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Deg I. Chem. Hons, Paper - II

Topic :- Abnormal Colligative Properties

There are number of solutes mostly electrolytes such as KNO_3, $NaCl$, Na_2SO_4 etc for which the experimental values of Colligative Properties are much different either greater or lower than theoretical values.

In such case the Colligative Properties are referred to as abnormal Colligative Properties.

These abnormal values are due to two reasons :-

(1) Association of the solute molecules in solution.

(2) Dissociation of the solute molecules in solution

Association : — Acetic acid, Phenol when dissolved in Benzene show values of Colligative Properties which are much lower than would be expected on the basis of Theory since colligative Properties depends upon the number of Particles molecules or ions.

Small values indicate that the number of Particles in the solution is much less than would be expected from the molar Concentration of the Solute.

This means that some of the molecules undergo association to form aggregates of higher molecular weight whereby the number of Particles is decreased.

$$2\ CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

$$2\ AB \rightleftharpoons (AB)_2$$

1 mole/l   0 mole/litre

$(1-x)$ mole/l $\frac{x}{2}$ mole/litre

suppose 1 mole/l is the Concentration of AB initially and let x be the degree of association, which is defined as the fraction of total electrolyte which undergoes association

Before Association $= 1 + 0 = 1$

After Association the total number of Particles $= 1 - x + \frac{x}{2}$

$$= 1 - \frac{x}{2}$$

$\therefore \dfrac{\text{Observed osmotic effect}}{\text{Normal osmotic effect}} = \dfrac{1-\frac{x}{2}}{1}$

Here osmotic effect implies for all colligative Properties.

since colligative Properties is directly Proportional to the Solute molecule and inversely Proportional to the molecular wt

$$\frac{\text{Observed molecular wt}}{\text{Normal molecular wt}} = \frac{\text{Normal number of solute molecule}}{\text{Number of solute particles after Association}}$$

$$= \frac{1}{1-\frac{x}{2}}$$

$$\frac{M_0}{M} = \frac{1}{1-\frac{x}{2}}$$

$$\text{or} \quad M = M_0\left(1-\frac{x}{2}\right)$$

$$\text{or} \quad \frac{x}{2} = \frac{M_0 - M}{M_0}$$

$$\text{or} \quad x = \frac{2(M_0 - M)}{M_0}$$

$x =$ Degree of association of electrolyte.