



Molecular simulation of ethylene-expanded methanol: Phase behavior, structure, and transport properties



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ABSTRACT

Ethylene is an important industrial feedstock for the generation of commodity chemicals and is increasingly abundant as a by-product of natural gas production. In some cases, the reaction of ethylene can be enhanced by using it to create a gas-expanded liquid with the co-reactants dissolved in an organic solvent. Here, we present a molecular simulation study of the phase behavior, structure, and transport properties of mixtures of ethylene and methanol, in which the ethylene mole fraction is controlled by changing the pressure. For this ethylene-expanded methanol system, we report phase equilibria, volume expansion, liquid structure, translational diffusion constants, and rotational correlation times. The simulation results show excellent agreement with experimental values, where available, and the ethylene and methanol models show promise for use in further studies on related systems.

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1. Introduction

Gas-expanded liquids (GXLs) are a general class of liquid mixtures in which a significant amount of a gas is dissolved under pressure into a liquid solvent. The properties of GXLs are modified significantly from those of the neat solvent, largely as a result of the lower density, allowing them to be tuned for optimal use as solvents for catalytic processes. The general properties, industrial benefits, and broad range of applications of GXLs have been thoroughly reviewed [1,2]. To date, most studies of GXLs have focused on carbon-dioxide-expanded liquids (CXLs), which have found success as novel media for chemical processing. However, with the increased availability of ethylene from natural gas production as a chemical feedstock, there has been increasing interest in the properties and applications of ethylene-based GXLs in chemical processing.

Recently, ethylene-expanded methanol has been used to develop sustainable catalytic pathways for the production of ethylene oxide (EO) through solution phase epoxidation of ethylene

[3,4] at modest temperatures (20–40°) and pressures (up to 50 bar), which significantly lowers the risk of burning ethylene to form carbon dioxide. Currently, industrial production of ethylene oxide, an important commodity chemical intermediate that is produced industrially in high volume, involves direct gas-phase reaction of ethylene with oxygen (or air) at relatively high temperatures (200–300°). Unfortunately, the high temperatures involved result in a significant burning of the feedstock and product to form CO₂ with up to 15% loss, making this process second only to ammonia in the production of greenhouse gases (GHG) in commodity chemical production [5]. By allowing significantly lower temperatures, life cycle analysis shows that the use of ethylene-expanded methanol has the potential to significantly lower greenhouse gas emissions while preserving the economic viability of the process [3].

As with carbon dioxide, the critical point of ethylene is reached at fairly low temperature and pressure (about 9.2 °C and 50.4 bar, respectively) and thus near-critical behavior can be exploited under relatively mild operating conditions. For processes in which ethylene is a reactant, an ethylene-expanded liquid has great utility because of its relatively high concentration of ethylene and more favorable transport properties than the unexpanded solvent due to decreased density. Ethylene-expanded methanol is a major component of a previously reported ethylene epoxidation process [4] in which ethylene is oxidized by hydrogen peroxide within a

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silica mesopore doped with a metal catalyst. Despite their utility, the detailed phase equilibria, transport properties, and molecular-scale molecular structure of GXLs is not well characterized, especially for non-CO₂ gases (including ethylene) and mixed solvents. This is especially true for GXLs under confinement, such as within the silica nanopores used for ethylene epoxidation. Because experimental studies on bulk and confined GXLs are difficult, molecular modeling can play a leading role in determining both the macroscopic and molecular phenomenology. By providing predictions of the phase equilibria and transport properties of complex GXL mixtures, in bulk and under confinement, molecular modeling can provide crucial information necessary to optimize reactor design for catalytic processes in nanoscale pores.

In this work, we use Gibbs Ensemble Monte Carlo (GEMC) and molecular-dynamics (MD) simulations to examine the phase equilibria, transport, and local structure of bulk ethylene-expanded methanol. The primary aims of this study are to validate the interaction between force fields used through a comparison of binary phase equilibrium predictions to existing experimental data and to make predictions of both transport coefficients (translational and rotational) and local solvation structure. The validation of the potentials will be especially important in future studies of the properties of this GXL under confinement in silica mesopores, as experimental data for benchmarking in such systems is lacking. In addition, the ethylene/methanol binary system is of considerable theoretical interest in its own right. The properties of methanol are strongly determined by its hydrogen-bonding network and the degree to which high concentrations of ethylene disrupt that network is an open question.

The remainder of the paper is organized as follows. In the next section (Section 2) we outline the details of the intermolecular force fields and summarize the simulation protocol. The results for molecular simulations of ethylene-expanded methanol (phase diagrams, transport and structure) are presented in Section 3 for temperatures in the range 20–40° and for pressures from 5 to 55 bar. Phase equilibrium results are compared with the experiments of Ghanta et al. [3], Ohgaki et al. [6], Brunner [7], and Karimi et al. [8] to validate the force fields used in the simulation. Finally, in Section 4 we summarize and conclude.

2. Methods

2.1. MeOH and C₂H₄ force fields

The Transferrable Potentials for Phase Equilibria-United Atom (TraPPE-UA) potential was chosen to model methanol (MeOH) [9]. This potential was chosen because, unlike many alternative models, TraPPE-UA methanol was optimized for the prediction of liquid–vapor phase equilibria. This three-site model consists of a methyl (CH₃) pseudo-atom, oxygen (O) atom, and hydrogen (H) atom. Charges are placed on the three (pseudo-)atom sites and 12–6 Lennard-Jones (LJ) sites are placed on O and CH₃ atoms. The non-bonded (LJ and Coulomb) intermolecular interactions $u(r_{ij})$ take the form

$$u(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

where r_{ij} , ϵ_{ij} , σ_{ij} , q_i , and q_j are the internuclear separation, LJ well depth, LJ size, and charges on atoms i and j , respectively. Lorentz-Berthelot combining rules [10,11] are used to determine parameters for dissimilar ($i \neq j$) LJ interactions.

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (2)$$

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad (3)$$

The cutoff distance for the non-bonded interactions is 14 Å, at which an analytic tail correction [12,13] is applied and beyond which interactions are no longer calculated. The bond lengths r_{CO} and r_{OH} are held fixed. In addition, the usually flexible methanol bond angle is held rigid, so that all molecules in the simulation (methanol and ethylene) are rigid in the MD simulations. This approximation is validated by the observation that the harmonic angular force constant in the TraPPE-UA model is quite high ($k_\theta/k_B = 55400$ K/rad²) and the distribution of angles around the equilibrium position is narrow, $\pm 4^\circ$.

While there exists a TraPPE-UA potential [14] for ethylene (C₂H₄), our preliminary calculations indicated that this potential is incompatible with TraPPE-UA MeOH for our purposes. TraPPE-UA ethylene lacks an explicit quadrupole, and we found that the solubility of TraPPE-UA ethylene in TraPPE-UA methanol is significantly underestimated relative to experiment. To remedy this, we have chosen instead the quadrupolar ethylene potential of Weitz and Potoff [15] (referred to here as qC₂H₄), which gives excellent vapor–liquid equilibria results for neat ethylene, on par with TraPPE-UA ethylene, but with a considerably improved description of ethylene solubility in methanol. This model consists of two positively charged methylene (CH₂) pseudo-atoms bonded to a massless center-of-mass (COM) dummy atom, where a negative charge is placed to mimic the electron density located in the double bond. The charges were chosen to give the model the observed quadrupole moment of ethylene in the gas phase [15,16]. The C–C bond length is held fixed at all times. The force field parameters for ethylene and methanol used in this work are summarized in Table 1.

2.2. Gibbs Ensemble Monte Carlo simulations

Using MCCC's Towhee [17], we employ the Gibbs Ensemble Monte Carlo (GEMC) simulation method [18,19] for the calculation of phase equilibria and volume expansion. For the vapor–liquid equilibrium (VLE) of the pure substances, canonical (NVT-) GEMC is used, and for mixture VLE, isothermal-isobaric (NPT-) GEMC is used, due to the Gibbs phase rule [20]. In both cases, the two simulation boxes equilibrate to a coexistence state with the vapor and liquid phases having identical temperature, pressure, and chemical potentials for each species. Average vapor and liquid densities are calculated for the VLE of the pure substances, and average ethylene mole fractions are calculated for the mixture VLE.

The experimentally determined phase diagrams are available [6,21,22], and we use these data to validate our two molecular models. To reduce computational time, we initialize our systems to the approximate experimental densities (for NVT-GEMC) or mole fractions (for NPT-GEMC) for a given thermodynamic state, leading to simulations with varying total numbers of molecules, namely

Table 1
Force field parameters for TraPPE-UA methanol and qC₂H₄ ethylene.

	$q(e)$	$\sigma(\text{Å})$	ϵ/k_B (K)	Bonds (Å)	Angle (°)
CH ₃	0.265	3.750	98.0	$r_{CO} = 1.430$	$\theta_{COH} = 108.5$
O	−0.700	3.020	93.0	$r_{OH} = 0.945$	
H	0.435	0.0	0.0		
CH ₂	0.850	3.720	83.0	$r_{CC} = 1.330$	
COM	−1.700	0.0	0.0		

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