Effect of a Phase Transition on the Solubility of a Solid

Theoretical investigation shows that a transition in the solid state from form I to form II affects the solubility of a solid in a liquid. Experimental results for the solubility of phenanthrene in pyridine, which has a lambda-point transition between 331 and 361 K, conform generally to the theoretical predictions.

P. B. CHOI and EDWARD MCLAUGHLIN

Department of Chemical Engineering
Louisiana State University
Baton Rouge, LA 70803

SCOPE

The solubility of solids in liquids, in the absence of a phase transition, has been thoroughly investigated. In the cases where a solid-phase transition takes place, the solubility equation for temperatures below the transition point must include terms for the effect of the phase transition. An equation is derived in this paper for a lambda point transition. As phenanthrene undergoes a lambda point transition from around 331 to 361 K, the solubility of phenanthrene in a solvent in which it exhibits close to ideal behavior, such as pyridine, can be used to verify the equations derived by theory. The solubility data curve yields three distinct regions, a straight-line portion for temperatures below the beginning of the phase transition, a transient portion during the lambda transition, and a straight-line portion at temperatures above the end of the phase transition. The solubility of phenanthrene in pyridine is predicted by the equations using the Scatchard-Hildebrand regular solution theory for the estimation of the activity coefficient of the solute in the liquid. The predicted solubility is compared with the experimental solubility data for confirmation of the equations.

CONCLUSION AND SIGNIFICANCE

The solubility of phenanthrene predicted by equations which take into account the existence of a phase transition in the solid phase agree with the experimental solubility data with an average deviation of 0.8%, provided that the activity coefficients of the solid are estimated by the Scatchard-Hildebrand regular solution theory. This close agreement suggests that the solubility equations given in this paper properly represent the solubility of solids at temperatures below the end of a lambda point transition.

THEORY

The solubility of solids in liquids is given by (for example, Prausnitz) Eq. 1 in terms of the mole fraction of solute X_2:

$$-\ln X_2 = \frac{\Delta s_2^f}{R}\left(\frac{T_m}{T}-1\right) - \frac{\Delta C_p}{R}\left(\frac{T_m}{T}-1\right) + \frac{\Delta C_p}{R}\ln\frac{T_m}{T} + \ln\gamma_2 \quad (1)$$

on assuming that no phase transition in the solid phase takes place from the system temperature T to the melting point T_m. When a solid undergoes a first-order phase transition, the solubility equation below the temperature of phase transition T_p must include a term for the contribution of the transition as given, for example, by Weimer and Prausnitz.

$$-\ln X_2 = \frac{\Delta s_2^f}{R}\left(\frac{T_m}{T}-1\right) + \frac{\Delta s_2^p}{R}\left(\frac{T_p}{T}-1\right) - \frac{\Delta C_p}{R}\left(\frac{T_m}{T}-1\right) + \frac{\Delta C_p}{R}\ln\frac{T_m}{T} + \ln\gamma_2 \quad \text{for } T \leqq T_p \quad (2)$$

Transitions in the solid phase below the melting point are of the lambda type rather than first order; thus, the appropriate equation for a lambda-type transition is obtained and its verification made by experimental measurement of the solubility phenanthrene in pyridine which has such a transition. Figure 1 shows schematically the enthalpy-temperature changes for a solid in state 1 going to a subcooled liquid in state 4 and includes the existence of a lambda-point transition in the solid phase. The change of Gibb's free energy from states 1 to 4 can be obtained from Eq. 3:

$$\Delta g_{2\ 1\to4} = \Delta h_{2\ 1\to4} - T\Delta s_{2\ 1\to4} \quad (3)$$

where the total change of enthalpy Δh_2 and entropy Δs_2 must include those for the phase transition.

In that case, Δh_2 and Δs_2 become

$$\Delta h_{2\ 1\to4} = \Delta h_{2\ 1\to5} + \Delta h_{2\ 5\to6} + \Delta h_{2\ 6\to2} + \Delta h_{2\ 2\to3} + \Delta h_{2\ 3\to4} = \int_T^{T_p} C_{ps}^I dT + \int_{T_p}^{T_t} C_{pS}^{II} + \int_{T_t}^{T} C_{pl}dT + \int_{T_a}^{T_b} C_p dT + \Delta h_2^f \quad (4)$$

$$\Delta s_{2\ 1\to4} = \Delta s_{2\ 1\to5} + \Delta s_{2\ 5\to6} + \Delta s_{2\ 6\to2} + \Delta s_{2\ 2\to3} + \Delta s_{2\ 3\to4} = \int_T^{T_p} \frac{C_{pS}^I}{T}dT + \int_{T_p}^{T_t} \frac{C_{pS}^{II}}{T}dT + \int_{T_t}^{T} \frac{C_p^l}{T}dT + \int_{T_a}^{T_b} \frac{C_p}{T}dT + \Delta s_2^f \quad (5)$$

where C_{pS}^I and C_{pS}^{II} are the specific heats per mole of solid phases I and II, respectively. If we assume that $C_{pS}^I = C_{pS}^{II} = C_{pS}$ and that $\Delta C_p = C_{pl} - C_{pB} = C_{pl} - C_{pS}$ then

$$\Delta h_{2\ 1\to4} = \int_{T_a}^{T_b} (C_p - C_{pB})dT + \Delta h_2^f + \int_{T_t}^{T} \Delta C_p dT \quad (6)$$

and

$$\Delta s_{2\ 1\to4} = \int_{T_a}^{T_b} \frac{(C_p - C_{pB})dT}{T} + \Delta s_2^f + \int_{T_t}^{T} \frac{\Delta C_p}{T}dT \quad (7)$$

where C_{pB} is the base line of the specific heat during the phase transition. The change of Gibb's free energy, on the other hand,

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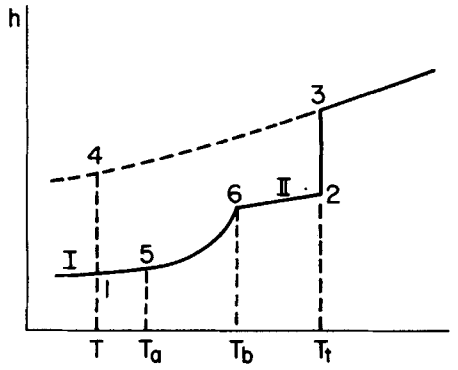

Figure 1. Enthalpy-temperature diagram for a lambda point transition.

is related to the composition and the activity coefficient by the relations

$$\Delta g_2 = \mu_2^{ol} - \mu_2^S \tag{8}$$

$$= RT \ln \left(\frac{f_2^{ol}}{f_2^S}\right) \tag{9}$$

$$= -RT \ln (X_2 \gamma_2) \tag{10}$$

Combining Eqs. 3, 6, 7 and 10 with the assumptions of $T_t \cong T_m$ and ΔC_p = constant leads to

$$-\ln X_2 = \frac{\Delta s_2^f}{R}\left(\frac{T_m}{T} - 1\right) - \frac{\Delta C_p}{R}\left(\frac{T_m}{T} - 1\right) + \frac{\Delta C_p}{R} \ln \frac{T_m}{T} + \ln \gamma_2 + \lambda \qquad \text{for } T \leqq T_a \tag{11}$$

In Eq. 11, the additional effect of the lambda point transition λ is given by

$$\lambda = \frac{1}{RT}\int_{T_a}^{T_b} (C_p - C_{pB}) dT - \frac{1}{R}\int_{T_a}^{T_b} \left(\frac{C_p - C_{pB}}{T}\right) dT \tag{12}$$

$$= \frac{\Delta h_2^g}{RT} - \frac{\Delta s_2^g}{R} \tag{13}$$

Obviously if $T_a \leqq T \leqq T_b$ then the lower limit of integration in Eq. 12 is replaced by T and Δh_2^g and Δs_2^g in Eq. 13, rather than being for the whole transition between T_a and T_b, are the portions between T and T_b. In addition when $T_a = T_b$, $\lambda = 0$ and Eq. 1 is recovered provided there is no discontinuity in the specific heat.

In summary, Eq. 2 represents the solubility of solids undergoing a first order transition at temperatures below T_p, and Eq. 1 represents the solubility at temperatures from T_p to T_t. For a lambda point transition, Eq. 11 represents the solubility of a solid at temperatures below the start of the phase transition and Eq. 1 represents the solubility at temperatures from the end of the phase transition to T_m. For the temperature interval between the beginning and end of a lambda point transition, the solubility of solids can be expressed by Eq. 11 by replacing T_a by T. In that case the term λ in the equation represents the overall effect of the phase transition on the solubility of the solid from the solution temperature T to the end of the phase transition T_b. Obviously in this region the nature of the transition between phases requires a continuous change rather than a discontinuity in the solubility curves.

PHYSICAL PROPERTIES OF PHENANTHRENE

To use Eq. 11 for the prediction of solubility, we must know the physical properties in the equation Δs_2^f, ΔC_p, C_p, C_{pB}, T_a, T_b and T_m and, in addition the activity coefficient of the solute γ_2. When the enthalpy and entropy data are available, Δh_2^g and Δs_2^g may be directly used as indicated by Eq. 13.

Phenanthrene undergoes a lambda point transition from around 331 to 361 K (Arndt and Damask, Casellato et al., and Finke et al.). The observed temperature and entropy of phase transition are

TABLE 1. TEMPERATURE, ENTHALPY AND ENTROPY CHANGES IN THE SOLID-PHASE TRANSITION FOR PHENANTHRENE

Literature Sources	T_p K	$\Delta h_2^g \times 10^{-3}$ J·mol^{-1}	Δs_2^g J·mol^{-1}·K^{-1}
Arndt et al.	331–361	1.591[a]	—
Casellato et al.	331–344	1.256	—
Finke et al.	347.5	1.307[b]	3.835[b]

[a] They obtained 1.424×10^3 J·mol^{-1} from another measurement.
[b] Calculated from the enthalpy, entropy and heat capacity data of Finke et al.

given in Table 1. The specific heat data of the solid taken by Finke et al. is plotted in Figure 2 as a function of temperature. The specific heat data at temperatures below 316 K and above 360 K are interpolated by a least squares fit and give an expression for the continuous base line as

$$C_{pB}/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = 44.38 + 0.434171\ T + 0.59352 \times 10^{-3}\ T^2 \tag{14}$$

Finke et al. reported 16.474×10^3 J·mol^{-1} for the heat of fusion of phenanthrene at its triple point of 372.4 K. From this data, one can obtain 44.255 J·mol^{-1}·K^{-1} for Δs_2^f if the difference between Δs_2^f at T_m and that at T_t is ignored. From their specific heat data, ΔC_p is evaluated to be 12.586 J·mol^{-1}·K^{-1} at T_t. T_a and T_b are found from Figure 2 to be 314.0 and 360.0 K, respectively. The observed melting temperature 372.8 K is used for T_m. Δh_2^g and Δs_2^g are calculated to be 1.307×10^3 J·mol^{-1} and 3.835 J·mol^{-1}·K^{-1}, respectively, by subtracting the integration of Eq. 14 from the enthalpy and entropy changes which are calculated from the data given by Finke et al. At $T < T_a$, Δh_2^g and Δs_2^g remain constant with the values given in Table 1. When $T_a < T < T_b$, Δh_2^g and Δs_2^g vary with the solution temperature T since they then represent the effect of the phase transition from T to T_b. For the activity coefficient we have found that the Scatchard-Hildebrand regular solution equation can be used successfully to predict the activity coefficients of aromatic hydrocarbons in simple solvents and so Eq. 15 can be used to determine γ_2

$$\ln \gamma_2 = \frac{v_2^l}{RT}\left(\frac{x_1 v_1^l}{x_1 v_1^l + x_2 v_2^l}\right)^2 (\delta_1 - \delta_2)^2 \tag{15}$$

where component 1 stands for pyridine and 2 for phenanthrene. v_1^l and δ_1 calculated at 298 K from the liquid density and enthalpy of vaporization data of pyridine given by Timmermans are 80.86 $\times 10^{-6}$ m^3·mol^{-1} and 2.167×10^4 (J/m^3)$^{1/2}$. v_2^l and δ_2 at 298 K are given by Hildebrand et al. to be 158×10^{-6} m^3·mol^{-1} and 2.005×10^4 (J/m^3)$^{1/2}$, respectively. Accordingly, the effect of a phase transition on the solubility of solids, as expressed by Eq. 11, can be checked by the solubility measurements of phenanthrene in a suitable solvent.

EXPERIMENTAL PROCEDURE

Phenanthrene purchased from Eastern Chemical Company, was purified by chromatography on activated alumina using toluene as eluant. It was

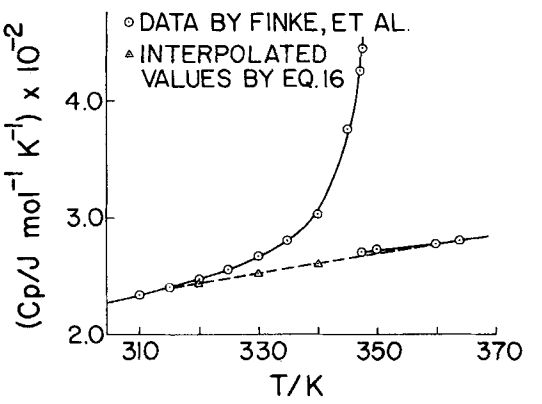

Figure 2. Specific heat of phenanthrene in solid phase (Finke et al.).

TABLE 2. SOLUBILITY OF PHENANTHRENE IN PYRIDINE

Temp. T/K	Mol Fraction of Phenanthrene by Experiment (X_2) Exp.	Mol Fraction of Phenanthrene Predicted (X_2) Pred.	Δ %
299.8	0.2459	0.2517	2.4
307.7	0.3011	0.3035	0.8
314.3	0.3513	0.3526	0.3
316.6	0.3690	0.3709	0.5
323.4	0.4283	0.4281	0.0
342.8	0.6170	0.6245	1.2
349.6	0.6961	0.7015	0.8
355.6	0.7651	0.7724	0.9
361.0	0.8349	0.8401	0.6
366.5	0.9111	0.9125	0.2

then recrystallized and toluene removed by evaporating in a vacuum. The recrystallized solid sample was analysed by a G.C. Mass Spectrometer. The purity was 98.67 wt % minimum (the observed melting point of the sample of the present study was 372.8 K while the triple point of the sample of Finke et al. was 372.4 K). The liquid samples were "gold label" quality Aldrich products and were used without further purification.

Solid-liquid mixtures of known composition were made up in glass ampoules, and the ampoules sealed off while frozen in dry ice and attached to a drying tube. They were then placed in a constant temperature bath, and the temperatures at which the last trace of solid disappeared were visually determined while the bath temperature was increased by 0.1 K every 1,200 seconds. At this time the ampoules were rotated at about 0.25 rps. The experimental system was similar to that of McLaughlin and Zainal.

DISCUSSION OF THE RESULTS

The solubility data for phenanthrene in pyridine were taken mainly in two temperature regions, one below the start of the phase transition and the other after it had ended. The data, given in Table 2, are plotted in Figure 3. The solubility plot produces two different lines, the equations for which are obtained by a least squares fit of the data. For the upper line

$$-lnX_2 = 2.0676 \times 10^3 \frac{1}{T} - 5.5487 \qquad (16)$$

and for the lower line

$$-lnX_2 = 2.3096 \times 10^3 \frac{1}{T} - 6.3020 \qquad (17)$$

From the plot, one can see that the solubility data at 323.4 K lies below the lower line. This means that the phase transition already has started and thus affects the solubility of phenanthrene at this temperature. This fact is also seen when we examine the specific heat curve in Figure 2. Bondi has suggested that the existence of a phase transition would produce a kink in the curve which is confirmed here.

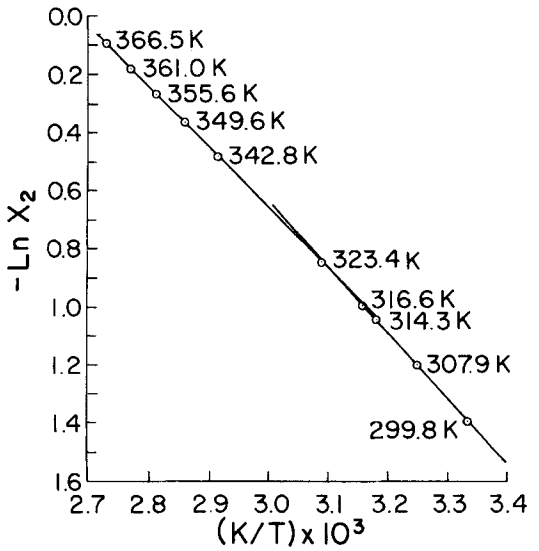

Figure 3. Solubility of phenanthrene in pyridine.

Using the physical constants of phenanthrene evaluated previously, x_2 is calculated by Eq. 11 at temperatures below T_b and by Eq. 1 at temperatures from T_b to T_m. The results are illustrated in Table 2, where the solubility of phenanthrene at temperatures below T_b is predicted by Eq. 11 with an average deviation of 0.8% for 6 data points. The solubility of the solid at temperatures between T_b and T_m is predicted by Eq. 1 with an average deviation of 0.6% for 4 data points. The deviation, in this case, is defined by

$$\Delta = \left| \frac{(X_2)\text{exp} - (X_2)\text{pred}}{(X_2)\text{exp}} \right| \times 100 \qquad (18)$$

This close agreement suggests that Eq. 11 properly represents the solubility of solids in liquids at temperatures during and below the solid phase transition.

NOTATION

ΔC_p = specific heat difference between the subcooled liquid and solid state
C_{pB} = base line of specific heat during lambda point transition
C_{pl} = specific heat of a subcooled liquid
C_{pS} = specific heat of a solid
f_2^{ol} = fugacity of a pure solute in its subcooled liquid state at the system temperature
f_2^S = fugacity of a pure solute at its solid state at system temperature
Δg_2 = change of the Gibb's free energy of component 2 between the subcooled liquid and solid states
Δh_2 = change of molar enthalpy of component 2
R = gas constant
Δs_2 = change of molar entropy of component 2
T = system temperature
T_a = temperature at which a lambda transition starts
T_b = temperature at which a lambda transition ends
T_m = melting temperature
T_p = temperature of a first order phase transition
T_t = triple point temperature
v_1^l = molar liquid volume of component 1
v_2^l = molar liquid volume of component 2
X = mole fraction

Greek Symbols

γ_2 = activity coefficient of component 2
δ_1 = solubility parameter of component 1
δ_2 = solubility parameter of component 2
μ_2^{ol} = chemical potential of component 2 at its subcooled liquid state
μ_2^s = chemical potential of component 2 at its solid state

Subscripts

f = fusion
p = phase transition
I = solid state I
II = solid state II
1 = solvent
2 = solute (solid)

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Manuscript received October 27, 1981; revision received March 29, and accepted April 19, 1982.

Avoiding Unwarranted Inflection Points in Fitting of Data

This paper presents a method for correlating univariable experimental data, which avoids unwarranted inflection points by means of mathematical constraints fitted to sections of the data. The method was applied successfully to correlate thermodynamic data which are otherwise difficult to fit in without inflection points.

YEHUDA TAITEL
School of Engineering
Tel-Aviv University
Tel-Aviv 69978, Israel

and

ABRAHAM TAMIR
Department of Chemical Engineering
Ben-Gurion University of the Negev
Beer-Sheva 84120, Israel

SCOPE

In the correlation of thermodynamic or other kinds of data, one usually strives to achieve simultaneously the following objectives: high accuracy and a minimal number of parameters in the series expansion. The latter is particularly important because, by increasing the number of parameters, inflection points tend to appear in unexpected locations due to mathematical reasons rather than physical. There are many physical cases, especially those of thermodynamic properties as a function of concentration, where functional dependence is known to be smooth and free of inflection points, either in the entire range or at several known sections. In such a case, correlation of empirical data that introduces false inflection points, caused by improper mathematical correlation or inaccurate noise bearing data, may cause serious distortion of the implied thermodynamic behavior. For example, when a search is made for azeotropic behavior of vapor pressure as a function of concentration, improper correlation may alter the implied azeotropic properties of such a system.

The available correlation methods (Landis and Nilson, 1962; Klaus and Van Ness 1967; Tamir, 1981) provide simplicity, interpolation ability, smoothness and low-ordered polynomials. However, no mathematical constraints were imposed in the process of fitting of the data so as to avoid the appearance of unwarranted inflection points. The object of this work is to establish a method which can avoid unwarranted inflection points. This is achieved by incorporating the method of "sectionwise fitting" while imposing the constraint that avoids inflection points. "Sectionwise fitting" is the term used for the method in which the entire range of data points is divided into sections which are correlated separately.

CONCLUSIONS AND SIGNIFICANCE

The principal significance of this work is the development of a method for correlating data by means of cubic polynomials with one independent variable, which incorporates mathematical constraints that would prevent the appearance of undesirable inflection points. In order to improve the goodness of fit, the method of "sectionwise fitting" is used.

The method has been applied successfully to vapor-liquid equilibrium data, which otherwise is difficult to correlate without inflection points. Correlation is obtained by minimizing the sum of the squares (S.O.S.) of deviations between the experimental points and the analytical representation, subject to constraint of continuity of the first derivative. The S.O.S. defines the loss function for inaccuracy; however, other loss functions may also be chosen, though the S.O.S. is the most common one. An additional constraint of smoothness of the second derivative can also be imposed. In spite of that, less accuracy is achieved by increasing the number of constraints, namely, the S.O.S. is increased.

This method is also useful for data exhibiting more than one extremum, for example, a binary mixture with two azeotropes or heat of mixing data with negative and positive values.

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