Phase Equilibria and Transport in Carbon Dioxide-Expanded Solvents

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Introduction

Carbon dioxide-expanded liquids are obtained by mixing organic liquids with compressed carbon dioxide. These liquids are being investigated as novel media for environmentally friendly chemical processing at the Center for Environmentally Beneficial Catalysis at the University of Kansas. We present the results of atomistic modeling of phase equilibria and transport properties of several expanded liquid systems.

Simple intermolecular potential models available in the literature [1, 2, 3, 4, 5, 6] were used to simulate the phase equilibrium properties of binary mixtures of carbon dioxide with acetonitrile, methanol, ethanol, acetone, acetic acid, toluene, and octene. The calculations were performed using the Gibbs ensemble Monte Carlo (GEMC) method [7, 8, 9, 10] with the standard Lorentz-Berthelot combination rules. Calculations in the canonical ensemble (NVT) were performed to determine the coexistence curve of the pure-component systems. A total of N = 512 molecules in liquid and gas phases was used in all pure-component simulations. Binary-mixture were simulated in the isobaric-isothermal ensemble (NPT) with a total of N = 600 molecules placed in the two simulation boxes.

For pure carbon dioxide, pure acetonitrile and CO_2-acetonitrile mixtures we have also performed calculations of translational and rotational diffusion coefficients, which are basic measures of molecular mobility. These calculations involved nanosecond length molecular dynamics simulations with the program CHARMM [11] for systems of N=1024 total molecules under NVT and NPT conditions.

Results

Vapor-Liquid coexistence curves of pure component systems were computed to test the potential model of each molecule. The simulations reproduced accurately experimental data of saturated liquid and vapor densities for carbon dioxide, methanol, ethanol, acetone, acetic acid, toluene, and octene. 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 450 K while the liquid phase densities is approximately 15% low over the entire temperature range.

For the binary mixtures composed of carbon dioxide and organic solvents, we calculated the volume expansion of the liquid phase defined as the total volume divided by the volume of the pure organic solvent liquid. Calculations for pressures up to 50 bar were performed for each mixture. Volume expansion results of our simulations are in close agreement with experimental data for carbon dioxide expanded acetonitrile, methanol, ethanol, acetone, and toluene systems. For acetic acid and octene binary mixtures with carbon dioxide, deviations of the volume expansion from the experimental values were observed at higher pressures.

The transport coefficients of pure CO_2 and pure acetonitrile at 298 K and 1 atm were in good agreement with experimental data. The translational and rotational diffusion coefficients for the binary CO_2-acetonitrile mixtures exhibited smooth variation between the values of the pure components as the CO_2 mole fraction was varied between 0.1 and 0.9.

Conclusions

Use of published force field parameters and standard combination rules allowed us reliable predictions of properties for a number of carbon dioxide-expanded organic liquids. The simulations may thus serve to complement and even substitute for experimental measurements for these novel liquids which are being applied to limit the use of organic solvents and tailor media physical properties in chemical processing.

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References

[1] J.G. Harris and K.H. Yung, Carbon dioxide's liquid-vapor coexistence curve and critical properties as predicted by a simple molecular model J. Phys. Chem. **99**, 12021 (1995).

[2] Y. Hirata, Molecular dynamics simulation study of the rotational and translational motions of liquid acetonitrile J. Phys. Chem. A **106**, 2187 (2002).

[3] Kamath G., Cao F, and Potoff J.J., An improved force field for the prediction of the vapor-liquid equilibria for carboxylic acids J. Phys. Chem. B **108**, 14130 (2004).

[4] B. Chen, J. J. Potoff, and J. I. Siepmann, Monte carlo calculations for alcohols and their mixtures with alkanes. transferable potentials for phase equilibria. 5. united-atom description of primary, secondary, and tertiary alcohols J. Phys. Chem. B **105**, 3093–3104 (2001).

[5] J. M. Stubbs, J. J. Potoff, and J. I. Siepmann, Transferable potentials for phase equilibria. 6. united-atom description for ethers, glycols, ketones, and aldehydes J. Phys. Chem. B **108**, 17596–17605 (2004).

[6] C. D. Wick, M. G. Martin, and J. I. Siepmann, Transferable potentials for phase equilibria. 4. united-atom description of linear and branched alkenes and alkylbenzenes J. Phys. Chem. B **104**, 8008–8016 (2000).

[7] Panagiotopoulos A. Z., Direct determination of phase coexistence properties of fluids by monte-carlo simulation in a new ensemble Mol. Phys. **61**, 813–826 (1987).

[8] A. Z. Panagiotopoulos, N. Quirke, Stapleton, and D. J. Tildesley, Phase-equilibria by simulation in the gibbs ensemble - alternative derivation, generalization and application to mixture and membrane equilibria Mol. Phys. **63**, 527–545 (1988).

[9] Panagiotopoulos A. Z., Direct determination of fluid-phase equilibria by simulation in the gibbs ensemble - a review Mol. Simul. **9 (1)**, 1–23 (1992).

[10] M. G. Martin, B. Chen, C. D. Wick, J. J. Potoff, John M. Stubbs, and J. I. Siepmann, Mcccs towhee, http://towhee.sourceforge.net/.

[11] B. R. Brooks, R. Bruccoleri, B. Olafson, D. States, S. Swaminathan, and M. Karplus, CHARMM: A program for macromolecular energy, minimization and dynamics calculations J. Comp. Chem. **4**, 187–217 (1983).

[12] D. M. Newitt, M. U. Pai, N. R. Kuloor, and J. A. W. Huggill, *In Thermodynamic Functions of Gases*, (Dim, F. Ed., Butterworth: London, 1956; Vol. 123).

[13] B. D. Smith and R. Srivastava, *Thermodynamic Data for Pure Compounds: Part B Hydrocarbons and Alcohols*, (Elsevier, Amsterdam, 1986).

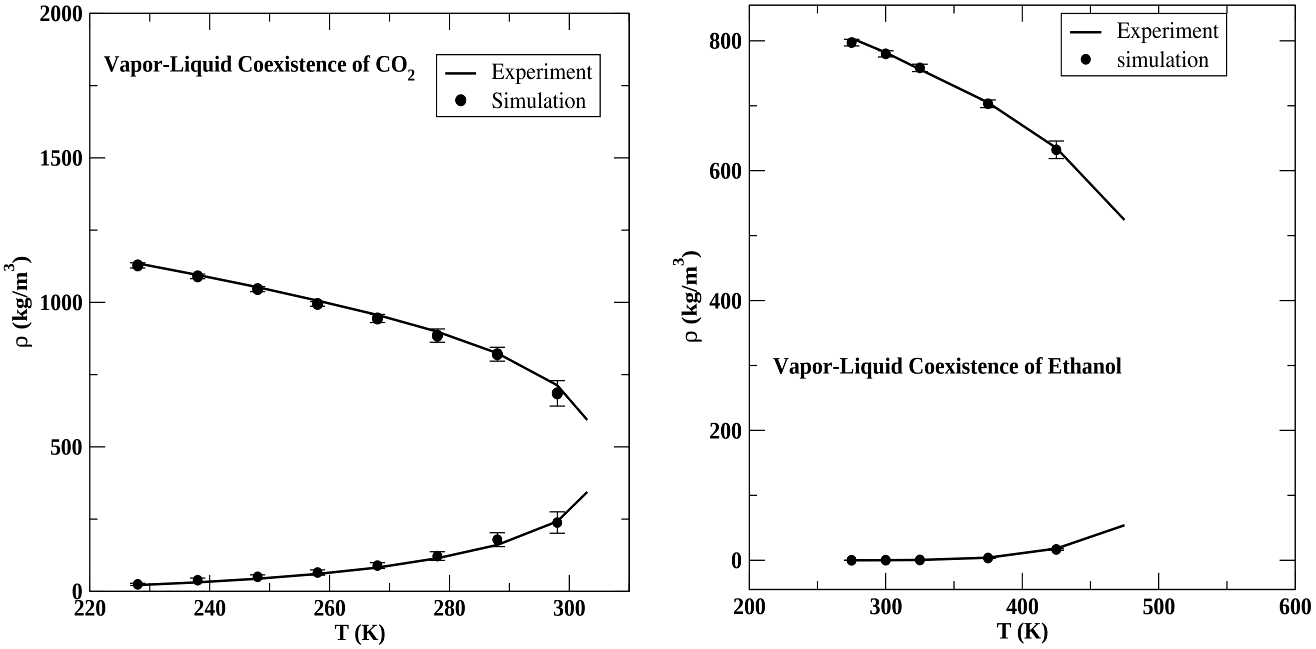

Figure 1: Vapor-liquid coexistence curves for carbon dioxide and ethanol. Experimental data were taken from ref. [12] for CO_2 and ref. [13] for CH_3CH_2OH.

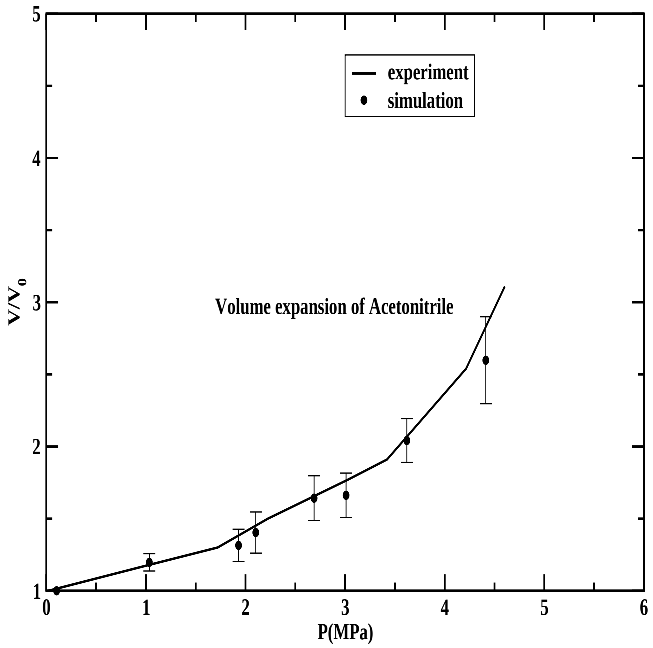

Figure 2: Volume expansion in carbon dioxide-acetonitrile system at 298.15 K. Experimental data and simulation results are shown as line and symbol, respectively.

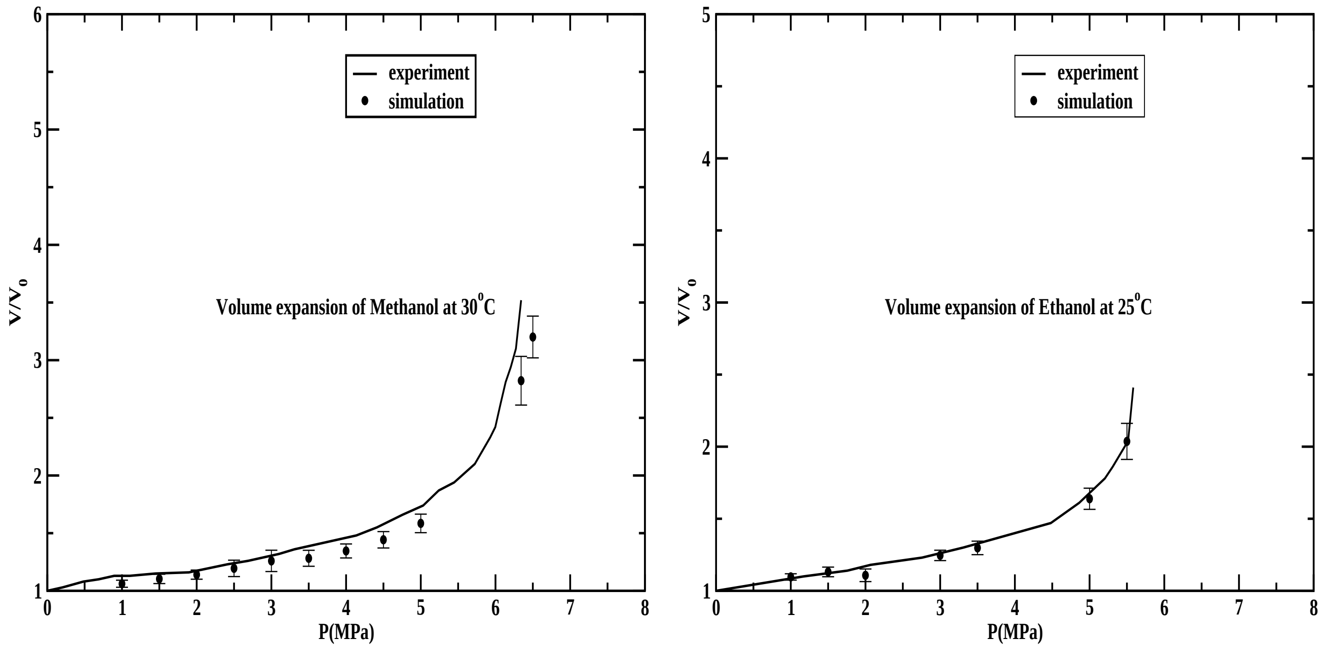

Figure 3: Volume expansions in carbon dioxide-methanol system at 303.15 K (right) and in carbon dioxide-ethanol system at 298.15 K (left). Experimental data and simulation results are shown as line and symbol, respectively.

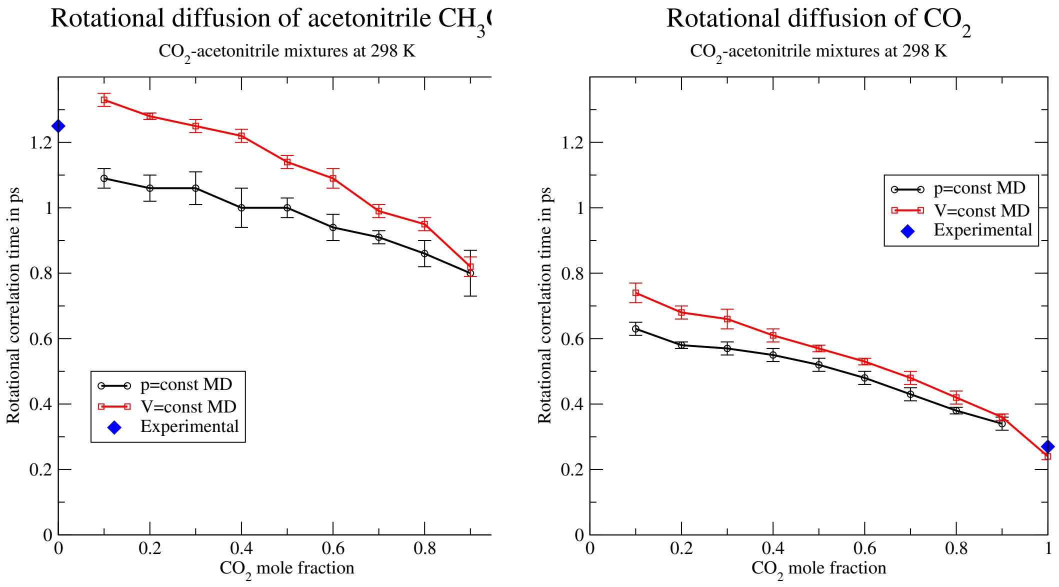

Figure 4: Translational diffusion coefficients of acetonitrile and carbon dioxide in binary mixtures. Results are for 298 K; pressures are 1 atm for pure acetonitrile and at vapor-liquid equilibrium values for mixtures and pure CO_2.

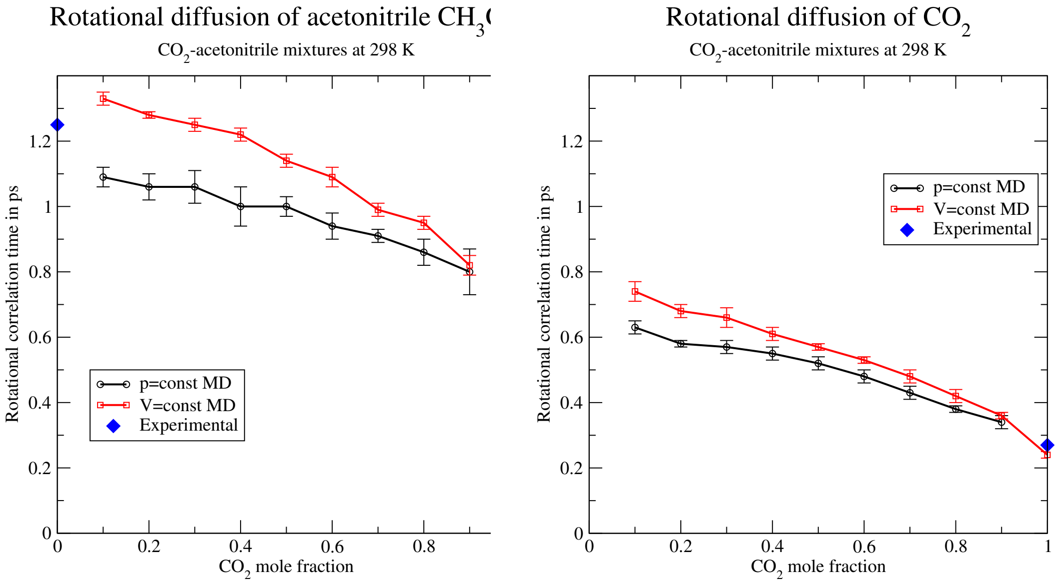

Figure 5: Rotational correlation times for reorientations of molecular axes of acetonitrile and carbon dioxide in binary mixtures. Results are for 298 K; pressures are 1 atm for pure acetonitrile and at vapor-liquid equilibrium values for mixtures and pure CO$_2$.