Bull. Chem. Soc. Jpn., 64, 3035—3038 (1991)

A Further Modification of the Born Equation

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(Received May 9, 1991)

By considering the distance-dependent relative permittivity of a solvent, the Born equation has been modified for a diatomic ion in which the charge is located on an atom deviating from the center of a spherical cavity. The new equation has been successfully applied to the diatomic ions of OH^-, SH^-, and CN^-.

The Born equation[1)] has long been widely applied in many fields regarding the solvation free energies of ions. The Born equation is written for 1 mol of ions of point charge Ze (where Z is the formal charge and e the charge of proton) located in a spherical cavity embedded in a continuous dielectric medium of solvent as

$$\Delta G_m^\circ=\frac{e^2LZ^2}{2a}\times\left(\frac{1}{\varepsilon_r}-1\right), \qquad (1)$$

where ΔG_m° is the increase in the standard molar Gibbs function due to electrostatic interactions when one transfers the ions from a vacuum to a solution at infinite dilution of the ionic species. Here, L is the Avogadro constant, ε_r the relative permittivity of the solvent, and a the radius of the spherical cavity. In the Born model, the charge is located in the center of the spherical cavity and the local relative permittivity in the immediate neighborhood of the ion is assumed to be equal to the bulk relative permittivity (ε_r) of the solvent. The latter defect was overcome by Abe[2)] by considering a distance-dependent relative permittivity of the solvent. In Abe's model, the point charge is still assumed to be located in the center of the spherical cavity, as in the case of the Born equation. This model is certainly valid for a monoatomic ion but is not valid for a polyatomic ion in which the charge located on an atom is not necessarily in the center of the cavity. In the case of a polyatomic ion, such as a diatomic ion, the point charge usually deviates from the center. Recently, Rashin and Namboodiri[3)] have presented a general method for calculating the hydration enthalpy for a single charged molecule of arbitrary shape, using the Born equation and the boundary element technique. They obtained excellent results. However, applying the boundary element technique employed to obtain a numerical solution of the Poisson equation is not easy. Recently, Zhou and Stell[4)] have obtained analytical equations for the pair correlation functions in the mean spherical approximation for the case of two hard-sphere ions in a model solvent of dipolar dumbbells and an expression for a single ion by letting the number density of the ionic species be infinitesimally small. The expression is similar to an empirical formula used for fitting experimental data to Eq. 1, and is currently not applicable to the present problem. In this paper, therefore, an attempt has been made to derive a simple equation that is easily applicable to a single diatomic ion in which the point charge deviates from the center of the spherical cavity, by considering the distance-dependent relative permittivity of the solvent.

Theory

As shown in Fig. 1, the point charge of Ze is located at position O in a spherical cavity (of radius a) embedded in a continuous dielectric medium of solvent whose bulk relative permittivity is ε_r. Inside the cavity, the relative permittivity is assumed to be equal to that of a vacuum. Let the origin be at position O, which deviates from the center (C) of the cavity by r_0. The z-axis is taken in the direction of line $\overline{CO}$. The distance of an arbitrary point (P) from O is denoted by r. The point at which line of $\overline{OP}$ crosses the cavity surface is denoted by Q. The angle between $\overline{OP}$ and the z-axis is denoted by θ. Then, one can write line $\overline{OQ}$ as

$$\overline{OQ}=\frac{-2r_0\cos\theta\pm\{(2r_0\cos\theta)^2+4(a^2-r_0^2)\}^{1/2}}{2}, \qquad (2)$$

since $a^2=r_0^2+\overline{OQ}^2-2r_0\overline{OQ}\cos(\pi-\theta)$. Here, $\overline{OQ}$ should be positive. From Eq. 2, therefore, one obtains

$$\overline{OQ}=-r_0\cos\theta+(a^2-r_0^2\sin^2\theta)^{1/2}. \qquad (3)$$

The electric field caused by Ze within the cavity is

$$E=\frac{Ze}{r^2}, \qquad (4)$$

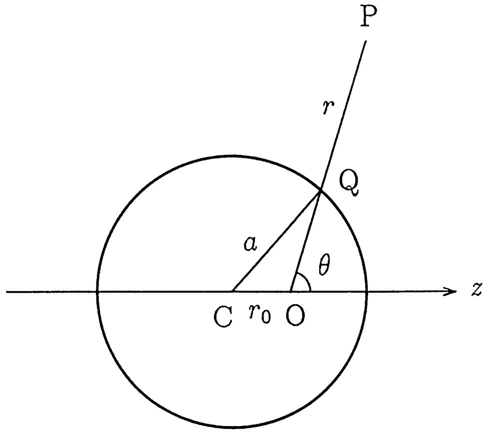

Fig. 1. Model.

while the electric field in the medium is written as

$$E_s = \frac{Ze}{\varepsilon(r)r^2}, \tag{5}$$

where $\varepsilon(r)$ is the distance-dependent relative permittivity. Here, the same formula for $\varepsilon(r)$ as was used in a previous paper[2)] is adopted,

$$\varepsilon(r) = e_r \exp(-\kappa/r), \tag{6}$$

where κ is determined under the condition $\varepsilon(r)=1$ for $r=\overline{OQ}$, i.e., $1=\varepsilon_r \exp(-\kappa/\overline{OQ})$ as

$$\kappa = \overline{OQ} \ln \varepsilon_r. \tag{7}$$

When $\varepsilon(r)$ is written as $\varepsilon(r)=\varepsilon_r \exp\{-(\overline{OQ} \ln \varepsilon_r)/r\}$, the potential Φ_i (due to Ze) inside the cavity can be written simply as Ze/r, which is the same expression as in a vacuum. The potential (Φ_o) outside the cavity is $Ze/\varepsilon(r)r$. These potentials obviously satisfy the two boundary conditions of $\Phi_i=\Phi_o$ and $(\partial\Phi_i/\partial r)\cos\theta'=\varepsilon(r)(\partial\Phi_o/\partial r)\cos\theta'$ (for the normal line ($\overline{CQ}$) components, where $\theta'=\angle CQO$) for $r=\overline{OQ}$, since $\varepsilon(r)=1$ for $r=\overline{OQ}$. This simple expression for Φ_i may be due to the fact that the polarization (P) given by $P=\{\varepsilon(r)-1\}\times E_s/4\pi$ is zero for $r=\overline{OQ}$ (i.e. on the cavity surface) in this case.

By following the same procedure that Slater and Frank[5)] used to calculate the total energy of an electron using a Poynting vector, the Born equation will be further modified. The infinitesimal area of the cavity surface contained in the solid angle between θ and $(\theta+d\theta)$ is given by $2\pi(a\sin\theta)(ad\theta)$. As in a previous paper,[2)] therefore, one can write the solvation free energy of 1 mol of ions with the charge Ze by using a Poynting vector as follows:

$$\begin{aligned}\Delta G^\circ_m &= \frac{L}{8\pi}\int_0^\pi\int_Q^\infty \{\varepsilon(r)E_s^2 - E^2\} \times 2\pi(r\sin\theta)(rd\theta)dr \\ &= \frac{L}{4}\int_0^\pi d\theta \sin\theta \int_Q^\infty \{\varepsilon(r)E_s^2 - E^2\} r^2 dr.\end{aligned} \tag{8}$$

Using Eqs. 4, 5, 6, and 7, one obtains the following integral calculation:

$$\begin{aligned}\int_Q^\infty \{\varepsilon(r)E_s^2 - E^2\}r^2 dr &= -\frac{Z^2e^2}{\varepsilon_r\kappa} \times \{1-\exp(\kappa/\overline{OQ})\} - \frac{Z^2e^2}{\overline{OQ}} \\ &= -Z^2e^2 \times \left(\frac{1-\varepsilon_r}{\varepsilon_r \ln \varepsilon_r} + 1\right) \times \frac{1}{\overline{OQ}}.\end{aligned} \tag{9}$$

Using Eqs. 3 and 9, one can rewrite Eq. 8 as follows:

$$\begin{aligned}\Delta G^\circ_m &= -\frac{Z^2Le^2}{4} \times \left(\frac{1-\varepsilon_r}{\varepsilon_r \ln \varepsilon_r} + 1\right) \times \int_0^\pi \frac{\sin\theta d\theta}{(a^2 - r_0^2 \sin^2\theta)^{1/2} - r_0 \cos\theta} \\ &= \frac{Z^2Le^2}{4a} \times \left(\frac{1}{\ln \varepsilon_r} - \frac{1}{\varepsilon_r \ln \varepsilon_r} - 1\right) \\ &\quad \times \left\{\frac{1}{1-(r_0/a)^2} + \frac{1}{2(r_0/a)} \ln \frac{1+(r_0/a)}{1-(r_0/a)}\right\},\end{aligned} \tag{10}$$

where $e^2L/2=69.45$ nm kJ mol^{-1}.

Discussion

When $r_0=0$ is put into Eq. 10, one should obtain the modified equation given in a previous paper.[2)] However, some modification of Eq. 10 is necessary for obtaining the ΔG°_m value for $r_0=0$, because it is impossible to put $r_0=0$ directly into Eq. 10. Expanding the terms of $1/\{1-(r_0/a)^2\}$ and $\ln\{1+(r_0/a)\}/\{1-(r_0/a)\}$ in Eq. 10 in series, one finally obtains

$$\begin{aligned}\Delta &= \frac{1}{2} \times \left\{\frac{1}{1-(r_0/a)^2} + \frac{1}{2(r_0/a)} \ln \frac{1+(r_0/a)}{1-(r_0/a)}\right\} \\ &= 1 + \frac{1}{2}\sum_{n=1}^{\infty}\left(1+\frac{1}{2n+1}\right)\left(\frac{r_0}{a}\right)^{2n}.\end{aligned} \tag{11}$$

This is obviously convergent, since $a > r_0$. Thus, one can write Eq. 10 as

$$\begin{aligned}\Delta G^\circ_m = \frac{Z^2Le^2}{2a} &\times \left(\frac{1}{\ln \varepsilon_r} - \frac{1}{\varepsilon_r \ln \varepsilon_r} - 1\right) \\ &\times \left\{1 + \frac{1}{2}\sum_{n=1}^{\infty}\left(1+\frac{1}{2n+1}\right)\left(\frac{r_0}{a}\right)^{2n}\right\}.\end{aligned} \tag{12}$$

When $r_0=0$, Eq. 12 is reduced to

$$\Delta G^\circ_m = \frac{Z^2Le^2}{2a} \times \left(\frac{1}{\ln \varepsilon_r} - \frac{1}{\varepsilon_r \ln \varepsilon_r} - 1\right). \tag{13}$$

This is a modified equation given in a previous paper.[2)] Ehrenson[6)] has shown that the solvent parameter of $\{1/\ln \varepsilon_r - 1/(\varepsilon_r \ln \varepsilon_r) - 1\}$ in Eq 13 is the best in the inverse exponential radial dielectric function family of the modified Born equations for correcting the free energies of solvation. In a comparison of Eq. 12 with Eq. 13, Δ (Eq. 11) is a factor which indicates the degree of deviation of the position of the charge from the center of the spherical cavity for ΔG°_m.

A plot of the Δ values vs. the r_0/a values is given in Fig. 2. This figure shows that the Δ value is approximately unity over the range of r_0/a values smaller than

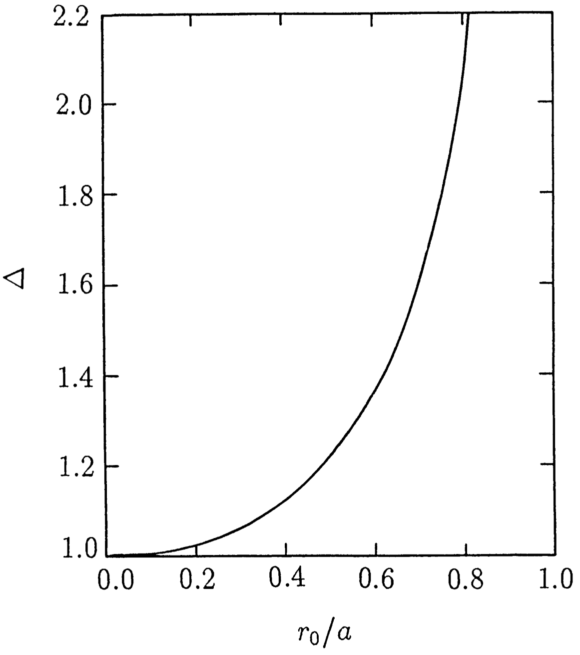

Fig. 2. Plot of Δ vs. r_0/a.

0.2. Therefore, Eq. 13 may be approximately used for an r_0/a value smaller than 0.2. However, Fig. 2 shows that the deviation of the $\varDelta$ value from unity can not be ignored for r_0/a values larger than ca. 0.25. In this case, therefore, Eq. 10 should be used instead of Eq. 13.

When the constant bulk relative permittivity of ε_r is used instead of $\varepsilon(r)$, one can easily obtain the following expression for ΔG°_m in the same way as in the derivation of Eq. 10:

$$\Delta G^\circ_m = \frac{e^2LZ^2}{2a}\times\left(\frac{1}{\varepsilon_r}-1\right)\times\varDelta. \tag{14}$$

This corresponds to a modified equation of Eq. 1 for the case of a deviation of the charge from the center of the cavity by r_0. In this case, the charges are induced on the cavity surface, since $P=(\varepsilon_r-1)E_s/4\pi\neq0$ for $r=\overline{OQ}$, where $E_s=Ze/\varepsilon_r r^2$. From the continuity of potentials at Q, the potential inside the cavity may be written as $\Phi_i=Ze/r+(1/\varepsilon_r-1)Ze/\overline{OQ}$. The second term of $(1/\varepsilon_r-1)Ze/\overline{OQ}$ (the reaction field) does not contribute to the electric field ($E=-\partial\Phi_i/\partial r=Ze/r^2$), since the term does not contain r, according to Eq. 3.

On the assumptions that only the electrostatic contribution is dominant and that a does not depend on the temperature, one can easily derive the following equations for the increase of standard molar entropy of solvation of a diatomic ion from Eqs. 1, 13, 14, and 10 according to $\Delta S^\circ_m=-(\partial\Delta G^\circ_m/\partial T)_p$ (where sufffix p denotes the constant pressure and T is the thermodynamic temperature (K)):

$$\Delta S^\circ_m = \frac{e^2LZ^2}{2a}\times\frac{1}{\varepsilon_r^2}\times\frac{d\varepsilon_r}{dT}, \tag{15}$$

$$\Delta S^\circ_m = \frac{e^2LZ^2}{2a}\times\frac{\varepsilon_r-\ln\varepsilon_r-1}{\varepsilon_r^2(\ln\varepsilon_r)^2}\times\frac{d\varepsilon_r}{dT}, \tag{16}$$

$$\Delta S^\circ_m = \frac{e^2LZ^2}{2a}\times\frac{1}{\varepsilon_r^2}\times\frac{d\varepsilon_r}{dT}\times\varDelta, \tag{17}$$

and

$$\Delta S^\circ_m = \frac{e^2LZ^2}{2a}\times\frac{\varepsilon_r-\ln\varepsilon_r-1}{\varepsilon_r^2(\ln\varepsilon_r)^2}\times\frac{d\varepsilon_r}{dT}\times\varDelta, \tag{18}$$

respectively, since the $\varDelta$ factor is independent of the temperature.

Applications

The present equations have been applied to the hydration of OH^-, SH^-, and CN^-, in order to compare with the experimental ΔG°_m values (298.15 K) for the hydration of these ions reported by Marcus,[7] as shown in Table 1. In these diatomic ions the negative charges are probably located on the atoms of O, S, and N, because the electronegativities of these atoms are larger than those of the corresponding bonding atoms and the negative charge of each ion may be located at one atom according to the adjacent charge rule of Pauling.[8]

In applying Eqs. 1, 10, 13, and 14, the reported data for a (Table 1)[7] and $\varepsilon_r=78.46$ (298.15 K)[7] were used and the r_0 values were approximated by the half values of the bond lengths of these diatomic ions, based on the assumption that the center of the bond length for each diatomic ion is located at the center of the spherical cavity. The values used for the bond lengths of OH^-, SH^-, and CN^- were 0.0970, 0.1336, and 0.11718 nm,[9] respectively. The results of calculations are listed in Table 1. The table clearly shows that the values calculated by both the Born equation (Eq. 1) and its modified equation (Eq. 14) derived by considering the deviation of r_0 are in worse agreement with the experimental values than those calculated by the modified equation (Eq. 13) derived by considering only the distance-dependent relative permittivity of the solvent; it also shows that a further modified equation (Eq. 10) derived by considering both the distance-dependent relative permittivity of a solvent and the deviation of r_0 best reproduces the experimental values among the 4 equations. Thus, Eq. 10 should be used instead of Eq. 13 for an ion in which the charge is located on one atom considerably deviating from the center of the spherical cavity.

Table 1. ΔG°_m Values

Ion	$a^{a)}$/nm	ΔG°_m/kJ mol^{-1}				
		Eq. 1	Eq. 13	Eq. 14	Eq. 10	Exp.$^{a)}$
OH^-	0.140	−490	−384	−534	−418	−439
SH^-	0.195	−352	−276	−382	−300	−303
CN^-	0.191	−359	−281	−384	−301	−305

a) Ref. 7.

Table 2. ΔS°_m Values

Ion	ΔS°_m/J K^{-1} mol^{-1}				
	Eq. 15	Eq. 16	Eq. 17	Eq. 18	Exp.$^{a)}$
OH^-	−29	−111	−32	−121	−161
SH^-	−21	−80	−23	−87	−101
CN^-	−21	−82	−23	−87	−80

a) Ref. 7.

The experimental ΔS°_m values (298.15 K) for the hydration of these ions are reported also by Marcus,[7] as shown in Table 2. In applying Eqs. 15—18, the $d\varepsilon_r/dT$ value[10] of $-0.3595\ K^{-1}$ for water was used. The results calculated for ΔS°_m are shown in Table 2. The table shows that Eq. 18 best reproduces the experimental values among the 4 equations.

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