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Experimental and Modelling of liquid –solid equilibria

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Abstracts

Solid-liquid equilibria are less considered in inorganic thermochemistry, comparatively to the other two types of phase equilibria involving vapour and/or liquid phases. The great majority of the relevant models, particularly for the calculation of the activity coefficient, concern these last two cases, although their use is extended to handle the solid-liquid equilibria.

The first part of the present work concerns an experimental study for the determination of the liquid –solid phase equilibrium diagrams, for various binary systems such as salicylic acid in water, ethanol and chloroform, and naphthalene in phenol, by the means of Differential Scanning Calorimetry. The second part consists of a modeling of these phase equilibria by means of various thermodynamic models such as NRTL, UNIFAC which are also tested for binary systems such as naphthalene in organic solvents.

The use of these models requires interaction parameter values which are not always available. Therefore, this work was an opportunity to compute these parameters for the different systems considered.

The results obtained experimentally and by modeling, concerning the phase diagrams showed a good agreement, particularly for the NRTL model, compared to UNIFAC which is based on the concept of group contribution and thus is approximate.

Keywords: Solubility; Solid-liquid phase equilibria; Solute; Solvent; NRTL; UNIFAC; Calorimetry

1. INTRODUCTION

In any design problem concerning separation equipment, the knowledge of the phase equilibria data is an essential step. The experimental measurement of such data is a complex task and therefore the use of thermodynamic models for its prediction is very important. This has encouraged the present study, by considering liquid-solid systems.

Binary systems were considered to determine, experimentally, the variation of the solute solubility in the solvent, with temperature. Generally, the techniques of solubility determination of a solute in a solvent are relatively simple. However they require a great care, due to the difficulty to reach a complete state of equilibrium of the solid in the liquid solution. Therefore it is necessary to maintain an intimate and prolonged contact between both phases.

As a second part of this work, the modeling of the solid-liquid equilibria obtained as well as the solubility of naphthalene in various organic solvents was performed using different thermodynamic models such as NRTL and UNIFAC.

2. EXPERIMENTAL

The present experimental study concerns measurements of liquid-solid phase equilibria for binary systems, by means of the differential scanning calorimetry technique, using a SETARAM DSC92 calorimeter.

2.1 Chemicals

The different solvents (99% purity) such as ethanol and phenol as well as the solutes such as naphthalene and salicylic acid, used in the present study, were provided by Fluka, Switzerland. Water was bi-distilled locally using a GFL 2001/4 distillation unit.

2.2 Experimental procedure

Solution samples were prepared in a jacketed glass beaker using tap water to keep a constant temperature. The solutions were magnetically agitated at constant speed of 200 rpm for 30 minutes, to ensure good mixing of the dissolved solid and the liquid solvent. The solutions were then decanted and sufficient time is allowed for their solidification. Solid samples were then encapsulated in standard aluminium sealed pans with a pierced cover lids, ready for DSC analyses. The reference pan, used for each experiment, was empty and identical to the one used on the measuring side. Temperature scans were conducted over the temperature range from 273 K to 473 K with an average heating rate q = 1 K min^{-1} and a precision of ± 0.01K. This experimental procedure was repeated twice for each considered chemical system to ensure reproducibility of the results. All investigated samples had a mass of 23.4 mg. Temperature calibration was made using three reference standards, indium, zinc and lead.

The obtained deviations are negligible and may be due essentially to the solvent evaporation as well as to the titration method.

The experimental determination of the solubilities is performed by means of the thermal analysis using the DSC technique with an estimated precision on molar fraction of $\pm 10^{-4}$. As an illustration a typical thermogram obtained for the calibration of the apparatus using Indium, is shown by the following figure:

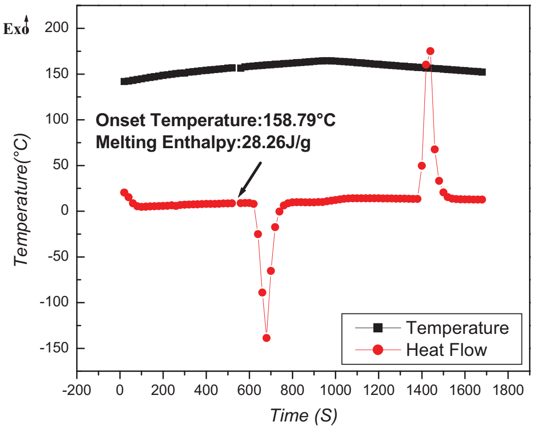


Figure 1: Calibration curve for Indium

The results are shown in the following table:

Table 1 Indium calibration results In

Trial N°	Enthalpy of Melting (J/g)	Melting temperature (°C)
1	-28.25	158.66
2	-28.35	158.88
3	-28.20	158.85

The left peak of heat flow versus time curve corresponds to melting (heating phase) whereas the right one characterises the recrystallisation of the sample.

In the literature the reported indium onset temperature for melting is generally around 156.6 and 157.6°C, for a melting enthalpy lying between -26.8 and -30.2 J/g [1]. Therefore the results shown in Table 1 are in these ranges and mean values are considered throughout this study.

2. SOLID-EQUILIBRIA MODELING

At a fixed temperature and pressure, the solid-liquid equilibrium is conditioned by the isofugacity criterion. For a given constituent A, this condition is expressed as follows:

$$x_A^S \gamma_A^S f_{A\ pur}^S = x_A^L \gamma_A^L f_{A\ pure}^L \qquad (1)$$

with S and L denoting the solid and liquid states, respectively, x_A the molar fraction of constituent A, γ_A the activity coefficient and $f_{A,\ pure}$ the fugacity of pure constituent in each phase.
This leads to the following solubility equation:

$$\ln(x_i \cdot \gamma_i) = \frac{\Delta H_{tp}}{R}\left(\frac{1}{T_{tp}} - \frac{1}{T}\right) - \frac{\Delta C_p}{R}\left(\ln\frac{T_{tp}}{T} - \frac{T_{tp}}{T} + 1\right) - \frac{\Delta V}{RT}\left(P - P_{tp}\right) \qquad (2)$$

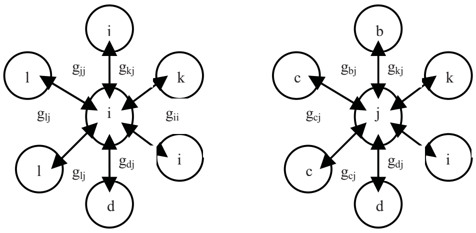
Where T_{tp} and ΔH_{tp} are the temperature and the enthalpy at the triple point respectively, ΔC_p and ΔV_p represent the differences in heat capacity and volume for the liquid with the solid.
However it is usual in the great majority of cases to neglect the effects of pressure and the variation of the heat capacity on the solubility and to consider safely the fusion temperature instead of the triple point which is generally not known for many constituents. These assumptions lead to the following general solubility equation:

$$\ln(x_i \gamma_i) = \frac{\Delta H_m}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \qquad (3)$$

Therefore reliable thermodynamic models are needed for the calculation of the activity coefficient, where the well known ones, namely UNIFAC and NRTL are tested in the present work. Briefly they are described as follows:

2.1 NRTL (Non Random Two Liquids) model

This model was originally proposed by Renon and Prausnitz [2]. It is mainly based on the introduction of the local composition concept with the hypothesis of a non random molecular distribution, similarly to the propositions put forward by Wilson [3] and Scott [4]. For a mixture of n constituents, n different elementary cells with different central molecules are considered. Figure1 shows schematically two different elementary cells as follows:



According to this model, the activity coefficient for a constituent i is expressed as follows:

$$\ln\gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k}\left(\tau_{ij} - \frac{\sum_l \tau_{lj} G_{lj} x_l}{\sum_k G_{kj} x_k}\right) \qquad (4)$$

with $G_{ji} = \exp\left(-\alpha_{ji} \cdot \frac{C_{ji}}{RT}\right)$; and $\tau_{ji} = \frac{C_{ji}}{RT}$

with α_{ji} the randomness parameter and $C_{ij} = g_{ij} - g_{ii}$, g_{ij} being the molar free energy due to the interaction between molecule i and j.

2.2 Model of UNIFAC (UNIQUAC Functional –group Activity Coefficient)

This model is based on a group contribution concept where the activity coefficient is defined as follows [5, 6]:

$$\ln\gamma_i = \ln\gamma_i^{\,C} + \ln\gamma_i^{\,R} \qquad (5)$$

With:

$$\ln\gamma_i^{\,C} = \ln\frac{\Phi_i}{x_i} + \frac{Z}{2}q_i\ln\frac{\Theta_i}{\Phi_i} + l_i\frac{\Phi_i}{x_i}\sum_j x_j l_j \qquad (6a)$$

$$l_i = \frac{Z}{2}(r_i - q_i) - (r_i - 1);\ \text{Z=10} \qquad (6b)$$

$$\Theta_i = \frac{q_i\cdot x_i}{\sum_j q_j\cdot x_j};\ \Phi_i = \frac{r_i\cdot x_i}{\sum_j r_j\cdot x_j} \qquad (6c)$$

x_i represents the molar fraction of constituent i and the summations are all over the constituents, Θ and Φ are the surface area and volume fractions, respectively, r_i and q_i are the molecular volume and surface area, respectively and can be calculated as follows :

$$r_i = \sum_K \nu_K^{(i)}\cdot R_K;\ q_i = \sum_K \nu_K^{(i)}\cdot Q_K \qquad (6d)$$

where $\nu_K^{(i)}$ is the number of type k groups in molecule i, R_k and Q_k are the group volume and surface parameters which are readily available in standard tables or can be calculated from the following relationships :

$$R_K = \frac{V_{wk}}{15.17};\ Q_K = \frac{A_{wk}}{2.5\times10^9} \qquad (6e)$$

With V_{wk} and A_{wk} the volume and the surface area of the considered group.

The residual term is given as follows:

$$\ln\gamma_i^{\,R} = \sum_k \nu_k^{\,i}\left(\ln\Gamma_k - \ln\Gamma_k^{(i)}\right) \qquad (6f)$$

Where Γ_k and $\Gamma_k^{(i)}$ are the residual activity coefficients of group k in the mixture and in pure liquid i, respectively.

The residual activity coefficient of group k is then expressed as follows:

$$\ln\Gamma_k = Q_k\left(1-\ln\left(\sum_m \Theta_m\cdot\Psi_{mk}\right)-\sum\frac{\Theta_m\cdot\Psi_{km}}{\sum_n \Theta_n\cdot\Psi_{nm}}\right) \qquad (6g)$$

$$\Theta_m = \frac{Q_m\cdot X_m}{\sum_n q_n\cdot x_n};\ X_m = \frac{\sum_j \nu_m^{(j)}\cdot x_j}{\sum_j\sum_n \nu_n^{(j)}\cdot x_j} \qquad (6h)$$

With Θ_m the group surface fraction in the mixture and X_m the group molar fraction in the solution.

The interaction parameter between groups m and n is then calculated from the following:

$$\Psi_{mn} = \exp\left(-\frac{u_{mn}-u_{nn}}{RT}\right) = \exp\left(-\frac{a_{mn}}{T}\right) \qquad (9)$$

Ψ_{mn} is the Boltzmann factor corresponding to the interaction parameter a_{mn} ($a_{mn}=U_{mn}-U_{nm}$).

3. RESULTS AND DISCUSSION

The results obtained both experimentally and by modelling of solid-liquid equilibria are presented for the various systems considered as follows:

3.1 Solubility of Salicylic acid in Ethanol, Water and Chloroform

Figure 2 shows the thermogram obtained by means of the DSC 92 for the salicylic acid, from which the obtained melting temperature and enthalpy are 434 K and 23.83 kJ/mole, respectively. The melting temperature is close to 432 K, the reported value in the literature [7], whereas the melting enthalpy value is of the same order of magnitude of reported results in the same source [7].

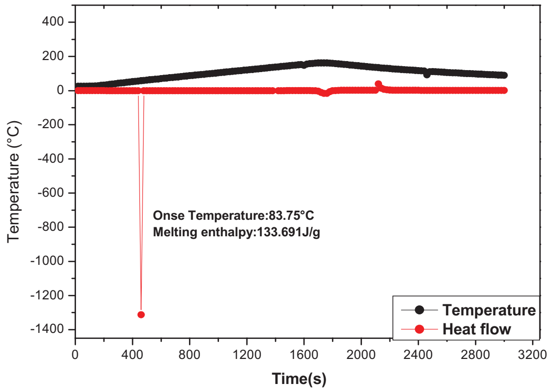


Figure 2 Salicylic acid thermogram from DSC92

The experimentally measured solubilities of salicylic acid in ethanol, water and chloroform, are shown in the figures 3, 4 and 5, respectively, as follows:

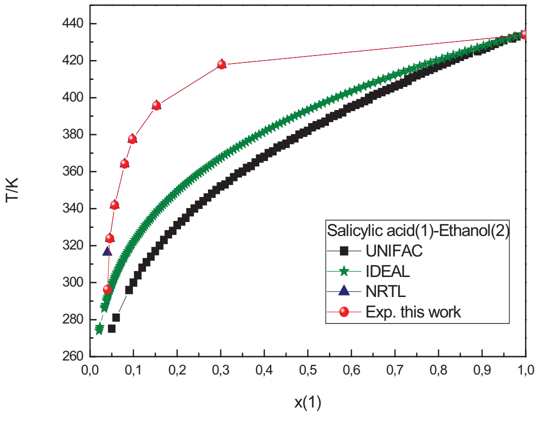


Figure 3 Solubility of salicylic acid in Ethanol

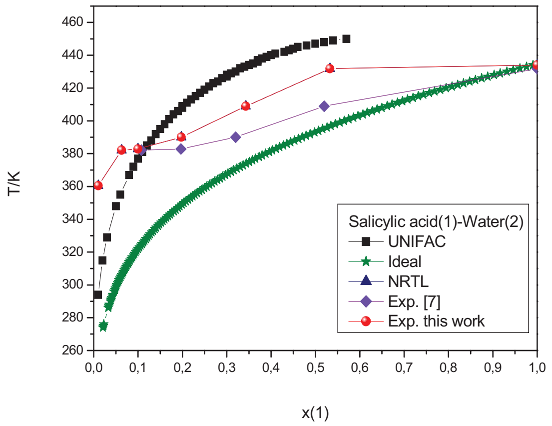


Figure 4 Solubility of salicylic acid in Water

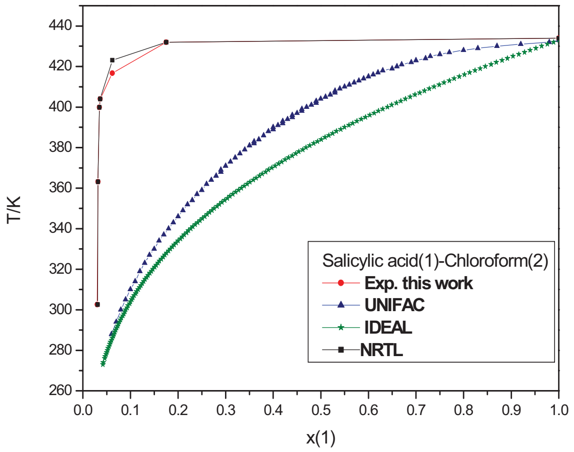


Figure 5 Solubility of salicylic acid in Chloroform

From the just above three figures, it can be concluded that acid salicylic exhibits similar behaviours in ethanol and water. However very low solubility is shown in chloroform for a large domain of temperature, as shown in the following figure:

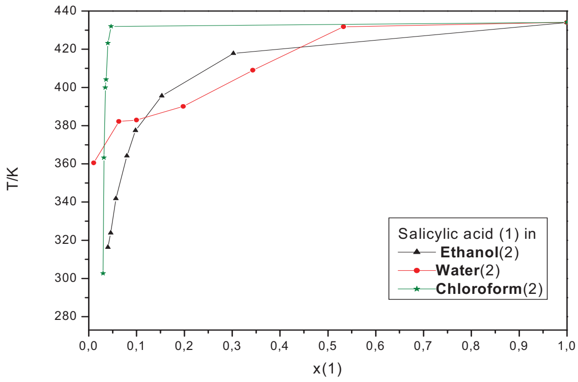


Figure 6 Comparison of salicylic solubilities in ethanol, water and chloroform

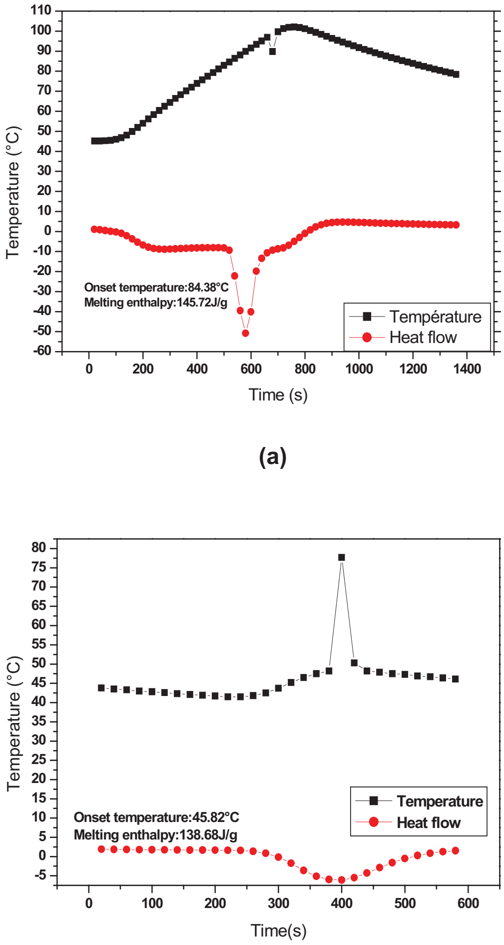
For the modelling of the results, the NRTL model gives results very close to the experimental values. The opportunity was taken to calculate interaction parameters for this model for the three systems and the results are presented in the following table:

Table 2: Calculated NRTL interaction parameters

System	τ_{12}	τ_{21}
Salicylic acid (1)- Ethanol (2)	-58.7326	62.5603
Salicylic acid (1)- Water (2)	-68.9271	73.5960
Salicylic acid (1)- Chloroform (2)	86.2353	-80.3362

3.2 The phenol- naphthalene system

The thermograms of both constituents are shown as follows:



(a)

(b)

Figure 7 Thermograms of a) Naphthalene; b) Phenol

The DSC measured melting properties for both constituents are shown in the following table:

Table 3: Measured and reported melting properties of Naphthalene and Phenol

Property	Naphthalene		Phenol	
	Exp.	From [9]	Exp.	From [10]
Melting temperature (K)	357.53	353.35	318.97	315.15
Molar melting enthalpy (J/mole)	18679.49	18784.92	130051.17	11278.55

The experimental results are very close to values reported in the literature, confirming the reliability of the DSC technique.

The experimentally measured and the calculated solid-liquid equilibria results are shown in the following figure:

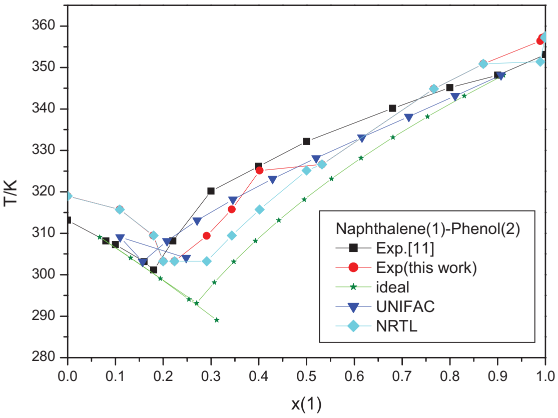


Figure 8: Experimental and calculated solid-liquid equilibria for Naphthalene-phenol system

The experimental results obtained from the DSC measurements, in the present study, follow the same trend as experimental values reported in the literature [11]. For this case UNIFAC seems to give the best results, close to both sets of experimental values, whereas the NRTL model gives the closest eutectic point value as shown by the following table:

Table 4 : Eutectic points

Method	Eutectic point (K)	Solubility (mol%)
Experimental [8]	301.278	0.1801
Experimental (this work)	303.396	0.2235
Ideal	293.129	0.2691
UNIFAC	306.343	0.1876
NRTL	303.22	0.2207

3.3 Modeling of Naphthalene in various organic solvents

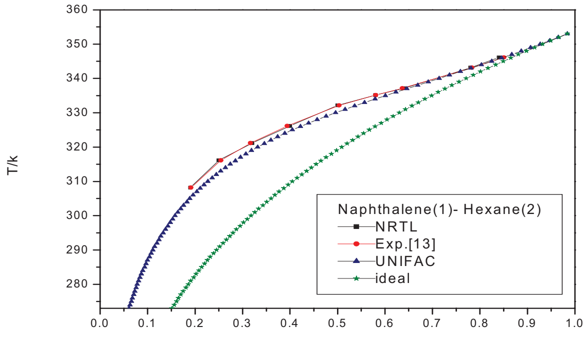
The above models are tested by considering binary systems. In total seven different binary systems were chosen, and involve naphthalene as the solute and some alcoholic and other organic compounds as the solvents.

For the first systems, the results are shown in the following figures (9a, b, c, d, e, f & g) and are compared with the experimentally measured values, reported in the literature [12]. It can be noticed that the obtained results are in a good agreement with the experimental values, excepted for the case where chloroform is the solvent.

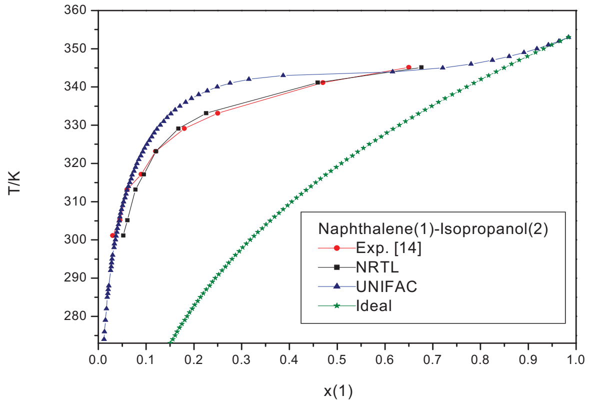
Table 5 shows the naphthalene solubility values at 40°C.

Table 5: Solubility of Naphthalene in different solvents at 40°C

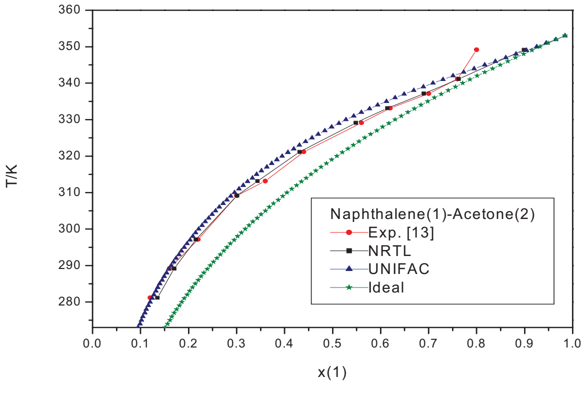
Solvent	exp	Ideal	UNIFAC [13]	UNIFAC [12]	NRTL
Methanol	4 .4	43.75	5.05	4.8	6.22
Ethanol	7.3	43.75	6.22	5.4	7.18
2-propanol	7.6	43.75	6.01	9.3	6.22
n-hexane	22.2	43.75	25.86	25.9	22.9
Acetic acid	11.7	43.75	12.66	12.5	9.9
Acétone	37.8	43.75	32.26	35.8	35.97
Chloroform	47.3	43.75	51.52	47.0	44.92



(a)



(b)



(c)

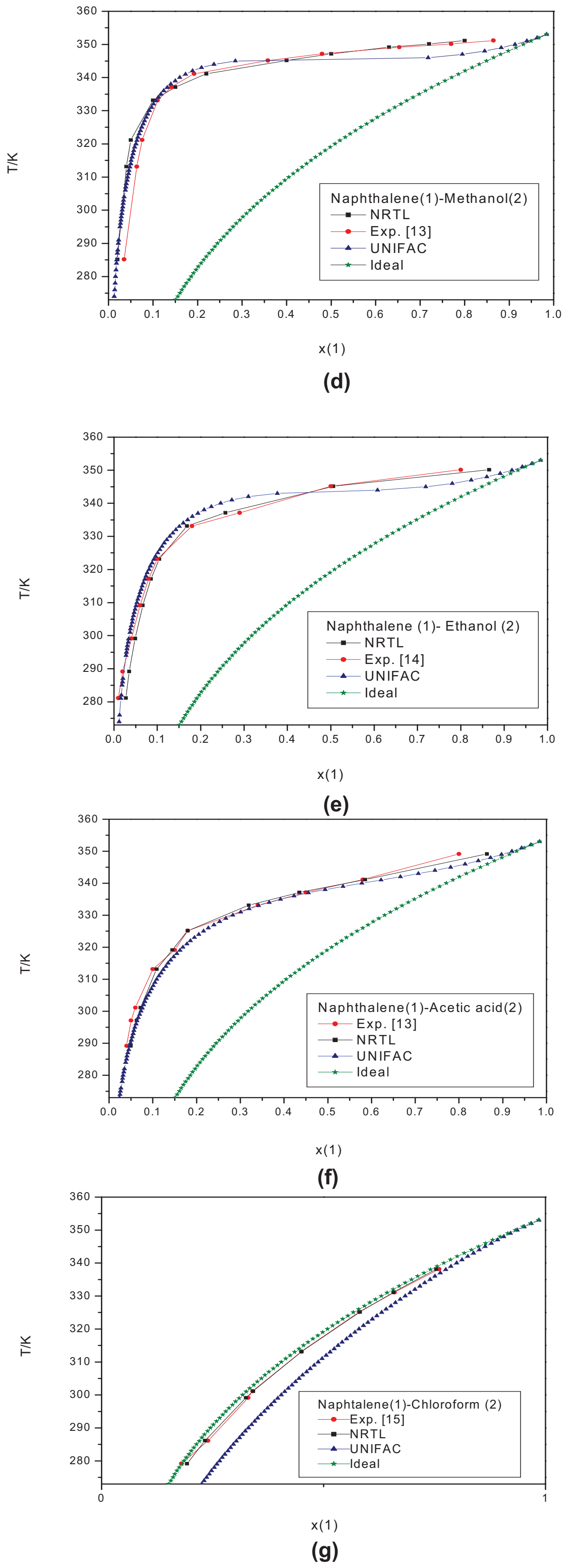


Figure 9: Solubility of Naphthalene in various organic solvents

4. CONCLUSION

In conclusion, for the considered systems it can be affirmed that the thermodynamic models used have shown to be reliable in predicting solid-liquid equilibria for various systems. However, they can be refined further by calculating updated interaction parameters by considering more systems.

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