❖ Ion-Size Parameter and the Theoretical Mean - Activity Coefficient in the Case of Ionic Clouds with Finite-Sized Ions

As we know that the total electrostatic potential at a distance *r* can simply be fragmented as given below.

$$\psi_r = \psi_{ion} + \psi_{cloud} \tag{156}$$

or

$$\psi_{cloud} = \psi_r - \psi_{ion} \tag{157}$$

The electrostatic potential at a distance *r* from an ion of finite size is

$$\psi_r = \frac{Z_i e_0}{\varepsilon} \frac{e^{\kappa a}}{(1 + \kappa a)} \frac{e^{-\kappa r}}{r} \tag{158}$$

Also, from the formulation of potential due to a single charge at a distance r, we know that

$$\psi_{ion} = \frac{Z_i e_0}{\varepsilon r} \tag{159}$$

After putting the values of ψ_r and ψ_{ion} from equation (158) and equation (159) into equation (157), we have

$$\psi_{cloud} = \frac{Z_i e_0}{\varepsilon} \frac{e^{\kappa a}}{(1+\kappa a)} \frac{e^{-\kappa r}}{r} - \frac{Z_i e_0}{\varepsilon r} \tag{160}$$

or

$$\psi_{cloud} = \frac{Z_i e_0}{\varepsilon r}\left[\frac{e^{\kappa(a-r)}}{(1+\kappa a)} - 1\right] \tag{161}$$

At this point, we must recall the relationship of mean activity coefficient and chemical potential change of the ion-ion interaction, i.e.,

$$RT \ln f_i = \Delta\mu_{i-I} \tag{162}$$

also

$$\Delta\mu_{i-I} = \frac{N_A Z_i e_0}{2}\psi \tag{163}$$

From equation (162) and (163), we have

$$RT \ln f_i = \frac{N_A Z_i e_0}{2}\psi \tag{164}$$

$$\ln f_i = \frac{N_A Z_i e_0}{2RT}\psi \tag{165}$$

Moreover, as the potential at the surface ($r = a$) of the ion must be

$$\psi = \psi_{cloud} \tag{166}$$

Which implies that ψ_{cloud} in equation (161) at $r = a$ should become

$$\psi_{cloud} = \frac{Z_i e_0}{\varepsilon a}\left[\frac{1}{(1+\kappa a)} - 1\right] \tag{167}$$

or

$$\psi_{cloud} = \frac{Z_i e_0}{\varepsilon a}\left[\frac{1 - 1 - \kappa a}{(1+\kappa a)}\right] \tag{168}$$

$$\psi_{cloud} = -\frac{Z_i e_0}{\varepsilon \kappa^{-}} \frac{1}{(1+\kappa a)} \tag{169}$$

After using the value of equation (169) in equation (165), we get

$$\ln f_i = -\frac{N_A Z_i^2 e_0^2}{2RT\varepsilon\kappa^{-1}} \frac{1}{(1+\kappa a)} \tag{170}$$

The mean ionic activity coefficient, in this case, will be

$$\log f_\pm = -\frac{AZ_+Z_-}{(1+\kappa a)} I^{1/2} \tag{171}$$

Where I is the ionic strength and A is Debye-Huckel constant. Now since the thickness of the ionic cloud is defined as

$$\kappa = BI^{1/2} \tag{172}$$

After putting the value of κ from equation (172) into equation (171), we have

$$\log f_\pm = -\frac{AZ_+Z_- I^{1/2}}{1 + a\, BI^{1/2}} \tag{173}$$

Which is the equation for the mean ionic activity coefficient when the central ion has a finite size. Now recall the equation for mean ionic activity coefficient when the central ion was considered as point charge i.e.

$$\log f_\pm = -AZ_+Z_- I^{1/2} \tag{174}$$

Hence, the two equations differ only in respect of denominator $1 + \kappa a$. The rearranged form of the equation (171) is

$$\log f_\pm = -\frac{AZ_+Z_-}{(1 + a/\kappa^{-1})} I^{1/2} \tag{175}$$

At large dilution, $a \ll \kappa^{-1}$, and the denominator tends to approach unity. Therefore, at very large dilution, the equation (175) becomes equal to equation (174), proving the correspondence principle.

The most obvious approach to estimate the ion size parameter is the sum of the crystallographic radii of the cation and anions present in the electrolytic-solution. This is because the two ions cannot come closer than the sum of their individual ionic radii. However, since ions are hydrated in aqueous solutions, one might think the ion size parameter as the sum of the hydrated radii instead. Nevertheless, the hydrated radii would face some compression during the course of the collision of ion. All this suggests that the magnitude of 'a' must be greater than the sum of the individual crystallographic radii and should be less than the sum of their individual hydrated radii. Therefore, the "mean distance of closest approach" should be more appropriate for this situation. The best way to estimate the ion-size parameter is to calibrated equation (175) to match the experimental value of mean ionic activity coefficient. After knowing the ion size parameter at one concentration, the value of mean ionic activity coefficient can easily be determined at other concentrations.

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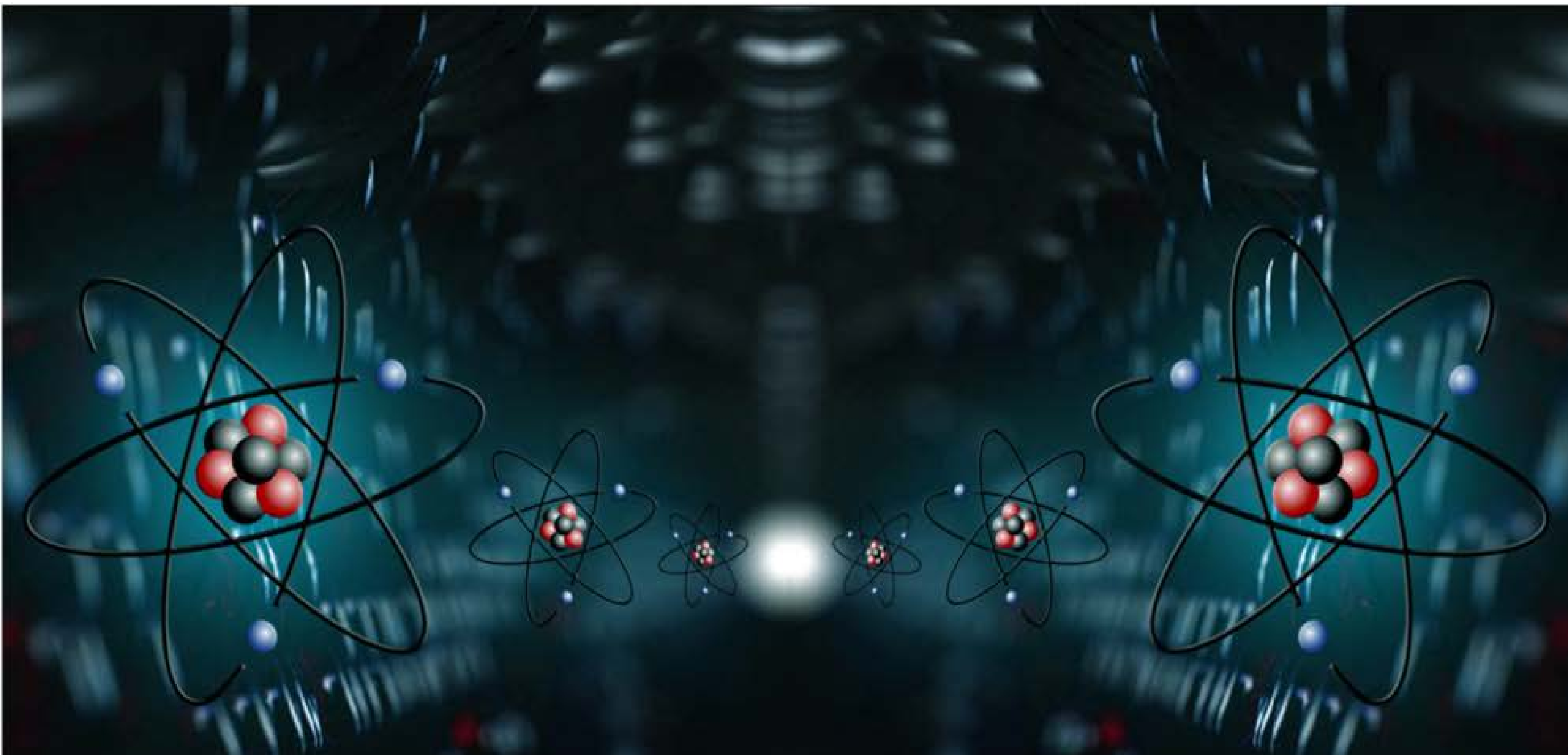

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