

Numerical study of the dissolution of carbon dioxide in an ionic liquid



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HIGHLIGHTS

- We model the dissolution of CO₂ in ionic liquids.
- The model accounts for the moving phase interface and variable liquid density.
- The initial diffusivity of CO₂ in [bmim][BF₄] is overestimated with a reduced model.
- The diffusivity increases with the dissolution of CO₂ in the ionic liquid.
- The equilibrium diffusivity given by correlations is 28% less than the actual value.

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ABSTRACT

This work investigates the dynamics of the dissolution of carbon dioxide in an ionic liquid using a computational fluid dynamics model. The system is composed of liquid and gas phases separated by a moving boundary. The transport process comprises only one-way mass transfer (from gas phase to liquid phase) since the solubility of ionic liquids in carbon dioxide is immeasurably low in general. The model accounts for the changes in the position of the liquid free-surface and liquid phase molar volume during the dissolution process. Thermodynamic equilibrium condition is valid at the liquid-vapor interface where the discontinuity in the mole fraction of carbon dioxide is formulated using the concept of internal boundary condition. The model is applied to the experimental data obtained for the [bmim][BF₄]-CO₂ system at 323.15 K and 50 bar. The binary diffusivities are calculated and compared with those obtained from the literature and some correlations.

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1. Introduction

Supercritical fluids and ionic liquids are alternative solvents which have been widely investigated for their applications in reactions, extractions and material processing (Knez et al., 2014, Guo et al., 2015). Carbon dioxide is commonly used as a supercritical solvent due to its favorable properties, and developing novel applications of supercritical CO₂ (scCO₂) is of interest also in the context of valorization of CO₂ generated in biochemical and petrochemical processes. Based on the application, the properties of scCO₂ can be fine-tuned by adjusting the operating temperature and pressure (Ramsey et al., 2009; Olajire, 2013). Ionic liquids, on the other hand, as molten salts at room temperature, have unique characteristics such as nonvolatility, high thermal stability and wide liquid range. They can be tailored with the selection of cations and anions forming them, and can dissolve both polar and nonpolar compounds (Ghandi, 2014).

The combination of dense carbon dioxide with an ionic liquid to generate solvent systems with application-specific properties is an active research area. CO₂-expanded ionic liquids offer lower viscosities (higher mass transfer coefficients) compared to ionic liquids, and allow lower processing pressures compared to scCO₂. They are composed of liquid and gas phases even at elevated pressures, and biphasic reactions are an application area of these systems. In biphasic reactions, the catalyst and the reactants are dissolved in the ionic liquid rich phase and products are transferred to the gas phase based on the phase equilibrium conditions. In order for these systems to work, the gas phase should not be contaminated by the liquid solvent. This constraint is satisfied by ionic liquids, which generally do not have measurable solubilities in CO₂ (Ahosseini et al., 2009).

Carbon dioxide-expanded ionic liquids belong to class III of gas-expanded liquids (GXLs). CO₂ has a high solubility in the ionic liquid, however the volumetric expansion of the liquid phase is low compared to class II GXLs (e.g. CO₂-expanded methanol) (Akien and Poliakov, 2009). In the ionic liquid network formed by the cation and anion, CO₂ occupies the empty positions which expand through ion displacements during the dissolution process.

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Therefore, during the formation of the CO₂-expanded ionic liquid system, the density of the liquid phase increases, and despite the high solubility, the volumetric expansion remains low (Cadena et al., 2004; Klahn and Seduraman, 2015). For example, at 40 °C and 70 bar, the solubility of CO₂ in methanol interpolated from the literature data is about 51 percent (Yoon et al., 1993) while the volumetric expansion is close to 90 percent with a molar volume decrease of around 9 percent (Jin, 2006; Sih et al., 2007). On the other hand, at the same temperature and pressure, the solubility of CO₂ in [bmim][BF₄] is 0.47, yet the volumetric expansion remains at 17 percent with a molar volume decrease of 38 percent (Aki et al., 2004; Jessop and Subramaniam, 2007). Unlike CO₂-expanded ionic liquids, mass transfer in class II GXs can be two-way; the diffusion from the liquid phase to the gas phase must be considered in order to model the behavior of these systems accurately.

It is crucial to know the transport properties of carbon dioxide-ionic liquid systems to design their applications. Shiflett and Yozek (2005) determined the diffusion coefficients in [bmim][BF₄] by measuring the amount of dissolved CO₂ using a gravimetric microbalance. The value they reported at 323.15 K and 1 bar is 1.2×10^{-10} m²/s. Another group, Hou and Baltus (2007), found the diffusivities by tracking the change in pressure after the addition of CO₂ into a chamber containing a thin film of ionic liquid. Both research groups used a one-dimensional diffusion model to calculate the diffusion coefficients from the time dependent experimental data. Hou and Baltus ran experiments at a pressure in the range of 1–2 bar and reported a value of $\sim 4.5 \times 10^{-10}$ m²/s, as read from the figure, at 323.15 K which is higher than the former value. They discussed the possible reasons for the difference between the diffusivity values presented in these studies. Also, in a more recent study, Moya et al. (2014) examined the significance of the amount of ionic liquid used in the experiments when the gravimetric method was employed. They ran experiments using different amounts of the ionic liquids ([emim][Tf₂N], [omim][Tf₂N], and [bmim][PF₆]), and found that the mass of the liquid must be sufficiently high for the diffusion coefficients obtained using the one-dimensional model to converge to the same value.

In the present work, we focus on the formation of a carbon dioxide-expanded ionic liquid system which we model as the mass transfer between two phases separated by a moving interface. The mass transfer is one-way, and the phase interface moves upward as CO₂ diffuses into the liquid phase. The model accounts for the changes in the position of the phase interface using the Volume-of-fluid method, and the density of the liquid phase during the process. To determine the time dependent solubility values of CO₂ in the ionic liquid, we use an experimental setup consisting of a view-cell where pressure and temperature are continuously monitored, a high pressure syringe pump for carbon dioxide loading at constant pressure, and a cathetometer to measure the changes in the liquid level. We apply the model to the experimental data collected from the [bmim][BF₄]-CO₂ system at 323.15 K and 50 bar to determine the change in the diffusivities with the liquid phase CO₂ mole fractions. We examine the effects of variable molar volume and moving phase interface on the initial diffusivity and also, compare initial and equilibrium diffusivities with the literature values and those obtained from correlations.

2. Model equations

The addition of carbon dioxide to a system containing an ionic liquid initiates one way mass transfer. CO₂ dissolves in the liquid while the liquid does not diffuse into the gas phase in significant quantities. During the process, the phase interface moves upward and the liquid phase density changes (see Fig. 1).

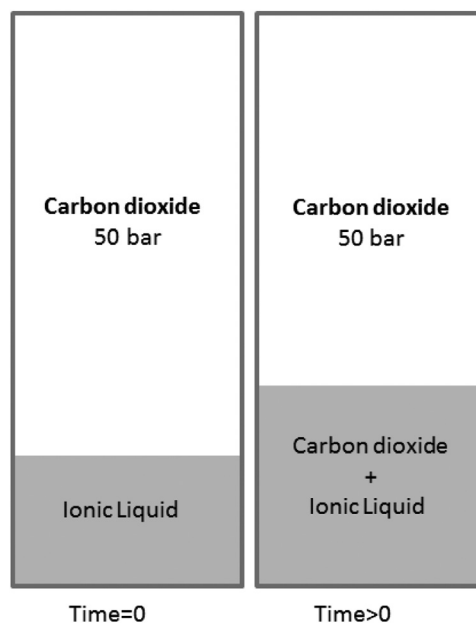


Fig. 1. Schematic of the system.

The position of the phase-interface is tracked by the Volume-of-fluid method (Hirt and Nichols, 1981) where a function for the liquid phase volume fraction is defined in every grid cell and advected by the velocity field as described by the following equation:

$$\frac{\partial(\alpha_L \rho_L)}{\partial t} + \nabla \cdot (\alpha_L \rho_L \mathbf{v}) = S_{\alpha L} \quad (1)$$

where α_L stands for the volume fraction of the liquid phase which takes a value between 0 and 1 if the computational cell contains the phase interface. The source term, $S_{\alpha L}$, is nonzero due to the interphase mass transfer and calculated using Eq. (2), where ρ_L , D and y^{CO_2} denote the liquid phase density, binary diffusion coefficient and mass fraction of carbon dioxide respectively.

$$S_{\alpha L} = -\rho_L D \nabla y^{CO_2} \cdot \nabla \alpha_L \quad (2)$$

The volume fraction of the gas phase is computed by the following constraint.

$$\alpha_L + \alpha_G = 1 \quad (3)$$

In the gas phase, the source term must be of equal magnitude but of opposite sign to satisfy mass conservation.

$$S_{\alpha G} = -S_{\alpha L} \quad (4)$$

The following momentum equation is solved for the entire flow field.

$$\frac{\partial(\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla P + \mu \nabla^2 \mathbf{v} + \rho \mathbf{g} \quad (5)$$

Where density and viscosity in a computational cell are defined as follows:

$$\rho = \rho_L \alpha_L + \rho_G \alpha_G \quad (6)$$

$$\mu = \mu_L \alpha_L + \mu_G \alpha_G \quad (7)$$

A commercial CFD package, ANSYS FLUENT, is used to solve the model equations. In Eq. (2), mass fraction gradient is required to calculate the source term. In FLUENT, in order to ensure that the gradient is calculated correctly at the phase interface, a scalar function for the mass fraction of carbon dioxide, ϕ , is defined in the entire domain. The conservation equation for ϕ , Eq. (8), is

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