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RESEARCH ARTICLE

THERMODYNAMIC CONTRIBUTION TO THE SOLUBILITY EQUATION

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ABSTRACT

An attempt to formulate the solubility equation was studied using thermodynamic data of both solute and solvent. The given equations predict quantitatively the solubility of different solutes in different solvents. Also, Miscibility and immiscibility of different solvents are estimated. The provided equations may be extended to be a general equations of solubility.

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INTRODUCTION

The task of solubility has been treated by various text books and articles. Solubility parameters have been introduced, Hildebrand solubility parameter and Hansen solubility parameters. Hildebrand solubility parameter is the total van der Waals force, however, which is reflected in the simplest solubility value. The solubility parameter is a numerical value that indicates the relative solvency behavior of a specific solvent. It is derived from the cohesive energy density of the solvent, which in turn is derived from the heat of vaporization. The Hildebrand solubility parameter for a pure liquid substance is defined as the square root of the cohesive energy density.

$$C = [(H_v - RT)/V_m]^{1/2}$$

where H_v is the heat of vaporization, and V_m the molar volume. (RT) is the ideal gas (PV) term, and it is subtracted from the heat of vaporization to obtain an energy of vaporization⁽¹⁾. Hansen Parameters is the most widely accepted three component system to date which divide the total Hildebrand value into three parts: a dispersion force component, a hydrogen bonding component, and a polar component.

$$t^{2=} + d^{2=} + p^{2=} + h^{2=}$$

Where

$t^{2=}$	Total Hildebrand parameter
$d^{2=}$	dispersion component
$p^{2=}$	polar component
$h^{2=}$	hydrogen bonding component

Thermodynamics requires that the free energy of mixing must be zero or negative for the solution process to occur spontaneously. The free energy change for the solution process is given by the relation:

$$G^M = H^M - TS^M$$

where

G^M is the free energy of mixing,
 H^M is the heat of mixing, T is the absolute temperature,
and

TS^M is the entropy change in the mixing process.

The Gibbs energy can be written in terms of chemical potentials of components A and B:

$$G(\text{mix}) = x_A \mu(A, T) + x_B \mu(B, T)$$

The thermodynamic activity is defined as:

$$RT \ln a_A = \mu(A) \text{ and } RT \ln a_B = \mu(B) \quad 2,3$$

An equation was reported to estimate the quantity of solute that saturates a solvent:

$$\ln x = \frac{\Delta H_{\text{fus}}}{R} \left(\frac{1}{T} - \frac{1}{T_M} \right)$$

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Where

x : mole fraction of solute

H_{fus} : enthalpy of fusion of solute

T : absolute temperature

T_M : melting temperature

However, the detailed content of this equation should not be treated too seriously because it is based on highly questionable approximations, such as the ideality of the solution. One aspect of its approximate character is that it fails to predict that solutes will have different solubilities in different solvents, for no solvent properties appear in the expression.^{4, 5} The term of solute activity in a certain solvent was added to the last equation in order to correct the solubility quantifications. The solubility of various compounds were determined using the corrected equation and computational methods like conductor-like screening (COSMO)-based activity coefficient models and conductor-like screening segment activity coefficient (COSMO-SAC)^{6,7}

METHODOLOGY

The solubility is considered as energy interaction between solute and solvent. The quantity of solute that will dissolve in a certain solvent is affected by different factors and the limit at which solubility stops. The factors affecting solubility are treated in this work as the breaking force which exhibit the capability of solvent to separate the molecules of solute, potential energies of both solute and solvent, and interpotential between solute molecules and solvent molecules. The limit at which solubility stops is related to the fusion energy of either solute or solvent which is lower. The limit of solubility does not mean the maximum quantity of solute that will dissolve but the maximum ratio of energy that limits the solubility, as will be illustrated below. The variables which will be used in this study are the energy of formation, the energy of vaporization, the energy of fusion and the lattice energy and the molar mass:

$$F = H_f - RT$$

Where F is the energy of formation (considered as the potential energy)

H_f is enthalpy of formation

R is gas constant = $8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

$$F_M = F/M$$

Where

F_M is the potential energy per unit mass

M is the molar mass

$$V = H_{vap} - RT$$

V is the energy of vaporization (considered as the interpotential energy)

H_{vap} is the enthalpy of vaporization

$$V_M = V/2M$$

Where

V_M is the interpotential energy per unit mass

$$E_M = F_M + V_M$$

E_M is the total potential energy per unit mass

$$J = H_{fus} - RT$$

Where

J is energy of fusion

H_{fus} is the enthalpy of fusion

$$Latt = H_{Latt} - RT$$

Where

$Latt$ is the lattice energy

H_{Latt} is the lattice enthalpy

T is the absolute temperature and set at 298 K

A. Solubility of solid in liquid

The solubility of solid materials in liquid is divided into two parts, solubility of non ionic solids and solubility of ionic solids.

A.1. Solubility of non ionic solids

The equation taking the general formula of

$$n = S_G \cdot S_T \cdot S_c \quad \text{Eq.1}$$

where

n is the number of moles of solute the dissolves in one mole of solvent.

S_G is the gradient ratio of solubility

S_T is the tunneling ratio of solubility

S_c is the correction factor

This formula has different factors as will be illustrated. The solubility equation of a solute in a certain solvent will be combined from this general form according to certain rules.

Gradient ratio of solubility (S_G)

The gradient term represents the ratio of solute that dissolves in solvent due to the difference in potential between solute and solvent.

$$S_G = S_{gf} \cdot S_{gr} \cdot S_{ge}$$

S_{gf} is the breaking force

S_{gr} is the gradient factor of solubility (ratio of solute that allowed to dissolve due to interpotential difference)

S_{ge} is the tunneling term between two limits of solubility

The Breaking Force (S_{gf})

The potential energy of molecule is taking as its energy of formation as considered by the semi-empirical method of calculation⁸. By simulation to the electric potential energy equation⁹, we will obtain:

$$F = q/4 \pi r$$

and by simulation to the electric force between two point charges⁽⁹⁾

(Force = $q_1q_2/4 \pi r^2$) we can approximate the breaking force between two different molecules 1, 2:

$$S_{gf} = F_1F_2/F_2^2 = F_1/F_2$$

Where F_1 , F_2 are the energy of formation of solvent and solute respectively.

S_{gf} is applied when $F_1 < F_2$ Rule. 1

$$F_{Latt} = F_1F_2/(Latt.)^2$$

F_{Latt} is additional breaking force in case of solubility of ionic compounds

The gradient factor of solubility (S_{gr})

The ratio of solute that is allowed to dissolve is limited by the fusion energy of solute or solvent which is lower in value and is taken as J/V. The potential difference that allow solubility is taken as V/F. Here we will deal with five categories:

1. $V_1/F_1 > V_2/F_2$
2. $V_1/F_1 < V_2/F_2$ ($V_1/F_1 > 0.95 V_2/F_2$)
3. $V_1/F_1 < V_2/F_2$
4. Solubility of solute with $E_{M2} < 1$ in solvent with $E_{M1} > 1$
5. Solubility of solute with $E_{M2} > 1$ in solvent with $E_{M1} < 1$

The subscripts 1,2 refer the solvent and solute respectively.

J/V tunneling factor (S_{ge})

The term tunneling is due to the similarity of this part of equation to the tunneling effect law in quantum mechanics.

$$S_{ge} = e^{-\left(\left|\frac{J_2}{V_2} - \frac{J_1}{V_1}\right|\right)^{1/2}}$$

It represents the tunneling between the two limit if solubility, J_1/V_1 and J_2/V_2 .

Now we will discuss the categories and incorporate the explanation of S_T, S_c during it.

Category. 1 : $V_1/F_1 > V_2/F_2$

This category is divided into three cases

1. $V_1/F_1 - V_2/F_2 > J/V$ (J/V of solvent or solute which is lower)
2. $V_1/F_1 - V_2/F_2 = J/V$
3. $V_1/F_1 - V_2/F_2 < J/V$

Case 1: $V_1/F_1 - V_2/F_2 > J/V$

The gradient factor is stated as follows:

$$S_G = \frac{F_1}{F_2} \cdot \frac{J/V}{\frac{V_2}{F_2} - \frac{V_1}{F_1}} \cdot e^{-\left(\left|\frac{J_2}{V_2} - \frac{J_1}{V_1}\right|\right)^{1/2}}$$

The tunneling part (S_T)

It represents the tunneling between different potentials of solute and solvent

$$S_T = e^{-(V_{M1} - V_{M2})^{1/2}} \cdot e^{-\left(\frac{E_{M2}}{E_{M1}}\right)^{1/2}}$$

Where

- $V_{M2} < V_{M1}$ Rule. 2
- $E_{M1} < 0.95 \cdot E_{M2}$ Rule. 3

The correction factor S_c

It is either decreasing factor S_{cd} or increasing factor S_{ci} depending on the relation between the total potential energy per unit mass of both solute and solvent.

Decreasing factor (S_{cd})

$$S_{cd1} = e^{-\left(\frac{E_{M1}}{2 \cdot E_{M2}}\right)^{1/2}}$$

- $4 \cdot E_{M2} > 0.95 \cdot F_{M1}$ Rule. 4
- $E_{M2} > 2 \cdot E_{M1}$ Rule. 5

Increasing factor (S_{ci})

$$S_{ci1} = e^{\left(\frac{E_{M2}}{E_{M1}}\right)^{1/2}}$$

Where

- $E_{M2} > 0.95 \times 1/2 \cdot F_{M1}$ Rule . 6

$$S_{ci2} = e^{\left(\frac{E_{M2}}{E_{M1}}\right)^{1/2}} \cdot e^{\left(\frac{F_1}{F_2} \cdot \frac{V_2}{V_1}\right)}$$

Where

- $E_{M2} > 1/2 \cdot F_{M1}$ Rule . 7

So the general equation for case. 1 is:

$$n = \frac{F_1}{F_2} \cdot \frac{J/V}{\frac{V_2}{F_2} - \frac{V_1}{F_1}} \cdot e^{-\left(\left|\frac{J_2}{V_2} - \frac{J_1}{V_1}\right|\right)^{1/2}} \cdot e^{-(V_{M1} - V_{M2})^{1/2}} \cdot e^{-\left(\frac{E_{M2}}{E_{M1}}\right)^{1/2}} \dots \text{Eq2}$$

n is subjected to correction factor under rules (4-7).
e.g. Resorsinol/Water, Naphthalene/ Benzene, Benzoic acid /Methanol, Phenol/ Water, Resorsinol/ Methanol.

Case. 2 : $V_1/F_1 - V_2/F_2 = J/V$

It taking the formula

$$n = \frac{F_1}{F_2} \cdot \left(\frac{V_2}{F_2} - \frac{V_1}{F_1}\right) \cdot e^{-\left(\left|\frac{J_2}{V_2} - \frac{J_1}{V_1}\right|\right)^{1/2}} \cdot e^{-(V_{M1} - V_{M2})^{1/2}} \cdot e^{-\left(\frac{E_{M1}}{E_{M2}}\right)^{1/2}} \dots \text{Eq3}$$

Where the factor $e^{-\left(\frac{E_{M1}}{E_{M2}}\right)^{1/2}}$ is applied when :

- $4 \cdot F_{M2} > E_{M1}$ Rule. 8
- n is subjected to decreasing factor under Rule.4,5 and increasing factor under Rule. 6
- Increasing factor S_{ci3} :

$$S_{ci3} = e^{\left(\frac{E_{M2}}{E_{M1}}\right)^{1/2}} \cdot e^{\left(\frac{VM_2}{VM_1}\right)}$$

The second part is applied only if $V_{M2} < V_{M1}$ Rule. 9
e.g Benzoic acid /Water, Benzoic acid/ Dimethyl ether, Stearic acid / methanol

Case. 3: $V_1/F_1 - V_2/F_2 < J/V$

Eq.3, rule. 8 are applied here and n is subjected to decreasing (S_{cd}) and increasing factors (S_{ci1} , S_{ci2}) under rules 4-7.

Category 2: $V_1/F_1 - V_2/F_2 (V_1/F_1 - 0.95 V_2/F_2)$

The solubility here depend on the interaction between energy per unit mass of solute and solvent (E_M):

It taking the formula:

$$n = \frac{F_1}{F_2} \cdot \frac{J_1/V_1}{J_2/V_2} \cdot e^{-(VM_1 - VM_2)} \cdot e^{(EM_2/EM_1)} \dots \dots Eq.4$$

e.g Salicylic acid / Methanol

Category 3: $V_1/F_1 < V_2/F_2$

This category is divided into two cases:

Case. 4: $V_1/F_1 - V_2/F_2 > J/V$

It is treated under Eq.2

e.g Succinic acid / Methanol, Oxalic acid / Methanol

Case. 5: $V_1/F_1 - V_2/F_2 < J/V$

It is treated under Eq.3

$$n = \frac{F_1}{F_2} \cdot \left(\frac{V_2}{F_2} - \frac{V_1}{F_1}\right) e^{-\left|\frac{J_2}{V_2} - \frac{J_1}{V_1}\right|^{1/2}} \dots \dots Eq.5$$

e.g Succinic acid /Water, Oxalic acid / Water, Salicylic acid / Chloroform

Decreasing factor

$$S_{cd2} = e^{-(E_{M2}/2.E_{M1})^{1/2}}$$

$E_{M1} < 1/4. F_{M2}$

Rule. 10

$$S_{cd3} = e^{-(E_{M1}/2.E_{M2})^{1/2}}$$

$E_{M2} < 1/4. F_{M1}$

Rule. 11

Increasing factor

$$e^{\left(\frac{E_{M2}}{E_{M1}}\right)^{1/2}}$$

Where

$E_{M2} > E_{M1}$, $E_{M1} > 1/2 F_{M2}$ Rule. 12

$E_{M1} > E_{M2}$, $E_{M2} > 1/2 F_{M1}$ Rule. 13

Category 4: Solubility of solute with $E_{M2} < 1$ in solvent with $E_{M1} > 1$

It is treated under the categories above (mainly Eq.1) with the following correction factors:

Decreasing factor

$$S_{cd4} = e^{-\left(5 - \left(\frac{EM_2}{EM_1}\right)\right)} \cdot e^{-\left(\frac{EM_1}{EM_2}\right)^{1/2}}$$

Where

5. $E_{M2} < 1/2 F_{M1}$ Rule. 14

e.g naphthalene/ water

Increasing factor

$$S_{ci4} = e^{\left(\frac{5 \cdot E_{M2}}{E_{M1}}\right)}$$

Where

5. $E_{M2} > 1/2 F_{M1}$ Rule. 15

e.g. naphthalene/methanol

Category 5: Solubility of solute with $E_{M2} > 1$ in solvent with $E_{M1} < 1$

It is treated under the categories above (mainly Eq.1)

$$e^{-\left(\frac{EM_2}{EM_1}\right)^{1/2}}$$

The factor

Which is used under rule.3 is transformed to

$$e^{-\left(\frac{EM_2}{5 \cdot EM_1}\right)^{1/2}}$$

Where

Rule. 16

e.g. Salicylic acid /Benzene

Increasing factor

$$S_{ci5} = \frac{E_{M2}}{5 \cdot E_{M1}} \cdot \frac{V_2}{V_1}$$

Where

Rule. 17

e.g. Benzoic/Benzene, Stearic/ Benzene, phenol/ Benzene

Effect of temperature

Here the temperature factor (T_f) is multiplied by all factors in the solubility equation or raised to a power equals to the number of factors in the equation. The increasing factor is not multiplied by T_f .

$$T_f = \left(\frac{T_s}{298}\right)^2$$

Where T_s is the absolute temperature
e.g. Resorcinol/Water at 80°C(353 K), Benzoic acid / Boiling Methanol

additional T_f factor is multiplied to become

$$\left(\frac{V_2}{F_2} - \frac{V_1}{F_1}\right) \cdot T_f^2$$

If n is not subjected to a decreasing factor additional T_f factor is multiplied also.

e.g Salicylic acid / Boiling Water, Benzoic acid/ Water at 95 °C.

A.2. Solubility of ionic solids

It involves two categories:

Category 1:

The factor F_{Latt} has to be compared with $S_{gr} \cdot S_{ge}$

$$\frac{F_1 \cdot F_2}{(Latt.)^2} \geq S_{gr} \cdot S_{ge}$$

The factor S_v has to be evaluated also
, $2 \cdot E_{M2} > F_{M1}$, a factor S_v has to be evaluated:

$$S_v = e^{-\left(\frac{E_{M2}}{F_{M1}}\right)^{1/2}} \cdot \frac{V_2 / F_2}{V_1 / F_1}$$

Case 1 $S_v > 1$

$$n = \frac{F_1}{F_2} \cdot S_{gr} \cdot S_{ge} \cdot S_{ci5} \dots \dots \dots Eq.6$$

S_{ci5} is considered $F_{Latt}/n < 90\%$

$$S_{ci6} = \frac{F_{Latt}}{S_{gr} \cdot S_{ge}}$$

e.g .NaCl/water, NaBr/ water,NaNO3/water
If $S_{ci6} > F_{M1}$

Rule. 18 it has to be multiplied by E_{M2}/F_{M1}
e.g KNO3/water

Case 2 : $S_v < 1$

$$n = \frac{F_1}{F_2} \cdot e^{-\left(\frac{2 \cdot E_{M2} / F_{M1}}{\frac{V_2}{F_2} \cdot \frac{V_1}{F_1}}\right)^{1/2}} \dots \dots \dots Eq.7$$

e.g. KNO3/methanol
NaNO3/methanol belong to category 2

The factor $e^{-\left(\frac{E_{M2}}{F_{M1}}\right)^{1/2}}$ In case 2 and 3: into the equation 6 If $E_{M1} < 0.95 E_{M2}$

$$n = \frac{F_1}{F_2} \cdot S_{gr} \cdot S_{ge} \cdot e^{-\left(\frac{E_{M2}}{F_{M1}}\right)^{1/2}} \dots \dots \dots Eq.8$$

NaCl/methanol

Effect of Temperature

1) If $2 \cdot E_{M2} < E_{M1}$
a factor T_{f2} is multiplied by n_{298} (solubility at 298 K)

$$T_{f2} = (S_{ci6})^{1/2} \cdot \frac{T_s}{298}$$

e.g. NaCl/water, NaBr/water, NaNO3/water, KNO3/water
2) If $2 \cdot E_{M2} > E_{M1}$ a factor T_{f3} is multiplied by n_{298} (solubility at 298 K)

$$T_{f3} = \left(\frac{E_{M2}}{F_{Latt} \cdot S_{gr} \cdot S_{ge}}\right)^{1/2} \cdot \frac{298}{T_s}$$

e.g. NaBr/methanol
If $E_{M2} < F_{M1}$

Category 2:

$$\frac{F_1 \cdot F_2}{(Latt.)^2} < S_{gr} \cdot S_{ge}$$

The following formula is applied

$$n = \frac{F_1}{F_2} \cdot \frac{F_1 \cdot F_2}{(Latt.)^2} \cdot e^{-\left[\frac{(Latt.)^2 + (F_2)^2}{F_1 \cdot (Latt.)}\right]^{n_i/q}} \cdot \frac{V_{M2}}{V_{M1}} \dots \dots \dots Eq.9$$

Where
(q equals to the absolute sum of charges)
 n_i is the total number of ions

The factor $\frac{V_{M2}}{V_{M1}}$ is applied where $q > n_i$

e.g LiF, CaF₂, HgBr₂, UO₂ in water

B. Miscibility

The solvents are to be miscible if they satisfy one of the conditions below:

1. $V_1/F_1 \quad V_2/F_2 \left(\frac{V_1}{F_1} / \frac{V_2}{F_2} \geq 0.95 \right)$
2. $E_{M1} \quad 1/2.E_{M2}$
3. The factor (m_1) is > 1

$$m_1 = \frac{J_2/V_2}{J_1/V_1} \cdot e^{-\left(\frac{E_{M2}}{E_{M1}}\right)^{1/2}}$$

The subscript 1,2 refer to lower and high values of the entioned factors respectively. In the case where one solvent is of $E_{M1} < 1$, the solvents become miscible if they satisfy one of the following:

1. $V_1/F_1 \quad V_2/F_2 \left(\frac{V_1}{F_1} / \frac{V_2}{F_2} \geq 0.95 \right)$
2. $E_{M1} \quad 1/2.E_{M2}$
3. The factor (m_2) is > 1

$$m_2 = \frac{J1/V1}{J2/V2} \cdot e^{-\left(\frac{EM2}{5.EM1}\right)^{1/2}}$$

Quantitation of the amount miscible in the immiscible solvents

The number of miscible moles of immiscible solvents with water can be obtained using the following formula:

$$n = \frac{V_w}{V_s} e^{-\left(\frac{J_2/F_2}{J_1/F_1}\right)} \cdot e^{-\left(\frac{E_{M2}}{E_{M1}}\right)} \dots\dots\dots Eq.10$$

Where

The subscripts w, s refer to water and the other immiscible solvent. The subscripts 1,2 refer to lower and higher values of the mentioned factors

(either for water or the other solvent).

Where $E_{M1} < 1$:

$$n = \frac{V_w}{V_1} \cdot e^{-\left(\frac{J_1/F_1}{J_w/F_w}\right)^{1/2}} \cdot e^{-\left(\frac{E_{Mw}}{5.E_{M1}} \cdot \left(5 - \frac{E_{M1}}{E_{Mw}}\right)\right)^{1/2}} \dots\dots\dots Eq.11$$

Where the subscripts w,1 refer to water and the other immiscible solvent.

RESULTS AND DISCUSSION

The potential energy of molecule is taking as its energy of formation as considered by the semi-empirical method of

calculation⁸. The interpotential between molecules is related to the energy of vaporization. As shown in Figure 1

The resultant force Is:

Repulsive from 0 to M. attractive from M to B but increasing with distance, and attractive from B to infinity but decreasing with distance. There is a position where the two forces balance, shown by M on the graph. This is the equilibrium position for molecules in the solid. For a molecule to be completely separated from its neighbour it must gain an amount of energy, represented by CM on the diagram which is the latent heat of vaporization¹⁰. The enthalpies of formation, vaporization, fusion and lattice¹¹⁻¹⁴ are subtracted from the value RT which R is gas constant and T is the absolute temperature (set at 298 K) to obtain the corresponding energies Tables (1-3). The solubility is a ratio between quantity of solute dissolved in a certain quantity of solvent so, we are studying the interaction between the ratios of energies of both solute and solvent; V/F, J/V and the ratios of the energies and the molar masses; F_M, V_M, E_M Table 4. The results are compared with reported practical solubility¹⁵⁻¹⁷.

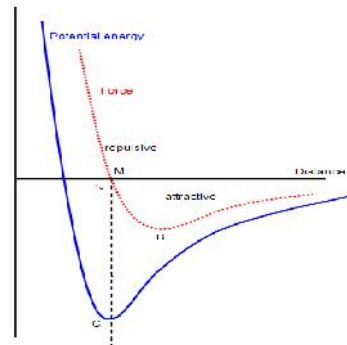


Figure 1 shows how the potential energy of two molecules

Table 1 The enthalpy of formation, vaporization, fusion and lattice

H _{Lattice}	H _{fus}	H _{Vap}	H _f	Name
Ionic Compounds				
1036	27.09	322	616	LiF
2630	30	441.4	1225.9	CaF ₂
2628	71.172	83.998	169.452	HgBr ₂
10644	70	619.3	1085	UO ₂
786	28.16	229	411.2	NaCl
747	26.11	218	361.1	NaBr
685.3	10.1	79.87	494.6	KNO ₃
756	15	97.4	467.9	NaNO ₃
Non ionic Compounds				
	32.4	117.5	940.5	Succinic acid
	25	98.1	829.9	Oxalic
	20.4	93.3	368	Resorcinol
	18.02	91.2	385.2	Benzoic acid
	11.51	68.7	165.1	Phenol
	14.2	95	589.9	Salicylic
	63	166.5	947.7	Stearic acid
	19.01	72.1	78.5	Naphthalene
Solvents				
	6.01	44.016	285	Water
	3.215	38.2	239.2	Methanol
	5.37	47.5	302.6	Propanol
	10.5	57	351.6	Pentanol
	23.7	70.9	426.5	Octanol
	9.87	33.83	49.1	Benzene
	4.94	19.2	203.3	ether
	10.48	35.6	479.3	Ethylacetate
	9.5	31.4	134.1	Chloroform

A. Solubility of solid in liquid

The solubility of solid materials in liquid is divided into solubility of non ionic solids and solubility of ionic solids.

solubility increases and vice versa. Different solutes and solvents with different energies were investigated to determine the concentration of the saturated solution or by other mean the solubility.

Table 2 The energies of formation, vaporization, fusion and lattice

Latt.	J	V	F	Name
Ionic Compounds				
1033.522428	24.612428	319.522428	613.5224	LiF
2627.522428	27.522428	438.922428	1223.422	CaF2
2625.522428	68.694428	81.520428	166.9744	HgBr2
10641.52243	67.522428	616.822428	1082.522	UO2
783.522428	25.682428	226.522428	408.7224	NaCl
744.522428	23.632428	215.522428	358.6224	NaBr
753.522428	7.622428	77.392428	492.1224	KNO3
683.522428	12.522428	94.922428	465.4224	NaNO3
Non ionic Compounds				
	29.922428	115.022428	938.0224	Succinic acid
	22.522428	95.622428	827.4224	Oxalic acid
	17.922428	90.822428	365.5224	Resorcinol
	15.542428	88.722428	382.7224	Benzoic acid
	9.032428	66.222428	162.6224	Phenol
	11.722428	92.522428	587.4224	Salicylic acid
	60.522428	164.022428	945.2224	Stearic acid
	16.532428	69.622428	76.02243	Naphthalene
Solvens				
	3.532428	41.538428	282.5224	Water
	0.737428	35.722428	236.7224	Methanol
	2.892428	45.022428	300.1224	Propanol
	8.022428	54.522428	349.1224	Pentanol
	21.222428	68.422428	424.0224	Octanol
	7.392428	31.352428	46.62243	Benzene
	2.462428	16.722428	200.8224	ether
	8.002428	33.122428	476.8224	Ethylacetate
	7.022428	28.922428	131.6224	Chloroform

Table 3 The energy / mass ratios of the studied compounds

E _M	V _M	F _M	Name
Ionic Compounds			
29.81047194	6.158874865	23.65159707	LiF
18.49850823	2.813605308	15.68490292	CaF2
0.576384235	0.113094015	0.463290219	HgBr2
5.151090972	1.142149541	4.008941432	UO2
8.699727367	1.8876869	6.812040467	NaCl
4.532837419	1.047343901	3.485493517	NaBr
5.250431672	0.382751869	4.867679802	KNO3
6.0339252	0.558367224	5.475557976	NaNO3
Non ionic Compounds			
8.430295893	0.48701172	7.943284173	Succinic acid
9.721577719	0.531058692	9.190519027	Oxalic acid
3.732028353	0.412416801	3.319611552	Resorcinol
3.497245676	0.363259204	3.133986472	Benzoic acid
2.079838933	0.351835235	1.728003698	Phenol
4.587920953	0.334934941	4.252986012	Salicylic acid
3.610916908	0.288284639	3.322632269	Stearic acid
0.864739346	0.271601888	0.593137458	Naphthalene
Solvents			
16.84953567	1.153845222	15.69569044	Water
7.950769582	0.557814304	7.392955278	Methanol
5.368280233	0.374562629	4.993717604	Propanol
4.269808758	0.309259376	3.960549382	Pentanol
3.518648867	0.262698411	3.255950457	Octanol
0.797575752	0.200694072	0.59688168	Benzene
4.540560929	0.181489342	4.359071587	ether
5.600268354	0.187981998	5.412286356	Ethylacetate
1.223686061	0.121135986	1.102550075	Chloroform

Table 4 The ratios of different energies of the studied compounds

J/F	J/V	V/F	Name
Ionic Compounds			
	0.077028796	0.520799914	LiF
	0.062704538	0.358766047	CaF2
	0.842665203	0.488221035	HgBr2
	0.109468179	0.569801061	UO2
	0.113376977	0.554220695	NaCl
	0.109651827	0.600973088	NaBr
	0.098490617	0.15726255	KNO3
	0.131922753	0.203948977	NaNO3
Non ionic Compounds			
	0.260144291	0.122622258	Succinic acid
	0.235534994	0.115566638	Oxalic acid
	0.197334826	0.248472928	Resorcinol
	0.175180373	0.231819255	Benzoic acid
	0.136395301	0.407215836	Phenol
	0.126698231	0.15750578	Salicylic acid
	0.368988734	0.173527863	Stearic acid
	0.237458366	0.915814317	Naphthalene
Solvents			
0.012503177	0.085040002	0.147027011	Water
0.003115159	0.020643278	0.150904282	Methanol
0.009637494	0.064244158	0.15001354	Propanol
0.022978839	0.147139962	0.156169938	Pentanol
0.050050249	0.310167713	0.161365115	Octanol
0.158559481	0.235784865	0.67247523	Benzene
0.012261718	0.147253019	0.083269723	ether
0.016782826	0.241601491	0.069464912	Ethylacetate
0.053352822	0.24280216	0.21973784	Chloroform

A.1. Solubility of non ionic solids

The solubility of non ionic solutes was found to be affected mainly by the interaction between energy per unit mass of both solute and solvent. As E_{M1} is higher and close to E_{M2}, the

Category. 1 : $V_1/F_1 > V_2/F_2$

Case 1: $V_1/F_1 - V_2/F_2 > J/V$

The solubility was expressed in mole/mole. There are some systems (Solute/Solvent) fall in this category. Table 5.

e.g. Resorsinol/Water, Naphthalene/ Benzene, benzene where E_{M2} of naphthalene is higher than 0.95. E_{M1} of Benzoic/Methanol, Phenol/ Water, Resorsinol/ Methanol. benzene.

Table 5 Calculated and reported value of solubility of non ionic compounds in different solvents

Solute/solvent	Calculated value of solubility	Reported value of solubility	Category
Resorcinol/Water	0.19	0.18	Category1, Case1
Resorcinol/ Methanol	0.453	0.4	Category1, Case1
Phenol/Water	0.0133	0.013	Category1, Case1
Benzoic acid/ Methanol	0.136	0.146	Category1, Case1
Naphthalene/Benzene	0.202	0.2	Category1, Case1
Benzoic acid/ Water	5.7×10^{-4}	5×10^{-4}	Category1, Case 2
Benzoic acid/ Dimethyl ether	0.16	0.17	Category1, Case 2
Stearic acid/Methanol	0.0072	0.007	Category1, Case 2
Salicylic acid /Water	1.9×10^{-4}	2.7×10^{-4}	Category1, Case 3
Salicylic acid / Dimethyl ether	0.188	0.15	Category1, Case 3
Salicylic acid / Methanol	0.09	0.1	Category 2
Succinic acid/Methanol	0.087	0.055	Category 3, Case 4
Oxalic/Methanol	0.27	0.18	Category 3, Case 4
Succinic acid/Water	0.0125	0.0117	Category 3, Case 5
Oxalic/ Water	0.036	0.028	Category 3, Case 5
Salicylic acid / Chloroform	0.01	0.013	Category 3, Case 5
Naphthalene/ Water	2.6×10^{-6}	3.6×10^{-6}	Category 4
Naphthalene/Methanol	0.019	0.015	Category 4
Salicylic/Benzene	0.0048	0.00532	Category 5
Benzoic/Benzene	0.074	0.07	Category 5
Stearic/ Benzene	0.075	0.07	Category 5
Phenol/ Benzene	0.1	0.08	Category 5

Table 6 Calculated and reported value of solubility of ionic compounds in different solvents

Solute/solvent	Calculated value of solubility	Reported value of solubility	Category
NaCl/Water	0.12	0.11	Category1, Sv>1
NaBr/Water	0.146	0.15	Category 1, Sv>1
NaNO ₃ /Water	0.17	0.19	Category 1, Sv>1
KNO ₃ /Water	0.056	0.06	Category 1, Sv>1
NaCl/ Methanol	0.0077	0.007	Category 1, Sv>1
NaBr/ Methanol	0.1	0.066	Category 1, Sv>1
KNO ₃ /Methanol	1.01×10^{-7}	insoluble	Category 1, Sv<1
NaNO ₃ /Methanol	0.0026	0.0016	Category 2
LiF/Water	5.3×10^{-4}	7.4×10^{-4}	Category 2
CaF ₂ /Water	5.07×10^{-6}	4.5×10^{-6}	Category 2
HgBr ₂ /Water	6.13×10^{-7}	4.02×10^{-7}	Category 2
UO ₂ /Water	3.37×10^{-14}	3.38×10^{-14}	Category 2

Table 7 Calculated and reported value of the amount dissolved of different solvents in water

Solvent A/solvent B	Calculated value of solubility	Reported value of solubility
Ether/Water	0.0245	0.0277
Ethyl acetate/Water	0.018	0.017
Pentanol/Water	2.34×10^{-3}	4.5×10^{-3}
Octanol/Water	8.95×10^{-5}	6.36×10^{-5}
Benzene/Water	4.24×10^{-4}	4.12×10^{-4}

The solubility of resorsinol in water was not subjected to any correction factor while, the solubility of resorsinol in methanol is subjected to increasing factor S_{ci2} because E_{M2} of resorcinol is higher than $1/2 F_{M1}$ of methanol. The solubility of benzoic acid in methanol is subjected to S_{ci1} because E_{M2} of benzoic acid is approximately equal to () $0.95.1/2 F_{M1}$ of methanol. The number of Phenol moles dissolved in mole of water is corrected by the decreasing factor S_{cd1} because E_{M2} of phenol is

lower than 0.95. $1/4 F_{M1}$ of water. The factor $e^{-\left(\frac{E_{M2}}{E_{M1}}\right)^{1/2}}$ is considered in determination of solubility of naphthalene in

Case. 2 : $V_1/F_1 - V_2/F_2 > J/V$

The solubility of Benzoic acid in water, Benzoic in dimethyl ether, Stearic acid in methanol are examples of this case. The system Benzoic acid / water is subjected to a decreasing factor S_{cd1} where Benzoic / Dimethyl ether, Stearic acid / Methanol are subjected to increasing S_{ci1} , S_{ci3} factors. Table 5.

Case. 3: $V_1/F_1 - V_2/F_2 < J/V$

Eq.3, rule. 8 are applied here and n is subjected to decreasing (S_{cd}) and increasing factors (S_{ci1} , S_{ci2}) under rules 4-7.e.g. Solubility of salicylic acid in water and salicylic acid in dimethyl ether. Table 5.

Category 2: $V_1/F_1 > V_2/F_2$ ($V_1/F_1 > 0.95 V_2/F_2$)

The solubility here depend on the interaction between energy per unit mass of solute and solvent (E_M).The solubility is corrected by the increasing factor S_{ci1} . Table 5 e.g Salicylic acid / Methanol

Category 3: $V_1/F_1 < V_2/F_2$

Case. 4: $V_1/F_1 - V_2/F_2 > J/V$

e.g Succinic acid / Methanol, Oxalic acid / Methanol The energy per unit mass E_{M2} of both succinic and oxalic acid are higher than E_{M1} of methanol. Also, E_{M2} of both solutes are higher than half of E_{M1} of solvent so, the increasing factor S_{ci1} is applied here. Table 5

Case. 5: $V_1/F_1 - V_2/F_2 < J/V$

e.g Succinic/Water, Oxalic/ Water, Salicylic/ Chloroform The energy per unit mass E_{M2} of both succinic and oxalic acidS are lower than E_{M1} of water. Also, E_{M2} of both solutes are

higher than half of E_{M1} of solvent so, the increasing factor S_{ci1} is applied here. Table 5

Category 4: Solubility of solute with $E_{M2} < 1$ in solvent with $E_{M1} > 1$

Dealing with energy per unit mass E_M less than one makes a calculation error and not matched with the experimental results. Multiplying the E_M by a factor of five gave a close results with the reported data.

e.g: Naphthalene/ Water, Naphthalene/Methanol

Where the solubility of naphthalene in water is corrected by the application of decreasing factor under rule 15. But the concentration of saturated solution of naphthalene in methanol is subjected to the increasing factor under rule 16. Table 5.

Category 5: Solubility of solute with $E_{M2} > 1$ in solvent with $E_{M1} < 1$

e.g. Salicylic/Benzene, Benzoic/Benzene, Stearic/ Benzene, Phenol/ Benzene

The solubility equation of salicylic acid in benzene contain the

factor $e^{-\left(\frac{EM}{5 \cdot EM} \cdot \frac{2}{1}\right)^{1/2}}$ under rule 17. Where the solubility of benzoic acid, stearic acid, phenol in benzene is treated by multiplying by the increasing factor S_{ci4} .

Effect of temperature

The temperature factor (T_f) is multiplied by all factors in the solubility equation of resorcinol in water at 80°C (353 K) and benzoic acid in boiling methanol

The solubility equation of resorcinol in water at 298 K is:

$$x = 0.773 \cdot \frac{0.085040002}{(0.248472928 - 0.147027011)} \cdot e^{-\left(\frac{0.197334826 - 0.085040002}{x}\right)^{1/2}} \cdot e^{-\left(\frac{1.153845222 - 0.412416801}{x}\right)^{1/2}}$$

Here we have four factors in the equation, so, the temperature factor T_f is raised to the fourth power. The solubility of resorcinol in water at 80°C (353 K) was calculated to be 0.778 versus the reported value 0.82¹⁵. Where that of benzoic acid in boiling methanol was 0.36 versus 0.22¹⁵. The solubility of salicylic acid in boiling water was calculated to be 0.00675 versus 0.008¹⁵ which is the reported value. The temperature factor (T_f) is raised to eighth power as the equation contain sex factors. The other two powers are put because there is no decreasing factor. Also, T_f is raised to the seventh power in case solubility of benzoic acid in water at 95 °C to give 0.011 versus 0.01¹⁵.

A.2. Solubility of ionic solids

The solubility equation here deals mainly with water as solvent. The solubility of ionic compounds in different solvents depends mainly on the difference between (V/F) of solute and solvents, as the difference increase, the solubility increases. Also, the lattice energy of the ionic compound, the higher the

lattice energy the lower the solubility. The solubility of NaCl, NaBr, NaNO3 in water belong to category 1, as they have F_{Latt}

S_{gr} , S_{ge} and $S_v > 1$. Their solubility equations are subjected to the increasing factor S_{ci5} except NaCl in water because F_{Latt}/n more than 90 % . In case of KNO₃ in water the increasing factor is multiplied by E_{M2}/E_{M1} . The solubilities of these compound in methanol were also treated in the same way. The

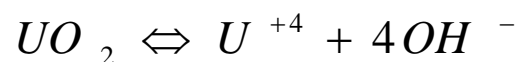
factor $e^{-\left(\frac{EM}{EM}\right)^{1/2}}$ is put in the equation of solubility of sodium chloride in methanol because $E_{M1} < 0.95 E_{M2}$. Table 6

Effect of Temperature

The temperature factor T_{f2} was applied for the determination of solubility of NaCl, NaBr, NaNO₃, KNO₃ in boiling water as 2. $E_{M2} < E_{M1}$. The results were 0.15 for NaCl in water versus 0.12¹⁵, 0.2 for NaBr in water versus 0.18¹⁵, 0.53 for NaNO₃ in water versus 0.35¹⁵ and 0.235 for KNO₃ in water versus 0.336¹⁵. The temperature factor T_{f3} was applied for the determination of solubility of NaBr in methanol as $2 \cdot E_{M2} > E_{M1}$. The result was 0.0886 versus 0.0612¹⁵. Solubility that belong to category 2 is characterized by $\frac{F_1 \cdot F_2}{(Latt)^2} < S_{gr} \cdot S_{ge}$

The solubility of sodium nitrate in methanol lies in this category and not in category 1 because $\frac{F_1 \cdot F_2}{(Latt)^2} <$

$S_{gr} \cdot S_{ge}$. The solubility of different ionic compounds with different solubility products⁽¹⁷⁾ are studied in water. The solubility products are converted to mole/ mole. Table 6 shows the comparison between the calculated values of solubility and the reported ones. The factor V_{M2}/V_{M1} is applied in the solubility equation of CaF₂, HgBr₂, and UO₂ in water where the total charges are higher than the total number of ions. Uranium oxide is dissolved in water to produces five ions and eight total charges⁽¹⁷⁾ so the ni/q equals 5/8.



B. Miscibility

The miscibility of liquids depend the ratio (V/F) and the energy per unit mass E_M . The solvents are to be miscible if they satisfy one of the conditions below:

1. $V_1/F_1 \cdot V_2/F_2 \left(\frac{V_1}{F_1} / \frac{V_2}{F_2}\right) \geq 0.95$
2. $E_{M1} \cdot 1/2 \cdot E_{M2}$
3. The factor (m_1) is 1

$$m_1 = \frac{J_2/V_2}{J_1/V_1} \cdot e^{-\left(\frac{EM}{EM}\right)^{1/2}}$$

The subscript 1, 2 refer to lower and high values of the mentioned factors respectively.

In the case where one solvent is of $E_{M1} < 1$, the solvents become miscible if they satisfy one of the following:

1. $V_1/F_1 \cdot V_2/F_2 \left(\frac{V_1}{F_1} / \frac{V_2}{F_2}\right) \geq 0.95$

2. $E_{M1} = 1/2 \cdot E_{M2}$
3. The factor (m_2) is 1

$$m_2 = \frac{J1/V1}{J2/V2} \cdot e^{-\left(\frac{E_{M2}}{5 \cdot E_{M1}}\right)^{1/2}}$$

Quantitation of the amount miscible in the immiscible solvents

The number of miscible moles of immiscible solvents with water are studied and found to be close to the reported values ^{15, 16}. Table 7.

CONCLUSION

The provided methodology in determining the concentration of saturated solution of a solute in a certain solvent resemble a scheme. The steps of this scheme have to be followed in order to reach to the solubility equation of the solute in the solvent of study. The solubility can be predicted without the need of complicated computer programs. The miscibility of solvents is easily to be predicted and the amount that will dissolve in an immiscible solvent can also be quantified.

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