

### ❖ Debye-Huckel-Onsager Theory for Non-Aqueous Solutions

Before we discuss the Debye-Huckel-Onsager theory for non-aqueous solutions, recall the same for aqueous solutions i.e.

$$\Lambda = \Lambda^0 - \text{constant}\sqrt{c} \quad (187)$$

or

$$\Lambda = \Lambda^0 - (A + B\Lambda^0)\sqrt{c} \quad (188)$$

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

$$A = \frac{FZe_0}{3\pi\eta} \left( \frac{8\pi Z^2 e_0^2 N_A}{1000\epsilon kT} \right)^{\frac{1}{2}} \quad (189)$$

and

$$B = \frac{e_0^2 \omega}{6\epsilon kT} \left( \frac{8\pi Z^2 e_0^2 N_A}{1000\epsilon kT} \right)^{\frac{1}{2}} \quad (190)$$

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. The quantity  $\omega$  is defined as

$$\omega = \frac{Z_+ Z_- 2q}{1 + \sqrt{q}}$$

Where  $q$  is defined as

$$q = \frac{Z_+ Z_-}{Z_+ + Z_-} \frac{\lambda_+ + \lambda_-}{Z_+ \lambda_+ + Z_- \lambda_-}$$

It is obvious from the Debye-Huckel-Onsager equation that the plot of conductance vs square root of the concentration will be a straight line with a negative slope and positive intercept. The intercept after extrapolation gives the value of conductance of such solutions at infinite dilution.

Now, it has been observed that the Debye-Huckel-Onsager equation can also be applied to non-aqueous solutions up to the fairly good agreement. For instance, consider the variation of equivalent conductivity as a function of the square root of the concentration for different alkali sulfocyanates in methanol as the solvent. The theoretical predictions show that the results of the Debye-Hückel-Onsager equation are in good agreement with the experiment up to  $0.002 \text{ mol dm}^{-3}$ .

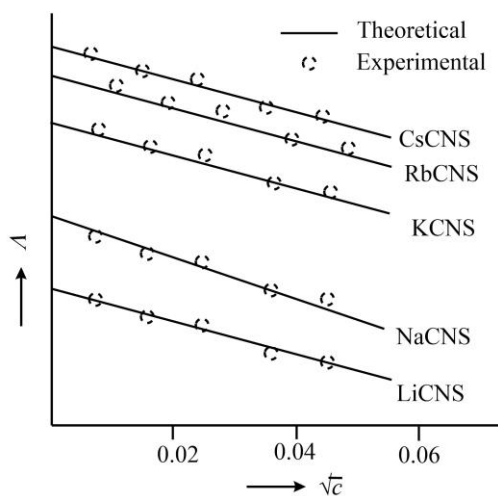


Figure 18. The variation of equivalent conductivity of alkali sulfocyanates vs  $c^{1/2}$  in  $\text{CH}_3\text{OH}$ .

In going from water to nonaqueous solvent, a significant variation in the quantities like dielectric constant of the medium, the distance of the closest approach, or viscosity is observed. Now since the Debye-Hückel-Onsager equation does have these quantities, the slope and intercept of the  $\Lambda$  vs  $c^{1/2}$  may also vary drastically.

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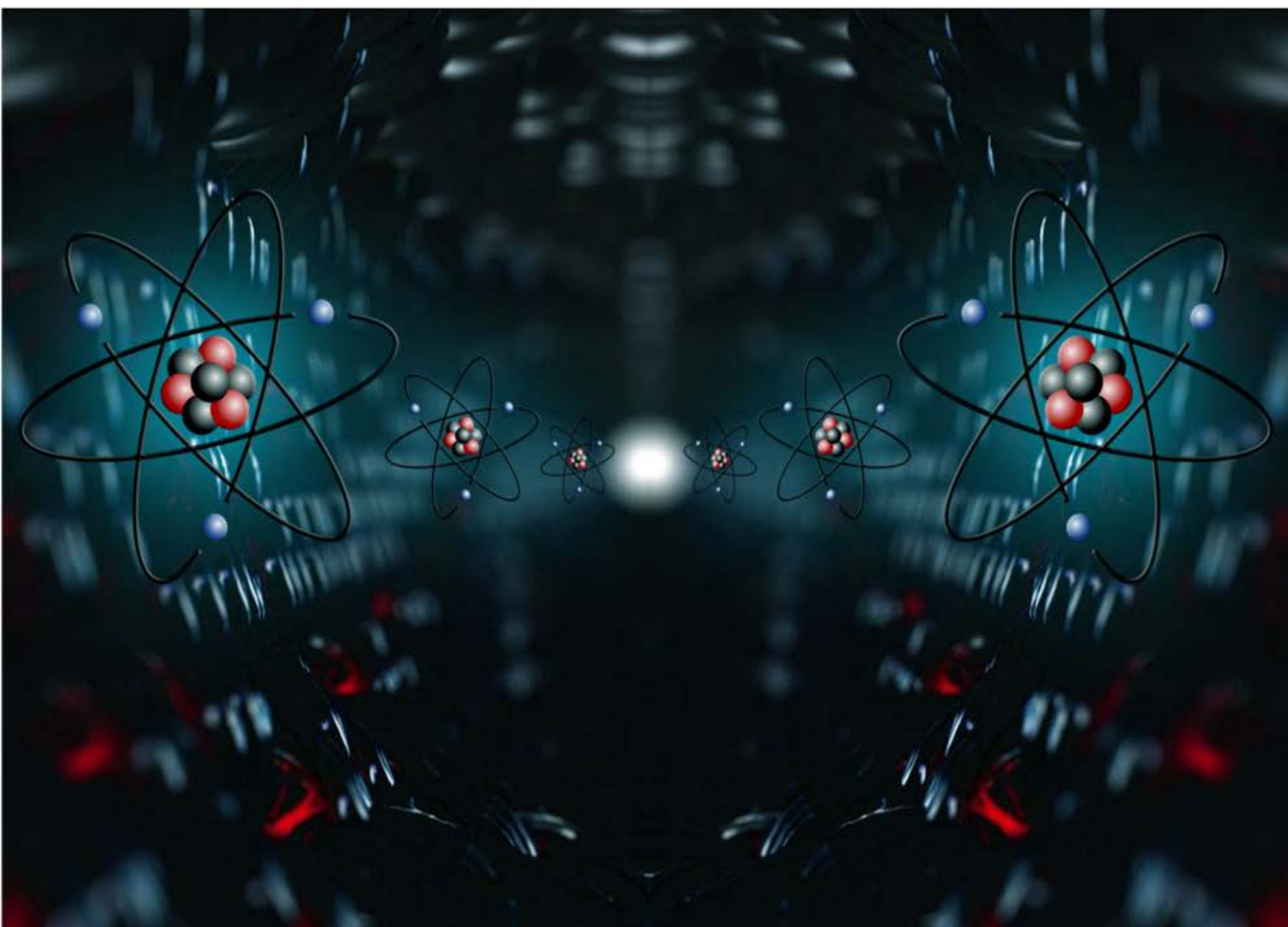
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**Volume I**

**MANDEEP DALAL**



*First Edition*

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