Transport properties of CO$_2$-expanded acetonitrile from molecular dynamics simulations

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Carbon-dioxide-expanded liquids, which are mixtures of organic liquids and compressed CO$_2$, are novel media used in chemical processing. The authors present a molecular simulation study of the transport properties of liquid mixtures formed by acetonitrile and carbon dioxide, in which the CO$_2$ mole fraction is adjusted by changing the pressure, at a constant temperature of 298 K. They report values of translational diffusion coefficients, rotational correlation times, and shear viscosities of the liquids as function of CO$_2$ mole fraction. The simulation results are in good agreement with the available experimental data for the pure components and provide interesting insights into the largely unknown properties of the mixtures, which are being recognized as important novel materials in chemical operations. We find that the calculated quantities exhibit smooth variation with composition that may be represented by simple model equations. The translational and rotational diffusion rates increase with CO$_2$ mole fraction for both the acetonitrile and carbon dioxide components. The shear viscosity decreases with increasing amount of CO$_2$, varying smoothly between the values of pure acetonitrile and pure carbon dioxide. Our results show that adjusting the amount of CO$_2$ in the mixture allows the variation of transport rates by a factor of 3–4 and liquid viscosity by a factor of 8. Thus, the physical properties of the mixture may be tailored to the desired range by changes in the operating conditions of temperature and pressure. © 2007 American Institute of Physics. [DOI: 10.1063/1.2434968]

INTRODUCTION

Carbon-dioxide-expanded liquids (CXLs), formed by adding compressed CO$_2$ to standard organic solvents, are a novel class of media for chemical processing. CXLs have intermediate properties between pure organic solvents and supercritical CO$_2$. The use of standard organic solvents allows the optimization of catalyst solubility, while causing concerns with toxicity and vapor emissions which may be toxic and form explosive mixtures in air. On the other hand, the use of supercritical CO$_2$ as solvent, while favorable from the point of view of pollution prevention, has drawbacks in the form of the low solubility of catalysts and the economic costs of operation at high pressures with low reaction rates. CXLs are a compromise between organic liquids and supercritical CO$_2$. From the processing standpoint, catalyst and reactant solubilities are sufficient to yield relatively high reaction rates. Replacement of part of the organic liquid by the benign CO$_2$ decreases the environmental concerns compared to organic solvents, while faster reaction rates and lower operating pressures improve the economic performance compared to supercritical CO$_2$. Additionally, adjusting the system pressure allows for smooth changes in CO$_2$ content and thus also in physical properties of the liquids.

In recent years a significant research effort has been undertaken to evaluate the efficacy of CXLs as novel media for chemical processing.$^{1–3}$ Studies of CXL-based chemical reactions are a major component of the investigations at the Center for Environmentally Benign Catalysis (CEBC) at the University of Kansas. Recent CEBC contributions include studies of several catalytic processes in CO$_2$ expanded solvents,$^{1–7}$ as well as modeling of the vapor-liquid equilibria of several CO$_2$-expanded organic liquids.$^8$

In this paper we continue our studies of CO$_2$-expanded organic liquids, presenting results of simulations of transport properties for a series of CO$_2$-acetonitrile mixtures of varying composition. We use previously published potential energy functions of CO$_2$ (Ref. 9) and acetonitrile$^{10}$ to generate nanosecond length molecular dynamics trajectories of the pure components and their mixtures. We calculate translational diffusion coefficients and rotational correlation times for both components as a function of CO$_2$ mole fraction. Our results indicate that the transport properties of CO$_2$-expanded acetonitrile may be varied in a smooth, predictable manner.

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by adjusting the pressure of the CO₂ component. We also compare our results with those of Li and Maroncelli, who recently reported simulations of transport properties for CO₂-acetonitrile mixtures using a different potential for CH₃CN and different simulation conditions.¹¹

The molecular models and computational methods are described in Methods, the results are described in Results and Discussion, and final conclusions are presented in Conclusions.

METHODS

CO₂ model

The carbon dioxide model was adapted from the three-site EPM model developed by Harris and Yung.⁹ The Lennard-Jones parameters and equilibrium C–O bond lengths (r₀=1.149 Å) were taken directly from Harris and Yung.⁹ In the original paper a harmonic term ½kₚθ(θ−θ₀)², with θ as the O–C–O angle, was used to describe the potential energy of CO₂ bending, with kₚ=305 kcal/(mol rad²) and θ₀=π radians as the equilibrium angle. In our simulations we added a harmonic energy term to describe bond stretching ½k_CO(r−r₀)², with r as the C–O distance. For our flexible model the values of the two force constants, k₂ =58 kcal/(mol rad²) and k₀=1150 kcal/(mol A²) were taken directly from the optimized vibrational force field of Suzuki.¹² These force constants yielded vibrational frequencies of 2492, 1302, and 682 cm⁻¹, for the asymmetric stretch, symmetric stretch, and bending modes, respectively, as calculated with the MOLVIB module of the program CHARMM.¹³ Given our highly simplified two-parameter vibrational force field, this is in reasonable agreement with the corresponding observed gas phase values of 2349, 1388, and 667 cm⁻¹, respectively.¹² In our simulations we used the standard Berthelot combination rules for the Lennard-Jones parameters, rather than the modified rules introduced by Harris and Yung.⁹ The same rules were employed for all atom pairs in the pure liquids and mixtures simulated here, allowing for a consistent and simple treatment of all these systems.

The motivation for introducing flexibility into the CO₂ model was twofold. First, this simple modification leads to a more physically realistic model, which may be consistently extended for use with other organic solvents. Second, preliminary simulations with the rigid bond model using the CHARMM program indicated the need for a 1 fs molecular dynamics (MD) time step in order to generate stable trajectories. This was due to the inefficiency of the SHAKE algorithm used to enforce bond constraints.¹⁴ With the flexible force field MD simulations were more efficient, as stable unconstrained trajectories could easily be generated with a 2 fs time step, producing savings both due to the doubling of time step and elimination of SHAKE use.

Acetonitrile model

The acetonitrile model was adopted from the three-site GROMOS model developed by Hirata.¹⁰ The Lennard-Jones parameters and equilibrium C–C and C–N bond lengths (1.46 and 1.17 Å, respectively) were taken directly from Hirata.¹⁰ Analogous to our CO₂ calculations, we defined a flexible force field for the acetonitrile model, by introducing three harmonic force constants, k₃C₃, k₃CN, and k₅CN describing C–C bond stretching, C–N bond stretching, and C–C–N bending, respectively. Initial values of the force constants were taken from the empirical force field based on gas-phase vibrations.¹⁵ The final values of the force constants, k₃C₃ =380 kcal/(mol Å²), k₃CN =1280 kcal/ mol Å², and k₅CN =20 kcal/(mol rad²), were obtained by optimizing the fit between the vibrational frequencies calculated within our three-point model and the subset of the corresponding observed vibrational frequencies of gaseous CH₃CN, using the MOLVIB module of CHARMM.¹⁵ The optimized force constants yielded CH₃CN vibrational frequencies of 2272, 922, and 364 cm⁻¹, for the C–N stretch, C–C stretch, and C–C–N bending modes, respectively. This was in excellent agreement with the corresponding observed values of 2267, 920, and 362 cm⁻¹.¹⁵

System preparation

For each simulated system, a cubic box with 512 molecules was prepared. For the pure liquids initial structures were generated by placing randomly oriented molecules on an 8×8×8 grid with 5 Å spacing. For mixtures with desired CO₂ mole fraction x an 11×11×11 grid with 5 Å spacing was filled with randomly oriented molecules, with the type of molecule selected at random; CO₂ has probability x and the cosolvent acetonitrile has probability 1−x. A system of desired composition, e.g., with 51 CO₂ and 461 acetonitriles for x=0.1, was then carved out of this larger box using CHARMM. Each system was prepared by a cycle of energy minimizations and constant pressure molecular dynamics simulations of total length of 1 ns, starting with an exaggerated cubic box size of side a=40 Å and leading to an equilibrated cubic box at 298 K and desired target pressure (see Table I). The pure CO₂ system was the exception, for which a 2 ns equilibration was needed to reach a state with stable density. The final structures from these equilibrations were employed as the starting points for 1 ns constant pressure (NPT) simulations. To create starting coordinates for constant volume (NVT) simulations, the NPT equilibrated structures of our systems were subjected to two stages of 500 ps constant volume MD, the first with a density intermediate between the target value and the one found in the constant pressure trajectory, and the second at the desired target value, corresponding to the experimental density. The basic thermodynamic parameters of the simulated systems are described in Table I. For pure acetonitrile, the target pressure was 1 bar in the NPT simulation and the target density d =0.776 g/cm³ (the experimental density at 298 K and 1 bar)⁶ for the NVT case. Analogously, for pure CO₂ the target pressure was p=64 atm for NPT and target density d =0.7301 g/cm³ for NVT, which correspond to the experimental conditions for liquid phase in equilibrium with its vapor at 298 K. For the mixtures, values of target pressure and density were obtained by linear interpolation from measurements of Kordikowski et al.¹⁷
Table I. Conditions for CO2-acetonitrile mixture simulations at 298 K. For NPT simulations the target pressures \( P \) and average densities \( d \) and cubic cell sizes \( a \) are given, for NVT simulations the actual densities and cell sizes. CO2 mole fractions: \( x \); number of CO2 molecules: \( N_{CO2} \); number of acetonitrile molecules: \( N_{acn} \).

<table>
<thead>
<tr>
<th>System</th>
<th>( P ) (atm)</th>
<th>( d ) (g/cm(^3))</th>
<th>( a ) (Å)</th>
<th>( d ) (g/cm(^3))</th>
<th>( a ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>512</td>
<td>1.0</td>
<td>0.7155±0.0015</td>
<td>36.54±0.03</td>
<td>0.776</td>
</tr>
<tr>
<td>0.10</td>
<td>51</td>
<td>4.0</td>
<td>0.7335±0.0017</td>
<td>36.32±0.03</td>
<td>0.786</td>
</tr>
<tr>
<td>0.20</td>
<td>102</td>
<td>12.0</td>
<td>0.7549±0.0021</td>
<td>36.06±0.04</td>
<td>0.812</td>
</tr>
<tr>
<td>0.30</td>
<td>154</td>
<td>20.0</td>
<td>0.7800±0.0037</td>
<td>35.76±0.06</td>
<td>0.835</td>
</tr>
<tr>
<td>0.40</td>
<td>205</td>
<td>26.0</td>
<td>0.7969±0.0016</td>
<td>35.58±0.03</td>
<td>0.865</td>
</tr>
<tr>
<td>0.50</td>
<td>256</td>
<td>33.0</td>
<td>0.8144±0.0035</td>
<td>35.41±0.06</td>
<td>0.870</td>
</tr>
<tr>
<td>0.60</td>
<td>305</td>
<td>40.0</td>
<td>0.8312±0.0057</td>
<td>35.25±0.09</td>
<td>0.889</td>
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<tr>
<td>0.70</td>
<td>358</td>
<td>48.0</td>
<td>0.8286±0.0028</td>
<td>35.37±0.04</td>
<td>0.897</td>
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<tr>
<td>0.80</td>
<td>410</td>
<td>55.0</td>
<td>0.8205±0.0072</td>
<td>35.57±0.11</td>
<td>0.893</td>
</tr>
<tr>
<td>0.90</td>
<td>154</td>
<td>20.0</td>
<td>0.8043±0.0162</td>
<td>35.88±0.24</td>
<td>0.878</td>
</tr>
<tr>
<td>1.00</td>
<td>512</td>
<td>64.0</td>
<td>0.7819±0.0094</td>
<td>36.31±0.15</td>
<td>0.713</td>
</tr>
</tbody>
</table>

Molecular dynamics simulations

For each system listed in Table I, 1 ns MD simulations were carried out under two kinds of conditions—constant volume (NVT) and constant pressure (NPT). The Nosé-Hoover algorithm was used to maintain a constant temperature of 298 K in all cases,\(^{18}\) while the Langevin piston method was used to maintain constant pressure in the NPT trajectories.\(^{19}\) This method has been found to eliminate problems with unphysical energy distributions which may occur if weak coupling is employed.\(^{18}\) For van der Waals nonbonded interactions, modeled by the Lennard-Jones 6-12 potential, an atom-based 12.0 Å nonbonded cutoff distance was employed, with a switching function between 10.0 and 12.0 Å. To avoid truncation effects, the particle-mesh Ewald method was used for electrostatic interactions, with roughly 1 Å grid spacing and parameter \( \kappa = 0.34 \text{ Å}^{-1} \).\(^{20}\) For acetonitrile, CO2, and their mixtures a 2 fs integration time step was employed without the use of SHAKE constraints. Simulations were performed on 46-CPU Xeon Linux cluster at the Center for Environmentally Beneficial Catalysis at the University of Kansas, using the program CHARMM version 30.\(^{15}\) Typically, a 1 ns simulation required about 8 h of simulation on one processor.

Calculation of transport properties

The translational diffusion coefficients \( D_{ij} \) of the molecules were calculated based on the expression\(^{21}\)

\[
D_{ij} = \lim_{t \to \infty} \frac{\langle \Delta r_{ij}^2(t) \rangle}{6t},
\]

where \( \Delta r_{ij}(t) \) is the displacement of the center of mass in time \( t \) and \( \langle \ldots \rangle \) denotes an average over starting times and all molecules of a given type. The values of \( D_{ij} \) were obtained by fitting to a straight line the center-of-mass displacements corrected for effects of the periodic boundary conditions, over a time range of 50–500 ps, where the \( \Delta r_{ij}^2(t) \) plots tended to be linear.

To obtain a description of rotational dynamics that may be related to experimental measurements, we calculated the second order correlation functions,

\[
C_2(t) = \langle \mathbf{n}(0) \cdot \mathbf{n}(t) \rangle^2 - 1)/2,
\]

where \( \mathbf{n}(t) \) is the direction of the molecular axis at time \( t \) and the averaging is performed over starting structures and all molecules of a given type. The correlation functions were fitted to single-exponential decays, yielding the second-order rotational correlation times \( \tau \).\(^{22,23}\) The molecular axes were taken to be unit vectors along the line between the two end atoms of CO2 and acetonitrile, respectively. In the rotational diffusion model, in which it is assumed that molecular reorientations occur in small independent steps, the correlation times \( \tau \) may be expressed in terms of components of the rotational diffusion tensor.\(^{22,23}\) Within our models, both CO2 and acetonitrile are linear molecules, and in that case their reorientations are described by a single rotational diffusion coefficient \( D_{ij} \), related to the correlation time by \( \tau = 1/6D_{ij} \).

The viscosity calculations were based on the Green-Kubo formula, involving integrals of the autocorrelation functions (ACFs) of the off-diagonal elements of the stress tensor \( J_{ij} \)\(^{24}\) e.g.,

\[
\eta_{xy} = \frac{1}{kT} \int_0^\infty \langle J_{xy}(0)J_{xy}(t) \rangle dt,
\]

with \( V \) as the system volume, \( k \) as the Boltzmann constant, and \( T \) as the temperature. The contributions from \( xy, xz, \) and \( yz \) components were averaged. For viscosity calculations, the existing NVT trajectories were extended by 500 ps, with coordinates and velocities saved every 2 fs and stress tensor components evaluated with CHARMM. The calculated autocorrelation functions exhibited fast fluctuations, changing sign with a period of 20–40 fs. The time integrals were evaluated up to a correlation time \( \tau_j \), after which it was assumed that the autocorrelation function fluctuations represent random noise. The correlation times were estimated as the point at which the magnitude of the ACFs fell to about 1% of their initial values. These values ranged from about 11 ps for
pure acetonitrile to 3 ps for pure CO$_2$. Extending the integration by a factor of 2 beyond these $\tau_f$ typically led to changes in viscosity values of 10%–20%.

**Error estimates**

Mean values of the calculated physical quantities, densities, translational diffusion coefficients, rotational correlation times, and shear viscosities were evaluated over the full 1 ns MD trajectories. To estimate statistical errors of the means, each trajectory was divided into five consecutive fragments (blocks). Values calculated from the fragments were used to obtain a standard deviation of the mean $s_b$, equal to 

$$ s = s / \sqrt{5}, $$

with $s$ as the standard deviation of the sample of five block data points. The reported errors are equal to $2.57 s_b$, i.e., they represent the 95% confidence interval of the $t$ distribution for five degrees of freedom.

**RESULTS AND DISCUSSION**

**Density and volume expansion**

As a test of the model, we have calculated the liquid densities from the constant pressure simulations for the pure components and their mixtures (Table I, Fig. 1). The calculated density of pure acetonitrile, 0.716(2) g cm$^{-3}$, is underestimated by about 8% compared to the experimental value of 0.776 g cm$^{-3}$ at 298 K and 1 bar.\textsuperscript{16} In turn, the calculated density of pure CO$_2$, 0.782(1) g cm$^{-3}$, is overestimated by about 10% compared to the experimental value of 0.713 g cm$^{-3}$ at 298 K and 63.5 bars.\textsuperscript{23} The calculated value is in accord with the 0.7772(6) g cm$^{-3}$ found in the Gibbs-ensemble Monte Carlo simulations of Harris and Yung using the unmodified EPM potential.\textsuperscript{9}

The densities of the acetonitrile-CO$_2$ mixtures tend to be lower than the experimental values, with underestimates in the range of 6%–8%. Interestingly, the density maximum reached at compositions of 0.6–0.7 CO$_2$ mole fraction is reproduced by the simulation results. A similar trend in the variation of density with composition was found by Li and Maroncelli, although these authors obtained better agreement of liquid densities with experimental data due to choice of a different potential energy for acetonitrile.\textsuperscript{11}

The calculated volume expansions of the CO$_2$-acetonitrile mixtures are presented in Fig. 2. The calculated results are highly similar to the experimental data.

**Translational diffusion**

The calculated translational diffusion coefficients $D_t$ are presented in Table II and Fig. 3. Experimental measurements for pure acetonitrile give $D_t = 0.43 \times 10^{-8}$ m$^2$/s.\textsuperscript{27} Our NPT trajectory predicts a value of 0.47(1) m$^2$/s at 298 K and 1 bar, while the NVT yields 0.33(1) m$^2$/s at 298 K and experimental density. These results are consistent with previous calculations of Hirata, who obtained $D_t = 0.44(2) \times 10^{-8}$ m$^2$/s at a slightly higher density of 0.79 g/cm$^3$.\textsuperscript{10} For pure CO$_2$, the measured value at 298 K and 68 bars, the thermodynamic point closest to our simulation conditions, is $D_t = 2.18 \times 10^{-8}$ m$^2$/s.\textsuperscript{28} The calculations

**TABLE II. Calculated translational diffusion coefficients in CO$_2$-acetonitrile mixtures at 298 K. Units: 10$^{-8}$ m$^2$/s.**

<table>
<thead>
<tr>
<th>x</th>
<th>NPT</th>
<th>NVT</th>
<th>NPT</th>
<th>NVT</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>...</td>
<td>0.47±0.01</td>
<td>0.33±0.01</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>0.69±0.04</td>
<td>0.51±0.02</td>
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<td>0.38±0.01</td>
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<td>0.20</td>
<td>0.71±0.02</td>
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</tr>
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<td>0.30</td>
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<td>0.54±0.02</td>
<td>0.41±0.01</td>
</tr>
<tr>
<td>0.40</td>
<td>0.79±0.04</td>
<td>0.61±0.02</td>
<td>0.59±0.02</td>
<td>0.44±0.02</td>
</tr>
<tr>
<td>0.50</td>
<td>0.80±0.01</td>
<td>0.68±0.01</td>
<td>0.59±0.01</td>
<td>0.50±0.01</td>
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<td>0.60</td>
<td>0.89±0.04</td>
<td>0.72±0.02</td>
<td>0.66±0.03</td>
<td>0.53±0.02</td>
</tr>
<tr>
<td>0.70</td>
<td>1.02±0.02</td>
<td>0.83±0.03</td>
<td>0.74±0.01</td>
<td>0.61±0.02</td>
</tr>
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<td>0.80</td>
<td>1.17±0.05</td>
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<td>0.70±0.01</td>
</tr>
<tr>
<td>0.90</td>
<td>1.33±0.11</td>
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</tr>
<tr>
<td>1.00</td>
<td>1.54±0.04</td>
<td>1.76±0.04</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>
predict coefficients of $1.54 \times 10^{-8}$ m$^2$ s$^{-1}$ (NPT at 298 K and 64 bars) and $1.76 \times 10^{-8}$ m$^2$ s$^{-1}$ (NVT at 298 K and experimental density). The deviations between the experimental and calculated results are significantly larger than the statistical errors of the former and fall into the 7%–30% range. This level of agreement is typical for cases when transport properties were not used to optimize the model parameters. We expect that this should be sufficient for us to make reliable predictions about changes in $D_t$ with composition.

There is a clear trend in the results, with translational diffusion rates of both CO$_2$ and acetonitrile increasing with increasing CO$_2$ mole fraction $x_{CO2}$. This effect may be rationalized based on the $D_t$ of the pure liquids, such that adding the more mobile CO$_2$ to the liquid phase speeds up translation of acetonitrile, while the CO$_2$ motions themselves are slowed down by collisions with the less mobile acetonitrile. Overall, our simulations predict that the rate of translational diffusion in CO$_2$-acetonitrile mixtures may be varied by a factor of 2–4 by changing the CO$_2$ content. The trends found by Li and Maroncelli were similar, with translation diffusion coefficients varying in the $(0.49–0.88) \times 10^{-8}$ m$^2$ s$^{-1}$ range for acetonitrile and $(0.65–2.3) \times 10^{-8}$ m$^2$ s$^{-1}$ range for carbon dioxide as $x_{CO2}$ is increased from the lowest to highest values.\textsuperscript{11}

The $D_t$ values calculated from the NPT and NVT simulations exhibit parallel variation with changes of CO$_2$ mole fraction, though the values at corresponding $x_{CO2}$ differ by more than their statistical errors. The differences may be explained by differences of liquid densities. Thus, in most cases, the NPT trajectories yield higher translational diffusion coefficients, as the simulated systems have underestimated densities. The only exception is pure CO$_2$, for which the NPT simulation overestimates the density and yields the higher $D_t$.

Molecular reorientations

The calculated values of the rotational correlation times are presented in Table III and Fig. 4. The experimental values for the pure liquids are $\tau=1.25$ ps for acetonitrile at 298 K and 1 bar,\textsuperscript{20} and $\tau=0.27$ ps for carbon dioxide at 298 K and 68 bars.\textsuperscript{30} Our calculations predict $\tau=1.13(3)$ ps (NPT, at 298 K and 1 bar) and 1.45(2) ps (NVT, 298 K and experimental 1 bar density) for pure acetonitrile, and $\tau=0.24(1)$ ps for pure CO$_2$ (both NPT at 298 K and 64 bars and NVT at 298 K and experimental 64 bar density). Thus, our calculated correlation times deviate by 5%–16% from measured values. This agreement is quite good for potentials that have not been specifically optimized for these properties.

As described in Methods, the correlation times $\tau$ are inversely proportional to rotational diffusion coefficients $D_r$. Thus, our simulation 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 rotational correlation times calculated using the NPT and NVT methods show similar agreement with experimental data for the pure components and follow parallel trends of decreasing values with increasing $x_{\text{CO}_2}$. Thus, these approaches appear to be equivalent in terms of prediction of \( \eta \). Except for pure \text{CO}_2, the NPT values of \( \eta \) are higher than the NVT results corresponding to faster reorientation in the NPT trajectories. As in the case of translational diffusion, this trend may be explained by the tendency to underestimate the densities in the NPT simulations.

Shear viscosities

The calculated values of the shear viscosities \( \eta \) are presented in Table IV and Fig. 5. The measured value of viscosity of pure acetonitrile at 298 K and 1 bar is 0.341 cP (1 cP=10^{-3} Pa s). The value calculated from our NVT simulation is 0.45(9) cP, overestimating the experimental result by 32%. For \text{CO}_2, the experimental value at 298 K and 64 bars is 0.057 cP, obtained from the formula defined by Eqs. (1), (3), (8) of Ref. 31. Our NVT simulations yield 0.059(3) cP for \text{CO}_2 at 298 K and its 64 bar experimental density. In this case the difference between experimental and calculated values is only 3%. Thus, our simulated viscosities of the pure components are in reasonable agreement with experimental data. This leads us to expect that we can reliably predict the viscosities of \text{CO}_2-acetonitrile liquid mixtures, with accuracy comparable to that achieved for the pure components.

The calculated viscosities of the mixtures exhibit a trend for systematic decrease with increasing \( x_{\text{CO}_2} \). Changing from pure CH$_3$CN to pure \text{CO}_2 along the 298 K isotherm leads to a ca. eight-fold decrease of calculated viscosity; the experimental data give a six-fold decrease. Thus, the viscosity of the liquid phase can be manipulated over a relatively large range by expanding acetonitrile with compressed carbon dioxide. The results of Li and Maroncelli are similar, predicting a smooth variation of the liquid viscosity from 0.34 cP for pure acetonitrile to 0.079 cP for pure \text{CO}_2.

**DISCUSSION**

**Variation trends**

The calculated transport properties show smooth, simple variation with composition, described by \( x \), the mole fraction.
of CO₂. The simplest correlations which could well represent the trends in the data are linear equations \( y = ax + b \) for the rotational correlation times \( \tau \) and shear viscosity \( \eta \) and inverse linear equations \( 1/y = ax + b \) for the translational diffusion coefficients. A summary of the fitting results is presented in Table V.

For translational diffusion coefficients, the inverse of \( D_t \), which in our units roughly represents the average time in picoseconds needed for a molecule to move by 1 Å, decreases linearly with CO₂ mole fraction for both acetonitrile and carbon dioxide components.

For reorientational motions, the rotational correlation times \( \tau \) for both components also decrease linearly with CO₂ mole fraction. In our units the correlation times roughly correspond to the average time in picoseconds for the molecular axis to reorient by 40°.

In the case of viscosity, straight lines drawn through the pure component data, either experimental or simulated, provide excellent models for variation with composition.

### Hydrodynamic parameters

Hydrodynamic theory predicts that both translation and rotational diffusion rates should be inversely proportional to solvent viscosity. For a spherical particle under stick boundary conditions,

\[
D_t = \frac{kT}{6\pi \eta a}
\]

and

\[
D_r = \frac{1}{6\tau} = \frac{kT}{6\eta V_h},
\]

where \( k \) is the Boltzmann constant, \( T \) is the temperature, \( a \) is the particle radius, and \( V_h \) is its volume.\(^{21,32}\) For nonspherical particles multiplicative correction factors may be found in the literature.\(^{32}\) For particles of fixed shape and size, we expect that the reduced diffusion rates \( D_r \eta \) and \( 6D_t \eta = \eta/\tau \) should remain constant at a constant temperature. The calculated reduced translational and rotational diffusion rates of both acetonitrile and carbon dioxide exhibit decreasing trends with rising CO₂ mole fraction (Fig. 6). This may be interpreted as the effect of increase of effective hydrodynamic sizes/volumes of both the components with increasing \( x_{CO₂} \). A similar effect was found by Li and Maroncelli.\(^{11}\) The explanation for these effects may be found in a detailed analysis of the local structure of the liquid mixture. This

![Fig. 6. Reduced transport coefficients in CO₂-acetonitrile mixtures. (a) Translational diffusion: \( D_t \eta \) from NVT MD. Units are 10⁻¹¹ N. (b) Rotational diffusion: \( \eta/\tau \) from NVT MD. Units are 10⁻⁹ Pa⁻¹.](image)

### Table V. Coefficients for linear models for variation of transport properties with CO₂ mole fraction

<table>
<thead>
<tr>
<th>Property</th>
<th>Equation</th>
<th>( a )</th>
<th>( b )</th>
<th>( n )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CN NPT translational diffusion coefficient ( D_t )</td>
<td>( 1/D_t = ax + b )</td>
<td>2.18</td>
<td>-1.20</td>
<td>10</td>
<td>1.5</td>
</tr>
<tr>
<td>CH₃CN NVT translational diffusion coefficient ( D_t )</td>
<td>( 1/D_t = ax + b )</td>
<td>2.96</td>
<td>-1.91</td>
<td>10</td>
<td>1.1</td>
</tr>
<tr>
<td>CO₂ NPT translational diffusion coefficient ( D_t )</td>
<td>( 1/D_t = ax + b )</td>
<td>1.62</td>
<td>-0.93</td>
<td>10</td>
<td>2.3</td>
</tr>
<tr>
<td>CO₂ NVT translational diffusion coefficient ( D_t )</td>
<td>( 1/D_t = ax + b )</td>
<td>2.18</td>
<td>-1.46</td>
<td>10</td>
<td>3.2</td>
</tr>
<tr>
<td>CH₃CN NPT rotational correlation time ( \tau )</td>
<td>( \tau = ax + b )</td>
<td>1.14</td>
<td>-0.34</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>CH₃CN NVT rotational correlation time ( \tau )</td>
<td>( \tau = ax + b )</td>
<td>1.43</td>
<td>-0.63</td>
<td>10</td>
<td>1.5</td>
</tr>
<tr>
<td>CO₂ NPT rotational correlation time ( \tau )</td>
<td>( \tau = ax + b )</td>
<td>0.69</td>
<td>-0.40</td>
<td>10</td>
<td>2.2</td>
</tr>
<tr>
<td>CO₂ NVT rotational correlation time ( \tau )</td>
<td>( \tau = ax + b )</td>
<td>0.81</td>
<td>-0.51</td>
<td>10</td>
<td>2.3</td>
</tr>
<tr>
<td>NVT shear viscosity ( \eta^s )</td>
<td>( \eta = ax + b )</td>
<td>0.34</td>
<td>-0.28</td>
<td>6</td>
<td>0.7</td>
</tr>
<tr>
<td>NVT shear viscosity ( \eta^b )</td>
<td>( \eta = ax + b )</td>
<td>0.45</td>
<td>-0.39</td>
<td>6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

\(^{a}\)Line through the two experimental data points for the pure liquids.

\(^{b}\)Line through the two NVT calculated data points for the pure liquids.
analysis will be part of a separate study of structure in CXLs which is under way at the CEBC and will be presented at a later date.

CONCLUSIONS

We present a molecular simulation study of the transport properties of liquid mixtures formed by acetonitrile and carbon dioxide, in which the CO$_2$ mole fraction is adjusted by changing the pressure, at a constant temperature of 298 K. We report values of translational diffusion coefficients, rotational correlation times and shear viscosities of the liquids as function of CO$_2$ mole fraction. We find that the calculated quantities exhibit smooth variation with composition which may be represented by simple model equations. The translational and rotational diffusion rates increase with CO$_2$ mole fraction for both the acetonitrile and carbon dioxide components. The shear viscosity decreases with increasing amount of CO$_2$, varying smoothly between the values of pure acetonitrile and pure carbon dioxide. Our results show that adjusting the amount of CO$_2$ in the mixture allows the variation of transport rates by a factor of 3–4 and the variation of liquid viscosity between pure acetonitrile and pure carbon dioxide values. Thus, the physical properties of CO$_2$-expanded acetonitrile may be tailored over a wide range by changes in the operating conditions of temperature and pressure.

Our calculations provide predictions of transport properties of CO$_2$-expanded acetonitrile, for which experimental data are lacking. Using potential energy functions taken from the literature, we have been able to reproduce the available experimental data for the pure components quite well. Thus we believe that our calculations also provide reliable, though approximate, results for the unknown properties of the mixtures. Additionally, the simulations provide insights into the microscopic properties of the mixtures. Thus, we found that transport rates tended to vary faster with composition than expected from calculated viscosities. This suggests that hydrodynamic parameters of the molecules change with composition. Our studies of the CO$_2$-acetonitrile mixtures provide important new information about the properties of this class of liquids and of CXLs in general. Studies of transport and structure in a variety of CXL systems will be the topic of our future studies.

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