

### ❖ Equivalent Conductivity ( $\Lambda$ ) vs Concentration $C^{1/2}$ as a Function of the Solvent

In order to understand the variation of equivalent conductivity with the square root of concentration for different solvents, recall the generalized Walden's rule, i.e.,

$$u^0 \eta r = \text{constant} \quad (196)$$

The  $u^0$  is the ionic mobility at infinite dilution and symbol  $r$  represents the radius of the ionic species considered in the solvent under examination. The symbol  $\eta$  represents the coefficient of viscosity of the solvent used. Also, as we know that the equivalent conductivity at infinite dilution can be obtained from the relation given below.

$$\Lambda^0 = F u^0 \quad (197)$$

Now, if the ionic mobility obtained using equation (196) is used in equation (197) for different nonaqueous solutions, it has been found that predicted values of equivalent conductivity are quite large and sometimes even outnumber the equivalent conductivity in water as the solvent. All this suggests that there should be no problem in using non-aqueous solutions in electrochemical systems. However, the quantity that is more important for practical applications is the specific conductivity ( $\sigma$ ) at a finite concentration rather than the equivalent conductivity at infinite dilution. In other words, the conjugative relationship of electrode geometry and specific conductivity dictates the overall electrolytic resistance of the system under consideration. At this point, one might ask why the electrolytic resistance is important. The answer lies in the fact that the magnitude of useful power wasted as heat in the electrolytic solution is  $I^2 R$  ( $I$  is the current passed); and therefore, it is the electrolytic resistance that  $R$  must possess a lower value for feasibility. The lower value of  $R$  implies a higher value of specific conductivity, and the relation of specific conductivity with equivalent conductivity at a certain concentration ' $c$ ' is

$$\sigma = \Lambda Z c \quad (198)$$

Now since the equivalent conductance  $\Lambda$  also depends on concentration, we cannot use equivalent conductance at infinite dilution in equation (198) to find out the specific conductivity. First of all, one must determine the equivalent conductivity at concentration ' $c$ ', which is possible from the Debye-Huckel-Onsager equation if the values of constants  $A$  and  $B$  are known. Hence, to proceed further, we must recall the Debye-Huckel-Onsager equation for the non-aqueous solution first, i.e.,

$$\Lambda = \Lambda^0 - (A + B \Lambda^0) \sqrt{c} \quad (199)$$

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

$$A = \frac{F Z e_0}{3 \pi \eta} \left( \frac{8 \pi Z^2 e_0^2 N_A}{1000 \epsilon k T} \right)^{\frac{1}{2}} \quad (200)$$

$$B = \frac{e_0^2 \omega}{6\epsilon kT} \left( \frac{8\pi Z^2 e_0^2 N_A}{1000\epsilon kT} \right)^{\frac{1}{2}} \quad (201)$$

Where  $F$  is the Faraday constant and  $N_A$  is the Avogadro number. The symbol  $\epsilon$  represents the dielectric constant of the medium whereas  $\eta$  is the coefficient of viscosity.  $Z$  is charge numbers of the cation and anion. The symbol  $e_0$  simply shows the electronic charge.  $\omega$  is a parameter defined earlier in this chapter.

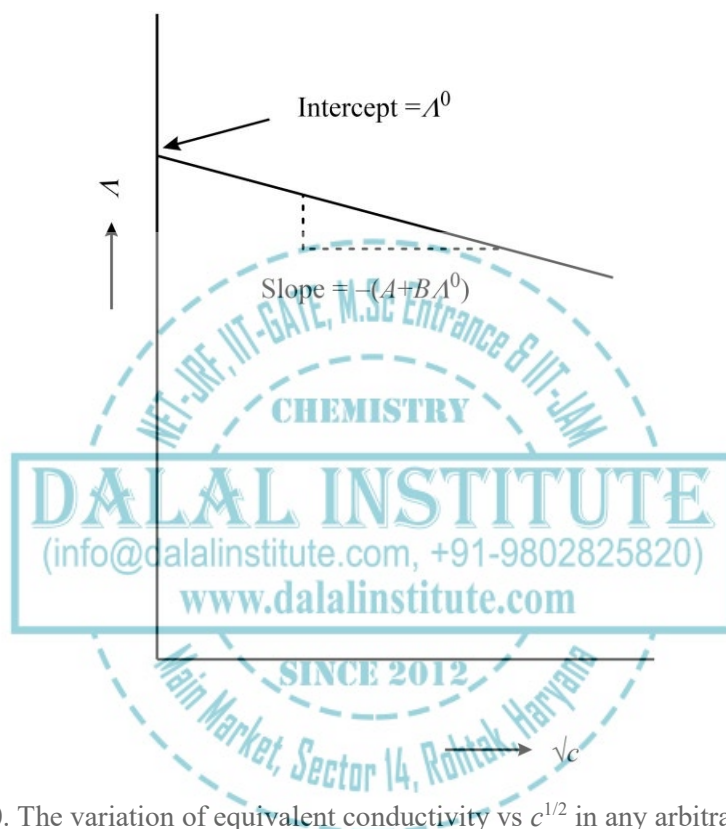


Figure 20. The variation of equivalent conductivity vs  $c^{1/2}$  in any arbitrary solvent.

It can be clearly seen that both the constants in the slope have the dielectric constant  $\epsilon$  in the denominator, and therefore, the equivalent conductivity as well as specific conductivity show decrease with the increasing  $\epsilon$ . In other words, we can say that the lower dielectric constant would result in stronger ion-ion interaction and vice-versa. Therefore, in the case of non-aqueous solvents with very low dielectric constants, the relative variation in the magnitude of equivalent conductivity with the square root of the concentration is very large. Consequently, all this result in a very low specific conductivity at any practical electrolytic concentration in non-aqueous solution than in water. Furthermore, in addition to the larger electrolytic resistance, non-aqueous solutions are hard to keep so because they can always absorb some moisture from the atmosphere.

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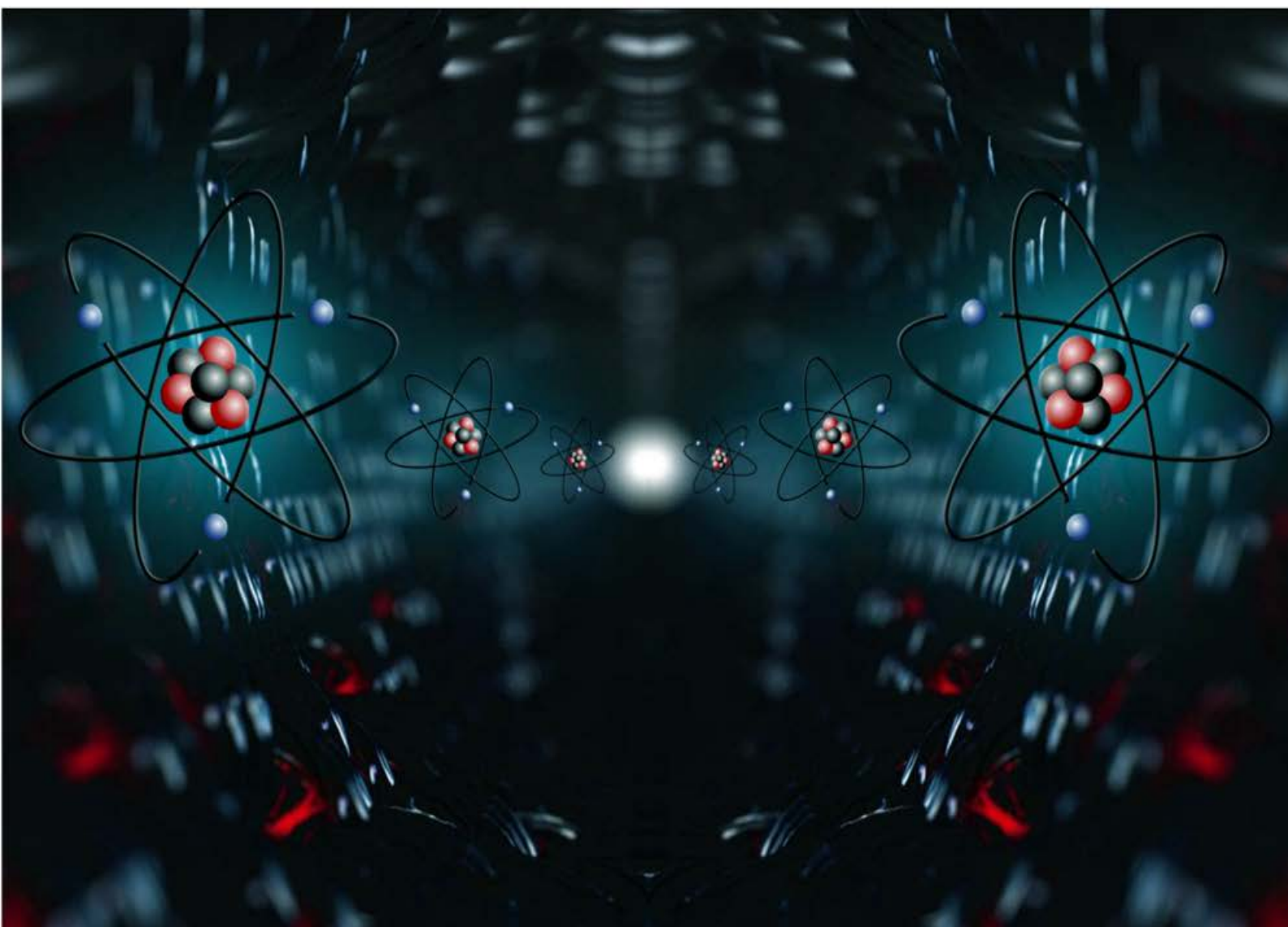
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**Volume I**

**MANDEEP DALAL**



*First Edition*

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