

Ideal and Real Solutions

- -**Ideal solution** when the components of solution **obey Raoult's law** (**adhesive forces =cohesive forces**)
- -**Real Solutions** when the components of solution **not obey Raoult's law** and are of two types:
 - a- **Negative deviated** (adhesive forces \gg cohesive forces)
Negative deviations lead to **increased solubility**
 - b- **Positive deviations** (cohesive forces \gg cohesive forces)
Positive deviations, leading to **decreased solubility**

The attractive cohesive forces, which may occur in gases, liquids, or solids, are called **internal pressures**.
- - **Liquid-liquid systems may be divided into 2 categories:**
 - 1) Systems showing **complete miscibility** such as **alcohol & water, glycerin & alcohol, benzene & carbon tetrachloride**.
 - 2) Systems showing **Partial miscibility** as **phenol and water**; two liquid layers are formed each containing some of the other liquid in the dissolved state.

Complete miscibility occurs when: The **adhesive forces** between different molecules (A-B) \gg **cohesive forces** between like molecules (A-A or B-B).

Partial miscibility results when: **Cohesive forces of the constituents** of a mixture are **quite different**, e.g. water (A) and hexane (B). $A-A \gg B-B$

The non polar molecules (B) will be squeezed out by the powerful attractive forces existing between the molecules of the polar liquid.

The term **miscibility** refers to the **mutual solubility of the components** in liquid-liquid systems.

Influence of Foreign Substances

If the added material is soluble in only one of the two components, the mutual solubility of the liquid pair is decreased.

Example, if naphthalene is added to a mixture of phenol and water, it dissolves only in the phenol, the miscibility is decreased.

If potassium chloride is added to a phenol-water mixture, it dissolves only in water and decreases the miscibility.

If the added material is soluble in both of the liquids, the mutual solubility of the liquid pair is increased.

Example, The addition of succinic acid or sodium oleate to a phenol-water system increases the mutual solubility.

The increase in mutual solubility of two partially miscible solvents by another agent is ordinarily referred to as **blending**.

SOLUBILITY OF SOLIDS IN LIQUIDS

- Systems of solids in liquids include the most important type of pharmaceutical solutions.
- There is ideal and real (non ideal) solution of solids
- **Ideal solution of solids**

The solubility of a solid in an ideal solution depends on

1- Temperature, (direct relationship)

2- Melting point of the solid, (inverse relationship)

3- Molar heat of fusion, ΔH_f ,

(The heat absorbed when the solid melts). In an ideal solution the heat of solution is equal to the heat of fusion, which is assumed to be a constant independent of the temperature.

Note:- Ideal solubility is not affected by the nature of the solvent.

The equation derived from thermodynamic considerations for an ideal solution of a solid in a liquid is

$$-\log X_2^i = \frac{\Delta H_f}{2.303R} \left(\frac{T_0 - T}{T T_0} \right)$$

where;

X_2^i is the ideal solubility of the solute expressed in mole fraction,

T_0 is the melting point of the solid solute in absolute degrees, and

T is the absolute temperature of the solution.

- - At temperatures above the melting point, the solute is in the liquid state, and, in an ideal solution, the liquid solute is miscible in all proportions with the solvent.

Therefore, the above equation no longer applies when $T > T_0$.

EXAMPLE 10-7

What is the solubility of naphthalene at 20°C in an ideal solution? The melting point of naphthalene is 80°C and the molar heat of fusion is 4500 Cal/mole. $R=1.987$ Cal/mole .k

$$-\log X_2^i = \frac{4500}{2.303 \times 1.987} \left(\frac{353 - 293}{293 \times 353} \right)$$

$$X_2^i = 0.27$$

Homework: calculate the solubility at 10 and 75 °C? You will see that the solubility increases as the temperature increased

Q12. The m.p and molar heat of fusion of three indomethacin polymorphs I, II, VII are:

polymorph	m.p °C(K)	ΔH_f Cal/mole	X_2^i
I	158(431)	9550	0.0069
II	153(426)	9700	0.0073
VII	95(368)	2340	0.4716

Calculate the **ideal mole fraction solubility** at 25 °C (298) three indomethacin polymorphs and rank the solubility in decreasing order, is the m.p or ΔH_f more useful in ordering the solubility.

According to m.p VII >II> I

According to ΔH_f VII >I> II

$$-\log X_2^i = \frac{\Delta H_f}{2.303R} \left(\frac{T_0 - T}{TT_0} \right)$$

$$\text{For I: } -\log X_2^i = \frac{9550}{2.303 \times 1.987} \left(\frac{431 - 298}{298 \times 431} \right)$$

$$X_2^i = 0.0069$$

$$\text{For II: } -\log X_2^i = \frac{9700}{2.303 \times 1.987} \left(\frac{426 - 298}{298 \times 426} \right)$$

$$X_2^i = 0.0073$$

$$\text{For VII: } -\log X_2^i = \frac{2340}{2.303 \times 1.987} \left(\frac{368 - 298}{298 \times 368} \right)$$

$$X_2^i = 0.4716$$

According to the solubility VII>II>I, so as the m.p increases, the solubility decreased

Non ideal Solutions

In non ideal solutions, the electrostatic and intermolecular forces should be considered.

The activity of a solute in a solution is expressed as the concentration multiplied by the activity coefficient. When the concentration is given in mole fraction, the activity is expressed as

$$a_2 = X_2 \gamma_2$$

where γ_2 on the mole fraction scale is known as the rational activity coefficient. Converting to logarithms, we have

$$\log a_2 = \log X_2 + \log \gamma_2$$

In an ideal solution, $a_2 = X_2^i$ because $\gamma_2 = 1$, and, accordingly, the ideal solubility equation can be expressed in terms of activity as

$$-\log a_2 = -\log X_2^i = \frac{\Delta H_f}{2.303R} \left(\frac{T_0 - T}{T T_0} \right)$$

By combining the 2 equations, we find that the mole fraction solubility of a solute in a nonideal solution expressed in log form, becomes

$$-\log X_2^i = \frac{\Delta H_f}{2.303R} \left(\frac{T_0 - T}{T T_0} \right) + \log \gamma_2$$

- Therefore, the mole fraction solubility in various solvents can be expressed as the sum of two terms: the solubility in an ideal solution and the logarithm of the activity coefficient of the solute.

As a real solution becomes more ideal, γ_2 approaches unity, the equation returns

$$-\log X_2^i = \frac{\Delta H_f}{2.303R} \left(\frac{T_0 - T}{TT_0} \right)$$

Q18. the mole fraction solubility of naphthalene (nonpolar solute) in different solvents at temperature 40 °C (313 k), m.p 80°C(353k), $\Delta H_f = 4500$ cal/mole. Calculate the γ_2 and find the relationship between X_2 and γ_2 .

X_2 for chlorobenzene(nonpolar solvent) = 0.444, for water = 1.76×10^{-5}

For chlorobenzene

$$-\log X_2^i = \frac{\Delta H_f}{2.303R} \left(\frac{T_0 - T}{TT_0} \right) + \log \gamma_2$$

$$-\log 0.444 = \frac{4500}{2.303 \times 1.987} \left(\frac{353 - 313}{313 \times 353} \right) + \log \gamma_2$$

$$\gamma_2 = 0.99$$

For water

$$-\log 1.76 \times 10^{-5} = \frac{4500}{2.303 \times 1.987} \left(\frac{353 - 313}{313 \times 353} \right) + \log \gamma_2$$

$$\gamma_2 = 25003$$

So there is inverse relationship between X_2 and γ_2

Solubility of Strong Electrolytes

The effect of temperature on the solubility of some salts in water is shown in Figure 10-6.

- A rise in temperature increases the solubility of a solid that absorbs heat (*endothermic* process) when it dissolves. Such as KBr
- Conversely, if the solution process is *exothermic*, that is, if heat is evolved, the temperature of the solution rises and the container feels warm to the touch. The solubility in this case decreases with an elevation of the temperature. such as cerium(III) sulfate
- Most solids belong to the class of compounds that absorb heat when they dissolve. Sodium sulfate exists in the hydrated form, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, up to a temperature of about 32°C , the solution process (dissolution) is *endothermic*, and solubility increase with temperature. Above this point, the compound exists as the anhydrous salt, Na_2SO_4 , the dissolution is *exothermic*, and solubility decreases with an increase of temperature.
- Sodium chloride does not absorb or evolve an appreciable amount of heat when it dissolves in water; thus, its solubility is not altered much by a change of temperature (*isothermic reaction*), and the heat of solution is approximately zero.

