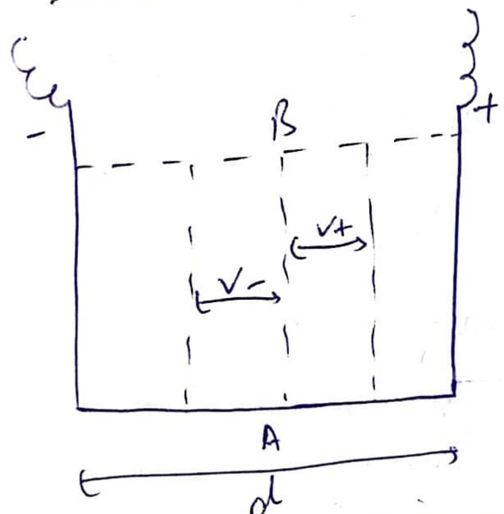
Debye - Falkenhagen Effect:

When high frequency (3×10^6 Hz) is used, ion changes their direction of motion so quickly that more sluggish atmosphere cannot adjust & follow the motion of ion. Both asymmetry & electrophoretic effect decreases & hence conductance increases.

Relationship between Ionic Mobility / Ionic velocity & ionic conductance



A potential ($\Delta\phi$) is applied

Let charge on each cation $= z_+$
charge on each anion $= z_-$
Total number of cations $= N_+$
Total number of anions $= N_-$
Average migration velocity of each cation $= v_+$
Average migration velocity of each anion $= v_-$

Since the solution is electrically neutral,
total positive charge ($N_+ z_+$) = Total negative charge ($N_- z_-$)

$$\text{velocity} = \frac{\text{distance}}{\text{time}}$$

If time = 1 sec, velocity = distance
$\therefore v_+ =$ distance travelled by cations per second.

Similarly, v_- = distance travelled by anions per second.

d = length of container

If 'd' distance has N_+ ions (for positive ions),

then 'v_+' distance travelled by positive ions has $\frac{N_+ v_+}{d}$ number of positive ions.

$d \rightarrow N_+$

$v_+ \rightarrow \frac{N_+ v_+}{d}$

So current carried by $\frac{N_+ v_+}{d}$ number of positive ions

$= I_+ = \frac{N_+ v_+}{d}(z_+ e)$

z_+ = charge on positive ion

e = electronic charge.

$z_+ e$ = Total charge carried by positive ions

$(I = \frac{Q}{t}$, time = 1 sec, $I = Q)$

So current carried = charge carried by ions.

Similarly, current carried by anions:

$$I_- = \frac{N_- v_-}{d} (|z_-| e)$$

I = Total current carried

$= I_+ + I_-$

$$= \frac{N_+ z_+ e (v_+ + v_-)}{d}$$

let 1 molecule of electrolyte gives ν_+ & ν_- ions

so 1 mole of electrolyte gives $\nu_+ N_A$ & $\nu_- N_A$ number of ions.

$\therefore N_+ = \nu_+ N_A$ & $N_- = \nu_- N_A$

$$\therefore I = \frac{N_A e (z_+ v_+ \nu_+ + |z_-| \nu_- v_-)}{d}$$

$$= \frac{F}{d} (z_+ \nu_+ v_+ + \cancel{\nu_-} |z_-| \nu_- v_-)$$ ($N_A e = F$ = Faraday's constant)

Molar conductance / conductivity of solution

$$= \Lambda_m = \frac{k}{c} = k \times V = k A d$$

$\therefore kA = \frac{\Lambda_m}{d}$ ($\because V = Ad$)

$$G = k \frac{A}{d}$$

$$= \frac{\Lambda_m}{d^2}$$

$V = IR$.

$\Delta\phi = IR$ or $I = \frac{\Delta\phi}{R} = \Delta\phi G = \Delta\phi \frac{\Lambda_m}{d^2}$

$$\frac{F}{d} (\nu_+ z_+ v_+ + \nu_- |z_-| v_-) = \Delta\phi \frac{\Lambda_m}{d^2}$$

At infinite delution,

$$\Lambda m = \nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty$$

$$\frac{F}{d}(\nu_+ z_+ V_+^\infty + \nu_- |z_-| V_-^\infty) = \frac{(\nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty)\Delta\phi}{d^2}$$

We can write,

$$\frac{F}{d} \nu_+ z_+ V_+^\infty = \frac{\nu_+ \lambda_+^\infty \Delta\phi}{d^2}$$

$$V_+^\infty = \frac{\lambda_+^\infty \Delta\phi}{d F z_+}$$

$$\frac{V_+^\infty}{\Delta\phi/d} = u_+^\infty = \frac{\lambda_+^\infty}{F z_+}$$

or $\boxed{u_+ = \frac{\lambda_+}{F z_+}}$ similarly, $\boxed{u_- = \frac{\lambda_-}{F|z_-|}}$

unit of $u = \frac{m s^{-1}}{V m^{-1}} = m^2 V^{-1} s^{-1}$.

The Walden's Rule :

When an ion in a solution is subjected to electrical field, it moves with a constant velocity. The ion attains this constant velocity when the accelerating electrical force = retarding frictional force

i.e. $ze E = 6\pi \eta r v$ (1.) $\xrightarrow{}$ Stoke's law.

$\left\{ \because \frac{F}{q} = E \right\}$ F → force, E → electric field, q → charge

ze = charge carried by each ion.

r = radius of ion

η = viscosity of medium

Rearranging (1.), $\frac{V}{E} = \frac{ze}{6\pi \eta r}$

$$\frac{v}{E} = u = \frac{z e}{6\pi \eta r} \quad \text{—(2)}$$

$$\Lambda = v_+ \lambda_+ + v_- \lambda_-$$

$$= v_+ u_+ z_+ F + v_- u_- |z_-| F \quad \left(\because u = \frac{\lambda}{zF}\right) \quad \text{—(3)}$$

$$\lambda = u z F.$$

Using value of 'u' from eq. (2) in eq. (3).

$$\Lambda = \frac{Fe}{6\pi\eta}\left[\frac{v_+ z_+^2}{r_+} + \frac{v_- |z_-|^2}{r_-}\right]$$

$\boxed{\Lambda \eta = \text{constant}}$ Walden's rule

But all other values are constant only for large ions & only η is variable. So this rule is applicable only for large ions.

For small ions, more solvation occurs & to different extent in different medium & hence value of r_+ & r_- will be different for same small ions in different medium (with different viscosity). So effective radius changes.

For larger ions, solvation is less & hence effective radius is nearly same in all solvents. Hence, Walden's rule is applicable.