Journal of Thermal Analysis, Vol. 37 (1991) 693-704

PHASE DIAGRAMS IN THE BINARY SYSTEMS OF TETRACYANOETHYLENE WITH MESITYLENE, DURENE AND PENTAMETHYLBENZENE

M. Radomska and R. Radomski

INSTITUTE OF ORGANIC AND PHYSICAL CHEMISTRY, TECHNICAL UNIVERSITY, 50 370 WROCLAW, POLAND

(Received April 7, 1990)

The phase diagrams of the binary systems of tetracyanoethylene (TCNE) with some methylbenzenes were determined by differential scanning calorimetry. In the durene–TCNE system a 1:1 complex was observed. The other two pairs of components form both 1:1 and 1:2 complexes. In all the systems, the complexes melted incongruently. Solid – solid phase transitions were found in the complexes in the pentamethylbenzene-TCNE system. The excess free energy of mixing of the liquid phase was estimated by fitting the modified van Laar equation to the measured liquidus lines. The enthalpy and the entropy of complex formation were used as the fitting parameters.

The object of this study was to explore the applicability of a previously presented model for calculation of the liquidus lines in binary systems involving a charge–transfer (CT) complex [1, 2]. The model is based on the assumption that, in a system involving an addition compound, the excess Gibbs energy for the liquid phase is the sum of two parts, related to complexing and non–complexing interactions.

Our earlier investigations concerned systems with 1,3,5–trinitrobenzene (TNB) as an acceptor (A) and polycyclic aromatic hydrocarbons as donors (D). The complexes observed in those systems were relatively weak, and the experimental liquidus lines differed from those calculated for the ideal case only insignificantly. This paper details further refinement of this model, and its application to systems involving strong complexes. Tetracyanoethylene (TCNE) was chosen as an acceptor because complexes with TCNE are known to be stronger than those with TNB [3a]. For the sake of comparison of the properties in a homologous series, the methylbenzenes were selected

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

as donors. In this part, the results for the systems with mesitylene (MES), durene (DUR) and pentamethylbenzene (PMB) are presented.

Experimental

Sample preparation

Mesitylene (Riedel, 98%) was twice distilled through a Vigreux column 50 cm in length. Durene (Koch–Light, pure) and pentamethylbenzene (Aldrich, 99%) were vacuum-sublimed and then zone-refined; approximately 200 zone passes were made. TCNE (Fluka, pure) was twice vacuum–sublimed; the first sublimation was through active carbon.

Weighed amounts of the desired components were placed into aluminium sample pans and then sealed under a nitrogen atmosphere.

In order to minimize the effect of sample size, the mixture masses were maintained relatively constant (about 5 mg).

The microbalance that was used (Cahn, model G) made it possible to determine masses within ±2 μg; consequently, the accuracy of the mole fraction was better than 0.08.

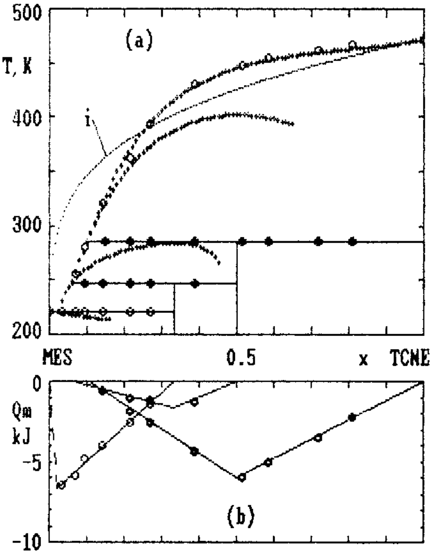

Fig. 1 (a) Phase diagram of the mesitylene – TCNE system. (b) Composition dependence of the molar heat of eutectic and peritectic melting. Circles and points represent the experimental results and calculated liquidus lines, respectively; i - ideal liquidus line of TCNE. See text for details

In order to ensure homogeneity, the samples were alternately heated and cooled over the temperature range covering all expected thermal events. This procedure was repeated until the thermal curve shape became reproducible. The measurements on the DUR–TCNE and PMB–TCNE systems were carried out on samples stored at room temperature for 2-3 weeks; the samples in the MES–TCNE system were maintained at about 220 K for 2–3 hours and then measured.

Calorimetric measurements

The experimental system consisted of a Perkin–Elmer DSC 1–B differential scanning calorimeter connected to an ELWRO 801 AT computer by means of a universal electrochemical meter (model EMU, produced by ELWRO, Poland). Special software was developed for the calorimeter control and the data acquisition and processing.

The enthalpy of transitions was determined by digital integration of the DSC curve part indicated by the user. The base line was approximated to a straight line. The standard error in the enthalpy measurements was 0.4 kJ mol^{-1}.

The low-temperature range of the calorimeter was calibrated with the following high-purity compounds used as standards: chloroform, *m*-xylene, fluorobenzene, *o*-xylene, water and *p*-xylene. Dibenzyl, naphtalene, phenanthrene, hexamethylbenzene, anthracene and hexachlorobenzene were used for the calibration of the superambient region of the calorimeter.

Both the original curve and its first derivative were used for the estimation of the transition temperature. A second-order polynomial was fitted to a set of data by the least-squares procedure. The standard deviation in the temperature residuals amounted to $\sigma = 1.07$ deg and $\sigma = 0.45$ deg for the sub- and superambient regions, respectively.

The line positions on the phase diagram were determined from the curves by using the procedure described previously [4].

Results and discussion

Phase diagrams

The experimental results for the phase diagrams of the considered systems, together with the calculated liquidus lines, are shown in Figs 1–3.

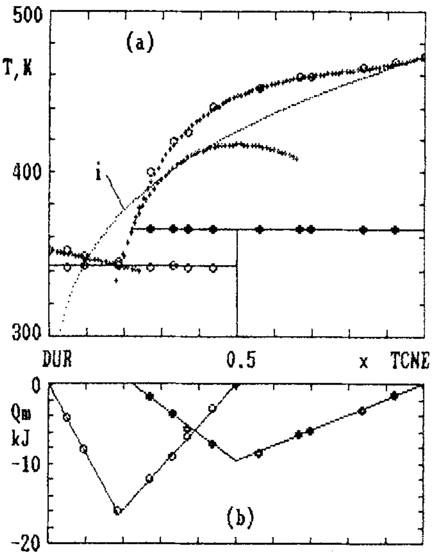

Fig. 2 (a) Phase diagram of the durene – TCNE system. (b) Composition dependence of the molar heat of eutectic and peritectic melting. Circles and points represent the experimental results and calculated liquidus lines, respectively; i - ideal liquidus line of TCNE. See text for details

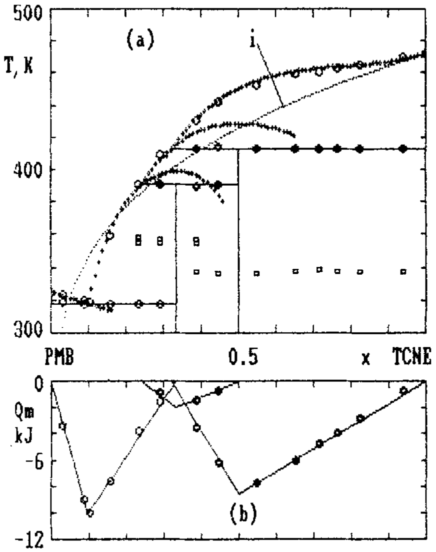

Fig. 3 (a) Phase diagram of the pentamethylbenzene – TCNE system. (b) Composition dependence of the molar heat of eutectic and peritectic melting. Circles and squares represent the experimental results; points depict the calculated liquidus lines, i - ideal liquidus line of TCNE. See text for details

In the DUR–TCNE system, a 1:1 complex was observed; in the MES–TCNE and PMB-TCNE systems, both complexes AD and AD_2 were found. In all the systems, the complexes melted incongruently. The complexes formed simple eutectics with the parent donors.

In the PMB–TCNE mixtures, a double transition was observed at 354.7 K and 357.5 K over the composition range 15–50 mpc of TCNE. The maxima in the composition dependence of the heat effects corresponded to 33.33 mpc of TCNE; thus, this transition was attributed to the complex AD_2. In the PMB–TCNE system, the complex AD also underwent the phase transition, as evidenced by the DSC curves recorded for the compositions from 33.33 to 100 mpc of TCNE.

Table 1 Calorimetric data for the components and complexes in the binary systems of TCNE with mesitylene (MES), durene (DUR) and pentamethylbenzene (PMB)

Compound/ Complex	Fusion		Solid–solid transition		Peritectic decomposition	
	T_f, K	ΔH_f, kJ·mol^{-1}	T_t, K	ΔH_t, kJ·mol^{-1}	T_p, K	Q_p, kJ·mol–1
TCNE	471.9	24.92				
MES	221.3	6.57				
DUR	352.4	20.90				
PMB	324.6	12.40				
TCNE·MES					285.2	12.3
TCNE·MES2					247.5	5.1
TCNE·DUR					365.4	19.6
TCNE·PMB			337.0	1.3	412.9	17.3
TCNE·PMB2			357.5	2.4	390.2	6.1
			354.7	4.8		

Table 2 Eutectic temperatures (T_E), composition (x_E) and heats (Q_E) in the binary systems of TCNE with mesitylene (MES), durene (DUR) and pentamethylbenzene (PMB)

Eutectic formula	TE, , K	xE mpc ofxE, TCNE	QE kJ·mol^{-1}
MES + TCNE·MES2	221.1	approx 2	6.65
DUR + TCNE·DUR	342.5	18.8	16.38
PMB + TCNE·PMB2	317.8	9.7	10.20

The peak shapes suggest transitions rather of the first-order type (Fig. 4). By analogy with the naphthalene–TCNE complex [5], the phase transitions in the PMB–TCNE complexes could be attributed to some molecular motions, but the elucidation of the nature of the transitions obviously requires the application of other techniques than DSC measurements.

A calorimetric characterization of the considered systems is given in Tables 1 and 2.

Calculation of liquidus lines

According to the regular solution theory, the deviations from ideality can be described by the expression

$$RT \ln \gamma_1 = A x_2^{-2} \tag{1}$$

where A is a parameter ("heat of mixing"), γ is the activity coefficient and x is the mole fraction. The subscripts 1 and 2 refer to the components of the binary system.

Inspection of Figs 1, 2 and 3 shows that the deviation from ideality of the experimental liquidus line of TCNE changes from a positive value at high temperatures to a negative value at low temperatures. These data are not interpretable in terms of a simple model of the regular solution, since the parameter A in Eq. 1 takes either a positive or a negtive value.

It seemed reasonable to assume two kinds of interactions in the binary mixtures A – D : (i) complexing ("chemical") and (ii) non-complexing ("physical"). According to this point of view, the excess Gibbs energy of mixing for the liquid phase G^E can be divided into chemical, G_c^E and physical, G_p^E contributions:

$$G^E = G_c^E + G_p^E \tag{2}$$

$$G_p^E = RTx_1 \ln \gamma_{p1} + RTx_2 \ln \gamma_{p2} \tag{3a}$$

$$G_c^E = RTx_1 \ln \gamma_{c1} + RTx_2 \ln \gamma_{c2} \tag{3b}$$

where γ_p and γ_c are the activity coefficients corresponding to physical and chemical interactions, respectively.

For evaluation of the γ_p values, we applied the solubility parameter theory [6], which leads to the equation

$$RT \ln \gamma_{p1} = v_1 \Delta\delta^2 \varphi_2^2 \tag{4}$$

where v is the molar volume, φ is the volume fraction, and $\Delta\delta$ is the difference in the solubility parameters of the components.

The chemical activity coefficient, γ_c, is equal to x^e/x, where x^e and x are the equilibrium and initial (free + complexed) mole fractions of the component, respectively.

According to the above definition, the γ_c–values are always less than 1. However, according to Eq. 4, the heat of mixing is positive and consequently $\gamma_p \geq 1$.

It should be noted that, as pointed out many years ago [6], a description in terms of the chemical activity coefficient is quite equivalent to Eq. 1 if a negative value is taken for parameter A.

The relationships between x and x^e for the three most common association models (1:1, 1:2 and 1:1 + 1:2) are given elsewhere [2]. In this work, we used the 1:1 model for all the considered systems, even those in which the crystalline complexes AD_2 were found. This assumption is justified since, as a rule, the dissociation AD_2 = AD + D is nearly complete after melting [2].

For a 1:1 association, A + D = AD, the chemical activity coefficient, γ_c, is given [1b] by

$$\gamma_c = \frac{K(2x-1)-1+\sqrt{(K+1)[K(2x-1)^2+1]}}{2Kx^2} \tag{5}$$

where K is an association constant expressed in the mole fraction scale.

The temperature dependence of the association constant was approximated by the van't Hoff equation:

$$\ln K = -\Delta H^{\circ}_{as}/RT + \Delta S^{\circ}_{as}/R \tag{6}$$

where ΔH°_{as} and ΔS°_{as} are the enthalpy and the entropy of complex formation, respectively.

An analysis of the liquidus lines was performed by means of the minimization method. The function being minimized was

$$f = \sum_{i} (T_{obs,i} - T_{cal,i})^2 \tag{7}$$

where $T_{\mathrm{obs},i}$ is the temperature measured for the ith data point along the pure component liquidus line, and $T_{\mathrm{cal},i}$ is the temperature predicted for this point from the van Laar equation adapted to the real solution, i.e.

$$T_{\mathrm{cal,i}} = \frac{\Delta H_f}{\Delta S_f - R\ln a_i}; \qquad a_i = x_i \gamma_{\mathrm{c,i}} \gamma_{\mathrm{p,i}} \tag{8}$$

where ΔH_f and ΔS_f are the enthalpy and entropy of fusion of the pure component, respectively, and a is the component activity.

The parameters varied to obtain the fit were the enthalpy and the entropy of association, $\Delta H^{\mathrm{o}}_{\mathrm{as}}$ and $\Delta S^{\mathrm{o}}_{\mathrm{as}}$. The fit was performed by using a subroutine for minimization based on the Powell method. For the DUR–TCNE and PMB–TCNE systems, the results for both donor and acceptor liquidus lines were taken into account; in the MES–TCNE system, only the acceptor liquidus was attainable experimentally.

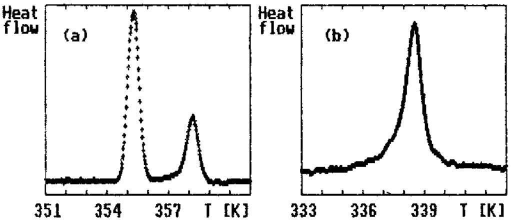

Fig. 4 Thermograms of the pentamethylbenzene–TCNE mixrures showing solid–solid transitions in the AD_2 complex (a) and in the AD complex (b). Sample composition (mpc of TCNE) = (a) 29.16 (b) 65.03; heating rate = 3.65 deg·min^{-1}

The physical activity coefficients were calculated from Eq. 4 by using the following values for the molar volume:v(MES) 139.11, v (DUR) 155.46, v (PMB) 171.65 and v (TCNE) 108.83 (all in cm^3, at 293 K), and for the solubility parameter: δ (MES) 16780, δ (DUR) 17125, δ (PMB) 16860 and δ (TCNE) 24610 (all in J$^{1/2}$·m$^{-3/2}$). The solubility parameter values were evaluated from the energy of vaporization, and the temperature dependence of the molar volume was estimated as described previously [1b].

Although relevant data are not available, it seems worthwhile to compare our results and those of others. The values of $\Delta H^{\mathrm{o}}_{\mathrm{as}}$ and $\Delta S^{\mathrm{o}}_{\mathrm{as}}$, as yielded from the fitting procedure, and the values of association constants, as calculated with Eq. 6, together with literature data, where available for TCNE complexes, are collected in Table 3.

A survey of the numerical values given in Table 3 indicates that the results of this work for the binary liquid system (A + D) are in agreement with those for the ternary liquid system (A + D + solvent) rather than with those for the binary gaseous system.

It is instructive to present the relation between the contributions for the complexing and the non-complexing interactions. Figure 5 shows the composition dependence of the excess Gibbs energy of mixing of the liquid phase calculated for the DUR–TCNE system by using Eqs 3 and 2. The γ_p values were calculated from Eq. 4. The chemical activity coefficient was obtained from the combination of Eqs 5 and 6, using the data given in Table 3.

The part of the excess free energy related to complexing, G_c^E is negative and strongly temperature dependent, in contrast with that associated with physical interactions, G_p^E (Fig. 5a). As a result, the total excess free energy G^E, changes negative values at low temperatures to positive ones at high temperatures to positive ones at high temperatures (Fig. 5b). This model provides a simple interpretation of the observed liquidus lines, as will become clear from the details presented below.

Table 3 Parameters from the fit experimental liquidus lines of pure components to modified van Laar equation with comparative data for binary systems of TCNE with mesitylene (MES), durene (DUR) and pentamethylbenzene (PMB)

System	Association enthalpy $-\Delta H^o_{as}$, kJ·mol^{-1}		Association entropy $-\Delta S^o_{as}$, J·mol^{-1}·K^{-1}		Association constant K_x (at 293 K)	
	This work[a]	Ref. 3b	This work[a]	Ref. 3b	This work[b]	Ref. 3b
MES–TCNE	24.07	18.9[s] 41.5[g]	47.44	40.2[s] 78.3[g]	65.1	17.5[s] 1020[g]
DUR–TCNE	26.02	21.2[s] 45.2[g]	52.99	38.6[s] 72.4[g]	74.4	53.5[s] 11200[g]
PMB–TCNE	26.10		51.34		93.7	

[a] Standard deviations amount to: $\delta(\Delta H^o_{as}) = 0.2$ kJ·mole^{-1} and $\delta(\Delta S^o_{as}) = 0.1$ J·mole^{-1}·K^{-1}

[b] Calculated from Eq. 5. Uncertainty of K was estimated from the formula for the propagation of errors and amounted to about 10%

[g] From measurement in gaseous phase

[s] From measurement in solution of CH_2Cl_2; recalculated in mole fraction scale

The same set of estimated values of ΔH^o_{as} and ΔS^o_{as} was used for the calculation of the liquidus lines of both the pure components and the complexes. The liquidus lines of the components were simulated by using Eq. 8.

The liquidus lines of the complexes were calculated by using the Vieland equation adapted to the real solution

$$T_{\mathrm{cal,i}} = \frac{\Delta H_{\mathrm{f,C}}}{\Delta S_{\mathrm{f,C}} - R \ln \left[\dfrac{a_{\mathrm{A,i}}\, a^{\nu}_{\mathrm{D,i}}}{a_{\mathrm{A,C}}\, a^{\nu}_{\mathrm{D,C}}} \right]} \tag{9}$$

where $\Delta H_{\mathrm{f,C}}$ and $\Delta S_{\mathrm{f,C}}$ are the enthalpy and the entropy of fusion of the complex, $a_{\mathrm{A,C}}$ and $a_{\mathrm{D,C}}$ are the activity of the acceptor and the donor in the neat complex liquid, and ν is the stoichiometry coefficient ($\nu = 1$ and $\nu = 2$ for the complexes AD and AD_2, respectively).

Table 4 Parameters from the fit experimental liquidus lines of complexes to modified Vieland equation for binary systems of TNCE with mesitylene (MES), durene (DUR) and pentamethylbenzene (PMB)

Complex	Fusion enthalpy $\Delta H_{\mathrm{f,C}}$, $\mathrm{kJ \cdot mole^{-1}}$	Fusion temperature $T_{\mathrm{f,C}}$, K
TCNE·MES	24.97	402.0
TCNE·MES2	32.80	283.9
TCNE·DUR	24.52	416.9
TCNE·PMB	23.64	434.0
TCNE·PMB2	26.82	398.6

First, the fusion enthalpy, $\Delta H_{\mathrm{f,C}}$ and the fusion temperature, $T_{\mathrm{f,C}}$, of the complex were estimated. The fitting procedure was applied to the experimental data along the liquidus lines of the complexes, including the

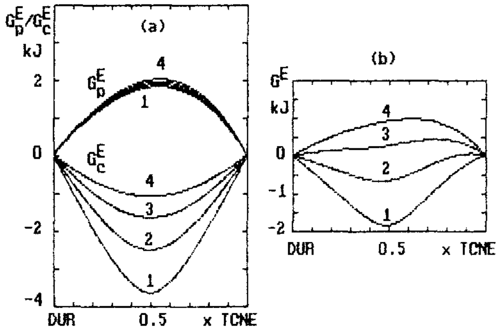

Fig. 5 Composition dependence of the excess free energy of mixing for the liquid phase in the durene–TCNE system calculated from Eq. 3 (a) and Eq. 2 (b). Temperature (K) = (1) 300, (2) 350, (3) 400 and (4) 450

results for the corresponding eutectic and peritectic points. The values of the fitted parameters are listed in Table 4.

Finally, the liquidus lines of the complexes were calculated by using Eq. 9.

As can be seen in Figs 1, 2 and 3, good agreement between the experiment and the calculations was obtained for the liquidus lines of both the pure components and the complexes.

An additional test of the model was a comparison of the experimental heat of the eutectic melting with the value calculated from the fusion enthalpies of the eutectic mixture components:

$$Q_E = [1-(\nu+1)x_E]\Delta H_{f,D} + x_E\,\Delta H_{f,C} \qquad (10)$$

where x_E is the eutectic composition in mole fraction of TCNE, $\Delta H_{f,D}$ is the experimental value of the fusion enthalpy of the donor and $\Delta H_{f,C}$ is the estimated value of the fusion enthalpy of the complex.

The Q_E values calculated from Eq. 10 were (the values in parenthesis are the measured values, all in kJ mol^{-1}) 6.86 (6.65), 17.65 (16.38) and 11.32 (10.20) for the MES–TCNE, DUR–TCNE and PMB–TCNE systems, respectively. Taking into account the error in the measured enthalpies, the agreement between the experimental and the calculated values is satisfactory.

* * *

We wish to thank M. Dankowski for his help in connecting the DSC apparatus to the microcomputer.

References

1 M. Radomska and R. Radomski, Thermochim. Acta, 40 (1980) 405 (a), *ibid* 40, (1980) 415 (b).
2 M. Radomska, R. Radomski and R. Klos, J. Chem. Soc., Perkin Trans. II (1987) 1563.
3 R. Foster, Organic Charge-Transfer Complexes, Academic Press, London and New York 1969, p. 40 (a), p. 184 (b).
4 R. Radomski and R. Radomska, J. Thermal Anal., 24 (1982) 101.
5 J. Boerio-Goates and E. F. Westrum Jr., Mol. Cryst. Liq. Cryst., 60 (1980) 237.
6 J. H. Hildebrand and R. L. Scott, The Solubility of Nonelectrolytes, Reinhold Publishing Corporation, New York 1955, p. 180.

Zusammenfassung — Mittels DSC wurden die Phasendiagramme der binären Systeme aus Tetracyanoethylen (TCNE) mit einigen Methylbenzolen erstellt. Im System Duren-TCNE wurde ein 1:1 Komplex beobachtet. Die anderen beiden Komponentenpaare bilden sowohl 1:1 als auch 1:2 Komplexe. In allen Systemen schmelzen die Komplexe inkongruent. Im System Pentamethylbenzol-TCNE wurde für die Komplexe eine Fest-Fest-Phasenumwandlung

gefunden. Durch Angleichen der modifizierten van Laar Gleichung an die gemessenen Liquidus-Kurven konnte die überschüssige freie Energie für das Mischens der flüssigen Phase geschätzt werden. Als Angleichparameter wurden Enthalpie und Entropie der Komplexbildung verwendet.