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Solvation of monovalent anions in acetonitrile and *N*,*N*-dimethylformamide: Parameterization of the IEF-PCM model

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Abstract

The present work reports the parameterization of the polarizable continuum model for predicting the free energies of solvation for monovalent anions in acetonitrile and *N*,*N*-dimethylformamide. The parameterization of the model for acetonitrile employed the experimental free energies of solvation for a set of 12 charged solutes, containing H, C, N, O, S, F, Cl, Br, and I atoms. For the *N*,*N*-dimethylformamide solutions, experimental solvation free energies for 11 monovalent anions were used. A mean absolute error of 0.7 kcal/mol in the solvation free energies has been achieved for the 12 anions in acetonitrile, whereas the mean absolute error for the 11 anions corresponds to 0.5 kcal/mol in *N*,*N*-dimethylformamide. These results indicate that the polarizable continuum model is a suitable methodology for the study of thermodynamic effects in solutions of monovalent anions in both solvents.

Keywords: Free energy of solvation; Polarizable continuum model; CH_3CN; DMF

1. Introduction

The influence of the solvent on chemical phenomena has been observed for a long time and it has received the attention of researchers from both, experimental and theoretical fields related with chemistry. For example, it is well known that the rate of a chemical reaction can change by many powers of 10 only by changing the reaction medium [1]. In addition to its impact on reactivity, the solvent also can modify the molecular structures and charge distributions as revealed by vibrational and electronic spectroscopy on molecules in solution [2]. Many of these phenomena have been explained by qualitative concepts or by empirical strategies based on the parameterization of experimental data for physical and chemical properties of solvents and the present intermolecular forces [3].

Using the intermolecular interactions that act between the solvent molecules and solutes, one may classify solvents into three categories [4]. Depending on the ability of solvent molecules to form hydrogen bonds with the solute molecules, we can classify the solvents as apolar aprotic, polar protic and aprotic. Apolar aprotic solvents have dielectric constants lower than 15, and possess low dipole moments. In this group, we include hydrocarbons, their halogen derivatives, tertiary amines, and carbon disulfide. Polar protic solvents posses molecular structures with hydrogen atoms bound to electronegative elements such as oxygen, and are hydrogen bond donors. These solvents are characterized by dielectric constants usually larger than 15. Good examples of protic solvents are water, ammonia, alcohols, carboxylic acids, amines and some amides. Protic solvents are usually good anion solvators due to their hydrogen bonding ability.

In this work, we are particularly interested in solvents belonging to the third group of solvent classes, namely the polar aprotic, or the non-hydrogen bond donor sol-

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vents. These solvents usually possess dielectric constants larger than 30, and their molecules exhibit dipole moments larger than 2.0*D*. Additionally, the presence of lone electron pairs makes them good cation solvators. The main solvents of this group are dimethylsulfoxide, nitromethane, *N*,*N*-dimethylformamide (DMF), acetonitrile (AN), acetone, nitrobenzene, cyclic ureas, hexamethylphosphoric triamide, sulfolane, among others.

The relevance of studying the solvation of ionic species in solvents with these characteristics is related to experimental evidences that some S_N2 type reactions are remarkably accelerated in polar aprotic solvents [5] when compared to protic solvents. A possible explanation for these observations is the weaker ability of aprotic solvents to solvate anions that consequently behave more freely to react with the saturated carbon atom [6] than in protic solvents, in which anions are hydrogen bound to the solvent molecules. Many other chemical reactions involve mechanisms via ions or charged transition states. Thus, the observation that anion solvation is correlated to the rate constants of chemical reactions motivated us to initiate a theoretical study modeling anion solvation in polar aprotic solvents. From this kind of studies, important principles can be established for the selection of solvents suitable for supporting specific chemical reactions and processes [4].

Due the development of new theoretical methodologies and computational tools in recent years, it became feasible to model physical and chemical phenomena in solution. Among the most important methodologies, we mention classical force field approaches such as Monte Carlo and Molecular Dynamics simulations [7]. Another promising concept is represented by the supermolecule approach in which the solute and the solvent molecules are explicitly treated in quantum mechanical calculations [8]. If quantitative yields are required, the supermolecule approach becomes computationally very expensive, but, nevertheless, there is an increasing trend in the use of such methods as more powerful computational tools become available. Finally, we mention methodologies based on continuum models for the solvent. In this approach, the solute is explicitly treated by quantum chemical methods, whereas the solvent surrounding the solute is considered as a continuous medium endowed with physical properties related to its electrostatic behavior. These methods have been widely adopted in recent years, especially in the description of the energetic characteristics of solvation [9–11]. In addition, models based on combinations of the cited approaches have been proposed [12–16].

In this work, we draw attention to a specific continuum model called the polarizable continuum model (PCM). This model presents good accuracy, reliability, adaptability, and a reduced computational effort in describing solvent effects [17–19]. The PCM simulates the solvation process by embedding the solute inside a cavity surrounded by the solvent which is represented by an infinite continuous bath characterized by its bulk physical parameters such as the dielectric constant. The solute is represented by an accurate charge distribution obtained from quantum mechanical calculation. According to this model, the solute's charge distribution polarizes the surrounding dielectric medium inducing apparent charges on the surface of the solute cavity. These charges generate a reaction field, which is introduced into the quantum mechanical Hamiltonian for the solute by a perturbation operator. This operator induces a rearrangement of the charge distribution of the solute. The new charge distribution induces a new reaction field and so on, leading to an iterative procedure aborted when self-consistency is reached. We skip over the mathematical details of this formalism, and address the reader to Refs. [9,10,20–23] for detailed reviews concerning the PCM.

The construction of the cavity for the solute is one of the crucial steps in the procedures of the PCM. Defining the solute/solvent boundary, the solute's cavity is carefully built according to the molecular shape of the solute with the cavity size depending on the atomic radii of the solute molecule and on the solvent under study [24]. Thus, for studying the solvation process, the PCM needs to be parameterized with the suitable solute's cavity in the solvent under consideration. This parameterization is usually undertaken by adapting a scaling factor to the solute's atomic radii. Generally, this scaling factor is chosen by maximizing the agreement between experimental data and computed values of some property for a representative group of solutes in a given solvent. Several parameterizations of the PCM, which make directly use of atomic radii and a suitable scaling factor, are described in the literature for the solvation processes of neutral molecules in water [16] and organic solvents such as chloroform [24], carbon tetrachloride [25], and octanol [26].

Less attention has been devoted to the application of PCM to solvation of charged molecules. We cite the parameterization for the solvation of ionic solutes in water [27,28] and, more recently, in dimethylsulfoxide [29]. In this work, we present the parameterization of the PCM for the solvation of anions in two polar aprotic solvents, namely AN and DMF. These two solvents are of great importance as indicated by their widespread use in several operations of chemistry [30].

2. Parameterization procedures

In our study on anion solvation in acetonitrile and *N*,*N*-dimethylformamide, we firstly chose a set of anions to be included in this work. Initially, we selected all the anions for which experimental values for the free energy of transfer from water to AN and DMF are available [31,32]. We combined these data with the aqueous free energy of solvation from Pliego and Riveros [33] for F^-, Cl^-, Br^-, I^-, N_3^-, CN^- and $CH_3CO_2^-$, the hydration free energy data for I_3^- and SCN^- anions from Marcus [34], the NO_3^- anion hydration free energy from Florian and Warshel [35], and the aqueous solvation free energy value for the picrate (Pic^-) anion from Kusakabe and Arai [36]. For the ClO_4^- anion,