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CALORIMETRIC STUDIES OF BINARY SYSTEMS OF 1,3,5-TRINITROBENZENE WITH NAPHTHALENE, ANTHRACENE AND CARBAZOLE. II. PHASE DIAGRAMS

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ABSTRACT

The phase diagrams of the binary systems of 1,3,5-trinitrobenzene (TNB) with naphthalene, anthracene and carbazole have been determined by differential scanning calorimetry and optical microscopy over the temperature range 180 K to just above the melting point. All systems show the same features: (i) systems form nearly ideal double simple-eutectic type phase diagrams with 1 : 1 complex, (ii) each one of three known modifications of TNB may exist as a component of the complex—TNB eutectic mixtures, (iii) measured liquidus lines of complexes agree within experimental error with those calculated by the Vieland equation for a completely dissociated complex in the liquid phase, whereas the experimental liquidus lines for the parent components deviate slightly from those predicted by the Schröder—van Laar equation, indicating some degree of complexing in the liquid phase.

The solubility parameter theory has been used to clarify this discrepancy. Applying this theory to the liquidus lines of complexes, we have found that these TNB complexes are still stable upon fusion, and an approximate degree of dissociation amounted to 90% at the melting point in all three cases.

The enthalpy of complex formation, ΔH^0, both in the liquid and solid state has been determined. The values of ΔH^0 show that in the solid state the carbazole—TNB complex is the most stable, and the naphthalene—TNB complex is the least stable.

INTRODUCTION

In Part I of this work [1] the results of measurements of some thermodynamic properties for the pure components and complexes in the binary systems of 1,3,5-trinitrobenzene (TNB) with naphthalene (NAP), anthracene (ANT) and carbazole (CAR) are reported. The melting, solid—solid phase transitions, and the stability of complexes in the solid state are also discussed.

This work presents the revision of the phase diagrams of binary systems of TNB with three selected donors, as well as an attempt to estimate the complex stability in the fused state.

Most investigations of complex formation have been concerned with reactions in some more or less inert solvent; few data referred to the gaseous

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phase, but investigations of binary mixtures of donor (D) and acceptor (A) over the entire composition range from pure A to pure D are much less common. In the present study we have applied the solubility parameter theory [2] for the evaluation of equilibrium constants from the data of phase diagrams.

EXPERIMENTAL

The components of binary systems were purified as described previously [1].

Alloys between two components were prepared by weighing appropriate amounts of zone-refined components into glass ampoules. The ampoules were then sealed under vacuum; in order to avoid the evaporation of naphthalene, the ampoules were held in liquid nitrogen. After sealing, the materials were melted, vigorously stirred, rapidly cooled to room temperature and then ground. The overall mole fractions were known to ±0.0002.

Preparation of the molecular complexes and the eutectic mixtures has been described previously [1]. Sample masses for the phase diagram measurements were in the range 5—10 mg. The phase diagrams were studied using a Perkin-Elmer DSC-1B differential scanning calorimeter. The results of calorimetric measurements were additionally tested by microscopic observations.

The positions of the lines on the phase diagrams were determined from the thermograms recorded at four heating rates: 4, 2, 1 and 0.5 K min^{-1} for samples sealed in a vapour-tight aluminium pan. For each sample the temperatures of the onset and termination of melting were plotted against the square root of scan rate and extrapolated to zero heating rate. All the lines on the phase diagrams, therefore, are quoted for zero heating rate.

PHASE DIAGRAMS

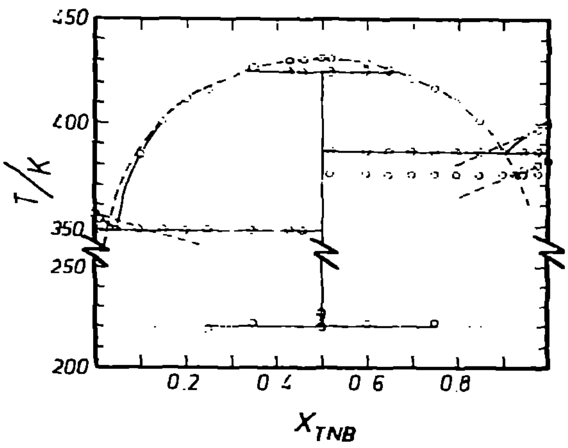
The phase diagrams of binary combinations of TNB with all used donors are shown in Figs. 1—3, together with the calculated liquidus lines. The liquidus lines of the pure components were calculated using the Schröder—van Laar equation

$$-RT \ln x_i = \Delta H_{\mathrm{f},i} - T\Delta S_{\mathrm{f},i} \qquad i = 1, 2 \tag{1}$$

and the liquidus lines of the complexes were calculated using the Vieland equation adopted for a 1 : 1 addition compound

$$-RT \ln \frac{x_i(1 - x_i)}{x_{i,\mathrm{AD}}(1 - x_{i,\mathrm{AD}})} = \Delta H_{\mathrm{f,AD}} - T\Delta S_{\mathrm{f,AD}} \tag{2}$$

where x_i = the mole fraction of component i at temperature T in the binary liquid along the liquidus line; $x_{i,\mathrm{AD}}$ = the mole fraction of component i in the hypothetical liquid at the complex composition; $x_{i,\mathrm{AD}} = 0.5$ in the case of a 1 : 1 complex; $\Delta H_{\mathrm{f},i}$ and $\Delta S_{\mathrm{f},i}$ = the enthalpy and entropy of fusion at the



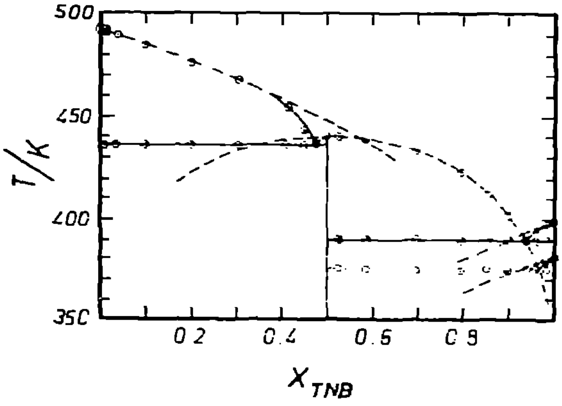


Fig. 1. The naphthalene—1,3,5-trinitrobenzene phase diagram. ———, · · · · · ·, Experimental lines; - - - - - -, lines calculated from eqns. (1) and (2).

Fig. 2. The anthracene—1,3,5-trinitrobenzene phase diagram. ———, · · · · · ·, Experimental lines, - - - - - -, lines calculated from eqns. (1) and (2).

melting point of the pure component; $\Delta H_{f,AD}$ and $\Delta S_{f,AD}$ = the enthalpy and entropy of fusion at the melting point of the complex.

If there is a transition in the solid state, eqns. (1) and (2) are valid only in the region $T_t < T < T_f$, where T_t and T_f are the transition and fusion temperature, respectively. In the region $T < T_t$, the term $\Delta H_{t,i} - T\Delta S_{t,i}$ or $\Delta H_{t,AD} - T\Delta S_{t,AD}$ were added to the right-hand sides of eqn. (1) or (2), respectively, where ΔH_t and ΔS_t are the enthalpy and entropy of transition.

We found that all those systems form "double simple-eutectic" type phase diagrams, which are consonant with the results reported by Kremann et al. [3—5], although there are small differences between our values of eutectic temperatures and compositions and those reported by Kremann (see Table 1).

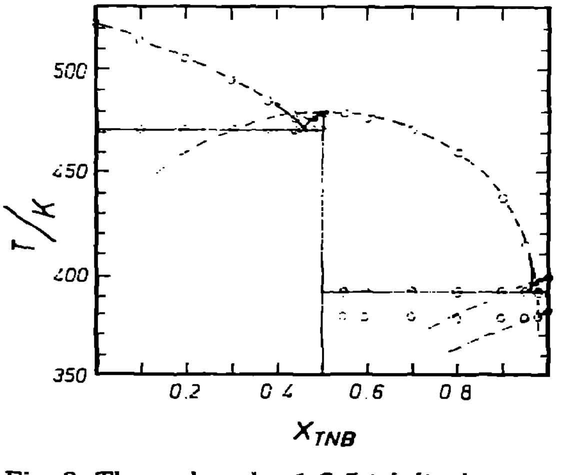


Fig. 3. The carbazole—1,3,5-trinitrobenzene phase diagram. ———, · · · · · ·, Experimental lines; - - - - - -, lines calculated from eqns. (1) and (2).

TABLE 1

Eutectic temperatures and compositions in binary systems of 1,3,5-trinitrobenzene (TNB) with naphthalene (NAP), anthracene (ANT) and carbazole (CAR)

Eutectic formula	Eutectic temp. (K)		Eutectic composition mole fraction of TNB	
	This work	Refs. 3—5	This work	Refs. 3—5
NAP + 1 : 1 NAP—TNB	348.5	350.2	0.05	0.07
1 : 1 NAP—TNB + TNB I	386.5	387.5	0.91	0.88
1 : 1 NAP—TNB + TNB II	375.0		0.93	
ANT + 1 : 1 ANT—TNB	437.0	435.2	0.485	0.445
1 : 1 ANT—TNB + TNB I	390.0	385.2	0.94	0.952
1 : 1 ANT—TNB + TNB II	375.5		0.96	
CAR + 1 : 1 CAR—TNB	471.0	468.2	0.46	0.382
1 : 1 CAR—TNB + TNB I	391.5	393.2	0.97	0.968
1 : 1 CAR—TNB + TNB II	378.5		0.98	

The essential disagreement between our and Kremann's results concerns the right-hand side of the phase diagrams, i.e. the region 0.5—1.0 mole fraction of TNB. The thermograms of samples in powder form, as well as those in frozen melt form, held for 1—2 months at room temperature displayed higher eutectic temperatures, as shown in Figs. 1--3. The DSC traces of freshly frozen samples revealed lower eutectic temperatures. Occasionally both eutectic melting peaks were observed.

It is well known that in some cases the eutectic mixture can be formed by the unstable solid phases of the components and remain in the metastable state for several months.

Two different eutectic lines in the composition range 0.5—1.0 mole fraction of TNB have been observed in all three systems under consideration. We think this phenomenon is associated with two modifications of TNB: stable I as a component of the higher melting eutectic and metastable II as a component of the lower melting eutectic (solid and dotted lines in Figs. 1, 2 and 3, respectively). Only one phase diagram of the complex—TNB systems has been reported by Kremann et al. [3—5], namely, that corresponding to the stable modification I of TNB. The eutectic temperatures and composition data are collected in Table 1.

The phase transitions in the solid state of pure components and complexes were also observed in two-phase mixtures. Both phase transitions in the NAP—TNB complex, viz. at 220 and 424.5 K [1], were observed as expected, i.e. the transition peak area decreased with decreasing complex concentration.

As mentioned above [1], the thermograms did not reveal the phase transition at 420 K reported by Robinson and Scott [6] in pure carbazole. For this reason this transition is not marked in Fig. 3, which shows the phase diagram deduced from thermograms and microscopic observations.

The phase transition TNB II → TNB III was occasionally observed within the composition range 0.5—1.0 mole fraction of TNB in all three systems.

When this transition occurred the eutectic temperatures were slightly different to those noted in Table 1. We suppose that modification III of TNB, similar to I and II, can also form the eutectic mixtures with complexes. Since the transition TNB II → TNB III was observed only exceptionally and rather accidentally, the third-type phase diagrams related to modification III of TNB are not noted in Figs. 1—3.

A comparison of the calculated and measured liquidus lines indicates that the binary systems of TNB with used donors reveal small but significant deviations from ideality. Seeking an explanation of these deviations, one should discuss the following assumptions, basic to the derivation of the Schröder—van Laar and Vieland equations:

(1) the two components of the eutectic system crystallize in pure form and do not form mixed crystals;

(2) the enthalpies of fusion of the components are independent of temperature. This is equivalent to the assumption that the difference in the heat capacities of the solid and liquid phases of the components is zero;

(3) the complex (addition compound) exists in the solid state only; in the liquid phase the complex is completely dissociated into the two parent components;

(4) the liquid phase is an ideal solution phase; this means that in the liquid phase the activity coefficients equal unity.

We have tested the validity of the above assumptions in the investigated systems in a systematic manner. In order to test the first assumption we applied the eutectic arrest method for evaluation of the mutual solubility of the components and complexes. The molar enthalpy of fusion of the eutectic portion of the samples is plotted vs. composition in Fig. 4.

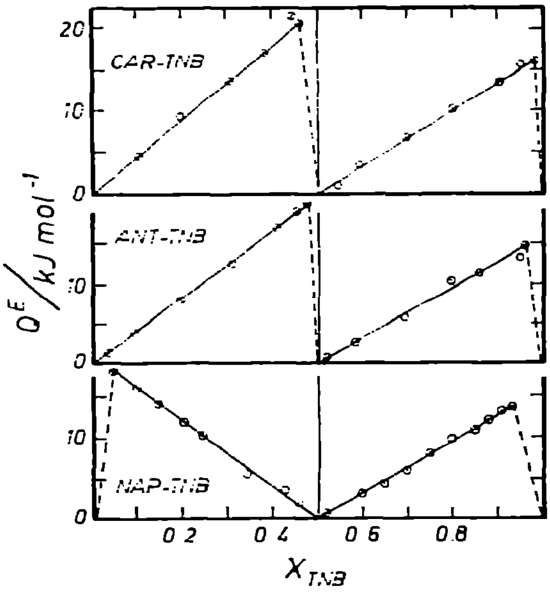


Fig. 4. The molar enthalpy of fusion of the eutectic portion of the alloys Q^E in the naphthalene—1,3,5-trinitrobenzene (NAP—TNB), anthracene—1,3,5-trinitrobenzene (ANT—TNB) and carbazole—1,3,5-trinitrobenzene (CAR—TNB) systems as a function of composition. The data correspond to the lower eutectic temperatures.

It seems that the systems under discussion show the occurrence of the double eutectic without remarkable forming of mixed crystals and the solubility in the solid phase is not greater than that limited by the defects.

It should be noted here, however, that there is a possibility of growing single crystals of the complexes with excess of component. For example, we have grown the single crystals of the ANT—TNB complex containing the excess 3 m.p.c. of anthracene by the vapour growth method described previously [7]. The single crystals were transparent, stable and of good quality, as revealed by X-ray measurements. However, the thermograms of the ground sample displayed the existence of a eutectic melting peak. Similar behaviour has been observed previously [7] in the anthracene—acridine system.

We think the special conditions which are employed during single crystal growth procedures are able "to constrain" the formation of a relatively stable phase beyond the region of its thermodynamical stability. The facility of formation of the metastable phase seems to be the feature of the organic molecular crystals under consideration.

To determine a consequence of the second assumption we have calculated the liquidus lines of anthracene and naphthalene using the following equation

$$-RT \ln x_i = \Delta H_{\mathrm{f},i} - T\Delta S_{\mathrm{f},i} + [C_{\mathrm{p},i}(\mathrm{l}) - C_{\mathrm{p},i}(\mathrm{s})]\left[T \ln \frac{T_{\mathrm{f},i}}{T} + T - T_{\mathrm{f},i}\right] \qquad (3)$$

where $C_{\mathrm{p},i}(\mathrm{l})$ and $C_{\mathrm{p},i}(\mathrm{s})$ are the heat capacities of liquid and solid phase of component, respectively, and using the heat capacity data for naphthalene [8] and anthracene [9]. The liquidus lines calculated by eqn. (3) were not far removed from those resulting from eqn. (1), the difference being about 0.3% for anthracene and 0.5% for naphthalene. Taking into account that the heat capacity of the complex is nearly equal to the sum of the heat capacities of the components, we suppose that the changes in the position of the liquidus lines for complexes are not much greater than those noted for anthracene and naphthalene. For these reasons we assume that the greatest deviations from ideality are caused by unfulfilment of the third and fourth assumptions.

It is well known that if the two components of a binary system form an addition compound in both the liquid and the solid state, then the melting point—composition curve shows a maximum at the stoichiometric point of the compound, and that the curvature of this line is related to the dissociation constant of the addition compound in the liquid. The liquidus lines of TNB complexes calculated using eqn. (2) are found to agree, within experimental error, with those measured (see Figs. 1—3). This result could indicate that the complexes used here completely dissociate upon melting. However, with such a conclusion there is inconsistency with analysis of the departure of the liquidus lines for pure components as well as with the fact that the melted complexes are coloured.

Inspection of Figs. 2 and 3 shows that the departure of the measured liquidus lines of the pure donors from those calculated shows some degree of complexing, particularly for anthracene. We have attempted to explain this contradiction by use of the solubility parameter theory [2].

For these systems in which complex formation takes place, it is often convenient to divide the deviation from ideal solution behaviour into "physical" and "chemical" contributions. The latter are due to the complex formation, the former arise from the non-specific, dispersion, London forces type of interactions. According to this point of view, for a non-ideal solution and a 1 : 1 complex, eqn. (2) may now be expressed in the form

$$-RT \ln \frac{x_1^s \gamma_{c1} \gamma_{p1} x_2^s \gamma_{c2} \gamma_{p2}}{0.25} = \Delta H_{f,AD} - T\Delta S_{f,AD} \tag{4}$$

where, x_1^s = the mole fraction of component 1 at temperature T along the experimental liquidus line, and at the same time $x_1^s + x_2^s = 1$; γ_c, γ_p = activity coefficients corresponding to "chemical" and "physical" deviations from ideality, respectively.

For evaluation of the coefficients owing to "physical" effects, γ_p, we applied the solubility parameter theory [2] which provides the equation

$$RT \ln \gamma_{p1} = v_1 \left[\frac{v_2 n_2}{v_1 n_1 + v_2 n_2} \right]^2 [\delta_1 - \delta_2]^2 \tag{5}$$

where, x_1^s = the mole fraction of component 1 at temperature T along the n_1, n_2 = the number of moles of component 1 and 2; δ_1, δ_2 = the solubility parameters of components 1 and 2.

For the activity coefficient, γ_c, related to complexing, the following equation was obtained

$$\gamma_c = \frac{K_x(2x^s - 1) - 1 + \sqrt{(K_x + 1)[K_x(2x^s - 1)^2 + 1]}}{2K_x(x^s)^2} \tag{6}$$

where, K_x = an association constant of complex expressed on a mole fraction scale. For reaction in the liquid state

$$\mathrm{A} + \mathrm{D} = \mathrm{AD}$$

where A, D and AD represent the acceptor, donor and complex molecule, respectively; the association constant K_x is defined by the equation

$$K_x = \frac{x_{AD}}{x_A x_D}$$

where x_A, x_D and x_{AD} are the equilibrium mole fraction of acceptor, donor and complex, respectively.

$$x_A = x_A^s \gamma_{cA} \quad x_D = x_D^s \gamma_{cD} \quad x_{AD} = 1 - x_A - x_D$$

As can be seen from comparison of eqns. (5) and (6), firstly, an effect of "physical" activity coefficient is in opposition to that of "chemical" coefficient, i.e. in all cases $\gamma_p \geqslant 1$ and $\gamma_c \leqslant 1$; secondly, an expression for γ_c is symmetrical to subscripts 1 and 2, whereas that for γ_p is unsymmetrical. Based on the above statements, our results for liquidus lines of complexes and components could be explained as follows: an agreement between

TABLE 2

Molar volumes, $V(298)$, and solubility parameters, δ, for naphthalene, anthracene, carbazole and 1,3,5-trinitrobenzene

Compound	$V(298)$ [b] (cm^3)	$\delta \cdot 10^{-3}$ ($J^{1/2}$ m$^{-3/2}$)
Naphthalene	123.0	19.8 [a]
Anthracene	161.2	19.8 [a]
Carbazole	150.8	19.6 [b]
1,3,5-Trinitrobenzene	130.3	22.0 [c]

[a] From the data in ref. 11.
[b] Calculated according to Bondi [10].
[c] Calculated by increments method using the values $18.4 \cdot 10^3$ and $20.0 \cdot 10^3$ $J^{1/2}$ m$^{-3/2}$ for benzene [11] and nitrobenzene [11], respectively.

experimental and calculated liquidus lines of complexes implies that there is $\gamma_{c1}\gamma_{p1}\gamma_{c2}\gamma_{p2} = 1$. A fulfilment of the latter condition does not mean, however, that at the same time the equations $\gamma_{c1}\gamma_{p1} = 1$ and $\gamma_{c2}\gamma_{p2} = 1$ must be fulfilled and the liquidus line of pure components may be deflected from ideal form.

We have tested the above supposition by applying eqns. (4), (5) and (6) to experimental lines of NAP—TNB, ANT—TNB and CAR—TNB complexes. The data used in calculations of "physical" activity coefficients γ_p are summarized in Table 2.

The temperature dependence of the molar volume of pure liquid components has been calculated according to Bondi [10]. The values of the equilibrium constant, K_x (the best fitting the experimental liquidus lines of complexes) as calculated from a combination of eqns. (4)—(6) are shown in Fig. 5.

The degree of dissociation of complex at the melting point has been cal-

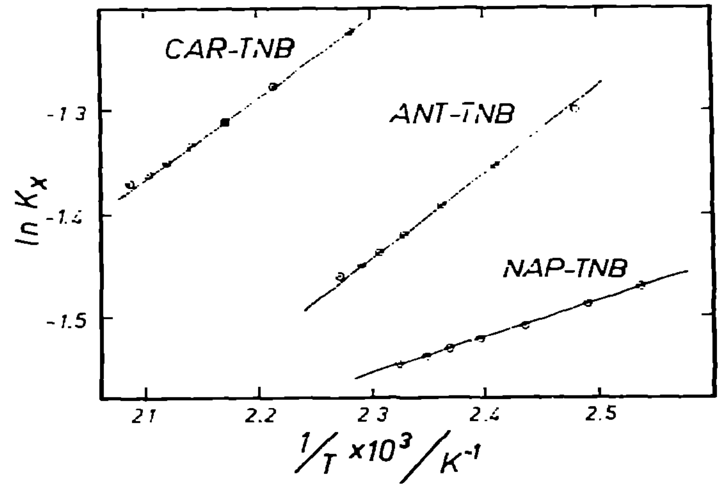


Fig. 5. The temperature dependence of the equilibrium constant K_x for 1 : 1 NAP—TNB, 1 : 1 ANT—TNB and 1 : 1 CAR—TNB complexes in the fused state.

culated by

$$\alpha = \sqrt{\frac{K_{\text{dys}}}{1 + K_{\text{dys}}}}$$

where $K_{\text{dys}} = K_x^{-1}$.

The enthalpy of complex formation in the liquid state, $\Delta H^0(\text{liq})$, has been calculated by applying the van't Hoff equation to the data shown in Fig. 5.

The enthalpy of complex formation in the solid state, $\Delta H^0(\text{solid})$, has been estimated as

$$\Delta H^0(\text{solid}) = \Delta H^0(\text{liq}) - \Delta H_{\text{f,AD}} + \Delta H_{\text{f,A}}(T_{\text{AD}}) + \Delta H_{\text{f,D}}(T_{\text{AD}}) \qquad (7)$$

where $\Delta H_{\text{f,AD}}$, $\Delta H_{\text{f,A}}(T_{\text{AD}})$ and $\Delta H_{\text{f,D}}(T_{\text{AD}})$ represent the enthalpy of fusion of complex, acceptor and donor, respectively, at the melting point of the complex. The values of $\Delta H^0(\text{solid})$ have been calculated using our results for ΔH_{f}, T_{f} and C_{p} [1].

It should be noted here that the values of enthalpies of complex formation, $\Delta H^0(\text{liq})$, as shown in Table 3, represent average values over the temperature ranges 395—430 K for NAP—TNB, 400—440 K for ANT—TNB and 435—480 K for CAR—TNB.

The equilibrium constant of the complex at 298 K (extrapolated for the supercooled liquid complex), the dissociation degree of complex at the melting point, and enthalpy of complex formation both in the liquid and solid state are shown in Table 3.

Comparison of our results and those of others is difficult since the numerical values of thermodynamical quantities are dependent on the concentration scale used and the choice of the standard state. Literature values, where available for TNB complexes, are concerned with reactions in solvents. Therefore, we list below only the average values of K and ΔH^0 for the aromatic hydrocarbons—TNB type complexes according to Mulliken and Person [12]

K_c(solution, 298): 0.2 to 12 (dm^3 mole^{-1})

ΔH^0(solution): —2.1 to —12.5 (kJ mole^{-1})

No enthalpies of formation of weak CT complexes in the solid state have

TABLE 3

Association constant, K_x, dissociation degree, α, enthalpy of complex formation in the liquid state, ΔH^0(liq), and in the solid state, ΔH^0(solid), for 1 : 1 complexes of 1,3,5-trinitrobenzene (TNB) with naphthalene (NAP), anthracene (ANT) and carbazole (CAR)

Complex	K_x(liq, 298)	α(m.p.) (%)	ΔH^0(liq) (kJ mole^{-1})	ΔH^0 (solid) (kJ mole^{-1})
1 : 1 NAP—TNB	0.305	90.8	—2.89	+0.51
1 : 1 ANT—TNB	0.560	90.1	—6.82	—2.36
1 : 1 CAR—TNB	0.679	89.3	—6.49	—6.32

been measured to date by direct methods (e.g., by combustion calorimetry). The enthalpy of formation of the TTF—TCNQ salt, as measured by combustion calorimetry, amounted to —37.41 kJ mole^{-1} [13]. The enthalpy of formation of the benzene—hexafluorobenzene compound, as estimated by an indirect method, was +1.0 kJ mole^{-1} [14].

Based on the calculated values of γ_c and γ_p for the anthracene—TNB system, the liquidus line for anthracene could be calculated. The agreement between the measured liquidus line and that predicted by the model used here is unsatisfactory but better than the result obtained by using the van Laar—Schröder equation for an ideal solution. For example, at the point $x = 0.5$ and $T = 440.2$ K, we obtained $\gamma_{c\text{ANT}}\gamma_{p\text{ANT}} = 0.994$, whereas the observed value was 0.893. According to us, this disagreement may be caused by the fact that the liquidus lines of complexes have been calculated using experimental values for $\Delta H_{f,\text{AD}}$ and $\Delta S_{f,\text{AD}}$, which refer to a partially dissociated complex, whereas Vieland's equation applies to the case of a completely dissociated complex. Despite the fact that the model applied in this work is a "zero-approximation", the results obtained by us for K_x and ΔH^0 seem to be in reasonable agreement with the present knowledge of weak charge-transfer complexes.

CONCLUSIONS

The three binary systems dealt with in this study form "double simple-eutectic" type phase diagrams with a 1 : 1 complex as a component of the eutectic mixtures. Each one of the three modifications of TNB can occur as a component of the eutectic mixtures, resulting in the marked difference in phase diagrams in the composition range 0.5—1.0 mole fraction of TNB.

Thermodynamical mutual solubility in solid phases seems to be no greater than that limited by the defects. However, under special conditions (e.g., by single-crystal growing methods), there is the possibility of obtaining the mixed crystals both at the boundaries of the phase diagram and in the complex region.

Measured liquidus lines of complexes agree within experimental error with those calculated by the Vieland equation for ideal solutions and this fact could imply the complete dissociation of complexes in the liquid phase. However, a comparison of liquidus lines measured and calculated by the Schröder—van Laar equation for the parent components evidences some degree of complexing in the liquid phase. Applying the solubility parameter theory to the considered systems, we found that the decomposition of these complexes upon fusion is not complete and the degree of dissociation at the melting point amounted to about 90% in all three complexes under consideration.

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