Journal of Thermal Analysis and Calorimetry, Vol. 84 (2006) 1, 47–52

DETERMINATION BY DSC OF SOLID–LIQUID DIAGRAMS FOR POLYAROMATIC – 4,4’DIAMINODIPHENYLMETHANE BINARY SYSTEMS

Analysis in terms of modified UNIFAC

K. Khimeche[1,2]* *and A. Dahmani*[2]

[1]Ecole Militaire Polytechnique EMP, BP 17 Bordj-el-Bahri, Alger, Algérie
[2]Laboratoire de thermodynamique et de modélisation moléculaire, Faculté de chimie, USTHB, BP 32 El-Alia
16111 Bab-Ezzouar, Alger, Algérie

Diamines are an important group of compounds in different fields of industry and particularly in the synthesis of a number of polymers. In this work, study of binary solid-liquid equilibriums SLE for (biphenyl+4,4’diaminodiphenylmethane), and (naphthalene+4,4’diaminodiphenylmethane) systems is done by differential scanning calorimetry.

Results obtained with this technique are compared with those predicted by modified UNIFAC (Larsen and Gmehling) models. It was found out that all the systems are eutectic and globally good agreement is obtained between experimental and predicted SLE.

Keywords: *diamines, polyaromatics, solid–liquid phase diagrams, UNIFAC model*

Introduction

The number of organic materials that are being separated and/or purified by crystallization in industrial scale operations is increasing rapidly because of the low energy consumption of such processes and the possibility of obtaining products with higher purity than can be achieved by other conventional separation operations. Apart from their application in chemical and petrochemical industry, solid–liquid equilibria are also of interest for the development of theoretical models. As long as eutectic behaviour is observed and the data for the pure substances are known it is possible to use the data obtained in any solid–liquid equilibrium experiment to calculate the activity coefficient in the liquid phase.

Of the methods of measuring SLE, it was shown that differential scanning calorimetry (DSC) is a rapid and sensitive technique, broadly used for the characterisation of any kind of phase of change [1–7]. It seemed interesting to test the application of DSC to the determination of SLE of complex systems including polyaromatics and aromatic diamine. These compounds are very important in different fields of industry and particularly in the synthesis of a number of polymers [8–10].

In this work the results obtained in a study of the thermodynamic properties of mixtures containing 4,4’diaminodiphenylmethane and polyaromatics are reported. A complete data obtained by differential scanning calorimeter (DSC) of solid-liquid equilibria (SLE) for (biphenyl+4,4’diaminodiphenylmethane), and (naphthalene+4,4’diaminodiphenylmethane) systems are compared with those predicted by modified UNIFAC (Universal Functional group Activity Coefficient) models. These models are employed with the major objective to extensively investigate the validity of UNIFAC (Larsen and Gmehling versions).

Theoretical models

UNIFAC model

Group contribution methods can be used for semi- quantitative predictions of activity coefficients in the liquid mixture. The basic idea of the group contribution methods is that the number of functional groups is much smaller than the number of chemical compounds.

Due to the availability of large group interaction parameter tables, UNIFAC group contribution method has gained widespread popularity in chemical engineering computations. Recent developments of the UNIFAC method make it possible to predict deviations to ideality of liquid mixtures in wide temperature ranges.

In this method the activity coefficient of a component *i* ($\ln\gamma_i$) is assumed to be made up two contributions: combinatorial ($\ln(\gamma_i)^C$) and residual ($\ln(\gamma_i)^R$) contributions.

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* Author for correspondence: kamel.khimeche@caramail.com

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

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

The combinatorial part represents the difference in size and shape of the molecule and is computed from pure-component properties. The residual part is due to intermolecular forces which assume the additivity of contributions [11–13].

Modified UNIFAC (Larsen) model

The modified UNIFAC model (version Larsen *et al.*) [11], is given in terms of these equations:

$$\ln(\gamma_i^c)=\ln\left(\frac{\varphi_i}{x_i}\right)+1-\frac{\varphi_i}{x_i}$$

$$\varphi_i=\frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \quad \text{with} \quad r_i=\sum_k \nu_k^i R_k$$

$$\ln(\gamma_i^R)=\sum_k \nu_k^i[\ln\Gamma_k-\ln\Gamma_k^i]$$

$$\ln\Gamma_k=\frac{z}{2}Q_k\left[1-\ln\left(\sum_m \theta_m\psi_{mk}\right)-\sum_m\left(\frac{\theta_m\psi_{km}}{\sum_n \theta_n\psi_{nm}}\right)\right]$$

$$\theta_m=\frac{Q_m X_m}{\sum_n Q_n X_n} \quad \text{and} \quad X_m=\frac{\sum_j \nu_m^j x_j}{\sum_j\sum_n \nu_n^j x_j}$$

$$\psi_{nm}=$$

$$\exp\left[-\frac{a_{nm}+b_{nm}(T-T_0)+c_{nm}\left(T\ln\frac{T_0}{T}+T-T_0\right)}{T}\right]$$

where: R_k=volume parameter for group k, Q_k=surface area parameter for group k, ν_k^i=number of groups type k in molecule i, a_{nm}, b_{nm}, c_{nm}=group interaction parameter between groups m and n, x_i=liquid mole fraction of component i.

Modified UNIFAC (Gmehling) model

In the modified UNIFAC (Dortmund) model [12], as in the original UNIFAC model, the activity coefficient is the sum of a combinatorial and a residual part.

The combinatorial part was changed in an empirical way to make it possible to deal with compounds very different in size:

$$\ln(\gamma_i^c)=1-V_i'+\ln V_i'-5q_i\left(1-\frac{V_i}{F_i}+\ln\left(\frac{V_i}{F_i}\right)\right)$$

The parameter V_i' can be calculated by using the relative van der Waals volumes R_k of the different groups.

$$V_i'=\frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}}$$

All other parameters are calculated in the same way as for the original UNIFAC model. In comparison to the original UNIFAC method, only the van der Waals properties were changed slightly, at the same time temperature-dependent parameters were introduced to permit a better description of the real behaviour (activity coefficients) as a function of temperature.

$$\psi_{nm}=\exp\left[-\frac{a_{nm}+b_{nm}T+c_{nm}T^2}{T}\right]$$

Experimental

Our products (Fluka, purity greater than 99 mol%) were used without further purification. A series of binary polyaromatic –4,4'diaminodiphenylmethane mixtures were prepared as follows.

The sample was heated very slowly inside a glass cell above the melting temperature of the major component. The liquefied sample with continuous stirring was solidified, and kept in a desiccator with silica gel. Then a small amount of solid (6 to 10 mg) was taken and sealed in a DSC 7 PerkinElmer pan for the analysis.

The measurements were made under fixed conditions of constant heating rate of 1°C min^{-1} and under nitrogen atmosphere (20 mL min^{-1}).

Before the analysis, the DSC 7 was calibrated with indium standard. Data acquisition and processing is done with PerkinElmer's Pyris software.

Results and discussion

Determination of solid-liquid phase diagrams (SLPD)

The heat and temperature of melting corresponding to the pure products are globally in fair agreement with literature data [14–16]. Physical properties of pure compounds are given in Table 1. The DSC curves as shown in the case of 4,4'diaminodiphenylmethane (1)+naphthalene (2) System (Fig. 1) illustrate that all the endothermic transitions are reversible. A typical DSC curves obtained are shown in Figs 2–3. The (biphenyl+4,4'diaminodiphenylmethane) and (naphthalene+4,4'diaminodiphenylmethane) mixtures are eutectic because the first peak appeared at the constant temperature. The area of the eutectic peak in a DSC curve is affected by the amount of the sample

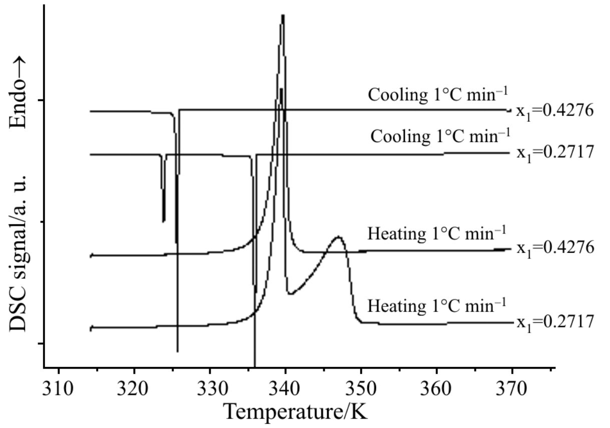

Fig. 1 Reversibility of the transitions evidenced by DSC for the 4,4'diaminodiphenylmethane (1)+naphthalene (2) mixture

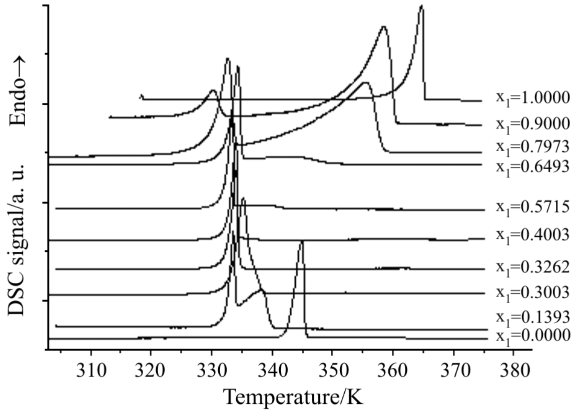

Fig. 2 DSC curves at different compositions for 4,4'diaminodiphenylmethane (1)+biphenyl (2) mixture

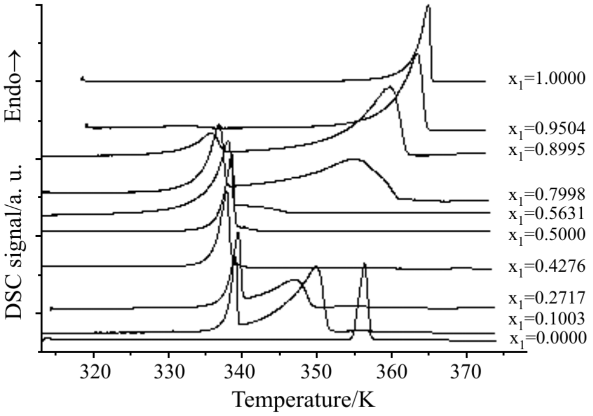

Fig. 3 DSC curves at different compositions for 4,4'diaminodiphenylmethane (1)+naphthalene (2) mixture

and heat of fusion of the melting component. Tables 2–4 list the experimental solid–liquid equilibrium temperatures for the different systems.

Table 1 Thermodynamic properties of pure compounds: T_m, melting point; ΔH_m, molar heat of fusion

Compound	T_m/K	ΔH_m/kJ mol^{-1}
4,4'diaminodiphenylmethane	362.69^a	19.69^a
Biphenyl	342.37^a 344.34^b	19.70^a 19.27^b
Naphthalene	354.69^a 353.30^c 353.40^d	19.55^a 18.78^c 18.24^d

^{a}This work; ^{b}Ref. [14]; ^{c}Ref. [15]; ^{d}Ref. [16]

Table 2 Experimental solid–liquid equilibrium temperatures for the system 4,4'diaminodiphenylmethane (1)+ biphenyl (2)

x_1	$T_{m(1)}$/K	$T_{m(2)}$/K
0.0000	342.37	
0.0203	340.92	
0.0340	339.68	
0.0495	338.43	
0.0691	337.61	
0.1000	336.33	
0.1393	334.86	
0.1906	333.77	
0.2506	332.45	
0.3262*	331.19*	
0.4003		332.11
0.4486		333.58
0.4988		334.67
0.5715		336.33
0.6103		337.80
0.6493		339.54
0.7381		342.69
0.7973		345.32
0.8217		346.44
0.9000		351.64
0.9387		355.39
1.0000		362.69

*corresponding to the eutectic point

Prediction of SLE

SLE data can be used to calculate activity coefficients of the mixture components. In the case of the systems studied, the components are not miscible in the solid phase and all diagrams present a simple eutectic. Therefore, the activity coefficient γ_i of the component i, in the liquid phase can be calculated according to the following expression [17, 18]:

$$\ln x_{\mathrm{i}}\gamma_{\mathrm{i}} = -\frac{\Delta H_{\mathrm{m,i}}}{RT}\left[1-\frac{T}{T_{\mathrm{m,i}}}\right] + \frac{\Delta C_{\mathrm{p,i}}}{R}\left[\ln\frac{T}{T_{\mathrm{m,i}}}+\frac{T_{\mathrm{m,i}}}{T}-1\right]-\frac{\Delta H_{\mathrm{tr,i}}}{RT}\left(1-\frac{T}{T_{\mathrm{tr,i}}}\right) \qquad (1)$$

where, $\Delta H_{\mathrm{m,i}}$, $T_{\mathrm{m,i}}$, $\Delta C_{\mathrm{p,i}}$, $\Delta H_{\mathrm{tr,i}}$ and $T_{\mathrm{tr,i}}$ are respectively the molar enthalpy of melting, the melting temperature, the molar heat capacity change (assumed to be independent of T) during the melting process, the enthalpy change corresponding to the transition and the transition temperature of the pure component *i*. Because of the lack of appropriate data representing $\Delta C_{\mathrm{p,i}}$, the related terms in Eq. (1) was neglected. The required physical constants of the pure compounds are collected in Table 1.

The modified UNIFAC, Larsen *et al.*, and Gmehling were used for the calculation of the activity coefficients and prediction of SLE. Values of the required geometrical and interaction parameters of our systems have been given elsewhere [11–12].

Table 3 Experimental solid–liquid equilibrium temperatures for the system 4.4’diaminodiphenylmethane(1)+ naphthalene(2)

x_1	$T_{\mathrm{m(1)}}$/K	$T_{\mathrm{m(2)}}$/K
0.0000	354.95	
0.0099	353.40	
0.0250	350.81	
0.0408	348.06	
0.0837	345.17	
0.1003	343.43	
0.2324	341.05	
0.2717	339.52	
0.2963	339.21	
0.3269	338.83	
0.3572	338.38	
0.4276^*	337.67^*	
0.5000		339.06
0.5631		340.36
0.5952		341.20
0.6741		343.86
0.7523		346.92
0.7998		347.61
0.8122		348.98
0.8702		351.95
0.8995		352.86
0.9298		355.08
0.9504		358.13
0.9765		360.35
1.0000		362.69

*corresponding to the eutectic point

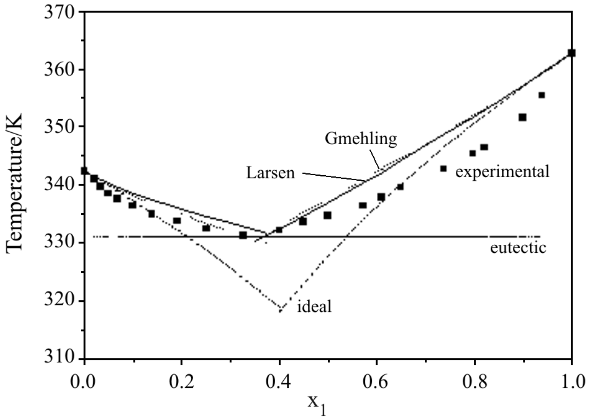

Fig. 4 Determined and calculated SLE for 4,4’diamino-diphenylmethane (1)+biphenyl (2) mixture

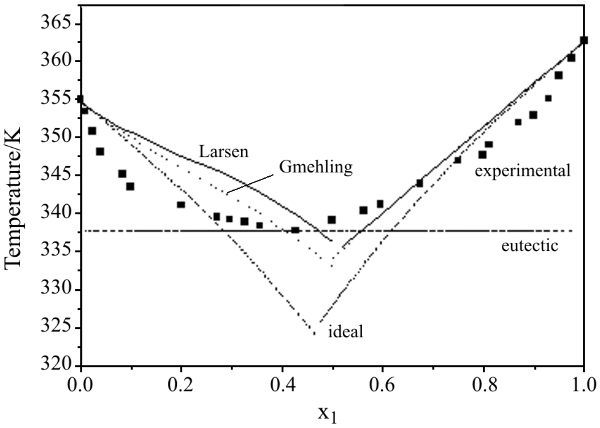

Fig. 5 Determined and calculated SLE for 4,4’diamino-diphenylmethane (1)+naphthalene (2) mixture

In the modified UNIFAC (Larsen version), the subgroups ACH and AC are used for description of the polyaromatics. For 4,4’diaminodiphenylmethane, the subgroups are ACH, AC, CH_2 and ANH_2. The structural subgroups in the modified UNIFAC (Gmehling version) are also ACH and AC for polyaromatics, but for 4,4’diaminodiphenylmethane, the used groups are ACH, AC, CH_2 and $ACNH_2$.

A graphical comparison between calculated SLE phase diagrams and experimental data is shown in Figs 4–5. For the binary polyaromatic –4,4’diaminodiphenylmethane mixtures higher SLE temperatures are recorded for modified UNIFAC (Larsen and Gmehling versions) and, in consequence, $\gamma_{\mathrm{theo}}>\gamma_{\mathrm{exp}}$, as illustrated by Figs 6–7. As shown in Table 4, the experimental values of T_{eu} and $x_{1\mathrm{eu}}$ corresponding to the eutectic points are close to those predicted by the different models. Table 5 lists the relative standard σ and the absolute mean Δ deviations of the equilibrium temperatures defined by:

Table 4 Comparison of experimental coordinates of eutectic points: T_{eu}/K and mole fraction, x_{1eu} with values calculated by UNIFAC (Larsen and Gmehling versions) and ideal models

System	T_{eu}/K		x_{1eu}	
	Exp.	Cal.	Exp.	Cal.
4,4’diaminodiphenylmethane (1)				
+biphenyl (2)	331.19	331.48[a] 330.55[b] 318.48[c]	0.3262	0.3742[a] 0.3576[b] 0.4047[c]
naphtalene (2)	337.67	335.49[a] 333.47[b] 324.65[c]	0.4276	0.5199[a] 0.4894[b] 0.4589[c]

[a]Calculated by UNIFAC (Larsen version); [b]Calculated by UNIFAC (Gmehling version); [c]Calculated (ideal model)

Table 5 Values of the relative standard deviations σ (Eq. (2)), and of absolute mean deviations Δ (Eq. (3)), of equilibrium temperatures obtained using modified UNIFAC and ideal models, N is the number of data points

System	N	Larsen		Gmehling		Ideal	
		Δ(K)	σ	(K)	σ	Δ(K)	σ
4,4’diaminodiphenylmethane+biphenyl	22	2.87	0.0103	2.81	0.0105	3.11	0.0134
4,4’diaminodiphenylmethane+naphthalene	25	3.22	0.0102	2.76	0.0084	3.24	0.0111

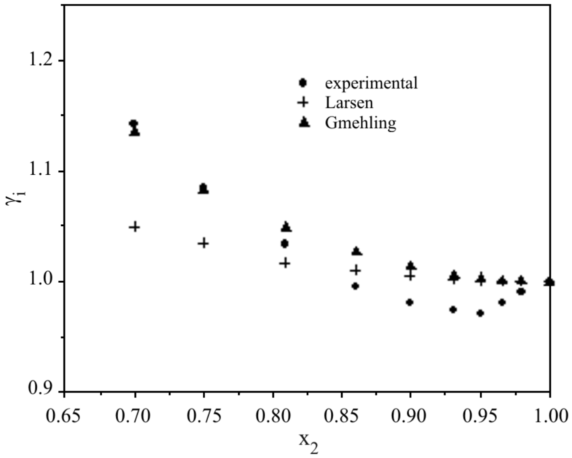

Fig. 6 Experimental and predicted activity coefficient, γ_i, *vs.* x_2 for 4,4’diaminodiphenylmethane (1)+biphenyl (2) mixture

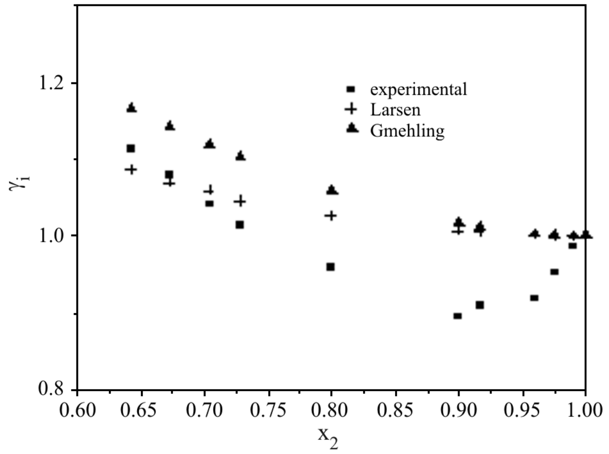

Fig. 7 Experimental and predicted activity coefficient, γ_i, *vs.* x_2 for 4,4’diaminodiphenylmethane (1)+naphthalene (2) mixture

$$\sigma=\left[\frac{1}{N}\sum_{\mathrm{i}=1}^{\mathrm{N}}\left(\frac{T_{\mathrm{ical}}-T_{\mathrm{iexp}}}{T_{\mathrm{iexp}}}\right)^{2}\right]^{1/2} \tag{2}$$

$$\Delta(K)=\frac{1}{N}\sum_{\mathrm{i}=1}^{\mathrm{N}}\left|T_{\mathrm{ical}}-T_{\mathrm{iexp}}\right| \tag{3}$$

where N stands for the number of data points of each system.

Theoretical phase diagrams for the SLE investigated in this work are characterized by positive deviations from Raoult’s law. An opposite behaviour is generally observed for experimental SLE. These deviations can be attributed to the hydrogen bonding between an amine and aromatic electrons and possible interactions between non bonding electron from N and an aromatic system.

Conclusions

The results confirm that the application of DSC method is effective in the study of solid-liquid equilibrium. The survey evidences the eutectic character of binary 4,4’diaminodiphenylmethane–polyaromatic systems and allows location of the eutectic point composition.

DSC illustrated that 4,4’diaminodiphenylmethane+biphenyl and 4,4’diaminodiphenylmethane+naphthalene mixtures form single eutectics corresponding respectively for diamine compositions: x_{eu}=0.3262, x_{eu}=0.4276 and temperatures T_{eu}=331.19 and 337.67 K.

Deviations were recorded between the values of the activity coefficients and diagrams given by the UNIFAC model and those resulting from the experiment. This can be explained by the weakness of group contribution model, in the description of complex systems like polyaromatics+diamine mixtures.

The presence of intermolecular effects, especially of the proximity effect which is more important in the presence of naphthalene, renders the widely used empirical methods quite inaccurate. This effect as cited in the literature [19–23] has a strong influence on the interaction parameters for polyfunctional molecules. It is obvious that in this case the assumption that the interactions are not influenced by the relative position of the groups and by the presence of a second group is not more valid.

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DOI: 10.1007/s10973-005-7167-9