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Note

Solid+liquid phase diagrams of mixtures of phenylenediamines with naphthols

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The study of solid+liquid equilibria is one of the best tools to investigate the formation of complexes in the condensed phases and provides information[1] about the type and melting temperature of the complex. With these objectives, the solid+liquid phase diagrams of the above-mentioned mixtures were studied.

EXPERIMENTAL

Materials

o-, *m*-, and *p*-Phenylenediamines (BDH) were fractionally crystallized from ethyl alcohol and distilled under vacuum. α-, and β-Naphthols (BDH) were fractionally crystallized from benzene and distilled under vacuum. The purities of the samples were checked by thin-layer chromatography and by determining the melting temperatures, which agreed to within ±0.1 K with the values reported in literature[2,3].

Procedure

Phase-equilibrium data for the systems were obtained by the thaw-melt method[4]. The heating and cooling rates were controlled to about 0.1 K min^{-1}. The temperatures were measured with a calibrated mercury in glass thermometer. The temperatures were corrected for the emergent stem of the thermometer. The measured temperatures were correct within 0.1 K. The solid+liquid equilibrium results were rechecked by the method of thermal analysis[5] and were found to agree within ±0.1 K with the corresponding values obtained by the thaw-melt method. The reproducibility of the results was 0.1 K.

RESULTS

Solid+liquid equilibrium results for the systems of *o*-phenylenediamine+α-naphthol, +β-napthol; *m*-phenylenediamine+α-naphthol, +β-naphthol; *p*-phenylenediamine+α-naphthol, and +β-naphthol are recorded in Table 1 and plotted in Fig. 1.

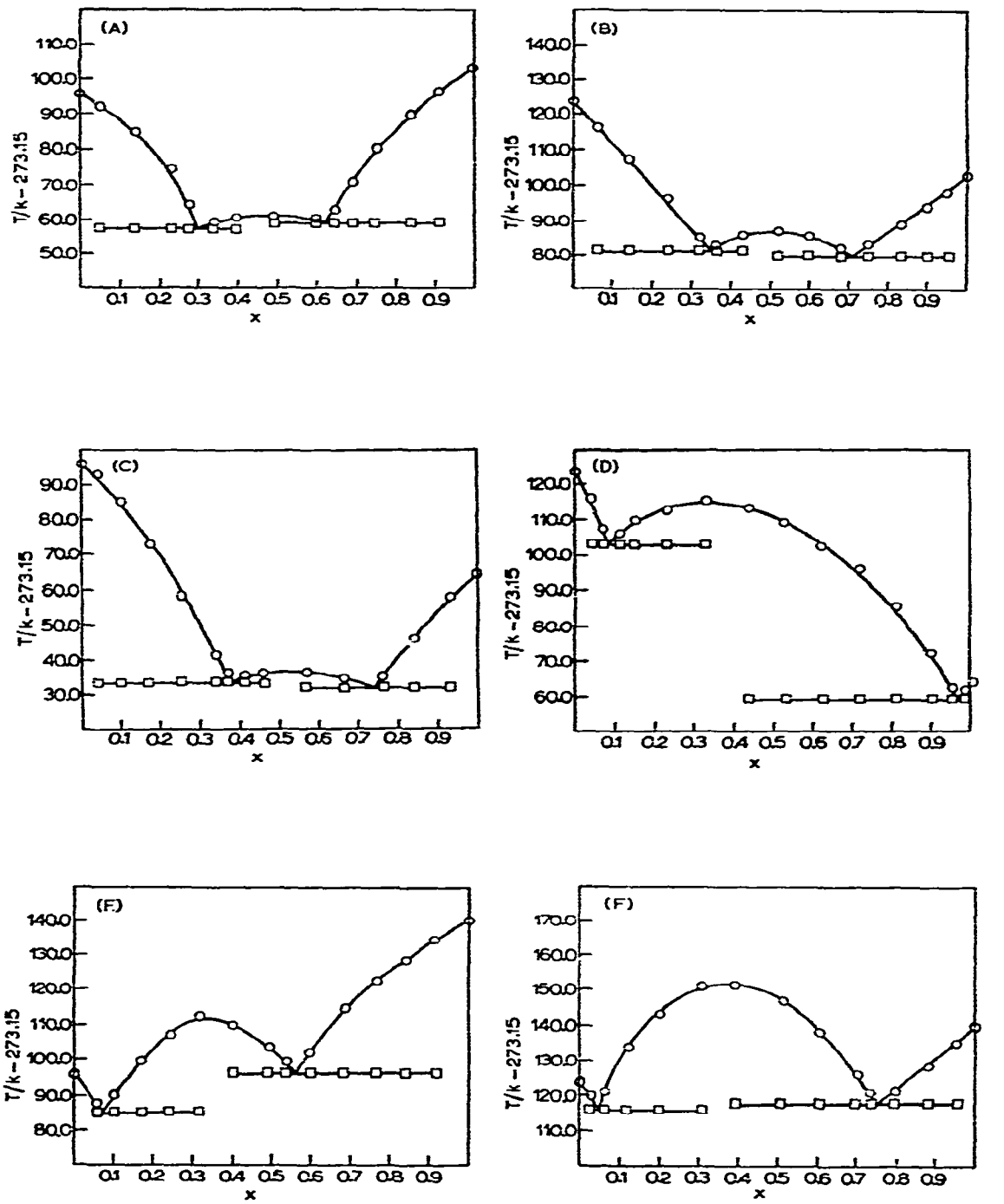

Fig. 1. Plots of melting temperature $T/K-273.15$ against mole fraction x of: (a) x *o*-Phenylenediamine+$(1-x)$ α-naphthol; (b) x *o*-Phenylenediamine+$(1-x)$ β-naphthol; (c) x *m*-Phenylenediamine+$(1-x)$ α-naphthol; (d) x *m*-Phenylenediamine+$(1-x)$ β-naphthol; (e) x *p*-Phenylenediamine+$(1-x)$ α-naphthol; (f) x *p*-Phenylenediamine+$(1-x)$ β-naphthol. O—O, Melting temperatures; □—□, thaw temperatures.

TABLE I

SOLID+LIQUID EQUILIBRIUM DATA OF THE MIXTURES

x	*Thaw temp., T/K − 273.15*	*Melting temp., T/K − 273.15*	x	*Thaw temp., T/K − 273.15*	*Melting temp. T/K − 273.15*
x o-Phenylenediamine + (1 − x) α-naphthol					
0.0000	—	95.8	0.6002	59.5	60.1
0.0502	58.4	92.2	0.6500	59.5	63.4
0.1394	58.4	85.0	0.6982	59.5	71.3
0.2304	58.4	74.9	0.7512	59.5	80.6
0.2813	58.4	65.0	0.8407	59.5	89.6
0.3423	58.4	59.1	0.9174	59.5	96.5
0.4088	58.4	61.2	1.0000	—	103.0
0.4976	59.5	61.4			
x o-Phenylenediamine + (1 − x) β-naphthol					
0.0000	—	123.9	0.6077	80.1	85.7
0.0612	81.3	116.3	0.6816	80.1	82.0
0.1483	81.3	107.2	0.7524	80.1	83.1
0.2450	81.3	96.2	0.8303	80.1	89.0
0.3203	81.3	85.0	0.9001	80.1	96.6
0.3645	81.3	82.7	0.9498	80.1	98.3
0.4311	81.3	86.2	1.0000	—	103.0
0.5205	80.1	87.2			
x m-Phenylenediamine + (1 − x) α-naphthol					
0.0000	—	95.8	0.4727	33.0	36.3
0.0398	33.0	93.1	0.5716	32.0	36.0
0.1022	33.0	85.4	0.6637	32.0	34.2
0.1747	33.0	72.8	0.7653	32.0	35.0
0.2502	33.0	58.4	0.8419	32.0	46.2
0.3398	33.0	41.0	0.9340	32.0	57.5
0.3688	33.0	35.2	1.0000	—	63.8
0.4109	33.0	34.6			
x m-Phenylenediamine + (1 − x) β-naphthol					
0.0000	—	123.9	0.5348	59.0	109.22
0.0413	103.2	116.1	0.6286	59.0	102.9
0.0749	103.2	107.6	0.7197	59.0	96.0
0.1088	103.2	106.0	0.8108	59.0	85.6
0.1502	103.2	109.9	0.9003	59.0	72.4
0.2304	103.2	112.8	0.9501	59.0	63.3
0.3314	103.2	115.7	0.9808	59.0	62.0
0.4425	59.0	113.8	1.0000	—	63.8
x p-Phenylenediamine + (1 − x) α-naphthol					
0.0000	—	95.8	0.5396	96.2	99.0
0.0596	85.0	87.6	0.6001	96.2	102.0
0.1091	85.0	90.0	0.6856	96.2	114.5
0.1707	85.0	99.8	0.7669	96.2	122.5
0.2418	85.0	107.4	0.8412	96.2	128.7
0.3255	85.0	111.6	0.9137	96.2	134.2
0.4003	96.2	109.8	1.0000	—	140.0
0.4889	96.2	104.5			

TABLE I (*continued*)

x _ '	*Thaw temp.*, $T/K - 273.15$	*Melting temp.*, $T/K - 273.15$	x	*Thaw temp.*, $T/K - 273.15$	*Melting temp.*, $T/K - 273.15$
x p-Phenylenediamine + (1 − x) β-naphthol					
0.0000	—	123.9	0.6093	118.1	138.0
0.0298	116.2	119.8	0.6997	118.1	126.0
0.0624	116.2	121.6	0.7311	118.1	121.1
0.1188	116.2	134.0	0.7902	118.1	122.0
0.2044	116.2	143.5	0.8810	118.1	129.4
0.3106	116.2	151.0	0.9496	118.1	134.9
0.3987	118.1	151.3	1.0000	—	140.0
0.5102	118.1	146.4			

DISCUSSION

From the analysis of Fig. 1, it is evident that these mixtures form congruent melting temperature type phase diagrams indicating the formation of complexes in the solid phase in these mixtures. The number, formula and melting temperature of the complexes were determined from these phase diagrams and are recorded in Table 2.

TABLE 2

TYPE AND MELTING TEMPERATURE T_m OF THE COMPLEXES

System	*Type of complex*	T_m/K
x o-Phenylenediamine + (1 − *x*) α-naphthol	1/1	335.15
x o-Phenylenediamine + (1 − *x*) β-naphthol	1/1	360.45
x m-Phenylenediamine + (1 − *x*) α-naphthol	1/1	309.65
x m-Phenylenediamine + (1 − *x*) β-naphthol	1/2	388.65
x p-Phenylenediamine + (1 − *x*) α-naphthol	1/2	384.65
x p-Phenylenediamine + (1 − *x*) β-naphthol	1/2	424.85

From Table 2, it is evident that 1/1 complexes are formed in the mixtures of *o*-phenylenediamine with naphthols; 1/2 complexes are formed in the mixtures of *p*-phenylenediamine with naphthols. *m*-Phenylenediamine formed 1/1 complex with α-naphthol and 1/2 complex with β-naphthol. It is difficult to find an explanation how the change of OH group from α- to β-position in naphthols changed the complex from 1/1 to 1/2 in the mixtures of *m*-phenylenediamine.

All these mixtures showed large deviations from ideal associated solution model[1] and the entropy of fusion values for these complexes were not determined from the solid + liquid equilibrium data. All these complexes are expected to be formed due to hydrogen bonding and large deviations from ideal associated solution model may be due to hydrogen bonding.

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