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Thermal Analysis of Systems Showing Apparently Horizontal Solidus and Liquidus[1,2]

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It was formerly believed that when a binary compound dissociates extensively on fusion, parts of the solidus and liquidus of the system become horizontal and therefore parallel. Since this is unacceptable in terms of the phase rule, thermal analysis was carried out with the picric acid–*m*-hydroxybenzaldehyde and naphthalene–*m*-dinitrobenzene systems which were hitherto considered as typical examples of such systems.

The phase diagrams reconstructed by the improved thaw-melt method showed two eutectic lines, closely adjacent but distinctly different. In both cases, the melting curves consisted of three parts and the central ones were gently curved but had maximums at equimolar composition. Thus, it is certain that these systems belong to the category forming a congruently melting compound with a combining ratio of 1 : 1, and that the so-called parallelism resulted from a lack of experimental accuracy and/or rather arbitrary drawing of the phase diagrams in the past.

In addition to the visual method, measurements by differential thermal analysis (DTA) and differential scanning calorimetry were done with the latter system. It was found that the melting point could not be determined in several cases; however, differentiation of the two close eutectic points was possible at a sufficiently slow rate of heating. Also, a small heat effect due to the metastable eutectic liquefaction was often recorded on the DTA curves. These findings show that the instrumental methods are useful for detecting the binary compound but by themselves are unsuitable for constructing the phase diagram of such a system.

Keywords——horizontal (parallel) solidus and liquidus; picric acid–*m*-hydroxybenzaldehyde system; naphthalene–*m*-dinitrobenzene system; thaw-melt method; differential thermal analysis; differential scanning calorimetry

It was formerly believed that when a binary compound with a congruent melting point dissociates almost completely on fusion, parts of the solidus and the liquidus in the phase diagram are often horizontal and therefore parallel.[3] Several such diagrams were reported successively by Kremann,[4] Rheinboldt,[5] and Kuroyanagi,[6] and they insisted that the combining ratio of the compounds could not be determined by thermal analysis alone. Since then, this type of phase diagram has been thought to be established, and no effort had been made to reexamine the results.

From the standpoint of the phase rule, the area surrounded by the solidus and liquidus is in solid–liquid equilibrium; however, as shown in Fig. 1, any binary mixture between the two horizontals must consist of two solid phases, since no tie-line crosses the liquidus. Such inconsistency is not permissible, and accordingly, the previous results require reexamination.

In the present paper, construction of the phase diagrams was attempted with the picric acid–*m*-hydroxybenzaldehyde[4,5] and naphthalene–*m*-dinitrobenzene[4] systems which were hitherto regarded as typical examples. The diagrams obtained were found to be ordinary ones belonging to the category forming a congruently melting compound. Thus, it was demonstrated that the parallel solidus and liquidus proposed by previous authors resulted from a lack of experimental accuracy of the methods adopted, and perhaps also rather arbitrary

drawing of the phase diagrams.

Experimental

Materials——Picric acid, *m*-hydroxybenzaldehyde, naphthalene and *m*-dinitrobenzene of the first grade were purified by recrystallization once or twice from distilled water, aqueous ethanol, methanol and ethanol, respectively. It was confirmed by the differential method that none showed polymorphic transition.

Isolation of the Molecular Compound——Yellow rod-like crystals of the molecular compound between picric acid and *m*-hydroxybenzaldehyde were isolated by fractional crystallization from an aqueous solution of both components. The thaw and melting points were found to be 90.1 and 90.4 °C, respectively. From elemental analysis, the combining ratio was found to be equimolar. *Anal.* Calcd for $C_6H_3N_3O_7 \cdot C_7H_6O_2$: C, 44.45; H, 2.58; N, 11.96. Found: C, 44.54; H, 2.72; N, 12.12.

Preparation of the Samples for Thermal Analysis——Two kinds of samples were used for the visual and instrumental analysis.

1) Evaporated Mixtures: Weighed mixtures of both components were treated with a small amount of ether or methanol and heated on a hot plate. After the solid components had completely dissolved, the solvent was evaporated off. The crystalline residue thus obtained was triturated to form a uniform powder.

2) Fused Mixture: The evaporated mixture in a capillary or sample cell was heated a little above its melting point, then allowed to solidify.

Visual Thermal Analysis——The modified thaw-melt method[7] under air-bubble stirring was employed. The heating rate was maintained at 1—3 °C/min. After thawing, the kind of primary crystals was visually discriminated as far as possible.

Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)——A semiautomatic DTA apparatus[8] using a pair of thermistors as heat sensors and permitting direct observation was employed for DTA. The heating rate was controlled manually at 0.25 and 0.5 or 1.0 °C/min. Ultra-fine KCl powder obtained by freeze-drying was used as the reference material. Appearance of liquid and disappearance of solid were visually observed in every run.

For DSC, two kinds of apparatus were used. One was a Perkin-Elmer DSC-1B differential scanning calorimeter, and the other was a Thermoflex CN 8059 L-1 (Rigaku Denki Co., Ltd.). The heating rate of the former instrument was 0.5, 4, 8 and 16 °C/min and that of the latter was 0.25, 1, 5 and 10 °C/min. During measurement, N_2 gas was introduced into the furnace.

In some cases, DTA and DSC were done with two different samples by alternate setting in the right and left positions of the furnace. By this procedure, the two samples were heated under the same conditions and the errors accompanying graphical extrapolation for determining the onset of liquefaction should be minimized. Thus, even a slight difference between two eutectic temperatures could be detected reliably.

X-Ray Powder Diffractometry——An X-ray diffraction analyzer, JDX-7F (Japan Electron Optics Laboratory Co., Ltd.), was used (Ni filter, Cu$K\alpha$ radiation = 1.542 Å). In the case of the naphthalene–*m*-dinitrobenzene system, measurements were done with once-melted mixtures having various compositions.

Results and Discussion

Picric Acid–*m*-Hydroxybenzaldehyde System

The phase diagram constructed by the improved thaw-melt method was clearly different from the ones previously obtained by the cooling curve method and the original thaw-melt method. As shown in Fig. 2 and Table I, two eutectic lines at 90.0 and 88.9 °C was observed in place of the single solidus in the Rheinboldt's diagram[5] (Fig. 1), and the first and second eutectic mixtures were found to contain 31.5 and 61% of the second component, respectively. Also, the liquidus consisted of three curves corresponding to both components and to the compound formed.

Although the curvature of the melting curve for the compound was large, a maximum appeared at the molar ratio of 1 : 1. The isolated crystals were found to contain the two components in the same ratio, and showed a characteristic X-ray pattern (Fig. 3); besides, when the isolated compound was mixed with either one of the components, the thaw point was observed at a fixed temperature of 90.0 or 88.9 °C according to the kind of added component. From these experimental results, it is clear that a single 1 : 1 compound was formed between the two components.

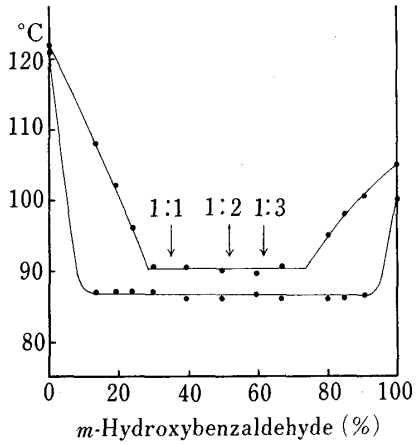

Fig. 1. Phase Diagram of the Picric Acid and *m*-Hydroxybenzaldehyde System According to Rheinboldt

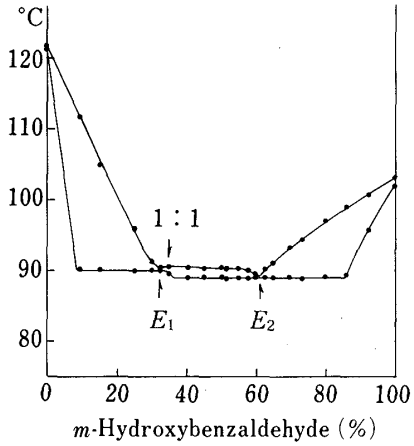

Fig. 2. Phase Diagram of the Picric Acid and *m*-Hydroxybenzaldehyde System

E_1, E_2: eutectic points.

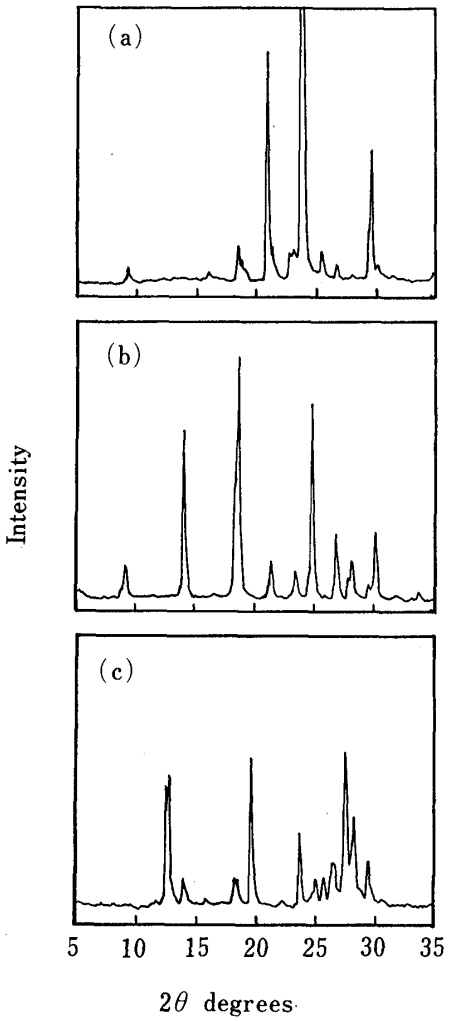

Fig. 3. X-Ray Diffraction Patterns of Picric Acid, *m*-Hydroxybenzaldehyde, and Their 1 : 1 Molecular Compound

(a) Picric acid. (b) *m*-Hydroxybenzaldehyde. (c) 1 : 1 Molecular compound.

The apparent parallelism in binary phase diagrams could arise if the middle melting curve is very gentle, as in this system, and only metastable eutectic liquefaction occurs during measurement. However, the expected value from the intersection of the extrapolations of both sides of the liquidus was far below the thaw point given by Rheinboldt. Thus, the above explanation is not applicable here.

Naphthalene–*m*-Dinitrobenzene System

As shown in Fig. 4 and Table II, a phase diagram was obtained by plotting values of the thaw and melting points. The first and second eutectic mixtures contained 46 and 59% *m*-dinitrobenzene and liquefied at 50.0—50.1 and 51.0—51.1 °C, respectively. The melting curve in the middle was not horizontal as in the Kremann's diagram,[4] but curved with a distinct maximum at 57%. Therefore, it is clear that a 1 : 1 compound with a congruent melting point of 51.8 °C was formed. This conclusion was also supported by the results of X-ray measurements (Fig. 5). Among various sample mixtures, only the one having an equimolar ratio showed a completely different diffraction pattern from those of other mixtures.

Previously, one of the authors demonstrated that the improved thaw-melt method[7] was

TABLE I. Picric Acid–*m*-Hydroxybenzaldehyde System

m-HB[a] (%)	Thaw point (°C)	Melting point (°C)	Primary crystals observed
0.0	121.3	121.7	
9.2	90.1	111.7	PA[b]
15.1	90.0—90.2	104.8	PA
25.1	90.0	95.9	PA
30.0	90.0	91.3	PA
32.5	90.0	90.4	
35.0	89.5	90.5	MC[c]
40.5	88.9	90.3	
45.2	89.0	90.3	
50.1	88.9—89.1	90.3	
51.6	88.8	90.2	
55.1	88.9	90.2	MC
57.8	88.9	90.0	
59.8	89.0	89.5	
62.7	88.9	90.2	
65.0	88.9	91.1	*m*-HB
69.7	89.0	93.2	*m*-HB
73.1	88.8	94.3	
79.9	89.0	96.9	
86.1	89.3	99.0	*m*-HB
92.2	95.7	100.7	
100.0	101.8	103.2	

a) *m*-HB: *m*-hydroxybenzaldehyde. *b*) PA: picric acid.
c) MC: mol. compd.

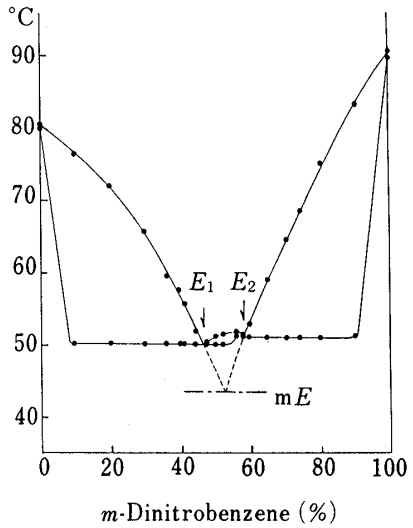

Fig. 4. Phase Diagram of the Naphthalene and *m*-Dinitrobenzene System

E_1, E_2: eutectic points.
mE: metastable eutectic point.

far more reliable than the original one.[5,9] However, the method is not objective in nature and so some doubt may still arise as to whether it is applicable to a case where the two eutectic temperatures differed by only one degree. For this reason, additional experiments were done by DTA and DSC.

As shown in Fig. 6, samples containing less than about 30% and more than about 70% *m*-dinitrobenzene showed two endothermic peaks in their DTA and DSC curves corresponding to eutectic liquefaction and melting of the primary crystals, while in the range of 30—70%, the second peak was represented by a shoulder or became hardly recognizable. As for the eu-

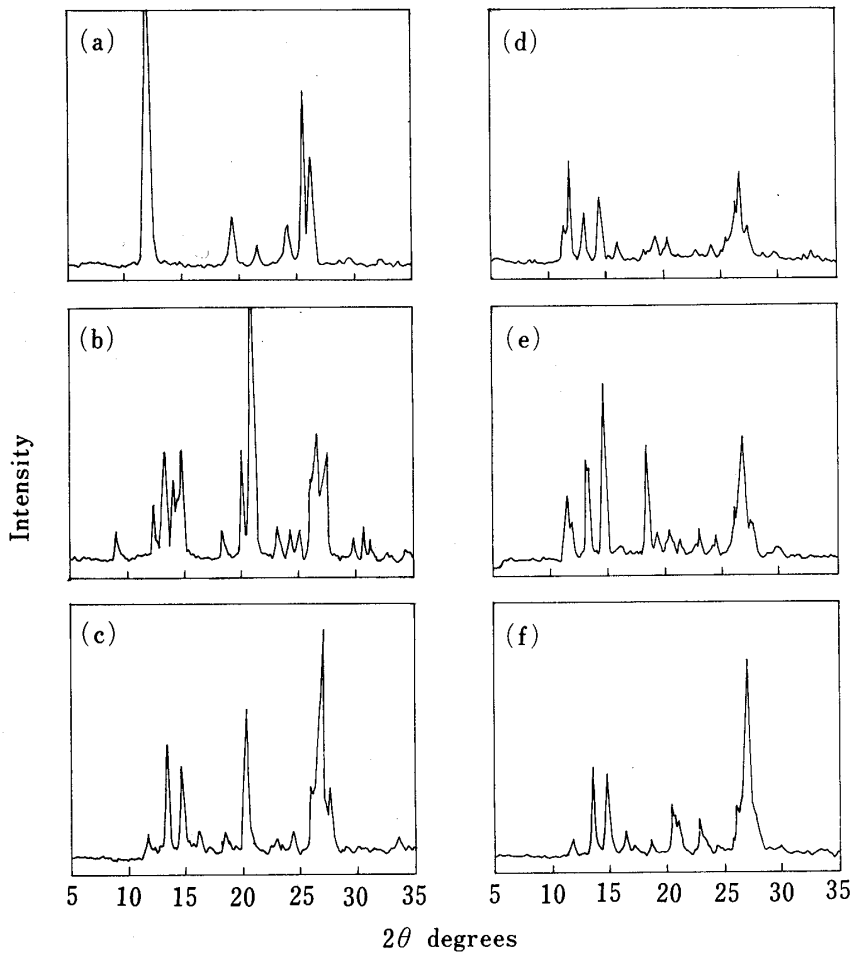

Fig. 5. X-Ray Diffraction Patterns of the Naphthalene and *m*-Dinitrobenzene System

(a) Naphthalene. (b) *m*-Dinitrobenzene. (c) *m*-DNB 57% (1 : 1). (d) *m*-DNB 46%. (e) *m*-DNB 50%. (f) *m*-DNB 59%.

tectic temperatures, they were almost indistinguishable at the comparatively rapid heating rates generally adopted in laboratories; however, when the rate was greatly decreased, the difference became pronounced, as depicted in Fig. 7. Also, it often happened that an additional small endothermic peak appeared in the DTA curves at 43—44 °C (Fig. 6). Since this peak was assignable to the metastable eutectic liquefaction, the presence of a binary compound was strongly suggested. The validity of the assignment was supported by the phase diagram obtained visually; the intersection of the extrapolated melting curves from both sides coincided quite well with the above temperature.

In the ordinary DTA and DSC methods, the eutectic temperature is determined by extrapolating the leading edge of the peak to the base line. Accordingly, some arbitrariness is inevitably involved. In order to avoid this, analysis was done without a reference substance by taking two different samples at a time. As shown in Fig. 8, the steep segment between the two opposite peaks suggests that different heat effects occurred successively. Besides, the extrapolations of the leading edges of the two peaks were found to intersect the base line at different points. In this way, more objective differentiation of the eutectic temperatures became possible in a single experiment.

The above results show that instrumental methods such as DTA and DSC alone may be inappropriate for constructing a precise phase diagram, at least under usual conditions. However, they are useful for detecting compound formation, if properly applied.

TABLE II. Naphthalene–*m*-Dinitrobenzene System

m-DNB[a] (%)	Thaw point (°C)	Melting point (°C)	Primary crystals observed
0.0	80.0	80.5	
9.9	50.0—50.1	76.4	Naph[b]
20.1	50.0—50.2	72.0	Naph
29.9	50.0—50.1	65.5	Naph
36.1	50.0—50.1	59.5	Naph
40.1	50.0—50.2	57.5	Naph
41.5	50.0—50.2	55.7	Naph
44.7	50.0—50.1	51.8	
47.8	50.0—50.1	50.4	MC[c]
50.2	50.0—50.1	51.1	
52.5	49.9—50.2	51.4	
56.4	51.2	51.8	MC
58.5	51.0—51.1	51.4	
59.8	51.0	52.9	*m*-DNB (rod form)
64.9	51.0—51.2	59.0	*m*-DNB (rod form)
70.5	51.0—51.2	64.5	
74.5	51.0—51.1	68.6	
80.3	51.0—51.1	75.1	*m*-DNB
90.3	51.0—51.4	83.2	
100.0	89.8	90.6	

a) *m*-DNB: *m*-dinitrobenzene. *b*) Naph: naphthalene.
c) MC: mol. compd.

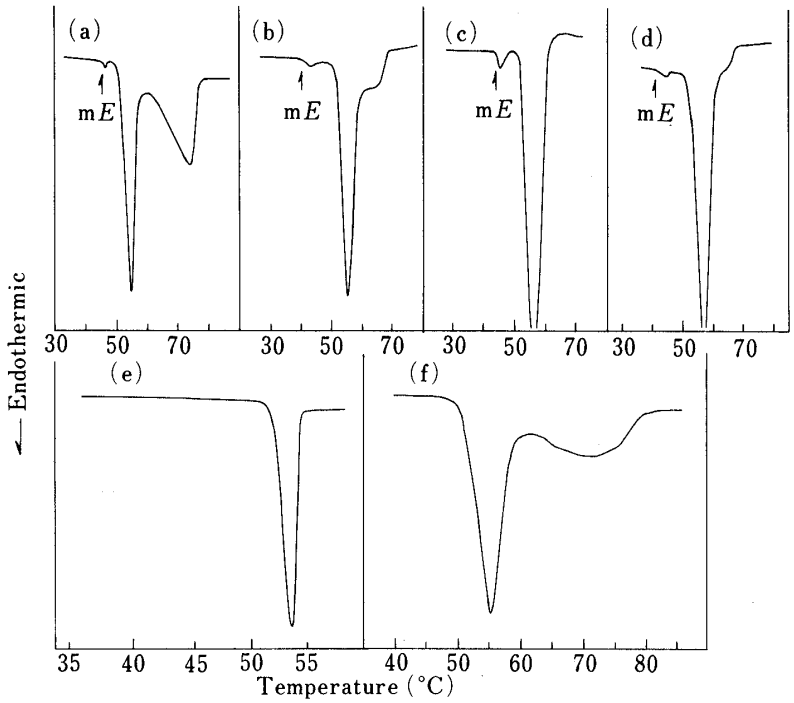

Fig. 6. DTA and DSC Curves of Naphthalene and *m*-Dinitrobenzene Fused Mixtures

(a) DTA, *m*-DNB 20.1%, 54.8 mg, 1±0.1 °C/min.
(b) DTA, *m*-DNB 30.1%, 52.0 mg, 1±0.1 °C/min.
(c) DTA, *m*-DNB 43.6%, 50.0 mg, 1±0.1 °C/min.
(d) DTA, *m*-DNB 70.1%, 53.6 mg, 1±0.1 °C/min.
(e) DSC, *m*-DNB 56.8%, 13.0 mg, 1 °C/min.
(f) DSC, *m*-DNB 79.8%, 99.3 mg, 1 °C/min.
m*E*: metastable eutectic point.

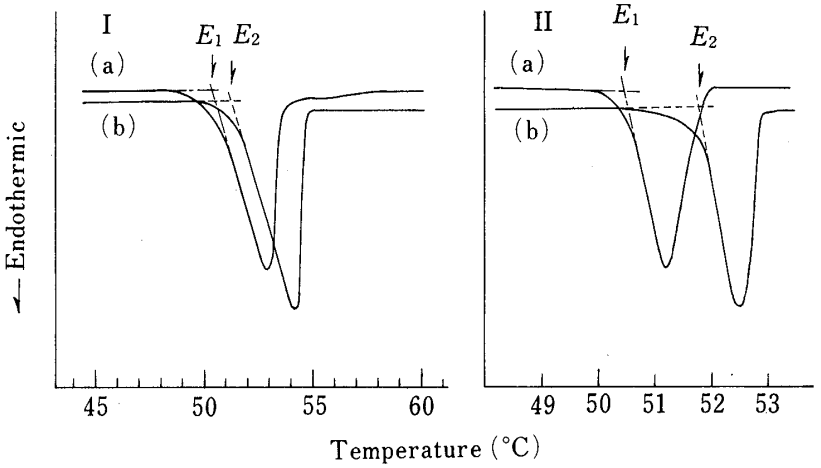

Fig. 7. DTA and DSC Curves of Naphthalene and *m*-Dinitrobenzene Eutectic Mixtures

I: DTA curves, 0.25±0.05 °C/min.
(a) *m*-DNB 39.9%, 54 mg. (b) *m*-DNB 59.0%, 53 mg.
II: DSC curves, 0.25 °C/min.
(a) *m*-DNB 45.7%, 9.7 mg. (b) *m*-DNB 58.9%, 8.7 mg.
E_1, E_2: eutectic points.

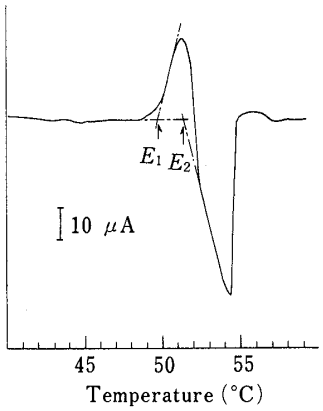

Fig. 8. DTA Curve of Each Eutectic Mixture of Naphthalene and *m*-Dinitrobenzene Measured at the Same Time

Ordinary sample side: *m*-DNB 59.0%, 63.1 mg.
Opposite reference side: *m*-DNB 39.9%, 61.2 mg.
Heating rate: 0.25±0.05 °C/min.
E_1, E_2: eutectic points.

References and Notes

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