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DTA INVESTIGATION OF THE SOLID–LIQUID EQUILIBRIUM FOR METHYL DERIVATIVES OF NAPHTHALENE WITH SOME NITROAROMATICS

I. Kotuła and *A. Rabczuk*

INSTITUTE OF CHEMISTRY, PEDAGOGICAL UNIVERSITY OF CZĘSTOCHOWA, POLAND

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The two-component solid–liquid phase eqilibria systems of some methyl derivatives of naphthalene with 2,4,6-trinitrophenol and 2,4,6-trinitrotoluene have been examined by DTA. All systems contain molecular complexes with 1 : 1 compositions.

The two-component solid--liquid phase equilibria of some methyl derivatives of naphthalene with 2,4,6-trinitrophenol (2,4,6-TNF) and 2,4,6-trinitrotoluene (2,4,6-TNT) have been examined.

Experimental

Materials

The following compounds were used in the investigations: 2,4,6-TNT, 1,5-dimethylnaphthalene (1,5-DMN) and 1,8-dimethylnaphthalene (1,8-DMN), produced by Merck–Schuchard, which were purified by crystallization from ethanol. β-Methylnaphthalene (β-MN), produced by POCh–Gliwice, was purified by rectification using a high-efficiency rectifying column. α-Methylnaphthalene (α-MN), 1,3-dimethylnaphthalene (1,3-DMN), 1,4-dimethylnaphthalene (1,4-DMN) and 1,6-dimethylnaphthalene (1,6-DMN), produced by Merck–Schuchard, were used without purification, 2,4,6-TNF, 2,3-dimethylnaphthalene (2,3-DMN) and 2,6-dimethylnaphtalene (2,6-DMN) were purified as described in [1].

Apparatus and procedure

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

Differential thermal curves (DTA) were recorded by means of a Paulik–Paulik–Erdey derivatograph, using 0.1 g samples in the smallest platinum crucible. The heating

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rate was 1.6 deg per min. The reference substance was Al_2O_3. Crystal decay temperature examination by Hill's method [2] was applied as a supplementary measurement. 4 g samples of mixtures of the same compositions as above were used. The heating rate near the melting point was 1.2 deg 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. A general interpretation of DTA curves is presented in [1]. As a particular example of this interpretation (Fig. 1), some DTA curves and a phase diagram based on those curves are presented for the system phenanthrene–2,4,6-TNF.

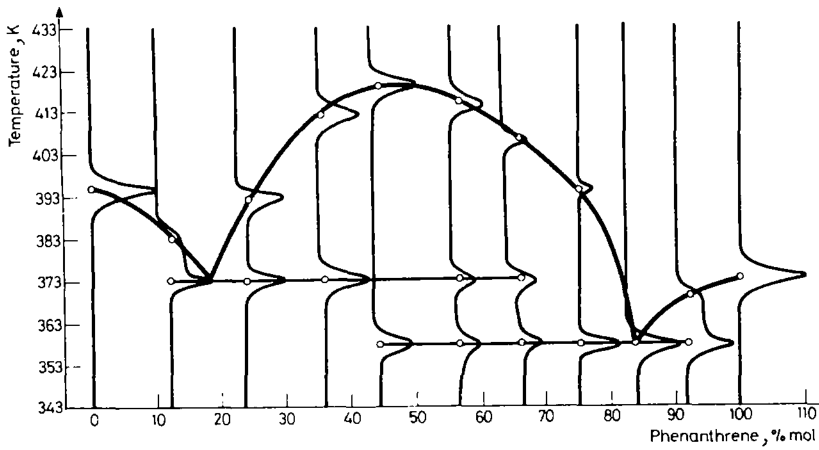

Fig. 1 Liquid–solid equilibrium for phenanthrene–2,4,6-TNF phase system

The temperatures, shapes and magnitudes of the thermal effects depend on the compositions of the mixtures. The DTA curves reveal some endothermic effects resulting from melting of the mixtures, and effects corresponding to melting of at least one of two eutectic mixtures in a congruent system. In the case of simple eutectic systems, only one effect of melting of a eutectic composition appears.

Results and discussion

The phase diagrams of 2,4,6-TNT and 2,4,6-TNF with dimethylnaphthalene isomers (Tables1–16) were determined using the interpretation presented in [1]. For some systems the determination was not complete, because of the low melting temperatures of the methylnaphthalenes (α-MN, 1,3-, 1,4- and 1,6-DMN).

All the examined phase systems gave marked maxima in the phase diagrams, certifying the presence of 1 : 1 molecular compounds.

The melting temperatures of the molecular compounds with 2,4,6-TNT are lower than of those with 2,4,6-TNF. The investigations proved that it is possible to determine phase equilibria by means of differential thermal analysis, which allows determinations of liquids as well as solidus curves in phase diagrams.

Table 1 Liquid—solid equilibrium for α-MN–2,4,6-TNF phase system

Mol % α-MN	T_1, K	T_2, K
0.0		395.6
4.3	379.0	393.5
9.6	379.0	387.5
14.7	379.5	387.5
21.1	378.0	395.0
29.1	378.0	400.0
38.1	379.0	406.0
50.0	329.0	411.0
53.5	328.0	410.0
60.1	328.0	407.0
69.3	328.0	403.0
76.7	329.0	398.0

E_1: 11.0 mol % α-MN 379.0 K
(1:1) 411.0 K

Table 2 Liquid—solid equilibrium for β-MN–2,4,6-TNF phase system

Mol % β-MN	T_1, K	T_2, K
0.0		395.6
8.3	375.0	387.0
15.8	375.0	380.0
20.3	374.5	377.5
29.5	375.0	378.0
40.6	375.0	384.5
50.0	302.0	389.0
52.1	301.0	388.0
62,1	301.0	383.0
70.1	300.0	376.0
78.1	303.0	367.0
86.7	302.0	306.5
92.9	300.0	303.0
96.8	301.5	305.0
100.0		307.1

E_1: 22.0 mol % β-MN 374.5 K
E_2: 88.5 mol % β-MN 302.0 K
(1:1) 389.0 K

Table 3 Liquid–solid equilibrium for 1,3-DMN–2,4,6-TNF phase system

Mol % 1,3-DMN	T_1, K	T_2, K
0.0		395.6
7.6	372.0	390.0
15.7	370.5	382.0
21.9	371.0	374.0
28.1	371.0	374.0
35.8	370.0	381.0
41.8	353.5	384.0
49.8	353.0	386.0
50.0	352.0	386.0
59.7	353.0	384.0
68.8	353.0	379.0
77.5	354.0	362.0

E_1: 24.5 mol % 1,3-DMN 371 K
(1:1) 386 K

Table 4 Liquid–solid equilibrium for 1,4-DMN–2,4,6-TNF phase system

Mol % 1,4-DMN	T_1, K	T_2, K
0.0		395.6
4.2	381.0	391.0
8.6	380.5	385.0
14.9	381.0	385.5
19.0	380.5	393.0
26.0	380.0	396.0
33.1	380.5	404.5
38.3	380.0	407.0
48.6	382.0	412.0
50.0		413.0
57.2		411.0
61.2		409.0
67.0		401.5
70.9		393.5
74.1		385.0

E_1: 10 mol % 1,4-DMN 380.5 K
(1:1) 413 K

Table 5 Liquid–solid equilibrium for 1,5-DMN–2,4,6-TNF phase system

Mol % 1,5-DMN	T_1, K	T_2, K
0.0		395.6
3.1	383.5	394.0
9.1	383.0	390.0
13.8	382.0	385.0
17.4	383.5	387.0
28.4	383.0	400.0
37.7	381.0	407.5
48.0	347.5	411.0
50.0	346.0	411.0
58.5	347.0	411.0
73.1	348.0	396.0
77.6	347.0	386.0
81.5	346.5	371.0
83.6	347.0	347.0
88.0	346.5	348.0
91.4	346.5	349.0
95.3	347.0	349.5
100.0		351.0

E_1: 16.0 mol % 1,5-DMN 383 K
E_2: 83.6 mol % 1,5-DMN 347 K
(1:1) 411 K

Table 6 Liquid–solid equilibrium for 1,6-DMN–2,4,6-TNF phase system

Mol % 1,6-DMN	T_1, K	T_2, K
0.0		395.6
5.4	368.0	390.0
14.0	368.0	378.0
18.1	368.0	372.0
27.5	368.0	375.0
31.7	368.0	378.0
41.3	368.0	380.0
49.7	355.0	381.0
50.0	356.0	381.0
52.0	356.0	379.5
62.0		381.0

E_1: 20.0 mol % 1,6-DMN 383 K
(1:1) 381 K

Table 7 Liquid–solid equilibrium for 1,8-DMN–2,4,6-TNF phase system

Mol % 1,8-DMN	T_1, K	T_2, K
0.0		395.6
4.6	380.0	393.5
12.5	380.0	386.0
17.0	380.5	382.0
23.6	380.5	396.0
33.4	379.0	416.0
42.3	330.5	423.0
50.0	331.0	426.0
56.0	330.0	425.5
64.3	330.0	423.5
79.0	331.5	394.0
87.9	331.0	367.0
92.1	330.0	348.0
96.1	331.0	331.0
97.5	330.0	332.0
98.9	330.0	332.5
100.0		335.0

E_1: 20.0 mol % 1,8-DMN 380.5 K
E_2: 96.1 mol % 1,8-DMN 331.0 K
(1:1) 426 K

Table 8 Liquid–solid equilibrium for α-MN–2,4,6-TNT phase system

Mol % α-MN	T_1, K	T_2, K
0.0		354.0
9.5	339.0	347.0
14.2	339.0	348.0
20.1	340.0	344.0
33.4	341.0	348.0
40.0	339.0	354.0
50.0		358.0
53.8	338.0	358.0
63.8		357.0
71.8		344.0
79.9		344.0

E_1: 27.0 mol % α-MN 341 K
(1:1) 358 K

Table 9 Liquid–solid equilibrium for β-MN–2,4,6-TNT phase system.

Mol % β-MN	T_1, K	T_2, K
0.0		354.0
8.8	336.0	349.0
15.7	335.0	341.0
20.1	336.0	338.0
28.6	335.0	337.0
40.6	337.0	341.0
50.0	300.0	342.0
52.6	298.0	342.0
61.7	298.5	339.0
70.6	298.0	335.0
79.6	299.0	323.0
86.5	297.0	304.0
92.6	297.0	300.0
96.8	297.0	304.0
100.0		307.1

E_1: 22.0 mol % β-MN 335 K
E_2: 88.0 mol % β-MN 297 K
(1:1)* 342 K

Table 10 Liquid–solid equilibrium for 1,3-DMN–2,4,6-TNT phase system

Mol % 1,3-DMN	T_1, K	T_2, K
0.0		354.0
8.8	330.0	349.0
17.3	328.0	343.5
25.6	327.0	338.0
33.2	328.0	331.0
39.2	329.0	332.0
44.5	321.0	336.0
49.3	320.0	338.0
50.0	320.0	338.0
54.2	322.5	338.0
58.9	321.0	337.0
68.5	322.0	333.0
72.3	322.0	325.0

E_1: 37.0 mol % 1,3-DMN 329 K
(1:1) 338 K

Table 11 Liquid–solid equilibrium for 1,4-DMN–2,4,6-TNT phase system

Mol % 1,4-DMN	T_1, K	T_2, K
0.0		354.0
5.0	337.0	351.0
11.8	338.0	345.5
13.9	337.0	345.0
19.7	338.0	340.0
26.1	337.5	341.0
29.8	339.0	343.5
36.3	338.5	350.0
40.5	338.0	353.5
50.0	339.0	357.0
58.9		355.0
66.2		352.0
75.7		330.0

E_1: 24.1 mol % 1,4-DMN 338 K
(1:1) 357.0 K

Table 12 Liquid–solid equilibrium for 1,5-DMN–2,4,6-TNT phase system

Mol % 1,5-DMN	T_1, K	T_2, K
0.0		354.0
5.3	338.0	350.0
10.1	337.0	345.5
16.0	337.0	340.5
20.4	337.0	339.0
26.5	337.0	344.0
38.4	337.0	351.0
49.5	337.0	355.0
50.0	340.0	355.0
58.0	399.0	354.0
68.9	340.0	349.0
77.1	340.0	346.0
81.5	340.0	342.0
85.9	340.0	341.5
92.3	340.5	347.5
96.5	340.5	349.5
100.0		351.0

E_1: 19.0 mol % 1,5-DMN 338 K
E_2: 83.0 mol % 1,5-DMN 340 K
(1:1) 355.0 K

Table 13 Liquid–solid equilibrium for 1,6-DMN–2,4,6-TNT phase system

Mol % 1,6-DMN	T_1, K	T_2, K
0.0		354.0
4.3	329.0	352.0
10.0	328.0	347.0
14.3	329.0	345.0
22.7	328.0	337.5
28.1	326.0	332.0
33.1		329.0
35.2	328.0	330.0
41.2	328.0	331.5
46.9	330.0	332.5
50.0		332.0
52.5	328.5	332.0
58.4		331.5
68.4		327.0
76.1		319.0

E_1: 31.5 mol % 1,6-DMN 328 K
(1:1) 332.0 K

Table 14 Liquid–solid equilibrium for 1,8-DMN–2,4,6-TNT phase system

Mol % 1,8-DMN	T_1, K	T_2, K
0.0		354.0
3.5	349.0	352.0
4.0	348.5	351.0
9.3	349.0	358.0
13.9	349.0	369.0
27.5	348.0	380.0
39.2	348.5	384.5
50.0	328.0	388.0
51.1	327.0	387.0
58.6	325.0	384.5
67,7	327.0	380.5
77.8	327.0	373.0
85.1	328.0	350.0
90.3	327.0	328.5
92.4	327.0	330.5
97.1	327.5	332.5
100.0		335.0

E_1: 6.0 mol % 1,8-DMN 349 K
E_2: 88.0 mol % 1,8-DMN 327 K
(1:1) 388 K

Table 15 Liquid–solid equilibrium for 2,3-DMN–2,4,6-TNT phase system

Mol % 2.3-DMN	T_1, K	T_2, K
0.0		354.0
3.1	342.5	353.0
6.1	342.0	350.0
9.8	342.0	345.5
14.0	342.5	343.5
29.5	342.5	360.0
38,5	343.0	363.5
49.4	343.0	366.0
50.0	343.0	366.0
59.2	350.0	364.5
65.4	353.0	360.0
70.9	351.0	355.0
76.5	351.0	357.0
85.5	353.0	367.5
92.7	352.5	372.0
100.0		378.0

E_1: 12.5 mol % 2,3-DMN 342,5 K
E_2: 72.5 mol % 2,3-DMN 351.0 K
(1:1) 366.0 K

Table 16 Liquid–solid equilibrium for 2,6-DMN–2,4,6-TNT phase system

Mol % 2,6-DMN	T_1, K	T_2, K
0.0		354.0
4.2	342.0	351.0
8.4	342.0	347.0
13.9	342.0	343.5
26.9	342.0	355.5
38.2	343.0	361.0
49.5	342.5	362.0
50.0	342.0	362.0
59.2	356.0	360.5
63.9	356.0	358.0
68.4	354.0	356.0
77.4	355.0	363.0
85.4	357.0	372.5
92.7	355.0	377.0
100.0		387.4

E_1: 12.0 mol % 2,6-DMN 342 K
E_2: 71.5 mol % 2,6-DMN 355 K
(1:1) 362.0 K

References

1 I. Kotuła and A. Rabczuk, J. Thermal Anal., 19 (1980) 143.

2 A. E. Hill, J. Am. Chem. Soc., 45 (1923) 1143.

Zusammenfassung — Zweikomponentige Fest-Flüssig-Phasengleichgewichtssysteme von einigen Methylderivaten von Naphthalen mit 2,4,6-Trinitrophenol und 2,4,6-Trinitrotoluol wurden mittels DTA untersucht. Alle Systeme enthalten Molekülkomplexe der Zusammenserzung 1 : 1.

Резюме — Методом ДТА изучено фазовое равновесие типа твердое тело - жидкость для двухкомпонентных систем метилпроизводные нафталина с 2,4,6-тринитрофенолом и 2,4,6-тринитротолуолом. Обе двухкомпонентные системы содержат молекулярные комплексы состава 1 : 1.