Properties of solutions

COLLIGATIVE PROPERTIES

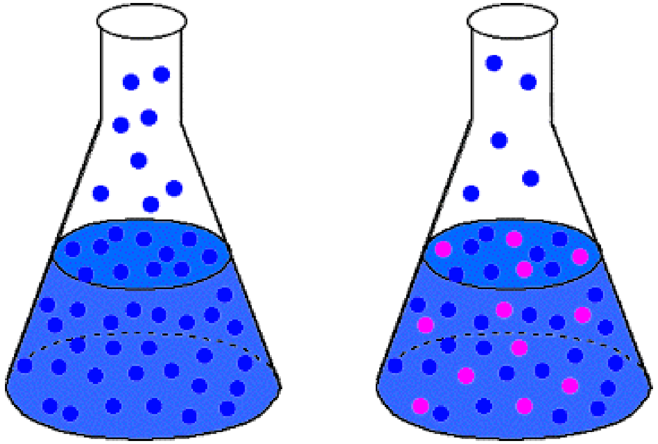
Colligative properties (or **collective properties**) are bound together by a common origin; that is, they all depend on the number of solute particles present, whether these particles are atoms, ions, or molecules. The colligative properties are

- Vapour pressure lowering
- Osmosis
- Boiling point elevation
- Freezing point depression.

VAPOR PRESSURE

- Vapor pressure depression takes place when a solute is added to a pure solvent. When a solute is added to a pure solvent, it depresses the vapor pressure of the solvent. The more solute added the more depressed the vapor pressure becomes.
- This is known as **Raoult's Law.**

VAPOR PRESSURE



If solute particles take the place of solvent molecules and these solute particles are non-volatile, they succeed in only blocking solvent molecules from vaporizing. Hence, the vapor pressure of the solvent will be less as a result of the presence of the solute particles. The more solute particles in the solution the more surface positions will be blocked

RAOULT'S LAW IN MATHEMATICAL FORM

$$p_1 = x_1 \cdot p_1^0$$

Where

- P_1 = vapor pressure of the solvent with added solute
- x_1 = mole fraction of solvent
- P_1^0 = vapor pressure of the pure solvent

RAOULT'S LAW IN MATHEMATICAL FORM

- For a two component solution: $X_1+X_2=1$, hence $X_1=1-X_2$
- If we substitute $1-X_2$ for X_1 in the equation, then:

$$P_1 = (1 - X_2)\, P_1^0$$

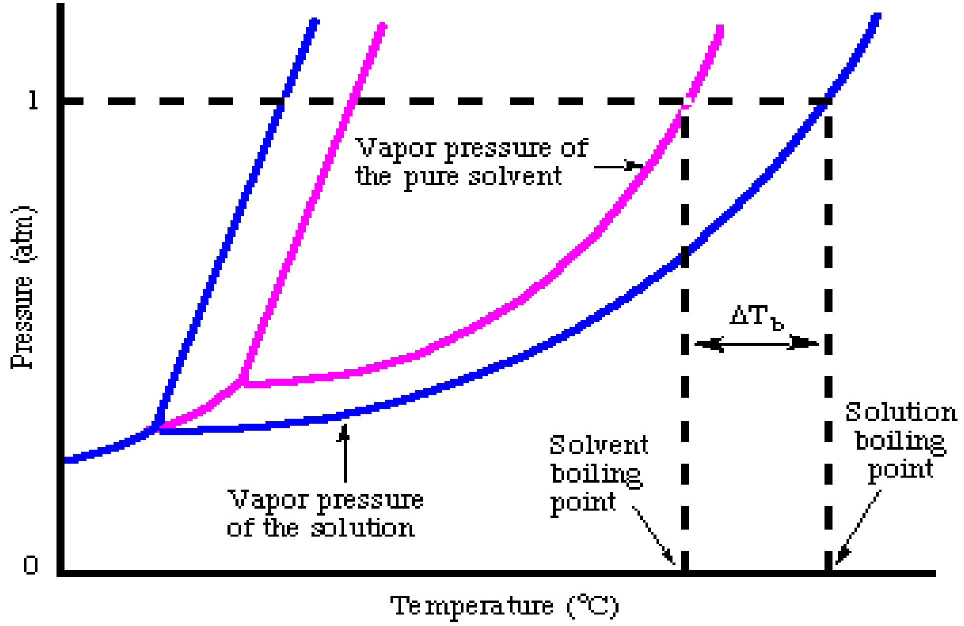
$$P_1 = P_1^0 - X_2 P_1^0$$

$$p_1^0 - p_1 = x_2 \cdot p_1^0 \text{ or } \frac{p_1^0 - p_1}{p_1^0}$$

THE VAPOR PRESSURE LOWERING

In pharmaceutical solutions, the solute is usually non-volatile and it does not contribute directly to the vapor pressure of the solution. However, its presence decreases the concentration of the solvent and its escape tendency, that is, the vapor pressure of the solution is lower than that of the pure solvent. **The vapor pressure lowering** is proportional to the number of solute molecular particles or ions. ***The effect of a solute on the vapor pressure may be determined in dilute solutions by applying the Raoult's law.***

BOILING POINT ELEVATION



Phase Diagram for a Solvent and its Solution with a Nonvolatile Solute

BOILING POINT

The boiling point of a liquid at a given pressure is the temperature T at which its equilibrium vapor pressure equals to P. The normal boiling point is the temperature at which vapor pressure of a liquid equal to 1 atm (bar).

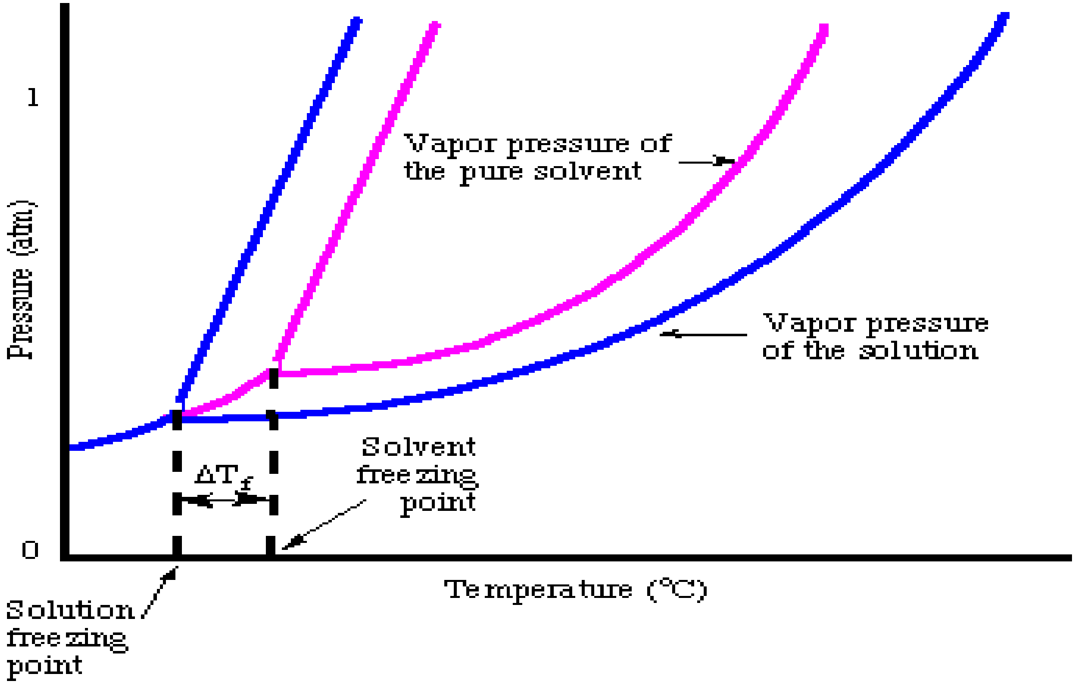
BOILING POINT ELEVATION

The vapor pressure of the solution is lower than that of the pure solvent. Because both pure solvent and solution need to reach the same pressure to boil, the solution requires a higher temperature to boil. If we represent the difference in boiling point between the pure solvent and a solution as **ΔT_b**, we can calculate that change in boiling point from the following formula:

$$\Delta T_b = K_b \cdot b(X)$$

Where **b(x)**, for the concentration, m, because molality is temperature independent. The term **K_b** is a boiling point elevation constant that depends on the particular solvent being used.

FREEZING POINT DEPRESSION



Phase Diagram for a Solution and the Pure Solvent Indicating the Freezing Point Depression

FREEZING POINT DEPRESSION

The freezing point is depressed due to the vapor pressure lowering phenomenon. The amount of the freezing point depression can be calculated by the formula:

$$\Delta T_f = K_f \cdot b(X)$$

APPLICATION

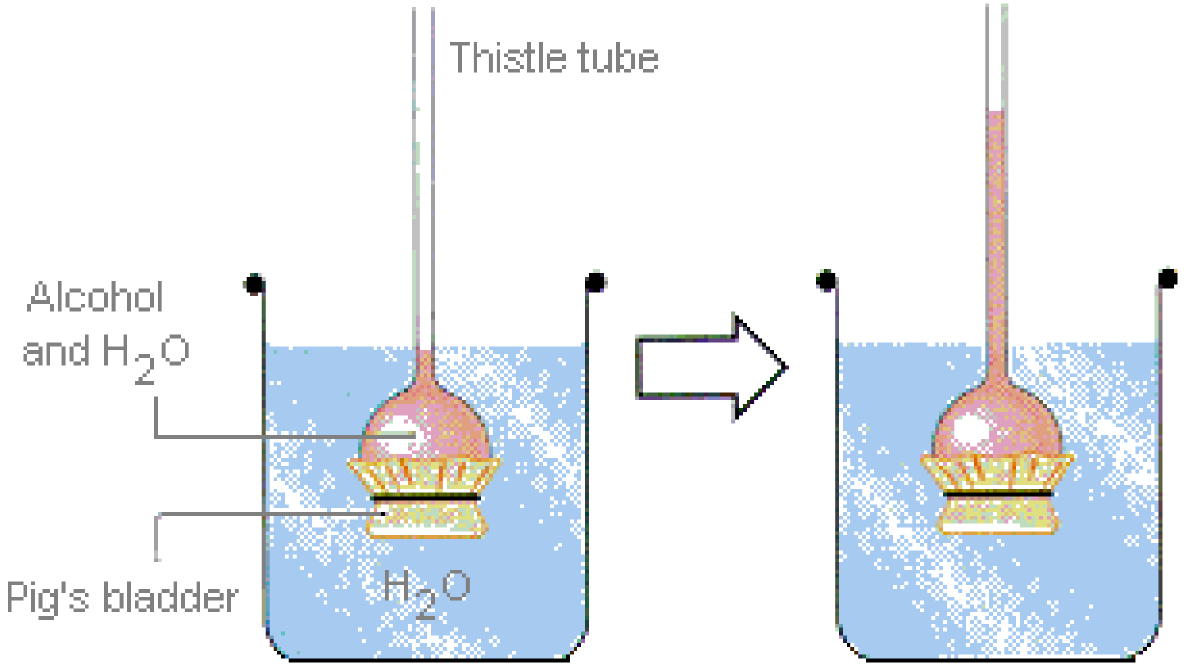
The molecular weight of the dissolved substance can easily by calculated if the cryoscopic or ebullioscopic constant of the solvent is known. The method of determination molecular weight by the freezing point lowering of a solvent is called **cryoscopic method (cryoscopy),** and by the boiling point elevation, **ebullioscopic method (ebullioscopy)**.

$$\Delta t = K \cdot \frac{m(x)}{M(x) \cdot m_{solvent}}$$

OSMOSIS

- **Osmosis** is the flow of one constituent of a solution through a membrane while the other constituents are blocked and unable to pass through the membrane. Experimentation is necessary to determine which membranes permit selective flow, or osmosis, because not all membranes act in this way. Many membranes allow all or none of the constituents of a solution to pass through; only a few allow a selective flow.
- **Osmosis** is the spontaneous net movement of solvent molecules through a semipermeable membrane from a region of high water potential (region of lower solute concentration) to a region of low water potential (region of higher solute concentration), in the direction that tends to equalize the solute concentrations on the two sides

OSMOSIS



OSMOTIC PRESSURE

The hydrostatic pressure establishing this equality of flow is called osmotic pressure. The **osmotic pressure**, like the pressure of a gas, *depends only on the number of molecules of the solute* at constant volume and temperature, and does not depend on the nature of the solvent. Osmotic pressure can be calculated by the formula:

$$p = CRT$$

LAW OF VAN'T HOFF

The profound analogy between gases and solutions is clearly expressed in the following principle known as the **Law of Van't Hoff**:

The osmotic pressure of a solution equals the pressure which would be exerted by the solute if it were in a gaseous state at the same temperature and occupied a volume equal to that of the solution.

SOLUTIONS

Depending on the relationship between the internal and external concentrations, the external solutions are called:

- Hypertonic
- Hypotonic
- Isotonic.

HYPERTONIC SOLUTIONS

- **Hypertonic solutions** *contain larger numbers of solute particles than the intercellular fluid.* A cell placed in a hypertonic solution shrinks because there is a net flow of intercellular water to the extracellular fluid.
- As the cell shrivels, it takes a *crenated* (*scalloped*) appearance. The event is called **plasmolysis (crenation)**.

HYPOTONIC SOLUTIONS

- **Hypotonic solutions** *contain fewer numbers of solute particles than the intracellular fluid*. A cell placed in hypotonic solution swells because the net flow of water is from the extracellular fluid to the intracellular fluid.
- If the cell swells too much, the membrane ruptures, just as overinflated bursts. When red blood cells rupture, it is called **hemolysis**. In case of erythrocytes – **lysis**.

ISOTONIC SOLUTIONS

- **Isotonic solutions** *contain the same numbers of solute particles as the intracellular fluid.* A cell placed in an isotonic solution retains its original shape.
- When body fluids are replaced intravenously, the injected fluid must be isotonic with the contents of red blood cells; otherwise, plasmolysis (crenation) or hemolysis will occur. A
- n aqueous solution containing 0.9% NaCl (*physiologic saline*) and one containing 5.5% glucose (called *dextrose* or *blood sugar solution*) are often used for intravenous injections because they isotonic with red blood cells.

ISOTONIC COEFFICIENT

- The Law of Van't Hoff is applicable only for dilute solutions. In the case of concentrated solutions considerable deviations from this law are observed. Even greater deviations are observed in aqueous solutions of electrolytes, substances which conduct current in aqueous solution.
- To extend this equation to solutions with "abnormal" osmotic pressure Van't Hoff introduced a correction factor **i** (called the isotonic coefficient) showing the number of times the osmotic pressure of the solution exceeds the normal value:

$$p = iCRT$$

ISOTONIC COEFFICIENT

The coefficient **i** was determined for each solution experimentally either by the vapour pressure lowering or by the freezing point lowering and boiling point elevation. Since all these values are proportional to the osmotic pressure, the number of times the osmotic pressure of the solution is higher than the normal value could be found by establishing the number of times any of the above values was greater than those calculated theoretically.

$$i = \frac{p'}{p} = \frac{\Delta t_{f.p.}'}{\Delta t_{f.p.}} = \frac{\Delta t_{b.p.}'}{\Delta t_{b.p.}} \quad \text{or} \quad i = 1 + \alpha(n - 1)$$

α is the ionization degree (for strong electrolytes $\alpha = 1$), **n** is a number of ions, which are formed in the ionization reactions.