

PHASE-DIAGRAMS AND ORGANIC MOLECULAR COMPLEXES

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Phase-diagrams for the mixtures *m*-nitraniline-*o*-phenylenediamine, *m*-dinitrobenzene-*o*-phenylenediamine, *m*-nitraniline-*m*-dinitrobenzene and *o*-phenylenediamine-*p*-nitraniline have been studied by thaw-melt method with the hope that the phase-diagram would belong to either congruent melting point or incongruent melting point type. The result showed that all these mixtures are eutectic in nature. The reason for this non-existence of complexes has been accounted on the basis of charge transfer theory of complexes. Phase-diagrams have been subjected to thermodynamic analysis and the problem is examined in the light of intermolecular forces in terms of the parameters δ and θ which are due to Prigogine.

INTRODUCTION

The formation of organic molecular complexes (Bennett and Wills 1929) by means of electronic theory of valency follows at once in many cases from Sidgwick's (1923) interpretation of Werner's theory. A number of different organic substances cannot be simply represented as having their constituent molecules united by means of molecular rather than atomic forces; the union is in fact attributed to the action of the fields of the residual valency of either molecules or group of atoms (Pfeiffer 1927). The large group of complexes formed by the union of benzoquinone or its substituted derivatives with aromatic hydrocarbons, amines and phenols have developed from the study of similar groups known as quinhedrons. The formation of complexes between amines and hydrocarbons suggests that quinones are the acceptor components in these molecular compounds. This is in agreement with the fact that the introduction of halogens into the nucleus of the quinones enhances its power of forming such compounds and the depth of the coloured products. The polar effect of halogen will facilitate their acceptance of electron and would oppose their donation.

An important group of organic molecular compound results from the union of nitro compounds on the one hand with various amines, aromatic

hydrocarbons or their derivatives on the other. The most stable and numerous of these are formed from bases. Moreover, the union of nitro compounds with bases is clearly analogous to the combination of acid and base. Kermann has in fact called amines and hydrocarbons heteropolar with respect to nitro compound. That the nitro group is involved in the complex formation follows, as Werner showed, from the formation of similar compounds by tetranitromethane.

Bennett and Wain (1936) have pointed out that in the large classes of complexes, formed between polynitro compounds on the one hand and bases or the aromatic hydrocarbons on the other, the relation between the two components must be that of acceptor and donor molecules respectively.

From the above review on the nature of the formation of complexes between organic compounds, one could expect the formation of complexes between nitro compounds and amino compounds much more effectively. With this point in view phase-diagrams of *m*-nitraniline-*o*-phenylenediamine, *m*-dinitrobenzene-*o*-phenylenediamine, *m*-nitraniline-*m*-dinitrobenzene and *p*-nitraniline-*o*-phenylenediamine were studied with the hope that phase-diagrams would show congruent or incongruent melting points and would prove the formation of compounds between the components selected.

2. EXPERIMENTAL STUDY

Materials and their purity.—*m*-nitraniline (A.R.), *o*-phenylenediamine (E. Merck), *m*-dinitrobenzene (A.R.) and *p*-nitraniline (A.R.) were used without further purification as their melting points agreed within $\pm 0.1^\circ\text{C}$.

		Melting point, $^\circ\text{C}$ (present work)	Melting point, $^\circ\text{C}$ (Rodd 1956)
<i>m</i> -nitraniline	..	113.9	114.0
<i>p</i> -nitraniline	..	147.0	147.0
<i>m</i> -dinitrobenzene	..	90.1	90.0
<i>o</i> -phenylenediamine	..	102.0	102.0

Determination of phase-diagrams.—Phase-diagrams were determined in the manner discussed earlier (Rastogi and Nigam 1960).

RESULTS

TABLE I

*Solid-liquid equilibrium data for the mixtures
m-nitraniline-o-phenylenediamine*

Mole- fraction of <i>m</i> -nitraniline	Thaw-point °C	Melting point °C
0.0000	—	102.0
0.0935	77.2	98.8
0.2029	77.2	91.4
0.2985	77.2	85.4
0.3905	77.2	81.1
0.5049	77.2	80.9
0.5859	77.2	94.7
0.6984	77.2	94.8
0.7930	77.2	101.5
0.8973	77.2	107.9
1.0000	—	113.9

TABLE II

*Solid-liquid equilibrium data for the
mixtures m-dinitrobenzene-o-
phenylenediamine*

Mole- fraction of <i>m</i> -dinitro- benzene	Thaw-point °C	Melting point °C
0.0000	—	102.0
0.1005	56.2	95.4
0.2021	56.2	91.3
0.3026	56.2	83.0
0.3961	56.2	73.9
0.4987	56.2	65.9
0.5964	56.2	60.9
0.6708	56.2	65.8
0.7791	56.2	76.5
0.9105	56.2	83.4
1.0000	—	90.1

DISCUSSION

From the phase-diagrams as shown in Figs. 1-4, it is evident that no addition compound is formed between the mixtures studied here. They

TABLE III

*Solid-liquid equilibrium data for the mixtures
m-nitraniline-m-dinitrobenzene*

Mole- fraction of <i>m</i> -nitraniline	Thaw-point °C	Melting point °C
0.0000	—	90.1
0.1071	59.3	83.7
0.2008	59.3	77.1
0.3056	59.3	67.1
0.3992	59.3	67.1
0.5090	59.3	79.9
0.5971	59.3	85.4
0.6911	59.3	93.8
0.7995	59.3	101.7
0.8997	59.3	107.1
1.0000	—	113.9

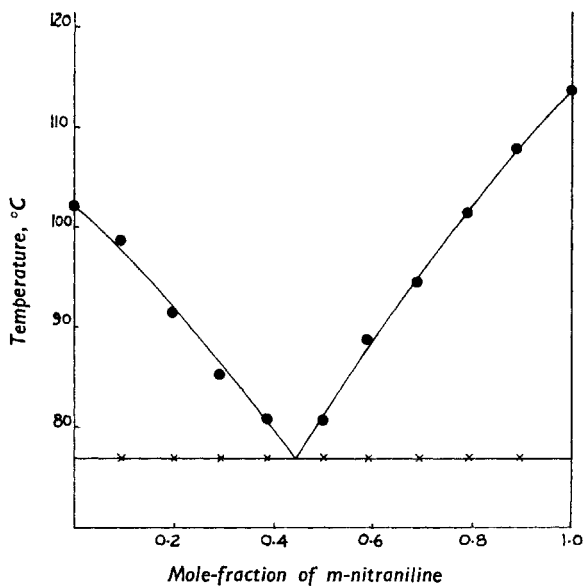
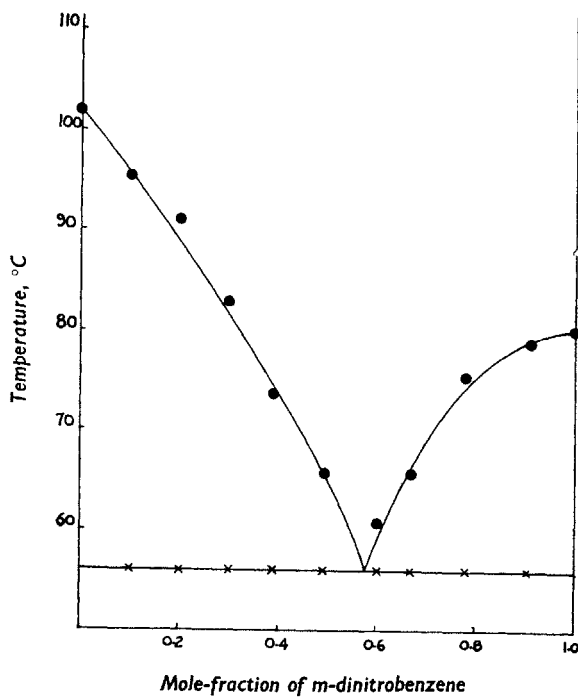
TABLE IV

*Solid-liquid equilibrium data for the mixtures
p-nitraniline-o-phenylenediamine*

Mole- fraction of <i>p</i> -nitraniline	Thaw-point °C	Melting point °C
0.0000	—	102.0
0.1025	84.3	98.4
0.1995	84.3	91.9
0.2997	84.3	87.3
0.4071	84.3	96.5
0.4987	84.3	107.6
0.5916	84.3	115.8
0.6966	84.3	129.2
0.7915	84.3	136.1
0.8995	84.3	143.7
1.0000	—	147.0

are simply eutectic type diagrams which is rather surprising. The reason for such a surprise could be given in the following manner.

It seems that charge transfer forces are mainly operative in the cases we have studied here. Mixtures containing one component having amine and the other as nitro compound or the keto compound, it is known that the electron attracting groups such as $-\text{NO}_2$, $-\text{Cl}$ or $-\text{COOCH}_3$ in the ring of nitro compounds promote the electronic drift by reducing the negative charge on the nitro

FIG. 1. Phase-diagram of *m*-nitraniline + *o*-phenylenediamine.FIG. 2. Phase-diagram of *m*-dinitrobenzene + *o*-phenylenediamine.

group, on the other hand electron repelling groups such as $-\text{NH}_2$ or $-\text{CH}_3$ in the ring of nitro compounds reduce its ability to polarize the amino compound

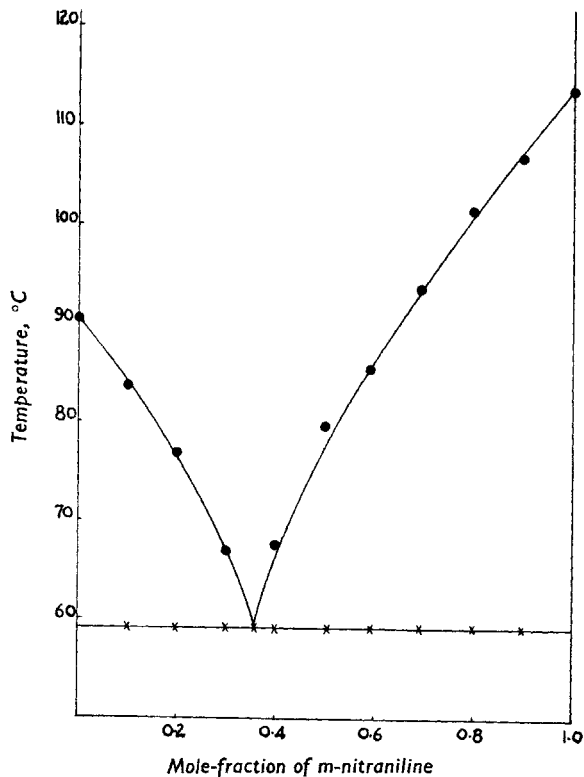
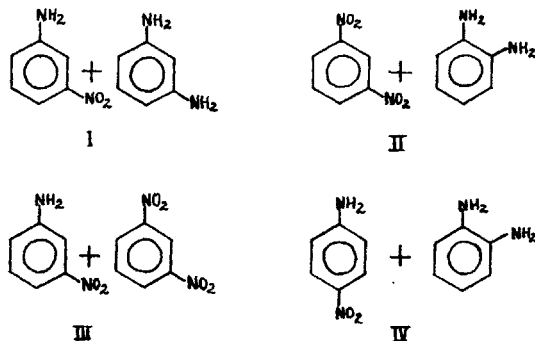


FIG. 3. Phase-diagram of *m*-nitraniline + *m*-dinitrobenzene.



both by their inductive effect and by their resonance effect. It appears, therefore, that there is a drift of electronic charge from the $-\text{NH}_2$ group to oxygen of $-\text{NO}_2$ with the consequent displacement of negative charge in N:O bond and in the polarizable aromatic nuclei when these groups come very close together in the solution.

In mixtures (I), (III) and (IV) the complex compounds are not formed on account of the simultaneous presence of $-\text{NH}_2$ and $-\text{NO}_2$ group in the first species. The non-existence of complex in (II) mixture is rather difficult to explain.

This aspect of the non-existence of complexes in the mixtures studied here could be explained with the help of Prigogine's parameter θ and δ relating to the intermolecular forces in the mixtures (Prigogine 1957); by assuming spherical field of forces which interact according to (6-12) interaction law.

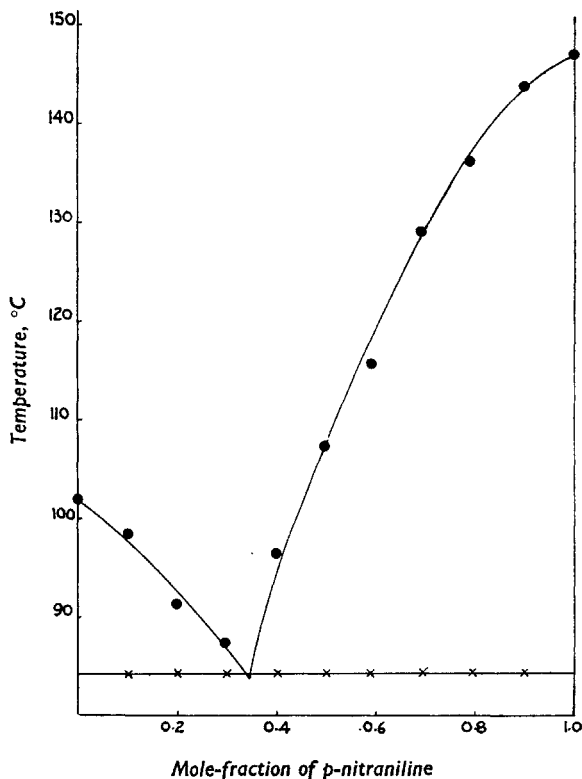


FIG. 4. Phase-diagram of *p*-nitraniline + *o*-phenylenediamine.

If we define the quantities δ , θ given by

$$\delta = \frac{1}{\epsilon_{AA}^*} [\epsilon_{BB}^* - \epsilon_{AA}^*] \text{ or } \epsilon_{BB}^* = \epsilon_{AA}^* (1 + \delta) \quad \dots \quad (1)$$

$$\theta = \frac{1}{\epsilon_{AA}^*} [\epsilon_{AB}^* - \frac{1}{2}(\epsilon_{AA}^* + \epsilon_{BB}^*)] \quad \dots \quad (2)$$

ϵ^* is the scale factor which depends on the pair energies AA , BB and AB .

The interaction between unlike spherical non-polar molecules to a good approximation is provided by the combining rule

$$\epsilon_{AB}^* = (\epsilon_{AA}^* \epsilon_{BB}^*)^{\frac{1}{2}}. \quad \dots \quad \dots \quad \dots \quad (3)$$

If we neglect higher order terms in δ which then corresponds to

$$\theta = -\frac{\delta^2}{8}. \quad \dots \quad \dots \quad \dots \quad (4)$$

When arithmetic mean law is applicable

$$\epsilon_{AB}^* = \frac{1}{2}(\epsilon_{AA}^* + \epsilon_{BB}^*). \quad \dots \quad \dots \quad \dots \quad (5)$$

The difference between eqns. (4) and (5) is generally rather small. Indeed the combining rule may be partly justified by the London theory of dispersion forces. If the interaction of pure substances ϵ_{AA}^* , ϵ_{BB}^* is of the same order of magnitude, while the interaction ϵ_{AB}^* differs markedly from the preceding one, we obtain from eqns. (1) and (2)

$$\delta = 0; \theta > 0.$$

This case corresponds to the case of a formation of addition compound. The values of ϵ^* were calculated for the like pairs of molecules in the mixtures by using the relation $\epsilon^* = 1.92 kT_m$ (Rastogi and Girdhar 1962) where k is the Boltzmann constant and T_m is the melting point of the pure compound. The ϵ_{AB}^* were calculated by using the combining rule, given in eqn. (3) (Prigogine 1957). The values so obtained are tabulated below for the mixtures studied.

Name of the mixture	$\epsilon_{AA}^* \times 10^{16}$ ergs	$\epsilon_{BB}^* \times 10^{16}$ ergs	$\epsilon_{AB}^* \times 10^{16}$ ergs	θ	δ
<i>m</i> -nitraniline- <i>o</i> -phenylenediamine	301.8	270.3	297.6	0.585	-0.11
<i>m</i> -dinitrobenzene- <i>o</i> -phenylenediamine	238.7	270.3	254.9	0.699	0.132
<i>m</i> -nitraniline- <i>m</i> -dinitrobenzene	301.8	238.7	268.4	0.598	-0.21
<i>p</i> -nitraniline- <i>o</i> -phenylenediamine	389.5	270.3	324.4	0.642	-0.31

From the table it is evident that the values of ϵ_{AB}^* are not very much different from ϵ_{AA}^* and ϵ_{BB}^* and the condition for the formation of addition compounds, i.e. $\theta > 0$; $\delta = 0$, is not obtained and hence no complex should be formed between the mixtures studied here. This is in agreement with our findings as the phase-diagrams are eutectic in nature.

Thermodynamic analysis of the phase-diagrams for the mixtures studied was made. For the equilibrium of solid and liquid phase in such a mixture

(Prigogine and Defay 1954), we have

$$-ln x_i^l \gamma_i^l = \frac{\Delta_f h_i^0}{R} \left(\frac{1}{T} - \frac{1}{T_i^0} \right) \quad (i = 1, 2) \quad \dots \quad (6)$$

where the pure component i separates. The terms x_i^l , γ_i^l , $\Delta_f h_i^0$ and T_i^0 are the mole-fraction, activity coefficient, heat of fusion and melting point of the component i , respectively. Thus γ_i^l can be calculated from the phase-diagram for different temperatures and compositions. Heat of fusion values for all the compounds in the mixtures, except that of *o*-phenylenediamine, were taken from International Critical Tables (1929). For *o*-phenylenediamine, $\Delta_f h_i^0$, was calculated from its entropy of fusion by taking it as 18 cal mole⁻¹ deg⁻¹ and was found to be 1836 cal mole⁻¹. All the mixtures on such an analysis were found to behave ideally. If the mixtures behave ideally, the eutectic temperature T_e and eutectic composition $(x_1^l)_e$ could be shown readily from equation (6) to be

$$1 = \exp \left[\frac{-\Delta_f h_1^0}{R} \left(\frac{1}{T_e} - \frac{1}{T_1^0} \right) \right] + \exp \left[\frac{-\Delta_f h_2^0}{R} \left(\frac{1}{T_e} - \frac{1}{T_2^0} \right) \right] \quad \dots \quad (7)$$

$$\frac{(x_1^l)_e \exp [1/\Delta_f h_1^0]}{[1 - (x_1^l)_e] 1/\Delta_f h_2^0} = \exp \left[\frac{1}{R} \left(\frac{1}{T_2^0} - \frac{1}{T_1^0} \right) \right] \quad \dots \quad (8)$$

The eutectic temperatures and compositions, calculated in this manner from eqns. (7) and (8), compared well with the experimental values as is clear from the following table:

Name of the mixtures	T_e °C		$(x_1^l)_e$		
	Calc.	Exptl.	Calc.	Exptl.	
<i>m</i> -nitraniline- <i>o</i> -phenylenediamine	77.2	77.2	0.46	0.47
<i>m</i> -dinitrobenzene- <i>o</i> -phenylenediamine	56.2	56.2	0.55	0.57
<i>m</i> -nitraniline- <i>m</i> -dinitrobenzene	54.3	54.3	0.32	0.32
<i>o</i> -phenylenediamine- <i>p</i> -nitraniline	84.3	84.3	0.34	0.34

It is rather surprising that the components of the mixtures, which were expected to form addition compounds, behaved ideally. It could be concluded that compounds having $-\text{NO}_2$ groups in one of the component in the mixtures and $-\text{NH}_2$ group in the other component might not give rise to the formation of addition compounds between them, which is normally expected at the first glance.

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