



# A semi-empirical Henry's law expression for carbon dioxide dissolution in ionic liquids

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## ABSTRACT

A simple model was developed to predict the solubility of carbon dioxide (CO<sub>2</sub>) in ionic liquids under normal processing and conditioning pressures for natural gas fluids. COSMO-RS was used to predict the unsymmetrical activity coefficients for CO<sub>2</sub> in ILs, and the Peng–Robinson equation of state was used to calculate the CO<sub>2</sub> fugacity coefficient. Using these two quantities, a correlation was developed which can be used to extrapolate solubilities for ILs where experimental data is not available. This study shows that the molecular mass of the ILs is an effective parameter to correlate the Henry's constant of CO<sub>2</sub>.

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## 1. Introduction

Natural gas is a mixture of light hydrocarbons saturated with water produced from underground reservoirs. Acid gases such as CO<sub>2</sub> and hydrogen sulfide (H<sub>2</sub>S) can be present in natural gas mixtures in considerable concentrations. H<sub>2</sub>S, a highly toxic substance, must be properly removed from the sales gas. CO<sub>2</sub>, also an acid gas, must be removed from the raw gas to ensure that heating value specifications are met. Flue gases produced by power plants are another industrial fluid rich in CO<sub>2</sub> which in the future may need to be treated before release to the atmosphere. Currently, absorption in alkaline solutions such as aqueous solutions of diethanol amine (DEA) and absorption in physical solvents such as polyethylene glycol dimethyl ether based agents such as Selexol are the common commercial processes used for treating high-volume gas streams containing H<sub>2</sub>S and/or CO<sub>2</sub> [1].

In the past decade, room temperature ionic liquids (RTIL), have received increasing attention as a class of non-aqueous solvents, with potential to be used as new solvents for gas treatment [2]. ILs are molten salts and are commonly formed by large organic cations and smaller organic or inorganic anions, allowing them to remain liquid at or near room temperature. One of the desirable characteristics exhibited by ILs for gas conditioning is their negligi-

ble vapour pressure and minimal waste to the environment when regenerated, *i.e.*, less solvent loss and greater recycle to the absorption system. There is the possibility of further tuning their intrinsic thermo-physical properties by changing their chemical structure at the synthesis stage. Furthermore, beyond the selective absorption of CO<sub>2</sub> and H<sub>2</sub>S there are a wide range of possible applications in the chemical industry including solvents, liquid support for chemical reactions, electrolytes and catalysts [3–8].

Given the potential of ILs for use as a selective solvent for the absorption of both CO<sub>2</sub> and H<sub>2</sub>S the availability of some experimental data for mixtures relevant to gas conditioning provides a useful starting point to search for efficient ionic liquids for use in industrial sweetening gas plants. However, there are many combinations of anions and cations that can be potentially used for the synthesis of ionic liquids of interest for gas conditioning. Many of these combinations may not have been studied experimentally, especially at the pressures and temperature commonly experienced in conditioning processes.

In order to perform conceptual studies for new gas conditioning plants it is required that a reliable method for the determination of acid gas standard state fugacities be determined to be used in conjunction with theoretical tools such as COSMO-RS [9] to provide a meaningful fugacity for the gas dissolved in the IL. This combination in turn allows us to estimate proper solubility curves of acid gas in ionic liquids that may not yet have been synthesized, or extend solubility curves to temperatures of interest which are beyond the experimental data.

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The availability of new theoretical tools [9] for the estimation of activity coefficients in complex polar liquid, the availability of key experimental solubility data and the desire to study the conceptual feasibility of using ILs is the motivation of this work. In this paper the issue of developing a correlation for the standard state of CO<sub>2</sub> in different ILs is studied in detail.

In order to develop a meaningful correlation for the standard state of CO<sub>2</sub> in ILs, a reliable model must be available to quantify the interactions between CO<sub>2</sub> molecules and the IL cations and anions. In this work the COSMO-RS model was chosen to calculate activity coefficients between carbon dioxide and ILs [10].

The COSMO-RS model is a theoretically based quantum chemical calculation which can be used to predict the thermodynamic properties of fluid mixtures [11–14]. For calculations with the COSMO model, a dielectric continuum of the solvent is assumed and the optimal geometry and electron density of the solute is calculated using an appropriate basis set for the molecular orbitals involved. Based on minimum geometry and electron density according to the COSMO-RS model, the solvent and solute interactions can be extracted from pair-wise surface segments and their local polarization charge densities. In these interactions van der Waals, electrostatic and hydrogen bonding energies are taken into account. Within COSMO-RS the information of the local polarization charge densities  $\sigma$ , reduces to a histogram  $P_i(\sigma)$ , which to define the chemical potential.

## 2. Theory

The pseudo-chemical potential,  $\mu_i$ , is defined by Eq (1) [15]

$$\mu_i = \mu_i^* - RT \ln x_i \quad (1)$$

where  $\mu_i^*$ , is the standard chemical potential.

The pseudo-chemical potential of compound  $i$  in the system can be calculated using Eq. (2)

$$\mu_i = \mu_i^C + \int P_i(\sigma)\mu_S(\sigma)d\sigma \quad (2)$$

where  $\mu_i^C$  is the combinatorial contribution to the chemical potential that takes into account the shape and size differences of the molecules in the system and  $\mu_S$  is the  $\sigma$ -potential and it can be interpreted as the affinity of the solvent S for the surface of polarity  $\sigma$ . The activity coefficient of the solute can be calculated using Eq (3),

$$\gamma_i = \exp\left(\frac{\mu_i - \mu_i^0}{RT}\right) \quad (3)$$

where  $\mu_i^0$  is the chemical potential of compound  $x$  in the pure compound reference state.

As an example of practical consequences of this type of approach, Zhang et al. [16], used the quantum calculations of COSMO-RS to predict the Henry's constant for CO<sub>2</sub> in several ILs at 298.15 K and inferred that more CO<sub>2</sub> can be absorbed in ILs with tris(pentafluoroethyl)trifluorophosphate (FEB) anion.

For this study, we applied the COSMO-RS method [11–14] implemented in the COSMOtherm software [17]. The quantum chemical COSMO calculations were performed on the density functional theory (DFT) level, utilizing the BP functional [18–20] with RI (resolution of identity) approximation and a triple- $\zeta$  valence polarized basis set (TZVP) [21,22].

In order to evaluate the applicability of the COSMO-RS as implemented in COSMOtherm we calculated the Henry's constant of CO<sub>2</sub> in several ILs at different temperatures and these were compared with experimental data. The calculated Henry's constant of CO<sub>2</sub> in IL was ca 40% less than the experimental data thus making the method inadequate for process design. A similar problem was reported by

Maiti in 2009 [23] where the partial pressure of the CO<sub>2</sub>–IL systems were 50% higher than the ones calculated by COSMO-RS. This problem also was reported in a recent COSMO-RS calculation for CO<sub>2</sub> solubility in organic carbonate solvents by Kolář et al. [24].

Maiti [23] used Eq. (3) along with the Soave–Redlich–Kwong equation of state [25] to correct the vapour phase equilibrium calculations and introduced a two-parameter empirical model, Eq. (4), to describe the chemical potential of compound  $i$  in the reference state of the pure compound and proposed Eq. (5) to calculate the saturation pressure of the system as described by Eqs. (4) and (5) pressure of the system,

$$\mu_i^0(T) = \mu_{T_C} + \alpha(T - T_C) \quad (4)$$

$$\mu_{T_C} = -18547.524$$

$$\alpha = -83.736$$

$$P(x_i, T) = \frac{x_i P^0}{\varphi(T, P)} \exp\left(\frac{\mu_i(x_i, T) - \mu_i^0}{RT}\right) \quad (5)$$

For process design Maiti's formulation is not ideal because process simulators normally use models based on fugacity versus chemical potential. The change from chemical potential to fugacity is easily done using standard thermodynamics. We start with the expression of fugacity equalities

$$f_i^v = f_i^l \quad (6)$$

As mentioned earlier, ionic liquids are low-melting salts, and they have negligible vapor pressure [26–44]. The fugacity of the vapour phase, assuming zero vapour pressure for the ionic liquid is given by,

$$f_i^v = P\varphi_i \quad (7)$$

The fugacity of the liquid phase is calculated using the asymmetric normalization scale and is given by Eq. (8),

$$f_i^l = \gamma_i^* x_i H_i \quad (8)$$

The unsymmetrical activity coefficient is calculated based on the symmetric activity coefficient calculated by COSMO-RS according to Eq. (9).

$$\gamma_i^* = \frac{\gamma_i}{\gamma_i^\infty} \quad (9)$$

The problem then can be reduced to the calculation of the Henry constant of CO<sub>2</sub> in different IL's. Ideally the dependency of  $H_i$  with specific IL's should be captured using a simple IL molecular parameter. If a meaningful relationship between the Henry constant of CO<sub>2</sub> in IL and a simple IL molecular parameter is found, then better solubility estimates can be provided and available experimental data extended in a semi-empirical way.

The determination of  $H_i$  is done through the use of experimentally measured CO<sub>2</sub> pressures over IL's, the concentration of CO<sub>2</sub> in the IL, the unsymmetrical activity coefficients from COSMOtherm and the temperature and the fugacity coefficient of CO<sub>2</sub> in the gas phase. The fugacity coefficient of CO<sub>2</sub> was calculated using the Peng–Robinson equation of state [45],

$$\ln \phi = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln\left(\frac{Z + 2.414B}{Z - 0.414B}\right) \quad (10)$$

where  $\phi$  is the fugacity coefficient of the pure component and  $Z$  is the compressibility factor. The parameter  $A$  and  $B$  are defined elsewhere [45].

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