Hydration of Ionic Species Studied by the Reference Interaction Site Model with a Repulsive Bridge Correction

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Abstract: We have tested the reference interaction site model (RISM) for the case of the hypernetted chain (HNC) and the partially linearized hypernetted chain (PLHNC) closures improved by a repulsive bridge correction (RBC) for ionic hydrated species. We have analyzed the efficiency of the RISM/HNC+RBC and RISM/PLHNC+RBC techniques for decomposition of the electrostatic and the nonpolar hydration energies on the energetic and the enthalpic parts for polyatomic ions when the repulsive bridge correction is treated as a thermodynamic perturbation, and investigate the repulsive bridge effect on the electrostatic potential induced by solvent on solute atoms. For a number of univalent and bivalent atomic ions, molecular cations, and anions, the method provides hydration energies deviating only by several percents from the experimental data. In most cases, the enthalpic contributions to the free energies are also close to the experimental results. The above models are able to satisfactory predict the hydration energies as well as the electrostatic potential around the ionic species. For univalent atomic ions, they also provide qualitative estimates of the Samoilov activation energies.


Key words: electrostatic solvent response; reference interaction site model; density functional theory

Introduction

Ion hydration is one of the most fundamental physicochemical processes occurring in chemical and biological systems. Many efforts have been spent for theoretical and experimental studies of ion hydration properties1–4 and various theoretical methods have been developed to investigate solvation effects. The dielectric continuum model5 treats solvent molecules in an implicit way, while molecular simulations6,7 and methods based on the integral equation theory (IET)8–32 are considered as explicit solvation models. Although the molecular simulations are more realistic and give the most reliable insight into microscopic processes, they dramatically increase the computational time required for the calculations. The IET provides an alternative “low-cost” technique for treating molecular effects in liquids.8–32 At present there are several approaches based on integral equations. The molecular Ornstein–Zernike (MOZ) theory is the method to calculate three-dimensional (3D) solvation structure in molecular liquids. The MOZ theory treats the orientation dependence of intermolecular interactions through the rotational invariant expansions of interaction potentials and correlation functions.9 The recent MOZ calculations10–14 have indicated that the theory is able to reproduce the thermodynamic, dielectric, and structural properties for aprotic solvents. Another method is the reference interaction site model (RISM) pioneered by Chandler and Andersen8 and then extended to the polar liquids by the XRISM treatment.17,18 The theory is based on calculations of radial distribution functions (RDF) via the site–site Ornstein–Zernike (SSOZ) integral equation. The theory has been successfully applied to calculate structural and thermodynamic properties of various chemical and biological systems.16,19 Recently, 3D extensions of the RISM theory have been developed to obtain 3D correlation functions of interaction sites of solvent molecules around a solute of arbitrary shape.20–31,33,34

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In the original XRISM procedure, the hypernetted chain closure (HNC) was employed to take into account the nonlinear response of solvent. The advantage of the RISM/HNC approximation resides in the fact it is well suited for the description of liquids containing polar solutes. However, the predictions coming from this method are rather poor for the thermodynamics of hydrophobic solvation and provide only a qualitative picture for the solvation of charged solutes, since the RDF amplitudes responsible for hydrogen bonding are overestimated. Although the 1D HNC closure provides physically reasonable results for polar polyatomic solutes hydrated in water at normal conditions, it can become divergent in the case of a very deep well of the attractive potential between the solute and individual solvent sites. To eliminate this artifact, a partial linearization of the HNC closure (PLHNC) have been proposed in Refs. 26, 27. In fact, it combines the HNC for the region of the density profile depletion and the mean spherical approximation for the regions of enrichment.

Beyond the RISM/HNC and RISM/PLHNC approximations, an additional effective repulsion has to be introduced to account solute steric constrains. The orientational average of the Boltzmann factor for a repulsive core potential of the whole solvent and structural properties of hydrated atomic and molecular ions. Among other quantities we will evaluate the correlation functions by the RISM equation:

\[ G = D + \Delta \mu. \]  

The change in the intramolecular energy \( \Delta E \) is due to the polarization of the solute electron density interacting with the solvent. To estimate this quantity, we employ the linear response theory (LRT) which gives us the following equation:

\[ \Delta E = \frac{1}{2} \sum_{\nu} V_{\nu} \Delta q_{\nu}. \]

where \( \Delta q_{\nu} \) is the change in partial charge of the \( \nu \)-site, which is determined as the difference between the partial charges of the solute in vacuum and solvent, respectively, while \( V_{\nu} \) is the electrostatic potential induced by the solvent at the solute \( \nu \)-site. In the case of the water solvent it can be expressed via total solute–oxygen (\( h_{\nu o} \)) and solute–hydrogen (\( h_{\nu h} \)) correlation functions

\[ V_{\nu} = 4\pi n_0 \int_{0}^{\infty} [2q_{\nu} h_{\nu o}(r) + q_{\nu} h_{\nu h}(r)] r \, dr, \]

where \( n_0 \) is the averaged water density, while \( q_{\nu} \) \( h_{\nu o} \) and \( h_{\nu h} \) are hydrogen and oxygen charges of water molecule. We calculate the correlation functions by the RISM equation:

\[ H^{\nu o} = W^{\nu} \ast C^{\nu o} \ast [W^{o} + n_0 H^{o}]. \]  

The superscripts \( v \) and \( u \) refer to the solvent and the solute, respectively, the symbol \( \ast \) corresponds to the convolution integration, the matrix elements of \( H \) and \( C \) are matrices built from the site–site total and the direct correlation functions, respec-
tively, and \( W \) is the intramolecular correlation matrix. The Fourier transform of the matrix elements of \( W \) is given by \( \tilde{w}_{ij}(k) = \delta_{ij}(1 - \delta_{ij}) \sin(kl_{ij}/k_{B}T) \), where \( i \) and \( j \) denote molecular sites of the same molecule, and \( l_{ij} \) is the intramolecular distance between \( i \) and \( j \) sites. In the above equation, the solvent matrices \( W' \) and \( H' \) do not change during the calculations and we regard them as input data. They are calculated separately and stored in computer memory. Both the matrices \( H \) and \( C \) can be obtained by eq. (4) coupled with a closure relation:

\[
c_{ij}(r) = \exp[-\beta U_{ij}(r) + \gamma_{ij}(r) + B_{ij}(r)] - \gamma_{ij}(r) - 1, \quad j = O, H,
\]

where \( U_{ij}(r) \) is the intermolecular site–site potential, \( \gamma_{ij}(r) = h_{ij}(r) - c_{ij}(r) \) is the indirect correlation function, \( B_{ij}(r) \) is a bridge function, \( \beta = (k_{B}T)^{-1} \) where \( k_{B} \) is the Boltzmann constant, and \( T \) is the absolute temperature. The case \( B = 0 \) corresponds to the HNC closure. The PLHNC\(^{26,27} \) applies linearization of the exponent in (5) depending on the sign of the index \( I_{ij}(r) = -\beta U_{ij}(r) + \gamma_{ij}(r) + B_{ij}(r) \):

\[
c_{ij}(r) = \exp[I_{ij}(r)] - \gamma_{ij}(r) - 1, \quad I_{ij}(r) < 0,
\]

\[
c_{ij}(r) = -\beta U_{ij}(r) \quad \text{if} \quad I_{ij}(r) > 0.
\]

The solute–solvent intermolecular potentials are represented by the Lennard–Jones (LJ) and the coulomb terms:

\[
U_{ij}(r) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] + \frac{q_{i}q_{j}}{r}.
\]

The LJ parameters \( \sigma_{ij} \) and \( \epsilon_{ij} \) are determined according to the standard combining rules, \( \sigma_{ij} = (\sigma_{i} + \sigma_{j})/2 \) and \( \epsilon_{ij} = \sqrt{\epsilon_{i}\epsilon_{j}} \).

To complete the expression for the hydration energy (1) we should derive the expression for the excess chemical potential \( \Delta \mu \) via correlation functions. In the case of HNC approximation, there is an explicit formula for \( \Delta \mu^{46} \):

\[
\beta \Delta \mu = -4\pi n_{0} \sum_{ij} \int_{0}^{\infty} \left[ c_{ij}(r) + \frac{1}{2} c_{ij}(r) h_{ij}(r) - \frac{1}{2} h_{ij}(r) \right] r^{2} dr,
\]

while for the PLHNC it is expressed as\(^{26} \)

\[
\beta \Delta \mu_{\text{PLHNC}} = -4\pi n_{0} \sum_{ij} \int_{0}^{\infty} \left[ c_{ij}(r) + \frac{1}{2} c_{ij}(r) h_{ij}(r) - \frac{1}{2} h_{ij}(r) \Theta(-h_{ij}(r)) \right] r^{2} dr.
\]

The Kirkwood charging formula\(^{47} \) can be employed in the general case, it is written in the site–site formalism as:

\[
\Delta \mu = 4\pi n_{0} \sum_{ij} \int_{0}^{\infty} \int_{0}^{\infty} \left[ 1 + h_{ij}(r, \lambda) \right] \frac{\partial U_{ij}(r, \lambda)}{\partial \lambda} r^{2} dr,
\]

where \( \lambda \) is the coupling parameter. This relation requires calculation of solute–solvent correlation functions \( h_{ij}(r, \lambda) \) at different values of \( \lambda \). Typically, two coupling parameters \( \lambda_{\text{elel}} \) and \( \lambda_{\text{el}} \) are introduced to calculate the nonpolar and the electrostatic free energy contributions, respectively.\(^{28} \) The former is considered as a scaling factor of the LJ radius, i.e., \( \sigma_{ij}(\lambda_{\text{elel}}) = \lambda_{\text{elel}} \sigma_{ij}(\lambda_{\text{el}}) \) while the coupling parameter \( \lambda_{\text{el}} \) is introduced as a scaling factor of the solute charge, \( q_{i} (\lambda_{\text{el}}) = \lambda_{\text{el}} q_{i} \). Thus, we express \( \Delta \mu \) as

\[
\Delta \mu = \Delta \mu_{\text{elel}} + \Delta \mu_{\text{el}}, \quad \Delta \mu_{\text{el}} = \sum_{ij} q_{i} \int_{0}^{\infty} V_{0}(\lambda_{\text{el}} q_{i}) d\lambda_{\text{el}}.
\]

Using linear approximation for integration over \( \lambda_{\text{el}} \), we rewrite it as

\[
\Delta \mu_{\text{el}} \approx \sum_{ij} q_{i} \left[ V_{0}(0) + \frac{q_{i}^{2}}{2} V'_{0} \right],
\]

where \( V_{0} \) is the matrix of the approximating coefficients, while \( V_{0}(0) = V_{0}(q_{i} = 0) \) is the nonzero potential arising even for nonpolar solute due to different distribution of oxygen and hydrogen sites of water molecules around the solute. It is responsible for asymmetry of solvation of cations and anions.\(^{48–50} \) The matrix \( V'_{0} \) is inverted to the charge response kernel \( \partial V_{0}/\partial q_{i} b_{ij} \). The latter is quite useful for assigning partial charges and to before overcome the ill-posed nature of the ESP fitting procedure.\(^{51} \) If the matrix \( V_{0} = \partial V_{0}/\partial q_{i} b_{ij} \) is charge independent, we have quadratic dependence of the solvation energy on the solute charge, which corresponds to the LRT approach. In general case, the dependence \( V_{0}(\lambda_{\text{el}}) \) is smooth and can be estimated with the use of few intermediate points of integration.

To reduce the overestimated hydrogen bonding in the RISM/HNC(PLHNC) models we use the repulsive bridge correction (RBC)\(^{29} \) in the corresponding closures:

\[
\exp[-B_{ij}(r)] = \prod_{ij} w_{ij}(r) \exp \left[ -4\beta c_{ij}^{46}(\frac{\sigma_{ij}}{r})^{12} \right].
\]

Such correction factor has been proposed for the 3D orientational reduction of the MOZ equation for an one-component molecular liquid.\(^{22} \) Similar empirical bridge corrections have been also employed to treat hydration of organic molecules by the 3D RISM scheme\(^{28} \) as well as to evaluate electronic structure of organic solutes by the combined 3D RISM/QM method.\(^{52} \) Kovalenko and Hirata\(^{29} \) proposed to take the repulsive core as the repulsive bridge correction factor (RBC)\(^{29} \) in the corresponding closures:

\[
\beta \Delta \mu_{\text{elel}} = \beta \Delta \mu_{\text{elel}}^{\text{HNC}} + 4\pi n_{0} \sum_{ij} \int_{0}^{\infty} g_{ij}(r) \exp[-B_{ij}(r)] - 1] r^{2} dr,
\]

where the coupling parameter \( \lambda_{\text{elel}} \) is calculated by the perturbation scheme proposed in Ref. 29.
In the case one does not need to calculate the derivative functions of only the solute–solvent interactions: these contributions is to express the excess chemical potential as each step of the temperature increase. Another way to calculate But this definition demands calculations of the solvent RDFs on of hydrated hydrophobic and polar organic solutes.29,53

exactly counterbalanced by a term in the solvation entropy. which does not contribute to the chemical potential since it is

OPLS force field,54,55 they are listed in Table 1 where we have

used the notations similar to that in Ref. 55. The small Lennard–Jones parameter \( \sigma_{H_2O} = 0.4 \) Å is attributed to the highly charged hydrogen sites in order to avoid numerical singularities. Although the OPLS force field require the geometric combination rule for the LJ solute–solvent parameters, we have employed the arithmetic rules described above, because the geometric rule results in the small size of hydrogen and hence to abnormal hydrogen bonding.

Since the hydration of ionic species depends significantly on the values of partial charges of solute atoms, we have derived the solute charges using QM calculations instead of direct use of the OPLS charges for the relevant molecular ions. To derive the partial atomic charges of the solutes, we have implemented the Kollman procedure56 with the deMon program based on the linear combination of Gaussian-type orbitals.57 This method is able to evaluate the charges by fitting the electrostatic potential (ESP). The ESP procedure leads to the following expression of the electronic charges58:

\[
q_i^{(e)} = - \sum_j D_{ij} r(PA)_j - \xi \sum_j D_{ij},
\]

where the matrix \( D \) is the inverse of the matrix whose elements are \( \sum_i \phi_i / \partial r_j, \delta r_{ij} \), where \( \delta r_{ij} = |r_i - r_j| \) is the distance between the grid point \( i \) and the solute atom \( j \), while \( \phi_i \) is its weight, \( P \) is the self-consistent density matrix and \( A \) is the supermatrix whose elements are:

\[
A_{ij}(\mathbf{r}) = \sum_j \phi_i \mathbf{\phi}_j \left( \frac{1}{|\mathbf{r} - \mathbf{r}_j|} \right),
\]

where \( \phi_i \) are the contracted cartesian gaussian functions. The Lagrange multiplier \( \xi \) can be expressed as:

\[
\xi = \frac{-\sum_i D_{ij} r(PA)_i - N_r}{\sum_i D_{ij}},
\]

Table 1. LJ Parameters and Atomic Charges for Molecular Ions.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Site</th>
<th>( \sigma(\text{Å}) )</th>
<th>( \epsilon(\text{kcal} / \text{mol}) )</th>
<th>( q )</th>
<th>( \Delta q )</th>
<th>Solute</th>
<th>Site</th>
<th>( \sigma(\text{Å}) )</th>
<th>( \epsilon(\text{kcal} / \text{mol}) )</th>
<th>( q )</th>
<th>( \Delta q )</th>
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<td>H_2O^+</td>
<td>HW</td>
<td>0.4</td>
<td>0.046</td>
<td>+0.518</td>
<td>+0.025</td>
<td>OH^-</td>
<td>HW</td>
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<td>0.046</td>
<td>+0.2463</td>
<td>-0.095</td>
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<tr>
<td></td>
<td>OW</td>
<td>3.166</td>
<td>0.1554</td>
<td>-0.559</td>
<td>-0.076</td>
<td></td>
<td>OW</td>
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<td>+0.071</td>
</tr>
<tr>
<td>NH_4^+</td>
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<td>1.2</td>
<td>0.0157</td>
<td>+0.4683</td>
<td>-0.009</td>
<td>NH_3^+</td>
<td>H</td>
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<td>0.0157</td>
<td>+0.2021</td>
<td>+0.087</td>
</tr>
<tr>
<td></td>
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<td>-0.8732</td>
<td>+0.038</td>
<td></td>
<td>N3</td>
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<td>0.17</td>
<td>-1.4042</td>
<td>-0.173</td>
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<tr>
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<td>0.086</td>
<td>-0.5693</td>
<td>+0.066</td>
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<tr>
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<td>-0.066</td>
<td>Cl</td>
<td>Cl</td>
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</tr>
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<td>0.046</td>
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<td>+0.071</td>
<td>HCC^-</td>
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<td>0.086</td>
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<tr>
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<td></td>
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<td>3.816</td>
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<tr>
<td>CH_3O^-</td>
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<td>0.3</td>
<td>+0.2024</td>
<td>-0.045</td>
<td>CHOO^-</td>
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<td>0.086</td>
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<tr>
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<tr>
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<td>-0.0741</td>
<td>0.049</td>
<td></td>
<td>HCl</td>
<td>2.5</td>
<td>0.03</td>
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</tr>
<tr>
<td>(CH_3)C^+</td>
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<td>3.55</td>
<td>0.07</td>
<td>+0.5588</td>
<td>+0.085</td>
<td>CH_3S^-</td>
<td>S</td>
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<td>0.5</td>
<td>-0.9352</td>
<td>-0.108</td>
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<td></td>
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<td>CH_3NH_3^-</td>
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<td>0.17</td>
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<td>+0.098</td>
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<tr>
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<td>-0.7809</td>
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<td></td>
<td>HCl</td>
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<tr>
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</tr>
</tbody>
</table>

where the correlation functions are taken at zero bridge function \( B_{ij}(r) = 0 \), and \( \Delta S^{\text{HNC}} \) is calculated by (8). The perturbation treatment is essentially simpler and faster than the complete thermodynamic integration, but provides reasonable accuracy for evaluations of hydrated hydrophobic and polar organic solutes.29,53

To describe the solvation properties, we decompose the excess chemical potential into the enthalpic and the entropic contributions. Since experiments are most commonly done at fixed pressure \( p \), it is convenient to decompose the hydration chemical potential into the excess solvation entropy \( \Delta S \) and the excess solvation enthalpy \( \Delta H \) in the following manner:

\[
\Delta S = \left( \frac{\partial \Delta H_{\text{solv}}}{\partial T} \right)_p, \quad \Delta E_s = \Delta \mu + T \Delta S. \tag{14}
\]

But this definition demands calculations of the solvent RDFs on each step of the temperature increase. Another way to calculate these contributions is to express the excess chemical potential as a sum of an energetic term and an entropic one which are both functions of only the solute–solvent interactions:

\[
\Delta E_{\text{solv}} = n_0 \sum_{nj} \int g_{nj}(r) U_{nj}(r) dr, \quad T \Delta S_a = \Delta E_{\text{solv}} - \Delta \mu. \tag{15}
\]

In the case one does not need to calculate the derivative \( \partial \Delta \mu / \partial T \) and, therefore, the integral (15) can be easily evaluated. The difference \( \Delta E_s - \Delta E_{\text{solv}} \) is the reorganization energy of the solvent, which does not contribute to the chemical potential since it is exactly counterbalanced by a term in the solvation entropy.

Computational Details

We have tested our approach for different atomic and molecular ions. The LJ parameters of the ions have been derived from the OPLS force field,54,55 they are listed in Table 1 where we have
where $N_e$ is the total number of the electrons. The extra grid points inside the 1.4 van-der-Waals radius were removed to avoid ESP singularities near to the nuclear position of the solute. We excluded also the grid points outside the 2.0 van-der-Waals radius because the ESP integration over them do not influence numerically the charge values. The ESP calculations were carried out using a fixed Lebedev grid of 99 radial shell points and 590 angular points for each shell. All calculations have been performed at local density approximation (LDA) level using the exchange correlation functional derived by Vosko et al.\textsuperscript{58} and double zeta for valence electrons plus one polarized function (DZVP)\textsuperscript{59} as basis set. To avoid calculations of the four-center coulomb integrals, Gaussian-type auxiliary A2 functions have been used. The numerical calculation of the density was performed employing directly the DZVP basis set for the numerical integration of the exchange correlation functional.

Although the self-consistent reaction field (SCRF) procedure can be adopted to evaluate the solvent-field solute charge polarization, the earlier estimates\textsuperscript{45} have indicated the contribution of the polarization energy to the hydration free energy to be small for the considered charged species, therefore one can apply less sophisticated procedure to evaluate this contribution. In this work we have used more simplified LRT version and applied the Polarizable Continuum Model (PCM) to estimate the polarization contribution. Comparison of the PCM and the RISM-SCF evaluations\textsuperscript{60} have indicated that both the methods predict similar mean force potentials, but there is a difference in the calculated polarization energies. Some advanced models\textsuperscript{42} could be more accurate for evaluating partial charges, but, as a whole, the influence of the procedure evaluating partial charges on the free energy of the studied charges species is to be minor (see the next section).

Table 1 reports the difference between the solute gas-phase charges and the solute SCRF charges calculated by the Kollman method.\textsuperscript{58} Although the deviation of the calculated charges from that parameterized by the OPLS\textsuperscript{55} is about 10–15% it essentially affects the polarization energy $\Delta E$ of solutes.

The ESP charges were used as input data for RISM calculations. We employed the modified version of the extended simple point charge model for water.\textsuperscript{61} The water density $\rho_0$ is assumed to be equal to 0.997 g/cm$^3$ at room temperature. For calculation of water RDFs we used a reformulation of the RISM with dielectric corrections.\textsuperscript{62,63} For accurate screening of the long-range interactions within the framework of this method, the intermolecular Coulomb potential $q_iq_j/r$ is rescaled as $A(\varepsilon)q_iq_j/r$ where the scalar factor $A$ is defined via the phenomenological dielectric constant $\varepsilon$ and the dipole moment $m$ of the water molecule as

$$A = \frac{1 + \varepsilon(3y - 1)}{3y(\varepsilon - 1)}, \quad y = \frac{4\pi\beta\rho_m^2}{9}. \quad (19)$$

We notice that this procedure is only applied for the solvent–solvent interaction potential, the solute–solvent Coulomb potential remains unchanged. This approach makes use of the known asymptotic form of the correlation functions and, in general, more sophisticated nontrivial closures can be applied.\textsuperscript{64}

The solute–solvent correlation functions for pure water have been calculated by the wavelet-based algorithm\textsuperscript{65–67} before fitting the charges and calculations of solute–solvent correlation functions. The method proposes an expansion of site–site correlation functions into the wavelet series and further calculations of the approximating coefficients. To solve the integral equations we have applied the hybrid scheme in which the coarse part of the solution is calculated by wavelets with the use of the Newton-Raphson (NR) procedure, while the fine part is evaluated by the direct iterations. The Coifman 2 basis set is employed for the wavelet treatment of the coarse solution. We generated wavelets with $n = 4096$ grid points and $\delta r = 0.02645$ Å step size, the number of approximating coefficients $s_{max}$ is equal to 25 for each site–site correlation function, while the level of resolution is $j_0 = 4$. As well as in the conventional scheme, to speed up convergence we have initially solved RISM equations for uncharged solute species and then we have repeated the same calculations by increasing the charge using the previous solution as an initial guess. The system was gradually charged up to the target charge. The set is solved iteratively until the required accuracy is achieved. The precision parameter determining the measure of the accuracy is the root mean square residual equal to $10^{-6}$ for the NR loop and to $10^{-5}$ for the Picard iterations.\textsuperscript{65,67} The electrostatic contribution $\Delta E_{el}$ to the free energy is calculated with the use of the charging procedure at five different values of coupling parameter $\lambda_{el}$.

Results and Discussion

Earlier, we have calculated the hydration free energies of atomic and molecular ions by the RISM/HNC within the OPLS force field,\textsuperscript{68,69} and indicated that the RISM/HNC model overestimates systematically the absolute values of hydration free energy for anions, and underestimates that for cations by 20–40%. Moreover, the RISM/HNC procedure is not convergent in several cases. All these effects are due to overestimation of RDF amplitudes responsible for hydrogen bonding. The discrepancy becomes to be more pronounced for small sized solutes where hydrogen bonding effect is stronger. In this paper, we have calculated the hydration energy for the series of atomic and molecular ions by the HNC+RBC and PLHNC+RBC models and decomposed the hydration energies into the enthalpic and entropic parts. Table 2 lists the calculated hydration energies, the enthalpys, and the entropies for atomic ions and the corresponding experimental data.\textsuperscript{65,70} There is a difference between the enthalpic and energetics parts due to the difference in the entropic changes at constant pressure and volume, i.e., $\Delta H = \Delta H - \Delta E_{v} = Tz_n\delta\partial\Delta\mu/\partial\delta n_0$, where $z$ is the isobaric thermal expansion coefficient of pure water. Since the difference is small under normal conditions (several kcal/mol) and comparable with the accuracy of our calculations, we ignore it to simplify the evaluations of the enthalpic changes. As it is seen, the models underestimate absolute values of the hydration energy for atomic ions. The predictive capabilities of the method decrease for very small and very large ionic solutes. The average error does not exceed 6%; however, the discrepancy becomes up to 20% in the case of $Cs^+$. The calculated electrostatic contribution to the
hydration entropy is a good agreement with the experimental data; however, the calculated total entropies deviate sufficiently from the experiment. This artefact is supposed to be mainly caused by inaccurate evaluations of the entropic part of nonelectrostatic contribution $\Delta_{nt}$. The agreement between the calculated and experimental results is better for cations than for anions due to minor effect of hydrogen bonding in the first case. Although the RISM/HNC model provides less deviation from the experiment than that obtained by the RISM/PLHNC model, the difference between these two models is insignificant.

To reveal structural properties of the atomic ions, we follow the idea of Hirata and Chong and calculate the activation energy required to strip a water molecule away from the first solvation shell of an atomic ion as compared to that for another water molecule to its next coordination shell, which is evaluated via force potential (mfp). Finally, the relative activation energy $D_{nl}$ of a water molecule in an ion coordination shell is calculated as $D_{nl} = E_{nl} - E_0$, where $E_0$ is the activation energy of a water molecule transferring from a first shell around another water molecule to its next coordination shell, which is evaluated via the corresponding hydrogen–oxygen mfp of pure water. Table 3 lists the results calculated by the PLHNC+$\text{RBC}$ model and the Samoilov data on the activation energies extracted from the viscosity experiments for various hydrated ions. As it is seen, there is qualitative agreement between the experimental and the calculated data for monovalent ions. The theory overestimates the activation energies by 0.4 kcal/mol for atomic cations and calculated data for monovalent ions. The theory overestimates the activation energies by 0.4 kcal/mol for atomic cations and nonlectrostatic contributions are less satisfactory for both the model and 3D evaluations.

We have also calculated the hydration energies, the enthalpies, and the entropies for polyatomic ions. Table 4 lists the experimental results and data calculated by the PLHNC+$\text{RBC}$ and HNC+$\text{RBC}$ models. Although the theory overestimates the absolute values of hydration energy for polyatomic cations and underestimates for polyatomic anions, the average deviation does not exceed 6%. The difference between the calculated and experimental hydration energies increases for very small and very large ionic solutes like as for atomic ions. The evaluations of the entropic contributions are less satisfactory for both the HNC+$\text{RBC}$ and the PLHNC+$\text{RBC}$ models. The influence of intramolecular solute contribution $\Delta_{nl}$ and nonlectrostatic contribution $\Delta_{nt}$ are small with respect to the electrostatic one $\Delta_{el}$. Such behavior is typical for ionic systems and has been reported before. Table 5 proves this effect, indicating the electrostatic

### Table 2. The Experimental and Electrostatic and Nonelectrostatic Contributions (in Parenthesis) to the Total Excess Chemical Potential, the Enthalpies, and the Entropies for Hydrated Atomic Ions (kcal/mol), Calculated by the PLHNC+$\text{RBC}$ and the HNC+$\text{RBC}$ Models.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$-\Delta G$</th>
<th>$-\Delta E_{nl}$</th>
<th>$-\Delta S$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HNC</td>
<td>PLHNC</td>
<td>Exp</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>107.3 (–0.6)</td>
<td>105.5 (–1.1)</td>
<td>122.1</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>89.9 (–2.7)</td>
<td>89.2 (–3.3)</td>
<td>94.8</td>
</tr>
<tr>
<td>K$^+$</td>
<td>76.2 (–6.2)</td>
<td>75.9 (–6.9)</td>
<td>80.6</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>71.6 (–8.2)</td>
<td>71.4 (–8.9)</td>
<td>75.5</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>65.2 (–12.1)</td>
<td>65.2 (–12.9)</td>
<td>67.8</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>426.4 (2.4)</td>
<td>418.3 (1.5)</td>
<td>454.2</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>364.6 (1.2)</td>
<td>357.6 (0.1)</td>
<td>379.5</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>333.2 (–1.6)</td>
<td>329.2 (–2.6)</td>
<td>339.7</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>304.9 (–4.1)</td>
<td>302.4 (–5.2)</td>
<td>314.0</td>
</tr>
<tr>
<td>F$^–$</td>
<td>117.9 (1.9)</td>
<td>116.4 (0.5)</td>
<td>107.0</td>
</tr>
<tr>
<td>Cl$^–$</td>
<td>81.3 (–5.5)</td>
<td>81.1 (–6.9)</td>
<td>78.1</td>
</tr>
<tr>
<td>Br$^–$</td>
<td>79.0 (–6.7)</td>
<td>78.9 (–8.0)</td>
<td>69.2</td>
</tr>
<tr>
<td>I$^–$</td>
<td>69.3 (–10.8)</td>
<td>69.2 (–12.2)</td>
<td>60.3</td>
</tr>
</tbody>
</table>

### Table 3. The Calculated (PLHNC+$\text{RBC}$) and the Experimental Activation Energies (kcal/mol) for Various Hydrated Ions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Mg$^{2+}$</th>
<th>Ca$^{2+}$</th>
<th>Li$^+$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Cs$^+$</th>
<th>Cl$^–$</th>
<th>Br$^–$</th>
<th>I$^–$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLHNC+$\text{RBC}$</td>
<td>3.7</td>
<td>2.4</td>
<td>1.3</td>
<td>0.65</td>
<td>0.1</td>
<td>–0.21</td>
<td>–0.23</td>
<td>–0.28</td>
<td>–0.61</td>
</tr>
<tr>
<td>Exp$^{44}$</td>
<td>2.61</td>
<td>0.45</td>
<td>0.73</td>
<td>0.25</td>
<td>–0.25</td>
<td>–0.33</td>
<td>–0.27</td>
<td>–0.29</td>
<td>–0.32</td>
</tr>
</tbody>
</table>
(S_elect), the nonelectrostatic (S_nonel), and the polarization (S_pol) contributions to the entropies of hydrated ions (kcal/mol). As it is seen, the nonpolar contribution is overestimated. By our opinion, this artefact is caused by that the thermodynamic perturbation theory is not appropriate for estimations in this case, since the main contribution is determined by the cavity effect. In principle, the latter may be eliminated by an appropriate choice of the bridge for the nonelectrostatic part, but the study of this effect is beyond the scope of this paper.

Figures 1 and 2 demonstrate the correlations between the computed and the experimental hydration energies and enthalpies for molecular and atomic ions, respectively. Therefore, the HNC+RBC and PLHNC+RBC models are satisfactory to estimate hydration energies of molecular and atomic ions, since it provides the hydration energies for the selected ions within 5–10% of accuracy. Although our results are dependent on the force field parameters, we believe that this drawback can be eliminated by an appropriate choice of the bridge functions. A "smart" strategy for making this choice will be a matter of our forthcoming study.

We have also studied how the improved RISM models treat the electrostatic properties of hydrated ions. Figure 3 shows the comparison of the data on the distance dependence of the electrostatic potential $\Phi(r) = 8\pi n_0 \int_{r}^{\infty} [h_{\text{tot}}(r) - h_{\text{tot}}(r)]rdr$ of Br$^-$ hydrated in water under normal conditions. Although the RDFs calculated by integral equations are different from what obtained by the MD with the use of the GROMACS package

<table>
<thead>
<tr>
<th>Ion</th>
<th>HNC</th>
<th>PLHNC</th>
<th>EXP</th>
</tr>
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<tr>
<td>OH$^-$</td>
<td>119.5</td>
<td>118.3</td>
<td>110.0</td>
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<td>CN$^-$</td>
<td>81.6</td>
<td>81.6</td>
<td>75.0</td>
</tr>
<tr>
<td>OCl$^-$</td>
<td>83.8</td>
<td>83.6</td>
<td>80.7</td>
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<tr>
<td>NH$_4^+$</td>
<td>86.8</td>
<td>84.0</td>
<td>81.0</td>
</tr>
<tr>
<td>HCOO$^-$</td>
<td>84.1</td>
<td>84.4</td>
<td>80.0</td>
</tr>
<tr>
<td>CH$_3$O$^-$</td>
<td>99.2</td>
<td>89.8</td>
<td>95.2</td>
</tr>
<tr>
<td>HCC$^-$</td>
<td>87.7</td>
<td>87.6</td>
<td>76.1</td>
</tr>
<tr>
<td>NH$_2^+$</td>
<td>108.7</td>
<td>108.2</td>
<td>92.3</td>
</tr>
<tr>
<td>HO$_2^+$</td>
<td>103.5</td>
<td>103.0</td>
<td>97.3</td>
</tr>
<tr>
<td>H$_3$O$^+$</td>
<td>103.1</td>
<td>99.5</td>
<td>105.0</td>
</tr>
<tr>
<td>CH$_3$COO$^-$</td>
<td>86.6</td>
<td>87.9</td>
<td>80.0</td>
</tr>
<tr>
<td>CH$_3$S$^-$</td>
<td>75.2</td>
<td>75.1</td>
<td>76.0</td>
</tr>
<tr>
<td>CH$_3$NH$_3^+$</td>
<td>59.4</td>
<td>59.4</td>
<td>71.0</td>
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Table 4. The Experimental$^{45,70}$ and the Electrostatic (S_elect), Nonelectrostatic (S_nonel), and the Polarization (S_pol) Contributions (in Parenthesis) to the Total Excess Chemical Potential, and the Enthalpies for Hydrated Polyatomic Ions (kcal/mol), Calculated by the PLHNC+RBC and the HNC+RBC Models.

<table>
<thead>
<tr>
<th>Ion</th>
<th>HNC</th>
<th>PLHNC</th>
<th>EXP</th>
</tr>
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<tr>
<td>OH$^-$</td>
<td>12.7</td>
<td>11.1</td>
<td>2.4</td>
</tr>
<tr>
<td>CN$^-$</td>
<td>3.9</td>
<td>3.8</td>
<td>3.0</td>
</tr>
<tr>
<td>OCl$^-$</td>
<td>7.2</td>
<td>6.9</td>
<td>5.6</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>4.8</td>
<td>3.7</td>
<td>2.0</td>
</tr>
<tr>
<td>HCOO$^-$</td>
<td>5.6</td>
<td>5.3</td>
<td>2.1</td>
</tr>
<tr>
<td>CH$_3$O$^-$</td>
<td>9.9</td>
<td>9.4</td>
<td>2.7</td>
</tr>
<tr>
<td>HCC$^-$</td>
<td>7.3</td>
<td>7.1</td>
<td>3.6</td>
</tr>
<tr>
<td>NH$_2^+$</td>
<td>11.0</td>
<td>10.3</td>
<td>3.1</td>
</tr>
<tr>
<td>HO$_2^+$</td>
<td>10.4</td>
<td>9.7</td>
<td>2.1</td>
</tr>
<tr>
<td>H$_3$O$^+$</td>
<td>4.7</td>
<td>4.9</td>
<td>1.8</td>
</tr>
<tr>
<td>CH$_3$COO$^-$</td>
<td>7.4</td>
<td>7.1</td>
<td>4.0</td>
</tr>
<tr>
<td>CH$_3$S$^-$</td>
<td>4.1</td>
<td>4.1</td>
<td>5.7</td>
</tr>
<tr>
<td>CH$_3$NH$_3^+$</td>
<td>1.6</td>
<td>1.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 5. The Experimental$^{45}$ and the Calculated Electrostatic (S_elect), Nonelectrostatic (S_nonel), and the Polarization (S_pol) Contributions to the Entropies of Hydrated Polyatomic Ions (kcal/mol).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>HNC</th>
<th>PLHNC</th>
<th>EXP</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH$^-$</td>
<td>12.7</td>
<td>11.1</td>
<td>2.4</td>
</tr>
<tr>
<td>CN$^-$</td>
<td>3.9</td>
<td>3.8</td>
<td>3.0</td>
</tr>
<tr>
<td>OCl$^-$</td>
<td>7.2</td>
<td>6.9</td>
<td>5.6</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>4.8</td>
<td>3.7</td>
<td>2.0</td>
</tr>
<tr>
<td>HCOO$^-$</td>
<td>5.6</td>
<td>5.3</td>
<td>2.1</td>
</tr>
<tr>
<td>CH$_3$O$^-$</td>
<td>9.9</td>
<td>9.4</td>
<td>2.7</td>
</tr>
<tr>
<td>HCC$^-$</td>
<td>7.3</td>
<td>7.1</td>
<td>3.6</td>
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<tr>
<td>NH$_2^+$</td>
<td>11.0</td>
<td>10.3</td>
<td>3.1</td>
</tr>
<tr>
<td>HO$_2^+$</td>
<td>10.4</td>
<td>9.7</td>
<td>2.1</td>
</tr>
<tr>
<td>H$_3$O$^+$</td>
<td>4.7</td>
<td>4.9</td>
<td>1.8</td>
</tr>
<tr>
<td>CH$_3$COO$^-$</td>
<td>7.4</td>
<td>7.1</td>
<td>4.0</td>
</tr>
<tr>
<td>CH$_3$S$^-$</td>
<td>4.1</td>
<td>4.1</td>
<td>5.7</td>
</tr>
<tr>
<td>CH$_3$NH$_3^+$</td>
<td>1.6</td>
<td>1.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>
the difference between the HNC+RBC and the MD data are minor. We have used the geometric rule for solute–solvent diameter $\sigma_{w}$, to compare the results with the MD data obtained by GROMACS with the OPLS force field. In contrast to the simple HNC closure the bridge correction is able to provide accurate calculations for the electrostatic potential at small distances.

To analyze the charge effect on the electrostatic potential, we have calculated the potential versus the charging parameter. The dependence of electrostatic potential on the charging parameter is close to the linear one, slightly deviating from the linear behavior at small solute charges. The employment of the repulsive bridge does not change qualitatively this behavior, although the nonlinear effects become more pronounced. Figure 4 shows the derivative of the electrostatic potential versus the charging parameters $\lambda_{cl}$ for $\text{NH}_4^+$ and $\text{OH}^-$ ions. As it is seen, this dependence is well approximated by the third-order polynomial like as for atomic charged solutes (see for example Fig. 4 in Ref. 75). But the approximating coefficients are quite different for anions and cations. Such behavior clearly indicates the asymmetry of the hydration for anions and cations; however, few universal classes of hydrated ions can be revealed. Such universal classes have been previously studied by MD for atomic ions. 76

We have also compared the accuracy of the computation of electrostatic potential. Figure 5 demonstrates the correlation

*Figure 1.* The computed (RISM/PLHNC+RBC) versus the experimental $^{45,70}$ hydration free energies for (in kcal/mol) for molecular and atomic ions. The atomic ions are indicated by open circles, while the polyatomic ones by filled circles.

*Figure 2.* The computed (RISM/HNC+RBC) versus experimental $^{45}$ hydrationenthalpies for molecular and atomic ions (in kcal/mol). The notions are the same as in Figure 1.

*Figure 3.* The distance dependence of the electrostatic potential $\Phi(r)$ measured in atomic units for $\text{Br}^-$ ion hydrated in water under normal conditions. The solid curve corresponds to the MD calculations, while the dashed one to the RISM/HNC+RBC, while the dotted one to the HNC evaluations. The inset shows the RDF $h_{\text{BrH}}(r)$ of $\text{Br}^-$ hydrated in water under normal conditions.

*Figure 4.* The derivative $V' = \partial V/\partial \lambda$ of the electrostatic potential with respect to the charge versus charging parameters $\lambda_{cl}$. Solid line corresponds to nitrogen in $\text{NH}_4^+$, while the dashed one to oxygen in $\text{OH}^-$. 

*Figure 5.* The correlation...
between calculations of absolute values of the electrostatic potential at atoms of molecular ions. The QM calculations are provided by the PCM, the RISM data by the HNC+RBC models. Thus, using the 1D RISM/HNC+RBC and the 1D RISM/PLHNC+RBC models we evaluated systematically the structural and thermodynamic properties for series of hydrated atomic and molecular ions. We have shown that the above models are able to satisfactorily predict the hydration energies as well as the electrostatic potential around the charged solutes. For univalent atomic ions, they provide qualitative estimates of the Samoilov activation energy. Although the evaluations of nonelectrostatic entropic contributions are not in agreement with that obtained by the QM methods, we believe that this drawback can be eliminated by an additional parameterization of the repulsive bridge similar to that has been done in Ref. 28.

The advantage of the models is that they operate only with the radial distributions of the solvent atoms around solute sites and, therefore, are essentially simpler and faster than the 3D RISM treatment. Within the framework of the models we have to evaluate only $\Delta H_{\text{abs}}$, $V_{\text{el}}(0)$, and $V_{\text{el}}$ for computing the solvation free energy of ions. This can be done before quantum computations and then stored. More sophisticated analysis of the accuracy of different hybrid RISM-SCF methods will be presented in the forthcoming paper.

References

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