

Computer Simulations of Phase Equilibria and Transport Properties in Carbon-Dioxide Expanded Acetonitrile

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September 15, 2006

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1 Introduction

Chemical catalysis plays an important role in the modern chemical industry. The high demand for the products of industrial catalysis increases the need for development of solvent media that are both economical and environmentally friendly. Previous research efforts have focused on primarily supercritical CO₂ (scCO₂) and mixtures of scCO₂ with other solvents such as acetonitrile, toluene, ethanol, etc[1]. However, the reaction benefits are

often marginal with scCO₂. In many cases, scCO₂-based reactions are limited by inadequate solubilities of preferred homogeneous catalysts. Additionally, CO₂ is non-polar, which usually results in relatively low reaction rates.

In recent years, investigations at the Center for Environmentally Beneficial Catalysis laboratories and elsewhere [1, 2, 3] have clearly demonstrated how a relatively new class of solvents, are promising alternative media for performing catalytic reactions. A carbon-dioxide expanded liquid (CXL) is a mixed solvent composed of CO₂ condensed into an organic solvent. By varying the CO₂, a continuum of liquid media ranging from the neat organic solvent to scCO₂ is generated, the properties of which can be adjusted by tuning the operating pressure; e.g., a large amount of CO₂ favors gas solubility and the presence of polar organic solvents enhances metal catalyst solubility.

To rationally exploit CXLs, a complete knowledge of CO₂/organic solvent mixtures properties is required. Of particular interest are the vaporliquid equilibria (VLE) and transport properties for each of the pure components and the multicomponent including binary mixtures. In this work, we use previously published molecular potential of CO₂ [4] and acetonitrile [5] and the Lorentz-Berthlot mixing rules [6] to simulate the phase equilibria and transport properties of the CO₂/acetonitrile binary mixture. The phase equilibria calculations were performed using the Gibbs Ensemble Monte Carlo (GEMC) method [7, 8, 9, 10] to determine the coexistence curve of the pure solvent systems and the volume expansion of the binary mixture. The molecular simulation results for the volume expansion of the binary mixture were found to be superior to the predictions based on the Peng-Robinson (PR) equation of state (EOS). The molecular dynamics method was used to study the transport properties of the binary system and we report values of translational diffusion coefficients, rotational correlation times and shear viscosities of the liquid mixtures at various CO₂ mole fractions. The results indicate that the transport properties of CO₂-expanded acetonitrile may be varied in a smooth, predictable manner by adjusting the pressure of the CO₂ component.

2 Results

Phase Equilibrium Properties

To validate our methodology and our potentials for phase equilibrium in CO₂ and MeCN, we first test their ability to predict vapor-liquid coexistence in the pure systems.

The saturated liquid and vapor densities for CO₂ are in good agreement with experiment [11] over a large range of temperature. The same agreement was found by Harris *et al.*[4]. For acetonitrile, the vapor-liquid coexistence data of our simulations is only in qualitative agreement with experiment. Accurate densities were obtained in the vapor phase for temperatures below 150 deg C while the liquid phase densities is approximately 15% low over the entire temperature range. In the current work, we are interested in volume expansion, which is always close to unity at low CO₂ solubility [12]. Thus, these deviations for acetonitrile simulations should not significantly affect our results for the binary CO₂-acetonitrile mixture.

Figure 1 shows simulations and Peng-Robinson equation of state results together with experiment data of the liquid phase volume expansion by CO₂ for acetonitrile at 25 deg C. Our simulations are in good agreement with experimental results. For both mixtures, the volume expansion of the liquid phase varies strongly with pressure (i.e., CO₂ addition), starting with a gradual increase at low pressures and leading to a progressively larger increase at higher pressure. Composition of 65% in CO₂ mole fraction were achieved at pressure below 5 MPa. The Peng-Robinson equation of state calculation results tend to underestimate the volume expansion.

Transport Properties

The results of the calculated translational diffusion coefficients D_t are presented in Figure 2. The translational diffusion rates of both CO₂ and acetonitrile increase with increasing CO₂ mole fraction, x_{CO_2} . Overall, our simulations predict that the rate of translational diffusion in CO₂-acetonitrile mixtures may be varied by a factor of 2-4 by changing the CO₂ content. For the rotational correlation times, our results show a clear trend for faster rotational

diffusion of both carbon dioxide and acetonitrile components with rising CO_2 mole fraction. This trend parallels the behavior of the translational diffusion coefficients described above, and may be analogously rationalized in terms of adding the more mobile CO_2 to the less mobile acetonitrile leading to slowing down of reorientations of the former while speeding up reorientations of the latter. The rate of reorientational motion in the mixtures may be varied by a factor of 2-3 by adjusting the amount of CO_2 . The calculated values of the shear viscosities exhibit a trend for systematic decrease with increasing x_{CO_2} . Changing from pure CH_3CN to pure CO_2 along the 298 K isotherm leads to a ca. 8-fold decrease of calculated viscosity.

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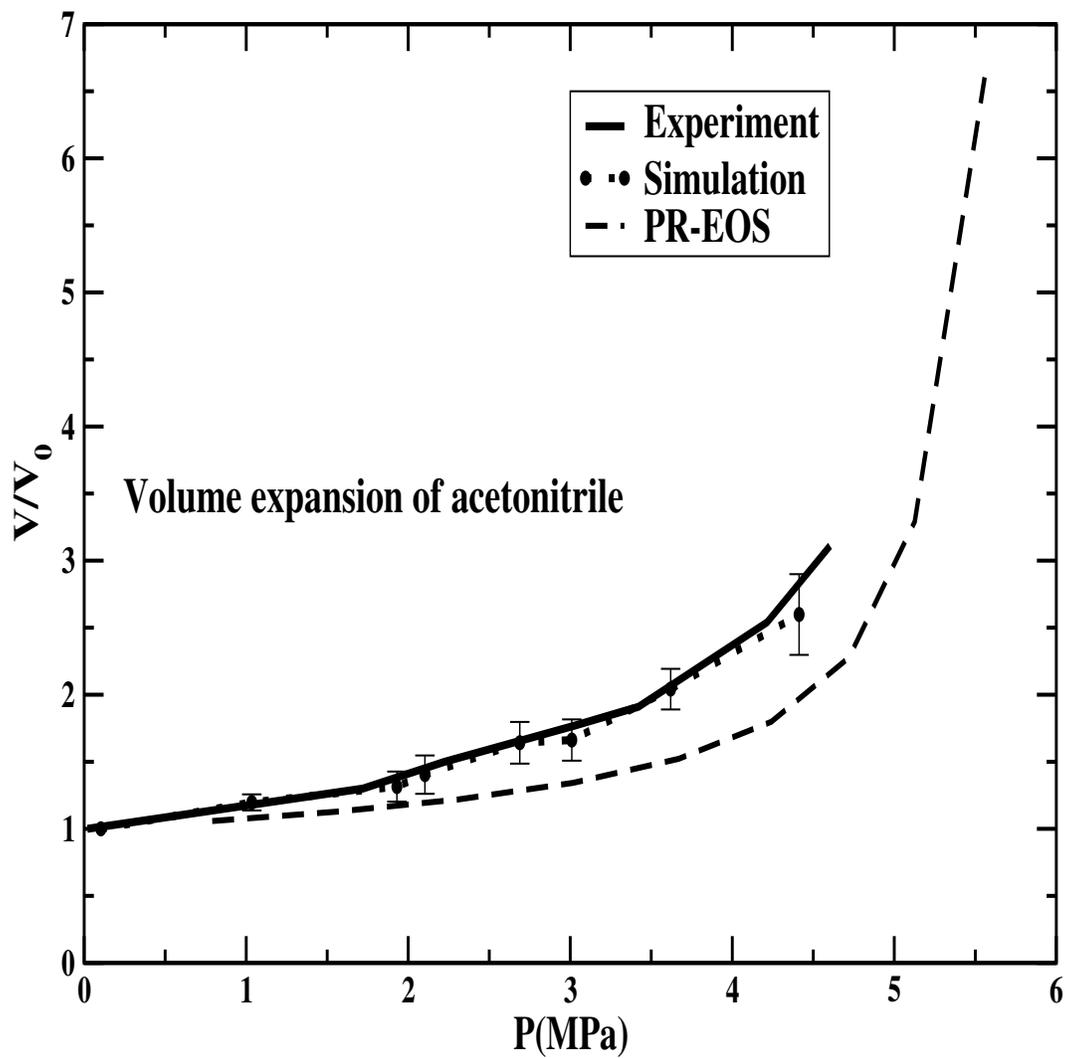


Figure 1: Volume expansion in carbon-dioxide-acetonitrile system at 25 deg C .

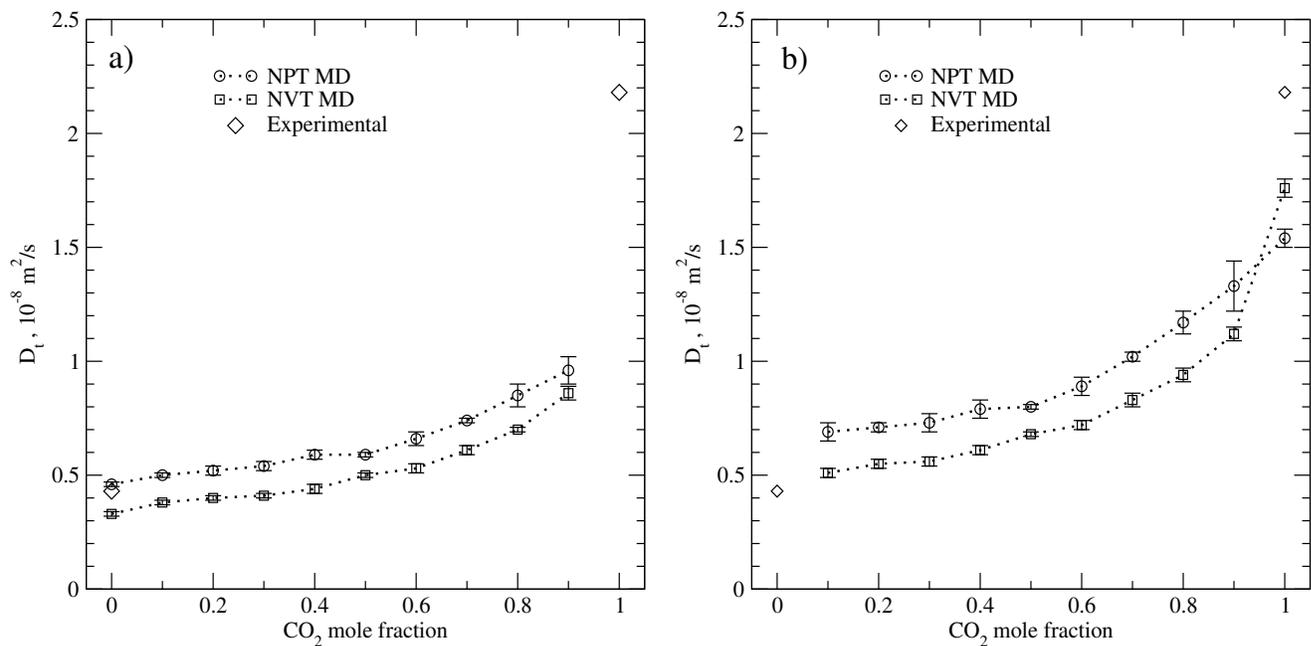


Figure 2: Translational diffusion coefficients in CO_2 -acetonitrile mixtures. Units are $\text{\AA}^2 \text{ps}^{-1} = 10^{-8} \text{ m}^2 \text{ s}^{-1}$. a) Calculated values for acetonitrile: circles - NPT, squares - NVT MD. Experimental value for pure acetonitrile at 1 bar and 298 K is marked by a diamond [13]. b) Calculated values for CO_2 : circles - NPT, squares - NVT MD. Experimental value for pure CO_2 64 atm and 298 K is marked by a diamond [14].