Excess properties of non-ideal binary mixtures containing water, methanol and ethanol by molecular simulation

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Svetlana Miroshnichenko, Jadran Vrabec *

Thermodynamics and Energy Technology, University of Paderborn, 33098 Paderborn, Germany

A B S T R A C T

Excess properties provide information about the nature of molecular interactions in binary mixtures. Since experimental measurements of these properties may be difficult and time consuming, their prediction is important. Monte Carlo simulations are used here to calculate the excess properties of binary mixtures. Excess volume and excess enthalpy are investigated by molecular modeling and simulation for aqueous, methanolic and ethanolic binary liquid mixtures with the following components: benzene, chloroform, dimethyl ether, ethylene oxide, toluene, tribromomethane and 2-bromo-2-chloro-1,1,1-trifluoroethane. These mixtures are of considerable interest because of their S-shaped composition dependence of excess thermodynamic quantities. The comparison with experimental data from the literature for excess volume and excess enthalpy shows that one binary interaction parameter per mixture typically needs to be adjusted for a quantitative agreement.

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1. Introduction

Reliable thermophysical properties of binary systems are of primary interest for process design and optimization in the chemical industry. These properties are important not only for a fundamental understanding of mixing processes, but also for many practical problems during the design of products, processes and industrial equipment [1]. Theoretically, it is possible to predict the thermodynamic properties of binary systems from the properties of their constituent components, but in many cases such calculations can be very inaccurate due to the complex structure of non-ideal mixtures [2]. There is a wide range of possible interactions between the components of a mixture, such as hydrogen bonding, molecular association, dipole–dipole or induced dipolar interactions. As a consequence, deviations from an ideal behavior of thermodynamic mixture properties occur. These deviations can be defined by excess properties, which provide fundamental information on the unlike intermolecular interactions between the components forming binary systems.

Excess properties can be studied by means of experimental methods, molecular simulation, theoretical or empirical approaches. Numerous works about excess properties of binary mixtures containing water, methanol or ethanol can be found in the literature [3–14]. Most of

these systems were studied by experiment in the 1970s. In the last decades, great advances were made in the field of equations of state (EOS), partially motivated by industrial interest. However, predictions for the excess properties, such as excess volume or excess enthalpy, are less common. Molecular modeling and simulation is an alternative method that is based on models for the intermolecular interaction forces and that can cover the thermodynamic properties of complex systems. These forces are described by potential functions that contain molecular parameters with a physical meaning, e.g. molecular size, dispersive energy or dipole moment. In classical molecular models, these parameters do not depend the thermodynamic conditions, such as temperature, pressure and composition.

There has been significant progress in studying and predicting excess properties of binary mixtures by molecular simulation. The first contributions were published in the 1970s: McDonald [15] described the application of the Monte Carlo method to the calculation of excess thermodynamic properties (volume, enthalpy and Gibbs energy) of liquid binary Lennard–Jones (LJ) mixtures. Recently, the study of excess properties of binary mixtures by molecular simulation has been an active field of research [16–24]. Chitra and Smith [16] reported molecular dynamics simulations of water + 2,2,2-trifluoroethanol, but could not achieve a quantitative agreement with experimental data. Milano and Müller-Plathe [17] calculated excess properties of cyclohexane + benzene which are in good agreement with experimental data. Gonzáles-Saldago and Nezbeda [18] studied the excess volume and excess enthalpy of water + methanol using realistic models (TIP4P for

* Corresponding author.
  E-mail address: jadran.vrabec@upb.de (J. Vrabec).

water and OPLS for methanol). These authors showed that the mixing properties are very sensitive to the potential model parameters and only properties related to the excess volume came out in a reasonably good agreement with experimental data. Yu et al. [19] used a polarizable model for methanol and the COS/G2 model for water for the simulation of water + methanol. Carvalho et al. [20] obtained by Monte Carlo simulations the excess volume and excess enthalpy for liquid binary mixtures of xenon and the linear alkanes ethane, propane and n-butane. Zhong et al. [21] predicted excess properties of the mixture water + methanol using non-additive interaction models: the TIP4P-FQ potential for water–water interactions and the CHARMM-based fluctuating charge potential for methanol–methanol as well as water–methanol interactions. Zhang et al. [22] used a polarizable, flexible force field for dimethyl sulfoxide and the TIP4P-FQ (fluctuating charge) water model to study the properties of dimethyl sulfoxide + water. Simulated excess volumes were underestimated in comparison to the experimental results. dos Ramos et al. [23] applied Monte Carlo simulation on the basis of TraPPE models to predict the excess thermodynamic functions of binary mixtures of short linear alkanes. Guevara-Carrion et al. [24] studied excess volume and excess enthalpy of methanol + ethanol. Their simulated excess properties correspond well with the experimental data of this nearly ideal mixture.

The aim of the present work is to investigate the S-shaped composition dependence of excess volume and excess enthalpy of binary mixtures containing water, methanol and ethanol by molecular simulation.

2. Methodology and simulation details

Excess quantities are properties of mixtures which characterize their non-ideal behavior. It is common practice to characterize liquid mixtures by means of excess functions

$$y^E = y^{Mix} - \sum_i x_i . y_i,$$ (1)

where y^{Mix} is the total molar property of the mixture, y_i the molar property of pure component i at the same temperature and pressure and x_i the mole fraction of component i.

The straightforward approach following McDonald [15] was used here to determine excess properties. Three simulations at specified temperature and pressure were carried out, two for the pure substances and one for the mixture at a given composition. Throughout, the excess volume or excess enthalpy was simulated at four different mole fractions: 0.2, 0.4, 0.6 and 0.8 mol/mol. The calculations of excess properties were carried out with the simulation tool $ms2$ [25]. All mixtures were simulated with the classical Monte Carlo simulation technique in the isothermal-isobaric (NpT) ensemble, where all mechanical degrees of freedom were attempted to be displaced once per loop. Starting from a face centered cubic lattice, a physically reasonable configuration was obtained by 5000 equilibration loops in the canonical ensemble, followed by 25,000 relaxation loops in the NpT ensemble. Thermodynamic averages were obtained over 300,000 loops. All simulations were made with a total number of 2000 particles and the long range interactions were considered appropriately [25].

3. Molecular models

In this work, molecular models of united-atom type without internal degrees of freedom from preceding work were used. The present molecular models include three groups of potential parameters. These are the geometric parameters, specifying the positions of different interaction sites, the electrostatic parameters, defining the polar interactions in terms of point charges, dipoles or quadrupoles, and the parameters that determine the attraction by London forces and the repulsion by electronic orbital overlaps. Here, the LJ 12-6 potential [26,27] was

used to describe the dispersive and repulsive interactions. The total intermolecular interaction energy thus writes as

$$
\begin{aligned}
U = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} &\Bigg\{ \sum_{a=1}^{S_i^{LJ}} \sum_{b=1}^{S_j^{LJ}} 4\varepsilon_{ijab} \left[\left(\frac{\sigma_{ijab}}{r_{ijab}} \right)^{12} - \left(\frac{\sigma_{ijab}}{r_{ijab}} \right)^6 \right] \\
&+ \sum_{c=1}^{S_i^e} \sum_{d=1}^{S_j^e} \frac{1}{4\pi\epsilon_0} \left[\frac{q_{ic}q_{jd}}{r_{ijcd}} + \frac{q_{ic}\mu_{jd} + \mu_{ic}q_{jd}}{r_{ijcd}^2} \cdot f_1(\omega_i, \omega_j) \right. \\
&+ \frac{q_{ic}Q_{jd} + Q_{ic}q_{jd}}{r_{ijcd}^3} \cdot f_2(\omega_i, \omega_j) + \frac{\mu_{ic}\mu_{jd}}{r_{ijcd}^3} \cdot f_3(\omega_i, \omega_j) \\
&+ \left. \frac{\mu_{ic}Q_{jd} + Q_{ic}\mu_{jd}}{r_{ijcd}^4} \cdot f_4(\omega_i, \omega_j) + \frac{Q_{ic}Q_{jd}}{r_{ijcd}^5} \cdot f_5(\omega_i, \omega_j) \right] \Bigg\},
\end{aligned}
$$ (2)

where r_{ijab}, ε_{ijab}, σ_{ijab} are the distance, the LJ energy parameter and the LJ size parameter, respectively, for the pair-wise interaction between LJ site a on molecule i and LJ site b on molecule j. The permittivity of the vacuum is ε_0, whereas q_{ic}, μ_{ic} and Q_{ic} denote the point charge magnitude, the dipole moment and the quadrupole moment of the electrostatic interaction site c on molecule i and so forth. The expressions $f_x(\omega_i, \omega_j)$ stand for the dependence of the electrostatic interactions on the orientations ω_i and ω_j of the molecules i and j [28,29]. Finally, the summation limits N, S_x^{LJ} and S_x^e denote the number of molecules, the number of LJ sites and the number of electrostatic sites, respectively. For a given molecule, i.e. for a pure fluid throughout, the interactions between LJ sites of different type were defined here by applying the standard Lorentz-Berthelot combining rules [30,31]

$$\sigma_{ijab} = \frac{\sigma_{iiaa} + \sigma_{jjbb}}{2},$$ (3)

and

$$\varepsilon_{ijab} = \sqrt{\varepsilon_{iiaa}\varepsilon_{jjbb}}.$$ (4)

The employed molecular models were taken from preceding publications of our group. The models for methanol and ethanol were developed by Schnabel et al. [32] and consist of two (methanol) or three (ethanol) LJ sites and three point charges each. The molecular models for benzene and toluene were developed by Huang et al. [35]. The model for toluene is composed of seven LJ sites plus five quadrupoles and one weak dipole. The quadrupole of the benzene model was equally divided into six parts and located on the six LJ sites representing the methine groups. Model parameters for ethylene oxide and dimethyl ether were published by Eckl et al. [36,37]. Both molecules were modeled by three LJ sites (one for the oxygen atom and one for each methyl/methylene group) as well as one dipole located in the center of mass and oriented along the symmetry axis of the molecule. The molecular models for chloroform, tribromomethane (R20B3) and 2-bromo-2-chloro-1,1,1-trifluoroethane (R123B1) were developed by Stoll et al. [38]. They are based on the two-center LJ plus point dipole (2CLJD) pair potential.

Numerous force fields for water were developed for their capability to describe and predict thermophysical properties. In several studies, some traditional water models have been re-parameterized to obtain a better agreement with experimental data. E.g., the TIP4P-type models have been re-parameterized for simulations with Ewald summation into the TIP4P-Ew model and the TIP4P/Ice model was developed for better predictions of the properties of ice. Further optimizations for the model type were suggested by Abascal and Vega [33] (TIP4P/2005) and Huang et al. [34]. The water model of Abascal and Vega is a rigid structure with OH bond lengths of 0.9572 Å and has a bond angle HOH of 104.52°. The partial charges are placed on the hydrogen atoms and on an additional site M, which is located midway along the HOH