



Transport properties of mixtures composed of acetone, water, and supercritical carbon dioxide by molecular dynamics simulation



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ABSTRACT

Transport properties of various mixtures of supercritical carbon dioxide, acetone, and water at different concentrations are evaluated at temperatures 313.15 K and pressure 150 bar by molecular dynamics simulations. The results show that the self-diffusion (viscosity) coefficient is increased (decreased) for all various mixtures studied when the concentration of the acetone is increased. In addition, the densities of the mixtures will rise (lower), when the supercritical carbon dioxide (acetone) concentrations is increased. We have observed that the first peak heights of the radial distribution functions will rise at very low mole fraction of water ($x_w = 0.016$) when the acetone and carbon dioxide concentrations are increasing, and hence the self-diffusion coefficients will decrease while its density and viscosity will increase.

1. Introduction

Knowledge of transport properties of fluids is very important in engineering applications that involve energy, mass, or momentum transfer. Hence, the availability of accurate experimental measurements and models to evaluate the viscosity and self-diffusion coefficients is the key to ensure efficient and safe engineering and designing in chemical and biochemical industries [1]. The development of thermodynamic models for the prediction of the solubility of gases in pure solvents as well as in solvent mixtures is still a demanding task in fluid phase equilibrium thermodynamics. The growing interest in high-pressure fluid applications, namely, hydraulic fracturing in mining and petroleum industries, the supercritical extraction in food and pharmaceutical production, the carbon dioxide capture and storage, and enhanced oil recovery techniques, have been followed by an increasing demand for thermodynamic and transport properties over a broad range of conditions, which can often include extreme temperature and pressure ranges [2–5]. Supercritical fluids are widely employed not only as extraction solvents but also as a reaction media because of their unique physical properties. And when used in reactors at industrial scales, knowing their transport properties most notably binary diffusion coefficients are necessary. For example, while designing reactors or predicting mass transfer rates under supercritical conditions, having their binary diffusion coefficients are significantly important [6]. Acetone is used in polymer industry for production of films, fibers and coatings where

viscosity plays a very important role. As a common solvent it is used in the textile industry for degreasing of wool and degumming of silk. Acetone-based solvents are also being explored in high-pressure extraction of plant seed oils, where viscosity information on the solvent and the solvent plus extracted material becomes important for access and removal of components from the plant matrix [7]. Pure acetone at high-pressures are favorably useful for process design, material casting industries, and polymer synthesis. Liquid thermophysical properties such as density and viscosity are basically required for applied research in chemistry, biochemistry [8] and industrial process design. These properties are also important key factors in theories of the liquid state theories [9]. High-pressure liquid solvent density and viscosity data for studying solution, particularly solution of soluble polymers have practical importance [8]. In mixtures and solutions, the properties of pure substances are drastically altered. For example, supercritical carbon dioxide/acetone/water mixtures often show quite different properties from those observed for the corresponding pure components. The transport properties play important roles in the theoretical study and technological application involving mass transfer present in chemical industries [10]. Understanding of fluid behavior at unusual thermodynamic conditions is required to support fluid production and processing operations. Even when pure substances such as carbon dioxide and acetone are concerned, the availability of experimental data decreases as the fluid conditions move away from common industrial application ranges. In addition, the majority of models employed to

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estimate transport properties lack a physical basis, and are often based on semi-empirical approaches [11–13] and are regressions of different sets of experimental data [14–16]. These models normally employ appropriate conditions of the experimental values, but extrapolation outside those conditions where the models were developed can be questionable.

An alternative route to obtaining transport properties is to use molecular dynamics methods, which rely only on the knowledge of intermolecular potentials to provide averages of macroscopic thermo-physical quantities and molecular structural information [17]. These methods have become particularly interesting with the increasing availability of computational resources and highly parallelized algorithms [18,19]. A major advantage of molecular dynamics over Monte Carlo methods is the ability to generate configurations of the system of interest that are dependent on time, and thus naturally, providing means to estimate time-dependent properties. The basic concept used to perform experimental measurements may be extended to simulation methods, i.e., transport properties can be obtained as a response of the fluid to an external perturbation that drives the system away from equilibrium [20]. In addition, from a microscopic point of view, knowledge of solution behavior is fundamental to understand and elucidate the mixture diffusion phenomenon. Molecular dynamics simulation is also a powerful tool to investigate the structural properties of solutions at a molecular level useful to study the aqueous solutions [15,16]. Recently, the dynamic properties of alcohol/water mixtures were calculated by molecular dynamics simulations [21,22]. In this work, transport properties of supercritical carbon dioxide, acetone, and water in their mixtures are studied as well as the concentration dependence of these properties. In the next section we will present the details of simulations. The obtained results and their meaning are discussed in subsequent sections.

2. Simulation details

molecular dynamics simulations were carried out by GROMACS 4.5.4 [22–24] using the gromos43a1 force field [25]. All simulations were performed in the constant number of particles, pressure, and temperature (NPT) ensemble.

We assessed the quality of molecules topologies produced automatically through the server PRODRG [26,27] under the GROMOS43a1 force fields [25]. For molecules having linear

groups (e.g., CO₂), a virtual site construction was included to the topologies to preserve the moment of inertia and the total mass, in order to keep the groups perfectly linear [28].

Molecular dynamics simulations of acetone/water in supercritical carbon dioxide various mixtures were performed in the temperature and pressure set at 313.15 K and 150 bar, according to ref. [29]. A steepest-descent algorithm was invoked to minimize the energy of each system. Molecular dynamics simulation for each system was run in two stages. In the first stage, position restraints is employed. In the second stage, each system was simulated with a time step of 2 fs for the total time 50 ns. To maintain constant temperature and pressure for various mixtures during simulation, the velocity rescaling and Parrinello-Rahman were employed for temperature- and pressure-coupling methods, respectively [30–32]. The coupling time intervals were set at 0.1 ps and 2.0 ps for temperature and pressure, respectively, compressibility was set at $4.5 \times 10^{-5} \text{ bar}^{-1}$, were used for a total time calculation. The neighbor grid searching method was applied and the neighbor list was updated every five steps. Twin range cut-offs were chosen for Lennard-Jones interactions, and the distance for the Lennard-Jones cut-off was equal to the cut-off distance for the short-range neighbor list (1 nm). For each component of the systems, Particle Mesh Ewald (PME) algorithm was applied to deal with the electrostatic interactions, and the periodic boundary conditions imposed throughout [33,34]. LINCS algorithm [35] was invoked to fix the chemical bonds between the atoms. Molecular dynamics simulations were carried over

Table 1

Transport coefficients of mixtures obtained from MD simulation at $x_a = 0.532$ and 313.15 K and pressure 150 bar.

x_c	ρ (kgm ⁻³)	$D \times 10^{-5}$ (cm ² s ⁻¹)	η (10 ⁻³ kgm ⁻¹ s ⁻¹)
0.053	838.235	4.3849 ± 0.3801	2.351
0.132	862.292	4.4092 ± 0.6284	0.796
0.239	909.21	5.3877 ± 1.1988	6.743
0.332	942.784	4.8463 ± 1.0995	0.3482
0.4	966.909	4.3683 ± 0.8346	0.289
0.432	978.114	4.4924 ± 0.7843	0.4766

Table 2

Transport coefficients of mixtures obtained from MD simulation at $x_a = 0.632$ and 313.15 K and pressure 150 bar.

x_c	ρ (kgm ⁻³)	$D \times 10^{-5}$ (cm ² s ⁻¹)	η (10 ⁻³ kgm ⁻¹ s ⁻¹)
0.052	825.877	4.7192 ± 0.5036	0.2611
0.132	850.693	4.6949 ± 0.4011	0.2225
0.232	889.469	5.4552 ± 1.2304	0.9151
0.29	909.093	5.1389 ± 0.8754	0.5812
0.332	923.112	5.05 ± 1.2930	2.808
0.352	929.697	5.2588 ± 1.3125	2.892

Table 3

Transport coefficients of mixtures obtained from MD simulation at $x_a = 0.732$ and 313.15 K and pressure 150 bar.

x_c	ρ (kgm ⁻³)	$D \times 10^{-5}$ (cm ² s ⁻¹)	η (10 ⁻³ kgm ⁻¹ s ⁻¹)
0.052	816.922	4.9723 ± 0.6258	0.2273
0.132	839.916	5.3948 ± 0.6004	0.2972
0.192	862.697	5.7877 ± 1.3267	0.292
0.232	875.458	5.412 ± 0.7607	0.3525
0.252	882.108	5.3209 ± 0.6836	0.4009

Table 4

Transport coefficients of mixtures obtained from MD simulation at $x_a = 0.832$ and 313.15 K and pressure 150 bar.

x_c	ρ (kgm ⁻³)	$D \times 10^{-5}$ (cm ² s ⁻¹)	η (10 ⁻³ kgm ⁻¹ s ⁻¹)
0.052	809.856	5.3715 ± 0.7788	0.1912
0.1	824.32	5.6868 ± 0.7341	0.303
0.115	829.032	5.5872 ± 0.585	0.2462
0.132	829.426	5.576 ± 0.9505	0.3023
0.152	840.253	5.3904 ± 0.6939	0.3756

at four different mole fractions of the acetone (from 0.532 to 0.832, at 0.1 intervals), different mole fractions of the carbon dioxide (x_c) as shown in Tables 1–4 according to ref. [29]. We fix the total number of particles in the cubic simulation box at $N = 1000$ with various concentrations of acetone, water, and supercritical carbon dioxide. The prepared mixtures were put into the 6.5nm × 6.5nm × 6.5 nm cubic boxes. Coordinates were saved every 2 ps for subsequent analyses. The obtained results are finally shown in graphs and tables.

3. Transport properties

Transport coefficients describing non-equilibrium flows of momentum and energy can be expressed in terms of decay of equilibrium fluctuations of pressure and heat flux, according to the Green–Kubo formulation [36,37]. For instance, the shear viscosity of a fluid of interest in the canonical ensemble can be defined by the time integral of the autocorrelation function of any off-diagonal component of the pressure tensor:

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