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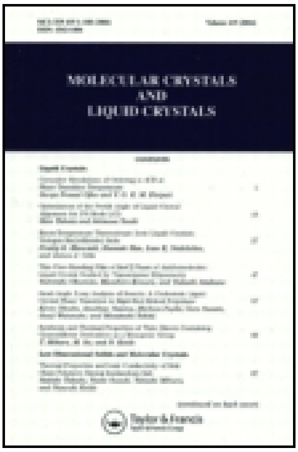

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n-Octane + n-Decane: a Eutectic System in the n-Alkane Family; Experimental Phase Diagram and Thermodynamic Analysis

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n-Octane + *n*-Decane: a Eutectic System in the *n*-Alkane Family; Experimental Phase Diagram and Thermodynamic Analysis

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The experimental temperature versus composition phase diagram of the system $n\text{-}C_8H_{18}$—$n\text{-}C_{10}H_{22}$ obtained by thermal analysis and X-ray powder diffraction is characterized by a simple eutectic and little miscibility in the solid state. The eutectic invariant is at 211.7 K and the eutectic composition is at a molar composition of 0.16 in C_{10}. The calculated phase diagram, obtained by thermodynamic analysis, is in full agreement with the experimental one. The value of the coefficient of crystalline isomorphism, ε_m^i, for this system is 0.76.

Keywords: n-alkanes -n-octane–n-decane binary phase diagram-Crystallographic and energetic characterization-Thermodynamic analysis

I. INTRODUCTION

In this work, we report detailed results on the binary solid-liquid phase diagram for $n\text{-}C_8H_{18}$—$n\text{-}C_{10}H_{22}$. To our knowledge this binary system has not been published before. Both *n*-octane C_8H_{18} and *n*-decane $C_{10}H_{22}$ belong to the family of *n*-alkanes C_nH_{2n+2}. The phase diagram, established by means of differential scanning calorimetry and X-ray powder diffraction, shows little miscibility in the solid state. The significance of the experimental data is supported by a thermodynamic analysis. In the following, the system is simply referred to as C_8–C_{10}.

The work is part of a research project on syncrystallization between components belonging to families of molecular substances.

II. EXPERIMENTAL

n-octane and *n*-decane were purchased from FLUKA. Their purities, carried out by gas phase chromatography coupled with mass spectrometry, were 99.5% and 98.9% respectively. No further purification has been made. The effect of impurities can be considered as negligible here since the values found for the DSC shape-factors of octane and decane correspond to the characteristic value of the family of even-numbered alkanes ($n = 8$ to $n = 16$).[1,2]

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II.1 CALORIMETRIC MEASUREMENTS

Calorimetric measurements were made with a Perkin-Elmer DSC-7 differential scanning calorimeter. The following conditions were adopted during the investigation:

- Sample weight: 4 mg.
- Scanning rate: 2 K/min.
- Three independent measurements for each sample.

From the DSC curves the liquidus temperatures were determined with the use of the shape-factor method[1]. Enthalpies effects were derived from the DSC recordings by integration.

II.2 CRYSTALLOGRAPHIC MEASUREMENTS

The cell parameters of the pure components at selected temperatures were determined by means of X-ray powder diffraction, using a Siemens D500 diffractometer. For the mixed samples, X-ray powder diffraction measurements were carried out with a Guinier-Simon camera. The wavelength of copper $K_{\alpha 1}$ radiation ($\lambda = 1,5406$ Å) is used in both cases.

III. PROPERTIES OF *n*-OCTANE AND *n*-DECANE

Both *n*-octane and *n*-decane crystallize in a triclinic structure ($P\bar{1}$, $Z = 1$). Their cell parameters measured with the D500 diffractometer at 173 K and 233 K respectively are given in Table I. There is good agreement with the results given by other authors.[3,4]

The temperatures and enthalpies of melting of both *n*-octane and *n*-decane are given in Table II.

TABLE I

Cell parameters of octane and decane

	C_8H_{18}		$C_{10}H_{22}$	
References	3	This work	4	This work
T(K)	193	173	?	233
a(Å)	4.16	4.16 ± 0.02	4.25	4.31 ± 0.01
b(Å)	4.75	4.76 ± 0.02	4.81	4.81 ± 0.01
c(Å)	12.13	12.4 ± 0.2	14.81	14.9 ± 0.2
α(°)	80.5	80.1 ± 0.9	82.1	81.6 ± 0.2
β(°)	64.5	62 ± 2	65.2	64.7 ± 0.2
γ(°)	74.9	75.4 ± 0.9	74.4	73.5 ± 0.1

TABLE II

Melting temperatures and enthalpies of octane and decane

	C_8H_{18}		$C_{10}H_{22}$	
References	5	This work	5	This work
T_m(K)	216.3	216.6 ± 0.8	243.5	243.0 ± 0.8
ΔH_m(kJ/mol)	20.8	21.8 ± 0.3	28.7	27.6 ± 0.6

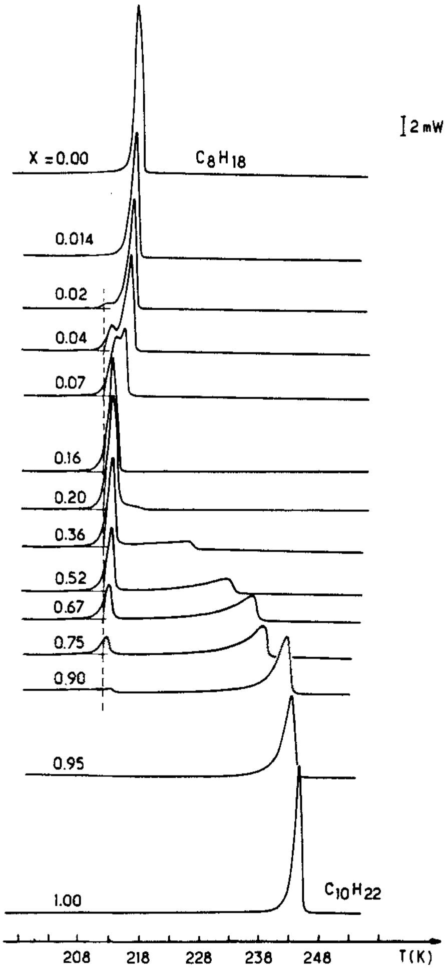

FIGURE 1 Evolution of the DSC curves.

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IV. EXPERIMENTAL PHASE DIAGRAM

Nineteen mixtures of C_8–C_{10} were studied by DSC. Figure 1 shows the most important curves as a function of composition. The set of curves clearly reveals the presence of a eutectic invariant.

The Tammann procedure was used to fix the right-hand boundary of the solid state miscibility gap (see Fig. 2). The intersection of the straight line with the horizontal axis (% in weight of C_{10}) is found at 91.0% which corresponds to a molar composition of 0.89 in C_{10}.

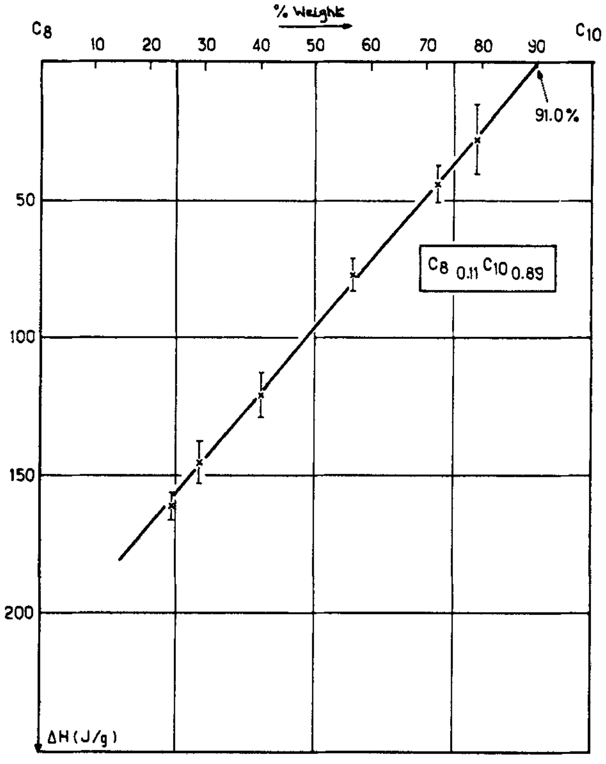

FIGURE 2 The plot of Tammann for C_8–C_{10}.

Obviously, at the C_8 side the DSC data does not allow the use of the Tammann procedure. For that reason and in view of the fact that *n*-octane and *n*-decane are isomorphous, a plot of ΔH_m (enthalpy of melting) versus composition was used to determine the positions of the two boundaries. Figure 3 shows the general behaviour of ΔH_m versus composition for a) binary systems with continuous miscibility in the solid state and b) a eutectic system.

Starting from the components A and B, the two curves follow the same path until the compositions x_K and x_M. For a eutectic system, the evolution of ΔH_m versus composition is a straight line inside the region of demixion. Thus x_K and x_M represent the limits of the two-phase region. Taking this into account, the curve of ΔH_m versus composition

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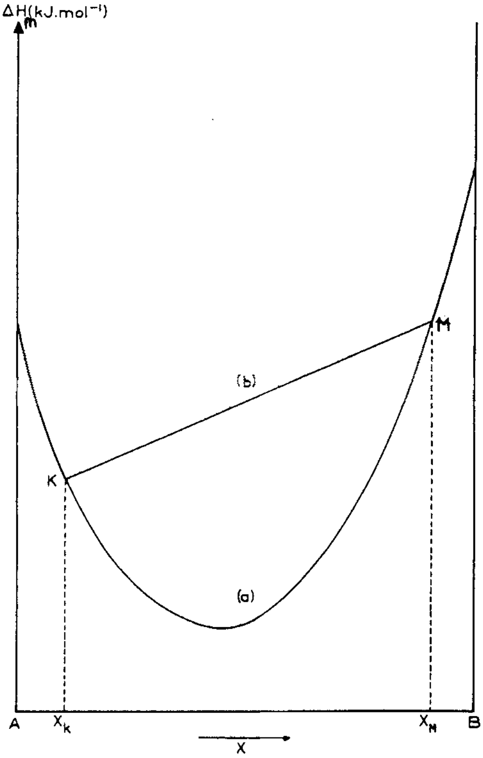

FIGURE 3 ΔH_m versus composition for a) binary system with complete miscibility in the solid state and b) a eutectic system.

of the system C_8–C_{10} was plotted. The values found for x_K and x_M are 0.03 and 0.89 respectively. It can be noted that x_M corresponds to the value found by the Tammann procedure. The plot is shown in Figure 4.

Five binary samples ($x = 0.04$, 0.25, 0.52, 0.75 and 0.95 in C_{10}) and the starting components were studied using the Guinier-Simon camera. The sample with $x = 0.95$ gave a single-phase and the others a double-phase diffraction pattern. Obviously, and in agreement with the results reported above, the sample with $x = 0.95$ is outside whereas the others are inside the region of demixing. In order to obtain the solid state solubility limits, we have used the d_{011} evolution with composition at a given temperature (203 K). These limits (Fig. 5) are approximately 0.02 and 0.90.

The experimental data are assembled in Figure 6 and correspond to a phase diagram showing a eutectic with partial solubility (around 10%) in the solid state for alloys rich in $C_{10}H_{22}$ and very low solubility of $C_{10}H_{22}$ in C_8H_{18}. The eutectic temperature is 211.7 ± 0.4 K and the eutectic composition $x_L = 0.16 \pm 0.01$.

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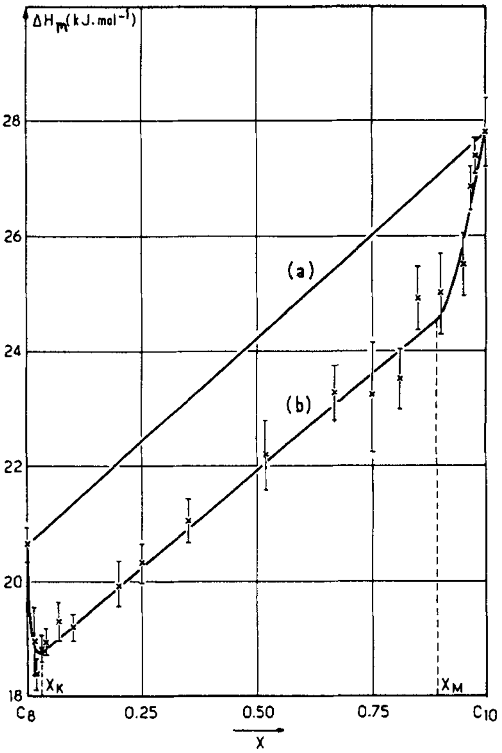

FIGURE 4 ΔH_m versus composition for the system C_8–C_{10}.

V. THERMODYNAMIC ANALYSIS

The TXFIT computer program[6] was used to calculate the excess Gibbs energy in the solid state. To perform the calculation, the properties of the pure components (entropy and temperature of melting) and the experimental liquidus and solidus points are required. The two components are supposed to be isomorphous and thus only one function $G(X)$ is used to describe the solid state at a given temperature. To start with, we supposed ideal behaviour of the liquid phase ($G^{E,\text{liq}} = 0$); the calculated phase diagram however did not completely fit the experimental data. So we took $G^{E,\text{liq}} < 0$ coupled with the previously calculated $G^{E,\text{sol}}$. A very good agreement between experimental and calculated diagram is obtained for:

$$G^{E,\text{sol}}(x) = x\cdot(1-x)\cdot[5750 + 1680\cdot(1-2x)]\ \text{J}\cdot\text{mol}^{-1}$$

$$= 5750\cdot x\cdot(1-x)\cdot[1 + 0.29(1-2x)]\ \text{J}\cdot\text{mol}^{-1}$$

$$G^{E,\text{liq}}(x) = x\cdot(1-x)\cdot[-300 - 250\cdot(1-2x)]\ \text{J}\cdot\text{mol}^{-1}$$

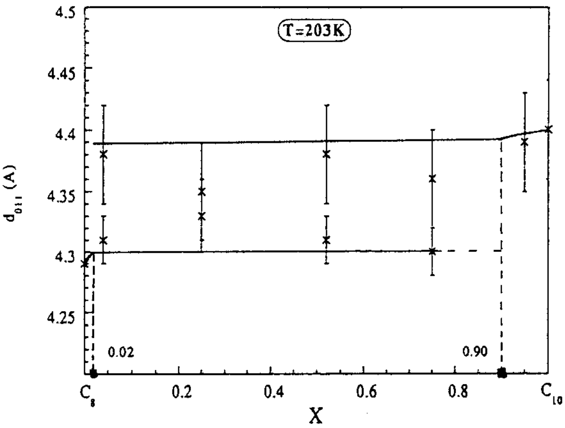

FIGURE 5 Variations of d_{011} versus composition in C_{10}.

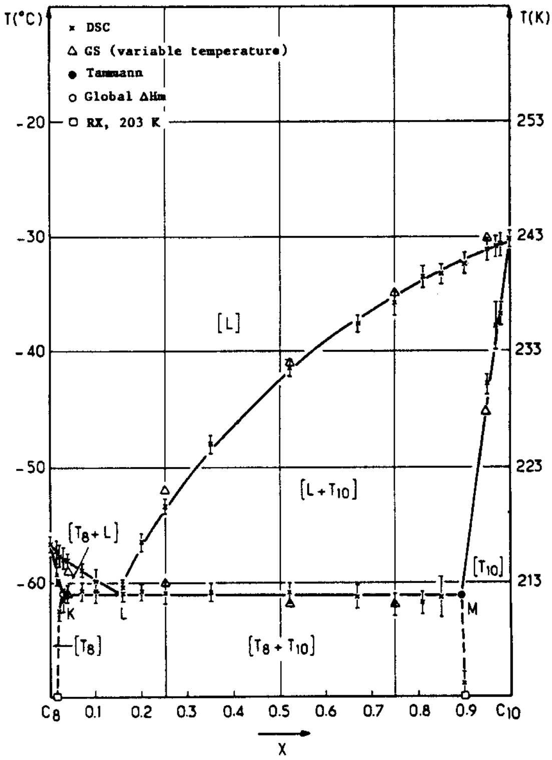

FIGURE 6 Phase diagram of C_8–C_{10}.

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VI. DISCUSSION

In spite of the similarity of the pure components (both are triclinic with slight differences in the lattice parameters) no continuous solid solubility (that is over the whole composition range) is observed. In fact, the region of demixion covers a very large part of the composition range. The Tammann procedure and the plot of ΔH_m versus composition show that the degree of solid solubility is more pronounced for compositions rich in C_{10} than for those rich in C_8. The asymmetry of the region of demixion finds expression in the 'asymmetry term', that is the value 0.29, in the excess Gibbs energy function of the solid state.

To explain the large two-phase region, we can consider the coefficient of crystalline isomorphism,[7] ε_m^i which is defined as: $\varepsilon_m^i = 1 - (\Delta_m/\Gamma_m)$ where Δ_m is the total volume due to the non-overlapping parts and Γ_m the volume due to the overlapping part when the two cells of the pure components are superimposed in such a way that their overlap is maximal. For the system C_8–C_{10}, we have found $\varepsilon_m^i = 0.76$.

The work done till now in the REALM (Réseau Européen sur les Alliages Moléculaires),[8–11] to which we belong, has shown that the value found here for ε_m^i is a weak intrinsic one and that in this case it is not surprising to observe little miscibility in the solid state.

If we consider the alkane family, we can compare our result with those found by P. Espeau:[12]

$$n\text{-}C_{15}H_{32}\text{—}n\text{-}C_{17}H_{36} : \varepsilon_m^i = 0.88.$$

$$n\text{-}C_{17}H_{36}\text{—}n\text{-}C_{19}H_{40} : \varepsilon_m^i = 0.89.$$

In these two binary systems, complete miscibility is observed.

On the contrary, for the system n-$C_{15}H_{32}$—$C_{21}H_{44}$,[13] the value for ε_m^i is 0.64 and the miscibility is only limited.

Our work confirms that the coefficient of crystalline isomorphism is a factor which classifies the extent of syncrystallization between components belonging to the same family of molecular substances, particularly when all the intermolecular interactions are the same (van der Waals forces for the alkane family).

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