6.6. Abnormal molar mass.

i) ~~In case of~~ The molecular masses can be obtained accurately in cases of solutes with non-electrolytes which do not undergo either dissociation or association in solution.

ii) In the case of electrolytes (acids, bases, salts) they undergo dissociation or association. leading to change in ~~number~~ number of particles.

iii) Since colligative properties are dependent upon the number of solute particles, so molecular which are inversely proportional to colligative

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properties must have different values from their normal values.

iv) Such a molar mass that is either lower or higher than expected or normal value is called abnormal molar mass.

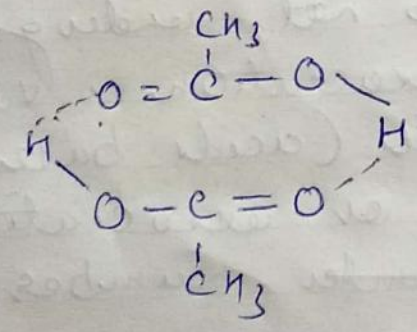
v) Association of solute particles - In certain non-polar solvents the particles of solute undergo association. So,

$$nA \rightleftharpoons (A)_n$$

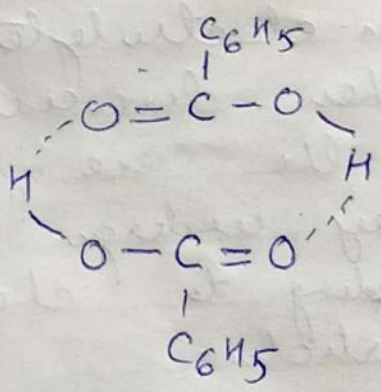
Single molecule associated molecule.

Total number of solute molecules in the solution decrease the colligative properties are expected to decrease while the molecular masses of the solutes involved are expected to increase. For example; in benzene solvent, both acetic acid and benzoic acid exist as dimers because of presence of intermolecular hydrogen bonding.

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2, \quad 2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$$



Acetic acid



Benzoic acid

The normal molecular mass of acetic acid is 60 u, and its observed molecular mass is expected to be 120 u when it undergoes dimerisation in benzene.

vi) Dissociation of solute particles: Solute particles in case of electrolytes are expected to undergo dissociation in polar solvents like water.

$$AB \rightleftharpoons A^+ + B^-$$

As a result, the number of ions (particles) formed will increase. The colligative properties increases so the observed molecular masses of solute decreases.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Thus, association or dissociation causes abnormal values of the molecular masses.

6.6.1. Van't Hoff factor (i)

'i' is to predict the nature of a particular solute in the solution as in extent of dissociation or association.

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}} = \frac{\text{observed colligative property}}{\text{calculated colligative property}}$$

$$i = \frac{\text{Total no. of moles of particles after association/dissociation}}{\text{No. of moles of particles before association/dissociation.}}$$

If $i = 1$, solute behaves normally in solution.
If $i > 1$, solute undergoes dissociation in solution.
If $i < 1$, solute undergoes association in solution.

According to van't Hoff factor,

i) Relative lowering of vapour pressure of solvent,

$$\frac{p_1^\circ - p'}{p_1^\circ} = i \cdot \frac{n_2}{n_1}$$

ii) Elevation of boiling point, $\Delta T_b = i k_b m$.

iii) Depression of freezing point, $\Delta T_f = i k_f m$.

iv) Osmotic pressure of solution, $\pi = i n_2 RT/V$.

Table 2.4 depicts values of the factor, *i* for several strong electrolytes. For KCl, NaCl and $MgSO_4$, *i* approach 2 as the solution becomes very dilute. As expected, the value of *i* gets close to 3 for K_2SO_4.

Table 2.4: Values of van't Hoff factor, *i*, at Various Concentrations for NaCl, KCl, $MgSO_4$ and K_2SO_4.

Salt	*Values of *i*			van't Hoff Factor *i* for complete dissociation of solute
	0.1 m	0.01 m	0.001 m	
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
$MgSO_4$	1.21	1.53	1.82	2.00
K_2SO_4	2.32	2.70	2.84	3.00

* *represent* i *values for incomplete dissociation.*