

SOLID+LIQUID PHASE DIAGRAMS, NMR AND COLORIMETRIC MEASUREMENTS OF MIXTURES

M. S. DHILLON AND G. S. DHILLON

Department of Chemistry, Guru Nanak Dev University, Amritsar, Punjab (India)

(Received 24 June 1976)

ABSTRACT

Solid+liquid equilibrium, NMR and colorimetric measurements have been made for the mixtures of *o*-phenylenediamine+phenol, *p*-phenylenediamine+hydroquinone, *m*-phenylenediamine+phenol, *m*-phenylenediamine+hydroquinone, *p*-phenylenediamine+phenol, and *p*-phenylenediamine+hydroquinone. The types and melting temperatures of the complexes formed in these mixtures were ascertained from phase diagrams. The nature of the complexes was ascertained from colorimetric and NMR data.

INTRODUCTION

Solid+liquid equilibrium data for *o*-, *m*-, and *p*-phenylenediamine with naphthols and nitrophenols have been reported earlier^{1,2}. In this paper we report the solid+liquid equilibrium data for phenylenediamines with phenol and hydroquinone. The study of solid+liquid equilibria is one of the best tools to investigate the formation of complexes in the condensed phases and provide information³ about the type and melting temperature of the complex. The colorimetric measurements^{4–7} may provide information about the nature and stability constant of the complex in solution phase. The NMR measurements may yield information about the complex formation due to hydrogen bonding.

EXPERIMENTAL

Materials

o-, *m*-, and *p*-phenylenediamines (B.D.H.) were boiled with activated charcoal, filtered while hot and crystallized. Phenylenediamines were repeatedly crystallized from ethyl alcohol. Phenol (A.R.) was fractionally crystallized from alcohol. Hydroquinone (B.D.H.) was fractionally crystallized from ether and dried.

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 the literature^{8,9}.

Procedure

Thaw-melt method. Phase equilibrium data for the systems were obtained by the thaw-melt method¹⁰. 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 measured temperatures were corrected for the emergent stem of the thermometer. The measured temperatures were correct to within 0.1 K. The solid + liquid equilibrium results were rechecked by the method of thermal analysis¹¹ 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.

Optical measurements

Mixtures of different concentrations were prepared by weight in alcohol. The concentration of one component was kept constant and the concentration of the other was varied and vice versa. Optical densities of various solutions were recorded with the help of an Erma Colorimeter. The measured optical density was found to be correct within 0.001.

NMR measurements

The NMR measurements of pure components and mixtures were made in CDCl₃ and TFA by NMR Spectrophotometer BS 487C.

RESULTS

Solid + liquid equilibrium results for the systems of *o*-phenylenediamine + phenol, *o*-phenylenediamine + hydroquinone, *m*-phenylenediamine + phenol, *m*-phenylenediamine + hydroquinone, *p*-phenylenediamine + phenol, and *p*-phenylenediamine + hydroquinone are recorded in Table 1 and plotted in Figs. 1-6.

Colorimetric data for the above-mentioned mixtures are recorded in Table 2 and plotted in Figs. 7-12.

TABLE 1

SOLID+LIQUID EQUILIBRIUM DATA FOR THE VARIOUS MIXTURES

<i>x</i>	Thaw temp. (K)	Melting temp. (K)	<i>x</i>	Thaw temp. (K)	Melting temp. (K)
<i>x</i> <i>o</i> -Phenylenediamine + (1 - <i>x</i>) phenol					
0.0000	—	316.15	0.5005	313.15	327.95
0.0742	302.65	312.35	0.5490	313.15	334.65
0.1880	302.65	305.65	0.6992	313.15	338.35
0.2148	302.65	303.25	0.8245	313.15	358.15
0.2999	302.65	313.15	0.8688	313.15	363.95
0.3995	302.65	323.65	0.9769	313.15	373.25
0.4249	302.65	326.26	1.0000	—	376.15

TABLE 1 (continued)

x	Thaw temp. (K)	Melting temp. (K)	x	Thaw temp. (K)	Melting temp. (K)
<i>x m</i> -Phenylenediamine + (1 - x) phenol					
0.0000	—	316.15	0.5995	313.15	324.65
0.0992	302.55	308.65	0.6750	313.15	312.15
0.1847	302.55	303.15	0.7599	313.15	316.65
0.2498	302.55	312.25	0.8542	313.15	320.25
0.3348	302.55	318.35	0.9541	313.15	331.35
0.4250	302.55	323.15	1.0000	—	336.95
0.5002	302.55	325.95			
<i>x p</i> -Phenylenediamine + (1 - x) phenol					
0.0000	—	316.15	0.4502	313.45	377.05
0.0248	313.45	315.75	0.5188	355.95	372.45
0.0488	313.45	324.95	0.5596	355.95	365.15
0.904	313.45	356.05	0.6084	355.95	366.75
0.1493	313.45	363.65	0.6944	355.95	390.35
0.2407	313.45	376.95	0.7902	355.95	397.25
0.3445	313.45	378.75	0.8832	355.95	406.25
			1.0000	—	413.15
<i>x o</i> -Phenylenediamine + (1 - x) hydroquinone					
0.0000	—	446.95	0.6146	377.45	379.45
0.0468	377.45	439.65	0.6572	377.45	380.55
0.1305	377.45	431.75	0.7102	365.45	380.15
0.2368	377.45	421.45	0.7999	365.45	376.95
0.3397	377.45	411.05	0.8594	365.45	369.95
0.4158	377.45	401.65	0.9546	365.46	371.35
0.4863	377.45	392.15	1.0000	—	376.15
0.5567	377.45	383.25			
<i>x m</i> -Phenylenediamine + (1 - x) hydroquinone					
0.0000	—	446.95	0.5922	335.15	398.35
0.0658	395.35	439.55	0.7004	335.15	389.75
0.0143	395.35	430.85	0.7932	335.15	376.75
0.2486	395.35	419.05	0.8685	335.15	361.85
0.3396	395.35	407.15	0.9244	335.15	339.15
0.3895	395.35	399.25	0.9723	335.15	336.15
0.4542	395.35	398.45	1.0000	—	336.95
<i>x p</i> -Phenylenediamine + (1 - x) hydroquinone					
0.0000	—	446.95	0.6164	408.15	464.35
0.0810	425.45	438.35	0.7326	408.15	454.95
0.1731	425.45	428.55	0.8143	408.15	442.15
0.2348	425.45	428.15	0.8817	408.15	424.35
0.2867	425.45	437.35	0.9141	408.15	413.15
0.3399	425.45	448.75	0.9637	408.15	401.15
0.4001	425.45	459.35	1.0000	—	413.15
0.5004	425.45	466.95			

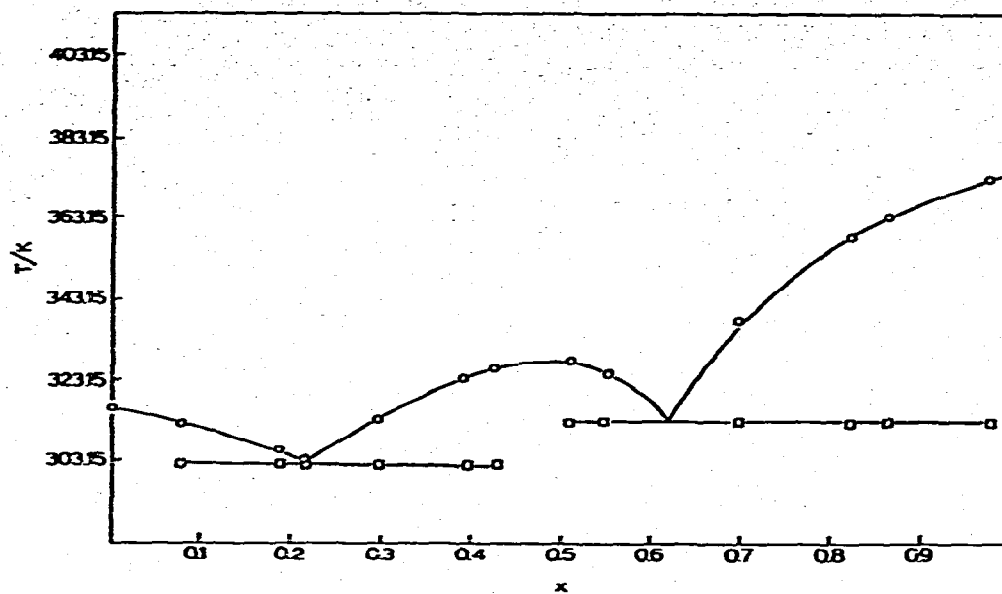


Fig. 1. Solid-liquid phase diagrams of x *o*-phenylenediamine+(1- x) phenol. O—O, Melting temperature; □—□, thaw temperature.

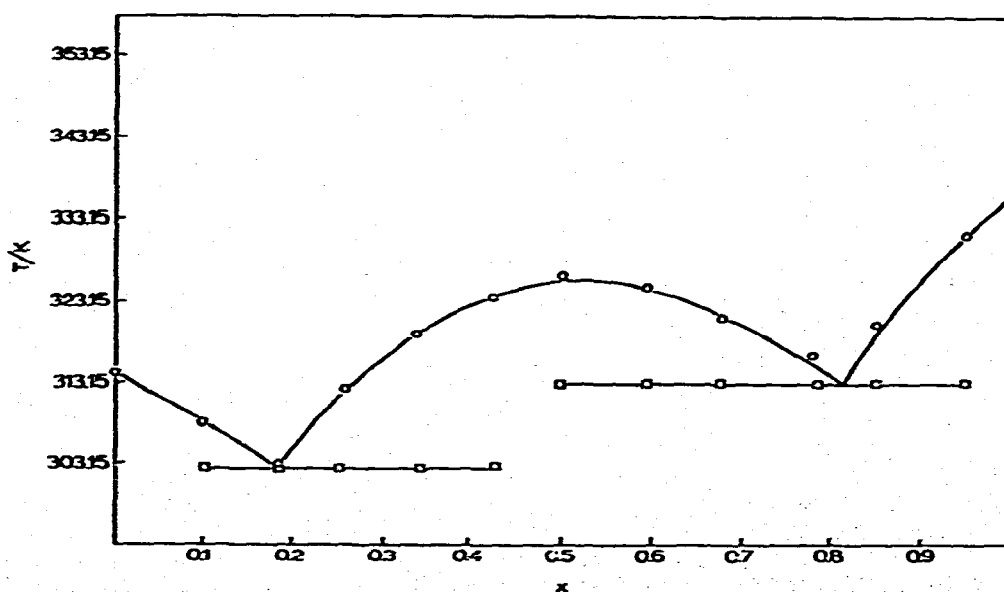


Fig. 2. Solid-liquid phase diagrams of x *m*-phenylenediamine+(1- x) phenol. O—O, Melting temperature; □—□, thaw temperature.

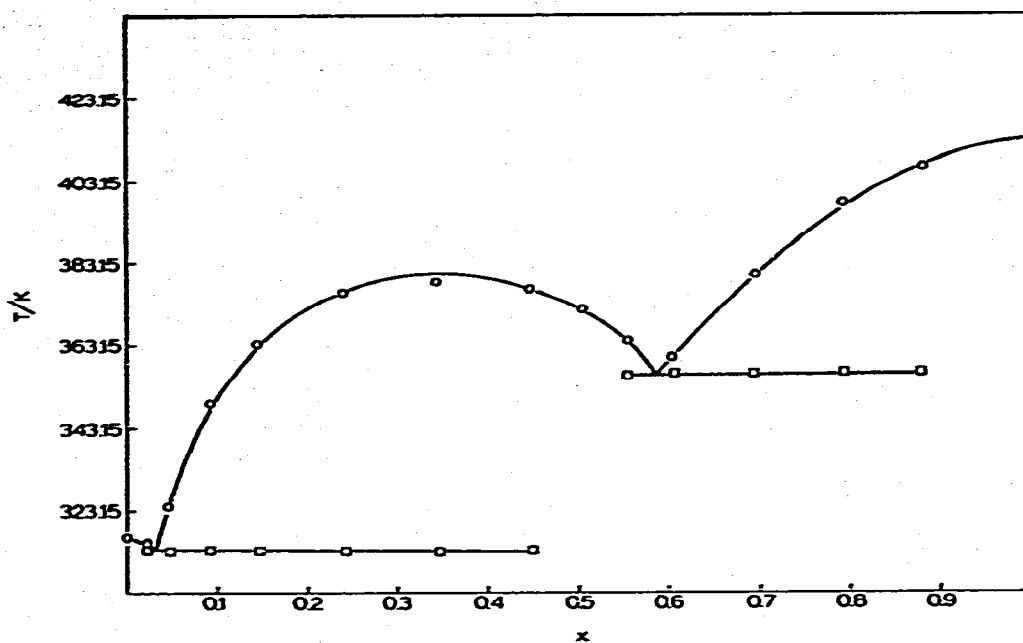


Fig. 3. Solid-liquid phase diagrams of x *p*-phenylenediamine + $(1-x)$ phenol. \circ — \circ , Melting temperature; \square — \square , thaw temperature.

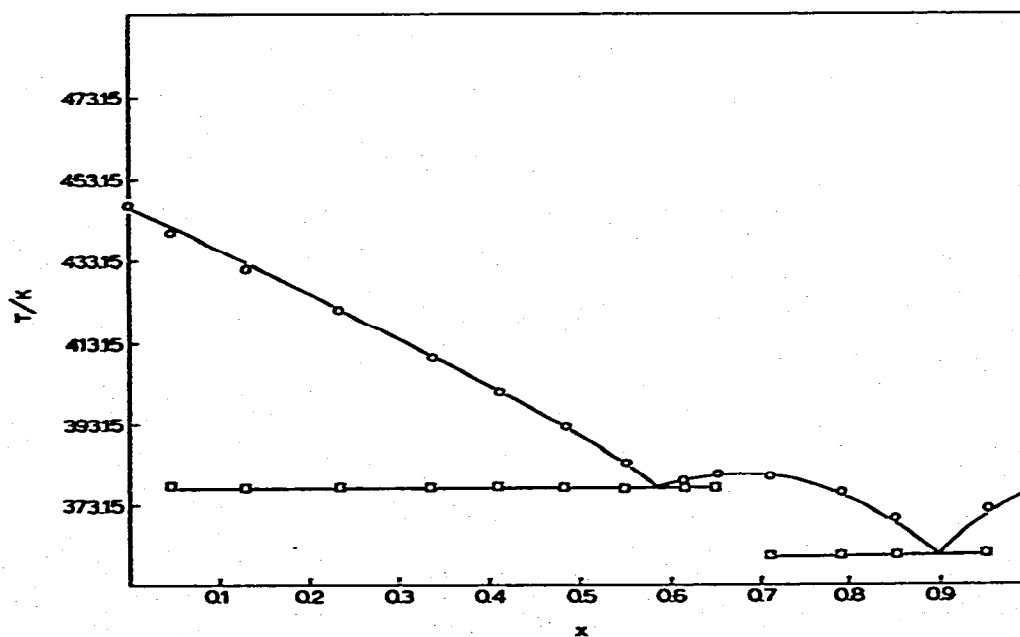


Fig. 4. Solid-liquid phase diagrams of x *o*-phenylenediamine + $(1-x)$ hydroquinone. \circ — \circ , Melting temperature; \square — \square , thaw temperature.

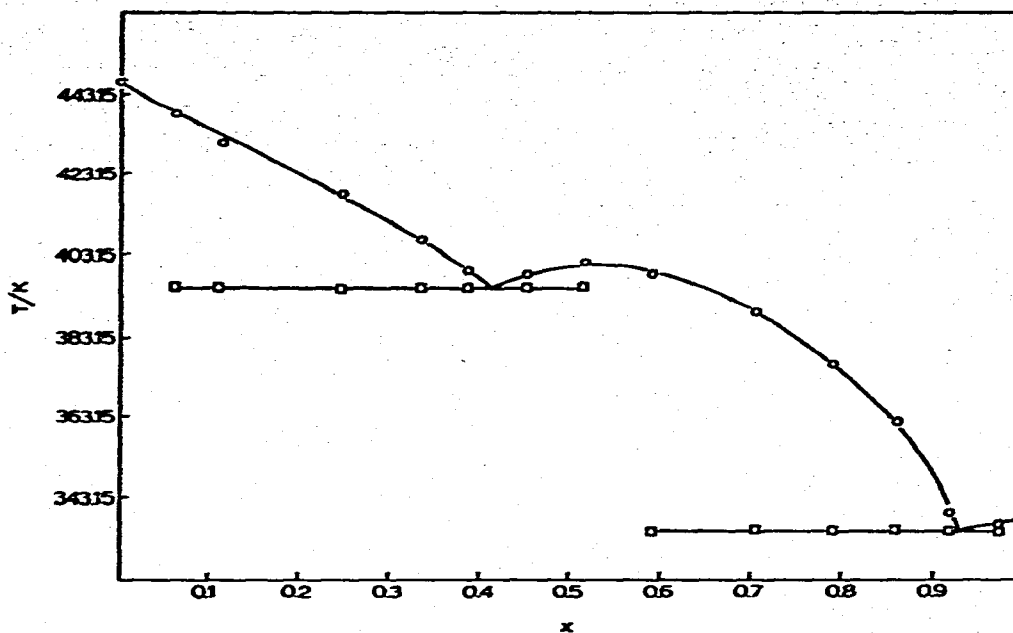


Fig. 5. Solid-liquid phase diagrams of x *m*-phenylenediamine + $(1-x)$ hydroquinone. \circ — \circ , Melting temperature; \square — \square , thaw temperature.

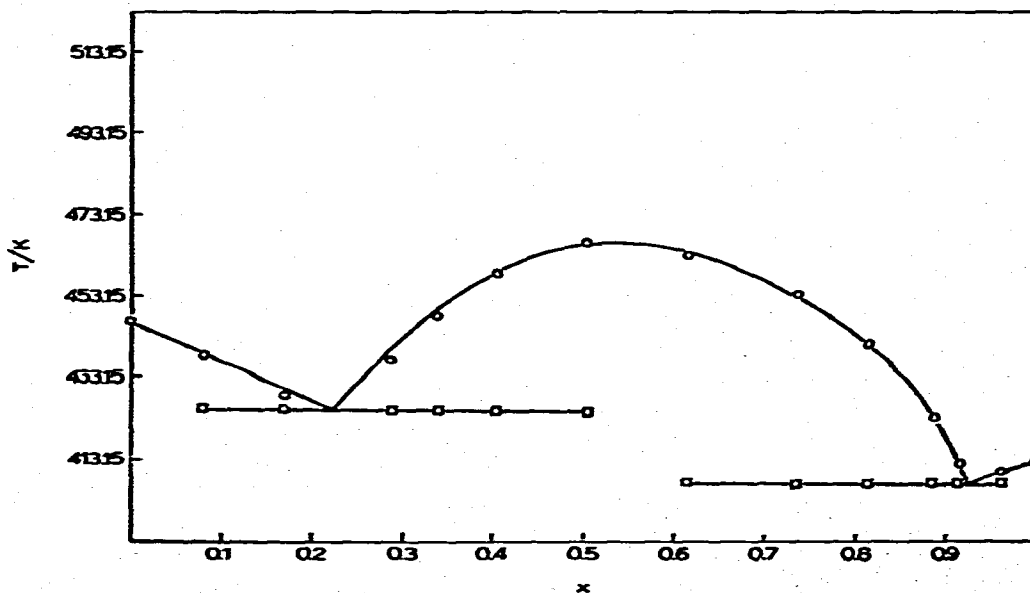


Fig. 6. Solid-liquid phase diagrams of x *p*-phenylenediamine + $(1-x)$ hydroquinone. \circ — \circ , Melting temperature; \square — \square , thaw temperature.

TABLE 2
OPTICAL DENSITY, MEASUREMENTS OF MIXTURES

Conc. of A ($\text{g mol}^{-1} \times 10^5$)	Conc. of B ($\text{g mol}^{-1} \times 10^6$)	Optical density	Conc. of B ($\text{g mol}^{-1} \times 10^6$)	Conc. of A ($\text{g mol}^{-1} \times 10^6$)	Optical density
<i>o</i>-Phenylenediamine (A) + phenol (B)					
3.06	0.53	0.065	1.14	0.69	0.005
3.06	1.06	0.070	1.14	1.30	0.010
3.06	2.02	0.080	1.14	2.08	0.015
3.06	3.45	0.095	1.14	3.40	0.028
3.06	4.08	0.100	1.14	4.20	0.035
3.06	4.50	0.105	1.14	4.75	0.039
<i>m</i>-Phenylenediamine (B) + phenol (A)					
1.14	1.20	0.025	1.03	1.50	0.165
1.14	2.20	0.036	1.03	2.60	0.175
1.14	2.90	0.045	1.03	3.50	0.185
1.14	4.09	0.055	1.04	4.01	0.187
1.14	4.50	0.065	1.04	5.75	0.200
1.14	5.30	0.075	1.03	6.10	0.207
<i>p</i>-Phenylenediamine (B) + phenol (A)					
1.14	1.10	0.030	1.03	1.80	0.385
1.14	2.30	0.062	1.03	2.60	0.400
1.14	3.10	0.090	1.03	3.40	0.425
1.14	3.40	0.105	1.03	4.20	0.430
1.14	4.40	0.140	1.03	5.20	0.446
1.14	4.90	0.152	1.03	6.25	0.0465
<i>o</i>-Phenylenediamine (A) + hydroquinone (B)					
1.04	0.68	0.040	4.50	2.93	0.040
1.04	1.68	0.045	4.50	6.20	0.066
1.04	2.50	0.048	4.50	11.80	0.100
1.04	3.02	0.050	4.50	14.80	0.135
1.04	4.09	0.055	4.50	18.00	0.150
1.04	4.61	0.060	4.50	23.03	0.185
<i>m</i>-Phenylenediamine (B) + hydroquinone (A)					
2.17	0.69	0.050	1.15	0.50	0.082
2.17	1.68	0.070	1.15	1.20	0.095
2.17	2.38	0.080	1.15	1.60	0.102
2.17	3.07	0.095	1.15	2.60	0.120
2.17	4.25	0.115	1.15	3.02	0.125
2.17	4.79	0.125	1.15	3.25	0.130
<i>p</i>-Phenylenediamine (B) + hydroquinone (A)					
1.16	0.60	0.140	1.03	0.68	0.950
1.16	1.62	0.340	1.03	1.81	1.000
1.16	2.54	0.560	1.03	2.56	1.050
1.16	3.17	0.660	1.03	3.47	1.100
1.16	4.14	0.900	1.03	4.38	1.200
1.16	4.75	1.020			

The NMR results of the pure components and the above mentioned mixtures are recorded in Table 3.

TABLE 3

NMR RESULTS OF PURE COMPONENTS AND THEIR MIXTURES

	¹ H NMR chemical shifts				
	Aromatic 4H (ppm)	NH ₂ (4H) non-bonded (ppm)	NH ₂ (4H) bonded (ppm)	OH (1H) non-bonded (ppm)	OH (1H) bonded (ppm)
<i>o</i> -Phenylenediamine	6.6	3.2	—	—	—
<i>m</i> -Phenylenediamine	5.9	4.4	—	—	—
<i>p</i> -Phenylenediamine	6.5	3.1	—	—	—
Phenol	7.2-6.7	—	—	2.6	—
Hydroquinone	6.4	—	—	1.9	—
<i>o</i> -Phenylenediamine + phenol	6.7	—	4.0	—	1.2
<i>m</i> -Phenylenediamine + phenol	5.9	—	4.4	—	1.2
<i>p</i> -Phenylenediamine + phenol	6.5	—	3.7	—	1.3
<i>o</i> -Phenylenediamine + hydroquinone	6.7	—	2.8	3.5	1.8
<i>m</i> -Phenylenediamine + hydroquinone	7.2-6.4	—	3.2	—	0.9
<i>p</i> -Phenylenediamine + phenol	6.5	—	2.17	—	1.6

DISCUSSION

It is evident from the analysis of Figs. 1-6 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 the melting temperature of the complexes were determined from phase diagrams and are recorded in Table 4. The heat of fusion of the addition compound A_{v₁}, B_{v₂} formed between the species A and B can be estimated from the freezing curve between the two eutectic temperatures from the relation,

$$\frac{1}{T} = -\frac{R}{\Delta_f h} \ln (x_A)^{v_1} (x_B)^{v_2} + \frac{R}{\Delta_f h} \ln (x_A)_c^{v_1} (x_B)_c^{v_2} + \frac{1}{T_c} \quad (1)$$

where $\Delta_f h$ is the heat of fusion of the addition compound, T_c its melting temperature, x_A and $(x_A)_c$ are the mole fractions of the species at temperature T and T_c , v_1 and v_2 are the integers. The plots of $(1/T - 1/T_c)$ against $-\ln (x_A)^{v_1} (x_B)^{v_2}$ showed large scatter from linearity indicating that these mixtures are far from being ideal. The

TABLE 4

TYPE AND MELTING TEMPERATURE T_m OF THE COMPLEX

System	Type of complex	T_m (K)
<i>o</i> -Phenylenediamine + phenol	1/1	327.95
<i>o</i> -Phenylenediamine + hydroquinone	2/1	381.15
<i>m</i> -Phenylenediamine + phenol	1/1	325.95
<i>m</i> -Phenylenediamine + hydroquinone	1/1	401.15
<i>p</i> -Phenylenediamine + phenol	1/2	378.75
<i>p</i> -Phenylenediamine + hydroquinone	1/1	466.95

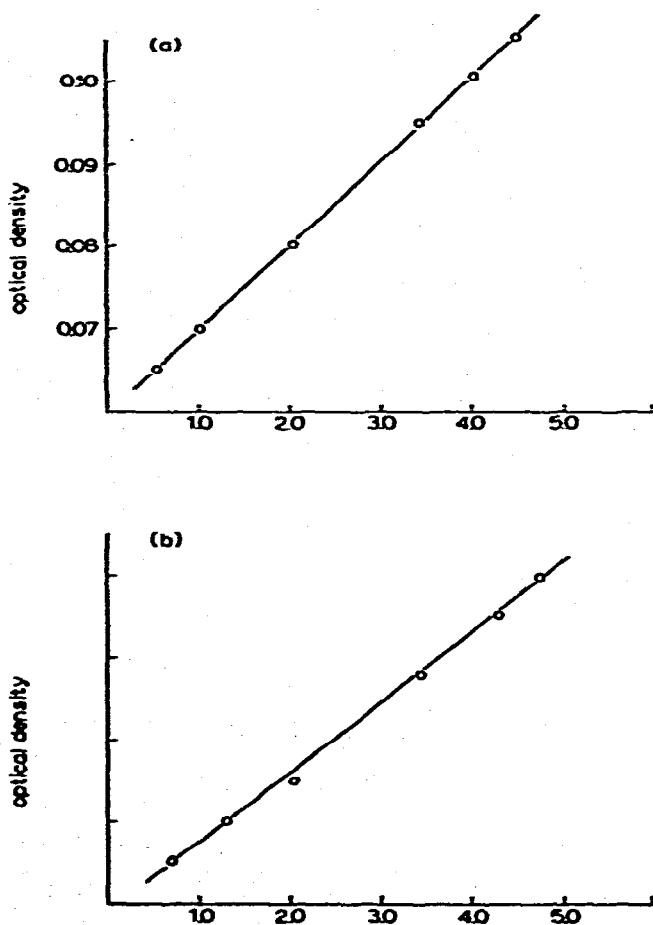


Fig. 7. Plots of optical density against concentration of *o*-phenylenediamine + phenol. (a) Concentration of phenol/ $\text{g mol l}^{-1} \times 10^6$. (b) Concentration of *o*-phenylenediamine/ $\text{g mol l}^{-1} \times 10^6$.

TABLE 5
TYPE OF COMPLEXES IN SOLUTION PHASE

System	Type of complex
<i>o</i> -Phenylenediamine + phenol	1/1
<i>o</i> -Phenylenediamine + hydroquinone	2/1
<i>m</i> -Phenylenediamine + phenol	1/1
<i>m</i> -Phenylenediamine + hydroquinone	1/1
<i>p</i> -Phenylenediamine + phenol	1/2
<i>p</i> -Phenylenediamine-phenol	1/2
<i>p</i> -Phenylenediamine + hydroquinone	2/1

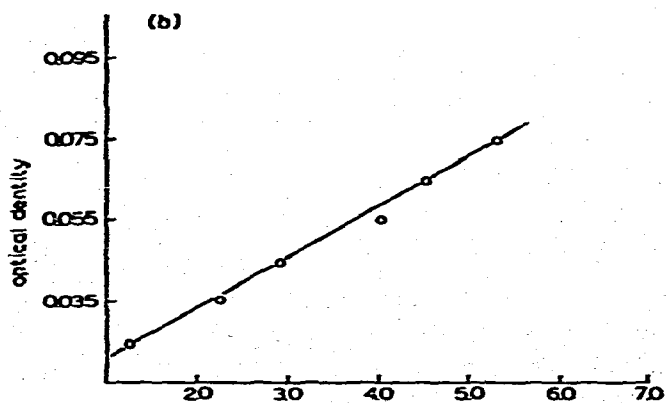
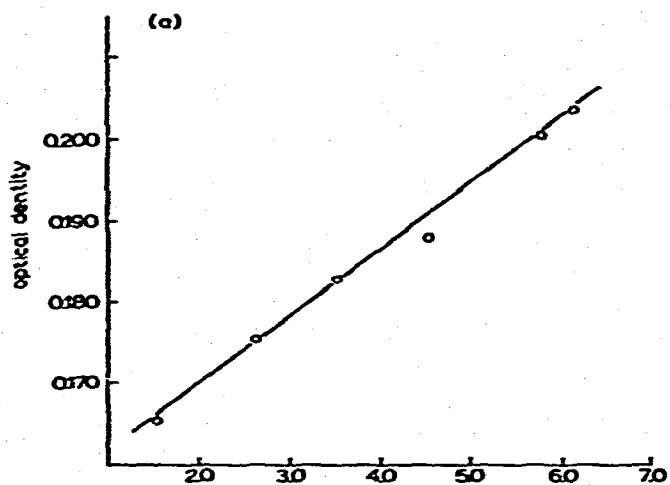


Fig. 8. Plots of optical density against concentration of phenol + *m*-phenylenediamine. (a) Concentration of phenol/ $\text{g mol l}^{-1} \times 10^2$. (b) Concentration of *m*-phenylenediamine/ $\text{g mol l}^{-1} \times 10^6$.

formation of the complex in these mixtures may be probably due to hydrogen bonding.

The nature of the complexes in solution phase was ascertained by the slope ratio method⁷.

In the reaction



If the concentration of B is constant and is in sufficient excess to make dissociation negligible, the equilibrium concentration of the complex $A_m B_n$ will essentially be proportional to the analytical concentration of A added in the reaction, so

$$E = \epsilon d C_A / m \quad (3)$$

where E is the measured extinction, ϵ the molecular extinction coefficient and d the

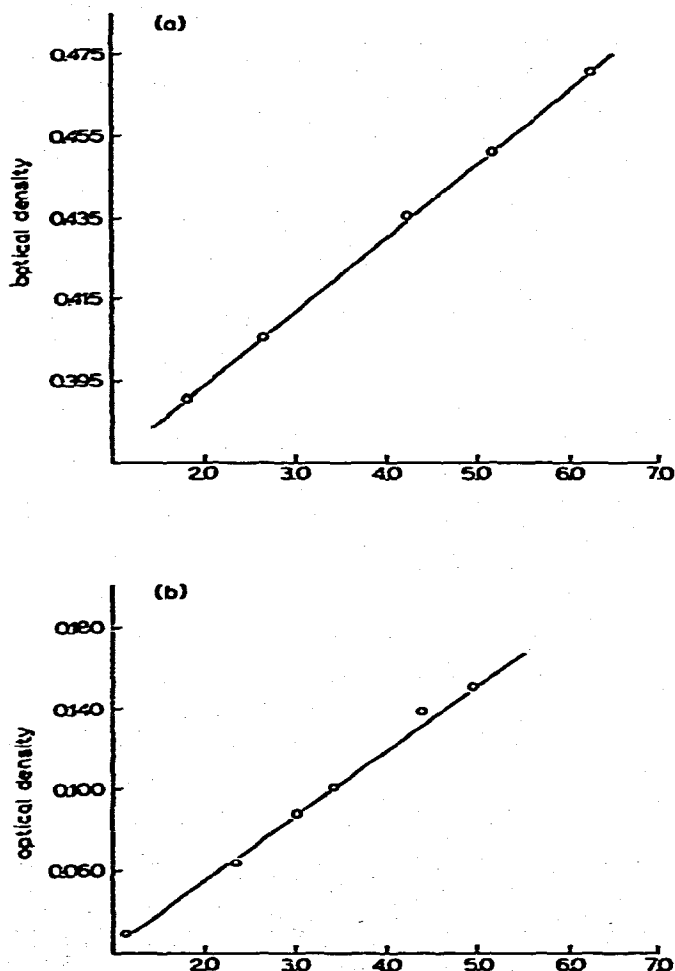


Fig. 9. Plots of optical density against concentration of phenol + *p*-phenylenediamine. (a) Concentration of phenol/ $\text{g mol l}^{-1} \times 10^6$. (b) Concentration of *p*-phenylenediamine/ $\text{g mol l}^{-1} \times 10^6$.

thickness of the cell in centimeters. If E is plotted against varying analytical concentrations of A, keeping the concentration of B constant and in excess, a linear plot is obtained whose slope is given by

$$\text{slope}_1 = \epsilon d/m \quad (4)$$

Similarly, when the concentration of A is kept constant and the concentration of B is varied, we get a slope

$$\text{slope}_2 = \epsilon d/n \quad (5)$$

The ratio of n to m in the complex may be determined by taking the ratio of the two slopes

$$\text{slope}_1/\text{slope}_2 = n/m \quad (6)$$

The slopes were determined by the method of least squares from Figs. 7-12 and the ratio of the slopes are recorded in Table 4.

It is clear from Table 4 that complexes, 1/1 complex in *o*-phenylenediamine+

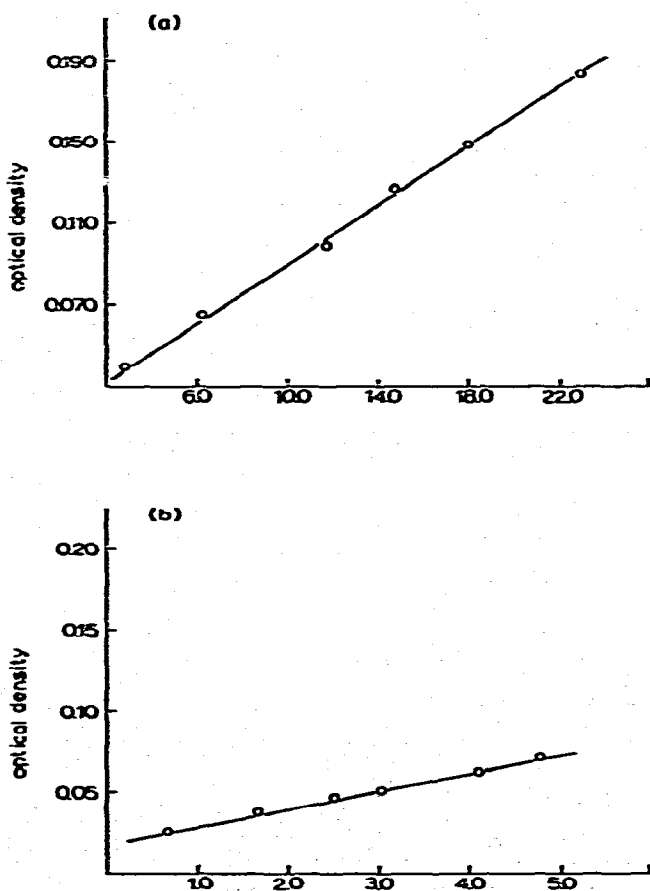


Fig. 10. Plots of optical density against concentration of *o*-phenylenediamine+hydroquinone. (a) Concentration of hydroquinone/ $\text{g mol l}^{-1} \times 10^5$. (b) Concentration of *o*-phenylenediamine/ $\text{g mol l}^{-1} \times 10^5$.

phenol, 1/1 complex in *m*-phenylenediamine + phenol, 1/2 complex in *p*-phenylenediamine + phenol, 1/2 complex in hydroquinone + *o*-phenylenediamine and 1/1 complex in *m*-phenylenediamine + hydroquinone, are formed which are in agreement with the results obtained from solid-liquid equilibria data.

In the case of *p*-phenylenediamine + hydroquinone the 2/1 complex is formed in solution phase and the 1/1 complex is formed in the solid phase.

It is expected that in *p*-phenylenediamine and hydroquinone the sandwich type compound may be formed with the overlap of benzene rings, and each -OH group covers one -NH₂ group of phenylenediamine with the result that the 1/1 complex is formed in the solid phase. While in the presence of solvent, this sandwich type structure is disturbed and the 2/1 complex is detected. It may be possible if each phenylenediamine attaches itself with one -OH group at the two ends.

Now we see these mixtures from NMR measurements. From Table 3 it is evident that ¹HNMR chemical shifts show a considerable change in the spectra of complexes in comparison with the spectra of pure compounds.

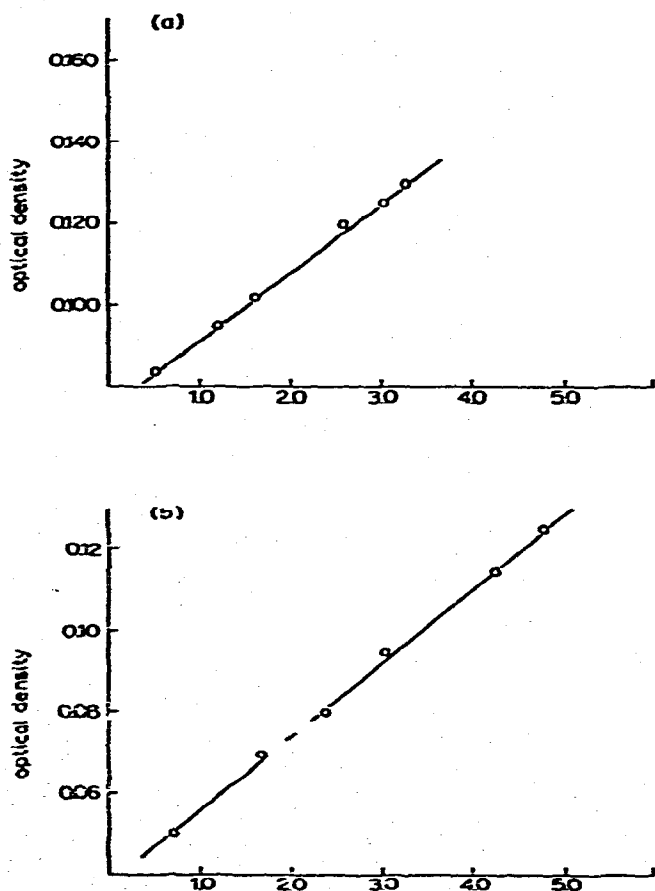
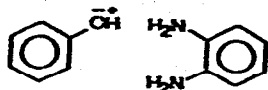


Fig. 11. Plots of optical density against concentration of hydroquinone + *m*-phenylenediamine. (a) Concentration of *m*-phenylenediamine/ $\text{g mol l}^{-1} \times 10^6$. (b) Concentration of hydroquinone/ $\text{g mol l}^{-1} \times 10^6$.

In *o*-phenylenediamine+phenol, the signal for proton ($-\text{OH}$) is at 1.2 ppm, while the signal for proton ($-\text{OH}$) in pure phenol is at 2.6 ppm. There is a shift of proton signal from lower field to higher field. The signal for proton ($-\text{NH}_2$) also changes in the complex from 3.2 ppm to 4.0 ppm. The shift of proton signal in ($-\text{OH}$) group to a higher field and the proton signal ($-\text{NH}_2$) to a lower field may be due to hydrogen bonding between the $-\text{NH}_2$ group of phenylenediamine and the $-\text{OH}$ group of phenol. The possible structure of the complex is given below.



In *m*-phenylenediamine+phenol, the proton signal of the $-\text{OH}$ group shifts from 2.6 ppm (phenol) to 1.2 ppm (complex) and the signal for proton ($-\text{NH}_2$) changes from 3.4 ppm (*m*-phenylenediamine) to 4.0 ppm (in complex). These shifts

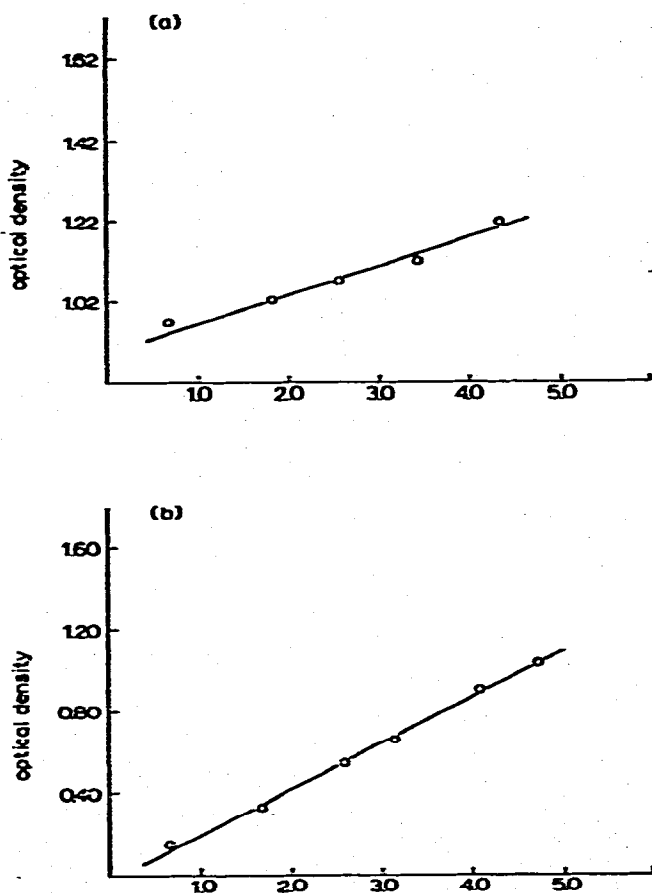
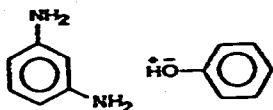
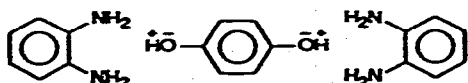


Fig. 12. Plots of optical density against concentration of hydroquinone+*p*-phenylenediamine. (a) Concentration of *p*-phenylenediamine- $\text{g mol l}^{-1} \times 10^6$. (b) Concentration of hydroquinone/ $\text{g mol l}^{-1} \times 10^6$.

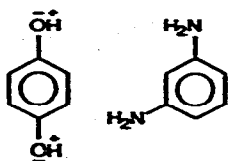
of signals may be due to hydrogen bonding between the $-NH_2$ group of phenylenediamine and the $-OH$ group of phenol. The possible structure of the complex is given below.



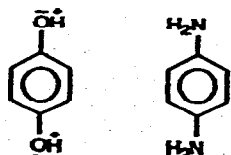
In *o*-phenylenediamine+hydroquinone, the signal for proton ($-OH$) shifts from 1.9 ppm (hydroquinone) to 1.8 ppm (complex) and the signal for proton ($-OH$) non-bounded is observed at 3.5 ppm. The signal for proton ($-NH_2$) changes from 3.2 ppm (*o*-phenylenediamine) to 2.8 ppm (complex). These shifts of signal for proton to a higher field may be due to hydrogen bonding between the $-NH_2$ group of phenylenediamine and the $-OH$ group of hydroquinone. From phase diagrams the formula of the complex was obtained to be 2/1. Hence, the possible structure of the complex is given below.



In *m*-phenylenediamine+hydroquinone, the signal for the proton ($-OH$) shifts from 1.9 ppm (hydroquinone) to 0.95 ppm (complex) and the signal for the proton ($-NH_2$) also changes from 3.4 ppm (*m*-phenylenediamine) to 3.2 ppm (complex). These shifts of proton signals to a higher field may be due to hydrogen bonding between the $-NH_2$ group of phenylenediamine and the $-OH$ group of hydroquinone. The possible structure is shown below.



In *p*-phenylenediamine+hydroquinone, the signal for the proton ($-OH$) shifts from 1.9 ppm (hydroquinone) to 1.6 ppm (complex) and the signal for the proton ($-NH_2$) also varies from 3.1 ppm (*p*-phenylenediamine) to 2.17 ppm in the complex. These shifts of proton signals to a higher field may be due to hydrogen bonding between the $-NH_2$ group of phenylenediamine and the $-OH$ group of hydroquinone. The possible structure of the complex is given below:



REFERENCES

- 1 M. S. Dhillon, *J. Chem. Thermodyn.*, 7 (1975) 1085.
- 2 M. S. Dhillon and S. P. Singh, *Thermochim. Acta*, 15 (1975) 555.
- 3 L. Prigogine and R. Defay, *Chemical Thermodynamics*, Longmans-Green, London, 1954.
- 4 H. F. Harvey and Dehwer, *J. Am. Chem. Soc.*, 72 (1950) 4488.
- 5 H. E. Bent and C. L. French, *J. Am. Chem. Soc.*, 63 (1941) 56.
- 6 H. F. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, 72 (1950) 1488.
- 7 W. C. Vosburg and G. R. Cooper, *J. Am. Chem. Soc.*, 63 (1941) 437.
- 8 J. Timmermans, *Physico-chemical Constants of Pure Organic Liquids*, Elsevier, New York, 1950.
- 9 R. C. Weast, *Handbook of Chemistry and Physics*, The Chemical Rubber Co., Cleveland, Ohio, 1972.
- 10 R. P. Rastogi and R. K. Nigam, *Proc. Nat. Inst. Sci.*, 26 (1960) 184.
- 11 R. P. Rastogi and R. K. Nigam, *Trans. Faraday Soc.*, 55 (1959) 2005.