Completely Immiscible liquids

P = Total vapour pressure = $P_A^{*0} + P_B^{*0}$

= Sum of vapour pressures of pure A & B.

So total vapour pressure of immiscible liquids is more than individual vapour pressures of A & B & as long as both liquids are present, total vapour pressure remains constant & will be independent of relative amounts of two liquids.

The mixture of immiscible liquids will boil at temperature lower than boiling points of either of the pure constituents & also boiling point of the mixture will remain constant & independent of relative amounts of two liquids.

Completely miscible liquids : Total vapour pressure will be in range of vapour pressure of both components.

Completely immiscible liquids : Total vapour pressure is always greater than vapour pressure of each component.

Composition of vapours can be calculated from Dalton's law of partial pressure :

$$\frac{P_A^\circ}{P_B^\circ} = \frac{y_A}{y_B} = \frac{n_A}{n_B} = \frac{m_A}{M_A}\frac{M_B}{m_B}$$

Or $$\boxed{\frac{m_A}{m_B} = \frac{P_A^\circ M_A}{P_B^\circ M_B}} \quad -(1.)$$

Amount of A in vapours will be equivalent to its vapour pressure & independent of other component.

The concept of immiscible liquids & eq. (1), is used in Steam Distillation.

Steam Distillation:

This process is utilized for purification of those liquids which either boil at too high temperature or decompose when heated to their normal boiling point.

Here, water is used as one of the immiscible liquids. Immiscible liquids ~~are~~ is heated directly along with water or by passing steam through it. Passing steam is preferred as it keeps system agitated & equilibrium between vapour & liquid is rapidly attained.

From eq. (1), we can say that if molar mass of the compound is larger & has appreciable vapour pressure at temperature near & just below boiling point of water, distillate will contain more proportion of the compound. This is the principle for distillation of ~~partially~~ immiscible mixture of organic compound with water (or separation of impurities).

Water or steam is the immiscible component. Actual efficiency of this process is slightly less than what is predicted theoretically from eq. (1).

e.g. Purification of aniline:

Boiling point of aniline = 180°C
Boiling point of water = 100°C.

Boiling or distillation takes place at 98.5°C. At this temperature, vapour pressure of water is 717 torr & that of aniline is 43 torr.

From eq. (1):

$$\frac{\text{Mass of aniline}}{\text{Mass of water}} = \frac{92 \times 43}{18 \times 717} = 0.309 \text{ or } 30\%.$$

Partial vapour pressure of aniline at boiling temperature is 8% of total (43 torr out of 717 + 43 = 760 torr) & relative proportion of aniline by mass in distillate is 30%.

Its vapour pressure is lower but high molar mass of aniline compensates for that, thereby increasing the amount of pure aniline in vapour, which is condensed to form liquid called distillate.