Colligative properties of solution of electrolyte

Some solutes which associate or dissociate in the solvent and yield abnormal results. In order to account for all abnormal cases, van't Hoff factor (i) is used.

Now, $i = \dfrac{\text{No. of moles after dissociation/association}}{\text{No. of moles initially present}}$

$= \dfrac{\text{Exp(Colligative property)}}{\text{Theoretical(Colligative property)}}$

- **For association of solute:**

Consider the association of a solute A into its associated form $(A)_n$, according to the reaction—

$$nA \rightleftharpoons (A)_n$$

where n is the number of molecules of solute, which combine to form an associated species.

$$\therefore \quad nA \rightleftharpoons (A)_n$$

	nA	$(A)_n$
At initially (moles):	c	0
At equilibrium moles:	$c - c\alpha$	$\frac{c\alpha}{n}$

$\therefore$ Total moles at equilibrium $= c - c\alpha + \dfrac{c\alpha}{n}$

$= c\left(1 - \alpha + \dfrac{\alpha}{n}\right)$

Now, $i = \frac{\text{No. of moles after association}}{\text{No. of moles for no association}}$

$$\text{or, } i = \frac{c\left(1-\alpha+\frac{\alpha}{n}\right)}{c}$$

$$\text{or, } i = 1-\alpha+\frac{\alpha}{n} = 1-\alpha\left(1-\frac{1}{n}\right)$$

$$\text{or, } i-1 = -\alpha\left(1-\frac{1}{n}\right)$$

$$\text{or, } \alpha = \frac{i-1}{-\left(1-\frac{1}{n}\right)} \quad \text{——— (1)}$$

If association is complete, i.e., $\alpha = 1$. So from equation (1), we get

$$i = \frac{1}{n} \quad \text{——— (2)}$$

That is the experimental value of a colligative property is $\frac{1}{n}$-times the theoretical value.

If no association occurs, i.e., $\alpha = 0$. So from equation (1), we get

$$i = 1 \quad \text{——— (3)}$$

That is, the experimental and theoretical value of colligative property will be equal.

- For dissociation of solute:

Consider an electrolyte, A_xB_y which partialy dissociates in solution yielding x ions of A^{y+} and y ions of B^{x-} and if α is the degree of dissociation and c is the initial concentration of the solute, then we can write

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

Initial concentration: C $\quad 0 \quad 0$

Concentration at equilibrium: $c - c\alpha$ $\quad x.c\alpha \quad y.c\alpha$

$\therefore$ Total moles at equilibrium $= c - c\alpha + cx\alpha + cy\alpha$

$= c[1 - \alpha + x\alpha + y\alpha]$

~~$= c[1 - \alpha(1 - x - y$~~

$= c[1 + x\alpha + y\alpha - \alpha]$

$= c[1 + \alpha(x + y - 1)]$

Hence, $i = \dfrac{\text{No. of moles after dissociation}}{\text{No. of moles for no dissociation}}$

or, $i = \dfrac{c[1 + \alpha(x+y-1)]}{c}$

or, $i = 1 + \alpha(x+y-1)$

or, $i - 1 = \alpha(x+y-1)$

$$\text{or, } \alpha = \frac{i-1}{x+y-1} \quad \text{——— (1)}$$

If the dissociation is complete, i.e., $\alpha = 1$. So from equation (1), we get

$$i - 1 = x + y - 1$$

$$\text{or, } i = (x+y) \quad \text{——— (2)}$$

That is, the experimental colligative property is $(x+y)$-times the theoretical value.

If no dissociation occurs, i.e., $\alpha = 0$. So from equation (1), we get

$$i = 1 \quad \text{——— (3)}$$

That is, the experimental and theoretical value of colligative property will be equal.