for the temperature and the composition of the liquid phase (pressure and composition of the vapor phase). For both gases, the prediction results for the fugacities in the liquid phase are slightly higher than the fugacities in the vapor phase. However, the mean absolute deviation in the fugacity of gas G

$$\Delta \bar{f}_{\text{G}} = \frac{\text{abs}[\sum_{j=1}^N (f_{\text{G}}^{\text{V}} - f_{\text{G}}^{\text{L}})]}{N} \quad (7)$$

Table 5. Simultaneous Solubility of CO₂ and H₂S in [C₈mim][Tf₂N]: Typical Results for the Influence of the Experimental Uncertainties on the Absolute Difference between f_G^V and f_G^L

experimental data (Jalili et al.)					calculation results	
<i>T</i> (K)	<i>p</i> (MPa)	<i>x</i> _{H₂S} (mol/mol)	<i>x</i> _{CO₂} (mol/mol)	<i>y</i> _{H₂S} (mol/mol)	$ f_{\text{CO}_2}^V - f_{\text{CO}_2}^L $ (MPa)	$ f_{\text{H}_2\text{S}}^V - f_{\text{H}_2\text{S}}^L $ (MPa)
303.15	0.7678	0.400	0.048	0.708	0.052	0.021
303.15	0.9603	0.114	0.218	0.131	0.042	0.005

is only 0.011 MPa (for CO₂) and 0.034 MPa (for H₂S). These deviations have to be compared with the uncertainties of the experimental data. For that discussion, the following experimental uncertainties were assumed: abs. uncertainty in pressure *p*, 0.001 MPa; abs. uncertainty in temperature *T*, 0.05 K; rel. uncertainty in the mole fraction of solute *G* in the liquid phase as well as in the vapor phase, 1%. Two typical examples for the influence of these estimated uncertainties on the difference ($f_G^V - f_G^L$) in the fugacities of *G* = H₂S and CO₂ in the coexisting phases as calculated with the predictive model described above are shown in Table 5. In those typical examples, the difference ($f_{\text{CO}_2}^V - f_{\text{CO}_2}^L$) is 0.052 and 0.042 MPa and the difference ($f_{\text{H}_2\text{S}}^V - f_{\text{H}_2\text{S}}^L$) is 0.021 and 0.005 MPa; i.e., these differences are of the same order of magnitude as $\Delta \bar{f}_{\text{CO}_2}$ and $\Delta \bar{f}_{\text{H}_2\text{S}}$ determined when the predictive model was applied.

Therefore, one can state that the model predictions (i.e., calculations without any interaction parameter between the solutes CO₂ and H₂S) agree almost within experimental uncertainty with the experimental data by Jalili et al.

Nevertheless, the numbers for $\Delta \bar{f}_{\text{CO}_2}$ and $\Delta \bar{f}_{\text{H}_2\text{S}}$ can be further, but only slightly, reduced by fitting interaction parameters between CO₂ and H₂S. For example, adjusting the binary interaction parameter between dissolved CO₂ and H₂S to

$$\beta_{\text{CO}_2, \text{H}_2\text{S}} = \beta_{\text{H}_2\text{S}, \text{CO}_2} = -0.045 \quad (8)$$

results in $\Delta \bar{f}_{\text{CO}_2} = 0.013$ MPa and $\Delta \bar{f}_{\text{H}_2\text{S}} = 0.029$ MPa, and the calculation results no longer systematically deviate from but scatter around the experimental results. Introducing further interaction parameters or considering an influence of temperature on $\beta_{\text{CO}_2, \text{H}_2\text{S}}$ gives no further improvement.

One of the most interesting aspects of the experimental results of Jalili et al. is the mutual influence of one of the gases on the solubility of the other gas in [C₈mim][Tf₂N]. As shown by Kumelan et al.,² one can estimate the influence of a gas *G*₁ on the solubility of a gas *G*₂ at constant temperature and constant fugacity of gas *G*₂ in the low gas concentration range by

$$(\Delta m_{\text{G}_2} / m_{\text{G}_2})_{T, f_{\text{G}_2}^V} \cong -2 \cdot \beta_{\text{G}_1, \text{G}_2} \cdot \frac{m_{\text{G}_1}}{m^\circ} \quad (9)$$

With the correlation result for $\beta_{\text{G}_1, \text{G}_2} = \beta_{\text{CO}_2, \text{H}_2\text{S}} = \beta_{\text{H}_2\text{S}, \text{CO}_2} \cong -0.045$, one recognizes that 1 mol of one of the dissolved gases increases the solubility of the other gas in [C₈mim][Tf₂N] by about 10%. A similar number (20%) was found for the influence of CO₂ on the solubility of hydrogen in [C₆mim][Tf₂N] (Kumelan et al.²).

CONCLUSIONS

The experimental data reported by Jalili et al. for the solubility of the single gases CO₂ and H₂S as well as for the simultaneous solubility of both gases in the ionic liquid [C₈mim][Tf₂N] can

be reliably described using the osmotic virial equation for the excess Gibbs energy of aqueous electrolyte solutions introduced by Pitzer. When the interaction parameters of that model are adjusted to reproduce the experimental results or the solubility of the single gases in [C₈mim][Tf₂N], reliable predictions for the simultaneous solubility of both gases are possible. However, as the predictions slightly, but systematically, deviate from the experimental data, introducing a single parameter for interactions between H₂S and CO₂ in the liquid phase results in a better agreement with the experimental data and allows one to estimate the mutual influence of one of the dissolved gases on the solubility of the other gas in [C₈mim][Tf₂N]. The correlations (for the solubility of the single gases as well as for the gas mixture) presented here require less parameters than the original correlation with the Pitzer model by Jalili et al. Furthermore, all interaction parameters have the correct order of magnitude, and therefore, the new correlation is expected to give better extrapolations, for example, to other temperatures and other solute concentrations.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Jalili, A. H.; Safavi, M.; Ghotbi, C.; Mehdizadeh, A.; Hosseini-Jenab, M.; Taghikhani, V. *J. Phys. Chem. B* **2012**, *116*, 2758.
- (2) Kumelan, J.; Tuma, D.; Maurer, G. *Fluid Phase Equilib.* **2011**, *311*, 9; **2012**, 329, 92.
- (3) Tuma, D.; Maurer, G. Gas Solubility in Ionic Liquids: Mixed Gases in Pure Ionic Liquids and Single Gases in Binary Liquid Mixtures. In *ACS Symposium Series Ionic Liquids Science and Applications 2012*; Visser, A., Bridges, N. J., Rogers, R. D., Eds.; in press.
- (4) Wagner, W.; Overhoff, U. *ThermoFluids*, version 1.0, build 1.0.0; Springer: Berlin, Heidelberg, Germany, 2006.
- (5) Lemmon, E. W.; Span, R. *J. Chem. Eng. Data* **2006**, *51*, 785.
- (6) Span, R.; Wagner, W. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1509.
- (7) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209–216.