Journal of Thermal Analysis, Vol. 19 (1980) 143–146

THERMAL INVESTIGATION OF SOLID–LIQUID EQUILIBRIUM IN THE NAPHTHALENE (AND SOME DIMETHYL DERIVATIVES)-PICRIC ACID SYSTEMS

I. Kotula and A. Rabczuk

Department of Physical Chemistry, Pedagogical University of Częstochowa, Poland

(Received September 14, 1979)

The equilibria of the naphthalene-picric acid and the 2,3- and 2,6-dimethylnaphthalene-picric acid systems were subjected to thermal investigation.

The naphthalene–picric acid system was earlier investigated by Kremann, Sapozhnikow and others [1, 5]. In view of the divergence of their data, reinvestigation of this system was considered necessary.

Experimental

Materials

Chemically pure picric acid (2,4,6-TNF) (POCh, Gliwice) was dissolved in hot water and neutralized with a saturated solution of sodium carbonate. The sodium salt was treated with hot dilute sulfuric acid to give picric acid (m.p. 122.6°) of 99.7% purity (determined by gas-chromatography).

2,3-dimethylnaphthalene (2,3-DMN) and 2,6-dimethylnaphthalene (2,6-DMN) (BDH) were purified by rectification using a high-efficiency rectifying column to give 2,3-DMN (m.p. 105°) of 99.98% purity and 2,6-DMN (m.p. 114.4°) of 99.96% purity (determined by gas-chromatography).

Naphthalene (POCh, Gliwice) was heated with bentonite and purified by rectification to give a product of 99.99% purity with m.p. 80.8°.

Apparatus and procedure

5 g samples of mixtures which differed in composition by weight in steps of 10% were prepared for measurements and ground to a uniform mass.

Differential thermal (DTA) curves were recorded by means of a Paulik-Paulik-Erdey derivatograph, using 0.3 g samples in the smallest platinum crucible. The heating rate was 0.9° per min. in the range 20–1500°. The reference substance was Al_2O_3.

Crystal decay temperature examination by Hill's method [3] as modified by Swierczek [4] was applied as a supplementary measurement. 4 g samples of mixtures of the same compositions as above were used. The heating rate near the melt-

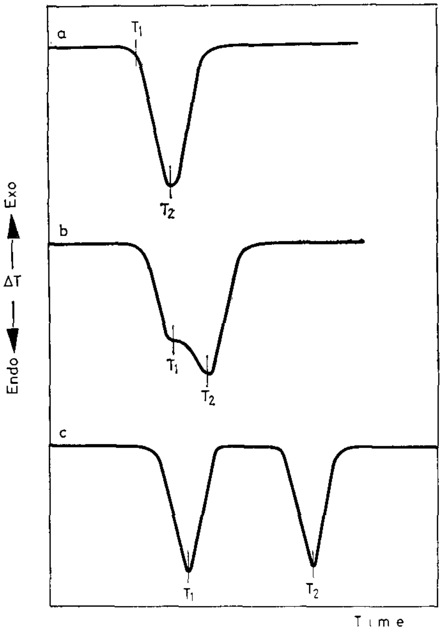

Fig. 1. Interpretation of DTA curves T_1 = temperature on solidus curve T_2 = temperature on liquidus curve

ing point was 1.2° per min. Temperature was measured with an Anschütz thermometer graduated to 0.05°.

This method allowed accurate identification of characteristic points in the DTA curve.

Because of their electron-donating properties, naphthalene and its methyl derivatives are able to form more or less stable EDA complexes with picric acid, with sharp melting points [5]. Compounds which form this kind of complex usually give a solid—liquid system with a compound which has a competitive melting point.

Analysis of DTA curves of each mixture and of melted samples of the organic compounds showed the possibility of accurate determination of the solidus as well as the liquidus curve. The points of the liquidus curve as determined by crystal decay temperature were exactly the same. Hence it may be assumed that interpretation of the DTA curves (Fig. 1) and the solid—liquid phase equilibrium diagram prepared from these was correct. Three DTA curves with endothermic effects were obtained. Curve A (Fig. 1) was obtained for samples with compositions similar to the eutectic composition. Curve B was obtained for pure compounds and the eutectic composition, whereas curve C was obtained for the mixtures and melted samples with compositions between the eutectic constitution.

Results and discussion

The solid – liquid phase equilibria of the naphthalene – 2,4,6-TNF, 2,3-DMN – 2,4,6-TNF and 2,6-DMN – 2,4,6-TNF systems are depicted in Tables 1, 2 and 3, respectively.

Table 1

Liquid phase equilibrium for naphthalene—2,4,6-TNF phase system

Mol % naphthalene	T_1 °K	T_2 °K
0		395.5
3.0	385.0	393.0
7.0	385.5	389.0
11.5	385.0	393.0
15.0	384.0	403.0
19.0	385.5	410.0
27.0	384.5	419.5
29.5	385.0	423.0
39.0	385.5	426.0
46.0	386.0	426.0
52.5	350.5	426.5
57.0	349.0	425.5
72.0	348.5	415.0
81.0	350.0	398.0
84.0	350.0	385.0
87.0	349.0	360.0
91.0	350.0	351.0
96.0	350.0	352.5
100.0		353.8

E_1:9.8 mol % naphthalene 427 K; E_2: 88 mol % naphthalene 350 K; (1 + 1) 427 K

Table 2

Liquid—solid phase equilibrium for 2,3-DMN—2,4,6-TNF phase system

Mol % 2.3 DMN	T_1 °K	T_2 °K
0		395.5
6.0	371.5	392.0
11.5	371.5	386.0
16.0	371.0	376.5
22.5	371.5	391.0
24.0	371.0	395.0
30.0	371.0	400.0
39.0	370.5	402.0
47.0	371.0	402.5
57.5	373.5	398.5
66.0	373.0	394.5
73.0	373.5	385.5
78.0	373.0	379.5
81.0	373.0	373.5
87.0	372.5	375.0
92.5	372.5	376.0
100.0	—	378.0

E_1: 15.5 mol % 2.3 DMN 371 K; E_2: 82.0 mol % 2.3 DMN 373.5 K; (1+1) 403 K

Table 3

Liquid—solid phase equilibrium for 2,6-DMN—2,4,6-TNF phase system

Mol % 2.6 DMN	T_1 °K	T_2 °K
0		395.5
4.0	383.0	389.5
8.0	382.5	386.5
12.5	382.5	384.5
16.0	383.0	393.0
22.5	383.0	404.5
31.0	382.0	412.5
41.0	382.5	417.0
48.0	383.0	418.0
53.0	372.0	417.5
56.0	371.5	416.0
66.0	372.0	407.0
71.0	372.0	393.0
75.0	372.0	372.5
83.0	372.5	376.0
90.5	373.0	380.5
100.0		395.5

E_1: 12 mol % 2.6 DMN 383 K; E_2: 76 mol % 2.6 DMN 373 K; (1 + 1) 418 K

A 1 : 1 complex is formed in each system. The melting point of each complex is higher than those of the pure compounds for the systems mentioned above being 427.0, 403 and 418.0 K, respectively.

The experiments proved that it is possible to determine the naphthalene and dimethylnaphthalene-picric acid phase systems by means of differential thermal analysis, which make possible determination of liquidus as well as solidus curves.

References

1. TIMMERMANS, Phisical-Chemical Constants of Pure Organic Conmpounds, Elsevier Publ. Comp. Inc., New York, 1970.
2. Beilsteins Handbuch der Organischen Chemie, Berlin, 1922.
3. A. E. HILL, J. Am. Chem. Soc., 45 (1923) 1143.
4. R. ŚWIERCZEK, Koks-Smoła-Gaz, 5 (1960) 74.
5. F. H. HERBSTEIN, Acta Cryst., B-31 (1975) 60.