

Contributions from Dispersion and Born Self-Free Energies to the Solvation Energies of Salt Solutions

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That the Born theory provides an accurate means of calculating solvation energies of ions in water has been demonstrated by Rashin and Honig (Rashin, A. A.; Honig, B. *J. Phys. Chem.* **1985**, 89, 5588). They could fit the experimental solvation energies of a number of salts nicely by a simple increase of 7% in the expected radii of all ions. However, as we demonstrate herein, there is an important previously ignored contribution due to the ionic dispersion self-free energy. The ionic parameters necessary to estimate the different contributions to solvation energy are the ionic radii, the ionic polarizabilities, and the ionization potentials. Whereas the polarizabilities and ionization potentials of a number of salts have recently been derived ab initio (in both vacuum and water), the appropriate choices of radii are less well-known. We pursue two different approaches to assign the ionic radii. In the first approach, we find that an increase of all expected radii by 23% gives reasonable agreement between theory and experiment (to within 6%). In the second approach, we increased the expected radii of six ions separately (10–30%) to obtain a best fit for the nine salts investigated. In this second approach, the deviations between theory and experiment were less than 0.1%. The essential point is that a proper theory must include contributions from both electrostatic (Born) and electrodynamic (dispersion) self-free energies.

I. Introduction

The Born theory¹ has provided a useful means of estimating the solvation energies of salt solutions² and the change in Gibbs free energy when an ion crosses a thin membrane.^{3,4} Rashin and Honig² gave the Born contribution to the solvation free energy of ions in water as

$$\Delta F_{\text{s,Born}} = \frac{e^2}{8\pi\epsilon_0 a} \left(\frac{1 - 1.357}{\epsilon(0)} - 1 \right) \quad (1)$$

where e is the net charge of a monovalent ion, a is the radius, and $\epsilon(0) = 80$ is the dielectric constant of water (and 1.357 is a correction² to the original Born formula that is due to the temperature dependence of the dielectric constant of water, valid in water at 298 K). It has been traditional to use ionic radii derived from crystal structures in the Born formula. Rashin and Honig² argued that the expected radius should be the covalent radius for cations and the ionic radius for anions. They then demonstrated that they could obtain good results for the heats of solvation for a large number of salts if these expected radii were increased by 7% for all ions.

However, the good agreement between theory and experiment obtained by Rashin and Honig is misleading. There is an additional, previously ignored, contribution that is a quantum electrodynamic dipolar polarization analogue of the electrostatic Born self-free energy. For consistency, this ionic dispersion self-free energy has to be included on the same level as the

electrostatic Born self-free energy (this is similar to the separation between electrostatic and electrodynamic forces in double layer theory that was shown to be incorrect by Ninham et al.^{5,6}). It is incorrect in that one part is treated in a linear theory and the other in a nonlinear approach. We demonstrate herein that, when this previously ignored contribution is included, the expected radius must be increased by 10–30% to find good agreement between theory and experiment.

II. Theory

For a long time, high-frequency dispersion interactions acting on ions, between ions and solvent, were totally ignored. It is only very recently that an understanding has emerged strongly that the excess polarizability of an ion has a crucial role.^{5–12} Mahanty and Ninham¹³ developed the concept of dispersion self-energy in atomic systems (with the radial dependence of the polarizability density approximated with a Gaussian function). It is a direct quantum electrodynamic dipolar polarization analogue of the Born electrostatic energy of a charged particle. Ions in both solution and vacuum have a different polarizability than the surrounding media. This means that there will be contributions from the dispersion self-free energy to the total self-free energy in both solution and vacuum. This contribution has to be included for consistency. The only interesting question is whether it makes a noticeable contribution or can, to a good approximation, be ignored. We demonstrate herein that it does indeed make an important contribution. Our analysis includes contributions to the dispersion self-energy from all electromagnetic correlation frequencies. As such, it includes the many-body extension of Keesom (permanent dipole) and Debye (permanent dipole–induced dipole) interactions, as well as

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TABLE 1: Ab Initio Results for Polarizabilities and Ionization Potentials for Various Ions in Vacuum and in Water Derived by Netz¹²

ion	α_{vacuum}^* (Å ³)	α_{water}^* (Å ³)	ω_{vacuum}^1 (rad/s)	ω_{water}^1 (rad/s)
Li ⁺	0.022	−0.04	1.14×10^{17}	6.87×10^{16}
Na ⁺	0.14	−0.11	7.14×10^{16}	4.29×10^{16}
K ⁺	0.81	0.062	4.78×10^{16}	2.74×10^{16}
F [−]	1.01	0.195	5.37×10^{15}	1.20×10^{16}
Cl [−]	3.67	1.63	5.44×10^{15}	1.04×10^{16}
Br [−]	6.61	4.29	5.14×10^{15}	0.98×10^{16}

induced dipole–induced dipole interactions. As such, ion-induced water structural effects are included in principle within the primitive model approximation.

We report here the result for spherically symmetric ions at finite temperature. It is straightforward to extend the result of Mahanty and Ninham¹³ to take into account the effect of surrounding media and finite temperature T . The contribution from dispersion self-free energy to the solvation of ions in water is

$$\Delta F_{\text{s,Disp}} = \frac{4k_{\text{B}}T}{\sqrt{\pi}a^3} \sum_{n=0}^{\infty} \left[\frac{\alpha_{\text{water}}^*(i\omega_n)}{\epsilon(i\omega_n)} - \alpha_{\text{vacuum}}^*(i\omega_n) \right] \quad (2)$$

where k_{B} is Boltzmann's constant and $\alpha^*(i\omega_n)$ is the excess ionic polarizability in a specific medium. The dielectric function of water $[\epsilon(i\omega_n)]$, which depends on temperature, was obtained from experimental optical data and a Kramers–Kronig relationship.¹⁴ The self-free energy change is obtained as a summation over discrete frequencies ($\omega_n = 2\pi k_{\text{B}}Tn/\hbar$), and the prime indicates that the $n = 0$ term carries a weight of $1/2$. The exact value of the numerical prefactor in the dispersion self-free energy is a consequence of the Gaussian form assumed for the polarizability distribution (some changes will be required if other polarizability distributions are used). Both the radius and excess ionic polarizability can, in principle, be different in the different phases. Netz¹² recently presented the result of ab initio calculations for the polarizability of ions in a vacuum. He demonstrated how one can use the result in a vacuum to obtain a good estimate for the corresponding excess polarizability of the ion in water. These calculations have all the usual limitations of theory but should provide a reasonable estimate. The parameters obtained by Netz for six ions are listed in Table 1. We model the excess polarizability with one adsorption frequency (ω^1) using the London approximation

$$\alpha^*(i\omega_n) = \frac{\alpha^*}{1 + (\omega/\omega^1)^2} \quad (3)$$

The parameters proposed by Kunz et al.¹⁰ for ions in water are different from the result of Netz.¹² The dispersion self-free energies for anions (cations) in water are substantially larger (smaller) when we use the parameters proposed by Kunz et al.¹⁰ instead of the parameters calculated by Netz.¹² We have used the parameters presented by Netz for demonstration purposes (but also because they are based on reasonable ab initio calculations). We suggest, however, that it is essential to investigate further the excess polarizability of ions in water using simulations that properly include interactions between ion and water molecules.⁷

The proper choice of radius is unfortunately not well defined. As we have already mentioned, Rashin and Honig argued strongly that the expected radius should be the covalent radius for cations and the ionic radius for anions. The dispersion self-free energy takes its major contributions from the visible and

TABLE 2: Theoretical and Experimental Values of the Free Energy of Solvation of Salts (in kcal/mol)^a

ion/salt	adjusted a (Å)	$\Delta F^{\text{Disp } b}$	$\Delta F^{\text{Born } c}$	$\Delta F^{\text{Calc } d}$	$\Delta F^{\text{Exp } e}$
Li ⁺	1.513	−10.41	−110.23	−120.64	
Na ⁺	1.932	−14.89	−86.32	−101.21	
K ⁺	2.498	−19.27	−66.76	−86.04	
F [−]	1.636	−7.62	−101.94	−109.56	
Cl [−]	2.228	−7.15	−74.85	−82.00	
Br [−]	2.400	−4.75	−69.94	−74.24	
LiF				−230.20	−245.2
LiCl				−202.64	−211.2
LiBr				−194.88	−204.7
NaF				−210.77	−217.8
NaCl				−183.21	−183.8
NaBr				−175.45	−177.5
KF				−195.6	−197.8
KCl				−168.04	−163.8
KBr				−160.28	−157.3

^a Radii for the six ions were found by increasing the expected radii² by 23%. ^b Theoretical contributions from dispersion self-free energy for different ions. ^c Theoretical contributions from electrostatic Born self-free energy for different ions. ^d Total theoretical free energies of solvation for different salts. ^e Total experimental^{2,15} free energies of solvation for different salts.

the ultraviolet regions. This depends on electronic densities, which are not affected much by the orientation of dipoles or the hydrogen bonding of water around the ion. We therefore make the reasonable approximation that we can use the same bare radius in water and in a vacuum.

III. Numerical Results

To test the importance of the additional correction to the heats of solvation of salts, we carried out calculations of both Born and dispersion contributions to the free energy for the six ions given in Table 1 and for the corresponding nine combinations of different anions and cations. We find excellent agreement for the NaCl solution when the expected radii² are increased by 23%. In Table 2, we report the results when all radii are increased by 23% compared to the expected value. We find that the theoretical heat of solvation is −230.2 kcal/mol for LiF, which is 15 kcal/mol smaller than the experimental value.^{2,15} For KCl, the theoretical results is 4.2 kcal/mol larger than the experimental value. A deviation of 6% (or less) between theory and experiment is not particularly surprising considering that we do not include explicitly any effects of water structure. The important point is that the correction due to dispersion self-free energy is of the same order of magnitude as the deviations between experiment and the pure Born theory without adjusted radii. It is clearly incorrect to ignore this contribution.

We finally demonstrate that it is possible to find agreement between theory and experiment to within 0.1% if all radii are increased separately. To fit the theoretical values, we have to arbitrarily select one ionic radius. We chose the radius of the bromide ion in such a way that we obtain the same free energy in our extended theory as Rashin and Honig found using the Born theory. In this way, we find that the radius of the bromide ion should be around 2.25 Å. This radius can be compared with the values of 2.087 Å used by Rashin and Honig², 1.96 Å used by Kunz et al.,¹⁰ and 2.34 Å used by Netz.¹² The other radii were then selected to optimize the agreement between theory and experiment. The results are summarized in Table 3. Although the agreement between theory and experiment for the majority of salts is directly caused by the fit, the better than 0.1% agreement even for the four salts that were not fitted provides some credibility to the fitting procedure.

TABLE 3: Theoretical and Experimental Values of the Free Energy of Solvation of Salts (in kcal/mol)^a

ion/salt	adjusted <i>a</i> (Å)	$\Delta F^{\text{Disp } b}$	$\Delta F^{\text{Born } c}$	$\Delta F^{\text{Calc } d}$	$\Delta F^{\text{Exp } e}$
Li ⁺	1.47	-11.36	-113.45	-124.81	
Na ⁺	1.99	-13.63	-83.81	-97.43	
K ⁺	2.69	-15.43	-62.00	-77.43	
F ⁻	1.51	-9.69	-110.45	-120.14	
Cl ⁻	2.13	-8.18	-78.30	-86.47	
Br ⁻	2.25	-5.76	-74.12	-79.89	
LiF				-244.92	-245.2
LiCl				-211.28	-211.2
LiBr				-204.70	-204.7
NaF				-217.57	-217.8
NaCl				-183.90	-183.8
NaBr				-177.32	-177.3
KF				-197.57	-197.8
KCl				-163.90	-163.8
KBr				-157.32	-157.3

^a Radii for the six ions were chosen to optimize agreement between theoretical and experimental free energies of solvation for nine different salts. ^b Theoretical contributions from dispersion self-free energy for different ions. ^c Theoretical contributions from electrostatic Born self-free energy for different ions. ^d Total theoretical free energies of solvation for different salts. ^e Total experimental^{2,15} free energies of solvation for different salts.

IV. Summary

It is important to point out that there is no physical motivation for the particular choice of radius for bromide used in the second fit. It is, in fact, possible to obtain a more or less equally good overall fit with a different choice (the same is true for the original Born theory). The purpose of this work is not to say that we find an excellent fit when both ionic dispersion self-free energies and Born self-free energies are included. Rather, we hope that an extension of the present work might accommodate experimental results without fitting parameters. A proper theoretical investigation, without any element of fitting, should preferably be based on excess polarizabilities and radii obtained from experimental data, e.g., refractive indices of solutions (complemented with ab initio calculations and/or simulations). If such a theory agrees with experiment for a large number of salt solutions, one can argue that the theory has captured the main ingredients. It is likely however that theory also has to include water structure effects, through molecular dynamics simulations, for example.⁷⁻⁹

We have demonstrated that the dispersion self-free energy contribution can be up to 30% of the Born energy. If the larger values for excess polarizabilities of anions proposed by Kunz

et al. are used, even larger dispersion contributions follow. The same is true if smaller values for the radii are used as the dispersion self-free energy varies as a^{-3} whereas the Born self-energy varies only as a^{-1} . With the present choice of excess polarizabilities and radii, we are most likely underestimating the relative effect of dispersion self-free energies. When we use the polarizabilities from Kunz et al. and the "expected" radii, the relative effect of dispersion self-free energies is much larger than what we have demonstrated here (30% or more for most cases). The solvation energies we then obtain are too large compared to experiments, but that does not mean that the theory is wrong, only that, as we expected, it does not include all contributions. The essential point is that it is clearly inconsistent to extend Born theory to include solvent effects if a major part of a first-order approximation is missing. The dispersion self-free energy is also highly ion-specific. In a proper continuum theory, one ought not to derive the self-energy for a charged electrostatic sphere and an uncharged atom separately and add them, but rather to take them together by writing down Maxwell's equations, including ionization equilibrium, current, and polarization (as for the double layer with charge regulation), and then do the adding of frequency contributions. We will address this very important point in a subsequent publication.

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