❖ 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.

$$\Lambda = \Lambda^0 - constant\sqrt{c} \tag{187}$$

or

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

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

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

and

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

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. The quantity ω 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 mol dm^{-3}.

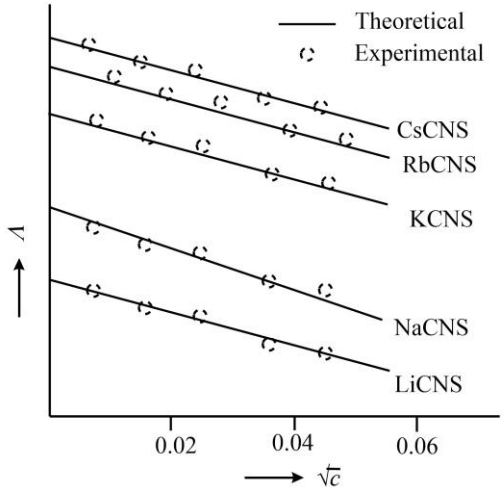
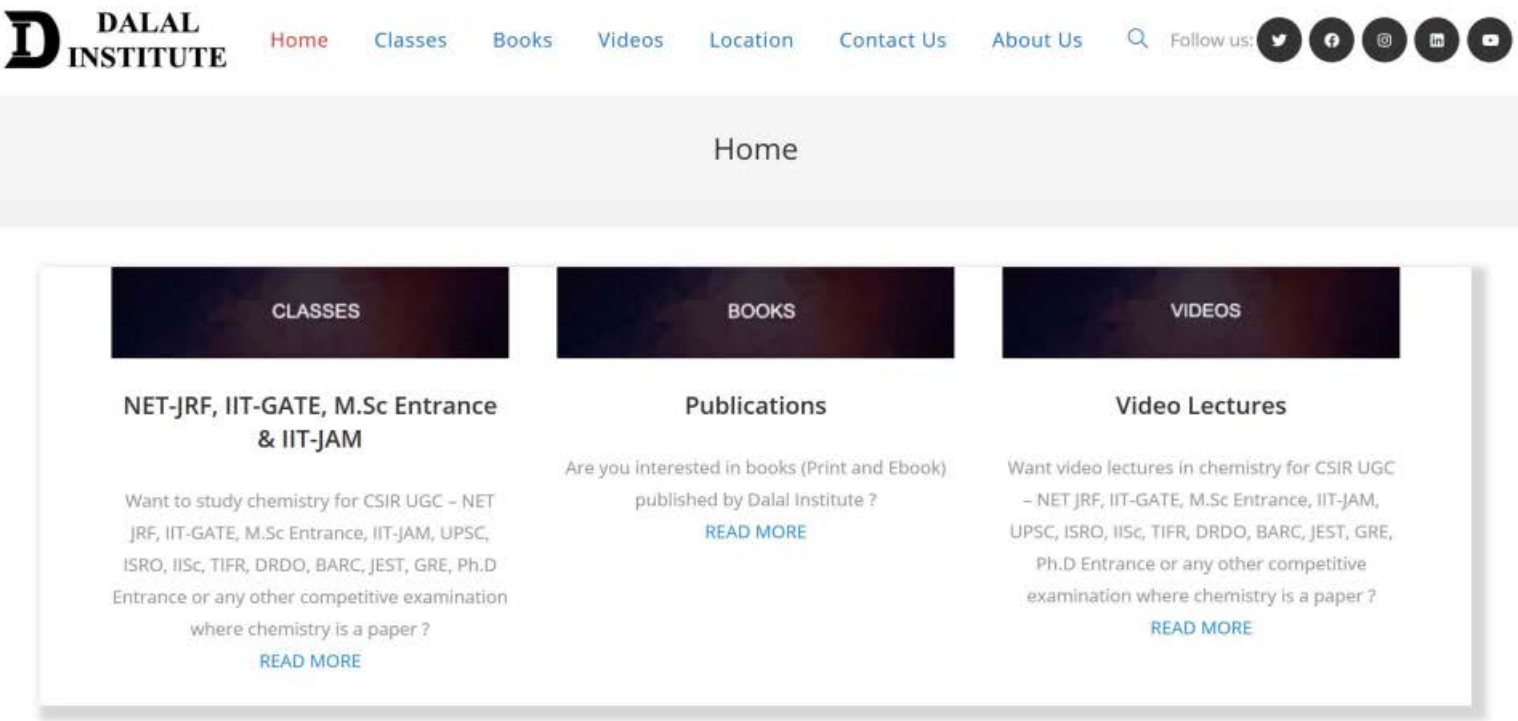


Figure 18. The variation of equivalent conductivity of alkali sulfocyanates vs $c^{1/2}$ in CH_3OH.

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 Λ vs $c^{1/2}$ may also vary drastically.



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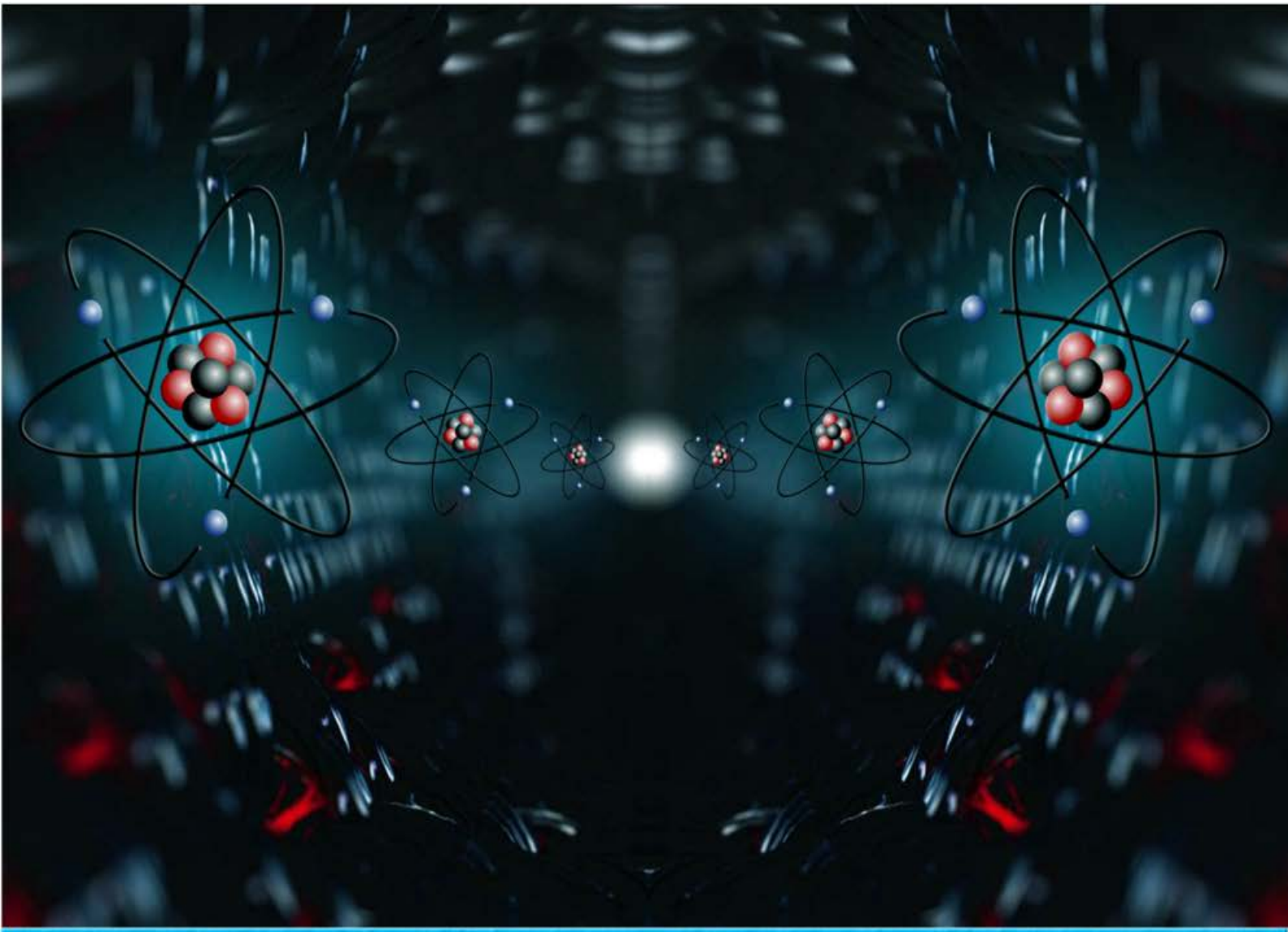

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