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Molecular Dynamics Simulations of Gas-Expanded Liquids

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Abstract

Gas-expanded Liquids (GXL's) are liquids whose volume is expanded by a pressurized gas. The incorporation of the gaseous compound and the expansion of the liquid phase lead to changes in solvation and transport properties of the new expanded phase.

This work aims at developing a Molecular Dynamics (MD) computational study for liquid methyl and ethyl acetates when expanded by CO₂ at pressures up to 120 bars and at temperatures between 298 and 393 K. Especially, density and viscosity of the liquid expanded phase were calculated by MD simulations. Good agreement with existing literature data has been obtained ascertained the validity of the method

Keywords: molecular dynamics, alkyl acetates, viscosity, density

1. Introduction

With the perspective of finding alternative benign media for different applications, solvent engineering represents an interesting alternative to propose innovative solutions to industrial problems. Gas-expanded liquids (GXLs), in particular CO₂-expanded liquids (CXLs), which are liquids whose volume is expanded by pressurized CO₂, represent a very promising strategy to perform solvent engineering.

A number of properties, including solvation properties, can be tuned by the addition of CO₂ to a liquid solvent (Jessop and Subramaniam, 2007) allowing the use of CXLs as “solubility switchers”. In many cases, solutes that are soluble in CO₂-expanded solvents will precipitate when CO₂ is removed and vice versa. For example, the addition of CO₂ to a biphasic system of a fluorinated solvent and an organic solvent causes the phases to become miscible (West et al., 2004). Opposite effect is seen in cases of water-soluble organics and an aqueous phase, where the addition of CO₂ forces the phases to split (Lu et al., 2004). Both systems may have applications in catalyst recycle and/or product recovery. Knowledge of phase equilibrium properties but also of transport properties is evidently important to design processes exploiting the peculiar behavior of these two phase systems.

Moreover, high-pressure experimental determinations of density and viscosity of systems involving hazardous compounds and/or at harsh conditions of pressure and temperature are usually problematic. As an alternative, numerical experiments with the help of molecular simulation, like Molecular Dynamics (MD) have gained interest in recent years as the performance of computational tools is continuously improving. In particular, MD

simulations have gained enormous progress in terms of 1) simulation methods, 2) understanding of complex phenomena, and 3) ability to model extremely complex systems.

MD simulations accuracy is highly dependent on the proper representation of the interaction forces acting on the molecules. This depends on the choice of a suitably parametrized force field and on a statistically representative sampling of the states of the system, with the help of Newton's equations integrator algorithm. Previous works on CO₂-expanded acetates (Smith et al., 1998; Byun et al., 2006; Kwon et al., 2007; Aida et al., 2010) describe some of these system properties, such as the Vapor-Liquid Equilibrium curves and the expanded phase density. However, no data were found about the viscosity of the alkyl acetates/CO₂ expanded phase, probably due to the difficulty of high-pressure expanded phase determinations.

Hence, in this work MD simulations were performed to numerically predict the value of the viscosity of CO₂-expanded acetates. The MD method and its accuracy were first evaluated for other CO₂-expanded solvents before predicting the densities and the viscosities of systems involving methyl and ethyl acetate. Indeed, Acetone (C₃H₆O) and Decane (C₁₀H₂₂) were chosen for this task for two main reasons: The available CO₂-expanded phase viscosity data and the presence of hydrocarbon chain in decane and the carbonyl group in acetone, both groups found in alkyl acetates.

2. Methods

2.1. Theory background

The fluctuation-dissipation theorem explains how transport coefficients associated to irreversible processes can be described using reversible microscopic fluctuations (Kubo, 1966). The Green-Kubo (Green, 1954; Kubo, 1957) relations give the exact mathematical expression for transport coefficients in terms of integrals of time-correlation functions. In the standard Green-Kubo method shear viscosity can be calculated by integrating the autocorrelation function of the stress tensor over time (1):

$$\eta = \frac{1}{k_B T} \lim_{\tau \rightarrow \infty} \int_0^\tau dt \langle P_{xy}(t) P_{xy}(0) \rangle \quad (1)$$

Where $\langle P_{xy}(t) P_{xy}(0) \rangle$ is the correlation function of the xy component of the stress tensor, V is the volume of the simulation box, k_B is the Boltzmann constant, T is the absolute temperature and t is the time.

2.2. Simulation details

The required liquid phase composition data at equilibrium was extracted from literature and from our own determinations.

Table 1. Amber_Cornell_Extended Force field bond and pairwise potentials

Bond	Angle	Improper	Dihedral (hybrid)
$E = K(r - r_0)^2$	$E = K(\theta - \theta_0)^2$	$E = K[1 + \cos(n\phi - d)]$	$E = K(X - X_0)^2$
VdW : L-J 12-6 $LJ(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] + S(r)$		Coulombic $C(r) = \frac{q_i q_j}{\epsilon r}$	$E = \sum_{i=1, m} k_i [1.0 + \cos(n_i \phi - d_i)]$

MD computations were carried out using the Materials Processes and Simulations (MAPS) Suite from Scienomics and in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code from Sandia National Laboratories. The “Amber_Cornell_Extended” force field was selected (Table 1).

Table 2: Fitted atomic center charges

	Atom	AM1	ESP		Atom	AM1	ESP
<i>Acetone</i>				<i>Decane</i>			
	C	-0,2041	-0,522162		C	-0,21	-0,326006
	C1	0,5631	0,811667		C1	-0,159	0,213133
	C2	-0,2041	-0,512053		C2	-0,158	0,05664
	O	-0,5311	-0,580332		C3	-0,158	-0,085466
	H	0,063033	0,141684		C4	-0,158	0,11713
	H1	0,063033	0,131853		C5	-0,158	0,12006
	H2	0,063033	0,131853		C6	-0,158	-0,087939
	H3	0,063033	0,138492		C7	-0,158	0,057575
	H4	0,063033	0,129499		C8	-0,159	0,213154
	H5	0,063033	0,129499		C9	-0,21	-0,324668
<i>Methyl Acetate (MA)</i>					H	0,072	0,068357
	C	-0,1501	-0,664509		H1	0,072	0,068324
	C1	0,6291	0,915207		H2	0,072	0,075387
	O	-0,4449	-0,433813		H3	0,078	-0,040085
	C2	0,1267	0,0011		H4	0,078	-0,040075
	O1	-0,541	-0,594817		H5	0,079	-0,018183
	H	0,0757	0,180868		H6	0,079	-0,018193
	H1	0,0757	0,178806		H7	0,079	-0,001635
	H2	0,0757	0,17922		H8	0,079	-0,001689
	H3	0,0617	0,084701		H9	0,079	-0,034637
	H4	0,0447	0,076499		H10	0,079	-0,034645
	H5	0,0447	0,076736		H11	0,079	-0,035151
<i>Ethyl Acetate (EA)</i>					H12	0,079	-0,035188
	C	-0,1501	-0,603183		H13	0,079	-0,001125
	C1	0,6311	0,910216		H14	0,079	-0,001192
	O	-0,4469	-0,51646		H15	0,079	-0,018348
	C2	0,1384	0,356665		H16	0,079	-0,018373
	C3	-0,1001	-0,34453		H17	0,078	-0,040213
	O1	-0,544	-0,613058		H18	0,078	-0,040178
	H	0,0517	0,011202		H19	0,072	0,075719
	H1	0,0517	0,011164		H20	0,072	0,068759
	H2	0,0757	0,16283		H21	0,072	0,06875
	H3	0,0757	0,167183				
	H4	0,0757	0,167011				
	H5	0,0467	0,078193				
	H6	0,0477	0,106401				
	H7	0,0477	0,106364				

The geometries for fitting the partial charges for all the alkyl-acetates molecules were optimized at the HF/6-31G+** level by using DFT quantum calculations. The partial charges were then fitted using two separate methods. The first one used the Electrostatic Potential method (ESP) on the optimized geometries at the HF/6-31G+** level. The second one used the AM1-BBC method, which includes the optimization of the initial geometry at the AM1 level, and after the calculation of the Mulliken charges, the BCC bond correction was applied (Semi empirical Quantum Mechanics). The fitted charges are displayed in Table 2.

After repeated tests, a number of molecules per box and a finite time of equilibration, production and integration were defined. The simulated boxes were set with periodic boundaries in all directions containing a total of 1000 molecules in the Isoobaric-Isothermal ensemble. The simulations were performed as follows: NPT equilibration and density production runs of 1,200,000 steps. Afterwards, NVT equilibration runs for 400,000 steps were followed by NVE viscosity production runs for 1,200,000 steps. All runs were performed with a 1fs timestep. The L-J and Coulombic cut-off was set to 8 Å with a switching distance of $r = 12$ Å. The simulations were started with randomly assigned velocities, the total momentum of the system was set to zero and Newton's equations of motion were solved with the standard Velocity-Verlet algorithm. Calculations were performed with the EOS super-calculator of CALMIP.

3. Results and Discussion

3.1. Density

Densities obtained by MD are shown in Figure 1 as function of CO₂ molar fraction at different temperatures and pressures.

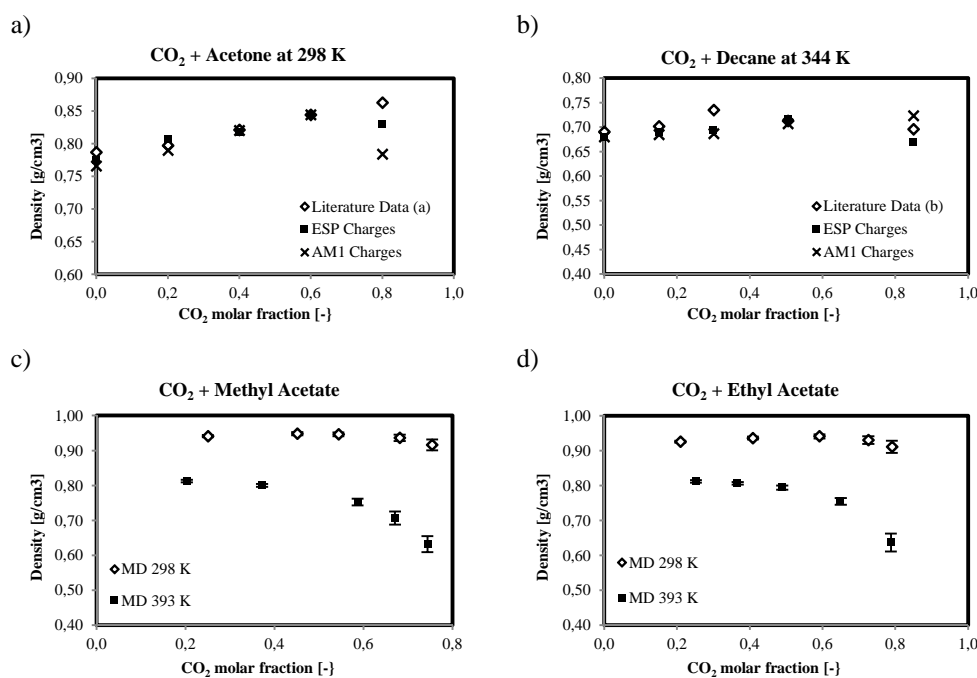


Figure 1. CO₂-expanded Density (g/cm³) vs CO₂ molar fraction. Refs a) (Sih and Foster 2008) b) (Cullick and Mathis 1984).

In Figures 1 c) and d) two distinct zones can be observed. Firstly, the density increases monotonically as the CO₂ solubilizes. Then, after a certain point ($x_{CO_2} \approx 0.7$), higher CO₂ molar fraction produces a drastic volume increment and the consequent decrease in density. Error bars correspond to Standard Deviation. This behavior has been explained by an increase in free volume observed in some CXLs (Li and Maroncelli, 2006), which would be responsible for their fluidity and solvation properties. Indeed, the initial solvent intermolecular spaces can first host the CO₂ to some extent, producing an imperceptible

increment in volume. Then, after a certain threshold in CO₂, its solubilisation induces a rapid volume expansion.

3.2. Viscosity

Calculated viscosities are shown in Figure 2 as function of CO₂ molar fraction at different temperatures and pressures. Literature data is plotted when available. Figure 2 shows a) CO₂+Acetone and b) CO₂+Decane systems for a single T with both charges sets; and c) CO₂+MA and d) CO₂+EA systems viscosity at different temperatures as a function of x_{CO₂}. For these two systems, no literature data was found concerning viscosity. Standard deviation for all systems falls under 5 · 10⁻¹⁰ due to integration over time smoothing. The behavior is nevertheless similar to other of CXL's (Li and Maroncelli 2006). In these systems, the viscosity decreases as a quasi linear function of CO₂ mole fraction. This general behavior is explained by the decrease of electrostatic forces between the solvent molecules due to the interposing CO₂ molecules, clustering around carbonyl groups. Calculating the intermolecular distances reveal that CO₂ molecules act as a Lewis acid and tend to gather around the carbonyl group of the acetates, at the free electrons pair of the oxygen (Aida et al. 2010).

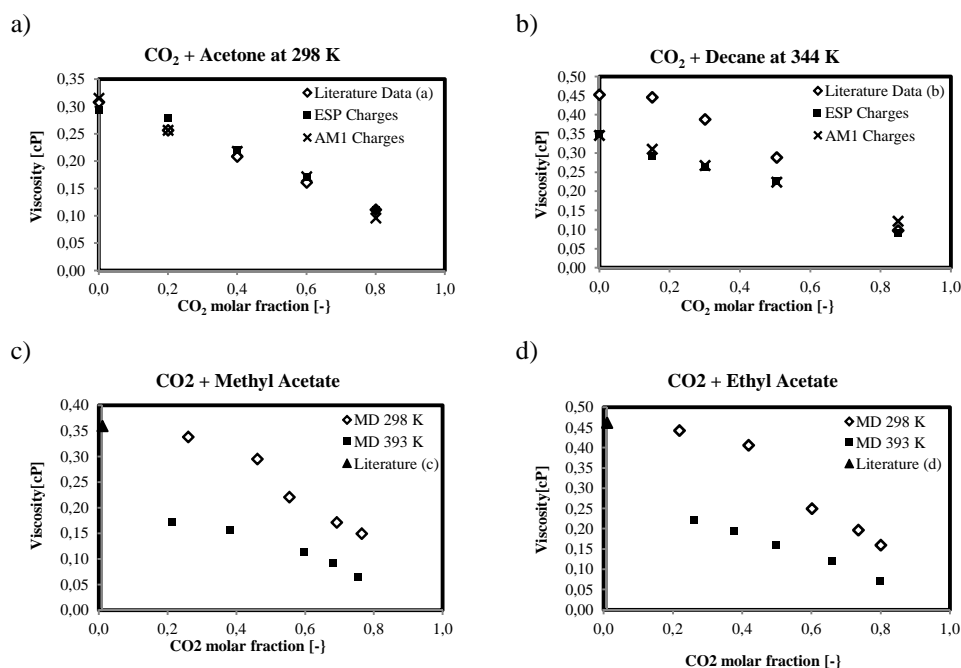


Figure 2. CO₂-expanded Viscosity (cP) vs CO₂ molar fraction. Refs a) (Sih and Foster 2008) b) (Cullick and Mathis 1984), c) (Lide 2004), d) (Trostin 1989).

4. Conclusion

MD simulations have been used to compute densities and viscosities of CO₂-expanded methyl and ethyl acetates; good agreement with existing literature data has been obtained. In this work, prediction of the densities and viscosities of the expanded liquid phases were

possible by this technique after good parameterization and by using the adapted model for CO₂.

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