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Surface Effects in the Born Solvation Model#

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The Born model is frequently used for calculating the work of solvation or free energy of ion–solvent interactions. The original Born equation does not reproduce the experimental data on solvation free energy, possibly due to the fact that the model does not take in account the changes in the structure of solvent in presence of an ion. The model also fails to account certain other experimental observations. A new derivation of the model is presented assuming the changes in the structure of solvent being analogous to surface phenomena. In addition to the successful checking its validity against experimental data, the revised expression can also yield the generalized Dupre rule for surface effects. Significance of new terms and their impact in accounting observed trends are discussed.

The classic Born model,[1)] though proposed more than 70 years ago, is considered a valuable tool in calculating the free energy of ion–solvent interactions useful in chemical, geochemical, and biological studies. In the model, an ion is viewed as a rigid sphere with radius r_i bearing charge q and the solvent is taken to be a structureless continuum. The model treats the structure of solvent around is exactly similar to that of bulk solvent. The original Born expression for calculating the amount of work, W_{ch} required to transfer an ion from vacuum to a solvent with dielectric constant ϵ_S is given by:

$$W_{ch} = -(q^2/2r_i)(1 - 1/\epsilon_s). \tag{1}$$

By considering a charged sphere equivalent to an ion, the Born model assumes that it is only the charge on the ion that is responsible for ion–solvent interactions. The interactions between the solvent and the ion are considered to be solely electrostatic in origin. Application of Eq. 1 to several salt–solvent systems yields very high values of W_{ch} or free energy of solvation.[2—5)] Several attempts[6)] have been made to tackle this problem by treating either or both r_i and ϵ_S as adjustable parameters. Attempts[3,7,8)] have also been made by accounting explicitly for the energy of transforming the discharged ion from vacuum to water.

Recently, we[9)] have shown that this model can yield reliable estimates of solvation energies by incorporating the polarization effect in the form of high frequency or local dielectric constant. The model was applicable to a variety of ions in different solvents and did not require any adjustable parameters. In all the modified models, including ours, the original form of the Born equation remained unaltered. A study of such modifications made for obtaining accurate solvation energies, reveals that the Born model cannot account for the linear effects,[10)] e.g. the dependence of electrostatic contribution to the entropy of the ions in water on the charge; when compared with experimental entropy data showed disagreement with the theoretical values. The Born equation is quadratic in nature and thus fails to account for such linear effects. The limitations,[4,11)] of the original Born model appears to arise mostly due to the assumption that the structure of solvent does not change in presence of an ion.

In this article, we present a revision of the Born model considering that the change in the structure of solvent near an ion is closely analogous to surface phenomena. We, therefore, incorporate surface effects in the Born model and demonstrate that, not only linear effects are accounted in the revised expression, but also the differences between the quantities expressing solvation energies for ions and valencies. In order to justify our assumptions, we show, in the end, that the revised Born version can be deduced to a generalized Dupre rule[12)] for the surface phenomena.

In order to include the surface effects in the Born model, we first attempt to obtain a suitable expression for grand thermodynamic potential, Ω, of the medium with a charge conducting sphere. The quantity Ω is a function of volume V, temperature T, and set of chemical potentials $\{\mu\}$. We can thus write,

$$\begin{aligned}(\partial\Omega/\partial q)_{T,V,\{\mu\}} &= n(r) \\ &= n(\infty) + \int_r^\infty \mathrm{d}r' E(r').\end{aligned} \tag{2}$$

In this equation, $n(r)$ is its potential; $n(\infty)$ is electrostatic potential of medium at ∞ distance from the sphere, while E denotes the strength of electric field in the medium.

We now intend to define the following quantities:

$$E_s(r_i') \equiv q/\epsilon_s r_i'^2$$

and

$$\Gamma \equiv -1/4\pi \int_r^\infty \mathrm{d}r'[E(r') - E_s(r')]. \tag{3}$$

In Eq. 3, symbol s refers to bulk phase of solvent. Γ denotes the excess polarization near the surface of sphere due to the change in the structure of the medium in the immediate vicinity of the sphere.

Substitution of the quantities given in Eq. 3 in Eq. 2 yields,

$$(\partial\Omega/\partial q)_{T,V,\{\mu\}} = n_s(\infty) - 4\pi\Gamma + q/\epsilon_s r. \tag{4}$$

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Since the change in structure of the medium, as discussed above is not related to the charge on the sphere, Γ can be assumed to be

$$\Gamma = \Gamma_\circ + \delta q/r^2. \tag{5}$$

Coefficients $\Gamma_\circ$ and δ indicate constant and induced parts of polarizations. The term $\Gamma_\circ$ can be related to the interfacial potential step $\Delta n_\circ$, (difference in electrical potential between the medium and a neutral substance corresponding to an ion) by $\Gamma_\circ = \Delta n_\circ/4\pi$.

Substituting Eq. 5 into Eq. 4 and on integrating, we obtain

$$\Omega = \Omega_\circ^{\mathrm{J}} + qn_{\mathrm{s}}(\infty) - 4\pi q\Gamma_\circ - 2\pi\delta q^2/r^2 + q^2/2\epsilon_{\mathrm{s}} r, \tag{6}$$

where $\Omega_\circ^{\mathrm{J}}$ refers to $\Omega_\circ\ (T, V, \{\mu\})$, which is equivalent to the value of Ω in the absence of the charge, but not of the sphere itself at given T, V, and $\{\mu\}$ conditions.

We distinguish the above $\Omega_\circ^{\mathrm{J}}$ from a quantity $\Omega_{\circ\circ}^{\mathrm{J}}$, indicating a situation where sphere is also absent. For this, we consider two media with bulk phases s_1 and s_2 rather than one medium and evaluate grand thermodynamic potential for transfer of the charged sphere from s_1 and s_2. On transferring the sphere initially in the medium with bulk phase s_1, Ω_1 is given through Eq. 6 and $\Omega_{\circ\circ}^{\mathrm{J,s_2}}$ as,

$$\Omega_1 = \Omega_\circ^{\mathrm{K}} + qn_{\mathrm{s}}(\infty) - 4\pi q\Gamma_\circ^{\mathrm{s_1}} - 2\pi\delta^{\mathrm{s_1}} q^2/r^2 + q^2/2\epsilon_{\mathrm{s}} r + \Omega_{\circ\circ}^{\mathrm{J,s_2}}, \tag{7}$$

with

$$\begin{aligned} \Omega_\circ^{\mathrm{k}} &= \Omega_\circ(T, V^{\mathrm{s_1}}, \{\mu^{\mathrm{s_1}}\}), \\ \Omega_{\circ\circ}^{\mathrm{J,s_2}} &= \Omega_{\circ\circ}^{\mathrm{s_2}}(T, V^{\mathrm{s_2}}, \{\mu^{\mathrm{s_2}}\}). \end{aligned} \tag{8}$$

Now we can write for the final state of the transfer process, when sphere is in medium s_2 as,

$$\Omega_2 = \Omega_{\circ\circ}^{\mathrm{J,s_1}} + \Omega_\circ^{\mathrm{J,s_2}} + qn^{\mathrm{s_2}}(\infty) - 4\pi q\Gamma_\circ^{\mathrm{s_2}} - 2\pi\delta^{\mathrm{s_2}} q^2/r^2 + q^2/2\epsilon_{\mathrm{s_2}} r. \tag{9}$$

It is clear from Eqs. 7 and 9 that two media can differ in terms of components and so in their chemical potentials.

Now Eqs. 7 and 9 can be employed to yield the work done in transferring the charged ion from s_1 to s_2 as,

$$\begin{aligned} \Delta\Omega &= \Omega_2 - \Omega_1 \\ &= W_\circ + q\Delta n - 4\pi q\Delta\Gamma_\circ - 2\pi q^2\Delta\delta/r^2 + q^2\Delta(1/\epsilon)/2r, \end{aligned} \tag{10}$$

where

$$W_\circ = \Omega_\circ^{\mathrm{J,s_2}} - \Omega_{\circ\circ}^{\mathrm{J,s_2}} - \Omega_\circ^{\mathrm{J,s_1}} - \Omega_{\circ\circ}^{\mathrm{J,s_1}}. \tag{11}$$

We note that $W_\circ$ denotes the work of transferring the uncharged sphere between the two media. We also note that r remains unaltered during the transfer process. Let us now examine the situation, where r varies, as discussed by others. In that case,

$$\Omega = W_\circ + q\Delta n - 4\pi q\Delta\Gamma_\circ - 2\pi q^2\Delta\delta/r^2 + q^2\Delta(1/\epsilon r)/2. \tag{12}$$

If Eq. 12 is used in connection with the transfer from vacuum to a liquid, then we have

$$\Delta\Omega = W_\circ + q\Delta n - 4\pi q\Gamma_\circ - 2\pi q^2\Delta(\delta/r^2) + q^2\Delta(1/\epsilon r)/2. \tag{13}$$

When r is constant,

$$\Omega = W_\circ + q\Delta n - 4\pi q\Gamma_\circ - 2\pi q^2\delta/r^2 + q^2(1/\epsilon - 1)/2r. \tag{14}$$

Equation 14 is an expression for the complete work of solvation, which can be rewritten for chemical work of solvation by subtracting term $q\Delta n$ to give,

$$W = W_\circ - 4\pi q\Gamma_\circ - q^2(1 - 1/\epsilon + 4\pi\delta/r)/2r. \tag{15}$$

Equation 15 demonstrates explicit dependence of work of solvation on electrical charge on ion. Let us examine the terms in the above Equations. The 5th term in Eq. 14 is nothing but Eq. 1, which is original Born equation. In Eq. 15, $W_\circ$ is independent of the charge and describes the work required to introduce a hypothetical particle into the solvent. This particle is uncharged but is identical to an ion in other aspects. The 2nd term i.e. $4\pi q\Gamma_\circ$ in Eq. 15 gives linear effect in a polar solvent. This linear term shows dependence of work of solvation on the sign as well as magnitude of charge. Contribution of this term to the solvation work for cations is negative, whereas for anions, opposite effect is seen. The 3rd term in Eq. 15 gives quadratic effect of the charge on ion. Recalling Eq. 1 explains us that even quadratic effects were not fully accounted in original Born equation. Additional constants appearing in the revised Born equation can be easily estimated, whereas the values of radius of an ion and dielectric constant of solvent are well established.

Equations, presented in this treatment, contain the linear term, which is a superior development over other attempts made so far. This permits us to account for the linear effects in the energetics of ion solvation. This can account for linear entropic effect, which could be ascribed to linear term in Eqs. 12, 13, 14, and 15. This term is strongly temperature dependent than the other terms, and can explain the linear experimental entropy dependence on the charge, as analyzed by the data of Powell and Latimer.[10] The present work also shows that ions with equal radii and valency don't have same free energy of solvation. Eventually, energy of solvation for such case differs by $8\pi q\Gamma_\circ$ and thus enthalpy of solvation by the $8\pi q[\Gamma - T(\partial\Gamma_\circ/\partial T)_{\{\mu\}}]$ term.[4,10]

The validity of the proposed model can be tested by comparing the calculated results obtained Eq. 15 with the experimental data on the free energy of solvation, ΔG_{i}. Values of constants ($\Gamma_\circ = 0.28\times10^{-18}$, $\delta = -0.026$) taken from elsewhere[4,5,9,13,14] when used in the proposed model yield accurate values of ΔG_{i} as compared with the experimental data.[4,9,15] We demonstrate such an agreement for a few ions in water in Fig. 1. In general for all mono and divalent cations, the deviation between experimental and calculated values does not exceed 3%,

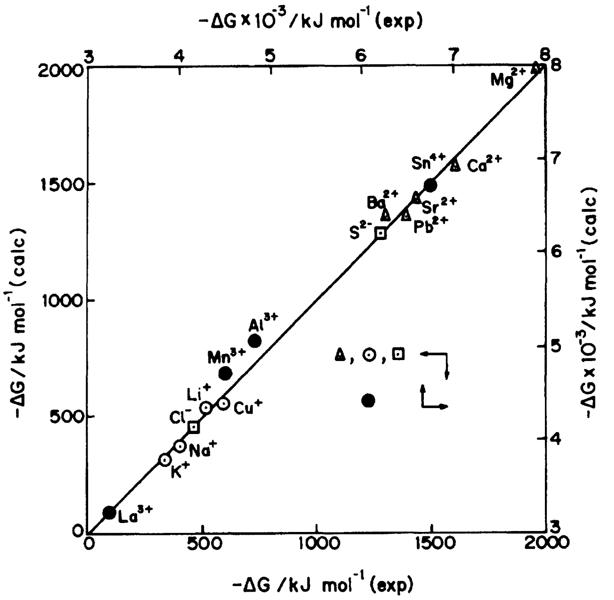

Fig. 1. Plot of experimental ΔG_i versus calculated ΔG_i by the proposed Born model; solvent=water.

whereas for higher valent ions, a higher value of about 8% is noted. In non-aqueous solvents like methanol and tetrahydrofuran, a good agreement of 4% between experimental and calculated ΔG_i for monovalent ions is obtained.

Let us now examine surface effect and the proposed Born equation. Recalling the classic paper of Dupre,[12] the work for wetting or adhesion for uncharged incompressible body is

$$W_o = A\Delta\gamma, \tag{16}$$

where A ($=4\pi r^2$) is the surface area and $\Delta\gamma$ indicates change in the thermodynamic surface tension. Equation 14 gives overall work of wetting or immersion for the charged body. Putting Eq. 16 into Eq. 14, we can obtain a generalized Dupre rule for a charged spherical body i.e.

$$\begin{aligned} n = {} & 4\pi r^2\Delta\gamma + q\Delta n - 4\pi q\Gamma_o \\ & - 2\pi q^2\delta/r^2 + q^2(1/\epsilon - 1)/2r. \end{aligned} \tag{17}$$

Equation 17 also shows that if the size of the sphere varies for a given surface charge density, the Born term becomes predominant.

To conclude, we have presented an entirely new expression for calculating the Born ion–solvent interaction free energy based on the argument that the change in the structure of solvent due to presence of an ion is analogous to surface effects. Although we realize that the revised version includes additional constants, our main objective was to couple the surface effects in the primitive model in order to eliminate the discrepencies observed. The version presented herein enhances our understanding on the ion–solvent interactions. The model is consistent with the generalized Dupre rule. Both the free energy of solvation and linear entropy effects can be explained by this model.

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