Scientific Paper

Modeling Simple Alcohols in Two Dimensions†

Barbara Hribar-Lee[1]*, and Ken A. Dill[2]

[1]*Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, 1000 Ljubljana, Slovenia.*
E-mail: barbara. hribar@fkkt.uni-lj.si

[2]*Department of Pharmaceutical Chemistry, University of California, San Francisco, California 94143-2240.*

Received 08-05-2006

† Dedicated to the memory of Prof. Dr. Davorin Dolar

Abstract

The alcohol-water mixtures were studied within a two-dimensional model. The MB model was used for modeling water and alcohol molecules were modeled as non-flexible chains consisting of two-dimensional Lennard-Jones disks with the first disk having two hydrogen-bonding arms. The model was explored using NPT Monte Carlo computer simulation. The results were compared with the experimental thermodynamic properties of methanol/water mixtures. The qualitative agreement was obtained for the excess volume of mixing, but due to the surface/volume effects not properly captured by two dimensional models, the excess enthalpy of mixing cannot be represented correctly by this model. Further, we studied the transfer of a single alcohol molecule into water, focusing on the trends exhibited by the methanol, ethanol, propanol, n-butanol series. While small alcohol molecules show the correct trend the flexibility of the alcohol molecules should be taken into account to improve the agreement for higher alcohols.

Key words: MB model, alcohol/water mixtures, thermodynamics, Monte Carlo

1. Introduction

The alcohols constitute the most thoroughly studied groups of the so-called mixed solute class. Such solutes contain groups that can hydrogen-bond with the water and so hold the solvent in the solution. At the same time they also contain a non-polar group which, by virtue of their large negative entropy of hydration, forces the solute out of the solution. The thermodynamic properties which characterize water-alcohol mixtures therefore exhibit a very specific behavior.[1] At low temperatures (< 283 K) and concentrations negative deviations from Raoult's law are observed, but at higher temperatures the mixtures show positive deviations.[1] The excess heats of mixing, ΔH^E, show a complex dependence on concentration.[2] Δc_P^E is large and positive[3], indicating the solute induced changes in the intermolecular structure of water. The excess volumes of mixing, ΔV^E, are negative, and the $\Delta V^E(x_2)$ curve has as inflection corresponding to a minimum in $\Delta \overline{V}_2^E(x_2)$.[4] These characteristics indicate that there are three concentration regions of interest in dilute alcohol solutions. The prevailing interpretation of the thermodynamic data is the following.[1] The minimum which is observed in the $\Delta \overline{V}_2^E(x_2)$ curves could be considered as being the point at which solute-induced reinforcement of solvent sheaths begins to be replaced by interference between solvent sheaths, since there is no longer sufficient solvent to support the full structuring ability of the solute molecules. The positive slopes which are observed beyond the characteristic minimum are taken to be indicative of structure breaking. At a higher concentration which corresponds to the minimum in ΔH^E, many of the physical properties give indication of a lower critical solution temperature.[1] This was further confirmed by recent neutron diffraction experiment suggesting incomplete mixing in the 7:3 molar ratio methanol-water solutions.[5]

The properties described so far, unless stated differently, were investigated at room temperature. As the temperature increases, the range of concentrations for which ΔH^E is negative, shrinks and almost disappears at 88 °C.[6] The effect could be the consequence of the temperature dependence of hydrophobicity. As stated previously, the regions of exothermic mixing is largely due to the enhancement of water-water interactions produced by the structural influence of the solute. In the number of studies dealt with the temperature dependence of the thermodynamic of solvation has been found that there exists a temperature, T_H, at which the enthalpy of solute transfer is zero. This implies that the insertion of solute and the attendant creation of a solvation shell in water lead to better hydrogen bonding. Thus, in cold water, solute insertion induces a shell of good hydrogen bonding. But solute insertion into hot water has the opposite effect: introducing a non-polar solute produces a shell of hydrogen bonds that is worse than in the corresponding bulk water solvent.[7-9]

In the last decades a number of spectroscopic procedures were developed to obtain more direct information about the interactions in the alcohol-water mixtures.[5, 10-18] Based on the IR spectroscopic measurements D'Angelo et al. discuss the possible mechanism of molecular aggregation in the various regions of alcohol concentrations.[15] At low concentrations the solutions are essentially monomeric: alcohol molecule forms hydrogen bonds with water molecules and enhances water-water interactions near the non-polar alkyl group. At intermediate concentrations one observes a progressive aggregation of alcohol molecules accompanied by the modification in hydrophobic hydration.[15] A detailed examination of methanol solutions at $x_2=0.7$ by Dixit et al. shows that at this concentration the water molecules are mostly found in the cavities formed by the »fluid« of methyl head-groups.[5] The local structure of these water clusters was surprisingly close to its counterpart in pure water and bridges neighboring methanol hydroxyl groups through hydrogen bonding. For each water molecule present in the mixture approximately 1 hydrogen bond was found to other water molecule and 1.9 to methanol molecules. The number of hydrogen bonds per methanol molecule was 1.2 to another methanol molecule and 0.8 to a water molecule, which sums up to 2 hydrogen bonds per methanol molecule found in a pure methanol[5]. Finally, at very large alcohol concentrations water presumably loses its hydrogen bond network completely and it mixes into the solution as a single molecule.[10]

To interpret the spectroscopic data, computer experiments on the liquids can be most valuable. Therefore, it is of no surprise that the number of computer simulations have been performed on the water-alcohol systems[5, 19-31], as also more analytical theories have been applied to them[27, 32-34]. Very different models for water and alcohol molecules have been used to describe the interactions between the water and alcohol molecules. The simplest one were two-dimensional models[23, 25], but the majority of the calculations were performed with more realistic three-dimensional potentials that proved useful in describing the properties of pure liquids. The Monte Carlo and Molecular Dynamics computer simulations were used to calculate mostly structural, but also some thermodynamic (excess enthalpy[19, 23, 26-27, 32], excess volume[23,24, 26-27], excess free energy [26, 32], and excess entropy[26, 32] for mixtures) and dynamic[22, 24, 29, 31] properties of the models. In most cases at least qualitative agreement with the observed experimental thermodynamic properties was obtained. The calculated structural properties generally agree with the conclusions drawn from the spectroscopic data that there is a certain stabilization of hydrated alcohol molecules. However, conclusions on its origin are quite in conflict.[21] Some authors find the hydrophilic part of the alcohol molecule to form hydrogen bonds with water and assume that the exothermic heat of solution is due to favorable solute-solvent interactions; the water structure itself is not significantly affected by the present of an alcohol molecule.[19, 29, 31] Others found the enhancement of the water-water hydrogen bonding in a clathrate hydrate-like structure of water triggered by the present of an alcohol molecule.[20-23, 30] Further, evidence was also found for the self-association (hydrophobic interaction), mostly for larger alcohols, of alcohol molecules with or without one water layer in between.[5, 21-22]

As cited, in spite of an increasing amount of experimental and theoretical work a consistent description of the water-alcohol mixtures in whole concentration range is still lacking.[5] In our work we decided to test the usefulness of a simple two dimensional model to describe the properties of these mixtures. Water molecules were modeled by the so-called MB model that was previously used to study the properties of liquid water and hydrophobic effect.[35] The model qualitatively correctly describes the anomalous properties of water, hydrophobic solubility and some properties of electrolyte solutions.[35-40] The model exhibits the T_H, which is at approximately 0.20 reduced temperature.[35-36] Also, the distributions in Voronoi volumes and surfaces around a water-sized hydrophobe for the model at temperatures below 0.20 shows the presence of clathrate-like formations [Figs. 9, 10 and Table 1 of ref. 35] that were supposed to be responsible for the $\Delta\overline{V}_2^E(x_2)$ behavior.[1]

2. The Model Description and the Simulation

The two-dimensional MB model was used to represent water molecules.[35-40] Each water molecule is represented as a two-dimensional disk that interacts with other molecules through a Lennard-Jones (LJ) interaction and through an orientational-dependent hydrogen-bonding (HB) interaction. The name »MB« arises because there are three hydrogen-bonding arms, arranged as in the Mercedes Benz logo (Figure 1). The model reproduces qualitatively many properties of pure water, hydrophobic effect, ion effects, and Hofmeister series.[40] We decided to test its ability to describe water solutions of simple mixed solutes – alcohols.

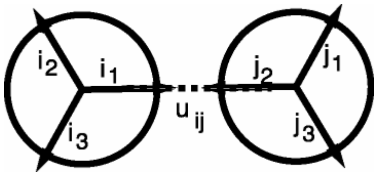

Figure 1. The MB model: the water molecules forming a hydrogen bond.

In the MB model, the energy of interaction between two waters is[35]:

$$U^{WW}(X_i, X_j) = U_{LJ}(r_{ij}) + U_{HB}(X_i, X_j) \qquad (1)$$

The notation is the same as in previous papers[35-40]: $\mathbf{X}_i$ denotes a vector representing both the coordinates and the orientation of the *i*th water molecule, and r_{ij} is the distance between the molecular centers of the molecules *i* and *j*. The LJ term is:

$$U_{LJ}(r_{ij}) = 4\varepsilon_{LJ}\left[\left(\frac{\sigma_{LJ}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{LJ}}{r_{ij}}\right)^{6}\right] \qquad (2)$$

where ε_{LJ} and σ_{LJ} are the well-depth and contact parameters, respectively. In addition, neighboring water molecules can form an explicit hydrogen bond when an arm of one molecule aligns with an arm of another water molecule, with an energy function that is a Gaussian function of separation and angle:

$$U_{HB}(X_i, X_j) = \varepsilon_{HB} G(r_{ij} - r_{HB}) \sum_{k,l=1}^{3} G(i_k \cdot u_{ij} - 1) G(j_l \cdot u_{ij} + 1) \qquad (3)$$

where G(x) is an un-normalized Gaussian function:

$$G(x) = \exp\left[-x^2/2\sigma^2\right] \qquad (4)$$

The unit vector $\mathbf{i}_k$ represents the *k*th arm on the *i*th particle (k=1, 2, 3), and $\mathbf{u}_{ij}$ is the vector joining the center of molecule *i* to the center of molecule *j* (Figure 1). H-bonding arms are not distinguished as donors and acceptors. The strength of the hydrogen bond is only determined by the degree of alignment.[35]

The model parameters are defined as previously.[35-40] The parameter ε_{HB} =-1 and r_{HB}=1 define the optimal hydrogen bond energy and bond length, respectively. The same width parameter σ=0.085 is used for both the distance and the angle deviation of a hydrogen bond. The interaction energy in the Lennard-Jones potential function, $\varepsilon_{LJ} = 0.1\varepsilon_{HB}$, and the LJ distance is 0.7 of that of r_{HB}.

The alcohol molecules were modeled as follows. Since it has been shown experimentally[5] that more than 90% of all the methanol molecules in the pure methanol is hydrogen bonded, with almost 2 hydrogen bonds per molecule indicating the dominance of chain formations[5, 41] (similar is true for higher alcohols[42-70]), we allowed the chain formation by putting two hydrogen bonding arms into an alcohol molecule (Figure 2). The angle between them was 120°, same as in the MB water molecule. The parameters for the hydrogen bond used were the same as those for the MB water. For each C atom in the alcohol molecule another Lennard-Jones disk of the same size was added into the molecule in the »missing« hydrogen bond direction such that the new disk's center was on the rim of the previous disk (Figure 2). The Lennard-Jones parameters were the same as in the case of MB water model described above.

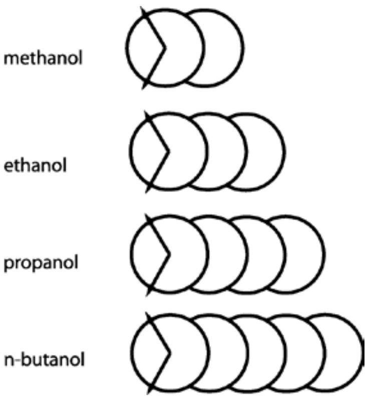

Figure 2: The model for alcohols.

Also, some results were obtained for the alkane-series. Alkanes were modeled in the same way as alcohols, except that there was no hydrogen bonding arms in the molecules and the series started with a single Lennard-Jones disk representing methane.

The Monte Carlo simulation method was performed at constant pressure ($P^* = P\, r_{HB}^2/|\varepsilon_{HB}| = 0.19$) in the NPT ensemble. Monte Carlo steps are displacements and rotations of the water and alcohol molecules. The simulations were performed using from 60 to 240 water molecules and corresponding number of alcohol molecules. The first 10^8 steps were used to equilibrate the system, and the statistics were collected over the following 5×10^8 steps. Pair distribution functions $g_{ij}(r)$ and thermodynamic properties (energy, enthalpy, volume) were calculated as ensemble averages.[35]

In addition, the free energy, enthalpy, and entropy of transferring an alcohol or an alkane molecule into water were calculated using the Widom test-particle method.[35]

3. Results and Discussion

All the Monte Carlo simulation results presented here were obtained at reduced temperature $T^* = k_BT/|\varepsilon_{HB}| = 0.20$ which roughly corresponds to the room temperature (T=298.15 K).[35] All the simulation results are given in reduced units: $T^* = k_BT/|\varepsilon_{HB}|$, $V^* = V/r_{HB}^2$,

$H^*=H/|\varepsilon_{HB}|$, and $P^*V^*=PV/|\varepsilon_{HB}|$. Some simulations were performed at a lower temperature ($T^*=0.18$) but due to little difference in structural and thermodynamic properties at different temperatures, the latter results are not presented here.

First, we studied the volumes of mixing of model methanol molecules with water. The excess volume of mixing, ΔV^E, of model methanol/water mixture is presented in Figure 3b. In all the concentration range the ΔV^E is negative. This is in agreement with the experimental results as seen in Figure 3a. The methanol molecules are small enough to distribute themselves in the cavities formed by the MB water molecules. One can see that the effects are relatively smaller for the model than they are for the real liquid. This is mostly due to the dimensionality of the model. While the molar volume of methanol is roughly twice the molar volume of water, the ratio of the »molar volume« within the model is only 1.3.

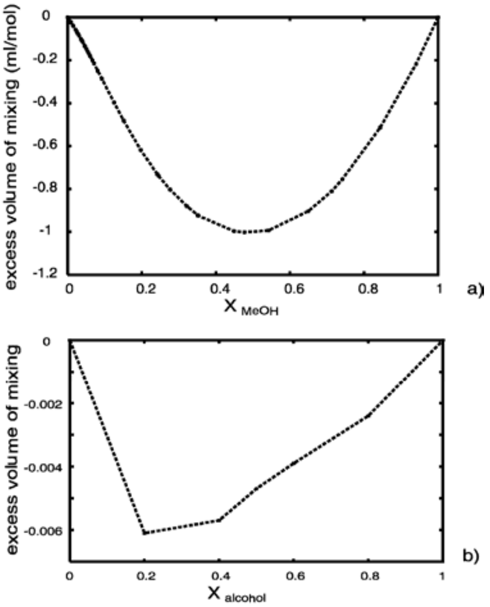

Figure 3. a) Excess volume of mixing for mixtures of water and methanol at T=298.15 K [4], and b) Excess volume of mixing in reduced units for model methanol in water.

While the volumes of mixing are an indicator of the empty space in the solution, the tendency of the formation of hydrogen bonds is reflected in the enthalpies of mixing. In the case of real liquid, an addition of methanol in the water has a structure making effect.[15] Methanol molecules induce structure ordering of water molecules and formation of more hydrogen bonds.[15] As a results, the excess enthalpies of mixing are negative (Figure 4a). This is not the case in our model. For model »methanol«/water mixtures, the enthalpies of mixing are positive in the whole concentration range (Figure 4b). A more detailed analysis of the complete set of data closer reveals that the formation of the »methanol«-water hydrogen bonds breaks the two-dimensional hydrogen bonding network of water molecules which leads to the higher enthalpy of the system. This problem arises due to the surface/volume effects that cannot be correctly captured by two dimensional models. It could be empirically fixed by setting the strength of the alcohol-alcohol hydrogen bond much larger than the strength of the water-water hydrogen bond.[45] However, our intention was to mimic the real conditions in these solutions, as close as possible.[12, 14, 17] The strength of the water-water hydrogen bond in real liquids differs from the strength of the methanol-methanol hydrogen bond only by few percents. The same is true for ethanol.[12, 14, 17]

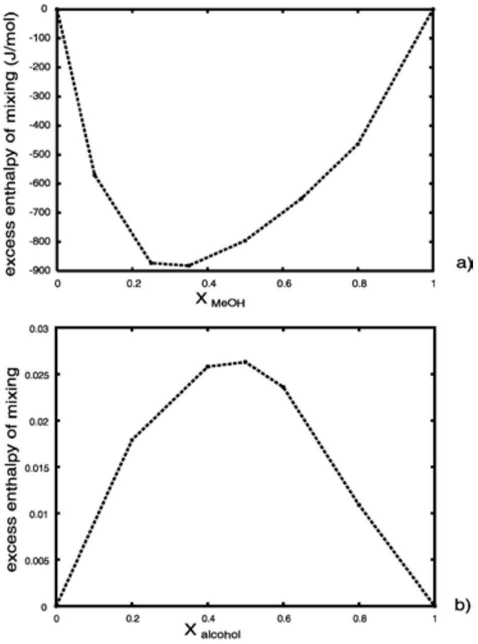

Figure 4. a) Excess enthalpy of mixing for mixtures of water and methanol at T=298.15 K [46], and b) Excess enthalpy of mixing in reduced units for model methanol in water.

To avoid the artifacts of the model due to its reduced dimensionality we further studied the alcohol/water solutions at infinite alcohol concentration. We performed two separate sets of Monte Carlo simulations, and namely, a transfer of a single alcohol molecule into MB water using the Widom method[35] and a simulation with one single alcohol molecule fixed in the middle of the simulation box.[35] Since we were mostly interested in the effect of the alcohol hydrogen bond on the solvation thermodynamics, we also performed simulations with the alkane-like molecules, for the comparison. The thermodynamic results for the model were compared with the corresponding experimental values for the transfer of gaseous molecules into water. The experimental results were adjusted for the Ben-Naim standard state.[7]

The results for the entropy of solvation are presented in Figure 5. The correct trend within the alcohol and alkane series is obtained: the longer alkane chain causes a larger decrease in entropy. The effects are larger for the corresponding alcohol molecules. The segments of the hydrophobic chain help the water molecules to order around them, forming more hydrogen bonds. In the case of alcohols, extra hydrogen bonds can be formed with alcohol hydrogen bonding arms, increasing the ordering of the solution. This can also be seen from the solute-water pair distribution functions. »Methanol«-water and »methane«-water pair distribution functions are for the illustration presented in Figure 7b. In the case of »methanol« the function is more structured. The peak at $r^*=1$ indicates a high probability of finding a water forming a hydrogen bond with the »methanol« molecule, while the hump at $r^*=0.7$ and peaks at $r^*=1.7$ and 2.7 show an increased probability of finding a water molecule in contact with an alkane chain segment. A typical distribution of water molecules around a model methanol described is shown in Figure 7c). At longer alkane chains the model curves showing the entropy of solvation slowly level out while the experimental entropy still decreases. We assume that this is a consequence of a non-flexible chains in the model. The real alkanes can fold, while in our model the chains just become longer slowly showing the properties of a planar surface.[9]

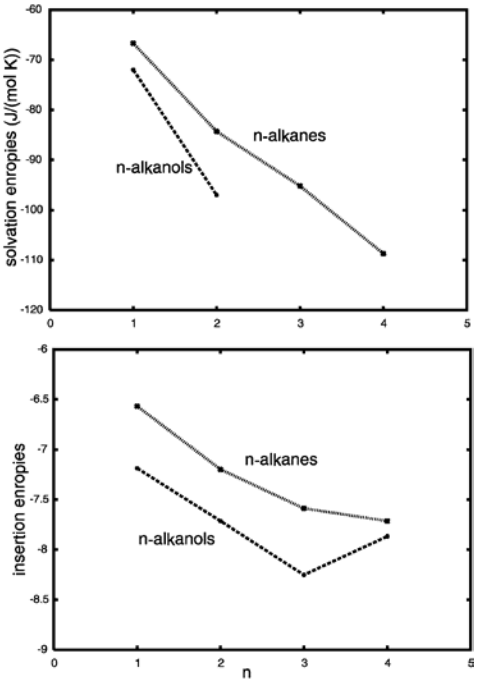

Figure 5. Experimental data for the entropy of transfer of some alkanes and alkanols into water at T=298.15 K. (The data are adjusted for the Ben-Naim standard state[7]), and simulation data for the same quantities (in reduced units). n represents the number of C atoms in the alkanols or alkanes respectively.

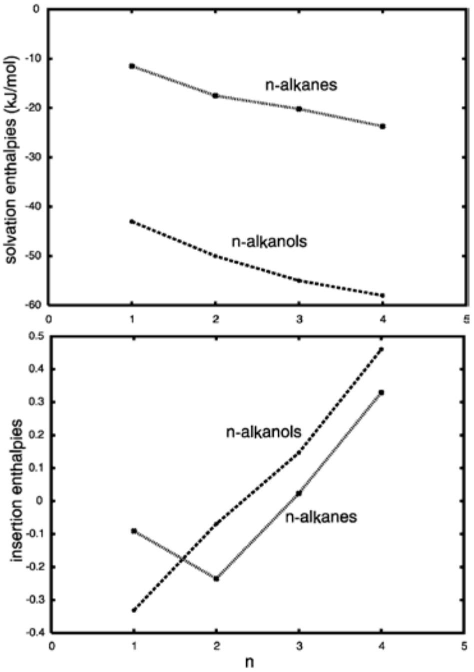

Figure 6. Experimental data for the enthalpy of transfer of some alkanes and alkanols into water at T=298.15 K. (The data are adjusted for the Ben-Naim standard state[7]), and simulation data for the same quantities (in reduced units). n represents the number of C atoms in the alkanols or alkanes respectively.

The non-flexibility of the chain has an even stronger effect on the enthalpy of solvation. For real n-alkanes and n-alkohols the enthalpy of solvation decreases with the increasing chain length and is higher for alkanes than for alcohols (Figure 6a). In our model the behavior is correct only for the short chains (Figure 6b). Due to the ability of forming hydrogen bonds, the solvation enthalpy of »methanol« is lower than the one for »methane«. At higher alcohols the influence of the hydrophobic part of the molecule prevails, and since the model alcohol molecules are bigger than the corresponding model alkanes, the latter have higher enthalpy of solvation in our model.

Last we present the water-water pair distribution function for the case of bulk water (dashed lines in Figure 7a), in comparison with water-water distribution function in the infinitely diluted "methanol" solution (solid lines in Figure 7a). Although the thermodynamic data suggest a decreased water structuring caused by the presence of "methanol" molecules (positive enthalpy of solvation – Figure 4b), the effects are too subtle to be observed in radial pair distribution functions.

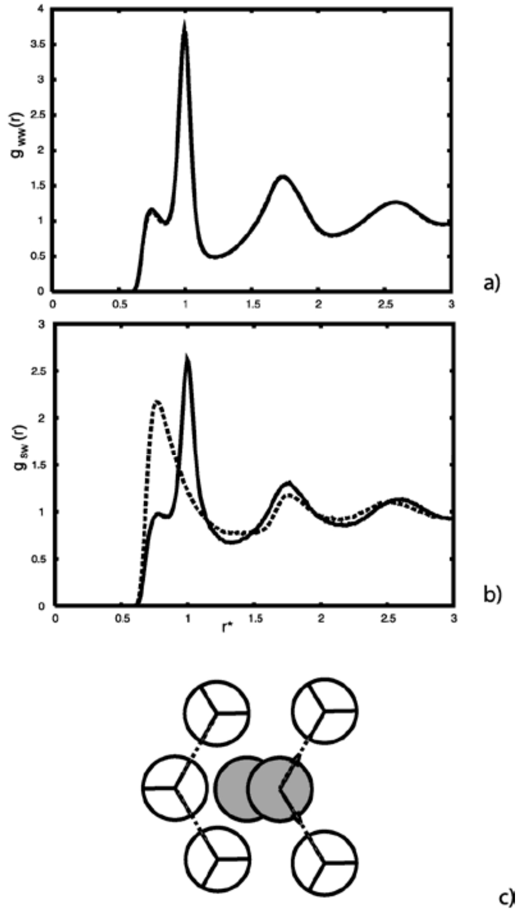

Figure 7. Radial pair distribution function for a) water-water ($g_{ww}(r)$) and b) solute-water ($g_{sw}(r)$) as obtained from Monte Carlo simulation. The solid line represents the »methanol«-water g(r) and dashed line »methane«-water g(r). c) A snapshot from the simulation showing a typical distribution of water molecules around the model methanol.

4. Conclusions

In this work we tested a simple two dimensional model for describing alcohol/water mixtures. For modeling water molecules we used the MB model which describes well the properties of pure water, simple electrolytes, and hydrophobic effect, for describing simple mixed solutes, alcohols. In constructing the alcohol model we followed the disposable experimental data, taking into account the dimensionality of the model.

Although the model successfully describes the excess volumes of mixing, it fails to capture the delicate balance of hydrogen bonding between alcohol and water molecules which reflects in the excess enthalpy of mixing. The latter is positive in the whole concentration range for our model. From the comparison with the experimental observation, we concluded that the reason for that is too many water-alcohol and too little alcohol-alcohol hydrogen bonds formed as predicted by our model. We speculate that the problem appears due to the dimensionality of the model and therefore our model cannot properly describe water-alcohol mixtures.

The artifacts of the model due to its reduced dimensionality could be overcome by studying the solvation thermodynamics of alcohols in water at infinitely small alcohol concentration (infinite dilution). The solvation thermodynamics show better qualitative agreement with experimental results, especially for low alcohols. At longer C-atom chains the behavior is not correctly captured as a consequence of non-flexibility of the model chains.

Our calculations suggest that the solvation thermodynamics of alcohols in water is a result of a combined effect of hydrophobic part of alcohol molecule promoting water-water hydrogen bonding, and alcohol molecules forming hydrogen bonds with water molecules.

The differences in experimental results for thermodynamics of solvation between alcohols and alkanes arise from the ability of alcohols to form hydrogen bonds.[7] Since our model correctly predicts these effects one can conclude that the model captures well the hydrogen bond characteristics of the mixed solvents, alcohols, in the infinite dilution, and with some refinement could be used to study more complicated systems.

5. Acknowledgement

We are grateful for the support from NIH grant R01 GM063592. B.H.L. appreciates the support of the Ministry of Science and Education of Slovenia under grants BI-US/05-06/006, P1-0201 and J1-6553.

6. References

1. *Water. A Comprehensive Treatise*., Vol. 2, ed. by F. Franks, Plenum Press, New York, **1973**.
2. *Landolt-Bornstein Numerical Data and Functional Relationship in Science and Technology*, Vol. 2, ed. by K. I. Schafer, Springer, New York, **1976**.
3. G. C. Benson, P. J. D'Arcy, O. Kiyohara, *J. Solut. Chem.* **1980**, *9*, 931–938.
4. G. C. Benson, O. Kiyohara, *J. Solut. Chem.* **1980**, *9*, 791–804.
5. S. Dixit, J. Crain, W. C. K. Poon, J. L. Finney, A. K. Soper, *Nature* **2002**, *416*, 829–832.
6. J. A. Larkin, *J. Chem. Therm* **1975**, *7*, 137–148.
7. A. Ben-Naim, *Solvation Thermodynamics*; Plenum Press: New York, **1987**.
8. N. Muller, *Acc. Chem. Res.* **1990**, *23*, 23–28.
9. N. T. Southall, K. A. Dill, A. D. J. Haymet, *J. Phys. Chem. B* **2002**, *106*, 521–533.

10. J. Turner, A. K. Soper, *J. Chem. Phys.* **1994**, *101*, 6116–6125.
11. D. T. Bowron, J. L. Finney, A. K. Soper, *J. Phys. Chem. B* **1998**, *102*, 3551–3563.
12. N. Nishi, K. Koga, C. Ohshima, K. Yamamoto, U. Nagashima, K. Nagami, *J. Am. Chem. Soc.* **1988**, *110*, 5246–5255.
13. A. K. Soper, J. L. Finney, *Phys. Rev. Lett.* **1993**, *71*, 4346–4350.
14. K. Nishikawa, T. Iijima, *J. Phys. Chem.* **1993**, *97*, 10824–10828.
15. M. D'Angelo, G. Onori, A. Santucci, *J. Chem. Phys.* **1994**, *100*, 3107–3113.
16. N. Nishi, S. Takahashi, M. Matsumoto, A. Tanaka, K. Muraya, T. Takamuku, T. Yamaguchi, *J. Phys. Chem.* **1995**, *99*, 462–468.
17. K. Egashira, N. Nishi, *J. Phys. Chem. B* **1998**, *102*, 4054–4057.
18. D. T. Bowron, A. K. Soper, J. L. Finney, *J. Chem. Phys.* **2001**, *114*, 6203–6219.
19. W. L. Jorgensen, J. D. Madura, *J. Am. Chem. Soc*. **1983**, *105*, 1413–1419.
20. S. Okazaki, K. Nakanishi, H. Touhara, *J. Chem. Phys.* **1983**, *78*, 454–469.
21. S. Okazaki, H. Touhara, K. Nakanishi, *J. Chem. Phys.* **1984**, *81*, 890–894.
22. H. Tanaka, K. Nakanishi, H. Touhara, *J. Chem. Phys.* **1984**, *81*, 4065–4073.
23. Y. Kataoka, *J. Chem. Phys.* **1984**, *80*, 4470–4477.
24. P. F. W. Stouten, J. Kroon, *Mol. Sim.* **1990**, *5*, 175–179.
25. M. Ferrario, M. Haughney, I. R. McDonald, M. L. Klein, *J. Chem. Phys.* **1990**, *93*, 5156–5166.
26. Y. Kataoka, *Advances in Therm. Fluct. Theor. Mix.* **1990**, *2*, 273–284.
27. H. Tanaka, K. E. Gubbins, *J. Chem. Phys.* **1992**, *97*, 2626–2634.
28. C. A. Koh, H. Tanaka, J. M. Walsh, K. E. Gubbins, J. A. Zollweg, *Fluid Phase Equil.* **1993**, *83*, 51–58.
29. A. Laaksonen, P. G. Kusalik, I. M. Svishchev, *J. Phys. Chem. A* **1997**, *101*, 5910–5918.
30. J. Fidler, P. M. Rodger, *J. Phys. Chem. B* **1999**, *103*, 7695–7703.
31. P. G. Kusalik, A. P. Lyubartsev, D. L. Bergman, A. Laaksonen, *J. Phys. Chem. B* **2000**, *104*, 9533–9539.
32. T. S. Van Erp, E. J. Meijer, *Chem. Phys. Lett*. **2001**, *333*, 290–296.
33. N. Laiken, G. Nemethy, *J. Phys. Chem.* **1970**, *74*, 3501–3509.
34. H. Adidharma, M. Radosz, *J. Phys. Chem. B* **2001**, *105*, 9822–9827.
35. K. A. T. Silverstein, A. D. J. Haymet, K. A. Dill, *J. Am. Chem. Soc.* **1998**, *120*, 3166–3175.
36. K. A. T. Silverstein, A. D. J. Haymet, K. A. Dill, *J. Chem. Phys.* **1999**, *111*, 8000–8009.
37. N. T. Southall, K. A. Dill, *J. Phys. Chem. B* **2000**, *104*, 1326–1331.
38. K. A. T. Silverstein, A. D. J. Haymet, K. A. Dill, *J. Am. Chem. Soc.* **2000**, *122*, 8037–8041.
39. B. Hribar, N. T. Southall, V. Vlachy, K. A. Dill, *J. Am. Chem. Soc.* **2002**, *124*, 12302–13311.
40. K. A. Dill, T. M.Truskett, V. Vlachy, B. Hribar-Lee, *Ann. Rev. Biophys. Biomol. Struct.* **2005**, 34, 173–199.
41. G. Palinkas, E. Hawlicka, K. Heinzinger, *J. Phys. Chem.* **1987**, *91*, 4334–4341.
42. A. H. Narten, S. I. Sandler, J. *Chem. Phys.* **1979**, *71*, 2069–2073.
43. W. L. Jorgensen, *J. Am. Chem. Soc.* **1981**, *103*, 345–350.
44. W. L. Jorgensen, *J. Phys. Chem.* **1986**, *90*, 1276–1284.
45. Yu. V. Kalyuzhnyi, *unpublished results*.
46. A. J. Easteal, L. A. Woolf, *J. Chem. Therm*. **1985**, *17*, 49–62.

Povzetek

V članku smo uporabili preprost dvodimenzionalni model za študij mešanic alkoholov in vode. Za molekule vode smo uporabili MB model, molekule alkoholov pa smo ponazorili kot nefleksibilne verige sestavljene iz dvodimenzionalnih Lennard-Jonesovih diskov, pri čemer je imel prvi disk v verigi dve »roki« za tvorbo vodikovih vezi. Model smo študirali z računalniško simulacijo Monte Carlo, in sicer v NPT ansamblu. Rezultate smo primerjali z eksperimentalnimi termodinamičnimi podatki za mešanice metanol/voda. Presežni volumni mešanja dobljeni za model se kvalitativno ujemajo z eksperimentalnimi podatki, vendar zaradi reducirane dimenzionalnosti model napačno opiše presežne entalpije mešanja. V nadaljevanju smo študirali termodinamiko prenosa molekule alkohola v vodo, pri čemer nas je zanimal predvsem trend, ki ga kaže vrsta metanol, etanol, propanol, n-butanol. V primeru nižjih alkoholov model kvalitativno pravilno opiše termodinamiko hidratacije alkoholov, pri višjih alkoholih pa bi bilo za boljše ujemanje potrebno upoštevati tudi fleksibilnost molekul alkohola.