❖ Ion-Size Effect on Potential

In the Debye-Huckel theory of ion-ion interaction, the central ion was simply treated as a point charge instead of its actual size. The scientific community realized that it might be one of the reasons behind the deviations observed from Debye-Huckel limiting law of activity coefficients. In order to understand the effect of ion size on the potential, recall the expression for the Debye-Huckel length (r_{max}) or κ^{-1}, i.e.,

$$r_{max} = \left(\frac{\varepsilon kT}{4\pi}\frac{1}{\sum_i n_i^0 Z_i^2 e_0^2}\right)^{1/2} \tag{140}$$

Where n_i^0 is the bulk concentration of the ith species and k is simply the Boltzmann constant. The symbol ε represents the dielectric constant of the surrounding medium. The symbol Z_i shows the charge number of the ion whereas e_0 represents the electronic charge. It is obvious from the equation (140) that the mean thickness of the ionic cloud (κ^{-1}) is actually inversely proportional to the concentration. This means that at higher concentrations, the mean thickness of the ionic cloud will be small and cannot outrank the size of the central ion anymore. In other words, at higher concentration, the size of the reference ion cannot be neglected at all, and therefore, the point charge approximation is no longer valid. For instance, At a concentration of 0.1*N*, the mean thickness of the ionic cloud is only ten times the radius of the reference ion.

Consider $4\pi r^2 dr$ as the volume element of a hollow spherical shell of thickness dr with the inner and outer radius as r and $r+dr$, respectively, with the size of the ion represented by the parameter a.

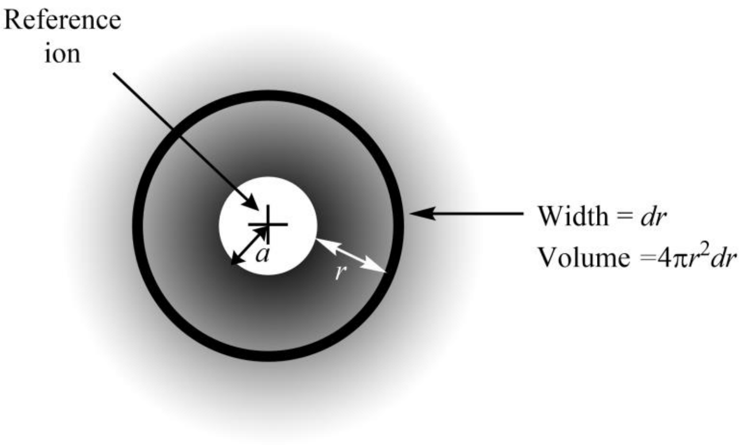

Figure 13. The depiction of excess charge density as a function of the distance r from the reference ion of finite size a.

Therefore, the ion-size must be considered for a more realistic picture of the actual situation. To do so, consider the linearized Poisson-Boltzmann equation which is free from both approximations, i.e., ion-size matters and the point charge consideration.

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right) = \kappa^2\psi_r \tag{141}$$

Where ψ_r is the potential at a distance r from the reference ion. The symbol κ is defined as

$$\kappa = \left(\frac{4\pi}{\varepsilon kT}\sum_i n_i^0 Z_i^2 e_0^2\right)^{1/2} \tag{142}$$

The general solution of the above equation is

$$\psi_r = A\frac{e^{-\kappa r}}{r} + B\frac{e^{+\kappa r}}{r} \tag{143}$$

Since the potential at $r = \infty$ must vanish, this boundary condition is satisfied only if $B = 0$. Therefore, the acceptable form of the equation (143) should be like this

$$\psi_r = A\frac{e^{-\kappa r}}{r} \tag{144}$$

To evaluate the value of constant A in this scenario, a slightly different route is followed. As we know that the total charge in the dr thickness of a spherical shell at distance r is

$$dq = \rho_r 4\pi r^2 dr \tag{145}$$

Now, the excess charge density at distance r from the reference ion will be

$$\rho_r = -\frac{\varepsilon}{4\pi}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right)\right] = -\frac{\varepsilon\kappa^2\psi_r}{4\pi} \tag{146}$$

Using the value of ψ_r from equation (144) into equation (146), we get

$$\rho_r = -\frac{\varepsilon\kappa^2}{4\pi}A\frac{e^{-\kappa r}}{r} \tag{147}$$

After putting the value of equation (147) into equation (145), we have

$$dq = -\frac{\varepsilon\kappa^2}{4\pi}A\frac{e^{-\kappa r}}{r}4\pi r^2 dr \tag{148}$$

or

$$dq = -\varepsilon\kappa^2 A e^{-\kappa r} r dr \tag{149}$$

Since the exponential part becomes zero only at $r = \infty$, the total charge around the reference ion can be obtained by integrating the equation (149) from an unknown parameter $r = a$ to $r = \infty$.

$$q_{cloud} = \int_{r=a}^{r=\infty} dq\ dr = \int_{r=a}^{r=\infty} -\varepsilon\kappa^2 A e^{-\kappa r} r dr \tag{150}$$

or

$$q_{cloud} = \int_{r=a}^{r=\infty} dq\ dr = -A\varepsilon e^{-\kappa a}(1+\kappa a) \tag{151}$$

Also as we know that the total charge on the ionic cloud must be equal and opposite to the charge on the reference ion i.e.

$$q_{cloud} = -Z_i e_0 \tag{152}$$

Equating the results of equation (151) and equation (152), we have

$$-A\varepsilon e^{-\kappa a}(1+\kappa a) = -Z_i e_0 \tag{153}$$

or

$$A = \frac{Z_i e_0}{\varepsilon}\frac{e^{\kappa a}}{(1+\kappa a)} \tag{154}$$

Using the value of *A* from equation (154) in equation (144), we get

$$\psi_r = \frac{Z_i e_0}{\varepsilon}\frac{e^{\kappa a}}{(1+\kappa a)}\frac{e^{-\kappa r}}{r} \tag{155}$$

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