Solvation Energy by Born Model

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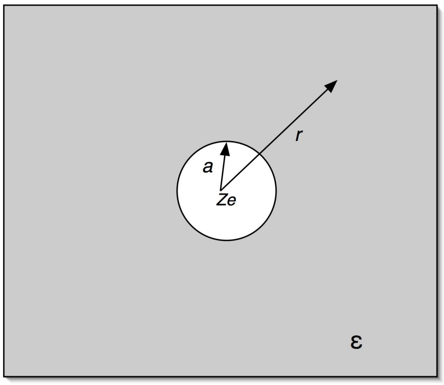
1 Born model

The (self-)energy of the electric .eld is given by (See Appendix.)

$$U = \frac{1}{2}\int d\mathbf{r}\mathbf{D}\cdot\mathbf{E}, \qquad \mathbf{D} = \epsilon\epsilon_0\mathbf{E} \tag{1}$$

Now we assume the ion has point charge Ze with radius a and the solvent is the dielectric continuum with dielectric constant ϵ. The electrostatic potential ϕ is



$$\phi(r) = \frac{Ze}{4\pi\epsilon\epsilon_0}\frac{1}{r} \tag{2}$$

The electric field is given by

$$\mathbf{E} = -\mathrm{grad}\phi = -(\mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z})\frac{Ze}{4\pi\epsilon\epsilon_0\sqrt{x^2+y^2+z^2}} = \frac{Ze}{4\pi\epsilon\epsilon_0}\frac{\mathbf{r}}{r^3} \tag{3}$$

The self-energy of the electric field becomes

$$U = \frac{1}{2}\int d\mathbf{r}\mathbf{D}\cdot\mathbf{E} = \frac{4\pi}{2}\int_a^\infty drr^2\frac{Z^2e^2}{16\pi^2\epsilon\epsilon_0}\frac{r^2}{r^6} = \frac{Z^2e^2}{8\pi\epsilon\epsilon_0}\int_a^\infty r^{-2}dr = \frac{Z^2e^2}{8\pi\epsilon\epsilon_0}[\frac{-1}{r}]_a^\infty \tag{4}$$

$$= \frac{Z^2e^2}{8\pi\epsilon\epsilon_0}\frac{1}{a} \tag{5}$$

In vacuum, the electric field energy U_0 is

$$U_0 = \frac{Z^2e^2}{8\pi\epsilon_0}\frac{1}{a} \tag{6}$$

The solvation energy is given by the energy difference

$$U_{\rm sol} = U - U_0 = \frac{Z^2 e^2}{8\pi\epsilon_0}\left(\frac{1}{\epsilon} - 1\right)\frac{1}{a} = -\frac{Z^2 e^2}{8\pi\epsilon_0}\left(1 - \frac{1}{\epsilon}\right)\frac{1}{a} \tag{7}$$

2 Modified Born model

(ref:Liquids, Solutions, and Interfaces: From Classical Macroscopic Descriptions to Modern Microscopic Details (Topics in Analytical Chemistry by W. Ronald Fawcett)

In the modified Born model the inverse of the radius $1/a$ is replaced by $1/(a+\delta)$. In the mean sphere approximation (MSA) the delta is given by

$$\delta = r_s/\lambda_s \tag{8}$$

Here r_s is the radius of the solvent (hard sphere is assumed) and λ_s is given by

$$\lambda_s^2(1+\lambda_s)^4 = 16\epsilon \tag{9}$$

From experiments $1/\delta$ has the linear relation with the donor number (DN) and acceptor number (AN) of the solvent.

$$\frac{1}{\delta} = a + b\mathrm{DN}, \qquad \frac{1}{\delta} = c + d\mathrm{AN} \tag{10}$$

Here DN is defined as the value of heat of reaction of the polar solvent with strong Lewis acid $SbCl_5$ when these 1:1 reactants are dissolved in 1,2-dichloroethane (Gutmann) and AN is the relative value of the P^{31} NMR chemical shifts produced by a given solvent with a strong Lewis base triethylphosphine oxide C2H5PO.(Mayer)

3 Appendix: Energy Conservation and Poynting Vector

$$\mathrm{div}\mathbf{D} = \rho \tag{11}$$

$$\mathrm{div}\mathbf{B} = 0 \tag{12}$$

$$\mathrm{rot}\mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{13}$$

$$\mathrm{rot}\mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \tag{14}$$

The equation of motion of point charges is [1]

$$m_i\ddot{\mathbf{r}}_i = \int d\mathbf{r}\left\{e_i\delta(\mathbf{r}-\mathbf{r}_i(t))\mathbf{E} + e_i\delta(\mathbf{r}-\mathbf{r}_i(t))\dot{\mathbf{r}}_i \times \mathbf{B}\right\}$$

[1] δ関数で与えられる点電荷は、電場・磁場からローレンツ力を受ける。

If we apply $(\sum_i \mathbf{v}_i \cdot)$ from the left, and the velocity is defined as $\mathbf{v}_i = \dot{\mathbf{r}}_i$

$$\begin{aligned}\sum_i m_i \mathbf{v}_i \cdot \dot{\mathbf{v}}_i &= \sum_i \int d\mathbf{r} \left\{ e_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \mathbf{v}_i \cdot \mathbf{E} + e_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \underbrace{\mathbf{v}_i \cdot [\mathbf{v}_i \times \mathbf{B}]}_{=0} \right\} \\ &= \sum_i \int d\mathbf{r} e_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \mathbf{v}_i \cdot \mathbf{E} \qquad (15)\end{aligned}$$

From the definition of the current and the Eq.(4).

$$\begin{aligned}\mathbf{J} &= \sum_i e_i \dot{\mathbf{r}}_i(t) \delta(\mathbf{r} - \mathbf{r}_i(t)) \qquad (16) \\ &= \mathrm{rot}\mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} \qquad (17)\end{aligned}$$

Then

$$\begin{aligned}\sum_i \frac{d}{dt}\left(\frac{1}{2} m_i \mathbf{v}_i^2\right) &= \int d\mathbf{r} \left(\mathrm{rot}\mathbf{H} - \frac{\partial \mathbf{D}}{\partial t}\right) \cdot \mathbf{E} \qquad (18) \\ \frac{1}{2}\frac{\partial}{\partial t}(\mathbf{E}\cdot\mathbf{D} + \mathbf{B}\cdot\mathbf{H}) &= \mathbf{E}\cdot\frac{\partial \mathbf{D}}{\partial t} + \mathbf{H}\cdot\frac{\partial \mathbf{B}}{\partial t} \\ &= \mathbf{E}\cdot\frac{\partial \mathbf{D}}{\partial t} - \mathbf{H}\cdot\mathrm{rot}\mathbf{E} \\ \frac{d}{dt}\left(\sum_i \frac{1}{2} m_i \mathbf{v}_i^2\right) &= \int d\mathbf{r} \left[-\frac{1}{2}\frac{\partial}{\partial t}(\mathbf{E}\cdot\mathbf{D} + \mathbf{B}\cdot\mathbf{H}) \right. \\ &\qquad \left. \underbrace{-\mathbf{H}\cdot\mathrm{rot}\mathbf{E} + \mathbf{E}\cdot\mathrm{rot}\mathbf{H}}_{=-\mathrm{div}(\mathbf{E}\times\mathbf{H})} \right]\end{aligned}$$

$$\frac{d}{dt}\left[\underbrace{\sum_i \frac{1}{2} m_i \mathbf{v}_i^2}_{\text{kinetic energy}} + \underbrace{\frac{1}{2}\int d\mathbf{r}(\mathbf{E}\cdot\mathbf{D} + \mathbf{B}\cdot\mathbf{H})}_{\text{total energy of electromagnetic field}} \right] = -\int dS \underbrace{[\mathbf{E}\times\mathbf{H}]}_{\text{Poynting vector}} \cdot\mathbf{n} \qquad (19)$$

From above equations the Poynting vector $\mathbf{S}[= \mathbf{E}\times\mathbf{H}]$ means the energy flux going out from the system.