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Fluid Phase Equilibria 240 (2006) 161–166

FLUID PHASE EQUILIBRIA

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Excess properties of aqueous mixtures of methanol: Simulation versus experiment

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Received 9 October 2005; received in revised form 6 December 2005; accepted 6 December 2005

Abstract

We report molecular simulation results for both the excess mixing and partial molar properties of water–methanol mixtures over the entire concentration range with the particular emphasis on the low concentration ends. It is shown that the mixing properties are very sensitive to potential models and that the used realistic potentials (TIP4P for water and OPLS for methanol) give a reasonably good agreement with experiment only for volumetric properties although the qualitative trend of the partial molar volume at low concentrations is not reproduced. As regards excess enthalpy, the results are rather bad and only its sign is predicted correctly.

Keywords: Aqueous mixtures; Water–methanol mixtures; Solutions of alcohol; Excess mixing properties; Partial molar properties

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1. Introduction

Aqueous solutions of alcohols have attracted a good deal of attention of both scientific and engineering community for decades for a number of reasons. From the technological point of view, such mixtures have served as useful industrial solvent media for a variety of separation processes; moreover, recently it has become popular to use them also in solar thermal systems [1]. Physical chemists have been attracted by their eccentric, unusual non-ideal behavior, especially in the low concentration range [2]. Aqueous solutions of alcohols are also ones of the simplest aqueous solutions with the solute having both a hydrophilic head and hydrophobic tail. They therefore attract nowadays also attention of biochemists because it is 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.

It is well known that the thermodynamic properties of water–alcohol mixtures are significantly smaller than the values that might be expected from an ideal mixture of the pure fluids. Structural properties underlying this behavior were reviewed by Frank and Ives in 1966 [3] and again in 1985 [4]. However, the wide-spread and commonly accepted explanation of these effects in terms of an enhanced structuring of water does not seem to be supported by modern diffraction experiments [5,6]. 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 [6].

In the light of the yet unsettled controversy as for the origin of the observed anomalies it is understandable that overwhelming majority of molecular simulation studies have focussed on the structure with very little attention paid to the thermodynamic properties [7–11]. However, it has been well established that not all interactions acting between the molecules contribute equally to establishing the structure [12]. Thus, although the observed macroscopic properties are superimposed on the underlying structure, they may result from a more complex interplay between various intermolecular interactions. Detailed simulation studies of the thermodynamic behavior revealing such relations seem therefore equally important.

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doi:10.1016/j.fluid.2005.12.007

Since the realistic potential models are too complex, they make it hardly possible to clearly link various observed phenomena to specific interactions. Such a link may however be established from a decomposition of the realistic potential into well-defined (and justified) individual contributions. One appealing possibility is the decomposition based on primitive models, i.e., the models that (i) descend directly from the considered realistic parent models, and that (ii) reproduce the structure of the parent fluids even semi-quantitatively [13,14]. The results obtained for the PM's may be compared directly with experimental data and from the obtained agreement/disagreement one may judge on the effect of different interactions. However, such a direct comparison may be misleading because there is no a priori guarantee that the parent realistic models themselves reproduce these data. Before drawing any conclusion on the molecular mechanism governing the observed behavior it must be therefore first known what type of behavior the parent models actually predict.

There is also another aspect of molecular studies of mixtures. Molecular simulations that have become a routine tool to study in detail properties of macroscopic systems from the molecular point of view rely on input Hamiltonians and agreement/disagreement of the simulation output with experimental data reflects the degree of their appropriateness. Extensive simulation studies have established that effective pair potentials can be devised that provide good prediction for both thermodynamic and structural properties for compounds made up of relatively small molecules. Typical models used in applications are pairwise additive which represents a certain compromise between accuracy and complexity. This may seem rather a crude approximation for strong polar and associating fluids but attempts to improve their performance by incorporating at least some flavor of non-additive effects (e.g., polarizibility) has turned out fruitless [15]. Quite different situation may however exist when dealing with mixtures, particularly if we account for the fact that their interaction models rely on various only purely empirical combining rules. It is therefore not surprising that there is yet unsettled controversy in scientific community whether the available realistic potential models are able at all to reproduce the observed behavior of water–alcohol mixtures which is associated with formation of specific clusters (as results from scattering experiments [6]).

Since we are not aware of any systematic simulation study of the thermodynamic properties of water–alcohol mixtures (and those that are available (i) focus only on excess volume and enthalpy and not on more important partial molar quantities, and, moreover, (ii) do not seem to yield results in mutual agreement [16–18]), the primary goal of the present paper is to examine to what extent common effective pair potential models of associating fluids, that have been obtained by fitting the properties of the pure components, are able to account also for the observed behavior of aqueous mixtures. Specifically, we consider water–methanol mixtures and perform extensive simulations over the entire composition range. It turns out that the used realistic models (TIP4P for water [19] and OPLS for methanol [20]) are able to reproduce reasonably well only the excess volume, to some extent qualitatively also the excess enthalpy, but seem to fail to reproduce, neither qualitatively, the composition dependence of the partial molar volume of methanol at its low concentrations.

2. Basic definitions and computational details

The considered realistic potentials of water and methanol have the form of common site-site potentials with a rigid monomer:

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

where the set (R_{12}, Ω_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 ϵ_{ij} and σ_{ij} are the Lennard–Jones (LJ) size and energy parameters, respectively. Specifically, for water we use the TIP4P model [19] which seems the most universal model predicting various properties of water fairly well [21,15], and for methanol the united atom OPLS model [20]; these two models have also been used in most previous studies of this mixture. Geometry of the models are defined in Table 1 where the potential parameters are given as well. For all models the geometric mean (i.e., Lorentz combining rule) is used not only for the energy to define the cross interactions between the LJ sites of all compounds but also for σ's:

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}, \qquad \sigma_{ij} = (\sigma_{ii}\sigma_{jj})^{1/2}. \quad (2)$$

Table 1
The Lennard–Jones parameters ϵ_i and σ_i, partial charges q_i, and geometries of the used potential models

Atom	ϵ/k_B (K)	σ (Å)	q (e)	Geometry
TIP4P water [19]				
O	78.08	3.1535	0.0	O–H: 0.9572 Å
H	0.0	0.0	+0.52	H–O–H: 104.5°
M-site	0.0	0.0	−1.04	O–M: 0.15 Å, along the H–O–H bisector
OPLS methanol [20]				
O	85.546821	3.070	−0.700	O–H: 0.945 Å
H	0.0	0.0	0.435	CH_3–O: 1.430 Å
CH_3	104.16583	3.775	0.265	CH_3–O–H: 108.5°