SOLUTION & COLLIGATIVE PROPERTIES

ABNORMAL MOLAR MASSES

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Theoretical molecular mass values, derived from colligative properties in solution calculations, can sometimes diverge from experimentally determined values, resulting in what is commonly known as abnormal molar masses. Van't Hoff proposed an explanation for this phenomenon, elucidating that when solutes dissolve in a solvent, they often dissociate into ions. Given that colligative properties are contingent solely on the number of solute particles, the dissociation of solute molecules into ions increases the particle count, consequently impacting colligative properties.

For instance, when 1 mole of NaCl dissolves in 1 kg of water and fully dissociates, the resulting solution contains 1 mole of Cl^- ions and 1 mole of Na^+ ions, totalling 2 moles of ions. However, in calculating the molar mass using colligative properties, only 1 mol of NaCl is considered present in the solution.

Certain substances exhibit association in the aqueous state, resulting in fewer ions or molecules in the solution compared to the actual number of molecules. Consequently, for substances that dissociate, the observed molar mass is lower than the actual mass, while for substances that associate, the real mass is lower than the observed molar mass.

The abnormality in molecular mass can be explained as follows:

- The dissociation of solute molecules into multiple ions increases the number of particles, subsequently elevating colligative properties.
- As the molar mass is inversely proportional to colligative properties, its value tends to be lower than anticipated.
- Conversely, when solute particles associate, the total particle count decreases, resulting in a reduction of colligative properties. In such cases, the observed molar mass values are higher than expected.

SOLUTE DISSOCIATION OR IONIZATION:

Abnormal colligative properties

It has been noted that the disparity between the observed and calculated molecular masses of a solute arises from the association or dissociation of solute molecules in the solution. This leads to a modification in the number of particles present in the solution.

Association of solute particles

Association refers to the creation of a larger molecule through the combination of two, three, or more solute molecules.

Let 'n' simple molecules combine to give an associated molecule as:

$$n(X) \stackrel{\stackrel{\text{non polar}}{\longleftarrow}}{\underset{\text{solvent}}{\overset{}}} (X)_n$$

one bigger

molecule.

n single molecules

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Consequently, the overall number of particles in the solution is reduced compared to the initial number of molecules dissolved, leading to lower values of colligative properties. Given that the molar mass of the solute is inversely proportional to colligative properties, the molar mass of the solute will exceed the theoretical value.

DISSOCIATION OF SOLUTE MOLECULES

Electrolyte molecules undergo ionization or dissociation in ionizing solvents, resulting in the formation of two or more particles in the solution.

For example, AB ionizes in solution to give two particles.

$$AB \xrightarrow{\text{ionizing}} A^+ + B^-$$
solvent

This dissociation leads to a rise in the overall number of particles, consequently causing higher values for the colligative properties of such solutions. Since colligative properties are inversely correlated with molecular weight, the molecular weight of an ionizable solute will be lower than the theoretical value.

Van't Hoff factor (i)

To quantify the degree of association or dissociation that specific solutes are anticipated to undergo in a solution, Van't Hoff introduced a factor in 1886 known as the Van't Hoff factor (i). The factor i is defined as:

$$i = \frac{observed colligative property}{Normal colligative property}$$

 $i = \frac{Normalor actualmolecular weight}{observed molecular mass.}$

When solute particles associate in a solution, resulting in an observed molecular weight higher than the standard, the factor 'i' has a value less than unity (i.e., i < 1). Conversely, for dissociation, where the observed molecular weight is lower than the normal molecular weight, the value of 'i' is greater than unity (i.e., i > 1).

Van't Hoff factor and degree of dissociation

The portion of the overall number of molecules that undergoes dissociation in the solution into simple ions or molecules is referred to as the degree of dissociation.

	i _ number of particlesafter dissociation			
	Number of particles initially taken.			
Calculation of 'i'				
Let, solute be A _x B _y				
	A _x B _y —	$\rightarrow x A^{y+} +$	- yB ^{x-}	
Initial mol	1	0	0	
after dissociation	1 - α	xα	уα	
Total no. of solute particles				
	$= 1 - \alpha + \alpha$	xα + yα		
	$= 1 - \alpha + \alpha$	$= 1 - \alpha + \alpha (x + y)$		
	$= 1 - \alpha + \alpha$	$= 1 - \alpha + n\alpha$		[where $x + y = n$ (total ions.)]

(i) observed colligative properties ∞ observed number of solute particles observed colligative properties ∞ (1 – α + n α)

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(ii) Normal colligative properties $\propto 1$

$$\frac{\text{eq }(i)}{\text{eq }(ii)} \rightarrow i = \frac{1 - \alpha + n\alpha}{1}$$
$$i - 1 = \alpha (n - 1)$$

$$\alpha = \frac{i-1}{n-1}$$

for strong electrolytes: $\alpha = 1$ or 100% so i = n (total no. of ions)

OSMOTIC PRESSURE OF MIXTURE OF TWO SOLUTIONS:

Case-1:

Let two solutions of same substance having different osmotic pressure π_1 and π_2 are mixed. The resultant solution has osmotic pressure is given by

$$\pi_1 V_1 + \pi_2 V_2 = \pi R(V_1 + V_2)$$

Equal volumes of two isotonic solutions are mixed.

$$\pi_{\text{resultant}} = \frac{\pi 1 V 1 + \pi 2 V 2}{V 1 + V 2} = \pi$$

Note: $\pi_1 = \pi_2 = \pi$ and $V_1 = V_2 = V$ are given.

Case-2:

Let n_1 and n_2 are the number of moles of two different solutes present in V_1 and V_2 volumes respectively. Then, the osmotic pressure of the mixture is given by

$$\pi = \pi_1 + \pi_2 = \frac{n_1 i_1 RT}{(V_1 + V_2)} + \frac{n_2 i_2 RT}{(V_1 + V_2)}$$

$$\therefore \qquad \pi = CRT$$

$$\therefore \qquad \pi = \frac{n_V}{V}RT$$

$$\pi = \frac{n_1 i_1 + n_2 i_2}{(V_1 + V_2)} \times RT$$

 $i_1\,\&\,i_2$ are Van't Hoff factors for two solutes