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Assessing the ability of force-fields to predict liquid–liquid equilibria of ternary systems of light alcohols + water + dodecane by Monte Carlo simulation

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ABSTRACT

Dodecane may be used as an extractive solvent to remove light alcohols from water in downstream processing in the Fischer–Tropsch process. In order to understand the ternary liquid–liquid phase behaviour for the systems and determine the effectiveness of alcohol removal with dodecane, both experimental liquid–liquid equilibria measurements and molecular simulations were undertaken as part of a previous study. Monte Carlo simulations for the systems proved to be difficult and therefore an assessment was undertaken to determine the effectiveness of the simple point charge (SPC) and TIP4P water models, in conjunction with the transferable potentials for phase equilibrium (TraPPE) model for the organics, in describing the liquid–liquid equilibria of such systems at atmospheric pressure. The light alcohols in question were methanol, ethanol, and propan-2-ol, and the temperatures for comparison with experimental data were at 313.14 and 333.15 K. It was found that the simulations agreed favourably with the experimental data for the system containing methanol over the entire composition range, and only within certain compositional bounds for the systems containing ethanol and propan-2-ol. The deviation of the molecular simulations from the experimental data increased with increasing alcohol carbon number.

1. Introduction

In order to remove light alcohols, typically alcohols with three or less carbon atoms, from aqueous solutions, solvent extraction followed by distillation is often undertaken in chemical processes in industry. A potential solvent in this liquid extraction process is dodecane which as a result of its relatively high boiling point may be recovered downstream via distillation. Such a process is being considered in downstream processing after the Fischer–Tropsch process.

The thermodynamic modelling of the solvent extraction process requires high-quality phase equilibrium data. In the case of the proposed process, liquid–liquid equilibrium (LLE) data are required. LLE data for such systems are frequently measured at atmospheric pressure [1–4], which can be a significant drawback when using conventional equipment with chemicals which have an appreciable volatility. This volatility at atmospheric pressure may limit the temperature ranges at which accurate LLE measurements can be undertaken. In order to expand the range of conditions for experimental LLE data, molecular simulation of ternary LLE for the light alcohols + water + dodecane system was investigated.

Molecular simulations are an increasingly attractive option to investigate phase equilibrium conditions which are difficult to obtain in the laboratory, as any desired conditions (i.e., temperature, pressure, volume) may be investigated via the simulations. It is however important to know which combinations of models or force-fields may be applicable to certain scenarios. If a prediction of the phase equilibrium behaviour of a particular system is desired, it is necessary for the force-fields to adequately represent the behaviour of the molecules in the system. To this end, it is necessary to determine whether or not a set of force-fields, either individually or in combination (as needs dictate) may be used for a particular application. This may be undertaken by comparison of the simulation results with available experimental data. If the description of the force-fields are found to accurately represent the real phase behaviour of the system, the said force-fields may be used. If not, it may be necessary to either determine a correction factor which may be applied to either the energy or size parameters (for Lennard-Jones species, for example).

Examples of Lennard-Jones parameter fitting include LLE of water + n-alkanes [5,6], in which the composition of the organic phase was used as the objective function in the fitting

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procedure, whilst the excess chemical potential of methane in the liquid phase was used in a study of dilute gaseous methane in water [7]. Other studies involving the fitting of Lennard-Jones parameters to experimental data involve, for example, binary and ternary phase equilibria in supercritical systems [8] and binary vapour-liquid equilibria of perfluoroalkanes with carbon dioxide [9]. A thorough study of the behaviour of Lennard-Jones fitting parameters [10] has found, however, that there may be no unique solution when attempting to fit to experimental data. Therefore, multiple values of Lennard-Jones correction factors may produce similar results, depending upon the quantity of interest for the fitting procedure itself (e.g., composition, density, etc.).

A significant shortcoming of molecular simulations, however, is that the quality of the results depends, necessarily, upon the force-fields and molecular models used in such simulations. These force-fields may be derived from first-principles quantum chemical calculations, but it may be prudent to refine any parameters by comparison with available experimental data. Therefore, simulations and experimental work may be used in a complementary manner, such that experimental measurements may be used to refine the force-field parameters. These refined parameters may then be used in further studies, where required. Additionally, such a complementary process may produce knowledge of the range of applicability of existing force-fields, as has been undertaken in this study.

Studies on similar and related systems have been undertaken recently; hexadecane + water + (acetonitrile or methanol) [11], 1-octanol + water + *n*-alkanes (methane to octane) [12,13], ethanol + water + 10-carbon alcohols [14]. These studies did not focus strictly on LLE, but on properties such as partition coefficient comparisons and free energies of solvation. It was demonstrated that systems containing methanol which involve solvation or transfer between liquid phases can be adequately described by molecular simulations [11]. The Gibbs free energies of solvation of *n*-alkanes in 1-octanol were found to be adequately predicted by both united-atom and all-atom force fields [12]. With regard to the hydration free energy of *n*-alkanes, the choice of water force fields did not play a role in the values obtained, although the hydration free energies obtained from simulations were noticeably higher than in experiments [13]. The extraction of ethanol from aqueous solutions by 10-carbon alcohols was shown to be adequately predicted using molecular simulations [14].

By considering the findings of the above studies, it can therefore be predicted that the role of the water force field may not play a role in differences in water + dodecane interactions in the present study, although the solubility between water and dodecane may not be accurately described. In addition, it can be presumed that the methanol + water + dodecane system may be well-described by the simulations.

2. Theory and methods

In order to simulate LLE in this study, the standard two-phase Monte Carlo (MC) form of the Gibbs ensemble [13] was used, as implemented in the Fortran90 "Gibbs" computer programme [16]. Essentially, the Gibbs ensemble overcomes the influence of surface effects on systems consisting of relatively few numbers of molecules (of the order of 10^2 to 10^3, most commonly) by replacing the action of molecular transfer between phases by the possibility of swapping molecules between two "boxes" located deep within the bulk material of the phases in question.

The simple point charge (SPC) model [17] and the TIP4P model [18] have been used to describe the water molecules in this study. The SPC model consists of three interaction sites (the negatively charged oxygen site, and two positively charged hydrogen sites), whilst the TIP4P model makes use of four interaction sites (two positively charged hydrogen sites, the oxygen site, and a charge balancing site at the centre of mass of the water molecule). The SPC model was selected as it reproduces the experimental liquid density of water well, without being computationally complex [19]. Since LLE simulations were undertaken, the capability of a force field to reproduce the liquid density suggests validity in its use. With regard to the alcohol and dodecane molecules, the transferable potentials for phase equilibrium (TraPPE) model [20,21] was used. A previous study has shown that the combination of SPC water with TraPPE alkanes agreed favourably with experimental data for systems of alkanes + water [5]. All of the models concerned made use of a Lennard-Jones [23] intermolecular potential to describe the van der Waals interactions, along with the classical Lorentz [24] and Berthelot [25] combining rules to account for the interactions between unlike intermolecular pairs. A cut-off radius of 2.84 times the size parameter of the water force field (i.e., about 0.9 nm for both SPC and TIP4P water) was used for intermolecular Lennard-Jones interactions, with an analytical tail correction being applied beyond this distance. The cut-off radius used in this study were always less than half the box lengths. A plot of the simulation box lengths during the progression of a simulation run is shown for illustrative purposes in Fig. 1. Ewald summation [26] accounted for the electrostatic interactions of the system. The force field parameters are presented in Table 1.

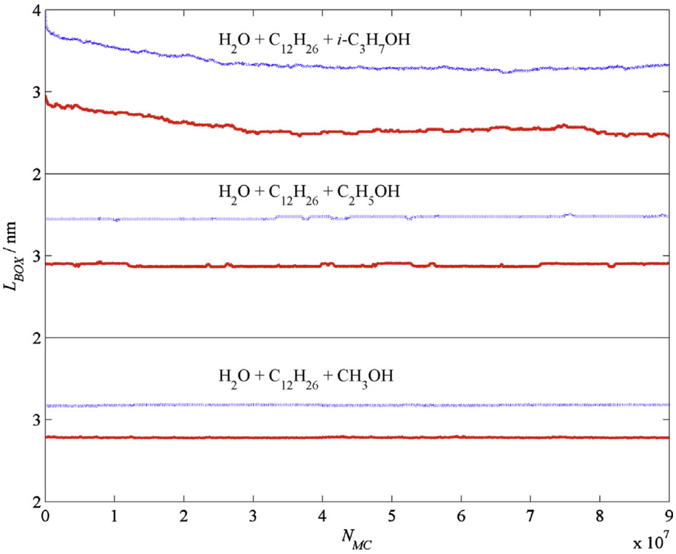

Fig. 1. Evolution of box length (L_{BOX}) versus the number of MC moves (N_{MC}) for one simulation run from each system. Aqueous phase (▬), organic phase (- -).

Within the framework of the Gibbs ensemble, the constant moles–pressure–temperature (NPT) ensemble has been used, due to the thermodynamic degrees of freedom of the system, as described by the Gibbs phase rule [27]. In addition, it is important to note that the NPT ensemble is analogous to laboratory experiments, where frequently, the system pressure and temperature are monitored and/or controlled, along with the amount of material charged into the equilibrium cell at the start of an experiment.

The system sizes in this study ranged from 300 to 500 molecules, which was in line with previous MC simulations of systems of water + organics [19]. Moreover, previous simulations of SPC water + alkanes showed no appreciable finite size effect when using 200, 500 or 1000 water molecules [28]. It should also be noted that these simulations used the minimum-image convention for the simulations of systems containing 200 water molecules, and a cut-off radius for the larger systems. In this study, the fact that the alcohols and especially dodecane contain substantially more