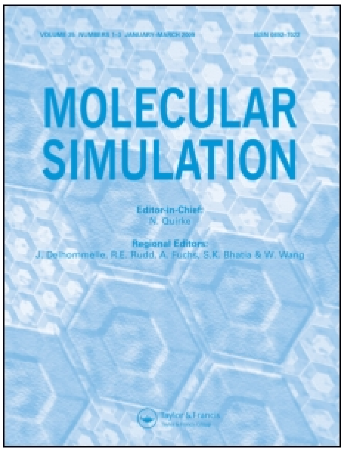

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Prediction of phase equilibria and transport properties in carbon-dioxide expanded solvents by molecular simulation

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Prediction of phase equilibria and transport properties in carbon-dioxide expanded solvents by molecular simulation

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We review our recent work on the calculations of the phase equilibrium and transport properties in carbon-dioxide (CO_2) expanded liquids (CXLs) via Monte Carlo and molecular dynamics (MD) simulations. Gibbs ensemble Monte Carlo simulations were performed to determine the volume expansion, the pressure–composition and pressure–density phase diagrams for CO_2 expanded acetonitrile, acetone, methanol, ethanol, acetic acid, toluene and 1-octene. MD simulations were conducted to compute the translational diffusion coefficients, rotational correlation times and shear viscosities in CO_2 expanded acetonitrile. Potential parameters for the pure component together with standard mixing rules were used to describe the interactions between the mixture components. A good agreement between simulation results and available experimental data is achieved. The simulation results for the volume expansion, the pressure–composition and pressure–density phase diagrams were in some cases superior to the Peng–Robinson (PR) equation of state correlations, showing the ability of molecular simulation to predict CXL properties for their use as solvent media in engineering processes.

Keywords: Molecular-dynamics simulation; Monte-Carlo-simulation; CO2-expanded liquids; Vapor-liquid-equilibria

1. Introduction

Solvent usage in chemical industries poses environmental concerns because of the high volatility and toxic nature of many common industrial solvents. The replacement of current solvents with more benign alternatives has become a necessity. In recent years, work at the Center for Environmentally Beneficial Catalysis [1–4] and in other research groups [5–17] has shown carbon-dioxide (CO_2) expanded liquids (CXLs) as promising alternate media for performing catalytic reactions, such as homogeneous catalytic oxidations [2], hydroformylation [3,18] and solid–acid catalyzed-reactions [4].

To optimize CXLs solvents for industrial use, the knowledge of the vapor–liquid equilibria (VLE) and transport properties for each of the pure components as well as the multicomponent, including binary mixtures, is essential. Experimental data on phase equilibria in CXLs are available in the literature [19–25]. However, because experiments are time-consuming, published data on CO_2 expanded solvents are sparse. For the transport properties, very little experimental data can be found in the literature. Sassiat and Morier [26] reported that the diffusion coefficients of benzene in CO_2-expanded methanol increased between 4 and 5 fold with CO_2 addition. Kho *et al.* [27] measured viscosities of CO_2-expanded fluourinated solvents using an electromagnetic viscometer. In the 25–35°C range and at pressures from 8–72 bar, Kho *et al.* report up to a 4–5 fold decrease in viscosity with CO_2 addition [27]. Thus, it would be useful to have a method to predict phase equilibria and transport properties for this promising novel class of solvent media.

The conventional approach to modeling for chemical engineering applications uses an empirical equation of state (EOS) such as the Peng–Robinson (PR) EOS [28]. These equations of state are simple two-parameter Van der Waals (vdW) type cubic EOS [29] and are usually excellent correlation tools for pure component properties. However, to reliably predict properties for mixtures, empirical EOS often use complicated mixing rules that must be optimized specifically for each mixture by using experimental data. A promising alternative to EOS models

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is the use of molecular simulation for the accurate prediction of thermodynamic and transport properties from pure component data. There have been few molecular simulations studies of CXLs [30–35]. The reported methods include Gibbs ensemble Monte Carlo (GEMC) [36,37] and molecular dynamics [38]. Li and Maroncelli [33] performed molecular dynamics (MD) simulations of CO_2-expanded cyclohexane, acetonitrile and methanol to calculate energies, local compositions, viscosities, diffusion coefficients and dielectric constants and relaxation times. Aida and Inomata [34] reported MD simulations of the self-diffusion and dielectric properties in CO_2/methanol mixtures. Shukla *et al.* [35] used MD simulations to study local solvation and transport effects in CO_2-expanded methanol and acetone.

Recently, we have employed GEMC and MD simulations for the calculations of the phase equilibria and transport properties in CXLs binary mixtures using simple pure component force fields available in the literature with the mixture interaction potential parameters determined by standard Lorentz–Berthlot combining rules [30–32]. For the phase equilibria simulations, the GEMC method [23,36,39,40] was used. In the canonical ensemble (*NVT*), we first computed the VLE coexistence curve of the pure component systems to validate the choice of the molecular potential parameters. Then, calculations within the isobaric-isothermal ensemble (*NPT*) were performed to determine the volume expansion of the mixtures

$$\frac{V(T,P)}{V_0(T,P_0)} \tag{1}$$

where V represents the total volume of the mixture liquid phase at temperature T and pressure P and V_0 is the total volume of the pure solvent at the same temperature and at atmospheric pressure.

For comparison, we have also calculated the volume expansion properties using the PR EOS model. The molecular simulation results for the volume expansion of the binary mixture were found in some cases to be superior to the correlations based on the PR EOS.

In the studies of the transport properties, we have used MD simulation methods to calculate the translational diffusion coefficients D_t, rotational correlation times τ and shear viscosities η for the CO_2 expanded acetonitrile liquid mixtures at various CO_2 mole fractions [32]. Our calculations reproduced the experimentally observed values of the pure components and made predictions about the unknown properties of the mixtures.

This paper reviews our recent work on the calculations of the phase equilibria and transport properties in CO_2 CXLs using molecular simulation methods. We continue this article with a brief description of the simulation and modeling methods. After a summary of the results of the VLE for the pure solvents, we present Monte Carlo simulation and PR-EOS calculations results for the volume expansion properties, and the pressure composition and density diagrams in the CXL mixtures studied. We then summarize the MD simulations results for translational and rotational diffusion, and shear viscosity in CO_2-expanded acetonitrile.

2. Models and simulation methods

In this section, we briefly describe the models and simulation methods used. More information can be found in our previous papers [30–32]. All molecules studied in this work are represented by the united-atom model in which CH_x groups (with $0 \leq x \leq 4$) is represented as a single interaction site that is located at the position of the carbon atom. The interaction between nonbonded sites is described by pairwise additive Lennard–Jones (LJ) 12–6 potentials and Coulombic interactions of partial charges

$$U(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \tag{2}$$

where r_{ij}, ϵ_{ij}, σ_{ij}, q_i and q_j are the separation, LJ well depth, LJ size, and partial charges, respectively, for interacting atoms i and j. Unlike interaction parameters ϵ_{ij} and σ_{ij} were calculated using Lorentz–Berthelot combining rules [38]. We used standard combination rules for simple and consistent treatment of a wide class of molecules with off-the-shelf potentials. For all simulations, an Ewald sum method was used to calculate the long-range electrostatic interactions [38,41].

The CO_2 and acetonitrile molecules used in the Monte Carlo simulations were modeled as rigid three-site. The EPM2 potential parameters developed by Harris and Yung [42] and optimized for VLE were used for CO_2. Acetonitrile interaction parameters were taken from the work of Hirata [43]. For the Monte Carlo simulations, all the other molecules intramolecular interactions were treated in the following way: the bond length between two neighboring pseudo-atoms was fixed. A harmonic potential is used to control bond angle bending

$$U_{\text{bend}} = \frac{k_0}{2}(\theta - \theta_0)^2 \tag{3}$$

where θ is the actual bending angle, θ_0 is the equilibrium bending angle and k_0 is the force constant. The dihedral rotations were controlled by a cosine series

$$\begin{aligned} U_{\text{torsion}} = & c_0 + c_1[1+\cos(\phi+f_1)] + c_2 \\ & [1-\cos(2\phi)] + c_3[1+\cos(3\phi)] \end{aligned} \tag{4}$$

where f_1, ϕ and c_i are phase factor, the dihedral angle and the i-th expansion coefficient, respectively.

For the MD simulations of CO_2/acetonitrile, the CO_2 and acetonitrile molecules were treated by flexible models in which the original force fields were modified by introducing bond stretching and angle bending potentials. Since flexible models are needed for larger molecules such as octene, this approach allows systematic treatment of

Table 1. Parameters for non-bonded interactions (Refs. [42,43,53–56]).

Molecule	*Atom/group*	*ϵ/k_b (K)*	*σ (Å)*	*q (e)*
Carbon-dioxide	C	28.129	2.757	0.6512
	O	80.507	3.033	−0.3256
Acetonitrile	CH_3	90.6	3.8	0.269
	C	105	3.0	0.129
	N	48.8	3.4	−0.398
Methanol	CH_3	98	3.75	0.265
	O	93	3.02	−0.7
	H	0	0	0.435
Ethanol	CH_3	98	3.75	0
	CH_2	46	3.95	0.265
	O	93	3.02	−0.7
	H	0	0	0.435
Acetone	CH_3	98	3.75	0
	C	40.0	3.82	0.424
	O	79	3.05	−0.424
Acetic acid	CH_3	98	3.75	0.12
	C	41.0	3.90	0.42
	O(=C)	79	3.05	−0.45
	O(−H)	93	3.02	−0.46
	H	0	0	0.37
Toluene	CH_3	98	3.75	0
	CH(aro)	50.5	3.695	0
	C(aro)	21.0	3.88	0
1-octene	CH_3	98	3.75	0
	CH_2(−C)	46	3.95	0
	CH	47.0	3.73	0
	CH_2(= C)	85.0	3.675	0

molecules of any size. More details about the models can be found in Ref. [32].

The parameters for the nonbonded interactions for all molecules studied in this work are listed in table 1. For the intramolecular interaction parameters the reader can consult Refs. [30–32].

Phase equilibria simulations for CO_2-expanded acetonitrile (CH_3CN), acetone (CH_3COCH_3), methanol (CH_3OH), ethanol (CH_3CH_2OH), acetic acid (CH_3-$COOH$), toluene ($CH_3C_6H_2$), and 1-octene (C_8H_{16}) were performed using the GEMC method [23,36,39] and the MCCCS Towhee program [40]. The coexistence curve of the pure-component systems were simulated in the *NVT* ensemble and the calculations of the binary mixtures were performed within *NPT* ensemble.

MD simulations for the transport properties of CO_2-expanded acetonitrile were carried out using the program CHARMM [44]. Both constant volume (*NVT*) and constant pressure (*NPT*) were employed in our recent work [32] for calculations in pure liquids and binary mixtures; here we report the *NVT* calculations. The Nosé–Hoover algorithm was used to maintain a constant temperature at 25°C in all cases [38].

For all binary mixtures, our results were compared to the values obtained using the PR EOS

$$P = \frac{RT}{v - b} - \frac{a(T)}{v^2 + 2bv - b^2} \tag{5}$$

where T, P, R and v are the temperature, pressure, the ideal gas constant and molar volume. For a component i, parameters a and b are given by

$$a_i = 0.457235 \frac{(RT_{\mathrm{ci}})^2}{P_{\mathrm{ci}}} \left[1 + k_i\left(1 - \sqrt{\frac{T}{T_{\mathrm{ci}}}}\right)\right]^2 \tag{6}$$

$$b_i = 0.077796 \frac{RT_{\mathrm{ci}}}{P_{\mathrm{ci}}}, \tag{7}$$

where T_{ci} and P_{ci} are the critical temperature and pressure of compound i. The k_i term has the form

$$k_i = 0.37464 + 1.54226 w_i - 0.26992 w_i^2 \tag{8}$$

where w is Pitzer's acentric factor.

For this EOS the mixture parameters a and b are determined using the conventional vdW mixing and combining rules

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{9}$$

$$a_{ij} = (1 - k_{ij})\sqrt{a_{ii} a_{jj}} \tag{10}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{11}$$

$$b_{ij} = (1 - l_{ij}) \frac{b_{ii} + b_{jj}}{2}. \tag{12}$$

The calculations of VLE were carried out by equating the fugacities ϕ_i of each component in the liquid phase and in the vapor phase and summing the mole fraction x_i and y_i in each phase to unity

$$\phi_i^L x_i P = \phi_i^V y_i P \tag{13}$$

$$\sum_{i=1}^{2} x_i = 1 \quad \text{and} \quad \sum_{i=1}^{2} y_i = 1. \tag{14}$$

The Newton–Raphson [45] (NR) method was used to solve the nonlinear equations (13) and (14).

For the binary systems CO_2/methanol, CO_2/acetic acid and CO_2/1-octene, the simplex optimization method was used to determined the cross interaction parameters k_{ij} and l_{ij} by minimization of the objective function

$$F = \sum_{m=1}^{n} |P_{\mathrm{calc},m} - P_{\mathrm{exp},m}| \tag{15}$$

where n is the number of experimental data points. In the case of CO_2/1-octene system, VLE data from our simulations were used since we could not find experimental VLE data.

We listed in table 2 the pure component and mixing parameters. More details about the PR-EOS calculations can be found in Ref. [30].

3. Vapor–liquid equilibria

3.1 Pure components

In order to validate the molecular models and the simulation method for phase equilibrium, we calculated

Table 2. Pure component and mixing parameters.

	Pure component parameters (Refs. [57,58])		
Component	*T_c(K)*	*P_c (MPa)*	*W*
Carbon-dioxide	304.2	7.38	0.225
Acetonitrile	545.5	4.83	0.327
Methanol	513	8.1	0.572
Ethanol	516.2	6.38	0.635
Acetone	508.1	4.70	0.309
Acetic acid	592.75	5.78	0.4624
Toluene	591.8	4.11	0.257
1-octene	567	2.68	0.386
	Mixing parameters		
System	*k_{ij}*	*l_{ij}*	*References*
CO_2/acetonitrile	0.070	0.000	Parameters from Ref. [19]
CO_2/methanol	0.057	0.002	Data from Ref. [59]
CO_2/ethanol	0.089	0.000	Parameters from Ref. [19]
CO_2/acetone	0.078	0.072	Parameters from Ref. [60]
CO_2/acetic acid	0.020	0.000	Data from Ref. [21]
CO_2/toluene	0.090	0.000	Parameters from Ref. [60]
CO_2/1-octene	0.020	0.004	Data from our simulation

the vapor–liquid coexistence curves of all the pure component systems. We reproduce in figure 1 the results presented in Ref. [30]. The saturated liquid and vapor densities are in good agreement with experimental data [46–50] for CO_2, methanol, ethanol, acetone, toluene and 1-octene. The simulation results for acetonitrile are only in qualitative agreement with experiment. As pointed out previously [30,31], this deviation from experimental data for the neat acetonitrile should not affect CO_2/actenonitrile mixture results at the temperatures considered.

3.2 Mixtures

At selected temperatures the vapor–liquid coexistence were determined for pressure up to 5 MPa by two-phase *NPT*-GEMC simulations of the binary systems CO_2+ acetonitrile at 25°C, acetone at 30°C, methanol at 30°C, ethanol at 25°C, acetic acid at 25°C, toluene at 30°C and 1-octene at 60°C.

In figures 2–4, we compared the simulations results for the volume expansion of the liquid phase defined by equation (1) to experimental data as well as with the PR EOS results. For the binary mixtures of CO_2 with acetonitrile, acetone, methanol, ethanol and toluene, the results are in good agreement with experimental results. For the binary mixtures of CO_2 with acetic acid and 1-octene, the experimental data is reproduced at low pressure. For pressures greater than 4 MPa, the calculated values are underestimated in CO_2 + acetic acid and overestimated in CO_2 + 1-octene. The PR-equation-of-state volume-expansion calculations for CO_2/methanol, CO_2/toluene and CO_2/1-octene are in close agreement with our simulation results. However, the PR-EOS results in CO_2/acetonitrile, CO_2/acetone and CO_2/acetic acid tend to underestimate the volume expansion. In these cases, our simulations give better agreement with experimental results than PR-EOS correlations.

The pressure–composition diagram is shown in figures 5–7. Good agreements are obtained between simulated results and the PR-EOS calculations. The simulated CO_2 mole fractions in the liquid phase are also compared to the experimental data from Ref. [19] for CO_2/CH_3CN in figure 5(a) and CO_2/CH_3CH_2OH in figure 6(b). As can be seen from the plots, our results are

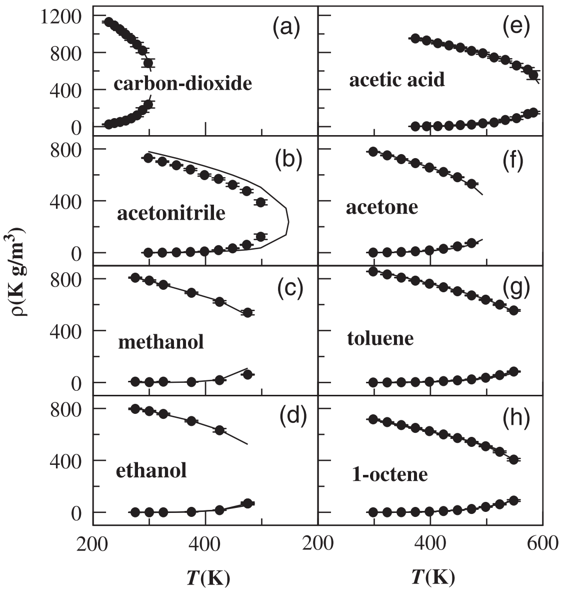

Figure 1. Vapor–liquid coexistence curves for the pure component systems: (a) CO_2; (b) acetonitrile; (c) methanol; (d) ethanol; (e) acetic acid; (f) acetone; (g) toluene; and (h) 1-octene. Simulation coexistence data (circles), experimental (lines) (Refs. [46–50]).

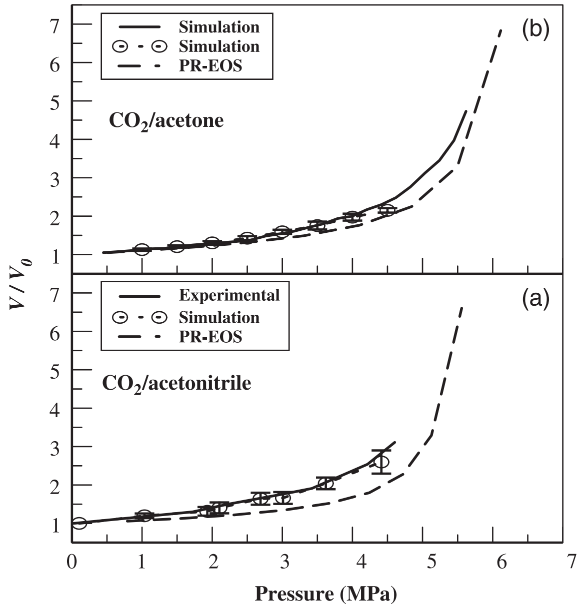

Figure 2. Volume expansion for CO_2-expanded: (a) acetonitrile (25°C); (b) acetone (30°C).

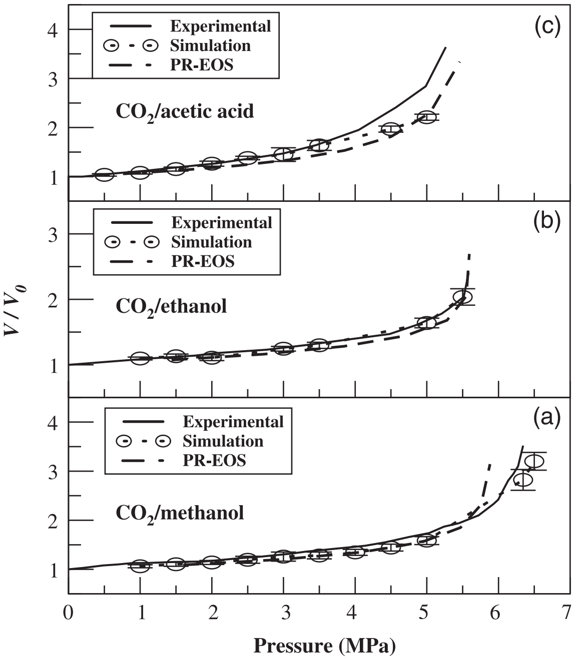

Figure 3. Volume expansion for CO_2-expanded: (a) methanol (30°C); (b) ethanol (25°C); (c) acetic acid (25°C).

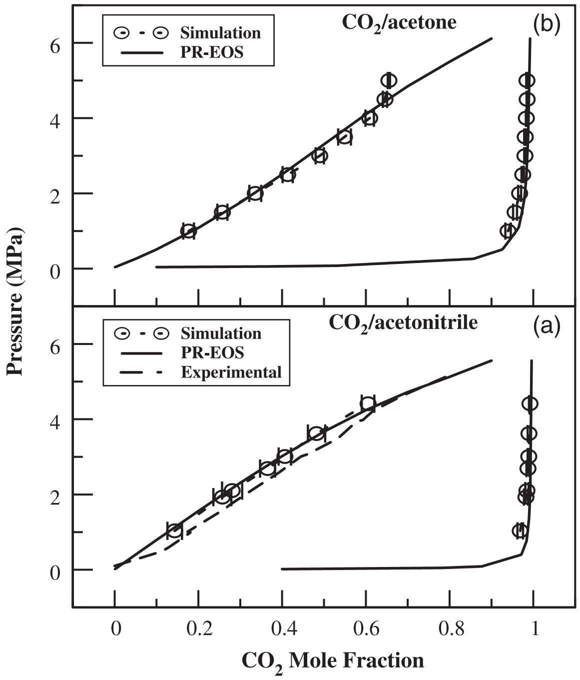

Figure 5. Pressure–composition diagrams for CO_2/acetonitrile at 25°C (a) and CO_2/acetone at 30°C (b).

in close agreement with the experimental data. For all seven binary systems, the CO_2 mole fractions in the vapor phase are close to unity indicating a CO_2 rich phase. In the liquid phase, the solubility of CO_2 approximatively increased linearly with pressure in the low pressure region (below 5 MPa). CO_2 solubility up to 65 mole % is achieved in the range of pressures studied.

Figures 8–10 show the densities of the coexistence phases in the binary systems studied. The PR calculations for the vapor phase density agree well with the corresponding simulation results, whereas the PR-EOS values are much lower than the simulated values for the liquid phase density except for the CO_2/ethanol and CO_2/toluene mixtures where results of the two methods agree. The comparison with the experimental data of Kordikowski *et al.* in figures 8(a) and 9(b) shows fair agreement with the simulation results for CO_2-expanded acetonitrile and ethanol. Interestingly for the former,

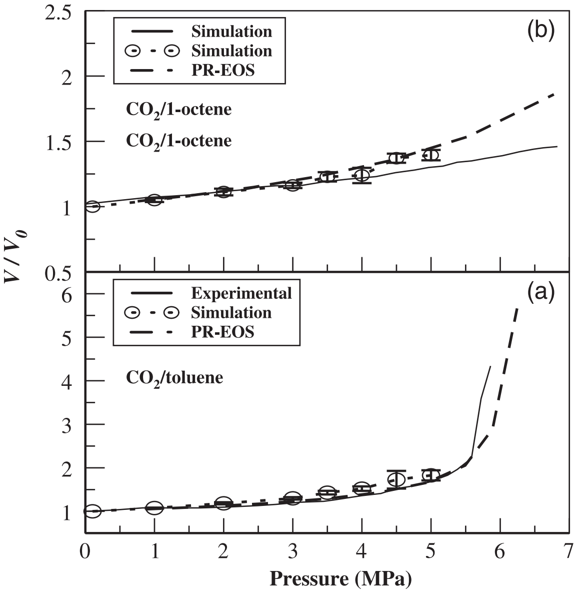

Figure 4. Volume expansion for CO_2-expanded: (a) toluene (30°C); (b) 1-octene (60°C); (c) acetic acid (25°C).

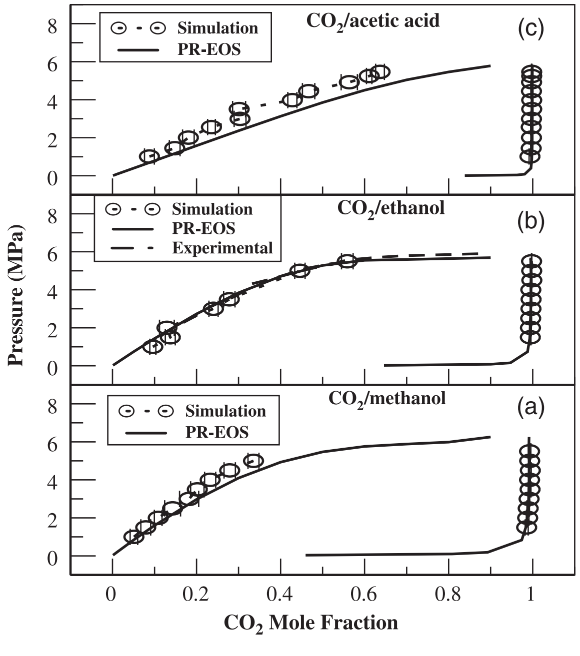

Figure 6. Pressure–composition diagrams for CO_2/methanol at 30°C (a), CO_2/ethanol at 25°C (b), and CO_2/acetic acid at 25°C (c).

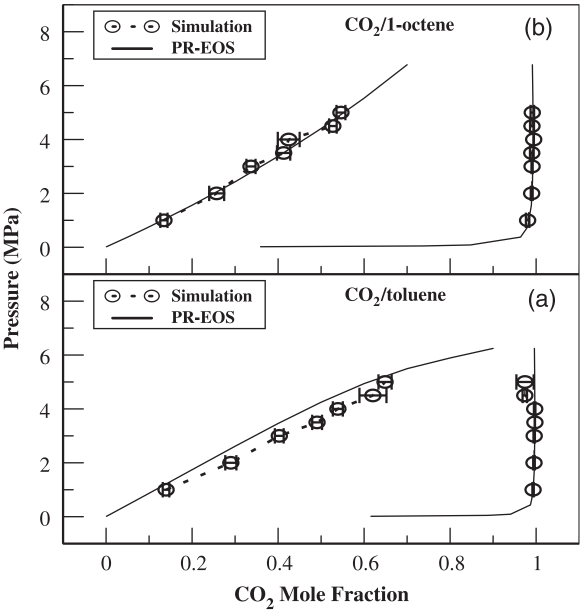

Figure 7. Pressure–composition diagrams for CO_2/toluene at 30°C (a), and CO_2/1-octene at 60°C (b).

the PR-EOS was not able to correlate the experimental data adequately.

4. Transport properties

In a recent paper [32], we studied the translational diffusion coefficients, the rotational correlation times and the shear viscosities in CO_2-expanded acetonitrile liquid. In this section, we summarize the *NVT* simulation results of these investigations.

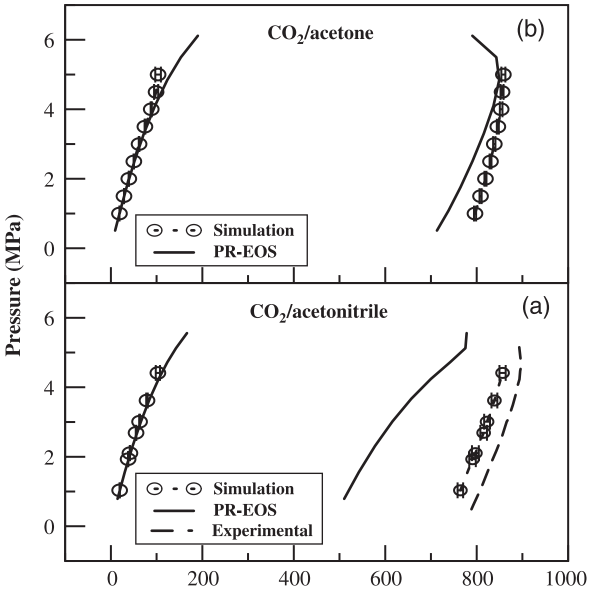

Figure 8. Saturated densities for (a) CO_2/acetonitrile (25°C) and (b) CO_2/acetone (30°C) mixtures.

The translational diffusion coefficients as functions of CO_2 mole fractions (x_{CO_2}) are plotted in figure 11. The available experimental values for the pure acetonitrile [51] ($x_{CO_2} = 0$) and pure CO_2 [52] ($x_{CO_2} = 1$) are also plotted for comparison. For the pure liquid, the deviations between our simulation results and experimental values are in the 19–23% range. These deviations are reasonable since the model parameters used in this work were not optimized for trasport properties. In the mixtures, the translational diffusion coefficients for both acetonitrile and CO_2 increase with CO_2 mole fraction. The simulation results show an inverse linear variation of the translational diffusion coefficients with x_{CO_2} in CO_2-expanded acetonitrile.

Figure 12 shows the mole fraction dependence of the calculated values of the rotational correlation times. The deviation between experimentally determined and simulated values fall in the 11–16% range indicating a quite good agreement since the potential models used were not optimized for these properties. The simulation data in figure 12 exhibit smooth variations of the correlation time with composition for both CO_2 and acetonitrile. The data can be well fitted using a linear equation in x_{CO_2}. With the diffusion coefficient being inversely proportional to the correlation time, figure 12 shows faster rotational diffusion of both CO_2 and acetonitrile with increasing CO_2 mole fraction for the CO_2/acetonitrile mixtures.

In figure 13, the simulation results for the shear viscosities are presented with the experimental values of the pure components for comparison. For pure acetonitrile, the simulation overestimates the experimental result by 32%. However, considering the statistical uncertainties (20%), the agreement with the experimental measurement is quite good. For CO_2, the difference between the calculated and measured values is only 3%. Overall, the simulated viscosities of the pure solvents are in reasonable agreement with experimental data. The predicted values of the viscosities of the mixtures presented in figure 13 decrease with increasing of x_{CO_2}. A viscosity decrease by a factor of 8 compared to pure acetonitrile is predicted in the studied composition range. The trend can be correlated with a linear equation. Similar results were also found by Li and Maroncelli [33].

5. Conclusion

The phase equilibrium and transport properties in CXLs were studied by molecular simulation using pure component pair potentials adopted from the literature and standard combining rules for the mixtures. The volume expansion, pressure–composition and pressure–density diagrams are obtained for CO_2 expanded acetonitrile, acetone, methanol, ethanol, acetic acid,

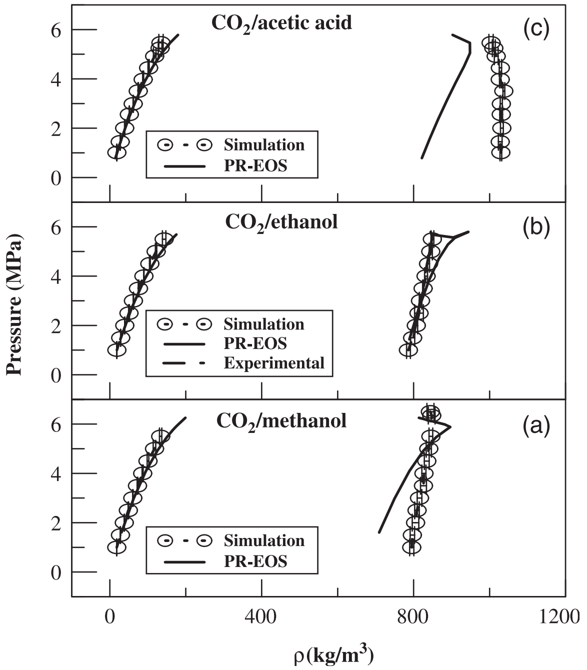

Figure 9. Saturated densities for (a) CO_2/methanol (30°C), (b) CO_2/ethanol (25°C), and (c) CO_2/acetic acid (25°C) mixtures.

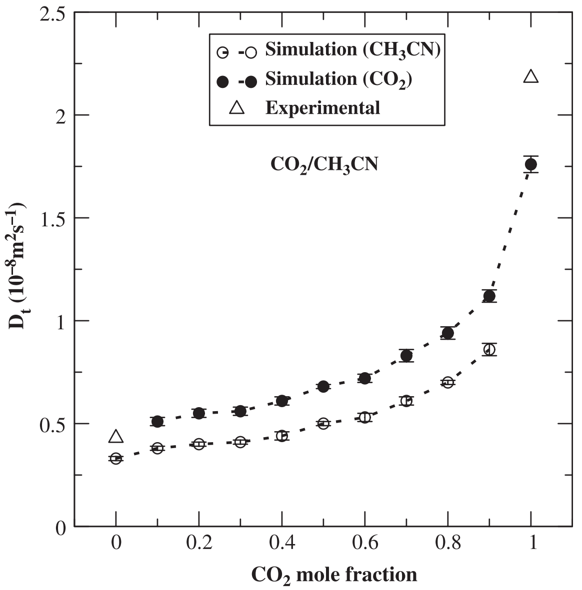

Figure 11. Translational diffusion coefficients in CO_2/acetonitrile (25°C) mixtures. The calculated values are represented by filled circles for acetonitrile and by filled circles for CO_2. The experimental values for the pure solvents (open triangles) are taken from Refs. [51,52].

toluene and 1-octene using both the GEMC method and the PR EOS. MD simulation results for translational diffusion coefficients, rotational correlation times and shear viscosities in CO_2 expanded acetonitrile were also reported. Good agreement between molecular simulations and available experimental measurements were obtained. Moreover, in some cases molecular simulations yield better results than the PR-EOS calculations. Overall, the results of our simulation show that the use of simple pure component force field parameters taken from the literature and standard combining rules can reliably model properties of CO_2-expanded organic solvents for engineering processes.

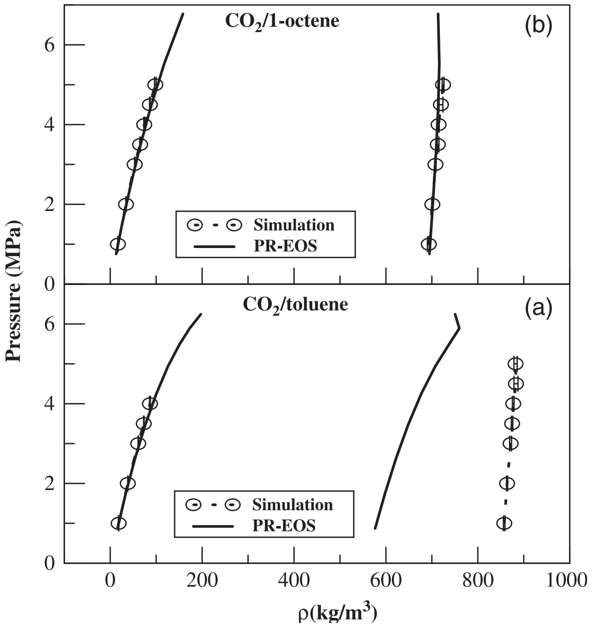

Figure 10. Saturated densities for (a) CO_2/toluene (30°C) and (b) CO_2/1-octene (60°C) mixtures.

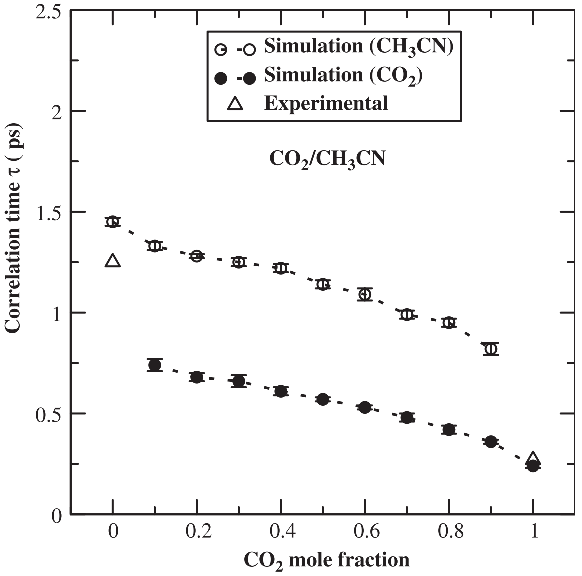

Figure 12. Rotational correlation times in CO_2/acetonitrile (25°C) mixtures. The calculated values are represented by open circles for acetonitrile and by filled circles for CO_2. The experimental values for the pure solvents (open triangles) are taken from Refs. [61,62].

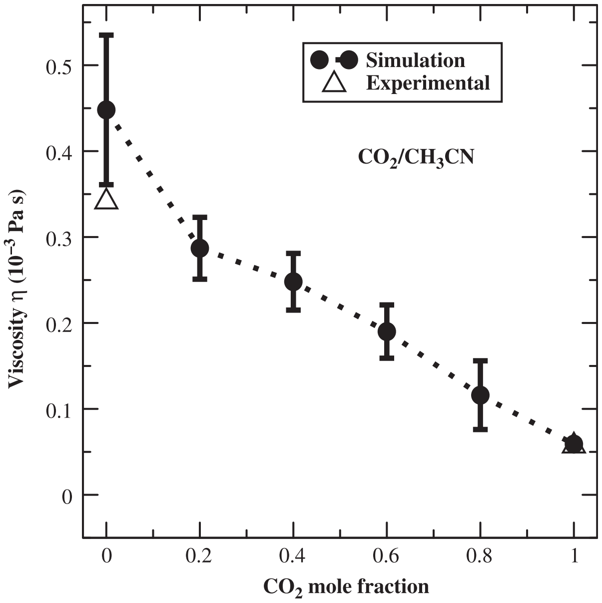

Figure 13. Shear viscosity in CO_2/acetonitrile (25°C) mixtures. The experimental values for the pure solvents (open triangles) are taken from Refs. [63,64].

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