❖ The Solvent Effect on the Mobility at Infinite Dilution

As we know that the asymmetry and electrophoretic effects are not active at infinite dilution because of their dependence on the size of ionic-cloud, the mobility of ions in such cases can be formulated simply from the Stokes law, i.e.,

$$u_{con}^{0} = \frac{Ze_0}{6\pi\eta r} \tag{191}$$

Where *r* represents the radius of the solvated ion and η is the coefficient of viscosity. Z is charge numbers of the cation and anion. The symbol e_0 simply shows the electronic charge. Now, if we imagine the same electrolyte in different electrolytic solutions, we can say

$$u_{con}^{0}\eta r = constant \tag{192}$$

Assuming further that the *r* is also independent of solvent type, we have

$$u_{con}^{0}\eta = constant \tag{193}$$

Thus, it is obvious from the equation (193) that ionic mobility is inversely proportional to the coefficient of viscosity. More viscous solvents would result in a slow drift of ions and vice-versa. It has also been found that the equation (193) is more valid for solvents other than water.

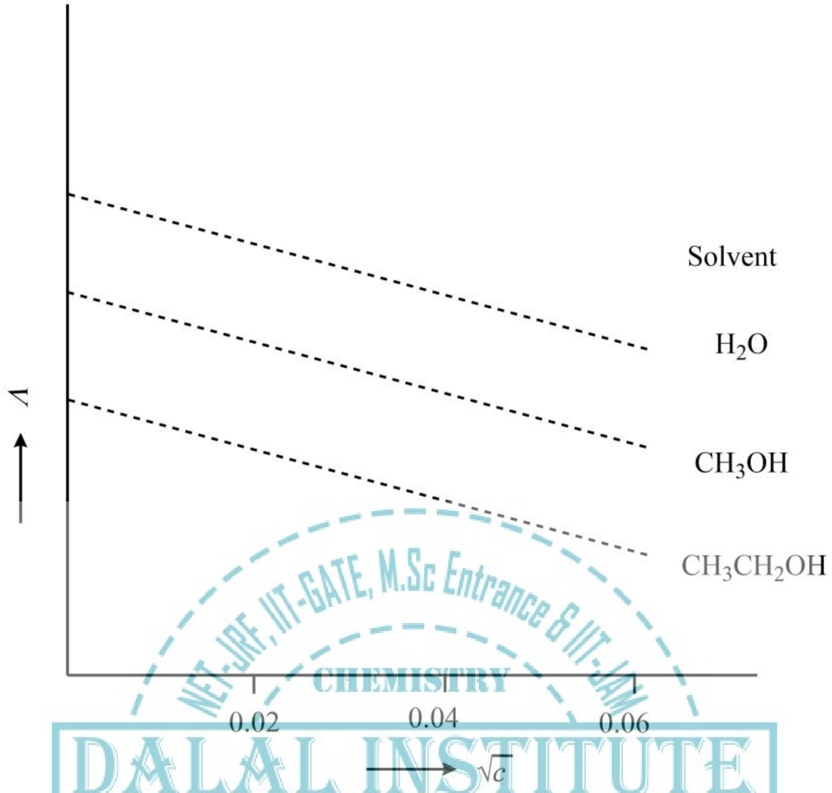

Figure 19. The variation of equivalent conductivity vs $c^{1/2}$ in different solvents.

Moreover, the radius of solvated ion may vary drastically in going from one solvent to another (in some cases it gets even double), the result of equation (193) does not find a very large application domain. This variation in the solvated radius is primarily due to the difference in the size of solvent molecules. For instance, the size of the solvated ion is larger in ethanol than in methanol, which in turn, is larger than what is observed in water. All this results in an opposite trend in the ionic mobilities, and therefore, in the equivalent conductivities as well. Recalling the simple Walden's rule i.e.

$$\Lambda\eta = constant \tag{194}$$

Where Λ is the equivalent conductivity of the electrolytic solution at concentration c. This simply means that equivalent conductivity and the viscosity of the solvent are inversely proportional to each other. However, the effect of the solvated radius must be considered for more accurate results. Therefore, we must more acceptable form of Walden's rule, i.e.,

$$u^0\eta r = constant \tag{195}$$

The symbol r represents the radius of the ionic species considered in the solvent under examination.

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