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Note

SOLID—LIQUID PHASE DIAGRAMS OF MIXTURES CONTAINING SUBSTITUTED PHENOLS AND AMINE MIXTURES

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As part of a program dealing with solid—liquid equilibria studies involving model compounds of asphaltenes [1], we report here investigations dealing with the phase diagrams of phenylphenols, hydroquinone and naphthol with various amines.

EXPERIMENTAL MATERIALS

All chemicals used were supplied by either Aldrich or B.D.H. and were purified by fractional crystallization from ether—petroleum ether mixtures and dried under vacuum. The purity of the samples was checked by determining the melting temperatures and by thin layer chromatography [2,3].

PROCEDURE

Physical mixtures of different systems were prepared by careful weighing, and then fused. The fused mixtures were ground to very fine powder in an agate mortar. All the heating—cooling curves were obtained with a Perkin—Elmer differential scanning calorimeter (DSC). The experimental details were the same as described previously [1].

RESULTS AND DISCUSSION

Solid and liquid equilibrium results for the various systems are plotted in Figs. 1—3 and recorded in Table 1.

It is evident from the analysis of Figs. 1—3 that mixtures of *p*-phenylphenol with *p*-chloroaniline, *p*-bromoaniline and *p*-anisidine form incongruent melting type phase diagrams indicating the formation of complexes (1 : 1) in the solid phases of these mixtures. The phase diagram of the mixture of *p*-iodoaniline with *p*-phenylphenol indicates the formation of a 1 : 1

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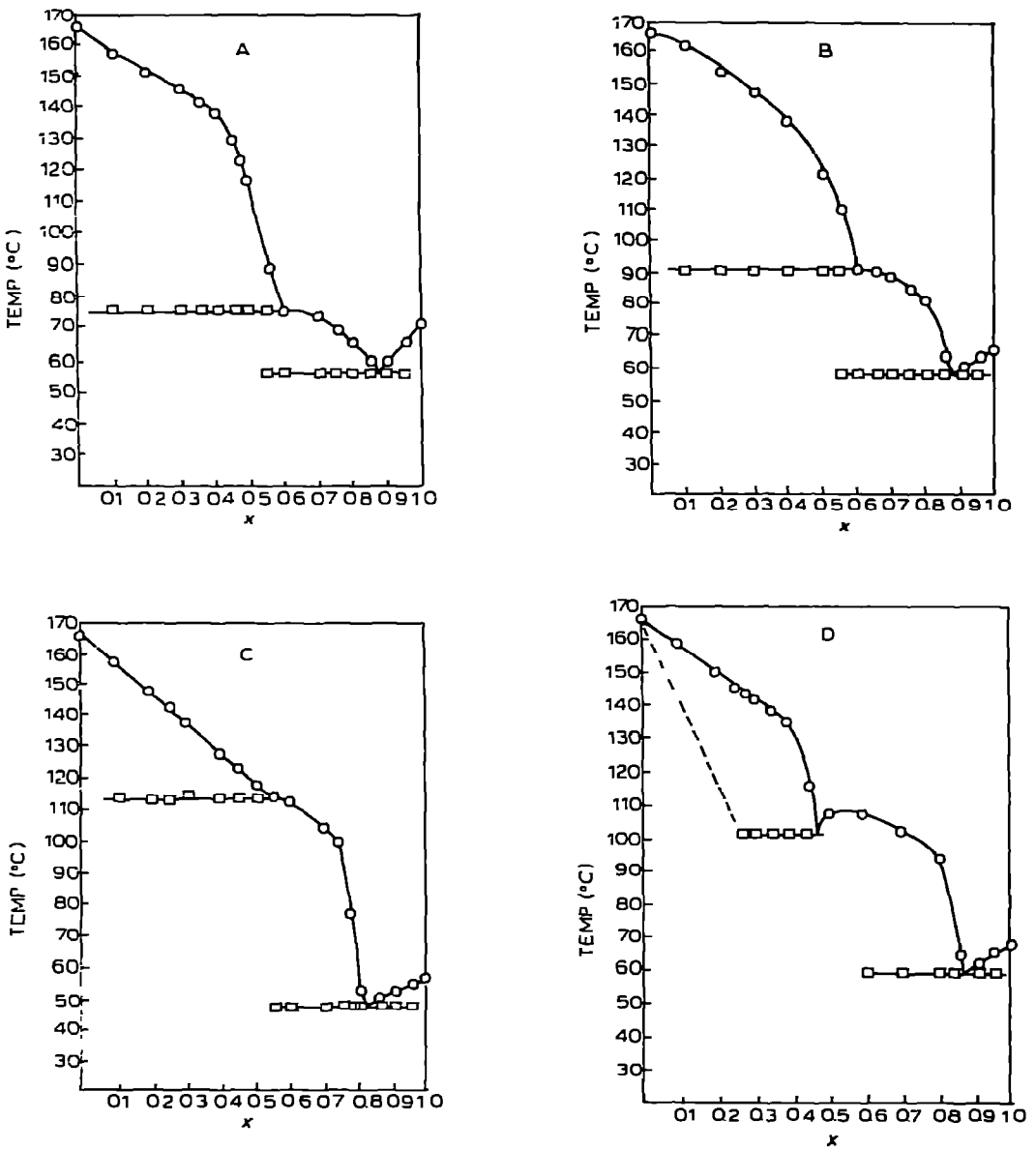

Fig. 1. Plots of melting temperatures against mol fraction x of: A, x *p*-chloroaniline + $(1-x)$ *p*-phenylphenol; B, x *p*-bromoaniline + $(1-x)$ *p*-phenylphenol; C, x *p*-anisidine + $(1-x)$ *p*-phenylphenol; D, x *p*-iodoaniline + $(1-x)$ *p*-phenylphenol.

complex and a limited solid solution of *p*-iodoaniline in *p*-phenylphenol. The mixtures of *o*-phenylphenol with *p*-anisidine and *p*-nitroaniline and α-naphthol with *p*-bromoaniline form congruent melting type phase diagrams with the formation of 1 : 1 complexes in the solid phase. Other mixtures in the present study form simple eutectic diagrams.

All these mixtures showed large deviations from the ideal associated solu-

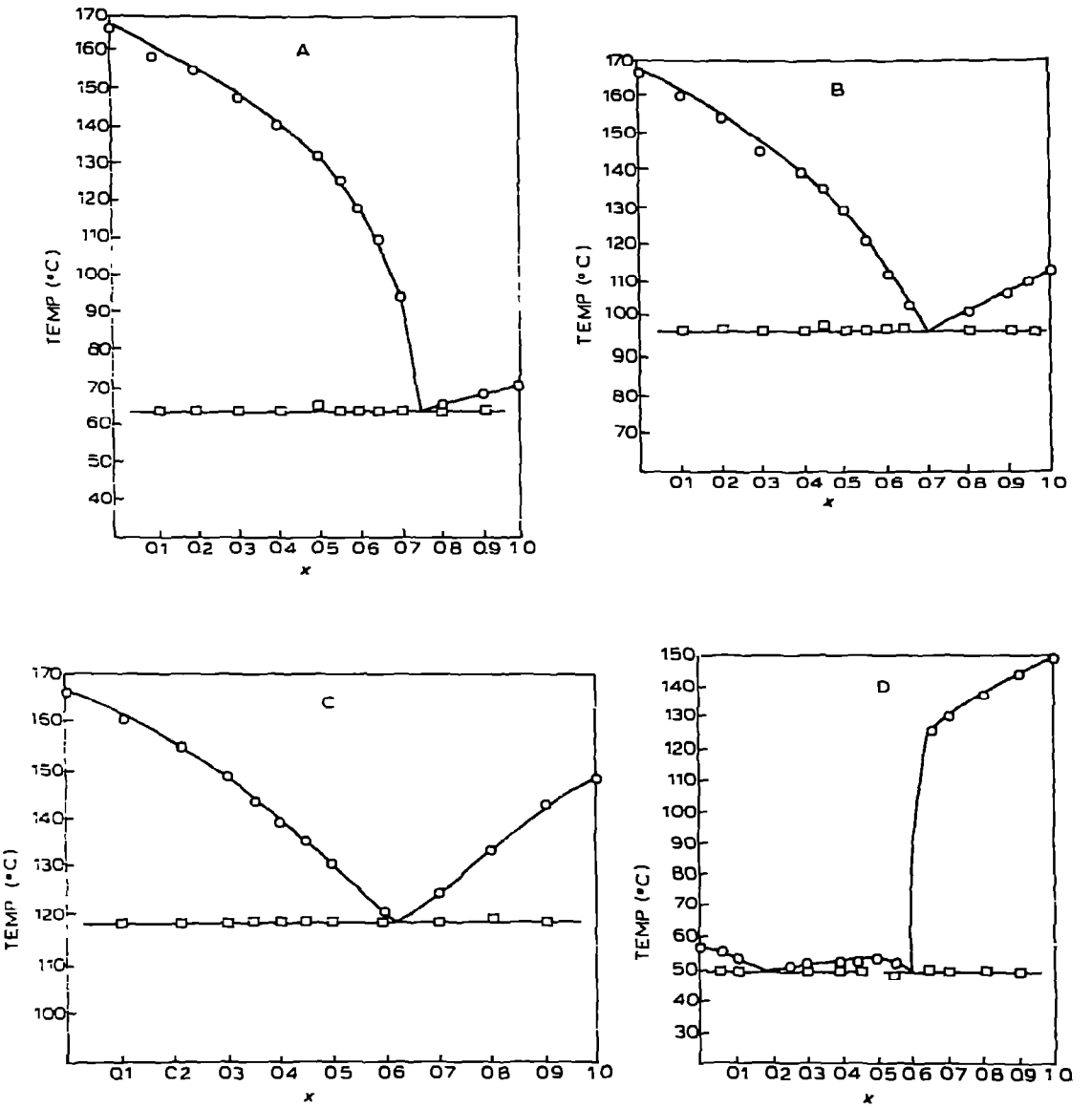

Fig. 2. Plots of melting temperatures against mol fraction x of: A, x *o*-nitroaniline + $(1-x)$ *p*-phenylphenol; B, x *m*-nitroaniline + $(1-x)$ *p*-phenylphenol; C, x *p*-nitroaniline + $(1-x)$ *p*-phenylphenol; D, x *p*-nitroaniline + $(1-x)$ o-phenylphenol.

tion model [4]; these deviations may be due to hydrogen bonding.

It is now planned to extend our study using low temperature DSC to study the systems involving solids (acidic components) and liquids (basic) such as phenylphenols, quinolines and coal-derived asphaltenes. These systems have already been investigated by spectroscopic [5] and calorimetric techniques [6].

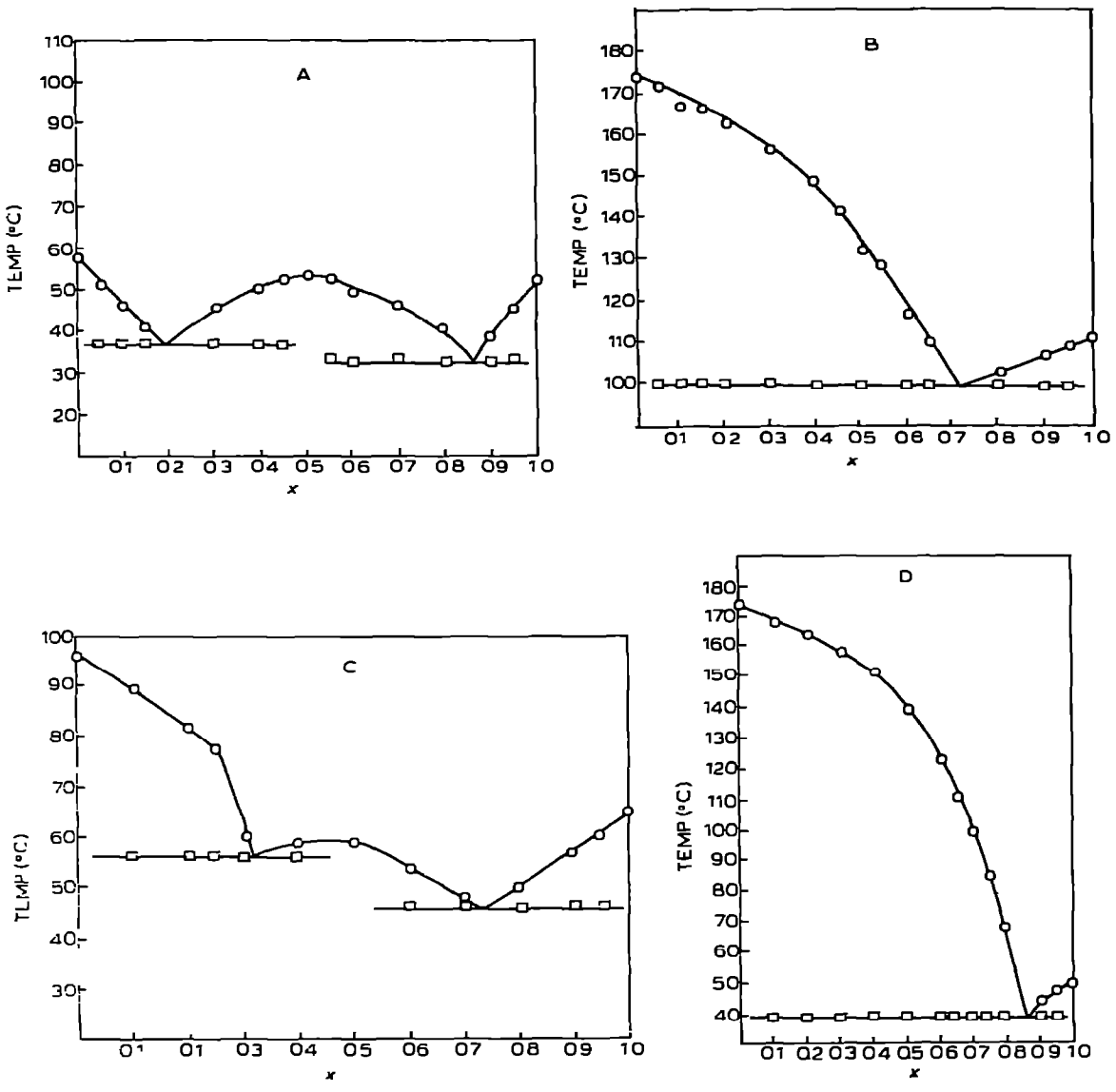

Fig. 3. Plots of melting temperatures against mol fraction x of: A, x *o*-phenylphenol + $(1-x)$ *p*-anisidine; B, x *m*-nitroaniline + $(1-x)$ hydroquinone; C, x *p*-bromoaniline + $(1-x)$ α-naphthol; D, x 2,5-dichloroaniline + $(1-x)$ hydroquinone.

TABLE 1

Solid + liquid equilibrium data for the various mixtures

x	t_E	$t_{P.E.}$	T.P.C.
(1—x) p-*phenylphenol* + x p-*chloroaniline*			
0.0000			166.0
0.1008		76.0	156.0
0.1992		75.8	151.0
0.3028		76.0	146.5
0.3517		76.0	141.5
0.4020		76.0	139.0
0.4511		76.0	129.0

TABLE 1 continued

x	t_E	$t_{P.E}$	T.P.C.
0.4981		76.0	117.0
0.5500	56.5	75.5	88.0
0.5953	56.2		75.0
0.6998	56.5		73.0
0.7999	56.5		65.0
0.8499	56.5		59.0
0.8994	56.5		58.5
0.9500	56.5		65.0
1.0000			72.0
(1—x) p-*phenylphenol* + x p-*bromoaniline*			
0.0000			166.0
0.1002		91.0	162.0
0.2006		91.0	153.0
0.3000		91.0	148.5
0.4007		91.0	139.0
0.5014		91.0	121.0
0.5501	57.5	91.0	110.5
0.5997	57.5		91.0
0.6672	57.5		90.2
0.6996	57.5		88.7
0.7500	57.5		86.0
0.7980	57.0		81.5
0.8497	57.5		63.0
0.8983	57.5		60.0
0.9497	57.0		63.0
1.0000			66.0
(1—x) p-*phenylphenol* + x p-*anisidine*			
0.0000			166.0
0.1014		114.0	158.0
0.2020		114.0	152.0
0.2506		114.0	142.0
0.3015		114.0	137.0
0.3995		113.5	127.0
0.4495		114.0	122.0
0.5014		114.0	117.0
0.5520	47.0		113.5
0.5976	47.0		112.0
0.6996	47.5		104.0
0.7490	47.0		99.0
0.7988	47.0		51.0
0.8482	47.0		49.0
0.9001	47.0		51.0
0.9500	47.0		54.0
1.0000			57.0

TABLE 1 continued

x	t_E	T.P.C.	x	t_E	T.P.C
(1—x) p-*phenylphenol* + x p-*iodophenol*					
0.0000		166.0	0.4997		107.0
0.0999		159.0	0.6006	59.0	106.0
0.2002		150.0	0.7016	59.0	101.0
0.2520		145.0	0.8001	59.0	93.7
0.2763	101.0	143.0	0.8507	59.0	63.0
0.3004	101 0	141.5	0.8994	58.5	61.0
0.3998	101.0	132.5	0.9495	59.0	63.0
0.4510	101.0	115.0	0.9744	58.5	65.5
			1.0000		67.0
(1—x) p-*phenylphenol* + x o-*nitroaniline*					
0.0000		166.0	0.5996	64.5	117.5
0.1000	64.5	159.5	0.6502	64.8	112.0
0.1997	64.5	156.0	0.6995	64.5	93.8
0.3006	64.5	147.0	0.7507	64.5	
0.4011	64.5	140.0	0.8003	64.8	66.4
0.5008	64.5	132.0	0.8992	64.5	68.5
0.5503	64.8	125.5	1.0000		71.0
(1—x) p-*phenylphenol* + x m-*nitroaniline*					
0.0000		166.0	0.5501	97.0	120.0
0.1000	97.0	160.0	0.6018	97.0	112.0
0.2008	97.0	155.5	0.6501	97.0	103.0
0.3007	97.0	145.0	0.6997	97.0	
0.3995	97.0	139.8	0.8000	97.0	101.0
0.4503	97.0	136.0	0.8997	97.0	107.0
0.4980	96.5	128.2	0.9500	97.0	109.0
			1.0000		113.0
(1—x) p-*phenylphenol* + x p-*nitroaniline*					
0.0000		166.0	0.5000	117.5	130.0
0.0999	117.5	159.5	0.6006	117.0	118.5
0.2064	117.5	154.0	0.7006	117.5	121.5
0.3009	117.5	148.5	0.7988	117.5	133.0
0.3497	117.5	142.8	0.8993	117.5	142.8
0.4008	117.5	139.0	1.0000		148.0
0.4503	117.5	135.0			
(1—x) o-*phenylphenol* + x p-*nitroaniline*					
0.0000		56.0	0.6001	49.0	
0.1003	49.0	51.3	0.6491	49.5	125.0
0.2018	49.0		0.7010	49.0	129.0
0.3006	49.0	51.0	0.7996	49.0	135.0
0.4003	49.0	51.5	0.9003	49.0	143.4
0.4997		53.0	1.0000		148.0
(1—x) p-*anisidine* + x o-*phenylphenol*					
0.0000		57.0	0.5510	32.0	52.1
0.1001	37.0	46.1	0.6000	32.0	49.0
0.2015	37.0	38.0	0.7050	32.0	46.0
0.3007	37.0	45.0	0.7996	32.0	40.0
0.4005	37.2	51.0	0.8500	32.0	
0.4501	37.0	52.0	0.9016	32.0	39.0
0.4998		53.5	0.9498	32.0	46.0
			1.0000		56.0

TABLE 1 continued

x	t_E	T.P.C.	x	t_E	T.P.C.
(1—x) hydroquinone + x m-nitroaniline					
0.0000		174.0	0.6009	100.1	119.0
0.1007	100.0	168.0	0.6925	100.0	102.5
0.2009	100.1	162.0	0.8000	100.2	103.6
0.3000	100.0	156.0	0.9010	100.1	107.0
0.4000	100.0	148.0	0.9500	100.0	109.0
0.4989	100.2	135.5	1.0000		113.0
0.5501	100.0	129.0			
(1—x) α-naphthol + x p-bromoaniline					
0.0000		94.0	0.6004	46.5	53.5
0.1006	56.0	89.0	0.7001	46.0	48.0
0.2009	56.0	81.5	0.8004	46.1	50.1
0.2489	56.5	78.0	0.9007	46.0	58.0
0.2996	56.0	59.0	0.9500	46.0	61.0
0.3997	56.0	58.0	1.0000		66.0
0.4999		58.2			
(1—x) hydroquinone + x 2,5-dichloroaniline					
0.0000		174.0	0.7000	39.0	100.0
0.1001	38.9	168.0	0.7497	39.0	85.0
0.1999	39.0	163.5	0.8004	39.0	68.0
0.3091	38.9	158.1	0.9000	39.1	43.5
0.3999	39.0	151.0	0.9506	39.0	47.0
0.5010	39.0	140.0	1.0000		50.0
0.5968	38.9	122.2			

T.P.C. = temperature of primary crystallisation (°C).
t_E = eutectic temperature (°C).
$t_{P.E.}$ = pereutectic temperature (°C).

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