PARTIAL MOLAR VOLUME OF METHANOL IN WATER: EFFECT OF POLARIZABILITY

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The available pairwise additive intermolecular interaction models used so far in simulations in combination with common combining rules do not seem to be able to reproduce the most distinct feature of aqueous solutions of alcohols, the minimum of the partial molar volume at low alcohol concentrations. Nonetheless, this fundamental failure seems to have been paid little attention to, partly because of very high requirements for accuracy and, hence, CPU time of simulations. As an attempt to go beyond empirical combining rules and account in a more physical and yet simple way for the cross interactions, a feasibility study has been undertaken using a polarizable model of water in molecular simulations of the water–methanol mixture at ambient conditions. It turns out that the inclusion of polarizability may qualitatively change the behavior of the mixture bringing the result in agreement with experiment.

Keywords: Water–methanol mixtures; Partial molar volume; Polarizability.

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. This approach has been found very successful for pure fluids but not so for mixtures. When dealing with mixtures, a common way is to choose some pure fluid intermolecular potential models of the constituent compounds and then to apply certain combining rules to estimate the interaction between the unlike species. This route has only a very weak theoretical justification with usually unpredictable results unless an ad hoc adjustment of the cross interaction to some experimental data on the mixture is made. Furthermore, even the validity of the pure fluid interaction models between like species in mixtures must be ques-

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tioned because it does not account for the effect of the presence of the other species.

An example of the systems for which the concept of pairwise additive interactions fails are aqueous solutions of alcohols. Not only that the available simulation results found in literature for excess properties exhibit very large scatter (see, e.g., ref.[1]), but we are not aware of any simulation result reported in the literature predicting the minimum in the partial molar volume of lower alcohols. It is also worth mentioning that although there has been a very large number of simulation studies of solutions of alcohols, an overwhelming majority of them have focused on the structure and further molecular details (see, e.g., ref.[2] and references therein) while only little attention has been paid to their thermodynamic properties beyond the excess ones.

To go beyond the pairwise additivity and empirical combining rules, the simplest and yet physically justified possibility to account for the effect of the cross interactions is to include polarizability of molecules. Simulations on the water–methanol mixture using polarizable models have been recently performed by Zhong et al.[3] but, again, in addition to a detailed analysis of the structure reporting only excess properties at not too many concentrations. Consequently, no conclusions can be drawn on the partial molar quantities. Thus, as an attempt to examine the effect of polarizability, particularly if it is able to change qualitatively the results for the mixture, we have considered a polarizable model of water and investigated the thermodynamic properties of the water–methanol mixture over the entire concentration range using a fine grid in the low methanol concentration range. From the available polarizable models of water we have chosen the BSV model[4], i.e., a modified TIP4P model[5] with added isotropic polarizability for its both accuracy and simplicity; for methanol we have used the KBFF model[6]. The main reason for this choice has been purely technical: no model of methanol compatible with the BSV model, i.e., a rigid molecule with a point polarizable dipole, is available. It is believed that for the purpose of the conducted feasibility study this combination should be sufficient and able to provide a first rough estimate of the effect of polarizability before one embarks on a very much time consuming full-scale project.

We carried out Monte Carlo (MC) simulations in an NPT ensemble at ambient conditions on a system made up of N_1 water and N_2 methanol molecules. The total number of particles $N = N_1 + N_2$ was 256 for all the simulations allowing one to set the potential cutoff to a reasonable distance of 9 Å. Because of the necessity to reach the electrostatic consistency after every single MC move, such simulations are extremely time consuming if

the common one-particle move MC method is used[7]. We have therefore used the recently developed multi-particle move MC method[8] which is at least by one order of magnitude more efficient than the one-particle move schemes. The geometric mean (i.e., the Berthelot combining rule) has been used for both the ε's and σ's to define the cross interactions between the LJ sites of the compounds. For further simulation details, including the long-range corrections, we refer the reader to the original paper[9] on the implementation of the method.

The partial molar volume is a quantity commonly used for characterization of the behavior of mixtures exhibiting very pronounced variations in the low concentration range. It is defined by the equation

$$v_i = \left(\frac{\partial V_{\mathrm{mix}}}{\partial n_i} \right)_{T,P,n_{j \neq i}} \tag{1}$$

where V_{mix} is the total measured volume of the mixture and n_i is the number of moles of compound *i*. Considering binary mixtures, the partial molar volume of component 1 is usually calculated from excess molar volume Δv via the relation

$$v_i = v_1^0 + \Delta v - x_2 \left(\frac{\partial \Delta v}{\partial x_2} \right)_{T,P} \tag{2}$$

where v_i^0 are the molar properties of pure compounds at the temperature and pressure of the mixture, $\Delta v = (V_{\mathrm{mix}} - \sum n_i v_i^0)/(n_1 + n_2)$, and x_i denotes the mole fraction of component *i*. 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. The commonly adopted way of differentiating the excess volume is via the Redlich–Kister parametrization[10], i.e., fitting of the Δv curve by a polynomial

$$\Delta v = x_1 x_2 \sum_{i=0}^{k} A_i (x_2 - x_1)^i \tag{3}$$

where parameters A_i are obtained by the least-square minimization and *k* should be determined by applying the *F*-test method. However, one cannot be certain that the derivative calculated from this fitted curve does provide an accurate description of the derivative of the measured data. An alternative, and perhaps a better way that we followed is to use a more

general method developed by Lubansky et al.[11] 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.

The results are shown in Fig. 1 where, for comparison, we show also experimental data and the results reported recently for non-polarizable models[1] (data themselves can be obtained from the authors upon request). As one can immediately see, the excess volume exhibits a concavity at low concentrations of methanol which must give rise to a minimum of its de-

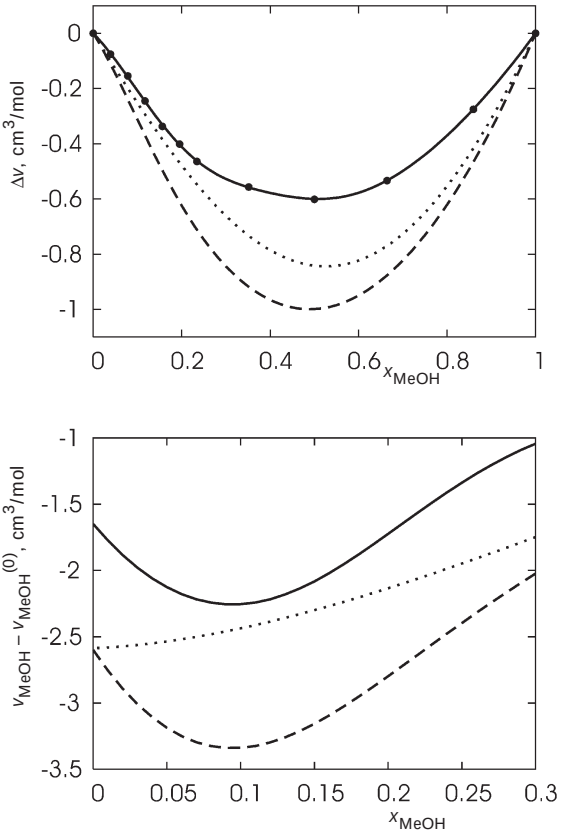

FIG. 1

The excess volume of the water–methanol mixture (upper graph) and the corresponding partial molar volume of methanol at low concentrations (lower graph). The solid lines and ● are the smoothed and raw simulation results, respectively, the dashed lines are smoothed experimental data[12], and the dotted lines are the results taken from ref.[1]

rivative regardless of the numerical method used. This behavior is in full (qualitative) agreement with experiment.

The quantitative disagreement is rather typical and therefore not surprising because the used potential models were fitted to pure fluid data and no information on the properties of the mixture has been used for the cross interaction. (We mention in passing that a similar disagreement has also been reported by Zhong et al.[3] who used the charge equilibration model.) Nonetheless, it has been found that accounting for the cross interactions by including polarizability the behavior of the mixture may be changed qualitatively bringing it to at least qualitative agreement with experiment and future development should proceed along this line. The obtained results thus justify further and more detailed and systematic research including also the effect of the combining rules for the non-electrostatic interactions.

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REFERENCES

1. Gonzales-Salgado D., Nezbeda I.: *Fluid Phase Equilib.* **2006**, *240*, 161.
2. Yu H., Geerke D. P., Liu H., van Gunsteren W.: *J. Comput. Chem.* **2006**, *27*, 1494.
3. Zhong Y., Warren G. L., Patel S.: *J. Comput. Chem.* **2008**, *29*, 1142.
4. Brodholt J., Sampoli M., Vallauri R.: *Mol. Phys.* **1995**, *86*, 149.
5. Jorgensen W. L., Chandrasekhar J., Madura J. D., Impey R. W., Klein M. L.: *J. Chem. Phys.* **1983**, *79*, 926.
6. Weerasinghe S., Smith P. E.: *J. Phys. Chem. B* **2005**, *109*, 15080.
7. Allen M. P., Tildesley D. J.: *Computer Simulation of Liquids*. Clarendon Press, Oxford 1987.
8. Moučka F., Rouha M., Nezbeda I.: *J. Chem. Phys.* **2007**, *126*, 224106.
9. Moučka F., Nezbeda I.: *Mol. Simul.*, in press.
10. Redlich O., Kister A.: *Ind. Eng. Chem.* **1948**, *40*, 345.
11. Lubansky A. S., Yeow Y. L., Leong Y. K., Wickramasinghe S. R., Han B. B.: *AIChE J.* **2006**, *52*, 323.
12. McGlashan M. L., Williamson A. G.: *J. Chem. Eng. Data* **1976**, *21*, 196.