



Molecular simulation study of the CO₂-N₂O analogy



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ABSTRACT

The validity of the CO₂-N₂O analogy concerning the Henry's law constant is investigated by molecular simulation of the solvents water, ethanol, as well as their mixtures. Molecular models for carbon dioxide (CO₂) and for the solvents water and ethanol are taken from the literature. For nitrous oxide (N₂O), two new molecular models are presented. They differ in their structure, but are both parametrized using pure component vapor-liquid equilibrium data. The models are used to study Henry's law constants of CO₂ and N₂O in pure water and pure ethanol over a wide range of temperatures. In the case of water, a slight adjustment in the water-solute interaction is necessary to achieve agreement with experimental data, whereas the gas solubilities in ethanol are predicted quantitatively without any adjustment. For mixed solvents containing both water and ethanol, the CO₂-N₂O analogy is found to be invalid, contradicting a widespread assumption.

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1. Introduction

The removal of carbon dioxide (CO₂) from gas streams is a common task in many industrial processes. Large scale applications are for example post combustion carbon capture processes and natural gas cleaning. The common process for CO₂ removal is reactive absorption with aqueous solutions of amines as solvents [1,2]. Upon absorption, CO₂ reacts with these solvents, forming carbonates and eventually carbamates. CO₂-loaded aqueous amine solutions may show complex phase behavior [3].

In the design of reactive absorption processes, the physical solubility of CO₂ in the solvent is a key property, as it is needed to describe both the phase equilibrium and the chemical equilibrium. A measure of the physical gas solubility is the Henry's law constant $H_{i,j}$ of the solute i in the solvent j . Unfortunately, for reactive systems, this property cannot be determined experimentally in many cases, namely when chemical and physical effects cannot be disentangled in the experiment. Therefore, for reactive systems with CO₂, the CO₂-N₂O analogy has been established as a workaround [4]. In contrast to CO₂, nitrous oxide (N₂O) normally does not react with the solvents used in reactive absorption processes, so that the Henry's law constant of N₂O in any of these solvents can be determined experimentally using standard methods. Furthermore, the Henry's law constant of both CO₂ and N₂O in pure water is

known [5,6]. In evaluating the Henry's law constant of CO₂ in water, the fact that CO₂ is a weak electrolyte is usually neglected, since the amount of reaction products of CO₂ is very small when the solvent is pure water [7–9]. The CO₂-N₂O analogy assumes that, for a given temperature, the ratio R_H of both gases' Henry's law constants does not depend on the solvent composition, i.e. for aqueous amine solutions:

$$R_H = \frac{H_{N_2O,water} \stackrel{!}{=} H_{N_2O,aqueous\ amine\ solution} \stackrel{!}{=} const.}{H_{CO_2,water} \stackrel{!}{=} H_{CO_2,aqueous\ amine\ solution}} \quad (1)$$

Relying on the validity of Eq. (1), the unknown Henry's law constant of CO₂ in an aqueous amine solution can be determined from the experimental data on the Henry's law constant of N₂O in that solution and the Henry's law constants of both gases in pure water.

The CO₂-N₂O analogy is generally considered to be a practically useful engineering rule [4,10,11]. The idea is loosely based on the similarity of the two molecules CO₂ and N₂O: Both are composed of three atoms, have a linear structure and the same molecular mass [12]. Furthermore, many pure component properties of CO₂ and N₂O, such as the vapor pressure, the saturated liquid and vapor density, and the enthalpy of vaporization, are similar, but not completely identical [13,14]. However, these similarities in the pure component properties do not imply that their behavior in mixtures is similar as well. Nevertheless, the CO₂-N₂O analogy assumes that a non-reacting CO₂ molecule is similar to a N₂O molecule when gas solubilities in various solvents are considered.

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As an alternative to experimental studies, molecular simulation can be used to study phase equilibria. When carried out properly, the quality of the simulation results solely depends on the quality of the employed molecular models. In this work, a simple approach for assessing the validity of the CO₂-N₂O analogy based on molecular simulation is presented. It is explored for the solvents water, ethanol, and their mixtures. Using molecular simulation, the Henry's law constants of CO₂ and N₂O are predicted for the pure solvents and their mixtures and the validity of the CO₂-N₂O analogy is assessed. The solvent ethanol is chosen here because experimental data on the solubility of both gases in ethanol are available in the literature [15–17]. The reactions of CO₂ with ethanol are negligible, as they are for water, and also N₂O does not react with ethanol. Additionally, experimental data also exist in the literature for the solubility of CO₂ in mixtures of water and ethanol [17]. Unless chemical reactions are modeled directly, e.g. by a reactive force field, classical molecular simulations consider only physical effects. Hence, even when a mixture is modeled in which CO₂ would react, e.g. an aqueous amine solution, the reactions are neglected and only the physical solubility is studied in the simulations.

A number of molecular simulation studies have been carried out for determining the solubilities of CO₂ in various solvents [18–26], whereas N₂O has drawn much less attention [25,27]. There is a large number of CO₂ models available in the literature, some of which describe the VLE of pure CO₂ reasonably well. For a detailed discussion, see the recent paper of Jiang et al. [28]. In contrast, there are only three N₂O models available to date [29–31], and none of them is able to describe the VLE with satisfactory accuracy. Therefore, two new molecular models for N₂O are developed in the present work, which differ in their structure, but are parametrized using the same data.

2. Molecular models and simulation methods

2.1. Molecular models

All molecular models used in the present study are rigid and non-polarizable. They contain Lennard-Jones (LJ) sites to describe dispersion and repulsion and partial charges or point quadrupoles to account for hydrogen bonding and polarity. Therefore, all potentials can be written as special cases of

$$U = U_{\text{LJ}} + U_{\text{CC}} + U_{\text{CQ}} + U_{\text{QQ}}$$

$$= \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left\{ \sum_{a=1}^{n_i^{\text{LJ}}} \sum_{b=1}^{n_j^{\text{LJ}}} 4\epsilon_{ijab} \left[\left(\frac{\sigma_{ijab}}{r_{ijab}} \right)^{12} - \left(\frac{\sigma_{ijab}}{r_{ijab}} \right)^6 \right] + \sum_{c=1}^{n_i^{\text{C}}} \sum_{d=1}^{n_j^{\text{C}}} \frac{1}{4\pi\epsilon_0} \left[\frac{q_{ic}q_{jd}}{r_{ijcd}} + \frac{q_{ic}Q_{jd} + q_{jd}Q_{ic}}{r_{ijcd}^3} f_1(\omega_i, \omega_j) + \frac{Q_{ic}Q_{jd}}{r_{ijcd}^5} f_2(\omega_i, \omega_j) \right] \right\}. \quad (2)$$

Here, a , b , c and d denote sites, i and j denote molecules. ϵ_0 is the vacuum permittivity, ϵ_{ijab} and σ_{ijab} are the Lennard-Jones energy and size parameters, r_{ijab} and r_{ijcd} are site-site distances, q_{ic} , q_{jd} , Q_{ic} and Q_{jd} are the magnitude of the point charges and quadrupole moments, respectively. Moreover, $f_1(\omega_i, \omega_j)$ and $f_2(\omega_i, \omega_j)$ are dimensionless angle-dependent expressions in terms of the orientation (ω_i, ω_j) of the electrostatic interaction sites [32].

The modified Lorentz-Berthelot combining rules are used [33,34] for the interaction between unlike Lennard-Jones sites

$$\sigma_{ijab} = \frac{\sigma_{iaa} + \sigma_{jbb}}{2}, \quad (3)$$

$$\epsilon_{ijab} = \xi_{ij} \sqrt{\epsilon_{iaa} \epsilon_{jbb}}. \quad (4)$$

The adjustment of a binary interaction parameter ξ_{ij} is only necessary for the systems 'water + CO₂' and 'water + N₂O' (cf. Section 3.2). Hence, the original Lorentz-Berthelot combining rules are retained in all other cases, i.e. $\xi_{ij} = 1$ for 'water + ethanol' as well as 'ethanol + CO₂' and 'ethanol + N₂O'. It would be desirable to replace the adjustment of the unlike pair interaction parameters by a predictive method, solely based on the knowledge of the interactions in pure components. However, there is no generally accepted way for doing this. There is a variety of mixing rules, but none of these achieves sufficient quantitative accuracy to omit the adjustment of binary parameters if a broad range of mixtures is of interest [35]. Of course, the description of the unlike interactions depends on the modeling level, and introducing more detail, like polarizability, could bring improvements, however at the expense of complexity. There are some promising recent efforts on the matter [26], but a universal, strictly predictive and quantitative description of mixtures has not been achieved yet.

The molecular models for the two solvents water and ethanol are taken from the literature: the water model is TIP4P/2005 [36], and the ethanol model is taken from previous work of our group [20]. Both models have been used successfully in several molecular simulation studies [37–42]. The ethanol model employed here is rigid, and the energetically most likely conformation as found by Jorgensen [43] is used (the *trans* conformation). With this rigid structure, many properties of pure ethanol can be described with high accuracy [20,38].

The binary mixture 'water + ethanol' as described by the models used in the present work was studied extensively by Guevara-Carrion et al. [38]. They found good agreement with experimental data for excess volumes and excess enthalpies as well as for diffusion coefficients and viscosities using predictive simulations based on the Lorentz-Berthelot combining rules. Also the structure of the mixture was considered using the power spectrum and reasonable results were obtained. Hence, no mixture parameters were adjusted here.

For CO₂, two different models are assessed, which are taken from previous work of our group. The model of Vrabec et al. [44] uses the two center Lennard-Jones plus quadrupole approach

(2CLJQ), employing two equal LJ sites and a point quadrupole in the center of mass. The model of Merker et al. [45] employs two equal LJ sites for the oxygen atoms and a different LJ site for the central carbon atom, while also describing the electrostatic interactions with a point quadrupole in the center of mass. This model is denoted as 3CLJQ in the present work. Both models show almost equal performance in the VLE of pure CO₂ and have also been applied successfully in studies of mixtures [20,22–24].

Inspired by the general idea of the CO₂-N₂O analogy, two new molecular models for N₂O were developed in the present work. They follow the same modeling approaches as their CO₂ counterparts: One model is of the 2CLJQ type, and the other model is of the

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