

New Six-site Acetonitrile Model for Simulations of Liquid Acetonitrile and its Aqueous Mixtures

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Abstract: A new six site flexible acetonitrile molecular model is developed. The AMBER force field was used for description of intramolecular parameters, the atomic charges were calculated from a high level *ab initio* theory and finally the Lennard–Jones parameters were tuned to fit the experimental density and evaporation heat. The obtained in this way model reproduces correctly densities of water–acetonitrile mixtures as well as provides qualitative description of the dielectric permittivity and self-diffusion coefficients.

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Key words: molecular dynamics; force fields; acetonitrile; aqueous solutions

Introduction

Calibration of force fields for molecular simulations is an important problem of computational chemistry. In the last decades, very much efforts have been devoted to the development of force fields describing molecules of different structures. However, even now it is still often a problem to find parameters of a force field which describe, with reasonable precision, the properties of even relatively small and simple molecules.

One of such molecules, interesting from the experimental point of view, and because of many technological applications, is acetonitrile. At present, there exist a number of molecular mechanical acetonitrile models.^{1–5} Many of these models consider acetonitrile molecule as a rigid body.^{1,2,4} Some of them have only three interaction sites, with the methyl group described as a united atom.^{2,4} It seems interesting to develop an acetonitrile model which: (a) reproduces experimental properties of not only pure component but also that of mixtures; (b) is developed in a regular manner according to some algorithm which can be used for other molecular liquids; and (c) is compatible with force fields and simulation packages of general use.

The success of the OPLS force field⁶ in description of many molecular systems has demonstrated that a force field can be developed largely on the basis of experimental thermodynamical data, such as densities, evaporation energies, and so on. Still, some force field parameters are difficult to determine exclusively from experimental data. Also, for many substances necessary experimental data are absent. A reasonable compromise was implemented in development of AMBER^{7,8} force field. For each chemical atom type, a

minimal transferable set of parameters are used. This condition is important for construction of a universal force field, it is also convenient for its systematic development. However, for some parameters, such as those defining torsion angle potential and partial charges, it is difficult to find well transferable values. That is why such parameters are typically defined from *ab initio* quantum calculations. Then, final tuning of parameters is carried out to fit available thermodynamical data. On this stage, mostly Lennard–Jones (Van der Waals) parameters are varied, since they have the most profound influence on the thermodynamical properties, and because they are generally poorly determined from quantum mechanical calculations.

In this work we have tried to implement the described above approach consequently to build an acetonitrile model. Our goal is to develop a model which describes reasonably well the thermodynamical properties of acetonitrile, and which is compatible with force fields of general use (AMBER, CHARMM, or OPLS). That is why this model consists of six sites (each site corresponding to a certain atom), interacting by the Lennard–Jones and the electrostatic potentials. The intramolecular interactions are described as a sum of harmonic bonds, harmonic angles, and torsion potentials. As a starting point, we used a model considered in ref. 9. We keep mostly the same intramolecular parameters (covalent bonds, angles, and torsions, see details below). We recalculated partial charges, using higher level quantum-mechanical calculations (MP2/6-311++G(3df,3p) versus HF/6-311+G* in ref. 9).

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The Lennard–Jones parameters were preliminarily adopted from the TraPPE force field,⁵ which correctly reproduces the thermodynamical properties of acetonitrile, and were optimized finally to fit the density and the heat of evaporation for the new model. The obtained in this way acetonitrile model was used for simulations of water–acetonitrile mixtures without further tuning. As a water model, we have used the flexible SPC model,¹⁰ which, being a model of the same type (all-atom and flexible), reproduces correctly thermodynamical properties of pure water as well as their diffusion and dielectric permittivity.

Computational Details

Quantum-chemical computations of charges for the acetonitrile model were carried out using PC-GAMESS 6.4 package.¹¹ Electrostatic potential derived charges were determined using an increased (relative to the standard) density of test points around the molecule, corresponding to the {3,5+}6,0 tessellations (see details of the procedure in ref. 12).

All molecular dynamics simulations were performed using MDynaMix (v.4.4) simulation package.¹³ The double time-step time-reversible integrator was used with a long time step 2 fs consisting of 10 short time steps. The short time steps were used for integration of the intramolecular forces and the intermolecular forces within 5 Å distance, and the long time step for forces outside 5 Å. The long-range electrostatic forces were treated by the Ewald method.¹⁴ The cut-off distance for the Lennard–Jones interactions and the real-space part of the Ewald sum was set to a half of the simulation box size, or 14 Å in simulations of larger systems. The long-range contribution from the Lennard–Jones interactions outside the cutoff was included into the energy and pressure. All simulations were carried out at temperature 298 K and pressure 1 bar. The temperature and pressure were regulated by the Nose-Hoover thermostat and barostat with relaxation times 30 fs and 1000 fs, respectively, according to the algorithm described in ref. 15.

All computations on parametrization of the model were made for 216 acetonitrile molecules in a cubic periodic box, with 200 ps simulation time for equilibration and 100 ps for average collection.

Two series of computations of water–acetonitrile mixtures using newly developed acetonitrile model were carried out. In the first one the total number of molecules was in the range between 216 (for pure acetonitrile) and 300. The equilibration part of each simulation

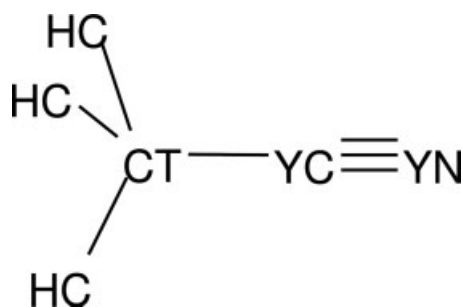


Figure 1. Acetonitrile molecule and molecular-mechanics atom types.

Table 1. AMBER Force Field Parameters.

| | $R^*(\text{Å})$ | $\epsilon(\text{kcal} \times \text{mol}^{-1})$ |
|-------------------------------|------------------------|---|
| Van der Waals parameters | | |
| YN | 1.824 | 0.17 |
| YC | 1.908 | 0.086 |
| CT | 1.908 | 0.1094 |
| HC | 1.487 | 0.0157 |
| | $r_0(\text{Å})$ | $K_b(\text{kcal} \times \text{mol}^{-1} \text{Å}^{-2})$ |
| Bond parameters | | |
| CT-YC | 1.458 | 400 |
| YC-YN | 1.157 ^a | 600 |
| CT-HC | 1.09 | 340 |
| | $\theta_0(\text{deg})$ | $K_\theta(\text{kcal mol}^{-1} \text{rad}^{-2})$ |
| Angle parameters ^b | | |
| CT-YC-YN | 180 | 80 |
| HC-CT-YC | 110 | 35 |
| HC-CT-HC | 109.5 | 35 |

^a1.150 in the original model.⁹

^bPotential for torsion angle x-CT-YC-x is zero.

was 400 ps followed by the production part of 400 ps. In the second series the size of the simulation box was increased twice in each direction, and the total number of molecules was in the range 1728–2400 for different compositions. The total simulation time in each run of the second series was 1 ns of which 500 ps was used for equilibration.

Force Field Development

Acetonitrile molecule with atom names used in the text is displayed in Figure 1. As a starting point of the force field development (denoted as Model 1), we have used the AMBER force field parameters adopted for acetonitrile in ref. 9. They are summarized in Table 1. The only change of the intramolecular parameters was an increase of the YC-YN bond length to 1.157 Å, in correspondence with our *ab initio* calculations of the optimized geometry. The partial atomic charges of work⁹ are given in column A of Table 2.

Note, that different force fields use different procedures to compute forces between atoms of the same molecule separated by 3 covalent bonds (the so-called 1–4 neighbors). For example, in the CHARMM force field the forces between such atoms are taken

Table 2. Potential derived atomic charges and dipole moments.

| | A ⁹ HF 6-311+G* | B ³ MP2 6-311+G* | C MP2 6-311++G(3df,3p) |
|-----------|-------------------------------|--------------------------------|---------------------------|
| YN | −0.532 | −0.494 | −0.5126 |
| YC | 0.481 | 0.475 | 0.4917 |
| CT | −0.479 | −0.552 | −0.5503 |
| HC | 0.177 | 0.19 | 0.1904 |
| μ (D) | 4.18 | 3.95 | 3.92 |

Table 3. Parametrization stages of acetonitrile model.

| Model | YC R^* (Å) | YC ϵ kcal/mol | YN R^* (Å) | YN ϵ kcal/mol | H_{ev} kJ/mol | ΔH_{ev} % | ρ g/cm ³ | $\Delta\rho$ % |
|---------------------------|--------------|------------------------|--------------|------------------------|-----------------|-------------------|--------------------------|----------------|
| <i>Experiment</i> | | | | | −33.4 | | 0.7768 | |
| 1. Initial ⁹ | 1.908 | 0.086 | 1.824 | 0.17 | −32.52 | −2.6 | 0.735 | −5 |
| 2. New charges | 1.908 | 0.086 | 1.824 | 0.17 | −30.05 | −10 | 0.722 | −7 |
| 3. Unit. atom LJ | 2.0485 | 0.13 | 1.7959 | 0.15 | −32.90 | −1.5 | 0.746 | −4 |
| 4. ref. 16 | 2.0019 | 0.15 | 1.755 | 0.17 | −33.94 | 1.6 | 0.790 | 1 |
| 5. OPLS ² | 2.0485 | 0.15 | 1.7959 | 0.17 | −35.61 | 6.6 | 0.763 | −1 |
| 6. R^* , ϵ^8 | 2.0019 | 0.0860 | 1.755 | 0.17 | −31.53 | −2.6 | 0.746 | −4 |
| 7. R^* , ϵ^4 | 2.0019 | 0.1300 | 1.755 | 0.15 | −33.60 | 0.6 | 0.764 | −1 |
| 8. TraPPE LJ ⁵ | 1.953 | 0.1341 | 1.6556 | 0.1331 | −33.62 | 0.66 | 0.795 | 2 |
| 9. Final | 1.99 | 0.1341 | 1.69 | 0.1331 | −33.51 | 0.03 | 0.773 | −0.5 |

Lennard–Jones parameters for YC and YN atom are given as well as computed heat of evaporation (H_{ev}) and density (ρ) with their deviations (ΔH_{ev} , $\Delta\rho$) from the experimental values. Statistical error is evaluated as 0.2 for the evaporation heat and 0.005 for the density. See the text for further details.

either as they are (scaling factor 1), or special Lennard–Jones parameters are introduced for such interactions. In the AMBER force field, the electrostatic force between 1 and 4 neighbors is usually scaled by factor $1/1.2 \approx 0.83$ and the Lennard–Jones forces by factor 0.5. Since we base our model on the AMBER force field, we use Amber’s scaling factors 0.83 and 0.5 for the 1–4 electrostatic and Lennard–Jones forces, respectively. We tested also scaling factor 1 for both electrostatic and Lennard–Jones forces and found essentially the same results as for the former set of the scaling factors, with difference of no more than 1% for the intermolecular energy, density, and diffusion. It is not surprisingly since in the acetonitrile molecule, the only 1–4 neighbors are HC and YN atoms, distance between which depends only on rather rigid covalent bonds and HC–CT–YC angle.

The density at pressure 1 bar and the evaporation heat of acetonitrile computed according to the Model 1 are given in Table 3. The evaporation heat was calculated from the average energy of intermolecular interaction as $H_{ev} = U_{inter} - RT$ (the correction on the intramolecular energy change upon transition from the liquid to the gas phase was not included since this energy was found to be the same in both phases, within the statistical uncertainty of the calculations). Both density and evaporation energy are lower than the experimental values. The authors of ref. 9 relate a too low density with a too large nitrogen radius. Indeed, as it will be discussed below, decreasing of the nitrogen radius leads to a better agreement with the experimental density.

The first step in reparametrization of the AMBER-based force field for acetonitrile was recalculation of the partial atom charges. In ref. 9, the charges were obtained from the electrostatic potential calculated within the Hartree–Fock approach in 6-311+G* basis. These charges are given in column A of Table 2. The dipole moment of acetonitrile calculated from these charges (4.12 D) is somewhat higher than the experimental one (3.92 D¹⁷ or 3.91 D¹⁸). Another set of charges, computed in ref. 3 with account for electron correlations on the MP2 level, is given in column B of Table 2. It is much closer to the experimental one. We recalculated the partial charges within the MP2 theory using an even larger basis (6-311++G(3df,3p)). They are given in column C of Table 2. These charges are close to that of column B, but provide even better agreement with the experimental dipole moment.

By substitution of set of charges “C” into original model “1”, we get “model 2”. Computations carried out for this model show worsening of results both for the density and the evaporation heat, see Table 3. As the second step, we varied the Lennard–Jones parameters for the nitrogen and YC carbon to reach a better agreement with the experimental density and evaporation heat, keeping the same set of charges. We tested a number of reported in the literature sets of parameters which are summarized in Table 3 as models 3–8. Model 3 uses values from a united atom force field for YN and YC atoms downloaded from site <http://pharmacy.man.ac.uk/amber/>. Interesting is that they improve agreement with the experiment comparing with the parameters of the all-atom AMBER. Model 4 employs parameters reported in ref. 16, with values of ϵ taken from the OPLS force field² and R^* fitted to reproduce the melting temperature of succinonitrile. Model 5 uses parameters of the united atom OPLS force field.² Model 6 combines R^* taken from work of Feng and Laird¹⁶ with ϵ taken from the original AMBER.⁸ Parameters of Model 7 are those defined in ref. 4, where values of ϵ were determined from *ab initio* computations, using 6-31G** basis set. Finally, the Lennard–Jones parameters of model 8 are taken from the TraPPE force field.⁵

Clearly, models 7 and 8 provide better agreement with the experiment among other models described earlier. Also, while the signs of deviation for the density and evaporation heat are different for model 7, they are the same for model 8. That is why we chose model 8 for the final tuning of parametrization. We increased the values of R^* for YN and YC atoms proportionally (model 9) and reached agreement with the experimental density and evaporation heat within 0.5%, which is within the statistical uncertainty of our simulations.

Results and Discussion

Structure of Pure Acetonitrile

Radial distribution functions between all pairs of heavy atoms for the newly developed acetonitrile model (model 9) are displayed in Figure 2. They are close to the RDFs computed in ref. 4 for three different three site acetonitrile models formulated in refs. 2, 4, 19,

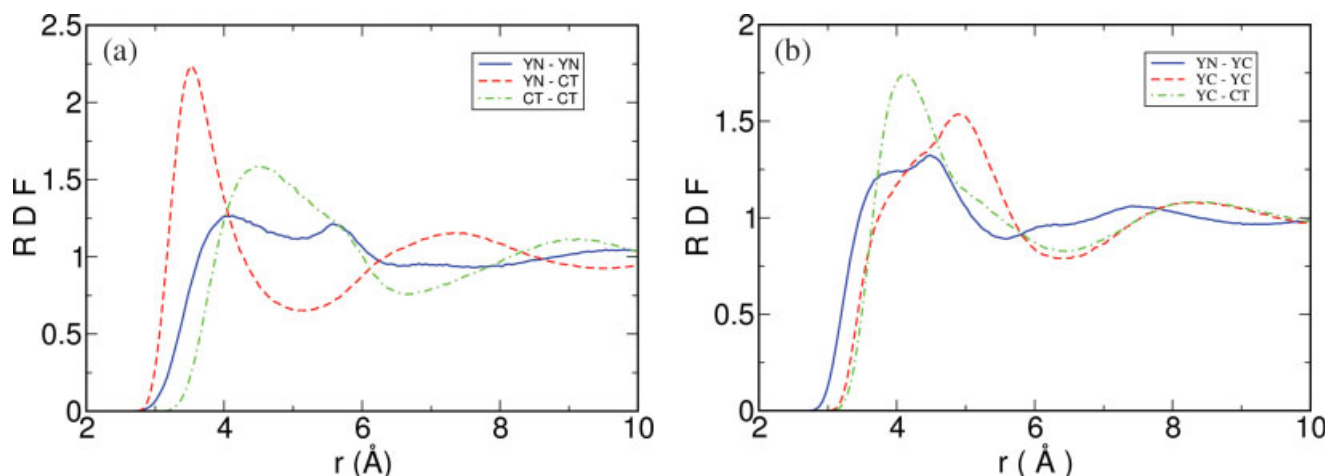


Figure 2. Radial distribution functions of pure acetonitrile. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

as well as to the RDFs of the six-site model by Garbuleda et al.⁹ (though in the later case the RDFs are rather noisy). One can see very similar positions and even amplitudes of most of maxima and minima, which indicates a rather weak (at least in the case of acetonitrile) sensitivity of RDFs to details of the model parameters. The only noticeable exceptions are the YN-YN and YN-YC RDFs. While YN-YN RDFs of all the three-site models considered in ref. 4 show the first peak of height 1.4 at about 4 Å followed by a shoulder of height 1.1 at 6 Å, our model shows two peaks, both of height 1.25, at the corresponding distances. The same trend is seen in the YN-YC RDF, where the second maximum at about 4.6 Å becomes higher than the first maximum at 3.6 Å, oppositely to the behavior of the three-site models. This means that our model gives somewhat lower probability of close coordination of nitrogen atom to the YN-YC part of another acetonitrile molecule, in comparison with the suggested earlier three-site models. The RDFs computed for 6-site model of Garbuleda et al. in ref. 9 show behavior more similar to that of our model. This indicates that the observed changes in the behavior of RDFs are caused by explicit description of hydrogens of the methyl group, which shifts slightly the nitrogen distribution toward the methyl part of the molecule because of the positive charge of the methyl hydrogens.

Another insight into structure of liquids can be reached by analyzing spatial distribution functions (SDF). In Figure 3, isosurfaces of SDFs of nitrogen and methyl carbon atoms around a reference acetonitrile molecule are shown. It is clear from the figure that acetonitrile molecules are preferentially oriented in an “antiparallel” manner. The both ends of the molecule are not equivalent: if distribution of the methyl group around the nitrogen atom has a shape of almost isotropic semisphere, the distribution of nitrogen atom around the methyl group has a shape of a ring, with angular axial structure mediated by methyl hydrogens. Only when threshold for the SDF is reduced to about 2, the isosurface of nitrogen around the methyl group adopts a shape of semisphere (data not shown). This picture demonstrates that the explicit description of hydrogen may have an effect on the structural properties of simulated liquid acetonitrile.

Densities of Water–Acetonitrile Mixtures

We tested the newly developed acetonitrile model in simulations of water–acetonitrile mixtures. Water was not used in parametrization of this model, therefore such simulations provide an independent test. Furthermore, an important property of a good molecular model is their ability not only to reproduce properties of a neat phase, but also to describe properties of these molecules in other environments and in mixtures. Simulation of mixtures of molecular liquids is often a challenging problem. Parameters, well optimized for pure components, do not often work for mixtures of these components.

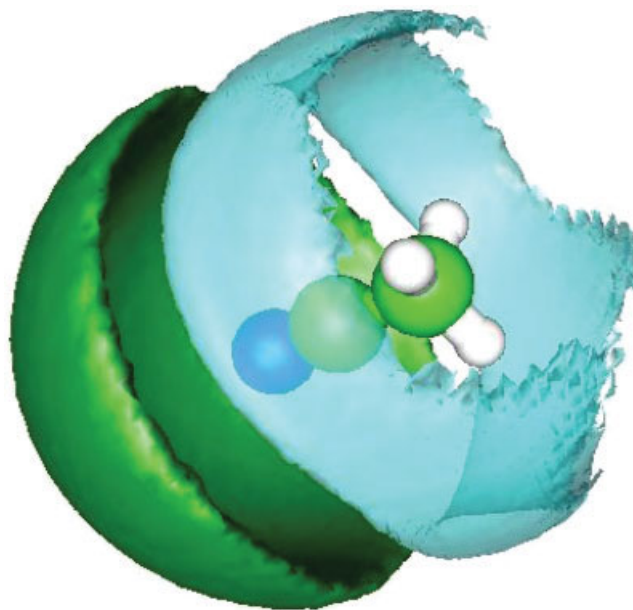


Figure 3. Isosurfaces of spatial distribution functions of YN (light blue transparent) and CT (dark green) atoms drawn at intensity level 3 for pure acetonitrile. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

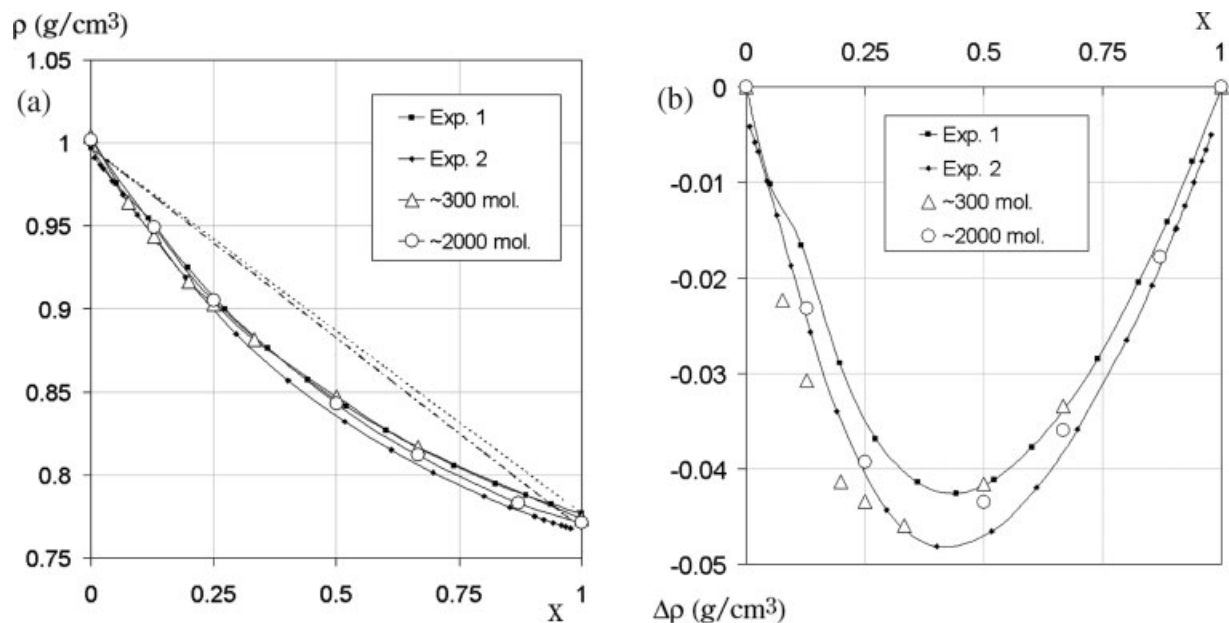


Figure 4. Density of acetonitrile–water mixture (a) and its deviation from the linear behavior (b), dependence on the molar fraction of acetonitrile x . Experimental data are from ref. 22 (Exp 1) and ref. 23 (Exp 2). Straight lines in panel (a) show the ideal linear behavior. Simulations with about 300 molecules were carried out with scaling factor 1 for 1–4 neighbors, whereas in simulations with about 2000 molecules 1–4 scaling factors were 0.83 and 0.5 for the electrostatic and Lennard–Jones interactions, respectively.

A typical problem is that a mixture of two solvents, which are well solvable in each other in any proportion in experimental conditions, is separated when simulated *in silico*. For example, it was demonstrated in ref. 20 that water–acetone mixture is separated in simulations despite the fact that each individual model (TIP4P water and Jorgensen model for acetone²¹) reproduces well properties of pure components.

Figure 4 shows densities of water–acetonitrile mixtures computed in constant-pressure simulations in comparison with experimental ones.^{22,23} Two sets of slightly different experimental data are shown. One can see that our data agree well with the experimental curves. Especially good agreement is observed between our data obtained in the large systems and the more recent experimental curve from work.²² Note also, that nonideality of water–acetonitrile

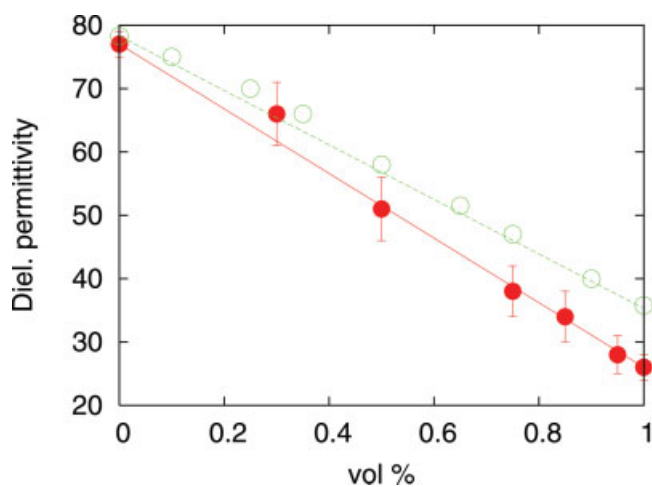


Figure 5. Dielectric permittivity of water–acetonitrile mixtures. Comparison of the simulation results (red filled circles) and experimental data from work ref. 26 (open green circles). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

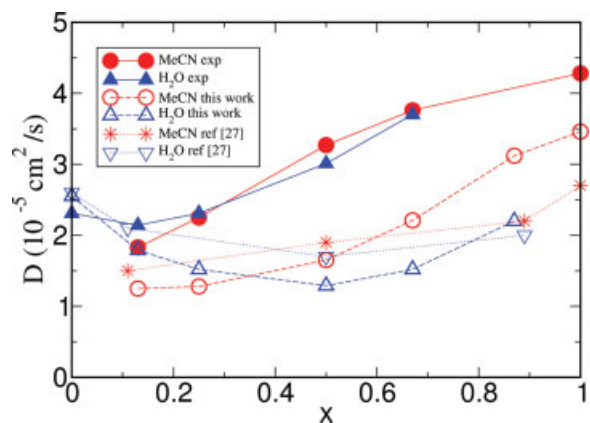


Figure 6. Self-diffusion coefficients of water and acetonitrile in water–acetonitrile mixtures, dependence on the molar fraction of acetonitrile x . Experimental data from refs. 27 and 28. Simulation data for about 2000 molecules. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mixing is rather strong, showing up to 5% lower density in comparison with the additive behaviour (straight line), and behavior of this nonideality is excellently reproduced throughout the whole concentration range.

Dielectric Properties

Another property of molecular systems, which can be directly compared with experiment and, which depends strongly on the potential model used, is the dielectric permittivity. In simulations of nonpolarizable molecules with Ewald summation in a periodic cell and tin-foil boundary conditions, the static dielectric permittivity can be determined from fluctuations of the total molecular momenta:²⁴

$$\epsilon = 1 + \frac{4\pi}{3kTV} \left\langle \left| \sum_i \bar{\mu}_i \right|^2 \right\rangle \quad (1)$$

where $\bar{\mu}_i$ is the dipole moment of molecule i and the sum is taken over all the molecules. For pure acetonitrile we obtained $\epsilon = 26 \pm 2$ which is below the experimental value $\epsilon = 36$. Interesting enough is that the dielectric constant of our model is very close to that of the three-site model of Guardia et al.,⁴ in which the partial charges were parametrized in *ab initio* computations and reproduce well the dipole moment. The three-site model by Edwards et al.¹⁹ shows dielectric constant closer to the experiment (estimated as 30 in ref. 4 and 28 in ref. 25) but it has a higher dipole moment (4.12 D) and shows a noticeable negative pressure at the experimental density.²⁵

The calculated dielectric permittivity of water–acetonitrile mixtures is displayed in Figure 5. In this figure, the acetonitrile/water ratio is given as a volume fraction. Experimental data²⁶ show that the dielectric permittivity of water–acetonitrile mixture is about linear in terms of the volume ratio. Our data shows also a nearly linear behavior, though our points are somewhat below the experimental ones because of the lower dielectric permittivity of pure acetonitrile in our model.

Self-Diffusion Coefficients

We have also determined self-diffusion coefficients of water and acetonitrile from the time dependencies of the mean square displacements. The results are shown in Figure 6, together with result of three site OPLS model²⁹ and experimental data. The measured diffusion coefficients are generally below the experimental ones^{27,28} (except the case of pure water where simulated diffusion is slightly higher than experimental). Diffusion of pure acetonitrile obtained in the simulations, $[(3.45 \pm 0.05) \times 10^{-5} \text{ cm}^2/\text{s}]$ is about 20% less than the experimental value. Our value is however larger (and closer to the experiment) than the self-diffusion coefficients calculated for other 3-site models, which are in the range $2.6 - 3.1 \times 10^{-5} \text{ cm}^2/\text{s}$.^{4,29}

For mixtures, diffusion of both water and acetonitrile is underestimated even stronger, about twice in the middle of the range. Still, some qualitative features of the simulated and experimental curves are similar, while the acetonitrile diffusion is monotonically increasing with the concentration, the water diffusion has a minimum. One can also see a convex behavior of the both acetonitrile curves in the region of high concentration. Taking also in mind that diffusion is

often very difficult to reproduce within available force fields, we consider our result for diffusion as satisfactory.

Conclusions

We have developed in this work an acetonitrile molecular model which:

- reproduces the dipole moment of acetonitrile in a gas phase
- reproduces the density and evaporation heat of liquid acetonitrile at ambient conditions
- reproduces nonadditivity of density of water–acetonitrile mixtures
- provides qualitative estimation of dielectric properties and diffusion as well as their concentration dependency in water–acetonitrile mixtures.

Being a flexible six-site model developed within the approach adopted in the general purpose force fields like CHARMM, AMBER, or GROMOS, this model can be easily included into existing simulation packages.

One of the key moments in derivation of the current model was determination of atom charges derived from the electrostatic potential. Instead of the traditional Hartree-Fock approach with 6-31G* basis set, a substantially bigger 6-311++G(3df,3p) basis was used, together with account for electronic correlations on the MP2 level. Also, an increased density of the test points for electrostatic potential fitting was used. The calculated set of atomic charges reproduces perfectly the dipole moment in the gas phase. We did not use the RESP methodology,³⁰ nor correct the charges to fit the dipole moment in the condensed phase. Still, we obtained a model well reproducing properties of pure acetonitrile and its aqueous solutions.

Acknowledgments

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