Excess Properties of Non-Ideal Binary Mixtures Containing Water, Methanol and Ethanol by Molecular Simulation

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Abstract

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 or 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.

Graphical abstract
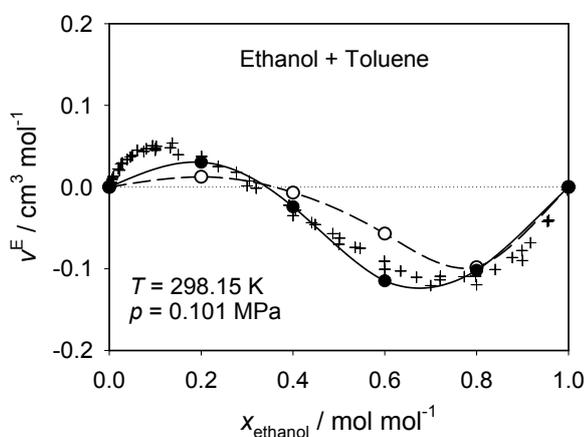
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Highlights

- Excess volume and excess enthalpy as functions of mole fraction are obtained by Monte Carlo simulation for seven liquid binary mixtures

- A S-shaped composition dependence of excess properties of binary mixtures containing water, methanol or ethanol is predicted

- The excess properties are highly sensitive on the unlike intermolecular interactions

Keywords: Molecular modeling and simulation; excess properties; excess volume; excess enthalpy; water; methanol; ethanol

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 1970ies. In the last decades, great advances were made in the field of the 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 1970ies: McDonald

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[15] described the application of the Monte Carlo method to the calculation of excess thermo-dynamic 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 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 a common practice to characterize liquid mixtures by means of excess functions

$$y^E = y^{Mix} - \sum_i x_i \cdot y_i, \tag{1}$$

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 were 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 25000 relaxation loops in the NpT ensemble. Thermodynamic averages were obtained over 300000 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

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

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 $f_x(\boldsymbol{\omega}_i, \boldsymbol{\omega}_j)$ stand for the dependence of the electrostatic interactions on the orientations $\boldsymbol{\omega}_i$ and $\boldsymbol{\omega}_j$ 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]

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

and

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

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 was modeled by three LJ sites (one for the oxygen atom and one for each methyl/methylene group) as well 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 thermopyhsical properties. In several studies, some traditional water models have been re-parametrized to obtain a better agreement with experiment. E.g., the TIP4P-type models have been re-parametrized 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 that 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 angle bisector, 0.1546 Å away from the oxygen atom. The TIP4P/2005 model was applied by many authors to predict the phase diagram and other thermophysical properties of water with great success. However, with respect to excess properties, problems were detected. It has been shown by Gonzalez-Salgado and Nezbeda [18] that the mixing properties are very sensitive to the underlying potential models and that different TIP4P water models yield a reasonably good agreement with experiment only for volumetric properties. With respect to the excess enthalpy, the results are rather poor and only its sign was predicted correctly. Considering these problems, we have selected the water model from preceding work of our group [34]. It also consists of one LJ site and three point charges. The magnitude of the point charges of this model is smaller than for any other TIP4P-type model and the attractive force is compensated by a relatively high LJ energy parameter ε.

In molecular simulations of a binary mixture $a + b$ with pairwise additive potentials, three different interactions occur: two like interactions between molecules of the same type a-a and b-

b, which are given by the pure component models, and the unlike interaction between molecules of different type a-b. In mixtures consisting of polar molecules, the electrostatic part of the unlike interaction is fully determined by the laws of electrostatics. However, there is no rigorous physical framework that yields reliable unlike dispersion parameters and thus unlike LJ parameters. For this purpose, combining rules were developed in the past based on physical and mathematical intuition or on empirical approaches. Following a recent investigation on combining rules and the sensitivity of vapor-liquid equilibrium properties on unlike LJ parameters by Schnabel et al. [39], the modified Lorentz-Berthelot combining rules were used here

$$\varepsilon_{ijab} = \xi \sqrt{\varepsilon_{iiaa}\varepsilon_{jjbb}}. \tag{5}$$

The state independent binary parameter ξ is introduced to account for polarizability effects and can be adjusted to experimental data. For VLE it was shown in [39] that ξ should be adjusted to a single binary vapor pressure data point. In the present work either the experimental excess volume or the experimental excess enthalpy at one liquid mole fraction was taken to adjust the binary parameter of the molecular mixture model. Table 1 lists the adjusted binary parameter ξ for all mixtures considered in this work.

4   Results and discussion

Based on the molecular models described above, excess volume and excess enthalpy were simulated for seven binary systems containing water, methanol and ethanol. These mixtures were chosen according to the availability of experimental data that exhibit a S-shaped form and the availability of molecular models. A single experimental data point near the extreme value of excess volume or excess enthalpy (maximum or minimum) was taken to adjust the binary parameter ξ.

4.1 Mixtures containing water

Several authors, such as Simond et al. [3], have examined excess properties of mixtures containing water. Simond et al. used molecular dynamics simulation to predict the excess enthalpy of water + alkanolamine systems. They indicated that water-water interactions play a major role in differentiating water + alkanolamine mixtures, which is a manifestation of the hydrophobic effect. Both the structural and energetic effects observed at the molecular level point to phenomena that have a strong composition dependence, in particular the interplay between the intramolecular hydrogen bond in the alkanolamine and the intermolecular hydrogen bonds with water [3]. Nakayama and Shinoda [4] have determined the excess enthalpy of water mixed with cyclic or linear ethers experimentally. In their work, the authors discuss the structural modifications of water around the ether molecules.

Water is a polar solvent with a structure that is determined to a large extent by hydrogen bonding. In mixtures of water with an organic liquid at least two effects must be taken into account: hydrogen bond formation between water and the polar group of the solute molecule and structural modification of water around the solute molecule [4]. According to Nakayama and Shinoda [4], the dependence of the excess enthalpy for the present mixtures may be explained as a balance between positive contributions (hydrogen bond rupture or dispersive interactions between unlike molecules) and negative contributions (intermolecular dipolar interactions or geometrical fitting between components).

Two binary mixtures containing water were studied here: water + dimethyl ether and water + ethylene oxide. Experimental data by Park et al. [5] and Glew and Watts [6] exhibit a S-shaped composition dependence of the excess enthalpy h^E. As shown in Figure 1, both mixtures behave similarly with respect to the excess enthalpy. We performed molecular simulations for the mixtures containing water using the TIP4P/2005 and Huang et al. water models to examine the ability of these models to reproduce the excess enthalpy. The data predicted by molecular simulation for both mixtures, i.e. without adjusting the binary parameter ξ, are positive over the entire composition range and similar for both models. Nevertheless, the predicted excess

enthalpy on the basis of the Huang et al. model, cf. Figure 1, agrees slightly better with the experiment than that from the TIP4P/2005 model.

The binary parameter ξ was adjusted here to the experimental excess enthalpy for a liquid mole fraction of water $x_{\text{water}} = 0.2$ mol/mol, cf. Table 1. In case of the TIP4P/2005 water model it was not possible to thereby match the simulation results with the experimental data, whereas in case of the Huang et al. model this procedure was successful. This can be explained by the differing magnitude of the LJ energy parameter of the two water models, $\epsilon/k = 93.2$ K (TIP4P/2005) and 208.05 K (Huang et al.), and their differing charge magnitudes. Because the Huang et al. model interacts relatively more via dispersion, it is more susceptible to variations of ξ. After adjustment, the values of h^E are positive in the water-poor region and decrease with rising mole fraction of water. The simulation results do exhibit the characteristic S-shaped mole fraction dependence, which has maximum at $x_{\text{water}} \approx 0.2$ mol/mol and minimum at $x_{\text{water}} \approx 0.9$ mol/mol. As shown in Figure 1, the present results match very well with the experimental data. For both aqueous systems, the binary interaction parameter ($\xi = 1.3$ for water + dimethyl ether and $\xi = 1.2$ for water + ethylene oxide) differs quite strongly from the value $\xi = 1$ that would be used for strictly predictive applications. As noticed by Huang et al. [34], this can be explained by the fact that the interactions of water are dominated by electrostatics so that the comparably weak unlike dispersive interactions have to be modified significantly to adjust mixture models.

4.2 Mixtures containing methanol

Methanol molecules do not only consist of hydrogen bonding sites like water, but also have a hydrophobic alkyl group. In this work, the excess enthalpy h^E was simulated for three binary mixtures: methanol + tribromomethane (or bromoform), methanol + 2-bromo-2-chloro-1,1,1-trifluoroethane (or halothane) and methanol + chloroform. The dependence of h^E on composition of these mixtures is S-shaped, cf. Figure 2. All mixtures are exothermic in the methanol-rich region and endothermic in the methanol-poor region. The binary parameter of methanol + tribromomethane $\xi = 1.083$ was adjusted to the experimental excess enthalpy measured by Singh et al. [7] at a liquid mole fraction of methanol $x_{\text{methanol}} = 0.2$ mol/mol. Despite the significant

deviations between simulated and measured excess enthalpy in the methanol-rich region, the qualitative agreement in terms of the S-shaped mole fraction dependence is satisfactory. The simulation results with adjusted binary parameter for the mixtures methanol + 2-bromo-2-chloro-1,1,1-trifluoroethane and methanol + chloroform are also in very good agreement with the experimental data by Costas et al. [8] and Morris et al. [9], cf. Figure 2.

The behavior of all considered systems containing methanol is governed by aggregate formation through hydrogen bonding, where methanol self-association and its complex formation with the proton donors compete. When methanol is diluted, there is a positive contribution to h^E from the breaking of hydrogen bonds between the alcohol molecules. This effect is relatively more important at low methanol concentrations than at high concentrations, where the dissociation of the less associated molecules predominates. The negative values of excess enthalpy in the methanol-rich region are then essentially due to the hydrogen bonded interaction between the hydroxyl oxygen of methanol and the hydrogen of the other compound and due to the specific interaction between the hydroxyl hydrogen of methanol with the halogen (bromine or chlorine) of the other component.

4.3 Mixtures containing ethanol

For the study of excess volume behavior two mixtures containing ethanol were chosen: ethanol + benzene and ethanol + toluene. The composition dependence of the excess volume v^E of these mixtures was examined by several authors [10–14]. Letcher et al. [14] investigated the excess volume for binary mixtures of toluene with an alcohol by using an association model. Tanaka and Toyama [11] reported on the excess molar volume, measured in a vibrating-tube densimeter for binary mixtures of ethanol + benzene and ethanol + toluene at a temperature of 298.15 K. Both mixtures exhibit a S-shaped excess volume behavior at ambient conditions. The excess volume of ethanol + benzene and ethanol + toluene was thus simulated here at 298.15 K and 0.101 MPa. The simulation results are compared with experimental data from the literature in Figure 3. The predicted excess volume of ethanol + benzene, i.e. without adjusting of the binary parameter ξ, is positive over the entire composition range. The binary parameter $\xi = 1.028$ was

adjusted to the experimental excess volume at a liquid mole fraction of ethanol $x_{\text{ethanol}} = 0.2$ mol/mol. In the ethanol-rich region the excess volume simulation results show some deviations from the experimental data. It can be seen that the excess volume of the mixture ethanol + toluene was well predicted by simulation. For $\xi = 1$, the results are close to the experimental data from the literature. For this system, the adjusted binary interaction parameter ($\xi = 1.003$) does not differ significantly from the value $\xi = 1$ that would be used in the strictly predictive approach. As shown in Figure 3, for both mixtures the simulated v^E is S-shaped and its sign changes from positive to negative with increasing mole fraction of ethanol. This composition dependence of the excess volume in selected mixtures can be qualitatively explained by considering the nature of the constituent molecules in their pure state and in the mixture. The ethanol molecule has a polar hydroxyl group end and a non-polar ethyl group end. Benzene is the simplest aromatic hydrocarbon with six carbon atoms bonded in a hexagonal structure. The positive v^E in the ethanol-rich concentration range is thus due to the breaking of hydrogen bonds formed between ethanol molecules. The negative v^E is due to the molecular size difference between ethanol and benzene/toluene.

5   Conclusion

Excess thermodynamic properties correspond to the difference between real and ideal mixing properties. The performance of molecular modeling and simulation for the prediction of a S-shaped composition dependence of excess thermodynamic properties was assessed focusing on binary mixtures containing water, methanol or ethanol. Excess volume and excess enthalpy as functions of mole fraction were obtained by Monte Carlo simulation for seven liquid binary mixtures. It turned out that the excess properties are highly sensitive on the unlike intermolecular interaction between the components in the mixture. It was found that the predictions obtained by molecular simulation without adjusting the binary interaction parameter ξ typically yield a qualitatively different form than the experimental data. Only for the mixture ethanol + toluene, predictive simulation results obtained with $\xi = 1$ show the correct composition dependence of excess volume and are very close to experimental data from the literature. The consideration of

interactions between unlike molecules is therefore very important for obtaining excess properties. In this work a single experimental data point, i.e. the extreme value of excess volume or excess enthalpy, was taken to adjust the binary parameter. The comparison between the simulation results and available experimental data is excellent after adjustment. This work shows that molecular modeling and simulation can successfully be used to predict thermodynamic excess properties even for highly non-ideal mixtures on the basis of a very narrow experimental data set.

Acknowledgements

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Table 1
Binary interaction parameter of the molecular models adjusted in the present work.

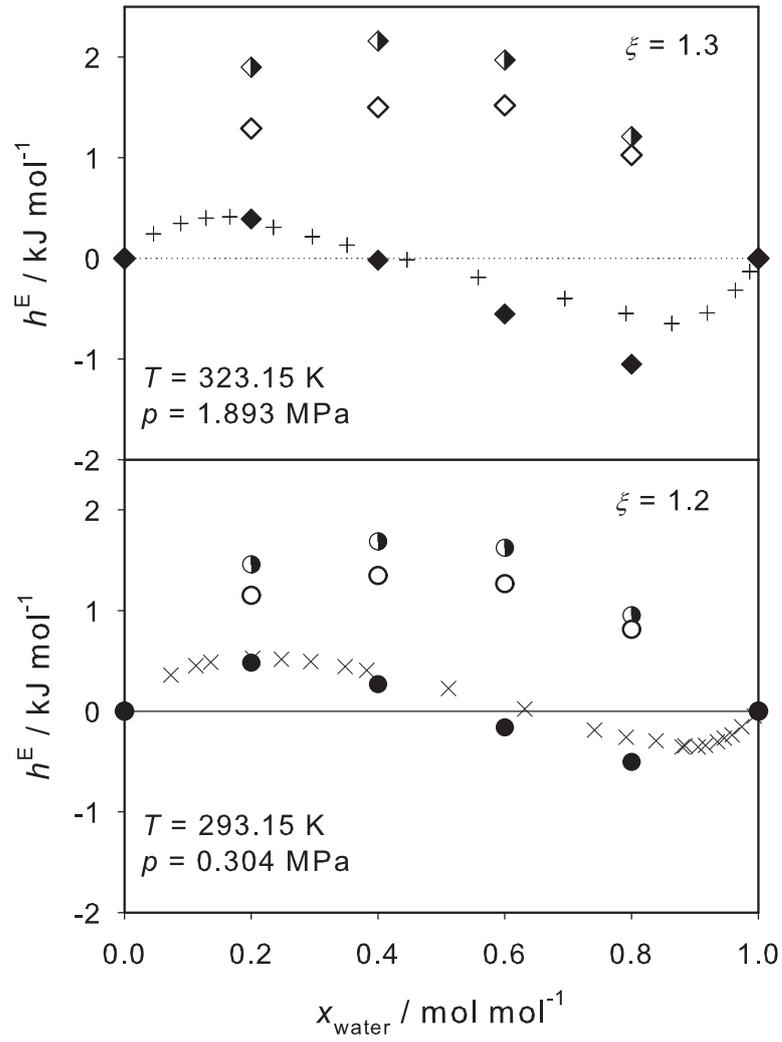| Mixture	ξ
water + dimethyl ether	1.3
water + ethylene oxide	1.2
methanol + tribromomethane	1.083
methanol + 2-bromo-2-chloro-1,1,1-trifluoroethane	1.110
methanol + chloroform	1.096
ethanol + benzene	1.028
ethanol + toluene	1.003

List of Figures

Fig. 1. Excess enthalpy of water + dimethyl ether (top) and water + ethylene oxide (bottom): present simulation results with adjusted binary parameter ξ (solid symbols) are compared to predictive simulation results with $\xi = 1$ (open symbols correspond to the Huang et al. water model [34] and semi-filled symbols correspond to the TIP4P/2005 water model [33]) and to experimental data by Park et al. [5] (+) and by Glew and Watts [6] (×). The statistical uncertainties of the present simulation data are within symbol size.
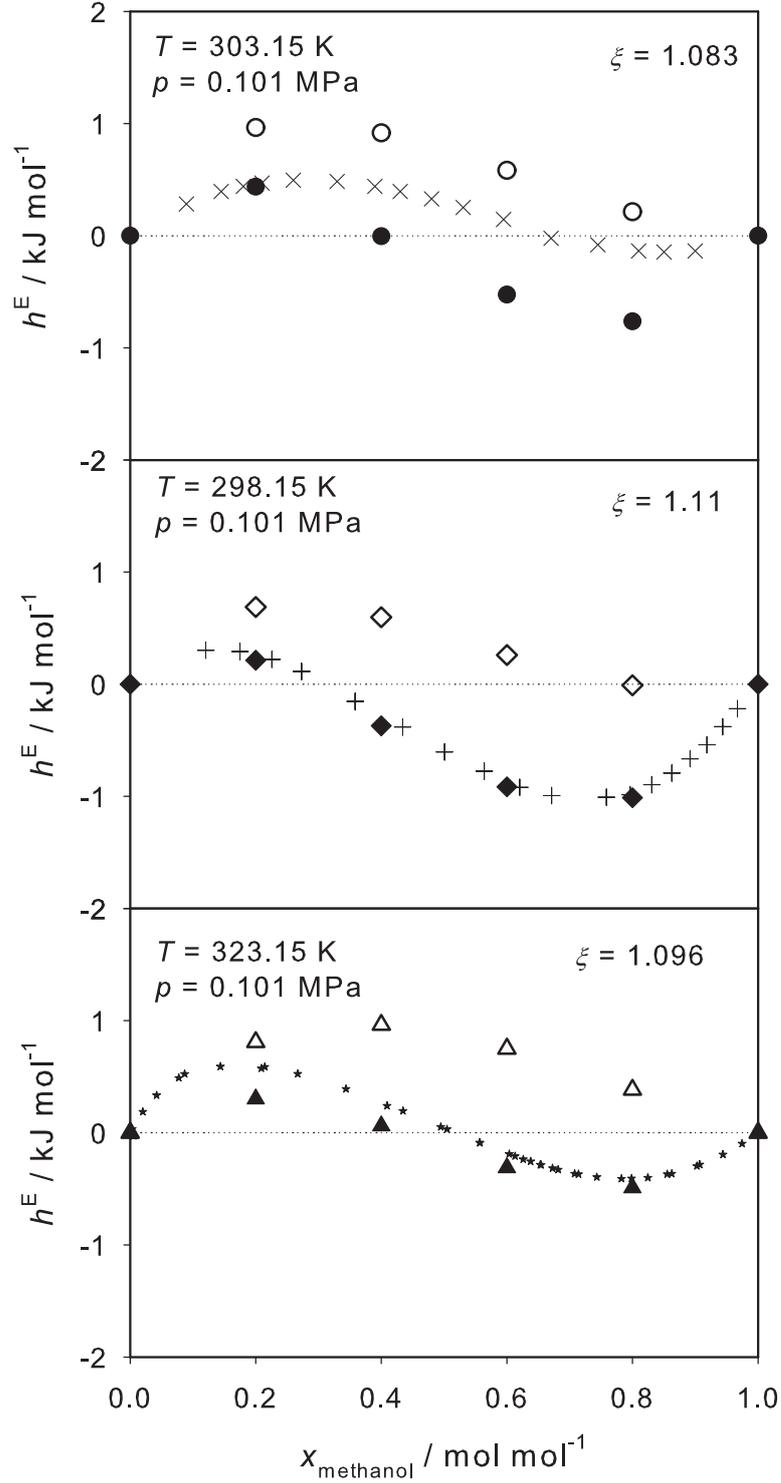
Fig. 2. Excess enthalpy of methanol + tribromomethane (top), methanol + 2-bromo-2-chloro-1,1,1-trifluoroethane (center) and methanol + chloroform (bottom): present simulation results with adjusted binary parameter ξ (solid symbols) are compared to predictive simulation results with $\xi = 1$ (open symbols) and to experimental data by Singh et al. [7] ($\times$), by Costas et al. [8] ($+$) and by Morris et al. [9] ($\star$). The statistical uncertainties of the present simulation data are within symbol size.
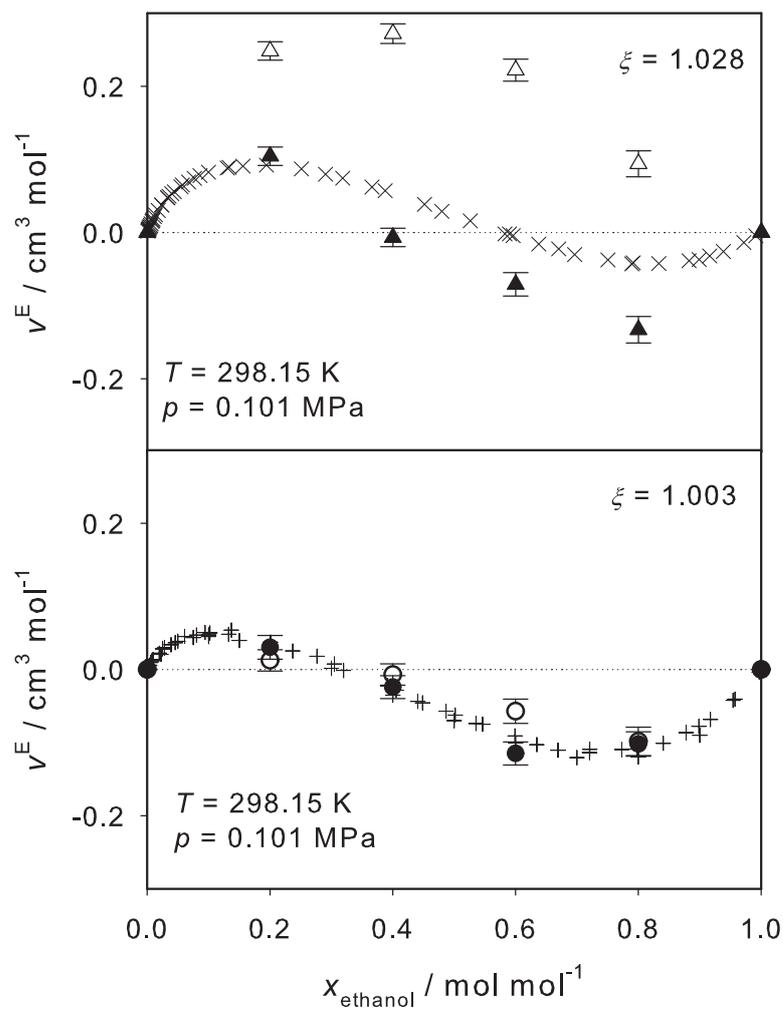
Fig. 3. Excess volume of ethanol + benzene (top) and ethanol + toluene (bottom): present simulation results with adjusted binary parameter ξ (solid symbols) are compared to the simulation results with $\xi = 1$ (open symbols) and to experimental data by Marsh and Burfitt [10], Tanaka and Toyama [11] ($\times$) and by Tanaka and Toyama [11], Kretschmer and Wiebe [12], Pardo and van Ness [13], Letcher et al. [14] (+).