Thermochimica Acta, 18 (1977) 323–328

Note

Solid + liquid phase diagrams of mixtures containing phenylenediamines, phenols and dihydroxyphenols

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(Received 24 June 1976)

Solid+liquid equilibrium data for *o*-, *m*-, and *p*-phenylene-diamines with naphthols, nitrophenols, phenol and hydroxybenzenes have been reported earlier[1–5]. In this paper we report the solid+liquid equilibrium data of phenylenediamines with phenylenediamines and phenols with dihydroxybenzenes. Solid+liquid phase diagrams provide information[6] regarding the presence or absence of compound formation between the components in the solid phase.

EXPERIMENTAL

Materials and methods

o-, *m*- and *p*-phenylenediamines (B.D.H.) were treated with activated charcoal and fractionally crystallized from alcohol. Phenol (A.R.), catechol, resorcinol and hydroquinone (B.D.H.) were fractionally crystallized from alcohol.

The purities of the purified 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[7,8].

The solid+liquid equilibrium data were obtained by the thaw-melt method[9–11].

The pure components were weighed to a prepare mixture of definite composition. This was taken in a glass tube which was sealed afterwards. The mixture was heated just above the melting temperature of the higher component in order to prevent vaporization. The tube was suddenly chilled and broken. The solid mass was very finely ground. This process was repeated three to four times. The mixture was taken in a specially designed capillary tube fitted with a mechanical stirrer and placed in an oil bath. The bath liquid was continuously stirred, heating and cooling rates were controlled to within 0.1 K min^{-1}. The measured temperatures were corrected for the emergent stem of the thermometer. Stem correction is given by

$$S = 0.00016n(t'-t)$$

where n is the length of exposed mercury column in terms of scale degrees, t' is the temperature of the bath and t is the average temperature of the emergent stem.

The measured temperatures were correct to within 0.1 K. The solid+liquid equilibrium results were rechecked by the method of thermal analysis[12] and were found to agree within 0.1 K with the corresponding values obtained by thaw-melt method. The reproducibility of the results was found to be 0.1 K.

RESULTS

The solid+liquid equilibrium results of *o*-phenylenediamine+*m*-phenylenediamines, +*p*-phenylenediamine, *m*-phenylenediamine+*p*-phenylenediamine, phenol+catechol, +resorcinol, and +hydroquinone are reported in Table 1 and are plotted in Figs. 1–6.

TABLE 1

SOLID AND EQUILIBRIUM RESULTS FOR VARIOUS MIXTURES

X	*Thaw temp.* (*K*)	*Melting temp.* (*K*)	*X*	*Thaw temp.* (*K*)	*Melting temp.* (*K*)
x m-phenylenediamine+(1−*x*) *o*-phenylenediamine					
0.0000	—	376.15	0.6444	314.15	321.35
0.0825	314.15	367.25	0.7025	314.15	316.95
			0.7750	314.15	316.65
0.2322	314.15	362.15	0.8301	314.15	322.05
0.2826	314.15	351.15	0.8890	314.15	327.15
0.3852	314.15	343.25	0.9502	314.15	322.25
0.4601	314.15	337.15	1.0000	—	336.95
0.5824	314.15	326.45			
x p-phenylenediamine+(1−*x*) *o*-phenylenediamine					
0.0000	—	376.15	0.5638	354.75	380.55
0.1031	354.75	368.25	0.6130	354.75	384.45
0.1987	354.75	361.55	0.6967	354.75	391.05
0.2762	354.75	356.85	0.7571	354.75	395.45
0.3448	354.75	359.35	0.8139	354.75	400.35
0.4009	354.75	365.55	0.8934	354.75	406.35
0.4638	354.75	371.75	0.9341	354.75	410.05
0.5001	354.75	375.45	1.0000	—	413.15
x m-phenylenediamine+(1−*x*) *p*-phenylenediamine					
0.0000	—	413.15	0.5651	320.15	334.15
0.0448	320.15	411.25	0.6750	320.15	324.10
0.1209	320.15	408.15	0.7302	320.15	320.25
0.2605	320.15	393.95	0.8140	320.15	330.65
0.3501	320.15	380.65	0.8853	320.15	333.35
0.4090	320.15	376.75	0.9605	320.15	335.95
0.5085	320.15	352.95	1.0000	—	336.95
(1−*x*) phenol+*x* catechol					
0.0000	—	316.15	0.5027	306.75	340.45
0.0766	306.75	311.25	0.5836	306.75	348.85
0.1147	306.75	309.65	0.6390	306.75	355.45
0.1413	306.75	308.85	0.6938	306.75	359.15

TABLE 1 (*continued*)

X	*Thaw temp.* (*K*)	*Melting temp.* (*K*)	*X*	*Thaw temp.* (*K*)	*Melting temp.* (*K*)
$(1-x)$ phenol + x catechol					
0.1927	306.75	312.55	0.7478	306.75	364.45
0.2641	306.75	317.75	0.7902	306.75	367.95
0.3041	306.75	323.85	0.8311	306.75	369.85
0.3732	306.75	328.25	0.8996	306.75	373.25
0.4540	306.75	335.75	1.0000	—	378.05
$(1-x)$ phenol + x resorcinol					
0.0000	—	316.15	0.5620	303.55	347.45
0.0863	303.55	310.55	0.6266	303.55	355.05
0.1146	303.55	307.45	0.7031	303.55	359.15
0.1402	303.55	304.35	0.7738	303.55	366.36
0.1936	303.55	310.15	0.8341	303.55	370.95
0.2448	303.55	316.05	0.8938	303.55	374.55
0.3040	303.55	323.40	0.9341	303.55	378.45
0.3833	303.55	330.55	0.9448	303.55	379.75
0.4910	303.55	340.65	1.0000	—	383.15
X-hydroquinone + $(1-X)$ phenol					
0.0000	—	316.15	0.5205	293.35	412.65
0.0514	293.35	311.65	0.5905	293.35	423.35
0.0995	293.35	308.25	0.7356	293.35	433.25
0.1750	293.35	296.35	0.8501	293.35	437.75
0.2525	293.35	347.85	0.9902	293.35	440.05
1.0000	—				
0.3515	293.35	378.35	1.0000	—	446.95
0.4256	293.35	398.25			

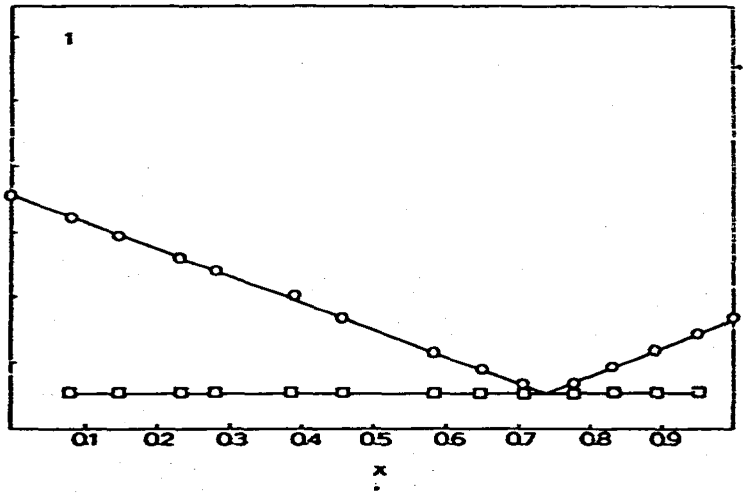

Fig. 1. Phase diagram of x *o*-phenylenediamine + $(1-x)$ *m*-phenylenediamine. O—O, Melting temperature; □—□, thaw temperature.

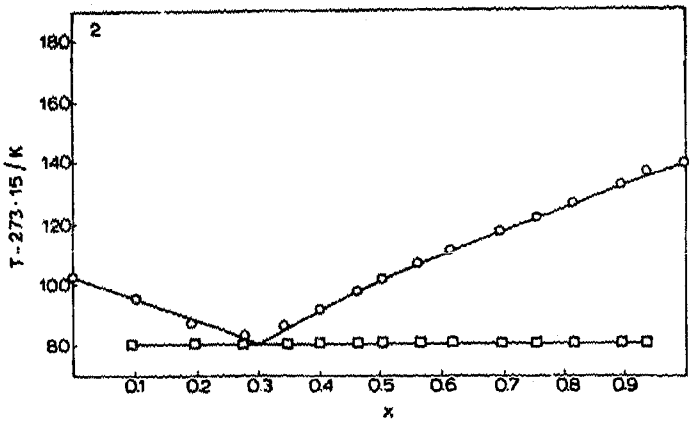

Fig. 2. Phase diagram of x *p*-phenylenediamine$+(1-x)$ *o*-phenylenediamine. ○—○, Melting temperature; □—□, thaw temperature.

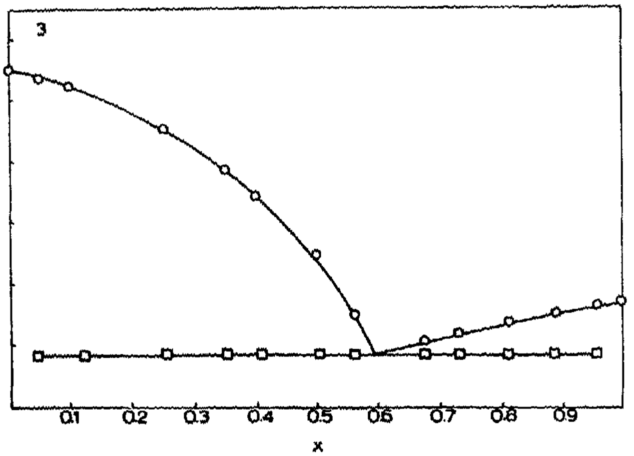

Fig. 3. Phase diagram of x *m*-phenylenediamine$+(1-x)$ *p*-phenylenediamine. ○—○, Melting temperature; □—□, thaw temperature.

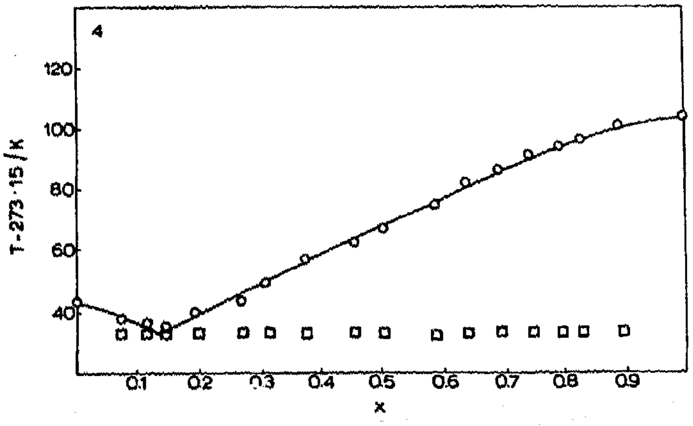

Fig. 4. Phase diagram of x catechol$+(1-x)$ phenol. ○—○, Melting temperature; □—□, thaw temperature.

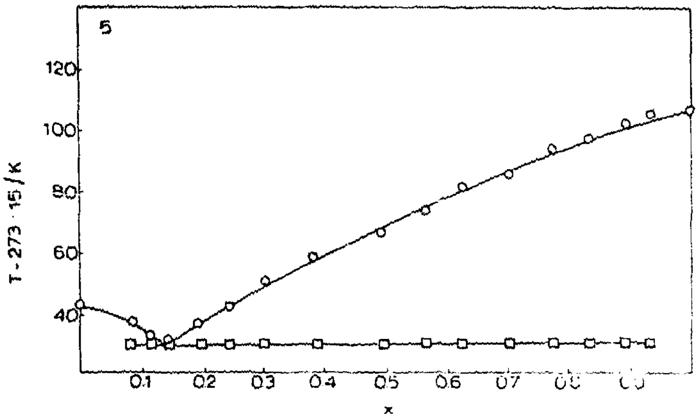

Fig. 5. Phase diagram of x resorcinol + $(1-x)$ phenol. ○—○, Melting temperature; □—□, thaw temperature.

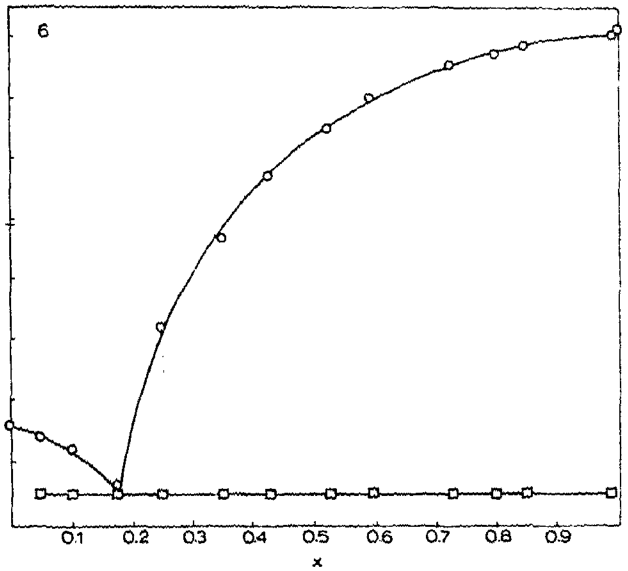

Fig. 6. Phase diagram of x phenol + $(1-x)$ hydroquinone. ○—○, Melting temperature; □—□, thaw temperature.

DISCUSSION

It is evident from Figs. 1–6 that eutectic type phase diagrams are formed in these systems indicating that no new compounds are formed in these mixtures. The activity coefficients can be calculated from the phase diagrams using the relation[6]:

$$-\ln x_i \gamma_i = \frac{\Delta_f h}{R}(1/T - 1/T_i^\circ)$$

where x_i is the mole fraction, $\Delta_f h$ the heat of fusion, R the gas constant, T and T_i° are the melting temperature of the mixture and the pure component. The activity coefficients of phenol + hydroquinone mixtures have been calculated and are recorded in Table 2. In the mixtures of *o*-phenylenediamine + *m*-phenylenediamine, + *p*-phenylene diamine, *m*-phenylenediamine + *p*-phenylenediamine, the components have approximately the same size, the same molar volume and the same $-NH_2$ groups. The components differ in the positions of $-NH_2$ groups only. It is expected that there should be no attractions between the components of these mixtures, and only dispersion forces may be present and no new compound may be formed in these mixtures. In the mixtures of phenol + catechol, + resorcinol, and + hydroquinone the components differ in sizes and molar volumes. It is expected that no attractive forces are operating between the components of these mixtures. It is expected that dispersion forces may be present between the components of these mixtures due to the presence of the $-OH$ group in phenol and $-OH$ groups in catechol, resorcinol, and hydroquinone. It is probable that no new compound may be present in these mixtures and eutectic type phase diagrams are formed.

TABLE 2

ACTIVITY COEFFICIENT FOR THE MIXTURE OF x HYDROQUINONE + $(1-x)$ PHENOL

X	*Temp. (K)*	*Activity coefficient*	*X*	*Temp. (K)*	*Activity coefficient*
0.0514	312.15	0.8074	0.7915	437.75	0.4160
0.0995	308.15	0.4674	0.8000	438.15	0.4279
0.5205	412.65	0.0099	0.8501	440.45	0.5883
0.5994	423.35	0.0553	0.9902	443.15	0.7633
0.7251	433.25	0.2237			

ACKNOWLEDGEMENT

The authors thank the Head of the Chemistry Department, Guru Nanak Dev University, for providing necessary laboratory facilities.

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