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Water–methanol mixtures with non-Lorentz–Berthelot combining rules: A feasibility study

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ABSTRACT

To examine a possibility to predict qualitatively correctly the properties of water–alcohol mixtures using pure fluid non-polarizable interaction potential models, a family of non-Lorentz–Berthelot combing rules was used in simulations on the water–methanol mixtures defined by the standard TIP4P (water) and OPLS (methanol) interaction models. A certain strategy to locate the region of the cross parameters yielding, potentially, a minimum in the partial molar volume of methanol has been adopted to reduce complexity of the problem and CPU time. It is found that a small deviation from the Lorentz rule along with a larger change in the Berthelot cross energy gives rise to a concavity of the excess volume at low methanol concentrations and hence to a minimum in the partial molar volume which is otherwise missing if the Lorentz–Berthelot rules are used. Nonetheless, it does not seem that non-Lorentz–Berthelot rules alone will be able to bring the results to a full quantitative agreement with experiment.

1. Introduction

Aqueous solutions of alcohols are of great interest from both technological and scientific points of view. They are among the simplest aqueous solutions with the solute having both a hydrophilic head and a hydrophobic tail and it is thus believed that the full understanding of their behavior may provide insight into the behavior of certain biological systems and may thus serve as a springboard for studying and modeling aqueous solutions of complex amphiphiles that are difficult to simulate. They also exhibit a number of rather unusual features, the most interesting of which is likely a minimum in the partial molar volume of alcohol at its low concentrations [1]. The wide-spread and commonly accepted explanation of this effect in terms of an enhanced structuring of water does not seem to be supported by modern diffraction experiments. Furthermore, neutron scattering experiments supported by molecular simulations based on an empirical potential obtained directly from the diffraction data show highly heterogeneous mixing across the entire concentration range despite apparent miscibility of both components [2,3].

It is therefore not surprising that a large number of simulation results for the water–alcohol mixtures have been reported with overwhelming majority of cases focussing primarily on structure and with much less attention paid to their thermodynamic properties. Nonetheless, despite large differences in the reported simulation results for excess functions (see, e.g., [4] and references therein), we are not aware of any simulation result which reproduces the course of the partial molar volume with a minimum. Although there may be several reasons for this failure, the primary cause seems the form of the used Hamiltonian, i.e., the intermolecular potential model describing the mixture.

A common molecular approach to estimate/predict the thermodynamic properties of fluids is to stick to pairwise additivity of intermolecular interactions and use effective pair potentials. When dealing with mixtures, then such pure fluid intermolecular potential models of the constituent compounds are directly used to describe the interaction between the like species also in the mixture and their certain combination for the interaction between the unlike species (cross interaction). It is more than evident that this is rather a crude approximation not only for the cross interaction but also for the interaction between the like species themselves. Whereas there is no problem with the cross electrostatic interactions, this route has only a very weak theoretical justification as regards the non-electrostatic interactions (typically Lennard-Jones; LJ). A large number of combining rules have been proposed, all of them being empirical without any a priori guarantee of success. The most common of them are the geometric mean rule (the Berthelot rule) for the energy parameter (the depth of the potential well), and the arithmetic rule (the Lorentz rule) for the length-scaling (excluded volume) parameter. The results obtained using such rules are, in principle, unpredictable unless an *ad hoc* adjustment of the cross interaction to some experimental data on the mixture is made. Moreover, even the validity of the pure fluid interaction models between like species in mixtures must be questioned because they do not account for the effect of the presence of the other species.

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A natural way to perform better for mixtures would be to develop potential models directly for mixtures (we remind in passing that a certain partial attempt along this line was made by fitting the Kirkwood–Buff integrals; although the computed excess volume was in a close agreement with experiment, the partial molar volume failed to exhibit the minimum [5]). However, a re-parametrization of the pure fluid potentials with respect to more realistic cross interactions and experimental data seems quite an unrealistic goal. To resolve the problem in a more realistic (feasible) way may be thus formulated as follows: How to account for the mutual effect of species in mixtures while keeping their pure fluid interaction models intact? There are (at least) two simple routes addressing this problem: (i) to include polarizability of molecules (modification of the electrostatic part of the interaction) and (ii) to modify the combining rules (modification of the non-electrostatic part of the interaction). A third possibility is then a combination of these two. We have recently followed the former route and showed that the inclusion of polarizability does bring about qualitative changes in the behavior of the mixture; specifically, using the polarizable BSV model of water, the minimum in the partial molar volume of methanol has been reproduced [6]. As regards the other route, we have recently conducted a feasibility study [7,8] to examine the effect of the cross interactions on the qualitative behavior of mixtures. Considering a model binary mixture of the LJ fluids we have found out, in full agreement with a similar finding by Boda and Henderson [9], that deviations from the Lorentz–Berthelot (LB) combining rules may bring about even qualitative changes in the behavior of the mixture.

Following the results obtained for this simple model mixture we consider in this paper a realistic water–methanol mixture defined by the common pure fluid potential models and examine the effect of a deviation from the LB rules on its thermodynamic properties. With respect to numerical complexity of the problem (too many degrees of freedom), our primary goal is not to find an empirical interaction model which would provide a quantitative agreement with experiment but rather to answer the question if it is possible at all, by deviating from the LB rule, to reach at least a qualitative (and only semi-quantitative) agreement with experiment by changes in the non-electrostatic cross interactions. After providing all necessary definitions and simulation details in the next section we lay out the adopted strategy to reach the goal in Section 3 and present and discuss there also the obtained results.

2. Basic definitions and computational details

To keep contact with previous studies, we consider the same intermolecular potential models as in our previous paper [4], i.e., the TIP4P model [10] for water and the united atom OPLS model [11] for methanol. Both models have the form of a site–site potential with a rigid monomer,

$$u(1,2)\equiv u(R_{12},\Omega_1,\Omega_2)=\sum_{i\in\{1\}}\sum_{j\in\{2\}}\left\{4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]+\frac{q_iq_j}{r_{ij}}\right\}, \tag{1}$$

where the set $(R_{12}, \mathbf{\Omega}_i)$ defines, respectively, the mutual position (separation R_{12} between the reference sites) and orientation of a pair of molecules, r_{ij} denotes the separation between site i on molecule 1 and site j on molecule 2, $r_{ij}=|\mathbf{r}_1^{(i)}-\mathbf{r}_2^{(j)}|$, q_i are partial charges, and σ_{ij} and ϵ_{ij} are the Lennard-Jones (LJ) size and energy parameters, respectively. For the geometry of the models and their parameters we refer the reader to the original papers.

For all cross LJ interactions we used the LB-like combining rules,

$$\sigma_{12}=\frac{1}{2}(1+\delta_\sigma)(\sigma_{11}+\sigma_{22})\equiv(1+\delta_\sigma)\sigma, \tag{2}$$

and

$$\varepsilon_{12}=(1+\delta_\varepsilon)(\varepsilon_{11}\varepsilon_{22})^{\frac{1}{2}}\equiv(1+\delta_\varepsilon)\varepsilon. \tag{3}$$

with, in general, $\delta_\sigma\neq 0$ and $\delta_\epsilon\neq 0$. If both δ_σ and $\delta_{\epsilon\varepsilon}$ are set to zero, the common LB rules are recovered.

It is a common practice to characterize liquid mixtures by means of excess mixing functions,

$$\Delta Y=Y_{\mathrm{mix}}-\sum n_i y_i^{(0)}, \tag{4}$$

where Y_{mix} is the total measured property of the mixture, $y_i^{(0)}$ are the molar properties of pure compounds (at the same T and P), and n_i is the number of moles of component i. However, in the case of mixtures exhibiting very pronounced variations in the low concentration range (which is also the case of aqueous mixtures of alcohols) partial molar quantities,

$$y_i=\left(\frac{\partial Y_{\mathrm{mix}}}{\partial n_i}\right)_{T,P,n_j\neq n_i}, \tag{5}$$

are the preferred functions. Considering binary mixtures, the partial molar function of component 1 is related to the excess function via the relation

$$y_1=y_1^{(0)}+\left(\frac{\partial\Delta Y}{\partial n_1}\right)_{T,P,n_2}=y_1^{(0)}+\Delta y-x_2\left(\frac{\partial\Delta y}{\partial x_2}\right)_{T,P}, \tag{6}$$

and similarly for the other component. Here x_i denotes the mole fraction of component i, and $\Delta y=\Delta Y/(n_1+n_2)$.

The excess molar volume can be evaluated directly from the set of values obtained during the molecular simulations. However, the calculation of the partial molar volume is somewhat complicated because the differentiation process amplifies the unavoidable noise in the data. Instead of the commonly used way of differentiating the excess volume via the Redlich–Kister parametrization [12], i.e., fitting of the Δv curve by a polynomial, we use a more general method developed by Lubansky et al. [13] which is based on the Tikhonov regularization; this method does not require any a priori assumption on the functional dependence of the data and the noise can be kept under control [14,15].

We used standard NPT Monte Carlo simulations with $N=500$ particles using a cubic box with periodic boundary conditions and the minimum image convention [16]. Molecular reference points were chosen as weighted averages of positions of all the molecular interaction sites with absolute values of their partial charges used as the weights. Both LJ and electrostatic intermolecular interactions were cut beyond $R_c=9$A. In the case of LJ interactions the cutoff was applied directly to the Lennard-Jones sites, in the case of Coulombic interactions it was applied to the molecular reference points in order to keep the molecules electroneutral. Long range corrections were applied in the usual way to the Lennard-Jones interactions and the reaction field method with the metal-like boundary condition ($\varepsilon_r=\infty$) was used for the Coulombic interactions. Simulations started from a configuration with randomly oriented particles placed on a low density FCC grid and the species were distributed evenly throughout the FCC grid.

Simulations were organized in cycles with each cycle consisting of n_D translational and rotational moves and $n_V=30$ volume changes. The types of moves were selected at random with a fixed probability so that the ratio n_D:n_V equal to N:1 was maintained. Acceptance ratios were set to 30% for all the moves. Initial period of equilibration of length 1×10^4 cycles was followed by production runs of length about 5×10^6 cycles to compute the internal energy, U, and volume, V.