

❖ Effect of Ion Association Upon Conductivity (Debye-Huckel-Bjerrum Equation)

According to the Debye-Huckel theory of ion-ion interaction, the ions produced by the dissociation of electrolytes are randomly distributed in the solution with oppositely charged ionic-cloud surrounding them. Nevertheless, the possibility that some negative ions might get very close to the positively charged reference ion was neglected. In such a situation, the translational thermal energy would not be enough to make the ions to move independently, and an ionic-pair may be formed. Being a combined entity of two equal and opposite charges, these ion pairs are completely neutral and distributed randomly in the electrolytic solutions. These neutral ion-pairs are not influenced by the reference ion under consideration. Therefore, the fraction of ions participating in these ion pairs must be obtained for a more accurate picture of the electrochemical properties of the solutions.

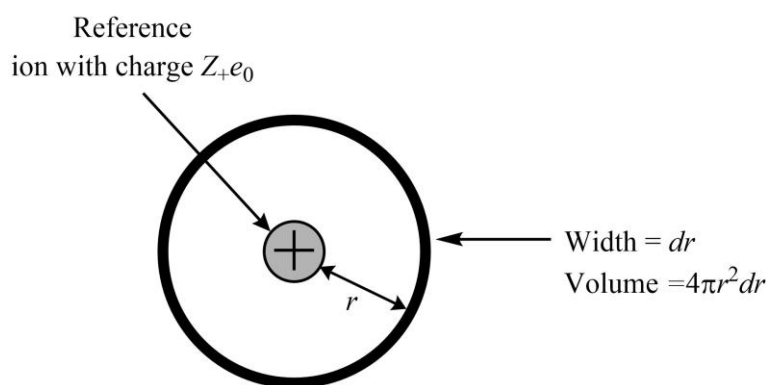


Figure 21. The probability of finding an oppositely charged ion i.e. Z_-e_0 at distance r in dr thickness around the reference ion.

In order to understand the concept, imagine a spherical shell at a distance r from the reference ion with dr thickness. The probability of finding the anion (P_r) in the spherical shell is proportional to three main factors. The first one is the ratio $4\pi r^2 dr$ volume element to the total volume V , the second one is the total number of anions i.e. N_- and the third is the $e^{-U/kT}$ (U represents the potential energy of anion situated at distance r). Mathematically, we can formulate this as

$$P_r = \left(\frac{4\pi r^2 dr}{V} \right) (N_-) (e^{-U/kT}) \quad (202)$$

Now because N_-/V represents the anions' concentration n_-^0 , the above equation takes the form

$$P_r = 4\pi r^2 dr n_-^0 e^{-U/kT} \quad (203)$$

Furthermore, after recalling the value of U , i.e.,

$$U = -\frac{Z_+Z_-e_0^2}{\epsilon r} \quad (204)$$

Equation (203) becomes

$$P_r = 4\pi r^2 n_-^0 e^{Z_+Z_-e_0^2/\epsilon r kT} dr \quad (205)$$

Where ϵ is the dielectric constant of the medium and e_0 is the electronic charge. Now define a new parameter λ as

$$\lambda = \frac{Z_+Z_-e_0^2}{\epsilon kT} \quad (206)$$

Therefore, we can write

$$P_r = (4\pi n_-^0) e^{\lambda/r} r^2 dr \quad (207)$$

Similarly, the probability of finding a positively charged ion at distance r in dr thickness around a negatively charged reference ion will be

$$P_r = (4\pi n_+^0) e^{\lambda/r} r^2 dr \quad (208)$$

Therefore, the probability of finding i th type of ion at distance r in dr thickness around a k th type of reference ion can be formulated as

$$P_r = (4\pi n_i^0) e^{\lambda/r} r^2 dr \quad (208)$$

where

$$\lambda = \frac{Z_i Z_k e_0^2}{\epsilon kT} \quad (209)$$

The variation of probability of finding one type ion around other types shows a strange behavior with distance.

Table 1. The total number of oppositely charged ions as a function of distance.

r (pm)	Number of ions in shell $\times 10^{22}$
200	1.77
250	1.37
300	1.22
350	1.17
400	1.21

When r varies from very small to moderate value, the magnitude of P_r decreases because of the factor $e^{\lambda/r}$. However, after a certain value, the probability starts to rise due to the dominance of the directly correlated factor of r^2 . Hence, we can say that the probability of finding the oppositely charged ion at distance r from the reference ion first decreases and then increases as we move away from the central ion.

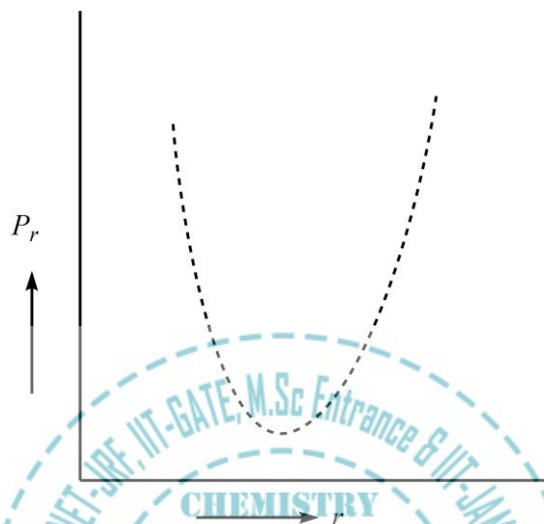


Figure 22. The variation of the overall probability of finding an ion around ion under consideration as a function of distance.

Since the probability of finding a negative ion within a certain distance around a positive ion is obtained by applying the lower and upper bounds, we need to find these limits first. Now, because the ion-pair can be formed only if the participating ions close enough so that the electrostatic attraction can outshine the thermal forces; let this distance be represented by q .

In other words, we can say that the formation of ion-pair takes place only if the separation between the cation and anion is less than q . Since the cation and anion cannot approach each other closer than the ionic-size parameter (a), i.e., (the distance of closest approach), the ion-pair will be formed for an interionic separation of greater than a but less than q . The probability of the ion-pair formation is the number of i th type of ion participating in the ion-association to the total number of the same type of ions. Therefore, the probability of ion-pair formation (θ) can be formulated as

$$\theta = \int_a^q P_r dr = \int_a^q (4\pi n_i^0) e^{\lambda/r} r^2 dr \quad (210)$$

Owing to the divergent nature of the integral, the upper limit can be set to the overall probability minima (q) as shown below.

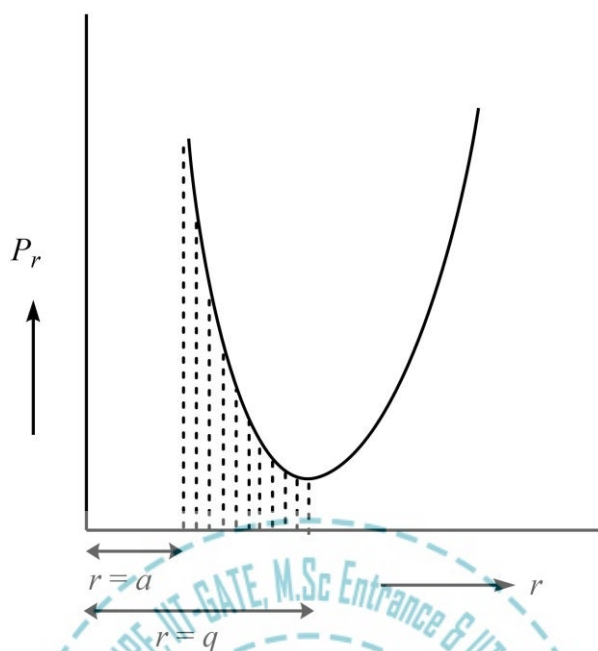


Figure 23. The depiction of the overall probability of finding an oppositely charged ion around reference ion from a to q .

To find the minima, differentiate equation (208) with respect to r and then put equal to zero, i.e.,

$$\frac{dP_r}{dr} = 4\pi n_i^0 e^{\frac{\lambda}{r}} 2r - 4\pi n_i^0 r^2 e^{\frac{\lambda}{r}} \frac{\lambda}{r^2} \quad (211)$$

or

$$2r_{min} - \lambda = 0 \quad (212)$$

or

$$q = r_{min} = \frac{\lambda}{2} \quad (213)$$

After putting the value of λ from equation (206) into (213), we get

$$q = \frac{Z_+ Z_- e_0^2}{2\epsilon kT} \quad (214)$$

Bjerrum claimed that only Coulombic interactions (short-range) lead to the formation of ion-pair; and if the separation of cation and anion larger than q , they should be treated as free ions. In other words, we can say that the formation of ion-pair is feasible if $a < q$ and infeasible if $a > q$.



The law of mass action can also be used to give association constant as

$$K_A = \frac{a_{IP}}{a_M^+ a_A^-} \quad (220)$$

Where a_M^+ , a_A^- and a_{IP} are the activities of the cation, anion and ion-pair, respectively. Moreover, it can also be seen that the association constant is just the reciprocal of dissociation constant. Now, θ is the fraction of ions forming ion-pair, whereas θc and $(1 - \theta)c$ are the concentrations of ion-pair and free ions, respectively. Therefore, the association constant in terms of activity coefficients can be written as

$$K_A = \frac{\theta c f_{IP}}{(1 - \theta) c f_+ (1 - \theta) c f_-} \quad (221)$$

or

$$K_A = \frac{\theta}{(1 - \theta)^2} \frac{1}{c} \frac{f_{IP}}{f_+ f_-} \quad (222)$$

Where f_+ , f_- and f_{IP} are the activity coefficients for cation, anion and ion-pair, respectively. In terms of mean ionic activity coefficient and analytical concentration c_a , the equation (222) can also be written as

$$K_A = \frac{\theta}{(1 - \theta)^2} \frac{1}{c_a} \frac{f_{IP}}{f_{\pm}^2} \quad (223)$$

Now because the ion pairs are neutral species, and therefore, do not participate in ion-ion interactions; the activity coefficients ion-pairs can be taken as unity. Therefore, equation (223) can be written as

$$K_A = \frac{\theta}{(1 - \theta)^2} \frac{1}{c_a} \frac{1}{f_{\pm}^2} \quad (224)$$

or

$$\theta = K_A (1 - \theta)^2 c_a f_{\pm}^2 \quad (225)$$

At this stage, the only thing that is needed for further treatment is the relation between θ and the conductivity of the electrolyte used. To do so, recall the correlation between the concentration of free ions and specific conductivity (σ) i.e.

$$\sigma = ZF(u_+ + u_-) c_{free\ ions} \quad (226)$$

Where F is the Faraday constant.

$$\sigma = ZF(u_+ + u_-) \frac{c_{free\ ions}}{c_a} c_a \quad (227)$$

The term $c_{free\ ions}/c_a$ is the fraction of ions that are free (not associated), and therefore

$$\frac{c_{free\ ions}}{c_a} = 1 - \theta \quad (228)$$

Using the result of equation (228) in equation (227), we get

$$\sigma = ZF(u_+ + u_-)(1 - \theta)c_a \quad (229)$$

Furthermore, after converting the specific conductivity to equivalent conductivity ($\Lambda = \sigma/Zc_a$), the equation (229) takes the form

$$\Lambda = F(u_+ + u_-)(1 - \theta) \quad (230)$$

Imagine a situation if no ion-association occurs ($\theta = 0$), then the equation (230) would reduce to

$$\Lambda_{\theta=0} = F(u_+ + u_-) \quad (231)$$

Using equation (231) in equation (230), we get

$$\Lambda = \Lambda_{\theta=0}(1 - \theta) \quad (232)$$

or

$$\frac{\Lambda}{\Lambda_{\theta=0}} = 1 - \theta \quad (233)$$

or

$$\theta = 1 - \frac{\Lambda}{\Lambda_{\theta=0}} \quad (234)$$

Now putting the values of θ and $1 - \theta$ from equation (234) and (233) in equation (225), we have

$$1 - \frac{\Lambda}{\Lambda_{\theta=0}} = K_A \left(\frac{\Lambda}{\Lambda_{\theta=0}} \right)^2 c_a f_{\pm}^2 \quad (235)$$

Rearranging, we get

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_{\theta=0}} + \frac{K_A f_{\pm}^2}{\Lambda_{\theta=0}^2} \Lambda c_a \quad (236)$$

Rearranging equation (229) for $F(u_+ + u_-)$ and putting in equation (231), we get

$$\Lambda_{\theta=0} = F(u_+ + u_-) = \frac{\sigma}{Z(1 - \theta)c_a} \quad (237)$$

The above equation shows equivalent conductivity at zero ion-association at $(1 - \theta)c_a$ concentration. Therefore, we must use Debye-Huckel-Onsager equation to express the more appropriate conductivity at small concentrations i.e.

$$\Lambda_{\theta=0} = \Lambda^0 - (A + B\Lambda^0)\sqrt{1 - \theta}\sqrt{c_a} \quad (238)$$

Where the two constants, A and B , are defined as

$$A = \frac{FZe_0}{3\pi\eta} \left(\frac{8\pi Z^2 e_0^2 N_A}{1000\epsilon kT} \right)^{\frac{1}{2}} \quad \text{and} \quad B = \frac{e_0^2 \omega}{6\epsilon kT} \left(\frac{8\pi Z^2 e_0^2 N_A}{1000\epsilon kT} \right)^{\frac{1}{2}} \quad (239)$$

Where F is the Faraday constant and N_A is the Avogadro number. The symbol ϵ represents the dielectric constant of the medium whereas η is the coefficient of viscosity. Z is charge numbers of the cation and anion. The symbol e_0 simply shows the electronic charge. ω is a parameter defined earlier in this chapter. The equation (238) can be simplified as

$$\Lambda_{\theta=0} = \Lambda^0 W \quad (240)$$

Where W represents a continued fraction i.e.

$$W = 1 - w \left\{ 1 - w \left[1 - w (\dots)^{-1/2} \right]^{-1/2} \right\}^{-1/2} \quad (241)$$

Provided that

$$w = \frac{(A + B\Lambda^0)\sqrt{c_a}\sqrt{\Lambda}}{(\Lambda^0)^{3/2}} \quad (242)$$

Using the result of equation (240) into (236), we get

$$\frac{1}{\Lambda} = \frac{1}{\Lambda^0 W} + \frac{K_A f_{\pm}^2}{(\Lambda^0 W)^2} \Lambda c_a \quad (243)$$

or

$$\frac{W}{\Lambda} = \frac{W}{\Lambda^0} + \frac{K_A}{(\Lambda^0)^2} \frac{f_{\pm}^2 \Lambda c_a}{W} \quad (244)$$

After looking at the above equation, it is obvious that the formation of ion-pairs has changed the variation of equivalent conductivity with concentration drastically. When the formation of ion-pairs was ignored, the variation of equivalent conductivity with concentration was empirically explained by the Kohlrausch's law.

Nevertheless, in the case of non-aqueous solvents with low dielectric constant, a significant amount of ion-pair formation occurs, and therefore, W/Λ is plotted vs $f_{\pm}^2 \Lambda c_a / W$ with W/Λ^0 as intercept and $K_A/(\Lambda^0)^2$ as slope.

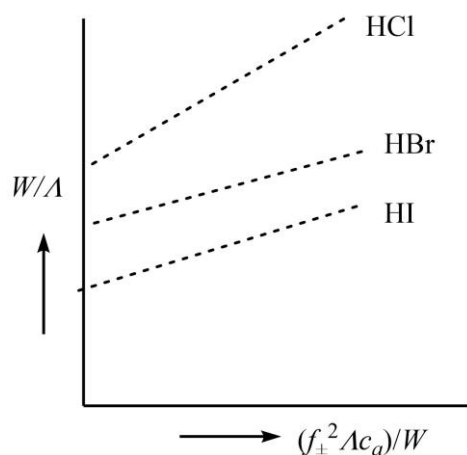


Figure 25. The variation of W/Λ is plotted vs. $f_{\pm}^2 \Lambda c_a/W$ for some typical electrolytic solutions.



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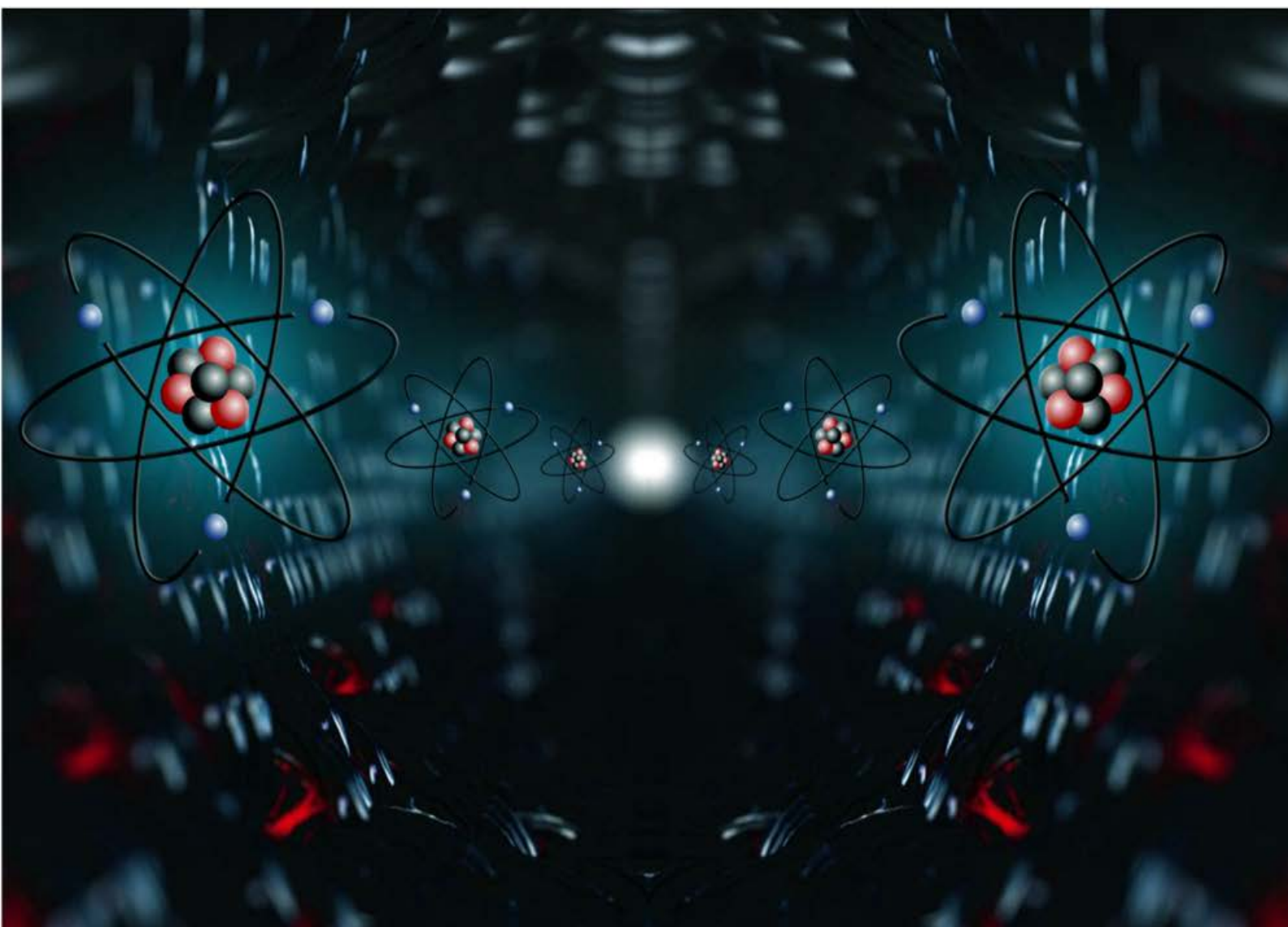
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Volume I

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Mandeep Dalal

(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)

Founder & Director, Dalal Institute

Contact No: +91-9802825820

Homepage: www.mandeepdalal.com

E-Mail: dr.mandeep.dalal@gmail.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands).

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