Correction in DTA purity determination

Xu-Wu An [a,1] and Raphaël Sabbah [b]

[a] *Institute of Chemistry, Academia Sinica, Beijing (People's Republic of China)*
[b] *Centre de Thermodynamique et de Microcalorimétrie (C.T.M.) du C.N.R.S.,
26 rue du 141è RIA, 13003 Marseilles (France)*

Abstract

An equation for calculating the melted fraction (F) in purity determinations by DTA has been derived, which makes a correction for the thermal lag of the sample cell during the melting process. A set of samples of benzoic acid containing different quantities of anthracene has been tested. There are two peaks in the melting thermograms and the calculated impurity contents in these samples without using the correction are less than those prepared. This binary system is assumed to form an eutectic; its composition and melting point are estimated as $X = 0.056$ mole fraction of anthracene and $T = 117.8°C$ respectively. Results obtained using naphthalene containing 0.415 mol% of fluorene show that the correction for the thermal lag of sample cell is necessary. In addition, a linear correction in the F calculation for the melting of eutectic and premelting of the main component is also desirable, giving a good straight line of the melting temperature T versus $1/F$ and a reasonable purity estimation

INTRODUCTION

Thermal analysis method for purity determination is commonly applied to various substances [1–3]. Its essential principle is based on measurement of the melting point depression of the substance (regarded as the solvent) in the presence of an impurity (regarded as the solute). According to thermodynamics the concentration of the impurity in the substance can be calculated from the slope of a straight plot of the melting temperature against the reciprocal of corresponding melted fraction of the substance during the melting process. The error in purity determination by this technique could come from at least two aspects: firstly, it depends on the solid–liquid equilibrium phase diagram of this system; secondly, thermal analysis is a dynamic technique and usually its result is more or less different from that

---

[1] Resident at the C.T.M. of the C.N.R.S. in Marseilles as a visiting scientist for six months according to the scientific and technological cooperation programme between Chinese Academy of Science and C.N.R.S. of France.

obtained under equilibrium conditions. In this paper we shall discuss these effects, derive a method for the calculation of the melted fraction of the sample and test it with benzoic acid–anthracene and naphthalene–fluorene binary systems.

A CORRECTION IN THE CALCULATION OF MELTED FRACTION FROM THE PEAK AREA

For an ideal case in which no solid solution appears in the solid and the liquid obeys the ideal solution law, the depression of melting point of a solvent in the presence of a solute can be calculated on the basis of thermodynamics.

$$d \ln(1 - X)/dT = \Delta H_m/RT^2 \tag{1}$$

For a dilute solution, the formula (1) is simplified approximately to

$$T = T_0 - RT_0^2 X/\Delta H_m \tag{2}$$

where T_0 is the melting point of the pure solvent, T is its melting point when containing X mol% of impurity, ΔH_m is the shortened form of $\Delta_{fus} H_m$ which is the molar enthalpy of melting of the solvent, and R is the gas constant.

If all the solute is in solution during the melting process, the mole fraction of solute, X, is equal to X_0/F, where F is the melted fraction of the sample and X_0 is the mole fraction of solute in the whole sample. Equation (2) can then be written

$$T = T_0 - RT_0^2(X_0/\Delta H_m)(1/F) \tag{3}$$

Usually a melting thermogram of DTA is like the one shown in Fig. 1, where T_j, T_r and T_s are the temperatures of surroundings, reference cell and sample cell respectively, $\Delta T = T_r - T_s$, t_i, t_f and t_m are the times at the beginning, end and maximum of the melting peak, S_m, S_c and S_0 are the peak areas from t_i to t_m, from t_m to t_f and the whole peak.

In the conventional method of calculation, the melted peak area S_t and the corresponding melting temperature T_t is obtained from the melting thermogram at a series of chosen times t and the melted fractions are calculated from the formula, $F_t = S_t/S_0$. A plot of T against $1/F$ is drawn as in Fig. 2. According to the formula (3), T_0 and X_0 are obtained from the ordinate intercept and the slope of the straight line extension, while ΔH_m is calculated from the whole peak area S_0. The use of S_0 in calculating the melted fraction $F_t = S_t/S_0$ implies that the sample completes its melting process at the time when $\Delta T = T_r - T_s = 0$. This is incorrect. Physically, when the melting process starts, the temperature rise of the sample cell is largely arrested and the increase of the magnitude of ΔT is mainly due to the temperature rise of the reference cell at the scanning rate. Therefore ΔT rises at first and reaches its maximum at the completion of the melting
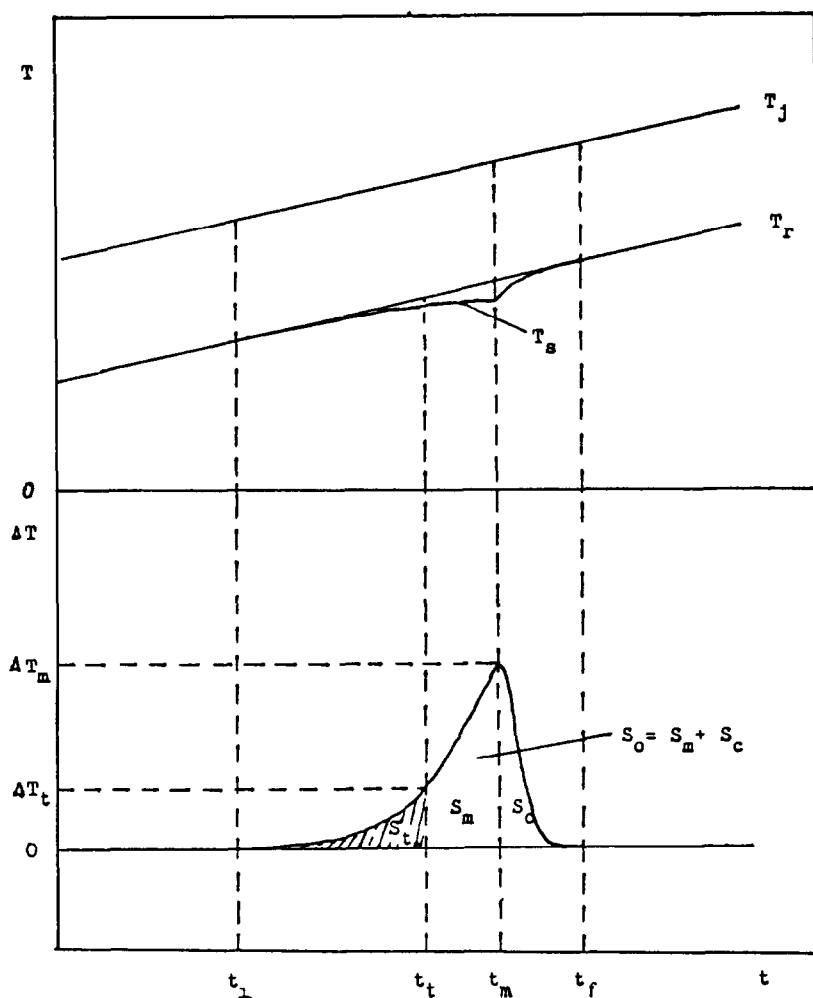
Fig 1 DTA melting thermogram.

process and then the temperature of the sample cell will gradually catch up with that of the reference cell and $\Delta T = 0$.

Let us consider the thermal exchange of both reference and sample cells with the surroundings during the melting process

$$dQ_r/dt = K_r(T_j - T_r) = C_r \, dT_r/dt \tag{4}$$

$$dQ_s/dt = K_s(T_j - T_s) = C_s \, dT_s/dt + (dm/dt)(\Delta H_m/M) \tag{5}$$

where the subscripts r and s are used to indicate the reference and sample cells respectively, dQ/dt and C are the heating power and the heat capacity of the cell, K is the thermal exchange coefficient of the cell with the
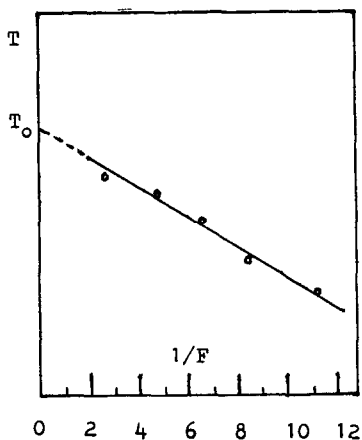
Fig. 2. Plot of T against $1/F$.

surroundings, m, ΔH_m and M are the mass, molar melting enthalpy and molar mass of the sample. If $K_r = K_s = K$ and $C_r = C_s = C$ approximately, then

$$dQ_s/dt - dQ_r/dt = K\,\Delta T = -C\,d\,\Delta T/dt + (\Delta H_m/M)(dm/dt) \qquad (6)$$

Integrating the formula (6) for the whole melting peak

$$\int_{t_i}^{t_f} K\,\Delta T\,dt = KS_0 = m\,\Delta H_m/M \qquad (7)$$

After t_m the sample has all melted, $dm/dt = 0$. Integrating (6) from t_m to t_f

$$\int_{t_m}^{t_f} K\,\Delta T\,dt = -C\int_{t_m}^{t_f} d\,\Delta T$$

$$KS_c = C\,\Delta T_m \qquad (8)$$

Transforming (6), we can obtain

$$dm/dt = (M/\Delta H_m)(K\,\Delta T + C\,d\,\Delta T/dt)$$

The melted fraction of sample at any time before t_m is

$$F_t = (1/m)\int_{t_i}^{t}(dm/dt)\,dt = (M/(m\,\Delta H_m))\left(K\int_{t_i}^{t}\Delta T\,dt + C\int_{t_i}^{t} d\,\Delta T\right)$$

$$= (M/(m\,\Delta H_m))(KS_t + C\,\Delta T_t) \qquad (9)$$

Substituting (7) and (8) into (9)

$$F_t = S_t/S_0 + (S_c/S_0)(\Delta T_t/\Delta T_m) \qquad (10)$$

It can be seen from (10) that the first term is the melted fraction calculated by the conventional method, and the second term is a correction for the peak area after the peak maximum. Neglecting the latter, the calculated purity of the substance will be larger.

PURITY DETERMINATION EXPERIMENTS FOR BENZOIC ACID CONTAINING ANTHRACENE AS IMPURITY

A set of samples of benzoic acid containing different quantities of anthracene was used for checking the formula (10).

The DTA instrument used is one built at the C.T.M. Laboratory in Marseilles; its structure and operating procedure have been described previously [4,5]. Benzoic acid 39i of NBS was used, of certified purity 99.997 mol%. Anthracene was A.G. pure from Fluka. The samples were prepared in the glass ampoules by weighing. After sealing the ampoules under vacuum, the samples were mixed by shaking under molten condition.

The melting thermograms are shown in Fig. 3. The heating rate was 0.2 K min^{-1}. The experimental results are listed in Table 1. The conventional method was used to calculate the melted fractions, i.e. $F_t = S_t/S_0$. It can be seen that the calculated mole fractions of anthracene in these samples are less than those prepared. In the thermograms of the benzoic acid-containing anthracene samples, a peak before the main melting peak of benzoic acid was always found, its area increasing with the concentration of anthracene.
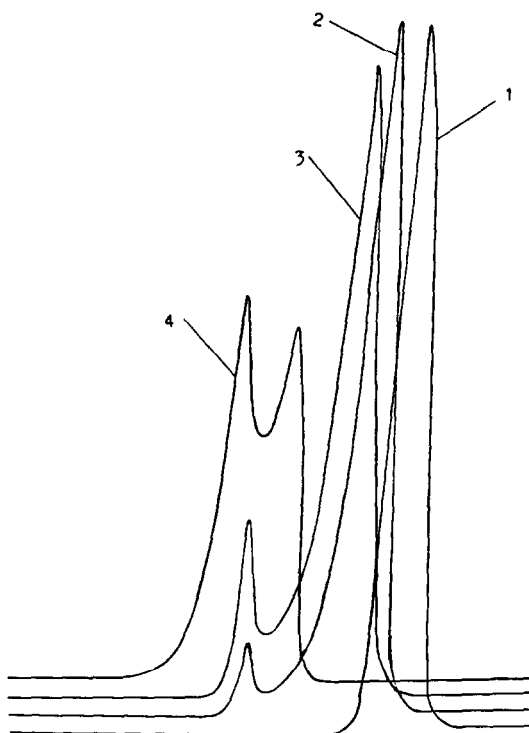

Fig. 3 Melting thermograms of benzoic acid containing different X mole fractions of anthracene: (1) benzoic acid, original purity 99.977 mol%; (2) $X = 0.295$ mol%; (3) $X = 0.662$ mol%; (4) $X = 2.97$ mol%.

TABLE 1

DTA results of purity and eutectic composition of benzoic acid containing anthracene

Expt. no	X_{01} [a] (mol%)	X_{02} [b] (mol%)	dX [c] (%)	A_1 (cm^2)	A_2 (cm^2)	X_e (mol%)	T_e (°C)
BA-0	0 003+0	0.023					
BA-1	0.003+0.295	0.208	−30	1.21	30.02	7.61	
BA-2	0.003+0 662	0.545	−18	3.81	28.63	5.64	
BA-3	0 003+2.97			15.25	13.16	5.53	117.8

[a] Content of impurity in original benzoic acid + content of anthracene added
[b] Content of impurities found in the sample.
[c] $dX = 100(X_{02} - X_{01})/X_{01}$.

For the sample for which $X \approx 3$ mol% (curve 4), this peak and the main peak have approximately the same area.

To explain the appearance of the first peak in the thermograms, we assumed [1,2] that this system forms a binary eutectic with an eutectic in which the mole fraction of anthracene is X_e and the eutectic temperature is T_e, (see Fig. 4). When heating a sample with $X < X_e$, the eutectic will melt at T_e first, with the appearance of the first peak. After the whole eutectic has melted, the pure benzoic acid begins to melt with the appearance of the main peak. If A_1 and A_2 are the areas of the two peaks, n_a and n_b are the moles of anthracene and benzoic acid in the sample, n_b^e is the moles of benzoic acid in the eutectic, and ΔH_a and ΔH_b are the shortened forms of
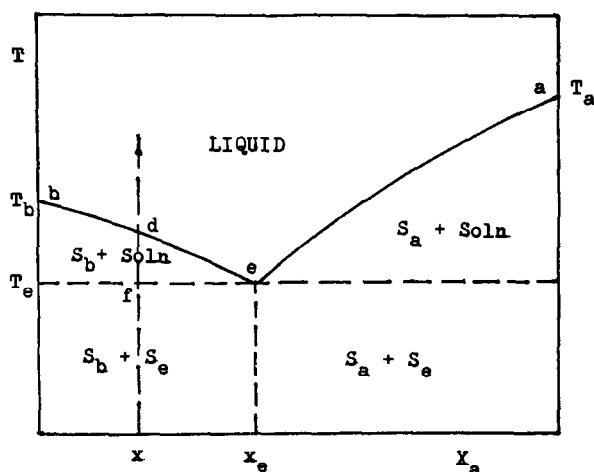

Fig. 4 An illustrated phase diagram of a binary eutectic T_a, T_b and T_e are the melting points of pure components a, b and eutectic. X_e and X are the compositions of eutectic and sample. S_a, S_b and S_e are the solid phases of pure components a, b and eutectic. Soln and L are liquid phases. For the system studied in the text, a = anthracene, b = benzoic acid, T_a = 217°C, T_b = 122.4°C, T_e = 117.8°C and X_e = 5.6 mol%

$\Delta_{fus}H_m$ which are the molar enthalpies of melting of anthracene and benzoic acid respectively, and further, it is assumed that the enthalpy of melting of the eutectic is equal to the sum of the enthalpies of melting of its components and the melting enthalpy of benzoic acid into the molten solution is constant and equal to the melting enthalpy of pure benzoic acid, then from $X = n_a/(n_a + n_b)$, $X_e = n_a/(n_a + n_b^e)$ and $A_1/A_2 = (n_a \Delta H_a + n_b^e \Delta H_b)/((n_b - n_b^e) \Delta H_b)$, we can deduce that

$$X_e = (A_1 + A_2)/[(A_1/X) + A_2(1 - (\Delta H_a/\Delta H_b))] \tag{11}$$

In these experiments $A_1/X \gg A_2(1 - (\Delta H_a/\Delta H_b))$, so eqn. (11) can be simplified as

$$X_e = (1 + (A_2/A_1)) X \tag{12}$$

The calculated values of X_e from the corresponding thermograms (Fig. 3) are listed in Table 1. It can be seen that these values are constant, about equal to 5.6 mol%, except for BA-1 where the area of A_1 is small and so the error involved in calculation of X_e is large. Thus we can say that the assumption of forming a binary eutectic in this system is reasonable. From the result of BA-3, $T_e = 117.8\degree C$.

EXPERIMENTS ON THE BINARY SYSTEM OF NAPHTHALENE AND FLUORENE

It is known that this system forms an eutectic at $T_e = 55.0\degree C$ with $X_e = 36.5$ mol% of fluorene [6]. The melting peak of the eutectic is far apart from the main melting peak of naphthalene; thus the two peaks would not interfere with each other.

Purified products of naphthalene and fluorene were used in the experiments. The purity of naphthalene was determined as 99.975 mol%. A sample was prepared with $X = 0.415$ mol% of fluorene; its melting thermogram was determined.

For comparison we have calculated the melted fraction F from this thermogram by four different methods: (I) $F_1 = S_t/S_0$; (II) calculating F_2 from formula (10) with an experimental value of $S_c/S_0 = 0.240$; (III) $F_3 = F_2 + F_e$, where F_e is the mole fraction of eutectic in the sample, $F_e = X/X_e = 0.0114$. In the three methods, the plots of T versus $1/F$ were curved and their curvatures decreased from method (I) to (III). A linear equation for each plot was obtained to fit the data in the range $3 \leq 1/F \leq 8$ [4]. Then X_0 and T_0 were calculated from this equation and eqn. (3). (IV) $F_4 = F_3 + \Delta F$, where ΔF is a correction for premelting [1,2]. After the eutectic has all melted, the "pure" solid naphthalene begins premelting; the deviation of ΔT from the baseline caused by this process is too small to be recognized by the instrument and it is thus included in the baseline. ΔF was estimated as 2.5 mol% by trial and error to give a good straight line of T versus $1/F$ in a wider range of $1/F$ (see Fig. 5).
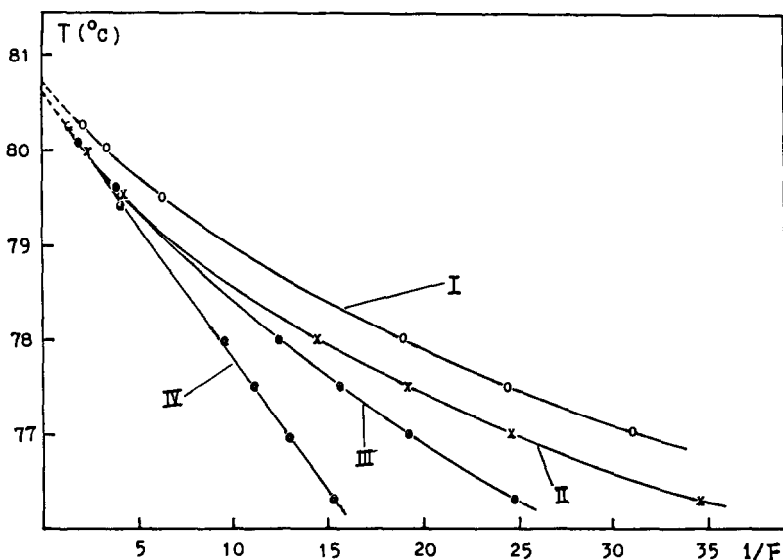
Fig 5. Plots of T against $1/F$ for naphthalene containing 0.415 mol% fluorene with different corrections in F calculation. Details for curves I–IV are given in the text.

The results estimated from these four curves for melting point of pure naphthalene and purity of the prepared sample are listed in Table 2. The impurity concentrations estimated are 38% less than the true value by the first method and 17% less by the second method, indicating the importance of the correction to the melted fraction calculation. When X is small, the correction for mole fraction of eutectic is small, and usually it is difficult in practice to know exactly what kind of impurities the sample contains. In this case, it can be included in the correction of premelting. Finally, the correc-

TABLE 2

DTA results of purity of naphthalene containing 0.415 mol% fluorene obtained with different corrections for F

Method [a]	X_{01} [b] (mol%)	X_{02} [c] (mol%)	X_{03} [d] (mol%)	dX [e] (%)	T_m (°C)
(I)	0.025	0.415	0.272	−38	80 50
(II)	0.025	0.415	0.364	−17	80.46
(III)	0.025	0.415	0.391	−11	80.48
(IV)	0.025	0.415	0.497	13	80.63

[a] See text.
[b] Impurity content in original naphthalene sample.
[c] Fluorene content added to the sample.
[d] Impurity content found in the sample.
[e] $dX = 100(X_{03} - X_{01} - X_{02})/(X_{01} + X_{02})$.

tion of premelting is important as it enables one to use more data in a wider melting range and to obtain a best straight line and less error.

REFERENCES

1 E.E Martı, Thermochim. Acta, 5 (1972) 173
2 E M. Barrall II and R D. Diller, Thermochim. Acta, 1 (1970) 509.
3 E.F. Palermo and J Chiu, Thermochim Acta, 14 (1976) 1.
4 R. Sabbah and I. Antipine, J Therm Anal , 32 (1987) 1929
5 R Sabbah and L. El Walik, J Therm. Anal., 36 (1990) 2299.
6 E W Washburn (Ed.), International Critical Tables of Numerical Data, Physics, Chemistry and Technology, Vol IV, McGraw-Hill, New York, 1928, p 180, No. 1566