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Solvation of monovalent anions in formamide and methanol: Parameterization of the IEF-PCM model

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Abstract

The thermodynamics of solvation for a series of monovalent anions in formamide and methanol has been studied using the polarizable continuum model (PCM). The parameterization of this continuum model was guided by molecular dynamics simulations. The parameterized PCM model predicts the Gibbs free energies of solvation for 13 anions in formamide and 16 anions in methanol in very good agreement with experimental data. Two sets of atomic radii were tested in the definition of the solute cavities in the PCM and their performances are evaluated and discussed. Mean absolute deviations of the calculated free energies of solvation from the experimental values are in the range of 1.3–2.1 kcal/mol.

Keywords: Free energy of solvation; Polarizable continuum model; Formamide; Methanol

1. Introduction

For many years, it is well known that the solvent may have an important influence on several chemical phenomena in solution. In general, the solvent affects chemical equilibria, rates and mechanisms of reactions, spectroscopic properties, etc. Some of these solvent effects can be explained on the basis of the solvation process of the solutes and the physical particularities of the solvents such as electrostatical or microscopic properties [1].

With the advances in computational tools and the development of theoretical methodologies, it became possible to model physical and chemical processes in solution. Several computational algorithms have been applied to the treatment of condensed phase phenomena. Among the most important methodologies, we cite the classical force-field approaches involved in Monte-Carlo and molecular dynamics (MD) simulations [2], simulations via *ab initio* MD [3], and the supermolecule approach treating both, the solute and the solvent molecules, explicitly by the quantum mechanical formalism [4]. Finally, we mention methodologies based on implicit solvent models [5–10], and combinations of the mentioned approaches [11–14] for the modeling of the solvation process.

The continuum models have been very useful in the description of the thermodynamics of solvation. In these models, the solute receives an explicit treatment whereas the surrounding solvent is treated implicitly as a continuous medium with conductor or dielectric properties depending on the specific model. In the present study, we apply the polarizable continuum model (PCM) [15,16] to study anion solvation. This particular model has been demonstrated to be very useful for describing the solvation of neutral and ionic species in different kinds of solvents. It is reliable

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and presents good accuracy at reduced computational costs. In recent years, the PCM has been adapted for the calculation of free energies of solvation for neutral molecules in the solvents water [17], chloroform [18], carbon tetrachloride [19], and octanol [20]. In addition, the process of anionic solvation described by the PCM has been developed for the solvents DMSO [21], water [22,23], acetonitrile and *N*,*N*-dimethylformamide [24], as well as nitrobenzene [25].

In this paper, we report the parameterization of the PCM for anion solvation in two polar protic solvents with broad application in chemical processes: methanol [26] and formamide [27]. The parameterization procedures involve the establishment of solvent dependent scaling factors for the atomic radii of the solutes with the purpose to obtain the solute's cavity inside a suitable boundary separating the solute from the continuum [28,29]. In most of the parameterization procedures reported in the literature, the scaling factors for the atomic radii are determined by a careful search for the best agreement between computed free energies of solvation for a set of solutes and available experimental data for the solvation in the investigated solvent. However, our choice for the scaling factors is based on structural informations from MD simulations on solutions of anions in the two solvents without the need of experimental data. Thus, we are enabled to employ experimental free energies of solvation in a second parameterization scheme to establish optimized parameters for the van der Waals contribution to the solvation energies.

We believe that these studies contribute to the improvement of theoretical principles for the selection of solvents for specific chemical tasks.

2. Compilation of experimental data

In a first step, of our solvation study of anions in formamide and methanol, we collected all experimental data available for the Gibbs free energies of solvation for anions in these solvents. In general, the literature reports for organic solvents the Gibbs free energy of transfer for the ions from water to the organic solvents. Therefore, in order to obtain the values for the Gibbs solvation energies in the organic solvents, we combined the experimental free energies of solvation for the anions in water (Gibbs free energy of hydration) with the transfer energies for the anions between the respective solvents (Gibbs free energy of transfer).

The experimental hydration energies for the anions F^-, Cl^-, Br^-, I^-, N_3^-, CN^-, $CH_3\ CO_2^-$, and benzoate ($PhCO_2^-$) have been adopted from the compilation of Pliego and Riveros [30]. The NO_3^- anion hydration free energy was taken from Florian and Warshel [31], and the aqueous solvation free energy for the picrate (Pic^-) anion from Kusakabe and Arai [32]. For the ClO_4^- anion, we have chosen the solvation free energy in water from the work of Abraham and Liszi [33]. Hydration free energies for I_3^-, SCN^-, BF_4^- and tetraphenylborate (BPh_4^-) have been published by Marcus [34]. When necessary, these experimental data were corrected in order to agree with the recently established standard value for the experimental solvation free energy for the proton in water, $\Delta G^{\circ}_{\mathrm{solv}}(H^+) = -264.0$ kcal/mol [35], corresponding to the process of transfer of the proton from ideal gas at 1 atm to ideal diluted solution at 1 mol per liter. Within the present study, we adopted a unique consistent standard state for discussing the Gibbs energy of solvation of all the anions in accordance to the definition given by Ben-Naim for the process of transfer of 1 mole of solute per liter of ideal gas to 1 mole per liter of ideal solution in the solvent [36]. Therefore, in this standard state, the Gibbs free energy of solvation for the proton is $\Delta G^{*}_{\mathrm{solv}}(H^+) = -265.9$ kcal/mol, where the relation,

$$\Delta G^{*}_{\mathrm{solv}} = \Delta G^{\circ}_{\mathrm{solv}} - RT\ln(\tilde{R}T) = \Delta G^{\circ}_{\mathrm{solv}} - 1.9\ \mathrm{kcal/mol}, \quad (1)$$

was used to convert the energies between the different standard states [30,37]. The compilation of Abraham and Liszi [33] reports the Gibbs energy of hydration for the anions with reference to a standard state describing the solvation process as the transfer of the solute from ideal gas phase at 1 atm to unit mol fraction solution. The conversion between this reference state and the Ben-Naim definition for the solvation process at 25 °C is given by

$$\begin{aligned}\Delta G^{*}_{\mathrm{solv}} &= \Delta G^{\mathrm{AL}}_{\mathrm{solv}} - RT\ln(d_{\mathrm{w}}RT/M_{\mathrm{w}})\\ &= \Delta G^{\mathrm{AL}}_{\mathrm{solv}} - 4.3\ \mathrm{kcal/mol}, \end{aligned} \quad (2)$$

where $\Delta G^{*}_{\mathrm{solv}}$ is the Gibbs free energy of solvation according to the Ben-Naim definition, $\Delta G^{\mathrm{AL}}_{\mathrm{solv}}$ the Gibbs free energy of hydration in the reference state reported by Abraham and Liszi, d_{w} the density of water under the considered temperature, and M_{w} the molar mass of water [33,38].

The Gibbs free energies of transfer between water and formamide were taken from the Marcus compilations of

Table 1
Experimental data for the Gibbs free energy of hydration $\Delta G^{*}_{\mathrm{hyd}}$, transfer from water to formamide, $\Delta G^{*}_{\mathrm{trans}}$(FA), solvation in formamide, $\Delta G^{*}_{\mathrm{solv}}$(FA), transfer from water to methanol, $\Delta G^{*}_{\mathrm{trans}}$(M), and solvation in methanol, $\Delta G^{*}_{\mathrm{solv}}$(M) for the set of anions

Anion	$\Delta G^{*}_{\mathrm{hyd}}$	$\Delta G^{*}_{\mathrm{trans}}$ (FA)	$\Delta G^{*}_{\mathrm{solv}}$ (FA)	$\Delta G^{*}_{\mathrm{trans}}$ (M)	$\Delta G^{*}_{\mathrm{solv}}$ (M)
F^-	−105.0	+6.0	−99.0 ± 2.0	+4.4	−100.6 ± 2.0
Cl^-	−74.6	+3.3	−71.3 ± 2.0	+3.1	−71.5 ± 2.0
Br^-	−68.6	+2.6	−66.0 ± 2.0	+2.6	−66.0 ± 2.0
I^-	−59.9	+1.7	−58.2 ± 2.0	+1.8	−58.1 ± 2.0
I_3^-	−34.8	−1.7	−36.5 ± 5.0	−3.0	−37.8 ± 5.0
N_3^-	−70.7	+2.6	−68.1 ± 2.0	+2.6	−68.1 ± 2.0
CN^-	−67.6	+3.2	−64.4 ± 2.0	+2.0	−65.6 ± 2.0
SCN^-	−55.3	+1.7	−53.6 ± 5.0	+1.4	−53.9 ± 5.0
NO_3^-	−61.5	–	–	+3.0	−58.5 ± 5.0
ClO_4^-	−51.3	−2.9	−54.2 ± 5.0	+1.5	−49.8 ± 5.0
OH^-	−105.0	–	–	+2.9	−102.1 ± 2.0
CH_3O^-	−95.2	–	–	+1.5	−93.7 ± 2.0
$CH_3CO_2^-$	−77.3	+4.8	−72.5 ± 2.0	+3.8	−73.5 ± 2.0
$PhCO_2^-$	−71.2	–	–	+1.8	−69.4 ± 2.0
Pic^-	−39.8	−2.3	−42.1 ± 5.0	−1.1	−40.9 ± 5.0
BF_4^-	−33.8	−0.1	−33.9 ± 5.0	–	–
BPh_4^-	+23.5	−5.7	+17.8 ± 5.0	−5.7	+17.8 ± 5.0

Units are kcal/mol.