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# Structure of a methanol–water microdroplet: a molecular simulation study

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**Molecular dynamics simulations provide evidence of strong reorientational effects of methanol molecules in the surface layer of a microdroplet, composed of an equimolar mixture of methanol and water, so that the orientational bias of methanol molecules in the mixture appears to be stronger than in droplets of pure methanol.**

The behaviour of amphiphiles in the interface between polar and nonpolar phases is one of the more interesting problems of the investigation of the water–amphiphile solutions. The simplest amphiphilic substances are alcohols, of which methanol is a prime example. Molecular simulations of alcohols and their mixtures by Monte Carlo (MC) and molecular dynamics (MD) methods were carried out in a number of studies. These simulations allow one to calculate in a straightforward manner the static and kinetic properties of the system under investigation. The surface properties of these systems were subject of a number of studies where the liquid–vapour interface of methanol and its aqueous solutions was considered.[1–6]

One of the principal quantities of interest in the investigation of the interface of liquid–vapour polar fluid is the surface potential $\chi$ which can be determined as the difference of the electric potentials of liquid $\varphi_l$(l) and gas $\varphi_g$(g) phases, that is $\chi = \varphi_l - \varphi_g$. The value of $\chi$ in the case of methanol and water–methanol mixtures was calculated in studies by Matsumoto *et al.*,[1,3] Baraclough *et al.*[2] and more recently by Zakharov and Brodskaya.[6] Unfortunately the results of these studies do not agree with each other and with experimental values.[7] The discrepancy between the results can partly be ascribed to different definitions of the surface potentials. Thus Matsumoto *et al.*[1,3] and Baraclough *et al.*[2] employ a definition, in which only dipolar contributions to the surface potential are included. Wilson *et al.*[8] have pointed out, that in addition to the dipolar contribution one should also include a purely quadrupolar term. Zakharov and Brodskaya[6] obtained the value of $\chi$ directly from a calculation of the local electric potential $\varphi(r)$ for small clusters of methanol, as described in earlier studies of water clusters.[9,10] Their results confirmed the importance of the quadrupolar contributions to the surface potential.

In this work we present preliminary results of MD simulations of a cluster, consisting of 128 molecules of equimolecular methanol–water mixture. For comparison clusters of pure water and methanol with the same number of molecules were considered as well. The average diameter of such micro-objects is about 20–30 A, which corresponds to about ten molecular diameters. Though the local density in the central region of the system approaches the value of the bulk liquid, the other local properties, such as energy and pressure, do not reach their bulk values. For this reason these microdroplets are usually referred to as clusters in order to stress their strong nonuniformity. One should be careful however to avoid possible confusion of such clusters, which are stable isolated objects, with the clusters arising inside a hydrogen bonded liquid by fluctuations, as presumed by a number of theories and observed in simulations of associating liquids.[11]

The success of the molecular simulations depends to a large degree on the quality of the molecular model together with the intermolecular potential. Reasonably efficient models are the empirical models proposed by Jorgensen both for water[12] and methanol.[13] Although not perfect these models describe the properties of liquid water and methanol at ambient pressures quite reasonably over a wide range of temperature.[13,14] The molecular dynamics simulations were carried out using constraint dynamics,[15] which take into account the rigidity of molecules. The temperature was about 300 K. The time step was equal to 1 fs, the equilibration time exceeds 200 ps, and duration of the production run was more than 900 ps. The coordinate origin is placed in the centre of mass of the system.

On the average the systems were spherically symmetrical, so that all one-body local properties are functions of the distance from the centre of the cluster. These functions are called the radial profiles. The systems of $N = 128$ molecules was placed in a loose spherical shell with a short-ranged, smooth repulsive field. The value of the radius $R_{sh}$ of this shell was nearly three times more than the radius of the equimolecular dividing surface $R_e$ which can be taken as a characteristic radius of the cluster size. This allows to avoid the influence of the shell on the properties of the cluster. This dividing surface is defined by the condition of zero excess density, *i.e.* zero adsorption:

$$3N = 4\pi[\rho_l R_e^3 - \rho_g(R_{sh}^3 - R_e^3)] \quad (1)$$

where $\rho_l$ and $\rho_g$ are the densities of the bulk liquid and vapour phases.

The first characteristic of the local structure is the local density, shown in Figure 1 which diplays the radial profiles of the partial density of water $\rho_w(r)$, the methanol oxygen density $\rho_O(r)$, the density of the methyl group $\rho_{CH_3}(r)$ and the total density $\rho(r)$. All densities are in atoms (molecules)/A$^3$. The radius of the equimolecular surface is about 10.7±0.5 A. It seems that methanol prevails in the surface layer, but in the central part of the cluster at $r < 6$ A the fraction of methanol is about 0.44.

It is interesting that the inner part of the surface layer inside the equimolecular sphere at 5 A $< r <$ 10 A is enriched by water and the partial local density of water has a maximum at $r = 7.5$ A. The tendency of such a behaviour for the local density of water in the surface of water–methanol solution was noticed recently by Benjamin[5] and Matsumoto *et al.*[3] In the case of the cluster this fact results in the higher value of the total local density $\rho(r)$. This feature is specific for the local density in the mixture and should be contrasted to the behaviour of the local density in clusters of pure water and methanol. In Figure 2 the local densities of all clusters are compared. It seems likely that the peculiarity of the local density in the mixture will disappear when the cluster size increases. But this assumption needs to be checked by considering larger clusters.

In comparison with the pure liquids the orientational structure of the surface layer of solution changes strongly. This can be seen clearly from the partial densities of the oxygen and methyl groups shown in Figures 1 and 2 for the clusters of the mixture and pure methanol (curves *3a* and *3b*). Although in both systems the methyl groups are directed towards to the vapour phase, this effect is much greater in the surface layer of solution. Such behaviour is characteristic of amphiphilic substances. At the same time a substantial change in the dipole orientations is observed. It is well known,[6,9] that in the surface layer of pure liquid the dipole moments are

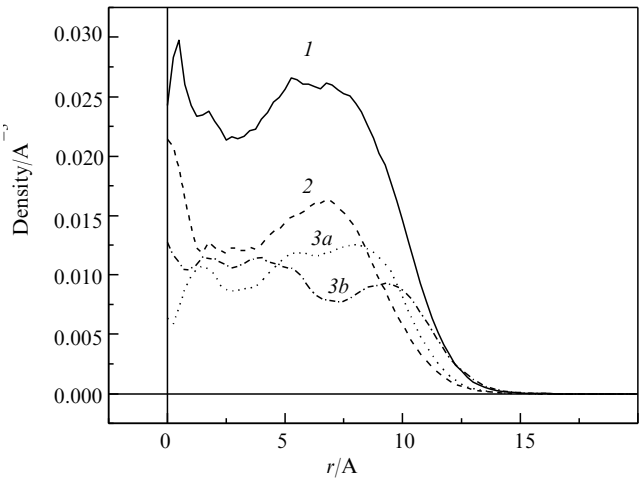


**Figure 1** The total and partial local densities in the cluster consisting of an equimolar mixture of methanol and water. *1* the total density, $\rho(r)$; *2* the oxygen density of water molecules, $\rho_w(r)$; *3a* the density of methanol oxygen atoms, $\rho_O(r)$; *3b* the density of methyl groups, $\rho_{CH_3}(r)$.

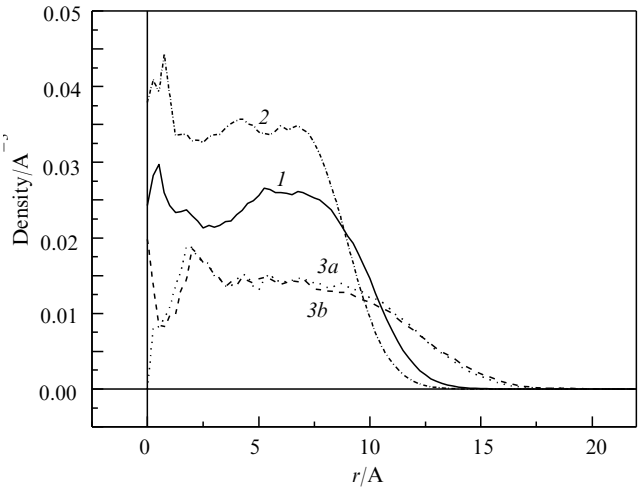


**Figure 2** The local density in the cluster of mixture (*1*), pure water (*2*), and pure methanol (*3*). *3a* the density of methanol oxygen atoms; *3b* the density of methyl groups.

oriented preferably along the surface both for methanol and water. In the surface layer of the mixture near the equimolecular surface the dipole moments of methanol prefer to be oriented towards to the vapour, whereas dipole moments of water point inwards towards the centre of the cluster. This results in some interesting local features of the electric potential, which are discussed below.

In Figure 3 the radial profiles of the total energy $e(r)$ for three clusters and the kinetic energy $e_k(r)$ for the cluster of mixture are displayed. The constancy of $e_k(r)$ in the range $2\,A < r < 12\,A$ indicates good thermal equilibrium in the system. The total energy per molecule in the case of mixture in this range is lower than the local energies for pure water and methanol. In the case of pure water and methanol the total energy in the central part of clusters reaches some plateau with the value very close to that of energy for bulk liquid. There is no such region in the cluster of mixture. This means that the cluster of mixture is nonuniform elsewhere relative to the energy. It is possible to estimate the local energy of mixing. For the minimum of $e(r)$ this value is about $-0.96$ kJ mol$^{-1}$, which is close to the experimental value of the enthalpy of mixing.[16] It should be noted also that in the minimum the partial energies of water and methanol in the cluster of mixture coincide almost.

The nonuniformity of the cluster of the mixture is reflected in the local electric potential shown in Figure 4. The local

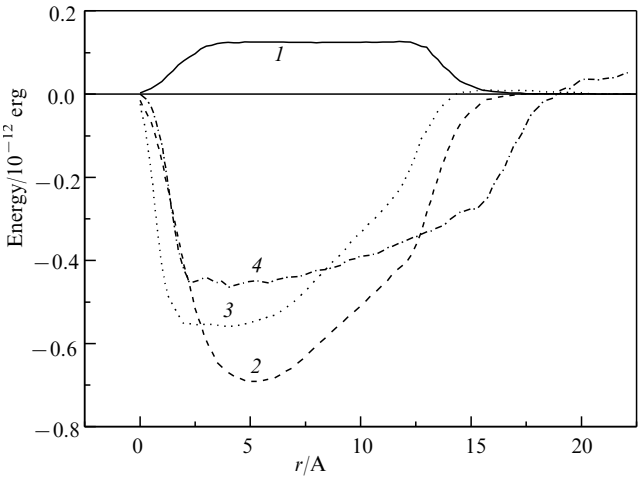


**Figure 3** The radial profiles of the kinetic energy (*1*) and total energy in the clusters of mixture (*2*) and pure water (*3*) and methanol (*4*).

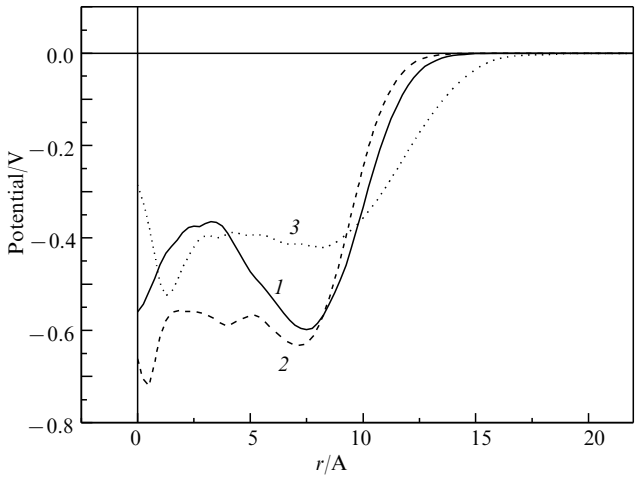


**Figure 4** The local electrical potential in clusters: (*1*) the equimolar mixture, (*2*) pure water and (*3*) pure methanol.

electric potential $\varphi(r)$ was calculated as follows:[9]

$$\varphi(r) = 1/(4\pi\varepsilon_0)\left\langle \sum_{r<r_i} q_i/r_i + \sum_{r>r_i} q_i/r \right\rangle, \quad (2)$$

where $q_i$ is the effective point charge of the molecule located at the distance $r_i$ from the centre of the cluster, the angular brackets denote a time average, $\varepsilon_0$ is the vacuum permittivity.

In Figure 4 the local electric potential $\varphi(r)$ for three clusters is shown. It is seen that the functions $\varphi(r)$ are negative elsewhere. According to the behaviour of $\varphi(r)$ inside the clusters of water and methanol it is possible to estimate the electric potential for liquid $\varphi_l$ as a mean value of $\varphi(r)$ within some region in the clusters. These values can be considered as the values of the surface potential $\chi$ since the value of $\varphi_g$ for the vapour can be neglected practically. The values of $\chi$ for water and methanol are given in Table 1. They are in agreement with the previous data both for water[10] and methanol[6] with clusters containing 64 molecules each. It can be noted only the slight increase of $\chi$ with the increase of the number of molecules from 64 up to 128. However the obtained values of the potential are more negative for methanol than the values obtained by Matsumoto and Kataoka[1] and Baraclough *et al.*[2] and differ even in sign for water.[2] As mentioned earlier, the reason of the discrepancy can be traced to the neglect of the quadrupolar contribution to the surface potential. The procedure used by Matsumoto *et al.*[1,4] and Baraclough *et al.* [2] is based entirely on the dipole polarization. The role of the molecular quadrupole was first noticed by Wilson *et al.*,[8] who proposed the following expression for $\chi$ in case of a flat interface between liquid (l) and gas (g):

**Table 1** The surface potential of water, methanol and their solutions from molecular simulations.

| System | | $\chi$/V | Reference |
|---|---|---|---|
| water | flat interface | 0.24 | 2 |
| | flat interface | 0.11 | 3 |
| | flat interface | −0.13 | 8 |
| | cluster, $N = 64$ | −0.66 | 10 |
| | cluster, $N = 128$ | −0.60 | this work |
| methanol | flat interface | −0.16 | 1 |
| | flat interface | −0.25 | 2 |
| | cluster, $N = 64$ | −0.44 | 6 |
| | cluster, $N = 128$ | −0.40 | this work |
| equimolar mixture | flat interface | −0.38 | 2 |
| | flat interface | −0.60 | 3 |
| | cluster, $N = 128$ | −0.44 | this work |

$$\chi = 1/\varepsilon_0\{\int_g^l P_d(z)dz - \Delta\rho Tr(Q)/3\}, \quad (3)$$

Here $z$ is the coordinate normal to the interface, $P_d(z)$ is the dipole moment per volume, $\Delta\rho$ is the difference of the density of liquid and gas, $Tr(Q)$ is the trace of the molecular quadrupole moment.

In our earlier studies[6,10] of small clusters of water and methanol special consideration was given to the estimation of each term in equation (3). Both for water and methanol the estimated values of the surface potential were negative mainly due to the negative contribution of the second term in the right-hand side of equation (3). If the source of the disagreement between this result with the data of Matsumoto and Kataoka[1] and Baraclough *et al.*[2] is the different approach to the definition of the surface potential, then the origin of the discrepancy between their data is not clear. It is more surprising that both those investigations were based on the same molecular model, the geometry of the system and the same procedure of the calculation of $\chi$.

In the case of methanol–water solutions[2,3] the surface potential was negative for molar fraction of methanol, $x$, larger than 0.1, but the dependencies of the surface potential on the composition were different in these simulations. In contrast to Matsumoto *et al.*, [3] Baraclough *et al.*[2] observed a smoothly varying function $\chi(x)$ with a shallow wide minimum. In present work for the cluster of mixture the local electric potential $\varphi(r)$ (Figure 4) lies between that for pure water and methanol and has a deep local minimum in the surface layer at $r = 7.5\,\text{A} < R_e$. It should be stressed that the quadrupole moments of water and methanol are very similar. Consequently, the minimum of $\varphi(r)$ can be explained only by influence of the purely dipolar contributions from water and methanol. The analysis of the orientational distribution for the dipoles shows that in this region the dipoles of water that prevails there are directed most likely outwards to the vapour. This fact provides the additional negative contribution to $\varphi(r)$. Unfortunately, according to the function $\varphi(r)$, it is rather difficult to judge of the electric potential $\varphi_l$ in the liquid solution and to make any conclusion about the surface potential in this case. It seems only that this value should be closer to the value of the pure methanol. The average value over $1\,\text{A} < r < 7\,\text{A}$ can be chosen as a rough estimation of the surface potential in this case. For the more exact determination of $\chi$ from such simulations it is necessary to consider larger clusters.

In the conclusion it should be said that this simulation shows that the surface layer of the mixture has much more complex structure than those for pure substances. Strong reorientation effect is observed in the surface layer of solution in comparison to the surface layers of pure liquids. Although the results did not allow to obtain a reliable value of the surface potential for the methanol–water mixture they showed that there is a considerable purely quadrupolar contribution to the local electric potential which was not taken into account in earlier studies.[1,2,4]

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