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CO_2 solubility in small carboxylic acids: Monte Carlo simulations and PC-SAFT modeling

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ABSTRACT

Carbon dioxide (CO_2) can electrochemically be converted to a range of products including formic acid (HCOOH) and acetic acid (CH_3COOH). The yield of the products in an electrolysis cell depends on the solubility of CO_2 in the (aqueous) mixture. In absence of experimental data, Monte Carlo simulations in the Gibbs ensemble are used to compute the VLE of the binary systems, CO_2-H_2O, CO_2-HCOOH and CO_2-CH_3COOH, and the ternary systems, CO_2-HCOOH-H_2O and CO_2-CH_3COOH-H_2O. In addition, the PC-SAFT equation of state (EoS) is used to model the VLE of these strongly associating mixtures. Both methods correctly predicts the liquid-phase compositions, but the gas-phase compositions are less accurately described. The challenges to model these systems are related to the simultaneous formation of dimers, rings, and chains, which requires accurate force fields and advanced biasing schemes in MC simulations, and association theories that can account for this effect.

1. Introduction

Electrochemical reduction of carbon dioxide (CO_2) to value-added products using renewable energy is an interesting route to develop carbon capture an utilization (CCU) [1,2]. CO_2 can be converted to a range of products including small carboxylic acids like formic acid (HCOOH) and acetic acid (CH_3COOH) according to the following half-cell reactions [3,4]:

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$$

$$2CO_2 + 8H^+ + 8e^- \rightarrow CH_3COOH + 2H_2O$$

The yield of the products primarily depends on the CO_2 solubility, since only the dissolved CO_2 is reduced at the cathode [5]. The reactions are typically performed in aqueous media, hence the CO_2 solubility is relatively low at atmospheric pressures. Therefore, using high pressures can be advantageous for the electrochemical process [6]. In order to design and operate high-pressure electrolyzers, vapor-liquid-equilibrium (VLE) data of CO_2 in the aqueous mixture are required. We are mainly interested in the formic acid system, but acetic acid is selected as a reference case since it shows a similar phase behavior and more experimental data have been reported for this system. Pure formic acid is susceptible to chemical decomposition and as a consequence gas solubility data is scarcely reported in the literature. The following binaries and ternaries are considered in this study: CO_2-H_2O, CO_2-HCOOH, CO_2-CH_3COOH, CO_2-HCOOH-H_2O, and CO_2-CH_3COOH-H_2O.

The system CO_2-H_2O has been studied extensively, both experimentally and theoretically by equations of state (EoSs) modeling [7–9] and molecular simulations [10,11]. The binary system CO_2-CH_3COOH was experimentally studied by Briones et al. [12], Rumpf et al. [13], Laugier et al. [14], and Bamberger et al. [15]. The system CO_2-HCOOH was studied by Byun et al. [16], but their data, as explained later, show some peculiar behavior. The ternary system CO_2-CH_3COOH-H_2O was experimentally studied by Bamberger et al. [17], Laugier et al. [14], and Panagiotopoulos et al. [18]. No experimental VLE data exist for the CO_2-HCOOH-H_2O system. The binary systems H_2O-HCOOH and H_2O-CH_3COOH have been studied by several researchers and are generally more challenging to describe [19–27]. Carboxylic acids are known to strongly self-associate and cross-associate with water forming dimers, rings, and chain-like structures [28–32], which complicates thermodynamic modeling of such systems. Bamberger et al. [15,17] modeled

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the phase behavior of CO_2 and (aqueous) acetic acid solutions using the Peng-Robinson (PR) EoS in combination of the chemical theory [33], which accounted for the dimerization reaction:

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

The problem with this approach is that in addition to the dimerization constant, the critical properties of the monomers as well as of the dimers need to be known. Perakis et al. [34] used the cubic plus association (CPA) EoS to model the VLE of CO_2 in acetic acid solutions. Satisfactory results were obtained using a 3-site water model, 1-site acetic acid model, and taking CO_2 solvation into account. Despite its industrial significance, the modeling of CO_2 and formic acid solutions has largely been ignored in the literature.

Here, we investigate the ability of Monte Carlo simulations in the Gibbs ensemble to compute the VLE of the binary systems, CO_2-H_2O, CO_2-HCOOH and CO_2-CH_3COOH, and the ternary systems, CO_2-HCOOH-H_2O and CO_2-CH_3COOH-H_2O. In addition, the PC-SAFT equation of state (EoS) is used to model the VLE of these strongly associating mixtures. A comparison with experimental data is provided and limitations of both methods are discussed.

2. PC-SAFT modeling

The thermodynamic perturbation theory (TPT) of Wertheim [35–38] forms the basis of all SAFT-type equations of state (EoSs). The perturbed-chain statistical association fluid theory (PC-SAFT) derived by Gross and Sadowski [39,40] utilizes a hard-chain reference fluid instead of a hard-sphere reference commonly used in other classical SAFT EoSs. In the PC-SAFT formalism, the residual Helmholtz free energy (a^{res}) of the system is expanded in terms of different molecular contributions:

$$a^{\text{res}} = a^{\text{hc}} + a^{\text{dis}} + a^{\text{ass}} \tag{1}$$

where $a^{\text{hc}}, a^{\text{dis}}, a^{\text{ass}}$ are contributions from a hard-sphere chain, dispersion, and association, respectively. Equations to compute the hard-sphere chain and dispersion contributions are provided by Gross and Sadowski [39,40], while details for the association-term can be found in Chapman et al. [41].

The PC-SAFT equation requires five pure component parameters for associating compounds, i.e., the segment number (m), the segment energy (ε/k), the segment diameter (σ), the association energy ($\varepsilon^{A_iB_j}$), and the association volume ($\kappa^{A_iB_j}$). The conventional Lorentz-Berthelot (LB) mixing rules were used for the segment diameter and the segment energy:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}; \quad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}(1 - k_{ij}) \tag{2}$$

where k_{ij} is the binary interaction parameter. Cross-association between associating molecules was described by Wolbach and Sandler (WS) [42] mixing rules:

$$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}}{2}; \quad \kappa_{A_iB_j} = \sqrt{\kappa^{A_iB_i}\kappa^{A_jB_j}}\left(\frac{\sqrt{\sigma_i\sigma_j}}{0.5(\sigma_i + \sigma_j)}\right)^3 \tag{3}$$

Strictly speaking, the WS mixing rules can only be applied to associating compounds [43]. Therefore, compounds that do not self-associate, but interact through cross-association (e.g., CO_2 dissolved in acids) require some special treatment regarding the WS mixing rules. For such compounds, the association energy parameter is set to zero, while the association volume parameter is either treated as an adjustable parameter or set equal to the value of the self-associating compound [44]. This approach to account for cross-association between a non-self-associating and an associating compound is referred to as ’induced association’ or ’solvation’. The pure component PC-SAFT parameters are often fitted to vapor-liquid equilibrium (VLE), vapor-pressure, and/or liquid density data [44]. All parameters used in this study were taken from literature and are listed in Table 1.

Typically, acids are described by the 1A or 2B association scheme of Huang and Radosz [45,46]. In the 1A scheme the molecule has a single site that can bond with a site of similar type on a second molecule. This model can describe dimerization, but lack the ability to form chains. On the other hand, the 2B scheme considers molecules with two different association sites A and B, but only intermolecular A-B bonds are admissible and bonds between sites of similar type (A-A or B-B) are not allowed. This model can capture chain formation, but lacks the ability to form dimers. More information on the thermodyanamic modeling of associating systems can be found in the book of Kontogeorgis and Folas [44], and Kleiner et al. [47].

3. Simulation details

Monte Carlo simulations in the Gibbs ensemble (GEMC) [48,49] were performed to compute the VLE of CO_2 in aqueous formic acid and acetic acid solutions. The TraPPE (united-atom) force field was used for CO_2 [50] and acetic acid [51]. The TIP4P/2005 model [52] was selected for water, and the force field of Schnabel et al. [53] was used for formic acid. CO_2, H_2O, and HCOOH molecules were considered rigid, whereas CH_3COOH was flexible in the simulations. The internal degrees of freedom of the flexible molecules were sampled using Configurational-bias Monte Carlo (CBMC) [54]. Lennard-Jones (LJ) interactions between dissimilar atoms were described by the Lorentz-Berthelot mixing rules, while the Ewald method was used with a relative precision of 10^{-5} to describe the long-range electrostatic interactions [55,56]. The LJ interactions were truncated at 12 Å and analytic tail corrections were applied. The VLE of the pure components and the mixtures were respectively computed in the Gibbs-NVT and the Gibbs-NPT ensemble. In both ensembles two simulation boxes are used and the temperature is fixed, while particles are rotated and displaced within each box, particles are transferred between the boxes, and the volume of the boxes are allowed to fluctuate (keeping the total volume constant in the Gibbs-NVT ensemble) [49]. The number of molecules in the GEMC simulations were computed from coexistence density data (either from experiments or an equation of state) to have a box-size of at least twice the cut-off radius. All MC simulations were performed with the molecular simulation software RASPA [57,58]. The GEMC simulations were started with an equilibration run of 50000 MC cycles followed by a production run of 0.5 million cycles. The number of steps in a MC cycle equals the total number of particles in the simulation box. The reported error bars represent the 95% confidence interval obtained from five independent simulations with different seed numbers and initial configurations.

4. Results and discussion

The VLE and vapor pressures of the carboxylic acids were computed to validate the force fields, see Figs. 1–3. The used force field can accurately describe the pure component VLE and vapor pressures of both acids. We note that in fitting the force field of formic acid, Schnabel et al. [53] drastically reduced the C-H bond-length to induce hydrogen bonding and to reproduce experimental VLE data. The critical temperature (T_c) and density (ρ_c) can be obtained by fitting the saturated densities (ρ_{liq} and ρ_{vap}) to the law of rectilinear diameters and the scaling law for the density [59],