

PREDICTION OF GAS SOLUBILITY IN IONIC LIQUIDS USING THE COSMO-SAC MODEL

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Dedicated to Prof. Leon Gradoń on the occasion of his 70th birthday

Thermodynamic principles for the dissolution of gases in ionic liquids (ILs) and the COSMO-SAC model are presented. Extensive experimental data of Henry's law constants for CO₂, N₂ and O₂ in ionic liquids at temperatures of 280-363 K are compared with numerical predictions to evaluate the accuracy of the COSMO-SAC model. It is found that Henry's law constants for CO₂ are predicted with an average relative deviation of 13%. Both numerical predictions and experimental data reveal that the solubility of carbon dioxide in ILs increases with an increase in the molar mass of ionic liquids, and is visibly more affected by the anion than by the cation. The calculations also show that the highest solubilities are obtained for [Tf₂N]⁻. Thus, the model can be regarded as a useful tool for the screening of ILs that offer the most favourable CO₂ solubilities. The predictions of the COSMO-SAC model for N₂ and O₂ in ILs differ from the pertinent experimental data. In its present form the COSMO-SAC model is not suitable for the estimation of N₂ and O₂ solubilities in ionic liquids.

Keywords: vapour-liquid equilibrium, ionic liquids, Henry's constant, solubility, carbon dioxide capture, COSMO-SAC model

1. INTRODUCTION

Due to the environmental effect of CO₂ emissions generated by power plants and energy-intensive industrial sectors such as the chemical industry, the necessity to develop effective CO₂ capture technologies is obvious. In recent years it has been concluded that, most probably, conventional chemical scrubbing will not be widely applicable on a large scale due to its high operating costs. There is thus an urgent need for highly efficient novel technologies that will compete with or complete established capture methods.

Ionic liquids have shown high selectivity towards CO₂ and have recently been considered as very promising reversible absorbents for CO₂ separation (Privalova et al., 2012). Ionic liquids are chemically inert, stable, and nonvolatile liquid organic salts at temperatures below 100 °C. CO₂ solubility in ionic liquids depends on their chemical composition, i.e. on the proper combination of cations, anions and substituents. Ionic liquids (ILs) offer an almost unlimited number of cation and anion combinations and their chemical structures. The problem of finding the best IL for the removal of carbon dioxide from flue gas is a challenging task, with experimental studies time-consuming and expensive. Therefore, the tool for predicting CO₂ solubilities in ILs may optimise the screening process and suggest a vast array of novel cation-anion configurations although, at some point, the predictions have to undergo a carefully planned verification procedure.

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In the present study the parameters needed for COSMO-SAC calculations are presented and discussed. This quantum mechanics model makes it possible to determine the data required for the estimation of Henry's law constants for a gas dissolved in ionic liquids (Lee et al., 2015). Henry's law constants for CO₂, N₂ and O₂ in ILs are estimated using the COSMO-SAC model and compared with the relevant experimental data.

2. THEORETICAL BACKGROUND

The description of phase equilibria is necessary for the design and optimisation of a number of processes at the core of chemical engineering, e.g. absorption, desorption, distillation, adsorption and crystallisation. The term "description" signifies, essentially, the concentrations of all the species of a system in thermodynamic equilibrium. These concentrations can be determined experimentally or predicted based on fundamental principles governing phase equilibria.

2.1. Vapour-liquid equilibrium

The solubility of gases in liquids can be described by an equation that relates the fugacity of a component in the gas phase with that in the liquid. At equilibrium we have (Lee et al., 2015):

$$y_i P \bar{\phi}_i = p_i \bar{\phi}_i = x_i \gamma_i f_i \quad (1)$$

At low pressures it may be assumed that the gas phase is an ideal gas mixture, and Eq. (1) becomes:

$$P y_i = p_i = x_i \gamma_i f_i \quad (2)$$

For low gas solubilities the concentration of the solute i in the liquid phase can be calculated using Henry's law:

$$\frac{p_i}{x_i} = H_i \quad (3)$$

with

$$H_i = \gamma_i^\infty f_i \quad (4)$$

It may be noted that at low pressures the fugacity of a pure gas in the liquid state corresponds to its saturated vapour pressure (Lee et al., 2015; Sandler, 1994):

$$f_i = p_i^0 \quad (5)$$

Saturated vapour pressures above a pure species can be determined experimentally (National Institute of Standards and Technology, 2016) or, alternatively, calculated from the relevant equations which relate the saturation pressure to temperature. To predict Henry's constant we also have to know the activity coefficient for the dissolved gas. This may be done using the COSMO-SAC model which makes it possible to estimate the activity coefficient of a gas dissolved in ionic liquids (ILs) (Lee et al., 2015; Shimoyama et al., 2010).

2.2. Segment activity coefficient (COSMO-SAC) model

There are a number of methods to calculate thermodynamic data for gaseous and liquid mixtures (e.g., the activity coefficients can be estimated using NRTL, UNIFAC, UNIQUAC or COSMO-SAC models,

to mention but a few). A major advantage of the COSMO-SAC approach lies in its relative simplicity compared with the other models – the calculations only require the knowledge of a structural formula and certain parameters commonly available in the relevant literature (Firaha et al., 2013; Mullins et al., 2006; Shah et al., 2012; Shah et al., 2013; Shimoyama et al., 2010).

In the COSMO-SAC model it is assumed that the molecule in a solution is surrounded by a sphere called molecular cavity. The solvent outside this cavity is treated as a continuum of a constant relative permittivity (Klamt et al., 1998). The shape of the cavity results from the overlapping of atomic spheres, and its surface is divided into small circles of similar dimensions. The radii of the atomic spheres for various elements are given as empirical parameters. (In the present study the values of these parameters are taken from the paper of Mullins et al. (2006)). Then, using quantum chemistry methods, the surface charge density σ_n^* is estimated over the n -th segment of the cavity, the probability distribution of surface charge density (the so-called sigma profile) is calculated, and the activity coefficient for gas i in a solution is determined.

In the COSMO-SAC model the activity coefficient of i in a mixture is expressed as a sum of two contributions, namely combinatorial (comb) and residual (res):

$$\ln \gamma_i = \ln \gamma_i^{comb} + \ln \gamma_i^{res} \quad (6)$$

The combinatorial term reflects differences in the size and structure of the molecules and is given as:

$$\ln \gamma_i^{comb} = \ln \left(\frac{\phi_i}{x_i} \right) + \frac{z}{2} q_i \ln \left(\frac{\theta_i}{\phi_i} \right) + l_i - \frac{\phi_i}{x_i} \sum_i x_i l_i \quad (7)$$

where:

$$\theta_i = \frac{x_i q_i}{\sum_i x_i q_i} \quad (8)$$

$$\phi_i = \frac{x_i r_i}{\sum_i x_i r_i} \quad (9)$$

$$l_i = \left(\frac{z}{2} \right) (r_i - q_i) - (r_i - 1) \quad (10)$$

$$r_i = \frac{V_i}{r} \quad (11)$$

$$q_i = \frac{A_i}{q} \quad (12)$$

The procedure for calculating the total volume, V_i , and the total surface area of the molecular cavity, A_i , is given in reference (Mullins et al., 2006); the other parameters are shown in Table 1.

The residual term results from molecular interactions. It can be predicted using the following relationship:

$$\ln \gamma_i^{res} = \frac{1}{a_{eff}} \sum_{\sigma_m} p'_i(\sigma_m) [\ln(\Gamma_s(\sigma_m)) - \ln(\Gamma_i(\sigma_m))] \quad (13)$$

where:

$$p'(\sigma) = p(\sigma) A_i \quad (14)$$

$$\ln \Gamma_s(\sigma_m) = -\ln \left[\sum_i \frac{p'_s(\sigma_n)}{A_i} \Gamma_s(\sigma_n) \exp\left(-\frac{\Delta W(\sigma_m, \sigma_n)}{RT}\right) \right] \quad (15)$$

$$\ln \Gamma_i(\sigma_m) = -\ln \left[\sum_i \frac{p'_i(\sigma_n)}{A_i} \Gamma_i(\sigma_n) \exp\left(-\frac{\Delta W(\sigma_m, \sigma_n)}{RT}\right) \right] \quad (16)$$

$$\Delta W(\sigma_m, \sigma_n) = \left(\frac{\alpha'}{2}\right)(\sigma_m + \sigma_n)^2 + c_{hb} \max[0, \sigma_{acc} - \sigma_{hb}] \min[0, \sigma_{don} - \sigma_{hb}] \quad (17)$$

The sigma profiles for the pure species i , $p'_i(\sigma_m)$, and for the solution, $p'_s(\sigma_m)$, were calculated based on the approach proposed in reference (Mullins et al., 2006), with numerical values of the relevant parameters based on literature data (Mullins et al., 2006).

Table 1. Values of the parameters in the COSMO-SAC model

Parameter	Symbol	Value	Unit
effective surface area of a segment	a_{eff}	7.5	\AA^2
hydrogen bonding constant	c_{hb}	85580.0	$\text{kcal}\cdot\text{\AA}^4\cdot\text{mol}^{-1}\cdot\text{e}^{-2}$
surface area normalization constant	q	79.53	\AA^2
volume normalization constant	r	66.69	\AA^3
average radius of a cavity fragment	r_{av}	0.81764	\AA
gas constant	R	0.001987	$\text{kcal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
coordination number	z	10	–
dislocation energy constant	α'	9034.97	$\text{kcal}\cdot\text{\AA}^4\cdot\text{mol}^{-1}\cdot\text{e}^{-2}$
hydrogen bonding correction	σ_{hb}	0.0084	$\text{e}\cdot\text{\AA}^{-2}$

3. COMPUTATIONAL DETAILS

A number of studies have been devoted to the prediction of gas solubilities in ionic liquids using the COSMO-SAC model. In their most recent paper Lee et al. (2015) calculate Henry's constants for several thousand systems consisting of gas (CO_2 , N_2 , H_2 , CH_4) – ionic liquid. It has to be noted, though, that the numerical results concerning Henry's law constant were compared with only 53 sets of experimental data, and even a cursory examination shows that some results may be affected by a considerable error.

In Lee et al.'s (2015) method the optimisation of the molecular geometry was performed separately for cations and anions. Similarly, sigma profiles were obtained separately for cations and anions. In some studies, however, a different approach is proposed – the cation and the anion are treated as a whole (Palomar et al., 2007). In the present paper a combination of the two approaches was employed. The optimisation of the molecular geometry is based on Lee et al. (2015) method, whereas the sigma profile is obtained for the ionic liquid molecule treated as a single entity.

The COSMO-SAC model provided the core element of the procedure whereby activity coefficients, γ_i^∞ , were predicted for ideally dilute solutions of CO_2 , N_2 or O_2 and ILs. The calculations were done using a software package (Materials Studio 5.5) and following the procedure described by Mullins et al. (2006).

Ionic liquids include an organic cation and an inorganic or organic anion. The simulation is started by drafting the three-dimensional structure of the cation, the anion and the gas, thus creating the initial

geometry. This geometry is then optimised for each of the species to find the most stable configuration. The optimisation is based on minimising the total energy of the molecule by altering the individual angles and bond lengths, and employs the density functional theory (DFT) as implemented in the software package used.

The complex structures of ionic liquids lead to a number of different conformations for which the energy may exhibit several local minima. Since optimisation results depend on the initial geometry, for larger molecules several conformation isomers were selected and the one most energetically favourable was eventually chosen.

In the next step the electron density for the optimised molecule is computed using the DFT method and the COSMO-SAC proper calculations are done. A dedicated algorithm draws a sphere around each atom, and then creates a molecular cavity surrounding the molecule. Klamt et al. (1998) suggest that in most cases the radius of the sphere should be assumed as equal to around 120% of the van der Waals radius. The values of these radii and the other parameters of the COSMO-SAC model are given in literature (Mullins et al., 2006).

The molecular cavity is divided into several smaller segments. For each segment the surface density charge, σ_n^* , is estimated based on the electron density of the molecule. Using the number of segments of the molecular cavity, the coordinates defining its shape, surface areas and surface charge densities for the segments, the charge distribution over the surface of the cavity (the sigma profile), $p(\sigma_m)$, is determined for the pure components (a gas and an ionic liquid) following the procedure proposed by Mullins et al. (2006). As already mentioned, it is assumed in the calculations that the cation and the anion form a single molecule.

The sigma profiles thus obtained were used to predict the activity coefficients, γ_i^∞ , of CO₂, N₂ and O₂ dissolved in an ionic liquid. The prediction employs the COSMO-SAC-VT-2005 program (Eqs. (6) – (17)) and constitutes the final stage of the COSMO-SAC procedure. It is assumed that for an ideally dilute solution the mole fraction of the solvent (IL) is at least 99.5%. In the present paper the concentration of the solvent was fixed at 0.995. The programs *Sigma-average.exe* and *COSMO-SAC-VT-2005.exe* are written in Fortran 90 and are available on the Internet (Virginia Polytechnic Institute and State University, 2006).

The estimation of the Henry's constant for a gas–IL system (Eq. (4)) requires the knowledge of the pure gas fugacity in its hypothetical liquid state. This was done using the following equation:

$$p_i^0 \approx \exp\left(A_i + \frac{B_i}{T} + C_i \ln T + D_i T^{E_i}\right) \quad (18)$$

The coefficients in Eq. (18) were estimated by Lee et al. (2015) using the relevant experimental data (saturated vapour pressure for pure species below the critical temperature and solubility in the supercritical region). In the present study it has been found, however, that Eq. (18) yields incorrect saturated vapour pressures for nitrogen. If this quantity is calculated using Eq. (18) and the coefficients given in Lee et al. (2015) (Table 1), the numerical results are an order of magnitude larger than the experimental data at $T < T_c$. Closer scrutiny reveals that the discrepancy is due to the erroneous value of the coefficient D , which should be 3.7676×10^{-3} rather than 3.7676×10^{-2} originally proposed in Lee et al. (2015).

Next the coefficients of Eq. (18) for oxygen were estimated using the experimental saturated vapour pressures for the pure gas, published by the National Institute of Standards and Technology (2016). The coefficients for the three gases (with the corrected value of D for N₂) are given in Table 2.

An important advantage of Eq. (18) results from the wide range of temperatures over which it may be used with appreciable accuracy. Below the critical temperature the fugacities agree very well with the

experimental data. Above T_C Eq. (18) may also be used; this is of special importance in the case of nitrogen and oxygen, as their critical temperatures are by far lower than those at which N_2/O_2 solubilities in ILs are studied.

Table 2. Coefficients in Eq. (18)

Gas	T	A	B	C	D	E
CO ₂	217 – 340	140.54	-4735	-21.268	0.040909	1
N ₂	64 – 343	30.895	-847.518	-1.999	0.0037676	1
O ₂	63 – 153	69.7277	-1426.2836	-10.3129	0.0447	1

4. RESULTS AND DISCUSSION

4.1. CO₂ – ionic liquid systems

To validate the parameter values and the principal assumptions extensive COSMO-SAC calculations were done concerning Henry's constants for a range of CO₂ – IL systems. The results were then compared with the pertinent experimental data. The ionic liquids analysed were composed of a number of different cation – anion combinations. The cations were C_nMIM⁺, C_nDMIM⁺ and C_nMpyrr⁺ (for the full names see the Appendix). The cations contained different alkyl groups, e.g. ethyl ($n = 2$), propyl ($n = 3$), butyl ($n = 4$), etc. ILs also contain inorganic (e.g. BF₄⁻, B[(CN)₄]⁻, PF₆⁻, DCA⁻) and organic (e.g. Tf₂N⁻, OTf⁻) anions. The structural formulae of these cations and anions are shown in Fig. 1.

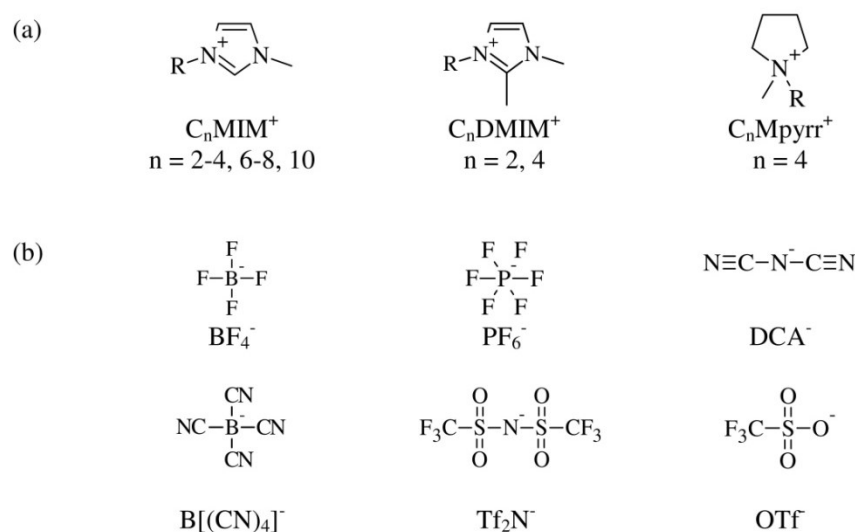


Fig. 1. Structural formulae of cations (a) and anions (b) analysed in this study

The comparison between the model predictions and experimental data for the system CO₂ – IL is presented in Fig. 2.

It may be seen from Fig. 2 that the model proposed in this work agrees better with the experiment. For 37 systems examined, only 4 deviate by more than 20% from the respective experimental data, and the average relative error is 10.3%. In the case of Lee et. al.'s (2015) calculations these numbers are, respectively, 13 and 16.7%; also, in a number of cases their results are visibly lower than the experimental values. This may be due to the fact that, in the present work, cations and anions were assumed to form a single compound, whereas Lee et al. (2015) determined the sigma profiles separately

for these two moieties. Moreover, a different equation was employed to calculate the energy of interaction between two surface segments, $\Delta W(\sigma_m, \sigma_n)$, Eq. (17).

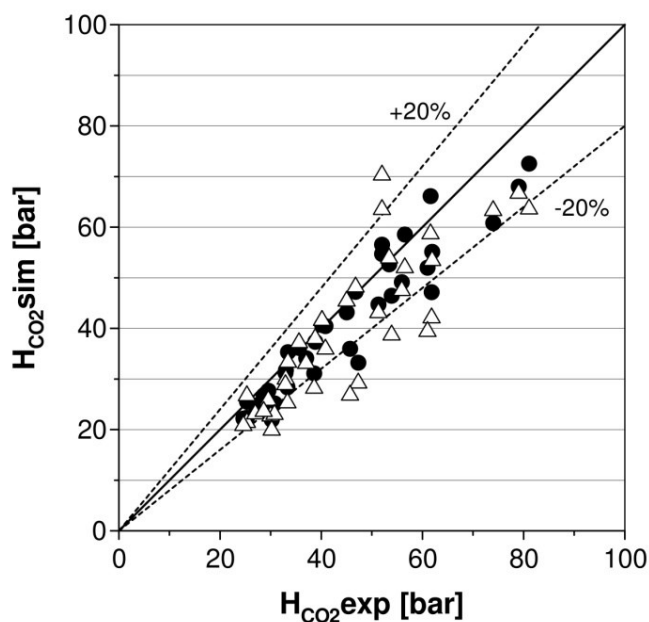


Fig. 2. Comparison of the experimental Henry's constants for CO₂ in ionic liquids with the COSMO-SAC predictions (circles – present study, triangles – results of Lee et al., 2015)

The average relative deviation is defined as:

$$ARD = \frac{1}{n} \sum \frac{|H_{sim} - H_{exp}|}{H_{exp}} \cdot 100 \% \quad (19)$$

In Fig. 3 142 values of Henry's constant are shown for CO₂ in 18 different ionic liquids at temperatures between 280 K and 363 K. These values are compared with the experimental data obtained by various authors (Lei et al., 2014).

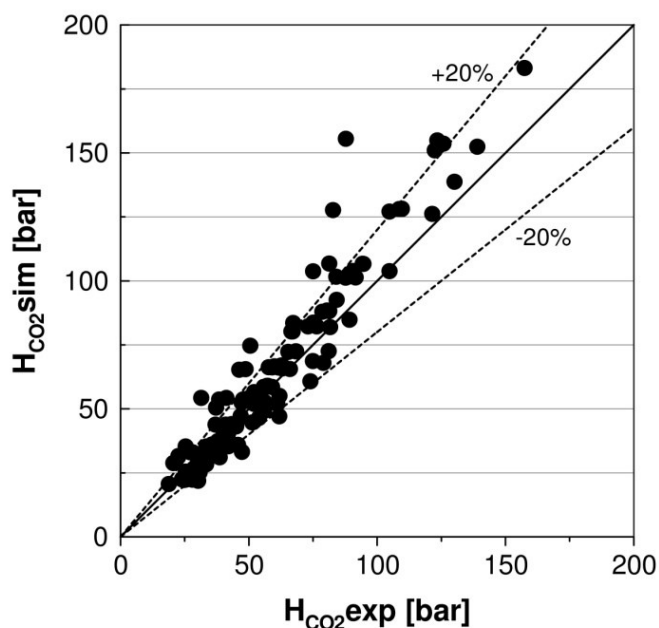


Fig. 3. Experimental Henry's constants for CO₂ in ILs vs. results of the COSMO-SAC model obtained in this work

It may be seen from Fig. 3 that most of the results are predicted with reasonable accuracy (deviation < 20%). However, there are 28 systems which deviate by more than 20% from the experimental values, especially for larger values of Henry's constants. The ARD is 13.2%.

It has to be noted that the coefficients in Eq. (18) were estimated based on experimental data measured mainly below the critical temperature for CO₂, while Fig. 3 includes 77 points close to or above T_C (31 °C) for CO₂. For these cases 18 points differ by more than 20% from their measured counterparts, and the average relative error is 16.0%. It may thus be concluded that the COSMO-SAC model can be employed for the prediction of Henry's constants over a wide range of temperatures.

Once the model has been validated the Henry's law constants for a range of CO₂ – IL systems at a specified temperature (say, 25°C) may be calculated. The results are shown in Fig. 4, where the ILs are grouped according to the type of the anion. The individual points for the same anion differ only in the nature of the cation (cf. Fig. 1).

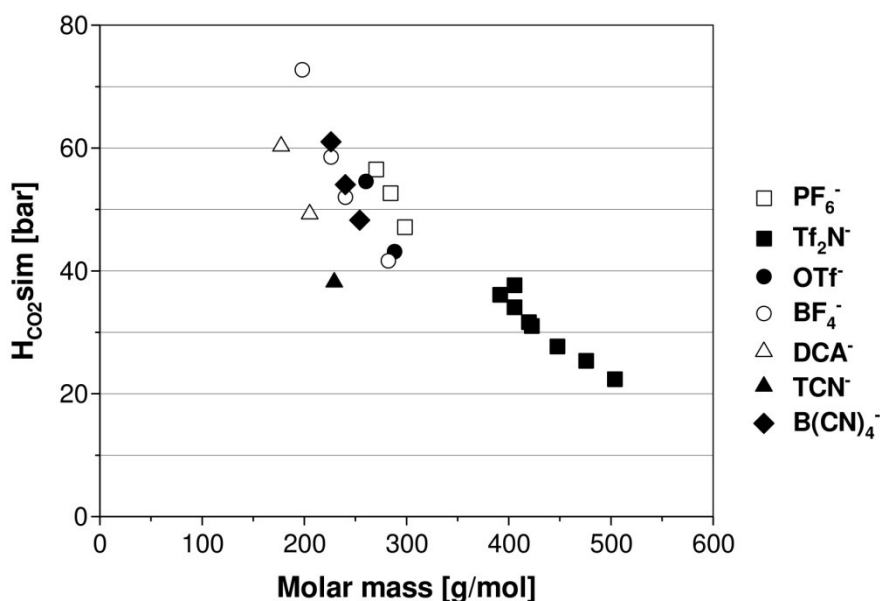


Fig. 4. Henry's constants for CO₂ in ionic liquids predicted by the COSMO-SAC model as a function of the IL molar mass

It may be seen from Fig. 4 that with an increase in the molar mass of ILs, Henry's constants tend to decrease (i.e., the solubility expressed in CO₂ mole fractions increases). Further, H_{CO_2} also depends on the anion and cation type, with anions having a more pronounced effect on H_{CO_2} than cations. It may also be noted that, at a constant temperature, for the three anions exhibiting the most obvious pattern, CO₂ solubility increases as the anions change in the following order: BF₄⁻ < PF₆⁻ < Tf₂N⁻. These results agree well with the data quoted in the literature (Anthony et al., 2005; Ramdin et al., 2012; Shimoyama et al., 2010).

4.2. N₂ – ionic liquid and O₂ – ionic liquid systems

The usefulness of the COSMO-SAC model in predicting the solubility of nitrogen in ionic liquids was examined. 32 Henry's constants were calculated for eight N₂ – IL systems over a range of temperatures (283 – 343 K). The results are shown in Fig. 5.

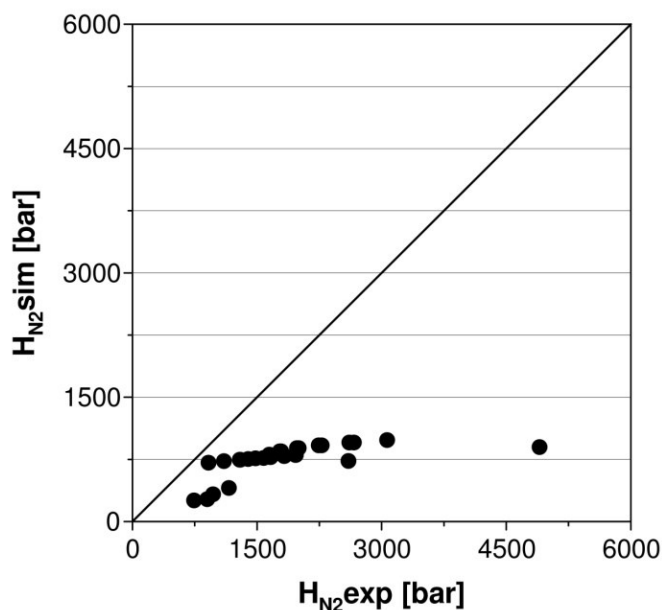


Fig. 5. Experimental Henry's constants for N₂ in ILs vs. results of the COSMO-SAC model obtained in this work

The results for nitrogen are far from satisfactory. A considerable discrepancy may be seen between the COSMO-SAC predictions and the experimental data, with the values obtained in the present study situated visibly lower. Unfortunately, the activity coefficients used, $\gamma_{N_2}^\infty$, cannot be verified with reasonable accuracy based on the available data.

Similar calculations were carried out for oxygen at temperatures between 283 K and 323 K. Again, in a number of cases the error exceeded 100%, thus limiting the usefulness of the model in this particular instance. Substantial errors for nitrogen and oxygen are reported in other studies (cf. e.g. Lei et al., 2014). This may be due to N₂ and O₂ solubilities being an order of magnitude smaller than that of CO₂; consequently, the relevant measurements are associated with a larger experimental error. Second, the calculations were performed using certain thermodynamic properties extrapolated well above the critical temperatures for N₂ and O₂, i.e. beyond their rigorous range of validity. Finally, the discrepancy may have resulted from the inherent deficiencies of the model itself.

Further studies will focus on using the COSMO-SAC model to predict the solubility of carbon dioxide in polyionic liquids (PILs). It is suggested that activity coefficients predicted for gas – IL systems may, under certain conditions, be extrapolated onto gas – PIL mixtures (Kuo et al., 2013). Based on the activity coefficient thus calculated it is possible to estimate the respective Henry's constant.

5. CONCLUSIONS

The COSMO-SAC model may successfully be employed to predict Henry's law constants for the CO₂ – IL system. The model may thus be useful in selecting the best candidate for the absorption of carbon dioxide. As the parameters required by the COSMO-SAC model are rather general, the examination of any new IL does not necessitate tedious experimental studies. Of the ILs so far investigated, the best CO₂ solubility is offered by those containing Tf₂N⁻. The effect of the anion on CO₂ absorption is more pronounced than that of the cation. Finally, in its present form the COSMO-SAC model is not suitable for the estimation of N₂ and O₂ solubilities in ionic liquids.

SYMBOLS

A_i	total cavity surface area, \AA^2
ARD	average absolute relative deviation, %
a_{eff}	effective surface area of a standard surface segment, \AA^2
c_{hb}	constant for hydrogen bonding, $\text{kcal}\cdot\text{\AA}^4\cdot\text{mol}^{-1}\cdot\text{e}^{-2}$
f_i	fugacity of pure gas in the hypothetical liquid state, bar
H_i	Henry's law constant of component i , bar
P	total pressure, bar
p_i	vapour pressure of gas i above the solution, bar
p_i^0	vapour pressure of pure component i , bar
$p'_i(\sigma_m)$	modified sigma profile of pure component, \AA^2
$p'_s(\sigma_m)$	modified sigma profile for a mixture, \AA^2
q	surface area normalisation constant, \AA^2
q_i	normalised surface area parameter
R	ideal gas constant, $\text{kcal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
r	volume normalisation constant, \AA^3
r_i	normalised volume parameter
T	temperature, K
T_C	critical temperature, K
V_i	total cavity volume, \AA^3
$\Delta W(\sigma_m, \sigma_n)$	exchange energy, $\text{kcal}\cdot\text{mol}^{-1}$
x_i	mole fraction of gas i in the liquid phase
y_i	mole fraction of gas i in the gas phase
z	coordination number
<i>Greek symbols</i>	
α'	constant for the misfit energy, $\text{kcal}\cdot\text{\AA}^4\cdot\text{mol}^{-1}\cdot\text{e}^{-2}$
γ_i	activity coefficient of component i in the liquid phase
γ_i^∞	infinite dilution activity coefficient of component i
γ_i^{comb}	combinatorial contribution to the activity coefficient of component i in solution
γ_i^{res}	residual contribution to the activity coefficient of component i in solution
$\Gamma_i(\sigma_m)$	segment activity coefficient of the solute
$\Gamma_s(\sigma_m)$	segment activity coefficient of the solvent
σ_{acc}	maximum of a set of σ_m and σ_n
σ_{don}	minimum of a set of σ_m and σ_n
σ_m	effective surface charge density on segment m , $\text{e}\cdot\text{\AA}^{-2}$
σ_n^*	surface charge density on segment n , $\text{e}\cdot\text{\AA}^{-2}$
$\overline{\phi}_i$	fugacity coefficient of gas i in the gas phase

Subscripts and superscripts

<i>exp</i>	experimental
<i>sim</i>	calculation

APPENDIX

Anion full names:

BF ₄ ⁻	tetrafluoroborate
B(CN) ₄ ⁻	tetracyanoborate
DCA ⁻	dicyanamide
PF ₆ ⁻	heksafluorophosphate
Tf ₂ N ⁻	bis(trifluoromethylsulfonyl)imide
OTf ⁻	trifluoromethanesulfonate; also triflate

Cation full names:

C _n MIM ⁺	1-alkyl-3-methylimidazolium; e.g.:
C ₃ MIM ⁺	1-propyl-3-methylimidazolium
C ₆ MIM ⁺	1-hexyl-3-methylimidazolium
C ₈ MIM ⁺	1-octyl-3-methylimidazolium
C ₂ DMIM ⁺	1-ethyl-2,3-dimethylimidazolium
C ₄ DMIM ⁺	1-butyl-2,3-dimethylimidazolium
C ₄ Mpyrr ⁺	N-butyl-N-methylpyrrolidinium

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