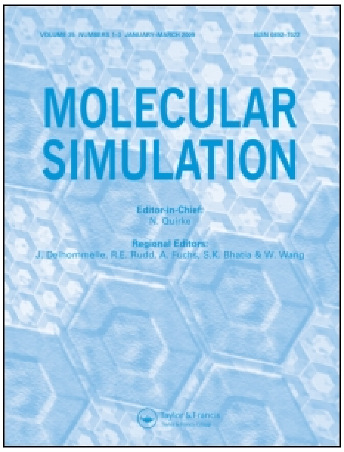

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Molecular dynamics simulation of aqueous solutions using interaction energy components: Application to the dielectric properties of the acetone-water system

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Molecular dynamics simulation of aqueous solutions using interaction energy components: Application to the dielectric properties of the acetone–water system

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Molecular dynamics simulation of aqueous solution of acetone was made using Lennard–Jones 12-6-1 potentials to describe the solute–solvent interactions and TIP4P to describe the water–water interactions. The Morokuma decomposition scheme and the ESIE solute atomic charges were used to reproduce the molecular parameters of the solute–water interaction potential. The results showed that the functions that use the EX-DIS-ES model improve the values of the dielectric properties, in particular, the dielectric constant and the dielectric relaxation time.

Keywords: Molecular dynamics simulation; Molecular interactions; Solute–solvent potential; Dielectric constant; Dielectric relaxation time

1. Introduction

The study of the liquid phase at a microscopic level has been the subject of a number of publications in the last decades [1–2]. One of the major difficulties in this type of study is the great number of interactions that are produced, so that a full quantum mechanical treatment is costly, and recourse is made to approximate methods. Although there exist procedures with an acceptable response to study the solvation of chemical systems, we shall use in the simulation of molecules in solution the classical method of molecular mechanics [3] with the aim of calculating the static and/or dynamic properties related to the solvation of molecules [4–5]. The description of the solute–solvent interaction, however, will be made by means of simple analytical functions whose molecular parameters come from fitting solute–solvent interaction energies calculated at the *ab initio* level, instead of using the geometric mean combining rules.

In recent years, our studies [6–10] have been dedicated to the search for potentials that suitably describe the solute–solvent interaction in chemical processes in solution, without excessively increasing the number of calculations required in the simulation of the system. We therefore opted to construct these potentials by fitting Lennard–Jones type functions, which include not only the van der Waals interactions but also the electrostatic interactions between the different atoms of the system, to the *ab initio* solute–solvent interaction energies at the MP2-CP level (considering both the correlation up to second order of Møller-Plesset theory [11], and the basis set superposition error correction by the CP method of Boys and Bernardi [12]).

A question that we have approached in the study of molecules in solution is the search for a procedure that improves the solute atomic charges that are best suited to the process being studied, since it is well known that the atomic charges play an important role in the description of chemical processes in solution. Recently, our research group has proposed a procedure to establish a new set of atomic charges which consists in looking for the charges that most accurately reproduce the Coulomb interactions between the solute and the water solvent [8–10]. The solute charges are derived from a fit of the electrostatic component of the bimolecular solute–water interaction energy, which will henceforth be denoted as ESIE. With respect to the molecular parameters that describe the van der Waals contribution of the interaction potential, we have recently proposed a fitting procedure based on using different components of the interaction energy, in particular, the repulsion-exchange and dispersion components for the repulsive and attractive contributions, respectively.

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This potential has been applied to systems at infinite dilution, studying thermodynamic properties where the solute–solvent interaction is the determining factor [10].

Furthermore, a significant test of the quality of a model is also to compare the theoretical and experimental properties of the surrounding medium. In this sense, simulations have seldom determined the macroscopic dielectric constant, although it is crucial in the response of the solvent to the charge distribution of a solute. In this context, the objectives of the present work are: (a) to use the molecular parameters fitted via the interaction energy decomposition technique of Morokuma *et al.* [13–14] to see to what extent this potential improves the description of the medium, and (b) to obtain values for the system's dielectric properties, in particular, the dielectric constant and the relaxation time, to validate the improvements made to the solute–solvent interaction potential.

We chose the acetone molecule as solute since it is widely used in chemistry and is soluble in water at all proportions. In addition, the acetone water mixture has been studied by molecular dynamics simulations [15–19], providing us with values of different thermodynamic properties that can be used as benchmarks. There have no studies, however, of this type for the dielectric properties.

2. Methods and working conditions

2.1 Solute–solvent potential

A grid of several hundred points was chosen to calculate SCF and MP2 solute–solvent interaction energies using the Gaussian/92 package [20]. These were then fitted by a Lennard–Jones 12-6 potential function that includes, besides van der Waals interactions, an additional Coulomb electrostatic term:

$$U_{\mathrm{sw}} = \sum_{ij} \frac{A_{ij}^{\mathrm{sw}}}{r_{ij}^{12}} - \sum_{ij} \frac{B_{ij}^{\mathrm{sw}}}{r_{ij}^{6}} + \sum_{ij} \frac{q_i^{\mathrm{s}} q_j^{\mathrm{w}}}{r_{ij}}. \tag{1}$$

The net charges on each solute atom q_i^{s} were obtained using the aforementioned ESIE procedure, which has been amply described in previous work [8–10]. It can be summarized as fitting the values of the Coulomb electrostatic component of the interaction energy $U_{\mathrm{sw}}(\mathrm{ES})$, using the variational scheme of Morokuma and co-worker [13,14], with the expression

$$U_{\mathrm{sw}}(\mathrm{ES}) = \sum_{ij} \frac{q_i^{\mathrm{s}} q_j^{\mathrm{w}}}{r_{ij}}, \tag{2}$$

where the Mulliken charges of the monomer water q_i^{w} are assigned previously.

The A_{ij}^{sw} and B_{ij}^{sw} parameters are obtained in a similar way to the q_i^{s}, but now the energies used in the fits are those that describe the exchange (EX) component of the interaction energy at SCF level, and the dispersion (DIS) component related to the MP2 correlation energy, i.e.

$$U_{\mathrm{sw}}(\mathrm{EX}) = \sum_{ij} \frac{A_{ij}^{\mathrm{sw}}}{r_{ij}^{12}}. \tag{3}$$

$$U_{\mathrm{sw}}(\mathrm{DIS}) = -\sum_{ij} \frac{B_{ij}^{\mathrm{sw}}}{r_{ij}^{6}}. \tag{4}$$

The parameters A_{ij}^{sw} and B_{ij}^{sw} obtained with this EX-DIS-ES model, together with those obtained with Mulliken and/or ESIE charges and with the total interaction SCF energy ($\mathrm{ABQ_M}$ and $\mathrm{ABQ_{ESIE}}$ models), were given in a previous paper [10].

2.2 Dielectric properties

The dielectric constant ε was calculated from the mean squared dipole moment $\langle M^2 \rangle$ of the medium using the "fluctuation formula" [21,22]

$$\frac{(\varepsilon - 1)(2\varepsilon_{\mathrm{rf}} + 1)}{3(2\varepsilon_{\mathrm{rf}} + \varepsilon)} = \frac{\langle M^2 \rangle}{9\varepsilon_0 k_{\mathrm{B}} T V}, \tag{5}$$

where $\varepsilon_{\mathrm{rf}}$ is a reference dielectric constant, V the cell volume, k_{B} Boltzmann's constant, T the temperature, ε_0 the vacuum permittivity and M the total dipole moment obtained from μ_{i} the individual dipole moment for each solvent molecule.

$$M = \sum\nolimits_{i=1}^{N} \vec{\mu}_i \tag{6}$$

The dielectric constant depends notably on the value taken for $\varepsilon_{\mathrm{rf}}$ to solve the equation (5), a problem which is usually avoided by setting $\varepsilon_{\mathrm{rf}} = \varepsilon$. In this case, equation (5) can be simplified to

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{\varepsilon} = \frac{\langle M^2 \rangle}{\varepsilon_0 k_{\mathrm{B}} T V}. \tag{7}$$

The correlation time τ can be calculated by means of the integral at infinite time of the dipole autocorrelation function $\Gamma_{\mu}(t)$,

$$\tau = \int_0^{\infty} \Gamma_{\mu}(t) \cdot \mathrm{d}t, \tag{8}$$

and the relaxation time τ_{rex} by fitting this function in the short-time zone to an exponential form

$$\Gamma_{\mu}(t) = \Gamma_{\mu}(0) \mathrm{e}^{-t/\tau_{\mathrm{rex}}}, \tag{9}$$

which allows us to obtain the Debye relaxation time τ_{D}

$$\tau_{\mathrm{D}} = \left(1 + \Gamma_{\mu}(0) \frac{\varepsilon - 1}{2\varepsilon_{rf} + 1}\right) \tau_{\mathrm{rex}}. \tag{10}$$

2.3 Simulation details

Molecular dynamics simulations of an acetone molecule in a cubic box (with an edge of 18.6 Å) of 216 solvent

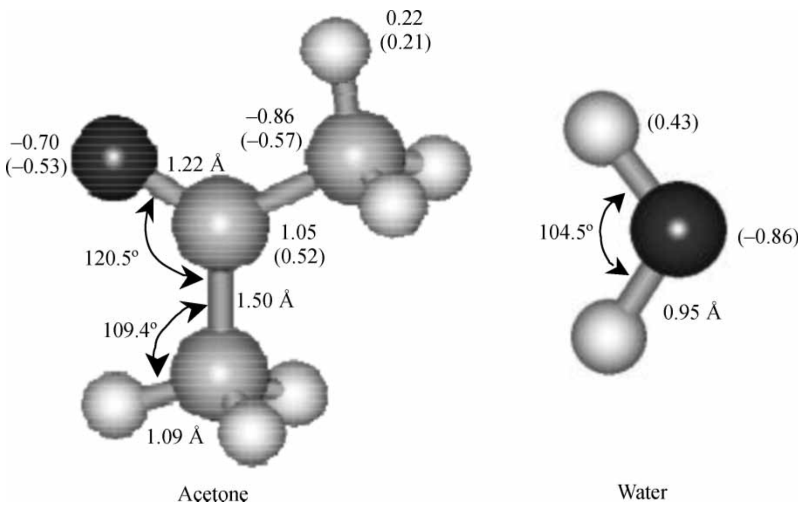

Figure 1. ESIE and Mulliken (in parentheses) charges and molecular geometries.

water molecules were carried out using the KGNMD program [23]. The temperature was kept constant at 298 K, and the time considered for the simulation was 1000 ps with time steps of 1 fs. The first 100 ps were taken to reach equilibrium, and the times remaining were used to store the positions required for an adequate evaluation of the total dipole moment. For the solvent–solvent interaction we used the TIP4P potential [24], although the MCY potential [25] was also considered with the aim of comparing some properties. No cut-off was applied in these simulations in order to eliminate the dependence of the dipole moment on the cut-off radius. For the solute–water interaction, the aforementioned Lennard–Jones 12-6-1 potential function was used, neglecting at the beginning of the simulation any water molecules that present an oxygen atom at a distance closer than 1.6 Å from any atom of the solute molecule. This criterion led to some of the 216 solvent molecules being left out of the simulation calculations. The electrostatic interactions were treated by the Ewald method [26] and the solute was kept rigid for the calculation of the properties using the SHAKE algorithm [27].

3. Results and discussion

Inspection of figure 1 shows that the ESIE charges accentuate the hydrophilic character of the carbonyl group C═O relative to the Mulliken charges, and that the charge on the hydrogen of the methyl group is similar in both cases. On the other hand we know that a hydrophobic solute produces “packing” of the molecules of the surrounding medium. Obviously, a hydrophilic solute has the opposite effect, breaking the stable structure of pure water.

The solvent–solvent energy in acetone–water solution was here found to be weaker than that of the pure solvent [10], a consequence of the predominance of the hydrophilic group over the hydrophobic groups in this solute. These values yield an important relaxation energy of the surrounding medium, and consequently the solvent molecules will have a weaker mutual interaction, with the result that the value of the $\langle M^2 \rangle$ mean squared dipole moment is less than in the pure solvent case. This is observed in table 1 only for the potential TIP4P and the ESIE solute charges.

Although these values are subject to major errors (these can be considerably reduced by eliminating those points whose deviation is larger than the mean standard deviation), their cumulative average converges after the first 100 ps of the simulation, as can be seen in figure 2.

These values of $\langle M^2 \rangle$ yield a dielectric constant of the system far from the experimental value of 78.5 [28] for the MCY case, although in better agreement for the TIP4P case. However, only the $\mathrm{ABQ}_{\mathrm{ESIE}}$ and EX-DIS-ES potentials reflect the decrease of the dielectric constant of the system when a solute such as acetone (of dielectric constant $\varepsilon = 21.4$ [28]) is introduced into the medium. The smallest underestimation with respect to the value of the pure solvent ($\Delta\varepsilon = 2.76$) is obtained when the EX-DIS-ES model is applied, and thus this potential can be considered as the best potential used in this work. These conclusions can also be applied to the Kirkwood factor G_{k}, which is better described with the TIP4P potential,

Table 1. Dielectric properties of acetone–water dilute solution.

Models	$\langle M^2 \rangle^a$	ε^b	τ^c	τ_D^c
MCY/pure water	7.34 ± 1.1	37.34	$3.87^{\mathrm{d}}(4.20)^{\mathrm{e}}$	5.80^{f}
MCY/$\mathrm{ABQ}_{\mathrm{M}}$	8.23 ± 1.3	41.80	5.69(5.31)	7.38
MCY/$\mathrm{ABQ}_{\mathrm{ESIE}}$	8.35 ± 1.3	42.40	5.51(5.30)	7.57
MCY/EX—DIS-ES	8.20 ± 0.8	41.65	6.11(6.02)	8.42
TIP4P/pure water	17.40 ± 0.8	87.80	3.09(3.97)	5.09
TIP4P/$\mathrm{ABQ}_{\mathrm{M}}$	17.51 ± 0.8	88.35	3.26(4.33)	5.47
TIP4P/$\mathrm{ABQ}_{\mathrm{ESIE}}$	16.14 ± 0.8	81.48	2.77(3.49)	4.43
TIP4P/EX-DIS-ES	16.85 ± 0.8	85.04	2.74(3.48)	4.43

a) In D^2; b) obtained using equation (7) with $\varepsilon_{\mathrm{rf}} = \varepsilon$; c) in ps; d) correlation time obtained using equation (8); e) relaxation time obtained using equation (9); f) Debye relaxation time obtained using equation (10).

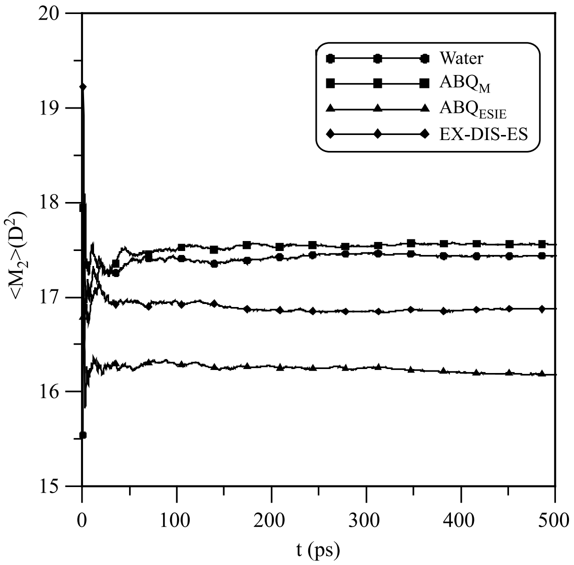

Figure 2. Cumulative average of squared moment dipole for the TIP4P potential.

although its value of 3.5 is larger than the experimental 2.9 for pure water [29].

With respect to the correlation time τ, evaluated from the integration of $\Gamma_\mu(t)$, we find again that only for the TIP4P case using solute–solvent interaction models with ESIE charges is the value obtained for the system lower than the value for pure water. The relaxation time τ_{rex}, calculated by fitting $\Gamma_\mu(t)$ to mono-exponential function, is also shorter than for the pure solvent when the ABQ$_{\text{ESIE}}$ and EX-DIS-ES potentials are used, as can be seen in figure 3. Likewise, the Debye relaxation times τ_D obtained with the three potentials are far from the experimental relaxation time of 8.3 ps for pure water [30]. Nevertheless the values obtained in this work are comparable to those presented by other authors [31–33].

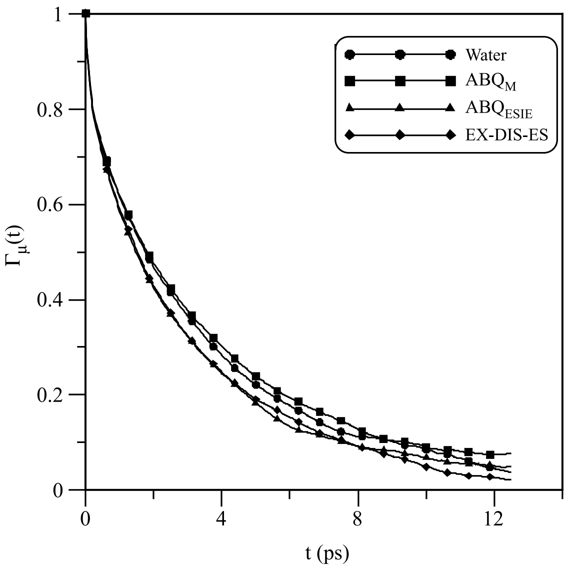

Figure 3. Dipole correlation function for the TIP4P potential.

In sum, obtaining the charges q_i^{s} and the parameters A_{ij}^{sw} and B_{ij}^{sw} by means of the interaction energy decomposition technique led to an acceptable description of the dielectric properties of the surrounding medium. The results were improved by appropriately modifying the solvent–solvent interaction with the TIP4P potential. The dielectric constant and the relaxation times obtained with the EX-DIS-ES procedure agreed well with those from other similar studies, thus confirming the goodness of the solute–solvent interaction model employed in the present work.

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