Notes on Debye-Hückel Theory

We seek:

$$\mu_i = \mu_i^o + RT \ln X_i + \mu_i^{ex},$$

where $\mu_i^{ex} = RT \ln \lambda_i$, or the deviation from ideal behavior due to long range interaction of ions in solution. μ_i^{ex} is electrical in nature.

From a theorem of electrostatics: "that the mutual energy of a system of charges is one-half the sum of the products of the charges of each and the potentials due to the others," we have for the ith ion:

$$\boxed{\mu_i^{ex} = \frac{z_i e \psi_i}{2}},$$

where $z_i e$ is the charge in coulombs and ψ_i is the potential on the surface of the ith ion due to all the other ions in solution. We want a simple expression for ψ_i.

One of the fundamental laws of electrostatics (Maxwell's first equation) is:

$$\vec{\nabla} \bullet \vec{E} = \frac{4\pi\varphi}{\varepsilon},$$

where $\vec{E}$ is the electric field vector, φ is the charge density per unit volume, and ε is the dielectric constant of the medium. Now, $\vec{E}$ is just $-\vec{\nabla}\psi$ (just like the force is the gradient of the potential energy), so:

$$\vec{\nabla} \bullet \vec{\nabla}\psi = -\frac{4\pi\varphi}{\varepsilon} \text{ or } \boxed{\nabla^2\psi = -\frac{4\pi\varphi}{\varepsilon}},$$

which is the Poisson equation.

For the ith ion: $\nabla^2\psi_i = -\dfrac{4\pi\varphi_i}{\varepsilon}$, where *we assume that ε is the same everywhere and is equal to the value for pure water*. φ_i is a function of radius about the ith ion.

Clearly, the charge on the ith ion added to the charge of every other ion in solution must sum to zero, i.e. $\sum\limits_i z_i e = 0$, since the solution is neutral. Thus,

$$\int_a^\infty 4\pi r^2 \varphi_i dr + z_i e = 0 ,$$

where $4\pi r^2$ is an element of surface area and a is the radius of the ith ion.

What does the charge density look like?

We assume the Boltzmann distribution,

$$C_j^{'} = C_j \exp\left(-E_j/kT\right),$$

where C_j is the number of j ions per unit volume, and $E_j = z_j e \psi_i$, the energy of the ion, is equal to its charge times the potential. Then,

$$\boxed{\varphi_i = \sum_j z_j e C_j \exp\left(-z_j e \psi_i/kT\right)}.$$

Expanding in a Taylor series (and keeping only the first two terms):

$$\varphi_i = \sum_j z_j e C_j - \sum_j z_j e C_j \left(z_j e \psi_i/kT\right) .$$

Note that the first of these sums is zero!

So, $\nabla^2 \psi_i = -\dfrac{4\pi\varphi_i}{\varepsilon}$ becomes

$$\nabla^2 \psi_i = \sum_j \frac{4\pi e^2 C_j z_j^2}{\varepsilon kT} \psi_i .$$

Setting $\kappa^2 = \sum_j \dfrac{4\pi e^2 C_j z_j^2}{\varepsilon kT}$, we have in Cartesian coordinates

$$\nabla^2 \psi_i = \kappa^2 \psi_i$$

or in Polar coordinates

$$\psi_i^{''} + \frac{2}{r}\psi_i^{'} - \kappa^2 \psi_i = 0 .$$

A solution is: $\psi_i = \dfrac{A}{r}e^{-\kappa r} + \dfrac{B}{r}e^{\kappa r}$

As $r \to \infty$, ψ_i must be finite, so B is zero. Thus, $\psi_i = \dfrac{A}{r}e^{-\kappa r}$, so

$$\varphi_i = -\sum_j \frac{C_j z_j^2 e^2}{kT} \frac{A}{r} e^{-\kappa r}$$

How do we determine the constant A?

From $\int_a^\infty 4\pi r^2 \rho_i dr + z_i e = 0$, we have

$$-\int_a^\infty 4\pi r^2 \sum_j \frac{C_j z_j^2 e^2}{kT} \frac{A}{r} e^{-\kappa r} dr = -z_i e \;,$$

and

$$A = \frac{z_i e}{\varepsilon} \frac{e^{\kappa a}}{1+\kappa a}$$

At last:

$$\psi_i = \frac{z_i e}{\varepsilon} \frac{e^{\kappa a}}{1+\kappa a} \frac{e^{-\kappa r}}{r}$$

If we are only interested in the potential field of all ions except the ith ion, we must subtract its potential, $z_i e / \varepsilon r$, from ψ_i, yielding

$$\psi_i^* = \frac{z_i e}{\varepsilon r}\left(\frac{e^{\kappa a} e^{-\kappa r}}{1+\kappa a} - 1 \right).$$

Therefore, the potential at the surface of the ith ion ($r = a$) due to the presence of all other ions in solution is given by:

$$\psi_{i,a}^* = -\frac{z_i e}{\varepsilon}\left(\frac{\kappa}{1+\kappa a} \right).$$

From $\mu_i^{ex} = \frac{z_i e \psi_i}{2}$, we get

$$\mu_i^{ex} = -\frac{z_i^2 e^2}{2\varepsilon}\left(\frac{\kappa}{1+\kappa a} \right) N ,$$

where N is Avogadro's number, to put the potential on a molar basis. So:

$$\ln \lambda_i = -\frac{z_i^2 e^2}{2\varepsilon kT}\left(\frac{\kappa}{1+\kappa a}\right).$$

Now we must modify $\kappa^2 = \sum_j \frac{4\pi e^2 C_j z_j^2}{\varepsilon kT}$ to convert C_j to M_j units. We divide by N and convert cc to liters (1000 cc/liter):

$$\kappa^2 = \sum_j \frac{4\pi N e^2 M_j z_j^2}{1000\varepsilon kT}.$$

To go from Molarity to molality we use the relation $M_j = \dfrac{m_j \rho^*}{1+\sum_k 0.001 m_k W_k}$, where W_k is the molecular weight of the kth component and ρ^* is the solution density. For geological (natural) fluids this expression may be simplified to $M_j \cong m_j \rho$, where ρ is the density of pure water, since

$$\rho^* \cong \left(1+\sum_k 0.001 m_k W_k\right)\rho.$$

These manipulations give us

$$\kappa^2 = \frac{4\pi e^2 N\rho \sum_j m_j z_j^2}{1000\varepsilon kT}.$$

If we define

$$\boxed{I = \frac{1}{2}\sum_j m_j z_j^2}$$

and call it the ionic strength, then

$$\kappa^2 = \frac{8\pi e^2 N\rho I}{1000\varepsilon kT}.$$

Hence:

$$\ln \lambda_i = \frac{-z_i^2 e^2}{2\varepsilon kT}\frac{\sqrt{\frac{8\pi e^2 N\rho}{1000\varepsilon kT}}\sqrt{I}}{1+a\sqrt{\frac{8\pi e^2 N\rho}{1000\varepsilon kT}}\sqrt{I}}.$$

Define

$$B_\gamma = \sqrt{\frac{8\pi e^2 N \rho}{1000 \varepsilon k T}}$$

and

$$A_\gamma = \frac{\sqrt{2\pi N} e^3 \sqrt{\rho}}{\ln(10)\sqrt{1000}\,(\varepsilon k T)^{3/2}} \ ,$$

and we get

$$\boxed{\log \lambda_i = \frac{-A_\gamma z_i^2 \sqrt{I}}{1 + a B_\gamma \sqrt{I}}}$$

Now we must convert rational to molal activity coefficients.

First note that

$$X_i = \frac{m_i}{55.51 + \sum_j m_j} \ ,$$

and

$$\mu_i = \mu_i^o + RT \ln(\lambda_i X_i) = \mu_i^{o,*} + RT \ln(\gamma_i m_i) \ .$$

So:

$$\frac{\mu_i^{o,*} - \mu_i^o}{RT} = \ln\left(\frac{X_i}{m_i}\right) + \ln\left(\frac{\lambda_i}{\gamma_i}\right)$$

As $m_i \to 0$,

$$\frac{\mu_i^{o,*} - \mu_i^o}{RT} \to \ln\left(\frac{1}{55.51}\right),$$

so

$$\ln\left(\frac{1}{55.51}\right) = \ln\left(\frac{1}{55.51 + \sum_j m_j}\right) + \ln\left(\frac{\lambda_i}{\gamma_i}\right).$$

Thus

$$\ln(\lambda_i) = \ln(\gamma_i) + \ln\left(1 + \sum_j m_j \Big/ 55.51\right).$$

Defining

$$\boxed{\Gamma_\gamma = -\log\left(1 + \sum_j m_j \Big/ 55.51\right)},$$

we have finally:

$$\log \gamma_i = \frac{-A_\gamma z_i^2 \sqrt{I}}{1 + aB_\gamma \sqrt{I}} + \Gamma_\gamma$$

This is the *Debye-Hückel* law.

At low concentrations

$$\log \gamma_i \rightarrow -A_\gamma z_i^2 \sqrt{I}.$$

This is the *Debye-Hückel Limiting* Law. Note that a is an ion parameter for the solution. A_γ and B_γ are f(T,P) and are tabulated by Helgeson and Kirkham (1974).