Phase Equilibria of Binary Systems containing Crystalline Inclusion Compounds. Part 1. The Perhydrotriphenylene–n-Heptane System

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The vapour pressure of saturated solutions containing the perhydrotriphenylene (PHTP)–n-heptane inclusion compound as a solid phase shows a maximum at *ca.* 10 °C below the m.p. of the crystalline adduct. A second pressure maximum, coincident with a eutectic point, is observed in the case of mixtures very rich in PHTP. Moreover, a sudden increase in pressure is observed in the case of pure or nearly pure inclusion compound in the close vicinity of the m.p. Such a behaviour is consistent with that predicted on the basis of the phase rule. The experimental values agree with those calculated by assuming the complete dissociation of the adduct in the liquid phase.

We have lately devoted much attention to the structure [1,2] and reactivity [3] of the inclusion compounds between perhydrotriphenylene (PHTP), a $C_{18}H_{30}$ tetracyclic saturated hydrocarbon, and guest molecules of different shape and dimensions. We have also examined the thermodynamic behaviour of these compounds, in particular the melting temperature, the heat of fusion, and the solid–liquid diagram. [4,5]

Our crystalline adducts may be described as binary compounds that undergo congruent (or incongruent) melting and incongruent vaporization. The existence of this class of compounds was discovered and discussed by Roozeboom [6] and by van der Waals [7] nearly a century ago. In spite of their quite different chemical nature, the phase diagram of gas hydrates, [6] salt hydrates, [6,8,9] complex metal halides, [10] and binary semiconductors [11] show the same essential features. A detailed analysis of the phases involved in these systems was reported by Ricci. [12]

Analogous systems exist in organic chemistry (*e.g.*, compounds which crystallize with molecules of solvent), but they have not been subjected to extensive studies from the point of view of the phase rule.

In this paper, we describe the pressure–temperature (*P–T*) diagram of PHTP–n-heptane mixtures over the whole range of composition, as an example of binary systems containing non-polar molecules (both components are saturated hydrocarbons), by assuming ideal behaviour in the liquid and vapour phases.

Before dealing with the case we are interested in, we briefly report on the behaviour of simpler binary systems that do not form addition compounds.

Saturated Solutions in Equilibrium with Pure Solid Constituents.—The *P–T* curve of ideal solutions of a non-volatile crystalline solute (B) in a volatile solvent (A) often shows a maximum in proximity to the melting temperature of the crystalline component. This phenomenon, also known as retrograde condensation, has been long known. [13-15]

The quantitative aspect is tackled on the basis of the Raoult and Van't Hoff equations. [16] The equilibrium pressure of an ideal solution is given by Raoult's law (1)

$$P = x_A P_A + x_B P_B \qquad (1)$$

which simplifies to (2) when the vapour pressure of the solute can be neglected.

$$P = x_A P_A \qquad (2)$$

In the case of ideal solutions and in the absence of mixed crystals, the solubility curve of component B is expressed by equation (3) where ΔH_B is the molar

$$\ln x_B = \ln (1 - x_A) = -(\Delta H_B/R)(1/T - 1/T_B) = -(\Delta H_B/RT) + B \qquad (3)$$

enthalpy of melting and T_B is the melting temperature of the pure solute. B is a constant of entropic nature. P_A is a function of temperature and may be expressed by two- or three-parameter equations. The latter, *e.g.* the Antoine equation, lead to better agreement with the experimental data, whereas the former allows a simpler elaboration of the equations. In fact, by employing equation (4) where ΔH_e is the molar vaporization

$$\ln P_A = -(\Delta H_e/RT) + A \qquad (4)$$

enthalpy of the solvent and A is a constant, and by introducing, following Korvezee, [16] equations (3) and (4) into equation (2), one obtains equation (5).

$$P = \exp [A - (\Delta H_e/RT)] - \exp \{A + B - [(\Delta H_e + \Delta H_B)/RT]\} \qquad (5)$$

Figure 1 illustrates the *P–T* curves calculated for a hypothetical solvent with ΔH_e 8 kcal mol⁻¹ (33.47 kJ mol⁻¹) and P_A 760 mmHg (101.3 kPa) at 400 K and for a hypothetical solute with ΔH_B 8 kcal mol⁻¹ (33.47 kJ mol⁻¹) and T_B 400 K.

The temperature of the maximum pressure point ($T_{P_{max}}$) is given by equation (6), obtained by Korvezee and Dingemans. [17] For $\Delta H_B \ll \Delta H_e$ a limiting value is

$$1/T_{P_{max}} = (1/T_B) + (R/\Delta H_B) \ln[1 + (\Delta H_B/\Delta H_e)] \qquad (6)$$

$$1/T_{P_{max}} = (1/T_B) + R/\Delta H_e \qquad (7)$$

obtained, according to equation (7). In the case shown in Figure 1, the lower limit of $T_{P_{max}}$ is 364 K, whereas the upper one is 400 K, equal to T_B.

When the vapour pressure is measured by an isoteniscope, the pressure drop after $T_{P_{max}}$ is clearly observed (curves MD or MD' depending on compo-

sition). Once the solid phase has disappeared, the pressure starts rising again and its value depends on composition according to equation (2). The maximum M corresponds to the pressure at which the curve of the vapour–liquid equilibrium touches the curve of the solid–liquid equilibrium.

The T–x diagram being known, the P–T curve may be calculated in the ideal case by equation (5), or, more accurately, by equations (3) and (2), using the Antoine equation for the P_A determination. Conversely, the T–x diagram at the equilibrium pressure may be drawn by the opposite procedure from the experimental vapour
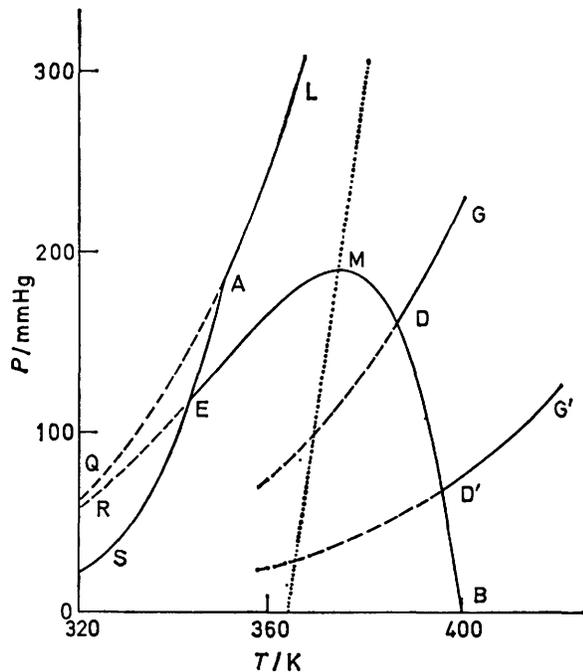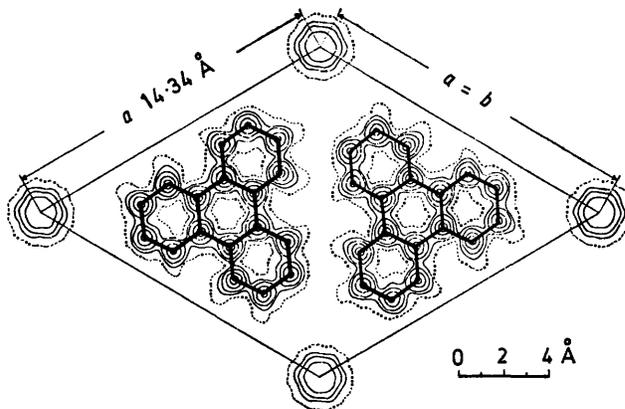

FIGURE 2 Crystal structure of PHTP–n-heptane inclusion compound

crease in pressure must be expected during crystallization. That evidently appears by observing the GDMR (or G'D'MR) curve upon decreasing the temperature. In some conditions, the pressure may increase even more if the solution undergoes much undercooling, i.e. if, before crystallization, the system is situated along the dashed lines.

P–T Curves in the Presence of an Inclusion Compound.—The structure of the PHTP–n-heptane inclusion compound, as well that of pure PHTP, has already been reported by us [1,2] and is shown in Figure 2.

The T–x melting diagram obtained by differential thermal analysis at a pressure between 1 and 2 atm is analogous to that of a binary compound with low stability,[19] which does not form mixed crystals with the pure constituents (Figure 3). It shows a maximum C at 120 °C for x_B ca. 0.8 (B = PHTP), corresponding to that of the pure inclusion compound, and a eutectic point at 118 °C between C and B. PHTP melts at ca.

FIGURE 1 P–T diagram of a binary system forming a simple eutectic mixture. The dotted line connects the $P_{max.}$ points calculated for different values of ΔH_m. DG (respectively D'G') is the vapour pressure curve of a solution with x_A 0.3 (0.1). Dashed lines refer to the metastable portions of the curves

pressure curve.[18] In most cases, such a diagram does not differ markedly from the isobaric plot obtained at $P > P_{max.}$

If the melting temperature of the solvent is not too low, a eutectic point E may be observed between A and B.* In the P–T diagram, E corresponds to the intersection between the liquid curve of B (curve REMB in Figure 1) and the sublimation curve of A (curve SEA). We are reminded that the sublimation pressure coincides with that of a saturated solution of A in B at the same temperature.[18] Below T_E, the pressure of the solid mixture is shown by the curve SE. Obviously, the maximum of the P–T curve cannot be observed if $T_E > T_{P_{max.}}$

As a consequence of the above, a considerable in-

* In the P–T diagrams, the letters A and B indicate the triple points of the pure components.
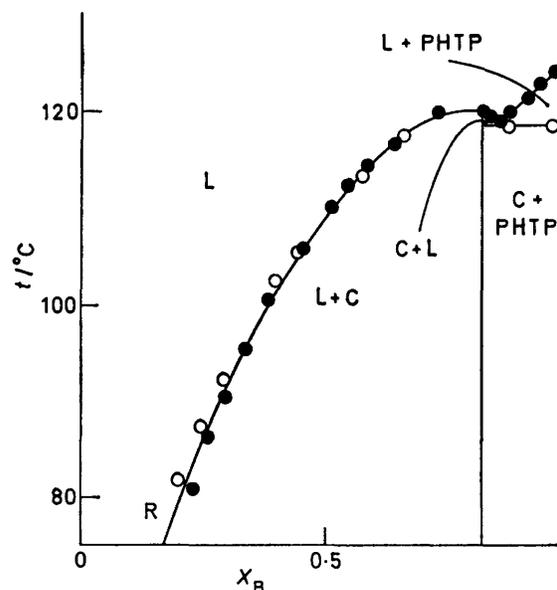

FIGURE 3 T–x diagram of PHTP–n-heptane mixtures. Open circles refer to differential thermal analysis measurements, full circles to vapour pressure measurements

125 °C. A second eutectic point should exist between A (n-heptane) and C at a temperature outside the experimental range of our instrument (below —90 °C) and with x_A ca. 1.

The experimental liquid curve is in good agreement with that calculated from the equation for binary compounds [20,21] given the hypotheses of complete dissociation, of ideal behaviour in the liquid phase, and of insolubility in the solid phase [equation (8) where x_A and

$$\ln(x_A/x_{0A}) + n \ln (x_B/x_{0B}) = -(\Delta H_C/R) (1/T - 1/T_C) \quad (8)$$

x_B are the molar fractions of the constituents in the liquid in equilibrium with the solid inclusion compound at temperature T, x_{0A} and x_{0B} are the molar fractions of the constituents in the pure inclusion compound, n is the stoicheiometric ratio between components B and A in the binary compound ($n = x_{0B}/x_{0A}$), ΔH_C is the melting enthalpy of the addition compound C referred to one mole of A (and assumed to be constant to a first approximation), and T_C is the temperature of congruent melting of the inclusion compound].

If an inclusion compound which contains a volatile guest molecule forms a crystalline phase differing from the pure host and does not form mixed crystals, the three-phase system, inclusion compound (crystal)–host (crystal)–vapour, is monovariant, i.e. at a given temperature it has a definite decomposition pressure, which varies with temperature according to the Clapeyron law.[22] In its simplest form, the integrated Clapeyron equation is (9) where ΔH_v refers to one mole of n-heptane in

$$\ln P = -(\Delta H_v/RT) + D \quad (9)$$

Inclusion compound (crystal) ⇌
  PHTP (crystal) + n heptane (vapour) (10)

reaction (10). By dividing P by P_A (vapour pressure of pure heptane at the same temperature), we obtain
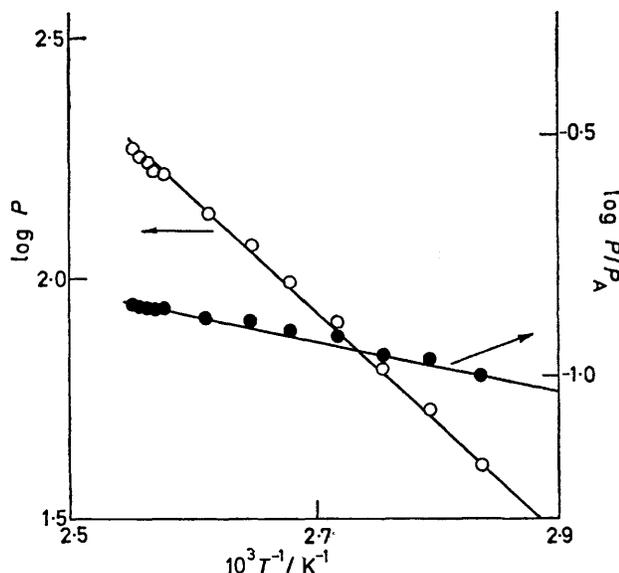

FIGURE 4   Decomposition pressure of the PHTP–n-heptane inclusion compound versus $1/T$
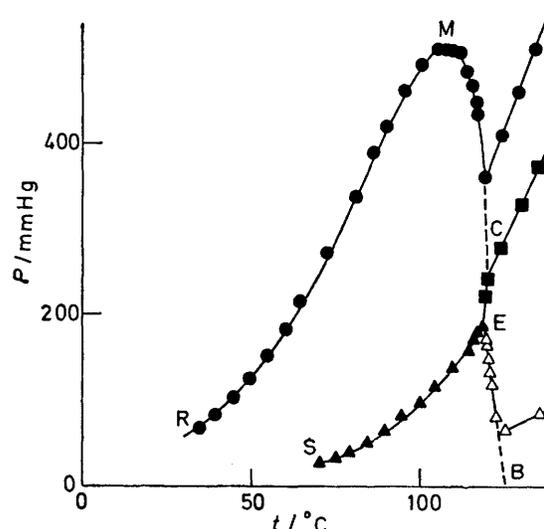

FIGURE 5 $P–T$ projection diagram of PHTP–n-heptane binary system. The vapour pressure curve of pure n-heptane is not reported

equation (11) where ΔH_{dec} ($= -\Delta H_{incl}$) refers to reaction (12).

$$\ln (P/P_A) = -(\Delta H_{dec}/RT) + D' \quad (11)$$

Inclusion compound (crystal) ⇌
  PHTP (crystal) + n-heptane (liquid) (12)

The validity of equations (9) and (11) has been experimentally confirmed (Figure 4). All mixtures of inclusion compound and PHTP with different compositions have the same vapour pressure. The good linearity of the logarithmic diagram indicates that ΔH_v and ΔH_{dec} are nearly constant with temperature.

We have extended the study of vapour pressures to the whole composition range and to temperatures between 30 and 140 °C. Two phenomena of retrograde condensation, with a pressure maximum, have been observed (Figure 5), one in the composition range $x_A > x_{0A}$ and the other in the range $x_A < x_{0A}$; furthermore, and this may seem even more peculiar at first sight, a sudden increase in pressure takes place during melting, for x_A equal to or slightly lower than x_{0A}.

Such findings are interpreted on the basis of the phase rule and of the essential features of $P–T–x$ projection diagrams. As first observed by Roozeboom [6f] and clearly pointed out by Ricci,[12] in the presence of a binary compound the $P–T$ diagram exhibits two invariant quadruple points, i.e. two eutectics, between A and C and between C and B. Our attention has been focused on the latter, called incongruent eutectic, since the composition of the vapour phase is outside the C—B range. In that point, phases V–C–L–B coexist (in the indicated order with increasing x_B). In the diagram, at least three lines converge at E, the liquid curve of the binary compound C (curve RMCE), the liquid curve of component B (BE), and the solid–vapour decomposition curve of the crystalline compound C (SE).

Three cases may be distinguished depending on composition.

(i) $x_A > x_{0A}$.—The P–T projection of the liquid curve of the inclusion compound C in the presence of an excess of n-heptane is obtained by introducing P_A values, calculated from the Antoine equation, and x_A values, from equation (8), into equation (2). Alternatively, we may write equation (13).

$$\ln\left[(n+1)P/P_A\right] + n\ln\left\{[(n+1)/n]\left[1 - (P/P_A)\right]\right\} = -(\Delta H_C/R)(1/T - 1/T_C) \quad (13)$$

The RMC curve is regarded as a solubility curve of the binary compound.[12] A pressure maximum exists at 510 mmHg and 108 °C. It arises from the combined action of two conflicting factors, the increase in P_A and the increase in solubility (and hence the decrease in x_A) with temperature. Above $T_{P_{max}}$, the pressure decreases very rapidly and, after complete dissolution, it rises again according to equation (2), by taking $x_A = $ constant. By linear regression analysis, we calculated the extrapolated congruent melting point of the inclusion compound C (t_C 120 °C), which coincides with that measured by differential thermal analysis.

(ii) $x_{0A} > x_A > x_{EA}$.—For compositions ranging between that of the inclusion compound and of the eutectic mixture containing C and B, equation (9), corresponding to the decomposition of the inclusion compound into pure host and vapour without formation of a liquid phase, holds at a temperature lower than T_E (curve SE). Above T_E, the inclusion compound decomposes into a liquid phase and vapour: the pressure follows the equations described in case (i) (curve CE). At point E, a clear discontinuity exists in the slope of the curve. In the system PHTP–n-heptane, the temperatures of points E and C are so close (*ca.* 1 °C) that the discontinuity in the slope simulates a discontinuity in the value of the pressure, a phenomenon which is inconsistent with equilibrium conditions. The CE curve portion is indicated [12] as the decomposition curve of compound C, according to the equation C $\rightleftharpoons$ L + V.

(iii) $x_A < x_{EA}$.—For compositions ranging between the eutectic point E and the pure constituent B, equation (9) holds below T_E. The pressure coincides with that of case (ii). Above T_E, the pressure decreases along the solubility curve of B, either expressed by equation (5) or obtained more accurately by introducing the Antoine equation and equation (3) into equation (2). Therefore, the eutectic point E represents a maximum pressure point for all mixtures with a large excess of PHTP.

With the hypothesis of ideal behaviour in the liquid and vapour phases, the P–T curves may be converted into the liquid curves of the T–x diagram (at the equilibrium pressure) by dividing P by P_A. The T–x curve is very close to that obtained by differential thermal analysis (Figure 2), in spite of the different nature of the experimental methods and of the approximations involved in the conversion of the diagrams.

The best values drawn from our experiments are reported in the Table.

Our results demonstrate that the behaviour of PHTP inclusion compounds fits well into the classical theory of

Thermodynamic parameters of PHTP–n-heptane binary system

P_{max}. 510 $\pm$ 2 mmHg (68.0 $\pm$ 0.3 kPa)
$t_{P_{max}}$. 108.0 $\pm$ 0.5 °C
t_C 120.0 $\pm$ 0.2 °C (extrapolated value)
t_E 119.0 $\pm$ 0.5 °C (intersection of curves CE, DE, and BE)
P_E 187 $\pm$ 5 mmHg (24.9 $\pm$ 0.7 kPa) (intersection of curves CE, DE, and BE)
t_B 125.3 $\pm$ 0.2 °C (extrapolated value)
ΔH_v 10.8 $\pm$ 0.2 kcal mol^{-1} n-heptane (45.2 $\pm$ 0.8 kJ mol^{-1} n-heptane)
ΔH_{dec} 2.8 $\pm$ 0.2 kcal mol^{-1} n-heptane (11.7 $\pm$ 0.8 kJ mol^{-1} n-heptane)

binary compounds, like racemates, solvates, hydrates, *etc.* The assumption of ideal behaviour in the liquid state is sufficient for a qualitative and a semi-quantitative analysis of the P–T curves in the PHTP–n-heptane system. However, some thermodynamic parameters, like ΔH_C and ΔH_B, have not been accurately determined.

A more quantitative approach, which seems necessary when considering polar guest molecules, may be carried out on the basis of the theory of regular solutions; this treatment will be discussed in a future paper. However it should be stressed that in the present case the deviation from ideality is small and the essential features of P–T and T–x curves are mainly related to the presence of the crystalline adduct, the formation of which depends, in turn, on the particular shape and symmetry of PHTP molecules and not on polar factors.

EXPERIMENTAL

Differential thermal analysis curves were obtained by a Mettler TA 2000 thermoanalyser, using sealed aluminium sample holders. Scan speed generally ranged between 1 and 2.5 °C min^{-1}.

Vapour pressures were measured by a Smith–Menzies isoteniscope,[23] modified for introduction of solid materials, using mercury as a confining liquid. Levelling of mercury in the U tube was observed by a kathetometer telescope. Pressure was measured by a mercury manometer and a kathetometer ($\pm$0.1 mmHg up to 500 mmHg, $\pm$1 mmHg above 500 mmHg). Corrections for expansion of scales and change in mercury density with temperature, as well as for the vapour pressure of mercury inside the isoteniscope, were taken into account.[24] Values of the constants of Antoine equation of n-heptane were taken from the literature.[25] Vapour pressure of PHTP was neglected, being lower than 1 mmHg at 140 °C.

Pure PHTP [26] placed in the bulb of an isoteniscope and the calculated amount of n-heptane (Carlo Erba, high purity g.l.c. standard) contained in a small flask were accurately degassed at 10^{-5} mmHg. The solvent was distilled into the isoteniscope through a vacuum line. During measurements, the temperature was kept constant ($\pm$0.03° up to 80 °C, $\pm$0.1° from 80 to 140 °C). Before each determination the isoteniscope was allowed to equilibrate for a time varying from 3 to 24 h depending on the conditions.

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