



# Phase equilibrium of a quaternary system: Methanol, ethylene, water and hydrogen peroxide

Zhenxing Wang<sup>a, b, c</sup>, Brian B. Laird<sup>a, b, \*</sup>

<sup>a</sup> Department of Chemistry, University of Kansas, Lawrence, KS 66045, USA

<sup>b</sup> Center for Environmentally Beneficial Catalysis, University of Kansas, Lawrence, KS 66045, USA

<sup>c</sup> Contemporary Amperex Technology Ltd., NingDe, Fujian 352100, China

## ARTICLE INFO

### Article history:

Received 19 September 2017

Received in revised form

5 January 2018

Accepted 12 January 2018

### Keywords:

Phase equilibrium

Methanol ethylene water hydrogen peroxide

Quaternary system

## ABSTRACT

In this work, we examine, using molecular simulation, the liquid-vapor phase equilibria and atomic-level structure of an ethylene-expanded mixture of methanol, water and hydrogen peroxide as functions of temperature and pressure. The motivation for this study is a recently proposed catalytic process for the epoxidation of ethylene to ethylene oxide in Nb-doped silica nanopores [J. Catal. **336** 75 (2016)], where the solvent (methanol) is expanded by the reactant (ethylene) in the presence of the oxidant (hydrogen peroxide in water). Optimal tuning of the reaction conditions can be greatly facilitated by detailed information as to the phase equilibrium and local structure (e.g., hydrogen bonding) of this quaternary mixture. In particular, we focus on the solubility of ethylene in this system as a function of water content. We compare this quaternary system to the recently studied ethylene/methanol/water ternary mixture [Fluid Phase Equilib. **429** 275 (2016)]. One major conclusion of this work is that for solutions in which the methanol to water/hydrogen peroxide ratio is greater than 50%, the solubility of ethylene in the quaternary mixture is identical within the statistical error to that of a corresponding ternary mixture, in which hydrogen peroxide is replaced by water. Given that these methanol-rich systems are precisely those of most utility in the epoxidation process, this observation greatly simplifies the phase-equilibrium analysis.

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## 1. Introduction

A gas-expanded liquid (GXL) is a novel liquid solution in which the volume of a solvent (typically an organic liquid) is expanded through the addition of a significant mole fraction of gas at high, but subcritical pressures [1]. Over the past two decades, GXLs have drawn great attention as support media in catalysis and separations, due to many factors, including enhanced mass transport, ease of post processing, high reactant and catalyst solubility and a reduction of amount of organic solvent needed [2,3]. Although most GXL studies and applications to date utilize carbon dioxide as the expansion gas (to form so-called “carbon dioxide-expanded liquids” or CXLs), efforts have been expanded to other expansion gases, such as propane [4], propylene [5], and ethylene [6].

In a recently proposed heterogeneous catalytic process for the

epoxidation of ethylene to ethylene oxide in niobium-doped silica nanopores, the reactant, ethylene, is used as an expansion gas with the aim of enhancing the reactant concentration in liquid phase [7–9]. Ethylene oxide is widely used in production of ethylene carbonate, which is the major component of electrolyte in commercial lithium-ion batteries. Specifically, the reaction mixture is an ethylene-expanded liquid (EXL) consisting of methanol (solvent), hydrogen peroxide (oxidant), water and the expansion gas, ethylene (reactant). Water is included here because the hydrogen peroxide used in the process is generally supplied as a solution with water. The use of ethylene as the expansion gas allows its concentration in the liquid phase to be easily tuned by adjusting the gas-phase pressure. The optimization of this catalytic process is hindered by the lack of reliable data on the Vapor-Liquid Equilibrium (VLE) for this quaternary system - especially with regard to the solubility of ethylene as a function of hydrogen peroxide/water content.

Determining the VLE of a quaternary system is challenging, both experimentally and in simulation. However, modern molecular simulation tools, such as Gibbs Ensemble Monte Carlo (GEMC) and

\* Corresponding author. Department of Chemistry, University of Kansas, Lawrence, KS 66045, USA.

E-mail address: [blaird@ku.edu](mailto:blaird@ku.edu) (B.B. Laird).

Grand Canonical Monte Carlo (GCMC), are well suited to the prediction of VLE, given a model for the intermolecular forces, while Molecular Dynamics simulation can be used to estimate the structural and thermodynamic properties of the calculated coexisting phases [10]. Previous simulations on GXLs using existing interaction models from the literature have been shown to give excellent agreement with experimental measurements for a variety of systems, especially CXLs [11,12]. In previous work we have examined the related binary EXL system (ethylene/methanol) (both in bulk [13] and under confinement in silica nanopores [14]), as well as the ternary EXL system where water is added to the ethylene/methanol mixture [15]. In these EXL studies, we obtained very good agreement with VLE experiments on these systems, exceeding the accuracy of standard equation of state modeling. In the binary [13] and ternary [15] EXL systems, we observed that decreasing temperature or increasing pressure not only increases the solubility of ethylene in the liquid, but also enhances diffusivity of all component species - a major advantage in process applications. In the ternary system, however, increased water content significantly lowered the ethylene solubility.

In this work, we extend our earlier calculations to the full quaternary reaction mixture (ethylene/methanol/water/hydrogen peroxide) for the aforementioned ethylene epoxidation reaction. As in our previous work on binary and ternary EXLs, we calculate the volume expansion as functions of temperature and pressure, while also varying the relative amounts of methanol and water/hydrogen peroxide. In addition, the compositional quaternary vapor-liquid phase equilibrium is studied and compared with our earlier results on the methane/ethylene/water ternary system. Finally we examine the local liquid structure as functions of temperature pressure and composition.

## 2. Methods

In this work, we use a United Atom (UA) model for methanol and ethylene in which the carbon atoms and those hydrogen atoms bonded to it are collapsed into a single “pseudoatom” sphere. While including all atoms in the simulation would yield perhaps a more realistic model, the computation of the additional interaction energies increases the computation time by an order of magnitude. Given the computational advantages, which are especially important for complex multicomponent phase equilibrium, and the observations that such UA models have been shown to give excellent results for phase equilibrium in similar systems [13,15], the UA force field is suitable for purposes of this work.

For ethylene we use a quadrupolar forcefield due to Weitz et al. [16], and, for methanol, the Transferable Potentials for Phase Equilibria-United Atom (TraPPE-UA) force field [17] with the C–O–H bond angle fixed to 108.5°. For water we use the SPC/E model [18]. All three species are treated as rigid molecules. For hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) we use a model by Cordeiro [19] with parameters for bonds, angles and torsions adapted from Koput et al. [20]. The short-range interactions as well as charges in this potential have been optimized to match liquid properties and the experimental free energy of hydration. Lorentz-Berthelot mixing rules are used for all short-range cross interactions and Ewald sums are used for the electrostatic interactions. The cutoff for all short-range interactions is chosen as 1.4 nm and Ewald Sum accuracy is 10<sup>-5</sup>.

In each NPT-GEMC simulation the vapor and liquid simulation boxes contain between 700 and 1000 molecules in total. Initially, the majority of ethylene molecules are placed in the vapor box with

the other species placed in the liquid simulation box. Between 250 K and 1 M Monte Carlo (MC) cycles (cycles = number of steps/number of molecules), depending upon the system conditions, were used to equilibrate the systems. During equilibration, the maximum MC displacements for translational, rotational, torsional and volume moves are adjusted to achieve a 50% acceptance rate. After this initial equilibration, the system is advanced for another 250 K cycles with fixed maximum displacements, followed by a 1 M cycle production run for the calculation of compositions and physical properties. These 1 M cycles are divided into 10 blocks for error estimation, using block-averaging and the Student's *t*-distribution with a 95% confidence level. To be consistent with the experimental conditions for all studied quaternary mixtures, the H<sub>2</sub>O/H<sub>2</sub>O<sub>2</sub> mass ratio is fixed to 1:1. Systems with 6 different initial compositions at various temperatures (20°C and 40°C) and pressures (5 bar, 30 bar and 50 bar) were analyzed. All NPT-GEMC simulations are carried out using the parallel MC program CASSANDRA [21]. Because the Ryckaert-Bellemans type function for dihedral angle energy, used in original hydrogen peroxide model [19], is not supported in CASSANDRA, the function is converted to an alternative OPLS type function and the fifth-order term is neglected. To validate this approximation, we have calculated dihedral energy differences at 36 evenly distributed positions between 0 and  $\pi$  and a Root-Mean-Square Error (RMSE) is found to be 0.0055 kcal/mol, which is acceptable.

The volume expansion is quantified by the *Volume Expansion Ratio*, defined as the ratio between the volume of gas-expanded liquid and the volume of neat solvent at the same temperature and 1 atm pressure. To be consistent with previous studies, the specific volume of the liquid phase is determined from NPT MD simulations. For each liquid phase a cubic simulation cell with initial edge length of 5 nm is created using phase composition predicted from the NPT-GEMC simulations. The simulation cell for the corresponding neat solvent is generated by simply removing ethylene from that of the quaternary system. The same force field parameters as in NPT-GEMC simulations are employed. The long range interaction is calculated using PPPM [22] with an accuracy of 10<sup>-6</sup>. The simulation cell is equilibrated at 100 K for 50 ps, then heated to the target temperature for another 100 ps. After 1 ns of equilibration, a 2 ns production simulation is performed to calculate densities and radial distribution functions (RDFs). In the whole procedure NVT ensemble is employed through Nosé-Hoover thermostat [23,24] with damping factor as 100 fs. The timestep is chosen to 1 fs and snapshots are collected every 100 steps. All MD simulations are conducted using LAMMPS [25].

Four-phase (quaternary) equilibrium is often difficult to visualize given the large number of components. To simplify this we note that, relative to ethylene, the liquid components methanol, water and hydrogen peroxide are nonvolatile; the equilibrium vapor phase will consist almost exclusively of ethylene. Therefore, as the pressure of ethylene over a given solution of methanol, water and hydrogen peroxide is increased at constant pressure and temperature, the relative fractions of methanol, water and hydrogen peroxide change relatively little. In addition, we fix the water and hydrogen peroxide ratio to 1. As such, in analogy to our previous study on ethylene-expanded methanol/water mixtures [15], we define for each solution a “solvent” methanol mole fraction

$$x_{\text{meth}}^s = n_{\text{meth}} / (n_{\text{meth}} + n_{\text{water}} + n_{\text{H}_2\text{O}_2}) \quad (1)$$

as the ratio of the number of moles of methanol to the total number of moles of the other relatively non-volatile liquid components.

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