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(Solid + liquid) equilibria of (phenanthrene + dichlorobenzenes)

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ABSTRACT

(Solid + liquid) equilibria (SLE) have been measured for phenanthrene + *o*-dichlorobenzene, phenanthrene + *m*-dichlorobenzene and phenanthrene + *p*-dichlorobenzene using differential scanning calorimetry (DSC) over the whole concentration range. It was found that all systems are simple eutectic systems. The eutectic point of (phenanthrene + *o*-dichlorobenzene) mixture is at −25.0 °C and 0.0767 mole fraction of phenanthrene, (phenanthrene + *m*-dichlorobenzene) mixture at −28.0 °C and 0.0530 mole fraction of phenanthrene and (phenanthrene + *p*-dichlorobenzene) mixture at 33.6 °C and 0.3060 mole fraction of phenanthrene. Furthermore, the activity coefficients of components in binary mixtures have been correlated by the Scatchard–Hildebrand expression with one adjustable parameter. This approach offers a useful procedure for estimating with good accuracy.

1. Introduction

The number of organic materials that is 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. The (solid + liquid) equilibrium (SLE) measurements of polycyclic aromatic hydrocarbon compounds with organic solvents provide the base data and academic foundation to crystallization processes and industrial magnification. On the other hand, the continued development of solution models for describing the thermodynamic properties of binary mixtures requires a large database to be available for assessing the applications and limitations of established expressions. Currently, only a little accumulation of these data exists for SLE of polycyclic aromatic hydrocarbon compounds in non-electrolyte solution [1–3]. For this reason, SLE have been measured for phenanthrene + dichlorobenzene isomers.

Various methods have been proposed to measure solid–liquid equilibria [4,5]. Classically, SLE is often determined by sampling saturated solutions and analyzing samples by spectroscopy or gas or liquid chromatography. Sample detection often requires a separation step and the presence of chromophores for detection. Errors can occur in sampling, particularly in systems with finely dispersed solute particles with little density difference between solid and liquid phases. Recently, methods of using output data of differential scanning calorimetry (DSC) are suggested. Of the methods of measuring SLE, it was shown that DSC is a rapid and sensitive technique, broadly used for determining the phase boundaries through the measurement of heat effect during the phase transformation process [6–8].

In this work, a complete data obtained by DSC of (solid + liquid) equilibria for (phenanthrene + *o*-dichlorobenzene), (phenanthrene + *m*-dichlorobenzene) and (phenanthrene + *p*-dichlorobenzene). Furthermore, the activity coefficients of components in (phenanthrene + dichlorobenzene) mixtures have been correlated by the Scatchard–Hildebrand solubility parameter expression to investigate the performance of this model for predicting SLE of phenanthrene with *o*-, *m*-, *p*-isomeric compounds, respectively. The results of an investigation of the (solid + liquid) phase diagram involving model compound of phenanthrene presented in this paper is also a continuation of the systematic study on solid–liquid equilibria of polycyclic aromatic hydrocarbon mixtures [9,10].

2. Experimental procedures

2.1. Materials

Phenanthrene was purchased from Alfa Aeasar with a molar purity greater than 99%. All other chemicals of *o*-dichlorobenzene, *m*-dichlorobenzene and *p*-dichlorobenzene were supplied by Tianjin Kewei Chemical Reagent Co., all of them were analytical reagent

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Table 1
Physical constants of pure compounds.

Compounds	T_m (°C)		H_m (J mol^{-1})		v (cm^3 mol^{-1}) [11]	δ (J$^{1/2}$ cm$^{-3/2}$) [12]
	Experimental[a]	Literature [11]	Experimental[a]	Literature [11]		
Phenanthrene	98.9	99.24	16,685	16,460	158.0 [10]	20.0
o-Dichlorobenzene	−17.3	−17.0	13,094	12,400	97.25 (20 °C)	20.5
m-Dichlorobenzene	−24.9	−24.8	12,510	12,600	98.57 (20 °C)	20.0
p-Dichlorobenzene	53.0	53.09	18,082	18,190	101.8 (55 °C)	19.8

[a] Our experimental values.

grade with purity higher than 99.5%. Their melting temperatures and enthalpies of fusion were measured using DSC (Metter DSC30). The melting points of the pure samples were in close agreement with literature data and no further purification was made. Properties of pure compounds are listed in Table 1.

2.2. Equipment

The calorimetry experiments were performed on a Metter DSC30 differential scanning calorimeter equipped with sample and reference standard aluminium crucibles, each with a capacity of 40 μl. During the scanning operation, high purity nitrogen gas was purged through the DSC chamber at 50 ml min^{-1}. The measurements were carried under fixed conditions of constant heating rate of 1 K min^{-1}. This scanning rate is low enough to approach the equilibrium measurement conditions. Before the analysis, the heat flow was calibrated using the heat of fusion of an exactly known quantity of indium; Temperature measurement with the Pt100 sensor was calibrated using a pan containing an exactly known quantity of indium as well as lead and zinc in separate compartments. The uncertainties of the measurements are estimated to be ±0.2 °C for the temperature and ±0.40 kJ mol^{-1} for the heats of fusion and phase transition.

2.3. Sample preparation

The sample was heated very slowly inside a glass tube at near the melting temperature of the major component. The liquefied sample with continuous stirring was solidified. Then a small amount of solid about 5 mg was taken and sealed in a Mettler sample crucible for the analysis.

2.4. SLE measurement

As described in detail previously [13], we adopted the method in which a liquidus and a solidus curves were estimated from the onset and peak temperatures obtained from the measured DSC curves. Fig. 1 shows a typical DSC curve of a eutectic mixture. The onset temperatures at each first peak almost show constant value for the eutectic temperature. The next peak temperatures were solidus temperature. This SLE measurement method was verified by comparing our results to published SLE data for (naphthalene + phenol). Fig. 2 shows that the results are in good agreement with literature data.

3. Results and discussion

3.1. Determination of solid–liquid phase diagrams

The equilibrium temperatures for varying mole fractions of phenanthrene with *o*-dichlorobenzene, *m*-dichlorobenzene and *p*-dichlorobenzene, respectively, are listed in Tables 2–4 and shown graphically in Figs. 3–5.

It was found that all systems are simple eutectic systems. The eutectic point of (phenanthrene + *o*-dichlorobenzene) mixture is at −25.0 °C and 0.0767 mole fraction of phenanthrene, (phenanthrene + *m*-dichlorobenzene) mixture at −28.0 °C and 0.0530 mole fraction of phenanthrene and (phenanthrene + *p*-dichlorobenzene) mixture at 33.6 °C and 0.3060 mole fraction of phenanthrene.

3.2. The equations for prediction of SLE

The equation of the solid-equilibrium curve of a pure solid component *i* including two first-order transitions is, for temperature

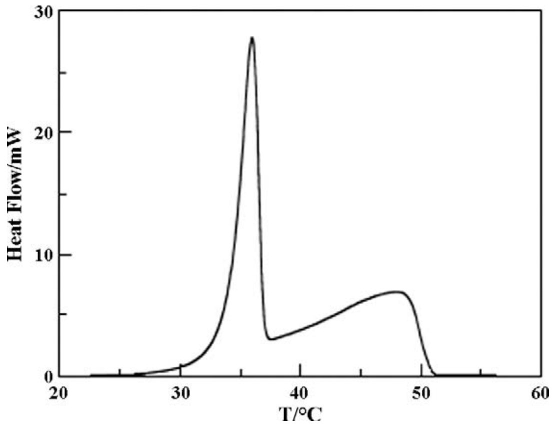

Fig. 1. A typical DSC curve exhibiting isothermal eutectic and solid–liquid transition peaks.

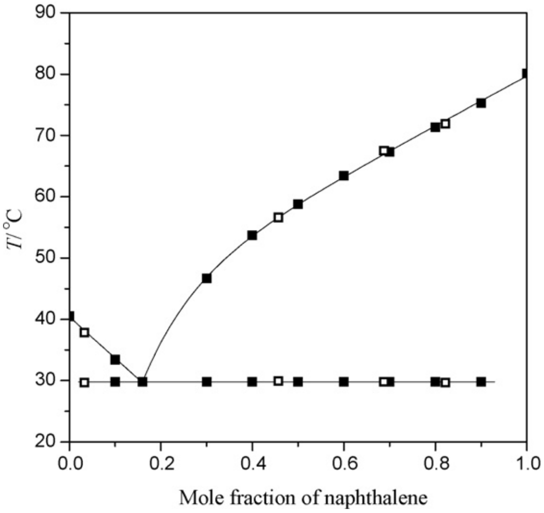

Fig. 2. Method validation, SLE phase diagram of (naphthalene + phenol): (□) SLE data measured by DSC; (■) literature data from reference [14].

Table 2
Measured solid–liquid equilibrium data for the system {phenanthrene (1) + *o*-dichlorobenzene (2)}.

x_1	T_E (°C)	T (°C)
1.0000		98.9
0.9511	−25.0	95.7
0.9242	−25.0	93.9
0.8800	−25.0	90.9
0.8279	−25.0	87.0
0.8010	−25.0	84.1
0.7605	−25.0	81.0
0.6968	−25.0	75.8
0.6241	−25.0	69.5
0.5579	−25.0	62.0
0.5062	−25.0	57.0
0.4690	−25.0	51.8
0.4311	−25.0	48.0
0.3752	−25.0	40.0
0.3403	−25.0	34.3
0.3118	−25.0	29.2
0.2719	−25.0	23.5
0.2382	−25.0	15.5
0.1913	−25.0	6.1
0.1506	−25.0	−4.1
0.1200	−25.0	−13.5
0.0000		−17.3

Table 4
Measured solid–liquid equilibrium data for the system {phenanthrene (1) + *p*-dichlorobenzene (2)}.

x_1	T_E (°C)	T (°C)
1.0000		98.9
0.9571	33.6	96.0
0.9255	33.6	93.8
0.9090	33.6	92.5
0.8374	33.6	86.7
0.8163	33.6	85.5
0.7458	33.6	79.8
0.7182	33.6	77.5
0.7023	33.6	76.8
0.6380	33.6	70.5
0.5590	33.6	62.9
0.5111	33.6	57.9
0.4464	33.6	50.6
0.4092	33.6	46.4
0.3583	33.6	40.3
0.3444	33.6	38.5
0.3060	33.6	33.6
0.1948	33.6	42.9
0.1518	33.6	45.0
0.1057	33.6	47.5
0.0518	33.6	50.1
0.0000		53.0

below that of phase transition [15],

$$\ln(\gamma_i x_i) = \frac{H_{m,i}}{RT}\left(\frac{T}{T_{m,i}} - 1\right) - \frac{\Delta c_{p,i}}{R}\left(\ln\frac{T_{m,i}}{T} - \frac{T_{m,i}}{T} + 1\right) \tag{1}$$

where x_i is the mole fraction and γ_i the activity coefficient of component i in the mixture at temperature T. $T_{m,i}$, $H_{m,i}$ and $\Delta c_{p,i}$, respectively, are the melting temperature in K, the molar enthalpy of melting in J mol^{-1} and the difference between the molar heat capacity of the component i in the solid and liquid states in J K^{-1} mol^{-1}.

In addition, in Eq. (1), the last term in the right-hand side containing Δc_p term almost cancel each other and of less importance than the remaining term. Therefore, a simplified form of this equation can be used:

$$\ln(\gamma_i x_i) = \frac{H_{m,i}}{RT}\left(\frac{T}{T_{m,i}} - 1\right) \tag{2}$$

Table 3
Measured solid–liquid equilibrium data for the system {phenanthrene (1) + *m*-dichlorobenzene (2)}.

x_1	T_E (°C)	T (°C)
1.0000		98.9
0.9600	−28.0	96.3
0.9082	−28.0	92.9
0.8548	−28.0	89.1
0.7878	−28.0	84.1
0.7452	−28.0	80.5
0.6981	−28.0	76.7
0.6620	−28.0	73.5
0.6010	−28.0	67.8
0.5443	−28.0	62.2
0.4912	−28.0	56.6
0.4576	−28.0	52.6
0.4102	−28.0	47.1
0.3543	−28.0	40.0
0.3031	−28.0	31.9
0.2678	−28.0	26.1
0.2188	−28.0	17.5
0.1612	−28.0	5.0
0.1151	−28.0	−7.0
0.0812	−28.0	−18.1
0.0000		−24.9

Predicting the liquidus line can be made easier by assuming that the system is eutectic. This is because the only information needed is the liquid non-ideality and the pure component properties.

In this study, the correlation equation in terms of Scatchard–Hildebrand theory [15] was applied to represent the activity coefficients of the components. When the non-ideality arises strictly from differential cohesiveness, the Scatchard–Hildebrand regular solution model

$$\ln\ \gamma_1 = v_1\phi_2^2(\delta_1 - \delta_2)^2/RT \quad \text{and} \quad \phi_2 = x_2v_2/(x_1v_1 + x_2v_2) \tag{3}$$

$$\ln\ \gamma_2 = v_2\phi_1^2(\delta_1 - \delta_2)^2/RT \quad \text{and} \quad \phi_1 = x_1v_1/(x_1v_1 + x_2v_2) \tag{4}$$

predicts the activity coefficients. The activity coefficient in the binary system can be calculated at any composition and temperature by implementing only solubility parameters δ_i and molar liquid volume v_i for the pure components. The solubility parameters δ_1 and δ_2 are the square root of the cohesive-energy densities. ϕ_1 and ϕ_2 designate volume fractions of components 1 and 2.

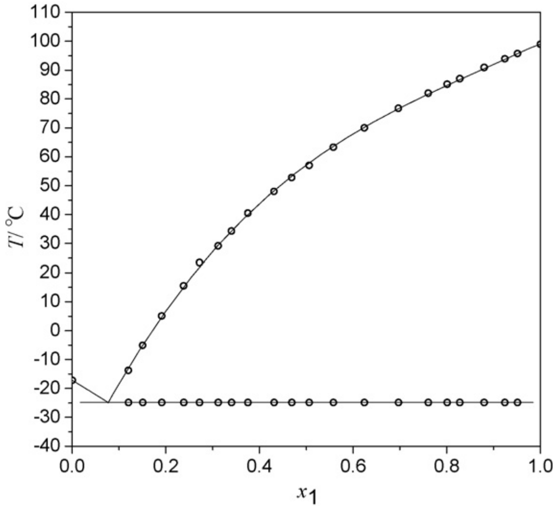

Fig. 3. Solid–liquid equilibrium diagram for {phenanthrene (1) + *o*-dichlorobenzene (2)} mixture: (○) our experimental data; (—) Scatchard–Hildebrand regular solution model predictions.

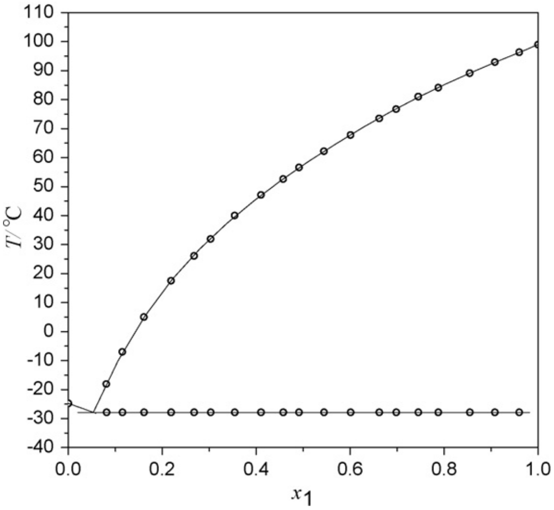

Fig. 4. Solid–liquid equilibrium diagram for {phenanthrene (1) + *m*-dichlorobenzene (2)} mixture: (○) our experimental data; (—) Scatchard–Hildebrand regular-solution model predictions.

For a mixture of hydrocarbons, the accuracy of prediction by the Scatchard–Hildebrand equation is improved if an adjustable binary parameter l_{12} is added to the equation, leading to the expression:

$$\ln\ \gamma_1 = v_1\phi_2^2 \left\lfloor (\delta_1-\delta_2)^2 + 2l_{12}\delta_1\delta_2 \right\rfloor /RT \tag{5}$$

$$\ln \gamma_2 = v_2\phi_1^2 \left\lfloor (\delta_1-\delta_2)^2 + 2l_{12}\delta_1\delta_2 \right\rfloor /RT \tag{6}$$

Eqs. (5) and (6), which are well known and their derivation process are omitted, show that the calculated activity coefficients are often sensitive to an adjustable constant l_{12}, although it is generally small compared with unity. As pointed out by author [16], for the aromatic hydrocarbon mixtures, even a small value of l_{12} can have a large effect on the predicted activity coefficient. For a special case $l_{12} = 0$, Eqs. (5) and (6) transform to Eqs. (4) and (5), respectively.

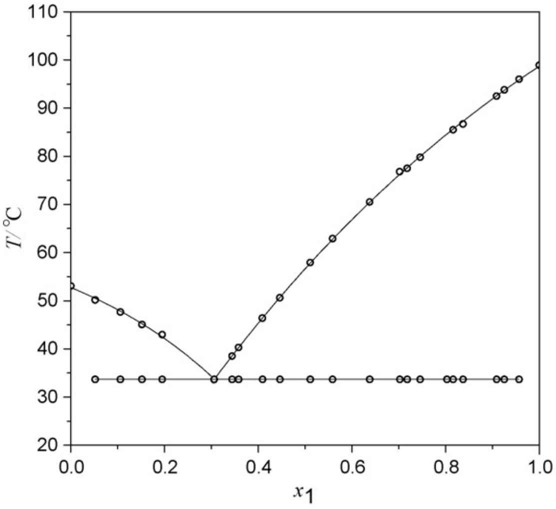

Fig. 5. Solid–liquid equilibrium diagram for {phenanthrene (1) + *p*-dichlorobenzene (2)} mixture: (○) our experimental data; (—) Scatchard–Hildebrand regular solution model predictions.

Table 5
Values of the root-mean-square deviations and of the absolute mean deviations obtained using Scatchard–Hildebrand regular-solution model.

System	n	l_{12}	σ	Δ
Phenanthrene (1) + *o*-dichlorobenzene (2)	22	−0.00472	0.80	0.61
Phenanthrene (1) + *m*-dichlorobenzene (2)	23	0.000698	0.64	0.49
Phenanthrene (1) + *p*-dichlorobenzene (2)	19	0.00124	0.29	0.19

3.3. Correlation of results based on Scatchard–Hildebrand regular-solution theory

The Scatchard–Hildebrand regular-solution model with binary parameter l_{12} (Eqs. (5) and (6)) was applied to forecast activity coefficient. It was reckoned for binary mixtures of (phenanthrene + *m*-dichlorobenzene) and (phenanthrene + *p*-dichlorobenzene) that non-miscibility in the solid phase. l_{12}-parameter was evaluated by minimizing the following objective function, F_{obj}, between the calculated and experimentally determined liquidus temperatures:

$$F_{\text{obj}} = \sum_{j=1}^{n} (T_{\text{cal},j} - T_{\text{exp},j})^2 \tag{7}$$

where the summation is over all jth data point. The molar liquid volumes and solubility parameters were directly taken from the literatures and listed in Table 1. The root-mean-square deviations on temperature are given by

$$\sigma = \left\{ \frac{1}{n-2} \sum_{j=1}^{n} (T_{\text{cal},j} - T_{\text{exp},j})^2 \right\}^{1/2} \tag{8}$$

and the absolute mean deviations are given by

$$\Delta = \frac{1}{n} \sum_{j=1}^{n} \left| T_{\text{cal},j} - T_{\text{exp},j} \right| \tag{9}$$

where n is the number of experimental points, and are reported in Table 5.

4. Conclusions

SLE for three binary mixtures of (phenanthrene + *o*-dichlorobenzene), (phenanthrene + *m*-dichlorobenzene) and (phenanthrene + *p*-dichlorobenzene) have been measured from the DSC experiments. It was shown that all systems are simple eutectic systems. The eutectic point of (phenanthrene + *o*-dichlorobenzene) mixture is at −25.0 °C and 0.0767 mole fraction of phenanthrene, (phenanthrene + *m*-dichlorobenzene) mixture at −28.0 °C and 0.0530 mole fraction of phenanthrene and (phenanthrene + *p*-dichlorobenzene) mixture at 33.6 °C and 0.3060 mole fraction of phenanthrene.

Relatively simple mathematical model, the Scatchard–Hildebrand regular-solution model, was used to present the SLE temperature of the binary systems of phenanthrene + *m*-dichlorobenzene and *p*-dichlorobenzene. It was demonstrated that the regular solution model using only one adjustable binary parameter can be predicted with good accuracy. The root-mean-square deviations on temperature were less than 0.8 °C.

List of symbols

Δc_p	capacity (J mol^{-1} K^{-1})
H_m	enthalpy of fusion at temperature T_m (J mol^{-1})
l_{12}	binary parameters used in Eqs. (5) and (6)
n	number of experimental data
R	gas constant, 8.314 J mol^{-1} K^{-1}

T	Temperature (K)
T_m	normal melting temperature (K)
v	molar volume ($\mathrm{cm}^3\ \mathrm{mol}^{-1}$)
x	mole fraction in the solution

Greek letters

γ	activity coefficient
δ	solubility parameter ($\mathrm{J}^{1/2}\ \mathrm{cm}^{-3/2}$)
Δ	absolute mean deviation
σ	root-mean-square deviation
ϕ	molar volume fraction

Subscripts

i	component
cal	calculated value
E	eutectic
exp	experimental data

References

[1] W.E. Acree Jr., Polycyclic aromatic hydrocarbons in pure and binary solvents, IUPAC Solubility Data Series, vol. 54, Oxford, 1994.

[2] W.E. Acree Jr., Polycyclic aromatic hydrocarbons: binary nonaqueous systems: Part 1 (solutes A–E), IUPAC Solubility Data Series, vol. 58, Oxford, 1995.

[3] W.E. Acree Jr., Polycyclic aromatic hydrocarbons: binary nonaqueous systems: Part 2 (solutes F–Z). IUPAC Solubility Data Series, vol. 59, Oxford, 1995.

[4] J. Nyvlt, Solid–liquid Phase Equilibria, Elsevier, Amsterdam, 1977.

[5] M. Matsuoka, N. Kanekuni, H. Tanaka, J. Cryst. Growth 73 (1985) 563–570.

[6] D. Dalmazzone, M. Kharrat, V. Lachet, B. Fouconnier, D. Clausse, J. Therm. Anal. Catal. 70 (2002) 493–505.

[7] C.C. Huang, Y.Y. Chen, Chem. Eng. Sci. 55 (2000) 3175–3185.

[8] A. Hammami, A.K. Mehrotra, Thermochim. Acta 211 (1992) 137–153.

[9] A. Gupta, S. Gupta, F.R. Groves Jr., E. McLaughlin, Fluid Phase Equilibria 64 (1991) 201–211.

[10] P.B. Choi, E. McLaughlin, AIChE J. 29 (1983) 150–153.

[11] D.R. Lide, CRC Handbook of Chemistry and Physics, 83rd edition, CRC Press LLC, New York, 2002–2003.

[12] Allan F.M. Barton, CRC Handbook of Solubility Parameters and Other Cohesion Parameters, 2nd edition, CRC Press, 1991.

[13] D.W. Wei, H.X. Jiang, J.T. Yuan, X. Jing, J. Chem. Ind. Eng. (China) 54 (2003) 1459–1462.

[14] J. Timmermans, Physico-chemical Constants of Binary System, Interscience Publish Inc., New York, 1960.

[15] J.M. Prausnitz, R.N. Lichtenthaler, E. Gomes de Azevedo, Molecular Thermodynamics of Fluid-Phase Equilibria, 3rd edition, Prentice-Hall, New York, 1999.

[16] E.W. Funk, J.M. Prausnitz, Ind. Eng. Chem. 62 (1970) 8–15.