



Calculations of shear viscosity, electric conductivity and diffusion coefficients of aqueous sodium perchlorate solutions from molecular dynamics simulations



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ABSTRACT

In this paper the shear viscosity, electric conductivity and diffusion coefficients under ambient conditions of sodium perchlorate solutions in two water models (tip3p and tip4p/2005) are evaluated using the classical molecular dynamics. While using the Green–Kubo formalism, the influence of simulation trajectory length and integration limit was examined. The obtained results are compared with the experimental data. The best results were obtained for shear viscosity calculations of tip4p/2005 solutions by means of the periodic perturbation method. In the case of electric conductivity the best agreement with the experimental data was obtained using tip3p and the Green–Kubo formula. Finally, perchlorate diffusion coefficients calculated using the mean square displacement depend linearly on the inverse of the length of simulation box. It allows to calculate the correction for the finite system-size dependence of diffusion coefficients.

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1. Introduction

The latest scientific studies show that liquid water forms dynamic hydrogen bond networks whose connectivity change constantly [1,2]. Moreover, the addition of electrolytes into water causes the rearrangement of water molecules in the solvation shell around the ions only which has been proved by Omta et al. [3] who investigated aqueous perchlorate and sulfate solutions by means of femtosecond pump–probe spectroscopy. Therefore the dynamically changing hydrogen bond network between the water molecules is only locally perturbed.

It is worth noting that the aforementioned anions belong to the Hofmeister series of so-called kosmotropic, structure-making, and chaotropic, structure breaking ions. The Hofmeister series arranges ions according to their ability to precipitate a given protein from solution. It seems that the commonly accepted “kosmotropic” and “chaotropic” terms erroneously define their effect on water structure. The concept of structure making and breaking is based only on the macroscopic properties of salt solutions and loses with the results of modern, molecular-level studies.

Kosmotropic cations and chaotropic anions increase the solution viscosity and water surface tension. One of the most chaotro-

pic anions in the Hofmeister series is aforementioned perchlorate, ClO_4^- . Although its water solutions are commonly used in many practical applications, e.g. as supporting electrolytes in electrochemical studies, there are only few papers related to NaClO_4 in water [3–10]. In this paper the recent results of shear viscosity, diffusion coefficients and conductivity calculations applying molecular dynamics simulations for different NaClO_4 concentrations in tip3p and tip4p/2005 water models are presented. The main intention of this paper is to calculate these intrinsic physico-chemical properties and to compare the obtained results with the experimentally determined data. Nevertheless the concise presentation of the calculation procedures of the above mentioned intrinsic parameters can be useful for readers who would like to perform similar studies. Computations confronted with further theoretical investigations of structure and dynamics of the first ClO_4^- hydration shell can be helpful with better understanding the ions' order of the Hofmeister series.

2. Theory

The way of calculations of the shear viscosity η of liquid by means of the molecular dynamics simulation was discussed in the brilliant paper by Hess [11]. Here we use subjectively the most useful methods: the method utilizing fluctuations of elements of stress tensor and method based on non-equilibrium molecular

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dynamics simulations. The first of them consist in using the Green–Kubo formula:

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{\alpha\beta}(t_0) \cdot P_{\alpha\beta}(t_0 + t) \rangle_{t_0} dt \quad (1)$$

which relates η to the autocorrelation function (ACF) of the off-diagonal components of the stress tensor $P_{\alpha\beta}$. In this method the viscosity can be calculated from an equilibrium simulation. It is worth noting that the Green–Kubo Eq. (1) is equivalent to the Einstein relation [12]:

$$\eta = \lim_{t \rightarrow \infty} \frac{1}{2} \frac{V}{k_B T} \frac{d}{dt} \left\langle \left(\int_{t_0}^{t+t_0} P_{xy}(t') dt' \right)^2 \right\rangle_{t_0} \quad (2)$$

Because the pressure in a simulation box fluctuates heavily, a proper computation of the shear viscosity requires a precise calculation of the ACF tail. This means long simulation times of the order of nanoseconds. The application of Eq. (1) was intensively studied by e.g. Gonzalez and Abascal [13] to determine the shear viscosity of different rigid water models. In order to obtain good statistics for the ACF, they extended the length of simulations of the order 20–60 ns. Reliable values of shear viscosity can be obtained using the integral upper limit of the order of 3–5 ps. Moreover, the stress components have to be saved frequently enough to obtain a smooth ACF function. As the system is isotropic, the off-diagonal elements of the stress tensor, P_{xy} , P_{xz} and P_{zy} are equivalent and the ACF function during computation can be averaged over three tensor components.

Instead of calculating of shear viscosity from equilibrium simulations, it can be determined applying an external force on a system. Such a way of viscosity calculation is known as the periodic perturbation method [11]. It makes use of the fact that energy added to the system by external forces is dissipated through viscous friction. Simulations have to be done under the periodic boundary conditions. The acceleration profile a_x is expressed by the cosine function:

$$a_x(z) = A \cos\left(\frac{2\pi z}{L_z}\right) \quad (3)$$

and is added to each particle in each simulation step. In Eq. (3) L_z means the length of simulation box and A is the shear rate. The proper choice of the shear rate A is crucial for the determined viscosity value. For most liquids A should be smaller than 0.1 nm/ps². Detailed description of the periodic perturbation method can be found elsewhere [11].

The next physical parameter considered in this paper is the electric conductivity of charged particles. This is related to the electric-current autocorrelation function by the Green–Kubo formula:

$$\sigma = \frac{1}{3Vk_B T} \int_0^\infty \langle J_z(0) \cdot J_z(t) \rangle dt \quad (4)$$

where the z -component of current $J_z(t)$ is expressed as the sum of the products of charge q and z -component of the velocity v_z of each atom in the system:

$$J_z(t) = \sum_{i=1}^n q_i v_{z,i}(t) \quad (5)$$

A valuable independent way to evaluate the results obtained by the Green–Kubo relation (4) is the Einstein–Helfand (EH) formula. It allows to determine σ from the slope of the mean square displacement of the translational dipole moments $M_J(t)$:

$$\lim_{t \rightarrow \infty} \langle [M_J(t) - M_J(0)]^2 \rangle = 6Vk_B T \sigma t \quad (6)$$

where

$$M_J(t) = \sum_{i=1}^n q_i r_i \quad (7)$$

and r_i is the coordinate of the center of mass of the ion i . The EH method produces an accurate value for the conductivity with much less statistics than the Green–Kubo relation (4). Furthermore, the linear fit of the mean square displacement of r_i allows to calculate the diffusion coefficient D :

$$\lim_{t \rightarrow \infty} \langle [r_i(t) - r_i(0)]^2 \rangle_i = 6Dt \quad (8)$$

The self-diffusion coefficient can be also calculated using the next Green–Kubo relation:

$$D = \frac{1}{3} \int_0^\infty \langle v_i(0) \cdot v_i(t) \rangle_i dt \quad (9)$$

which is the integral of the velocity correlation function. In contrast to the conductivity calculations, the velocity ACF converges faster than the mean square displacement [12]. Nevertheless, sometimes the long time contribution to the velocity ACF has to be taken into account [14]. The accurate ACF computation needs to satisfy all requirements described below Eq. (1).

Finally, it is worth mentioning the system-size dependence of diffusion coefficients. Yeh and Hummer [15] discovered that in contrast to shear viscosities, the diffusion coefficients show significant system-size dependences. Assuming simulations with the periodic boundary conditions in a cubic box [16]

$$D_0 = D + \frac{2.837k_B T}{6\pi\eta L} \alpha \quad (10)$$

where L is the length of a box and α is an empirical parameter introduced to account for deviations from the point-particle limit i.e. the case of polar and particularly charged particles in a polar or ionic medium. Eq. (10) can be used as the correction term for the diffusion coefficient D_0 for solutes with the infinite box size L and known solvent viscosity η . Moreover, when the viscosity is not known, having at disposal the diffusion coefficients D calculated for different system sizes, a linear fit of the plot D vs. $1/L$ provides both D_0 and η .

3. Simulations

Perchlorate ion is assumed to be of a regular rigid tetrahedron with the Cl–O distance 0.144 nm. The atomic charges for ClO_4^- were obtained by R.E.D. Server [17] using the RESP-A1A (HF/6-31G*) charge model and Gaussian 09 quantum mechanics program. The GAFF topology for perchlorate anion was generated using ACPYPE [18]. Atomic partial charges are as follows: Cl: +1.0786, O: –0.51965; the Lennard–Jones parameters: Cl: $\sigma = 0.347094$ nm, $\epsilon = 1.108760$ kJ mol^{–1}; O: $\sigma = 0.295992$ nm, $\epsilon = 0.878640$ kJ mol^{–1}; Na: $\sigma = 0.333045$ nm, $\epsilon = 0.011598$ kJ mol^{–1} (to be consistent with the common notations σ , instead of electric conductivity, it means the van der Waals radius here) [25].

Gonzalez and Abascal [13] showed that the adopted water model has significant influence on the results of shear viscosity calculations. The best agreement with the experiment was obtained for the case of tip4p/2005 water model. This is reparametrized tip4p water [19,20] and has an impressive performance for a wide variety of parameters and thermodynamic conditions [20]. Thus we decided to perform calculations in the two water models: tip3p and tip4p/2005.

The solution of sodium perchlorate in tip3p and tip4p/2005 with the concentrations of 0, 0.1, 0.5, 1.0, 2.0 and 4 mol/dm³ was prepared by putting on adequate amount of Na⁺ and ClO_4^- ions as well as water molecules into a cubic box of the length 3.679 nm to obtain the stable densities 1000.3, 1003.7, 1033.8, 1067.8, 1131.7 and 1299.1 kg m^{–3} respectively. Taking into account the size of perchlorate anion, the distance between two oxygens is 0.24 nm so the used 3.679 nm box length seems to be quite

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