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PHASE DIAGRAMS IN THE BINARY SYSTEMS OF *N*-ISOPROPYLCARBAZOLE WITH 2,4,7-TRINITROFLUOREN-9-ONE AND CARBAZOLE

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ABSTRACT

Phase diagrams of the binary systems formed by *N*-isopropylcarbazole (NiPC) and 2,4,7-trinitrofluoren-9-one (TNF) or carbazole (C) have been determined by differential scanning calorimetry and hot-stage microscopy. In the NiPC–C system a simple eutectic phase diagram has been found. In the NiPC–TNF system a congruently melting 1 : 1 charge transfer complex has been observed. A thermodynamic analysis of the two systems is also given.

INTRODUCTION

Complete phase diagrams were determined in our laboratory by differential scanning calorimetry (DSC) for the systems formed by 1,3,5-trinitrobenzene (TNB) [1] and 2,4,7-trinitrofluoren-9-one (TNF) [2] with several aromatic and heteroaromatic hydrocarbons. The experimental data and thermodynamic analysis for six binary systems formed by TNF with naphthalene, anthracene, pyrene, fluorene, carbazole and dibenzothiophene were described in detail [2]. In the 1 : 1 charge transfer (CT) complex formed by TNF with carbazole (C), a phase transition was observed. The temperature of this transition is 463.2 K, and its molar enthalpy is 14.7 kJ mol^{-1}. This phase transition was observed only in pristine samples, i.e. in the first run of DSC measurements. A hydrogen-bond-type interaction between C and TNF molecules was supposed as a possible cause of the transition. In an attempt to verify the hypothesis, a study of the phase diagram of TNF with *N*-isopropylcarbazole (NiPC) has been undertaken. In NiPC, a bulky isopropyl group replaces the hydrogen atom, thus no hydrogen bond can be formed.

The phase diagram of the binary system NiPC–C was also studied in order to check the mutual miscibility of the components.

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EXPERIMENTAL

Materials

In this work carefully purified substances were used, their purity being checked by DSC. NiPC and TNF were synthesised in this laboratory.

Crude samples of NiPC were contaminated by carbazole, an impurity highly resistant to simple purification techniques, i.e. crystallization or sublimation. A more extensive method of purification was thus proposed. After crystallization from heptane and repeated column chromatography on Al_2O_3, vacuum sublimation and finally zone melting (50 zone passes) were applied. NiPC purified in such a way melts at 395.2 K (T_f) (Reported values for $T_f = 395.0$ K [3], 393.0 K [4] and 396.0 K [5]).

TNF was purified by crystallization from glacial acetic acid and from concentrated nitric acid (ca. 50 wt.%), washed with water and finally dried under vacuum over phosphorus pentoxide. $T_f = 449.0$ K [2].

Carbazole (pure, Fluka) was crystallized from ethanol, sublimed and purified by zone melting (150 zone passes). $T_f = 519.5$ K [2].

Procedure

Samples for DSC analyses were prepared as described in Ref. 2(a). The phase diagrams were studied by scanning calorimetry (Perkin–Elmer DSC-1B) and hot-stage microscopy (Boetius).

The thermograms (DSC curves) were recorded from room temperature to the melting points of the samples. The scanning rate was 4 K min^{-1}. The DSC-1B apparatus was calibrated before the measurements as described in ref. 2(a).

RESULTS

DSC curves for NiPC, C and the 1 : 1 NiPC–TNF complex show no thermal effects additional to those of melting. Neither in the pure 1 : 1 NiPC–TNF complex nor in samples of any other composition in this binary system was any sign of a phase transition observed.

The thermodynamic data of the carefully purified materials under investigation are collected in Table 1.

The phase diagram of the NiPC–TNF binary system as obtained in this work is presented in Fig. 1, and that of the NiPC–C binary system in Fig. 2.

NiPC forms a brown 1 : 1 CT complex with TNF, which melts congruently at 448.0 K. Two eutectic points are found in the system: at 6.5 mol% of TNF, with $T_f = 388.0$ K, and at 79.0 mol% of TNF, with $T_f = 430$ K (Fig. 1).

TABLE 1

Thermodynamic data of pure components

Component	Abbre-viation	Melting point (K)	Heat of fusion ($kJ\ mol^{-1}$)	Reference
N-Isopropylcarbazole	NiPC	395.2	17.73	This work
Carbazole	C	519.5	21.17	2(a)
2,4,7-Trinitrofluoren-9-one	TNF	449.0	23.50	2(a)

A simple phase diagram with only one eutectic point at 7.0 mol% of carbazole was found in the NiPC–C system (Fig. 2). The temperature of the eutectic line is 385.7 K. There is no miscibility within the solid phase.

The compositions and the heats of fusion of eutectics were evaluated by the Tammann triangle method [6]. The values of the heat of fusion are given for one mole of the binary mixture. The molecular weight of the NiPC–C

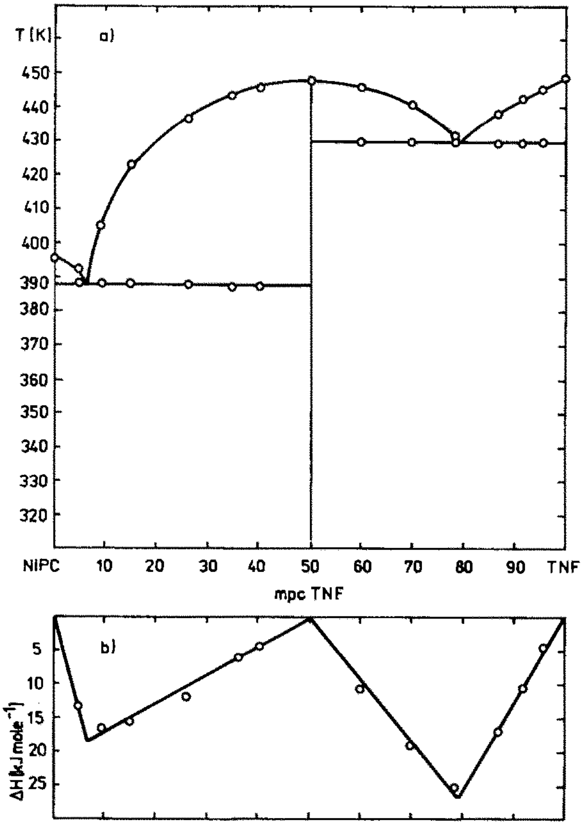

Fig. 1. (a) Phase diagram of the system NiPC–TNF: –o–, liquidus and eutectic lines; (b) molar heat of eutectic melting versus composition.

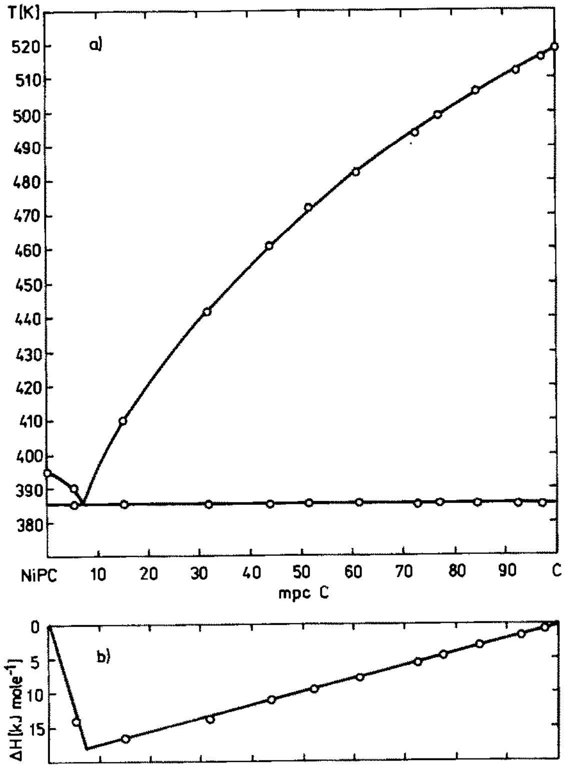

Fig. 2. (a) Phase diagram of the system NiPC–C: –o–, liquidus and eutectic lines; (b) molar heat of eutectic melting versus composition.

binary system was calculated by the equation

$$M_{av} = x_{NiPC} M_{NiPC} + x_C M_C$$

where x_{NiPC}, x_C are mole fractions and M_{NiPC}, M_C are the molecular weights of NiPC and C, respectively. For the NiPC–TNF binary system, eutectics were considered as mixtures of a DA (donor–acceptor) complex and an appropriate component X present in excess, then

$$M_{av} = x_{DA} M_{DA} + x_X M_X$$

where x_{DA}, x_X and M_{DA}, M_X are mole fractions of the DA complex and a component in excess in the eutectic mixture and their molecular weights, respectively. The characteristic thermodynamic data of these binary systems are collected in Tables 2 and 3.

If the composition of the eutectic and the molar enthalpies of fusion of the complex and its components are known, then the heat of eutectic melting can be calculated as follows:

(i) For the NiPC–TNF system

$$\Delta H^{\ominus}_{f,e,calc} = x_{eDA} \Delta H^{\ominus}_{f,DA} + (1 - x_{eDA}) \Delta H^{\ominus}_{f,X}$$

TABLE 2

Thermodynamic data of the CT complex in the NiPC–TNF system

Stoichiometry of the complex D:A	Melting point (K)	Heat of fusion (kJ mol^{-1})
1:1	448.0	42.78

TABLE 3

Composition of eutectic melts, temperature and molar heat of eutectic melting in the NiPC–TNF and NiPC–C binary systems

Eutectic points	Temperature of eutectic melting (K)	Composition of eutectic points (mol% of X)	Heat of eutectic melting (kJ mol^{-1})	
			found	calc.
TNF—NiPC–TNF	430.0	79.0 (TNF)	27.00	28.62
NiPC—NiPC–TNF	388.0	6.5 (TNF)	18.70	19.47
NiPC—C	385.7	7.0 (C)	18.00	17.97

where x_{eDA} is the mole fraction of complex in the eutectic mixture and $\Delta H^{\ominus}_{\mathrm{f,DA}}$ and $\Delta H^{\ominus}_{\mathrm{f,X}}$ are the molar heats of fusion of the complex and of a component X in the eutectic melt, respectively (cf. Table 3).

(ii) For the NiPC–C system

$$\Delta H^{\ominus}_{\mathrm{f,e,calc}} = x_{\mathrm{eNiPC}} \Delta H^{\ominus}_{\mathrm{f,NiPC}} + x_{\mathrm{eC}} \Delta H^{\ominus}_{\mathrm{f,C}}$$

where x_{eNiPC} and x_{eC} are mole fractions of NiPC and C in the eutectic and $\Delta H^{\ominus}_{\mathrm{f,NiPC}}$ and $\Delta H^{\ominus}_{\mathrm{f,C}}$ are their molar heats of fusion (cf. Table 3).

The data in Table 3 show a reasonable agreement between the values of the molar heats of eutectic melting found by the Tammann triangle method and those calculated from the heats of fusion of the pure components as well as the positions of eutectic points given in this work.

DISCUSSION

No phase transition was observed in the CT complexes of TNF studied hitherto except for the carbazole–TNF system.

No hydrogen bond was observed in solid carbazole [7], but in propyl ether solution carbazole is complexed with solvent and self-associated (probably dimerised) by hydrogen bonding, in contrast to *N*-ethylcarbazole [8].

The bond lengths in the TNF molecule [9] indicate that there is some interaction between the benzene ring and the carbonyl group or between the benzene rings. The nitro group in position 4 is twisted out of the benzene ring by 34° due to steric hindrance in this crystal.

It may be supposed that the presence of the N–H group in the carbazole molecule and the above mentioned interaction lead to formation of a hydrogen bond (HB), and the observed phase transition in the C–TNF complex is related to HB breaking in the high-temperature phase. The existence of HB in the low-temperature phase of the C–TNF complex is consistent with the broadening of the vibrational band of the N–H group in the 1 : 1 C–TNF complex, as compared with the N–H band in pure carbazole, which was found by us. Results of spectroscopic investigations will be given elsewhere [10].

The crystals of carbazole and NiPC are both orthorhombic, but they belong to different space groups: *Pnam* [7] and *Ic*2*a* [11], respectively. The molecules of carbazole and NiPC differ in shape and dimensions and cannot form mixed crystals, according to Kitaigorodsky's theory [12]. A phase diagram with a simple eutectic has been found in the system in accordance with the theory.

THERMODYNAMIC ANALYSIS

The position of the liquidus line in the phase diagram of a binary system may be determined theoretically (in the case of complete immiscibility in the solid phase) from the well-known van Laar–Hildebrand equation

$$\ln\left(x_i^1\gamma_i^1\right) = -\frac{\Delta H_{\mathrm{f},i}^{\ominus}}{R}\left(T^{-1} - T_{\mathrm{o},i}^{-1}\right) \tag{1}$$

where x_i^1 is the mole fraction of an i-th component at temperature T in the liquid phase, γ_i^1 is its activity coefficient, and $\Delta H_{\mathrm{f},i}^{\ominus}$ and $T_{\mathrm{o},i}$ are the molar heat of fusion and the melting temperature of the pure component, respectively. The values of $\Delta H_{\mathrm{f},i}^{\ominus}$, $T_{\mathrm{o},i}$ and temperature of fusion T at a given composition are usually known from independent experiments.

The liquid phase obtained by melting of a sample of a given composition may be considered as either a perfect solution with $\gamma_i^1 \cong 1$, or a regular solution with $\gamma_i^1 = \mathrm{f}(x_i^1, T)$, the activity coefficient of an i-th component in a regular solution being related to x_i^1 and T by the equation

$$\gamma_i^1 = \exp\left[\frac{4\Delta H^{\mathrm{M}}}{RT}\left(1 - x_i^1\right)^2\right] \tag{2}$$

where ΔH^{M} is the molar heat of mixing. From eqns. (1) and (2) and the experimental data it is possible to evaluate ΔH^{M}.

If components of a binary system form a complex in the solid phase, the problem of its dissociation in the melt should be considered. The complex may be undissociated, partially dissociated or completely dissociated. Equations which will be used to describe an equilibrium between the solid complex and liquid phases will be different in all these cases. It will be eqn. (1) which holds in the first case. For a dissociating complex one must consider the value of its dissociation constant in the melt. In the third case the liquid melt of the complex is assumed to contain the two components of a binary system only; i.e. the dissociation constant K is assumed to be infinity and $x_i = n_{o,i}$ ($n_{o,i}$ denotes the numbers of moles of pure components taken in preparation of the sample; for the sake of convenience we assume $n_{o1} + n_{o2} \equiv 1$).

The melt may be considered as a perfect or regular solution (for the latter one an activity coefficient must be defined). In the case of a partial dissociation of complex in the melt, the formula which describes the equilibrium between solid complex and binary melt reads [see eqn. (11) in ref. 2(b)]

$$\ln \frac{\left[x_1^1 \gamma_1^1 x_2^1 \gamma_2^1\right]_{n_{o1} \neq n_{o2}}}{\left[x_1^1 \gamma_1^1 x_2^1 \gamma_2^1\right]_{n_{o1} = n_{o2} = 0.5}} = -\frac{\Delta H_{\mathrm{eff}}^{\ominus}}{R}\left(T^{-1} - T_{o,12}^{-1}\right) \tag{3}$$

and in case of complete dissociation [cf. eqn. (13a) in ref. 2(b)]

$$\ln \frac{\left[n_{o1} n_{o2} \gamma_1^1 \gamma_2^1\right]_{n_{o1} \neq n_{o2}}}{\left[0.25 \gamma_1^1 \gamma_2^1\right]_{n_{o1} = n_{o2} = 0.5}} = -\frac{\Delta H_{\mathrm{eff}}^{\ominus}}{R}\left(T^{-1} - T_{o,12}^{-1}\right) \tag{3a}$$

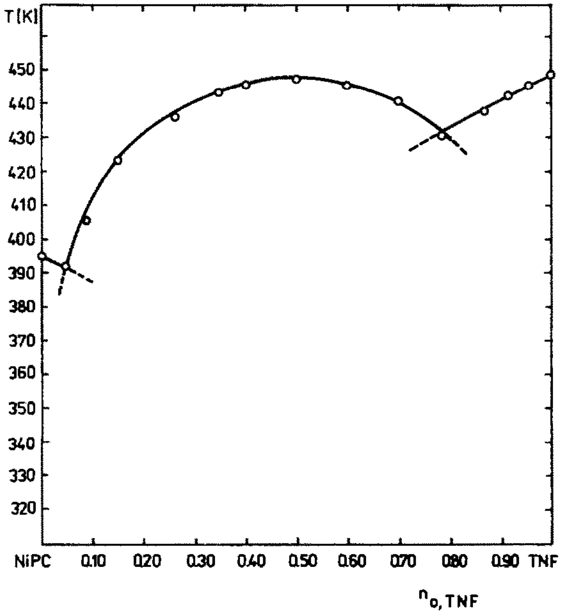

Fig. 3. Liquidus lines in the NiPC–TNF system: o, experimental results; ———, calculated for $\Delta H^{M} = 0$ and $K = \infty$.

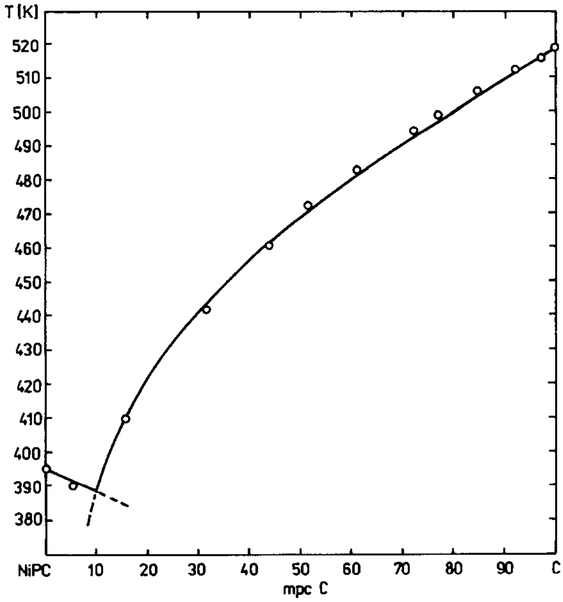

Fig. 4. Equilibrium temperature in the system solid NiPC–liquid NiPC + C and solid C–liquid C + NiPC: ○, experimental values; ———, calculated for $\Delta H^{\mathrm{M}} = 0.67$ kJ mol^{-1}.

where $T_{\mathrm{o},12}$ is the melting temperature of the complex and $\Delta H_{\mathrm{eff}}^{\ominus}$ is its effective heat of fusion. The meaning of $\Delta H_{\mathrm{eff}}^{\ominus}$ in eqns. (3) and (3a) is thus different (cf. ref. 2b).

For the NiPC–TNF system a reasonable fit of experimental data to calculated $T(n_{\mathrm{o}i})$ curves (liquidus lines) was achieved by applying eqn. (3a); i.e. by assuming complete dissociation of the complex in the melt treated as a perfect solution. The results are presented in Fig. 3. The equilibria between solid NiPC and the binary melt, and between solid TNF and the binary melt, calculated from eqn. (1) are also shown in the figure. $\Delta H_{\mathrm{eff}}^{\ominus}$ in eqn. (3a) denotes the experimental heat of fusion of the 1 : 1 complex.

Results obtained for the NiPC–C binary system by applying eqns. (1) and (2) and assuming the melt to be a regular solution with $\Delta H^{\mathrm{M}} = 0.67$ kJ mol^{-1} (calculated from experimental data) are shown in Fig. 4 for equilibrium between the liquid phase and each of the two pure solid components: NiPC and C.

CONCLUSION

For the NiPC–TNF system, where a congruently melting 1 : 1 complex is formed, the assumption of its complete dissociation in the liquid phase treated as a perfect solution ($\Delta H^{\mathrm{M}} = 0$ and $K = \infty$) well describes the experimental equilibria between solid and liquid phases.

The equilibria between solid and liquid phase in the binary system NiPC–C, where the components form a simple eutectic phase diagram, is better described by the model of a regular solution with a moderate value for the heat of mixing.

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