

# The Investigations of Water-ethanol Mixture by Monte Carlo Method

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**Abstract**—Energetic and structural results for ethanol-water mixtures as a function of the mole fraction were calculated using Monte Carlo methodology. Energy partitioning results obtained for equimolar water-ethanol mixture and ether organic liquids are compared. It has been shown that at  $x_{et}=0.22$  the RDFs for water-ethanol and ethanol-ethanol interactions indicated strong hydrophobic interactions between ethanol molecules and the local structure of solution is less structured at this concentration as at ether ones. Results obtained for ethanol-water mixture as a function of concentration are in good agreement with the experimental data.

**Keywords**—Ethanol, molecular liquids, Monte Carlo, water, thermodynamics.

## I. INTRODUCTION

THE importance of hydrogen-bounded liquids in physics, chemistry and biology kept them in the focus of experimental and theoretical attention for many decades. As prototype hydrogen-bonding molecules, water H<sub>2</sub>O and ethanol C<sub>2</sub>H<sub>5</sub>OH both hold special status. Ethanol has another point to be in the focus of attention – it is one of the simplest amphiphile-like molecules capable of hydrogen bonding. Understanding the behaviour of amphiphiles is a central aim of soft-condensed-matter physics. Amphiphiles are also widespread in the chemical industry, e.g. as detergents, are central in biology, most notably making up cell membranes. Clearly bipolar nature of ethanol molecule means that it can act as the starting point for fundamental understanding of the solvation of amphiphiles. The amphiphilic character of alcohols as solutes has been observed to affect both the structure of the surrounding water and to promote their aggregation in aqueous solution. This research area has broad significance for chemistry as the relationships between intermolecular interaction and properties of liquid and solutions are essentials to understand environmental effects on the structure and reactivity of molecules. Nevertheless, system of interest, the complexity of the intermolecular forces is an obstacle to the resolution of statistical mechanics equations by using standard mathematical methods. To overcome this difficulties, non-conventional methods, such as molecular dynamics (MD) and Monte Carlo (MC) simulations have been

used as alternative methodologies to obtain information about the behaviour of molecular amphiphilic liquids. This computer simulations of water-alcohol solutions have played an important role in providing insight into the structural and thermodynamical of solvation. No other method can give us more detailed information as molecular dynamics (MD) and Monte Carlo (MC) simulations. In the present work, we report MC simulation results for water-ethanol solutions in the isothermal and isobaric ensemble at T=300K and P=1atm.

## II. MODEL

Following usual procedures for force field calculations, the molecules were modeled by collections of interacting sites and energy between molecules represented by sum of Coulomb and Lennard-Jones potentials centered on the sites, that is [1]:

$$U = U_{LJ} + U_{Coul} = 4 \sum_j \epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_j \frac{q_i q_j}{r_{ij}} \quad (1)$$

where  $r_{ji}$  is the distance between site i and j,  $q_i$  and  $q_j$  are point charges located respectively at the i and j molecular sites. The point charges are distributed along the molecular geometry and their values optimized to reproduce the contribution from charge density asymmetry to intermolecular interaction energy.

In this work the ethanol and water molecules are presented by a three site rigid structure. The OPLS parameters and geometry of ethanol reported by Jorgensen and co-workers were used [2]. The OPLS potential was used for ethanol-ethanol interactions. It consists of three interaction sites; a positive charge  $q_H$  on the hydrogen of the OH group, a negative charge  $q_o$  on the oxygen, and a single site (the C<sub>et</sub>-site) for ethyl group. The water-water intermolecular interaction was described by either the SPCE potential [3]. This model has a charge  $q$  on the hydrogen atoms and a negative charge  $-2q$  on the bisector of the two hydrogen bonds, together with a soft core interaction between the oxygen pair. Methyl and ethyl groups of ethanol molecule treated as a pseudo-atoms (sites). In the particular in the case of calculating Lennard-Jones parameters to study binary liquids mixtures, we used Lorentz-Berthelot combining rules [1].

## III. SIMULATION EXPERIMENT

The simulations was performed using Monte Carlo method in a cubic box containing 216 molecules in NVT ensemble at

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300K using standard Metropolis algorithm, periodic boundary conditions and Ewald summation for long range Coulombic interaction [4]. The box length was calculated on the ground of experimental density for particular concentration. Each move to create a new configuration involved picking a molecule at random, translating it randomly along each of the space-fixed axes and rotating it by taking random displacements in all Euler angles. The maximum translation and rotations shifts were optimized to yield an acceptance ratio of about 50%. The simulation was initialized with random configuration of molecules, and equilibration needed  $10^6$  configuration. For sampling another  $2 \cdot 10^6$  configurations were used.

#### IV. RESULTS AND DISCUSSIONS

Monte Carlo simulations results obtained for interactions energies and distribution functions are presented in the section below.

##### A. Interaction Energy

This section presents Monte Carlo simulations results for average interaction energy of pure liquid water, ethanol and binary solution studied in this contribution. In each simulation, the number of water and ethanol molecules in the simulation box were chosen appropriately to produce the desired mole fraction. In the case of aqueous solution of ethanol the total interaction energy between molecules  $E_{\text{tot}}$  can be written as the sum of three terms:

$$E_{\text{tot}} = E_{w-w} + E_{w-e} + E_{e-e} \quad (2)$$

where  $E_{w-w}$  - the interaction energy between only water molecules,  $E_{w-e}$  the interaction energy between water and ethanol molecules,  $E_{e-e}$  - the interaction energy between only ethanol molecules.

Fig. 1 (a) shows the dependences of  $E_{\text{tot}}$ ,  $E_{w-w}$ ,  $E_{w-e}$ ,  $E_{e-e}$  from the concentration of ethanol in water. The behavior of the interaction energy follows the general pattern for binary liquid mixtures: the contribution of each component  $E_{w-w}$ ,  $E_{e-e}$  increase as the concentration of water and ethanol respectively increase. The data on Fig. 1(a,b) shows a general tendency towards an enhancement on water-water interaction energy as the water-organic liquid interaction energy decrease. The total interaction energy  $E_{\text{tot}}$  increases with the increase of ethanol concentration. It is easily to see that as the ethanol concentration in the solution increases the interaction energy  $E_{e-e}$  between ethanol molecules increases too but the interaction energy  $E_{w-w}$  between water molecules decreases. We see the opposite behavior as the ethanol concentration decreases. The results from Fig. 1(a) can be summarized as follow: a decrease in the population of water-organic liquid molecules interacting by hydrogen-bonding leads to an increase in water-water interaction. Therefore, the water-water average interaction energy is due to decrease in the population of water-ethanol molecules interacting through hydrogen bonding.

In the OPLS force field the hydrogen bonding is mainly represented by coulomb interaction between a site represented electronegative element such as water-oxygen and

electropositive site such as ethanol hydrogen atom, water hydrogen atom and i.e. It is seen that as the ethanol concentration Fig. 1(b) increases  $E_{ij}$  increases too but Coulombic component  $E_{\text{coul}}$  decreases. That says that at high ethanol concentrations in the solution take place strong hydrophobic interactions between the molecules of ethanol.

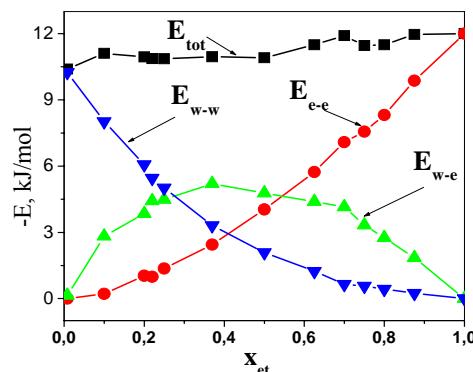


Fig. 1 (a) The dependence of the total interaction energy  $E_{\text{tot}}$  and its components  $E_{e-e}$ ,  $E_{w-e}$  and  $E_{w-w}$  on the ethanol concentration

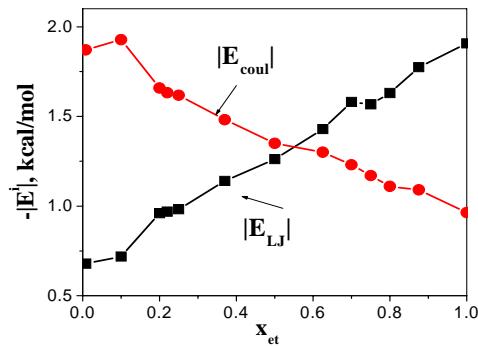


Fig. 1(b) The dependence of  $|E_{\text{coul}}|$  and  $|E_{\text{LJ}}|$  parts of the total interaction energy  $E_{\text{tot}}$  on the ethanol concentration

The behaviour of water-ethanol solute can be described by well known Le Chatelier's principle [5]: a decrease of water-solute interaction energy leads to an increase of water-water aggregation. From the other hand, the water-ethanol mixture is a example of non-ideal binary liquids and the properties of this solution depending on the relative strengths of the homo- and hetero-interactions between the component molecules. When the strengths are equal (concentrations  $x_{\text{et}} \sim 0.4$  at the Fig.1(a)), the mixture forms an ideal solution and follows Raoult's law. Derivations from Raoult's law [6] are seen in the asymmetric variations with composition of the thermodynamic functions like excess entropy, free energy of mixing or partial molar volume. The water-ethanol mixture characterized by a minimum volume ratio  $V/V_{\text{ideal}}$  [7]. In fact,

the values  $V/V_{ideal}$  decrease when small amounts of ethanol are added to water and display a relative minimum at  $0.2 < x_{et} < 0.3$ . Dependence of the heat capacity ( $C_V$ ) on the ethanol concentration is depicted in the Fig. 2. The calculations have been performed:

$$C_V = \frac{\langle \delta E_{tot}^2 \rangle_{NVT}}{k_B T^2} \quad (3)$$

where  $E_{tot}$  denotes fluctuation of total energy,  $k_B$  is the Boltzmann constant and  $T$  temperature in Kelvin. As a function of concentration, the  $C_V$  at the supercritical conditions shows maximum at  $x_{et}=0.22$ . Can be noted, that the activation enthalpy  $\Delta H_1^{act}$  and entropy  $\Delta S_1^{act}$  of the dominating dielectric relaxation process also display a distinct maximum at around  $x_{et}=0.22$  [7].

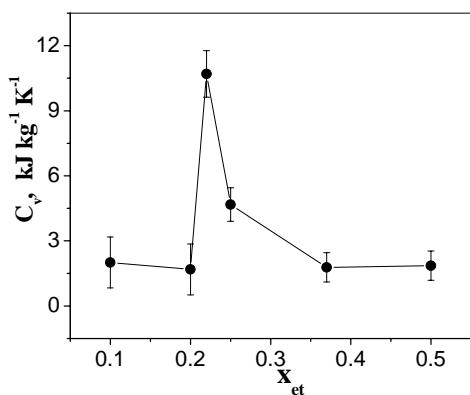


Fig. 2 Head capacity  $C_V$  as a function of  $x_{et}$  obtained from the present simulations at  $T=300K$

The results suggest, the maximum is indicating strong hydrophobic hydration of the solution. A widely accepted notion is that molecular association in water-alcohol media occurs mainly via hydrogen bonding, although hydrophobic forces also play a role in liquid structure [8]. It is a great interest to relate the thermodynamic behavior of the system with the nature of the interactions between the component molecules in the liquid.

#### B. Radial Distribution Function (RDF)

The structure of the solution is usually described by pair correlation function such as radial distribution function (RDF). To analyse the structure of water-ethanol solution eleven site-site RDFs, denoted as  $g_{xy}$ , where X, Y are atoms O<sub>w</sub>, H<sub>w</sub>, O<sub>et</sub>, H<sub>et</sub>, C<sub>et</sub> (C≡CH<sub>3</sub>-CH<sub>2</sub>) were calculated. The RDF shows how the structure of the solution changes as ethanol concentration increases. The most important six RDFs at three concentrations are plotted on Fig. 3-4. We calculated the most interesting RDFs for O<sub>w</sub>-O<sub>w</sub>, H<sub>w</sub>-O<sub>w</sub>, H<sub>w</sub>-H<sub>w</sub> interactions. Atom-atom pair correlation functions for H<sub>w</sub>-O<sub>w</sub> interactions is given in Fig. 3. The water-water RDFs have not changed

the position of the first maximum as ethanol concentration increases, that tells that the water geometric structure of water-ethanol diluted solution is almost the same as that of pure water. The RDFs O<sub>w</sub>-O<sub>w</sub> at all the concentrations show a high sharp first peak. The positions of the peaks of O<sub>w</sub>-O<sub>w</sub> RDF are similar to those found in pure water [3]. The position of the first and second peaks has not changed with increasing concentration of ethanol molecules in the solution.

At ethanol concentration  $x_{et} \sim 0.22$  the first maximum of RDF of type O<sub>w</sub>-O<sub>w</sub> a little increases whereas the first minimum of the same RDF slightly decreases in comparison with RDF of type O<sub>w</sub>-O<sub>w</sub> at  $x_{et} \sim 0.2$ . These results can be compared with experimental data from Raman spectroscopy [9]. The Raman spectra show in low frequency region at this concentrations existence of two association states of molecules: water aggregate state and that of ethanol aggregate. At lower ethanol concentration only water aggregation state has been found. It is known that the second peak of O<sub>w</sub>-O<sub>w</sub> RDFs at position of 0.45nm for pure water at ambient conditions reflects tetrahedral arrangement of the molecules. Hence the results indicate the low probability of tetrahedral arrangement of water molecules at concentrations less than  $x_{et} \sim 0.2$ .

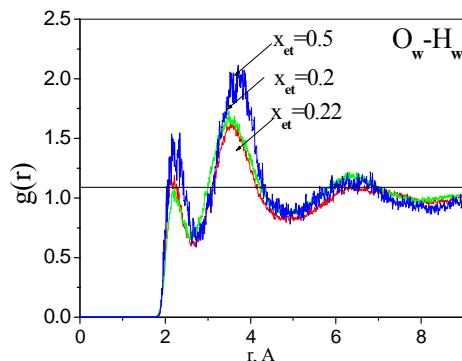


Fig. 3 RDF water-water, water-ethanol interactions at three ethanol concentrations  $x_{et}=0.2, 0.22, 0.5$  at  $T=300K$

The hydrogen-hydrogen H<sub>w</sub>-H<sub>w</sub> RDFs show the changing positions of first and second maxima from  $x_{et} \sim 0.22$ . The positions changing of the first minimum for oxygen-hydrogen (O<sub>w</sub>-H<sub>w</sub>) interactions have been not indicated for  $x_{et} \sim 0.22$ . This effect indicates hydrogen bond peculiarity of the solution at  $x_{et} \sim 0.22$ . Therefore, at  $x_{et} \sim 0.22$  the water structure is much pronounced than for the other concentrations.

The same discrepancies are found in the features of RDFs of type water-ethanol. The RDF O<sub>et</sub>-H<sub>w</sub>, which can be related to strong intermolecular interactions and has four distinct peaks. The clearly observed third peak confirms the need for a larger simulation box to describe more precisely the structure of the solution.

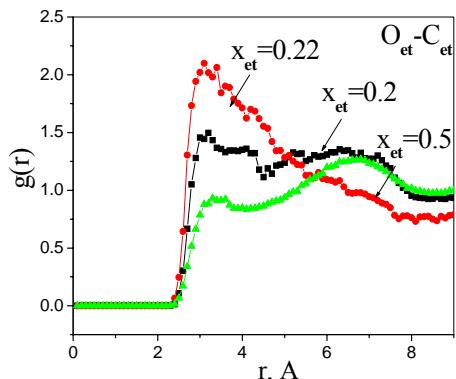


Fig. 4 RDF for ethanol=ethanol and water-ethanol interactions at three ethanol concentrations  $x_{et}=0.2, 0.22, 0.5$  at  $T=300K$

The most interesting aspect of hydrophobic effects in water-ethanol mixture is the ethanol-ethanol interactions  $O_{et}-O_{et}$ ,  $O_{et}-C_{et}$ ,  $H_{et}-O_{et}$ . The first maximum of the RDF  $O_{et}-O_{et}$  decreases as ethanol concentration increases. At the  $x_{et}=0.22$  can be seen the strong increasing of the first maximum, that one could conclude that the ethanol molecules have essentially become completely hydrated at lower than  $x_{et}\sim 0.22$  concentrations. By the next increasing concentrations the values of RDFs  $O_{et}-O_{et}$  are decreasing. The most interesting behavior shows the RDFs for  $C_{et}-O_{et}$  interactions (Fig.4). As we expected the RDF at  $x_{et}\sim 0.22$  shows the broadest first peak with maximum value. The first minimum shifted from  $4.5\text{\AA}$  at  $x_{et}=0.2$  to  $7.9\text{\AA}$  at  $x_{et}\sim 0.22$ . In this case the RDFs maximum can be indicated the strong hydrophobic interactions between ethanol molecules themselves. The RDFs for  $H_{et}-O_{et}$  interactions shows also the ethanol-ethanol interactions features at  $x_{et}=0.22$ . In this case have been indicated the shifts of the first minimum and second maximum, that tell as about existence the strong coulombic interactions at long distances without building hydrogen bonds. Curves for RDFs  $O_w-O_{et}$  water-ethanol pairs are shown in Fig.4. We find that the first peak become higher and that these RDFs generally become more structures as the ethanol content of these solutions increase. As we expected the largest peak heights for the equimolar solution where the number of possible cross-correlations is maximized. It is also apparent that the position of the second maximum shifts to slightly are agreement with increasing  $x_{et}$ . At the  $x_{et}=0.22$  the second maximum and the first minimum have a maximum values of RDF. This result suggest that at this concentration less structured as at ether concentrations.

## V. CONCLUSION

Energetic and structural results for ethanol-water mixtures as a function of the mole fraction were calculated using Monte Carlo methodology. Energy partitioning results obtained for equimolar water-ethanol mixture and ether organic liquids are compared. It has been shown that at  $x_{et}=0.22$  the RDFs for water-ethanol and ethanol-ethanol interactions indicated strong hydrophobic interactions between ethanol molecules and the local structure of solution is less structured at this concentration as at ether ones. Results obtained for ethanol-

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