The Madrid force field for electrolytes in water and some thoughts on our understanding of the dielectric constant in computer simulations

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In this work, we present the Madrid force field [1,2,3] for electrolytes in water . The force-field, denoted as Madrid-2019, does not include polarizability and uses the TIP4P/2005 [4] model of water and scaled charges for the ions. A charge of ±0.85e is assigned to monovalent ions. This new force field developed provides an accurate description of aqueous solution densities over a wide range of concentrations up to the solubility limit of each salt studied. The model is able to describe 35 different electrolytes. Good predictions of viscosity and diffusion coefficients are obtained for concentrations below 2 m. Structural properties obtained with this force field are also in reasonable agreement with the experiment. The number of contact ion pairs has been controlled to be low so as to avoid precipitation of the system at concentrations close to the experimental solubility limit. With this force field we estimate the freezing point depression [5] and the shift in the maximum in density provoked by the presence of the electrolytes [6] (including new experimental results in this case). The impact of the presence of salts on ice nucleation will be discussed [7]. Finally we shall discuss the role of the dielectric constant in computer simulations, and why it is a property absolutely different from the rest of properties determined in computer simulations. In our opinion, we have not properly understood its singular character in the past, and it is time to reformulate the problem properly [8].

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