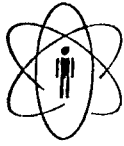




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X-RAY DIFFRACTION AND CALORIMETRIC PHASE STUDY OF A BINARY

PARAFFIN: $C_{23}H_{48}$ - $C_{24}H_{50}$

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STUDY OF A BINARY PARAFFIN: $C_{23}H_{48}$ - $C_{24}H_{50}$

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Introduction

From the early work of Muller [1] it was established in most of normal paraffins (C_nH_{2n+2}) the presence of a crystalline phase at low temperatures and a "rotator" phase at temperatures between the crystal and the liquid. The crystalline structure of paraffins has been characterized by a compact stacking of the molecular chains with their long axes perpendicular to the stacking plane in odd-numbered and tilted in even-numbered paraffins.

The crystalline lattice of odd-numbered paraffins with $n \leq 25$ is orthorhombic and its space group is Pcam. The even-numbered paraffins have a triclinic lattice and space group PT.

At temperatures above the crystalline phase, several disordered phases were found. In odd-numbered paraffins, hexagonal and/or quasi-hexagonal phases were identified [2][3]. The structure of the quasi-hexagonal phase, which is found in odd-numbered paraffins with $n \leq 25$, presents an orientational disorder of the molecular chains. This disorder increases with temperature and, for $C_{23}H_{48}$ and $C_{25}H_{52}$, an additional transition to an hexagonal structure occurs [4]. The paraffins with $n=19$ and 21 melt before the hexagonal symmetry state is reached. Even numbered paraffins with $22 \leq n \leq 26$ transform from the crystal directly to a "rotator" phase with hexagonal symmetry [5].

The previous studies of pure paraffins were carried out on samples with purity ranges from 97 to 99%*. We thought worthwhile to perform a systematic study of a mixture of two paraffins in order to establish the influence of the degree of purity on the

* The compositions are given in weight %.

structure. We selected for this study a binary system composed by $C_{23}H_{48}$ and $C_{24}H_{50}$. The $C_{23}H_{48}$ paraffin presents at increasing temperatures: primitive orthorhombic, centered orthorhombic (quasi-hexagonal), and hexagonal structures [4]. The $C_{24}H_{50}$ paraffin has a triclinic lattice at low temperatures and an hexagonal one below the liquid [5].

Most of the previous determinations of binary phase diagrams of paraffins were done without X-ray diffraction measurements and, consequently, the structures of the observed phases were not given or only suggested. A detailed study of a binary even-even paraffin ($C_{20}H_{42}$ - $C_{22}H_{46}$) involving calorimetric and diffraction experiments, showed a complete solid miscibility at high temperatures (rotator phases) and a complex phase behaviour at low temperatures [7]. Unfortunately the rotator phase region was not accurately studied in this work since the quasi-hexagonal and hexagonal phase were not distinguished.

Materials and methods

The compounds of $C_{23}H_{48}$ and $C_{24}H_{50}$ have been purchased from Fluka and their purity grade were 99% and >98% , respectively. The samples were prepared by mixturing weighted amounts of the pure components in liquid state. Binary mixtures covering the whole range of composition in steps of 2% near the edges and 10% in the center of the phase diagram were prepared. The components were mixed by shaking the melt and pouring it in the cells for thermal calorimetry and X-ray diffraction studies.

The differential thermal analysis (DTA) experiments have been performed on a Mettler ATD 2000 instrument. The X-ray diffraction measurements have been carried out on powder samples with a Guinier camera (CGR) equipped with a water-heated cell using focused monochromatic beam ($CuK\alpha_1 = 1.5403 \overset{0}{\text{\AA}}$). The samples

were held at constant temperatures ($\pm 0.2^\circ\text{C}$) during the X-ray diffraction measurements.

Calorimetric and X-ray results (phase diagram)

The differential calorimetric analysis was performed on twenty one binary mixtures and the two pure compounds. They were heated at a rate of $1^\circ\text{C}/\text{min}$, from room temperature to above the liquidus. Fig. 1 gives the set of calorimetric curves for every composition.

The DTA curves, which corresponds to pure $\text{C}_{24}\text{H}_{50}$, show two peaks. One of them is due to the transition triclinic crystalline phase (C_T) \rightarrow hexagonal rotator phase (R_{II}) which has been previously studied [5]. The other corresponds to the melting of the R_{II} phase. The DTA of pure $\text{C}_{23}\text{H}_{48}$ shows an additional weak peak. The sequence of peaks from low to high temperatures for $\text{C}_{23}\text{H}_{48}$ is associated with the following transitions: primitive-orthorhombic (crystalline) phase (C_0) \rightarrow face-centered-orthorhombic (rotator) phase (R_I) \rightarrow hexagonal (rotator) phase (R_{II}), whose features were discussed in previous works [2] [3].

Starting from the $\text{C}_{24}\text{H}_{50}$ side of Fig. 1 and at increasing $\text{C}_{23}\text{H}_{48}$ content, a clear lowering of the transition temperature $\text{C}_T \rightarrow \text{R}_{II}$ is apparent. The melting temperature weakly decreases. Starting from the $\text{C}_{23}\text{H}_{48}$ side, an important diminution of the $\text{C}_0 \rightarrow \text{R}_I$ transition temperature occurs. The transition temperature $\text{R}_I \rightarrow \text{R}_{II}$ diminishes from 0 to 20% of $\text{C}_{24}\text{H}_{50}$ and it remains approximately constant for higher $\text{C}_{24}\text{H}_{50}$ content up to 30%. The temperature of the transition $\text{R}_{II} \rightarrow$ liquid slightly increases with $\text{C}_{24}\text{H}_{50}$ content.

The X-ray diagrams corresponding to the quasi-pure compounds (with same % of the minority component) show the same fea-

tures than the diagrams obtained from pure paraffins. The powder X-ray diffraction diagrams of $C_{23}H_{48}$ with 0 to 70% of $C_{24}H_{50}$ have the same qualitative features, indicating a high solubility of $C_{24}H_{50}$ in solid phase. All the low temperature diagrams in this composition range were indexed under the assumption of primitive orthorhombic lattices. The structures of the rotator phases are similar than those of pure $C_{23}H_{48}$ (R_I and R_{II} phases). The lattice parameter variations were determined as a function of composition. They will be discussed in a next section.

The mixtures containing 2, 4, 6 and 8% of $C_{23}H_{48}$ do not present the $R_I \rightarrow R_{II}$ transition which occurs for higher $C_{23}H_{48}$ content: neither the DTA curves nor the X-ray diagrams bring evidencies of it. The width of the $C_T \rightarrow R_I$ or R_{II} DTA peak increases with the $C_{23}H_{48}$ content up to approximately 20%.

The low temperature X-ray diagrams of the binary systems with 18, 20 and 24% of $C_{23}H_{48}$ indicate the coexistence of a mixture of the C_T and C_0 phases for this composition domain. This two-phase region was found in these systems up to 40°C.

Fig. 2 represents the phase diagram which was determined from DTA and X-ray results, taking into account the thermodynamic constraints. The width of the two phase regions at high temperature has been determined by the difference between the DTA peak of the pure components and those of the different mixtures. The two phase domain of crystalline phases was established by determining the presence of a mixture of phases from the X-ray diagrams.

The main features of the phase diagram are the important solubility of both components (mainly $C_{23}H_{48}$ in $C_{24}H_{50}$), the lowering of the transition temperature $C_0 \rightarrow R_I$ and the approxima-

tely linear dependence on composition of the $R_{II} \rightarrow L$ transition temperature.

The phase diagram shows an eutectoid at a temperature of 40°C and, probably, a peritectoid at about 46°C and 6% of $C_{23}H_{48}$.

Primitive orthorhombic (crystalline) phase (C_0)

In the $C_{23}H_{48}$ side of the phase diagram up to 70% of $C_{24}H_{50}$, the same phases than those of pure $C_{23}H_{48}$ (C_0 , R_I and R_{II}) are present. The lattice parameters of the crystal (C_0) phase, obtained from the X-ray diffraction measurements, are given as a function of the composition in Fig. 3. We do not find significant variations with composition of the parameters \underline{a} and \underline{b} of the orthorhombic cell. The only apparent influence of the addition of $C_{24}H_{50}$ to pure $C_{23}H_{48}$ is the linear increase of the lattice parameter \underline{c} . Fig. 3 shows the approximate linear dependence on composition of $\underline{c}/2$ (molecular layer thickness).

Rotator phases (R_I and R_{II})

The structures of R_I and R_{II} phases are centered orthorhombic and hexagonal, respectively. The transitions $C_0 \rightarrow R_I \rightarrow R_{II}$ can be characterized by the quotient between the short lattice \underline{a} and \underline{b} parameters. The value of a/b in the crystalline orthorhombic phase is a constant near 1.50 for every composition as it can be seen in Fig. 4. A discontinuity at the $C_0 \rightarrow R_I$ transition temperatures and a continuous and important increase, starting from about 1.55 Å above the $C_0 \rightarrow R_I$ transition, are apparent in Fig. 4. The a/b quotient reaches the value $\sqrt{3}$ for every composition above the transition temperature $R_I \rightarrow R_{II}$ and remains constant at higher tem-

peratures up to the $R_{II} \rightarrow$ liquid transition. These results are equivalent to those obtained in a previous work on pure $C_{23}H_{48}$ [4]. The present work seems to indicate a weak discontinuity of b/a at the transition temperatures $T(R_I \rightarrow R_{II})$.

The long spacing of the rotator phase at 47°C was represented as a function of composition in Fig. 5; (at 47°C the mixture presents a R_{II} phase for almost the whole composition range). The long spacing of all the binary mixtures corresponds to a linear interpolation of the long spacing of the pure components. The short parameter a of the hexagonal lattice, which is also plotted in Fig. 5, has a constant value throughout the whole composition range.

Discussion

These calorimetric and X-ray studies of the binary mixture $C_{23}H_{48}-C_{24}H_{50}$ indicate the existence of four stable phases. Two of them, at low temperatures, are the ordered terminal solid solutions of the pure components: triclinic C_T ($C_{24}H_{50}$ side) and primitive orthorhombic C_O ($C_{23}H_{48}$ side). At high temperatures two disordered "rotator" phases occur. The hexagonal rotator (R_{II}) phase exists for all compositions below the liquid. The orthorhombic rotator (R_I) phase was detected for all compositions, excepted a narrow region of few percent near the $C_{24}H_{50}$ side of the phase diagram. The total miscibility between the R_{II} phase of the odd-numbered $C_{23}H_{48}$ and the R_{II} phase of the even-numbered $C_{24}H_{50}$ proves that the two phases are of the same nature and that it is safe to design them by the same symbol R_{II} . This criterion of classification has been developed by H. Sackmann et D. Demus [6] for thermotropic liquid crystals.

The constancy of the short lattice parameters a and b of the C_O phase for varying concentration (Fig. 5), means that there is no appreciable variation of lateral packing of the molecular chains in the different mixtures. The linear variation of the long parameter c with composition is consistent with the absence of voids between the terminal

molecular groups [7].

The high temperature phases of most of the mixtures are the same than those found in $C_{23}H_{48}$ paraffins [4]. As it was observed in the low temperature phases, the long parameter c (layer thickness) has a linear dependence on composition. The temperature dependence of the ratio a/b , which is similar to that found in pure $C_{23}H_{48}$ [4], indicates a continuous increase of the orientational disorder of the molecular chains around their long axis.

The domain of stability of the orthorhombic R_I phase increases from the $C_{23}H_{48}$ side and reaches a maximum at about 50% of $C_{24}H_{48}$. At higher $C_{24}H_{48}$ content the domain of R_I decreases to zero at about 95% of $C_{24}H_{50}$; the triclinic C_T phase is stable up to a rather high temperature preventing the formation of the R_{II} phases at low $C_{23}H_{48}$ concentration.

The phase behaviour of the binary system $C_{23}H_{48}$ - $C_{24}H_{50}$ is rather simple: the observed phases are solid solutions of the terminal phases. The additions of few percent of $C_{23}H_{48}$ in $C_{24}H_{50}$ and 70% of $C_{24}H_{50}$ in $C_{23}H_{48}$ do not change the type of structure of the pure components: only variations of the long spacing and the transition and melting temperatures were detected. The eutectoid involving C_O , C_T and R_I seems well established but the peritectoid region (C_T+R_I leading to R_{II} by rising temperature) is still schematic. In order to obtain a closer insight on this temperature and composition domain, further X-ray and calorimetric work is needed.

Small-angle X-ray diffraction were recently used to study molecular disorders in the rotator phases of several pure paraffins [8]. Because of the increase of the stability temperature domain of the rotator phase in mixtures, similar studies on this binary system would permit a more detailed analysis of the temperature dependence of the molecular disorders. This work is now in progress.

REFERENCES

- [1] A.Muller, Proc. Roy. Soc., A127, 417 (1930).
- [2] J.Doucet, I. Denicolo, A.Craievich, J. Chem. Phys., 75, 1523 (1981).
- [3] G.Ungar, J. Chem. Phys., 87, 689 (1983)
- [4] J.Doucet, I.Denicolo, A.Craievich, A.Collet, J. Chem. Phys., 75, 5125 (1981).
- [5] J.Doucet, I.Denicolo, A.Craievich, J. Chem. Phys., 78, 1465 (1983).
- [6] H.Sackmann, D.Demus, Fortschritte. Chem. Forsch. Berlin, Heidelberg, New-York, 12, 349 (1969).
- [7] H.Lüth, S.C.Nyburg, P.M.Robinson, H.G.Scott, Mol. Cryst. Liq. Cryst. 27, 337 (1974).
- [8] A.Craievich, J.Doucet, I.Denicolo. To be published (1983).

FIGURE CAPTIONS

- Fig. 1 - D.T.A. curves of $C_{24}H_{48} - C_{24}H_{50}$. Concentrations are given in weight fraction of $C_{23}H_{48}$. The arrows indicate the D.T.A. peaks corresponding to the $R_I \rightarrow R_{II}$ transition.
- Fig. 2 - Phase diagram of the $C_{23}H_{48} - C_{24}H_{50}$ system. Phases identified by X-ray diffraction are: \circ triclinic, \bullet primitive orthorhombic, \blacktriangle face-centered orthorhombic, \square hexagonal, \odot triclinic and primitive orthorhombic, \oplus triclinic and face-centered orthorhombic. The phase boundaries were determined from the D.T.A. measurements.
- Fig. 3 Lattice parameters of the primitive orthorhombic phase at $25^\circ C$ (crystal phase).
- Fig. 4 - Quotient of the short lattice parameters of the orthorhombic cells as a function of temperature. The curves were vertically displaced for clarity. The concentrations are given on the plots in weight % of $C_{24}H_{50}$.
- Fig. 5 - Short lattice parameter, a , and long spacing (layer thickness), d , as a function of composition at $47^\circ C$ (Rotator II phase).

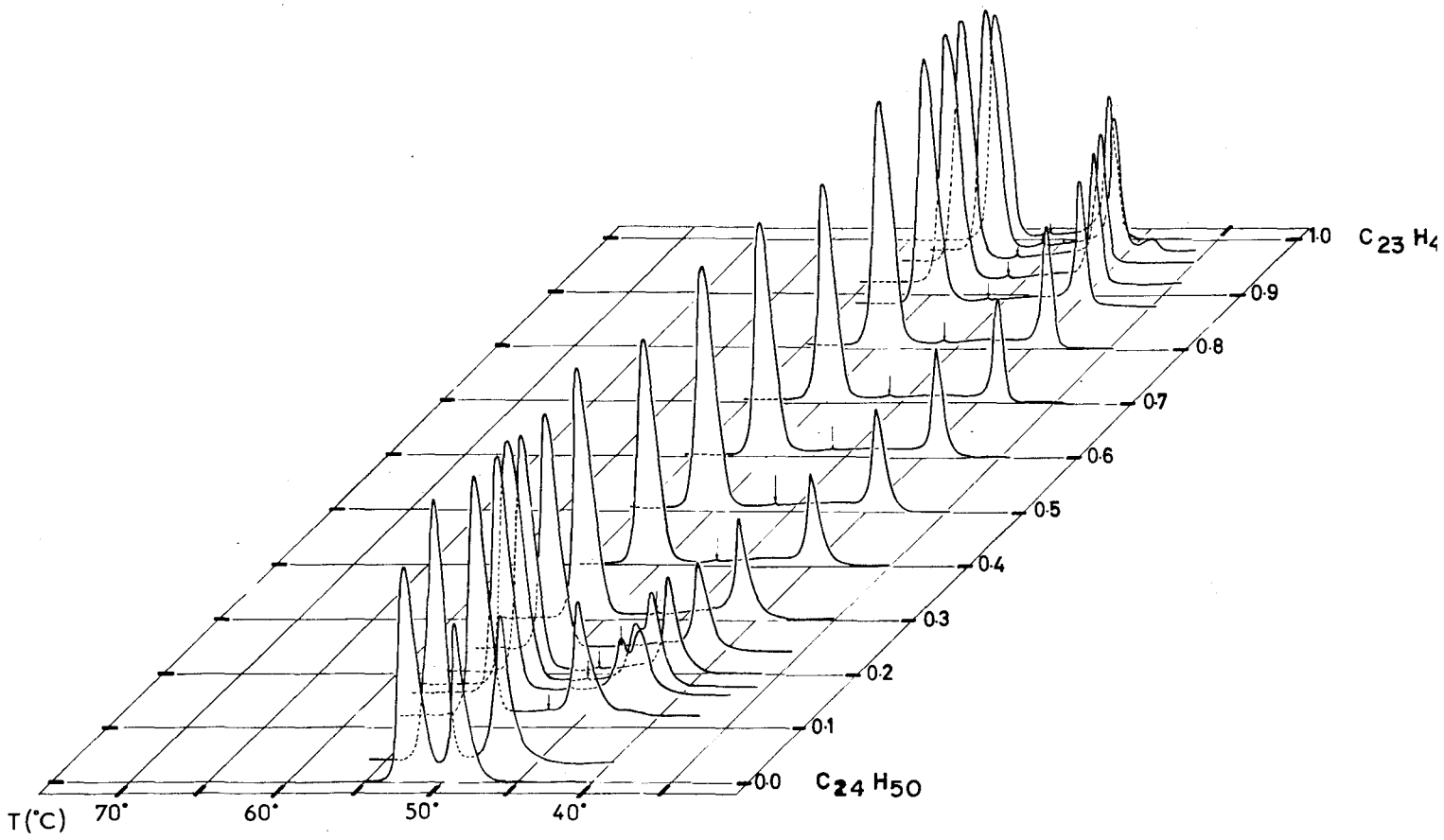


FIG. 1

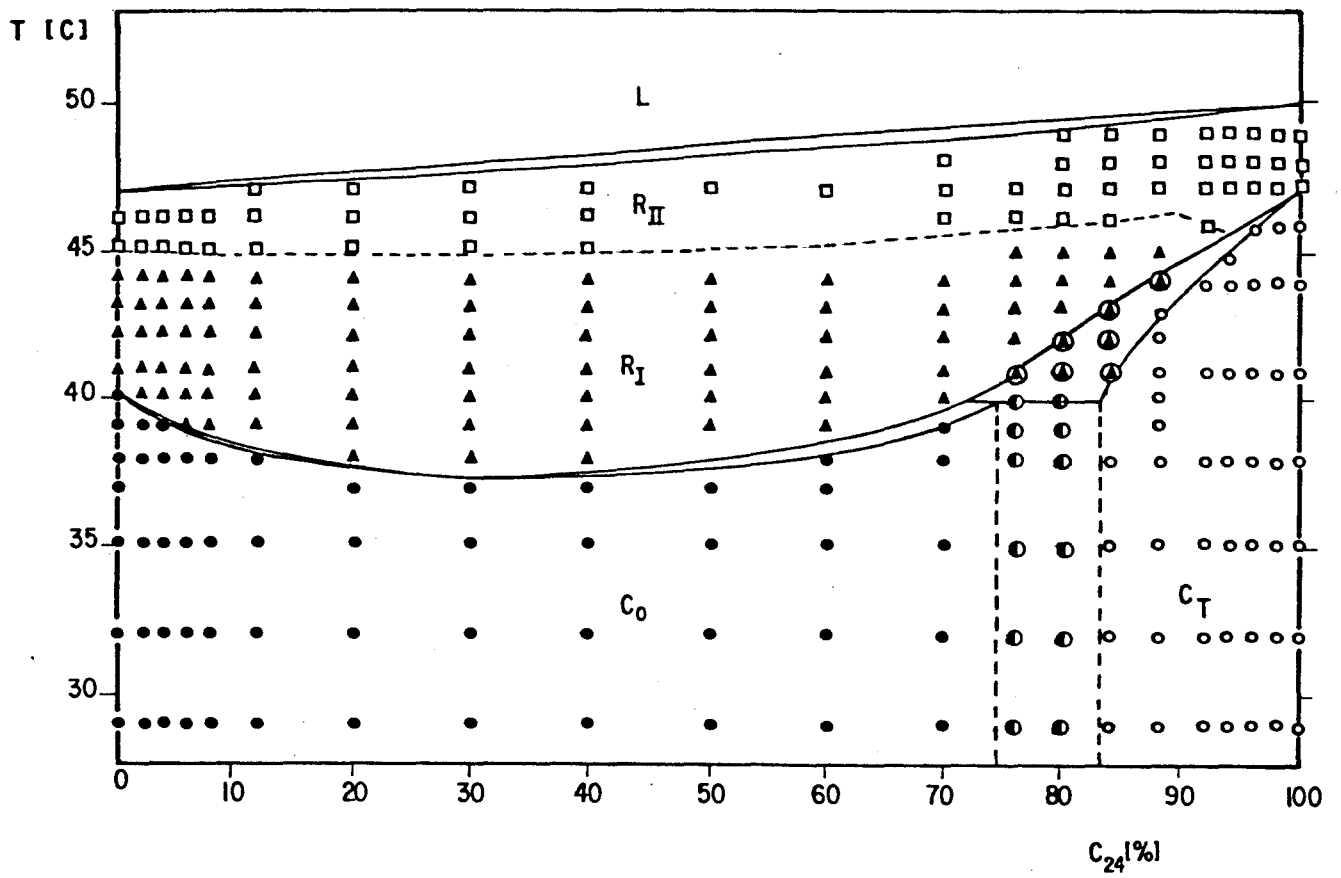


Fig. 2

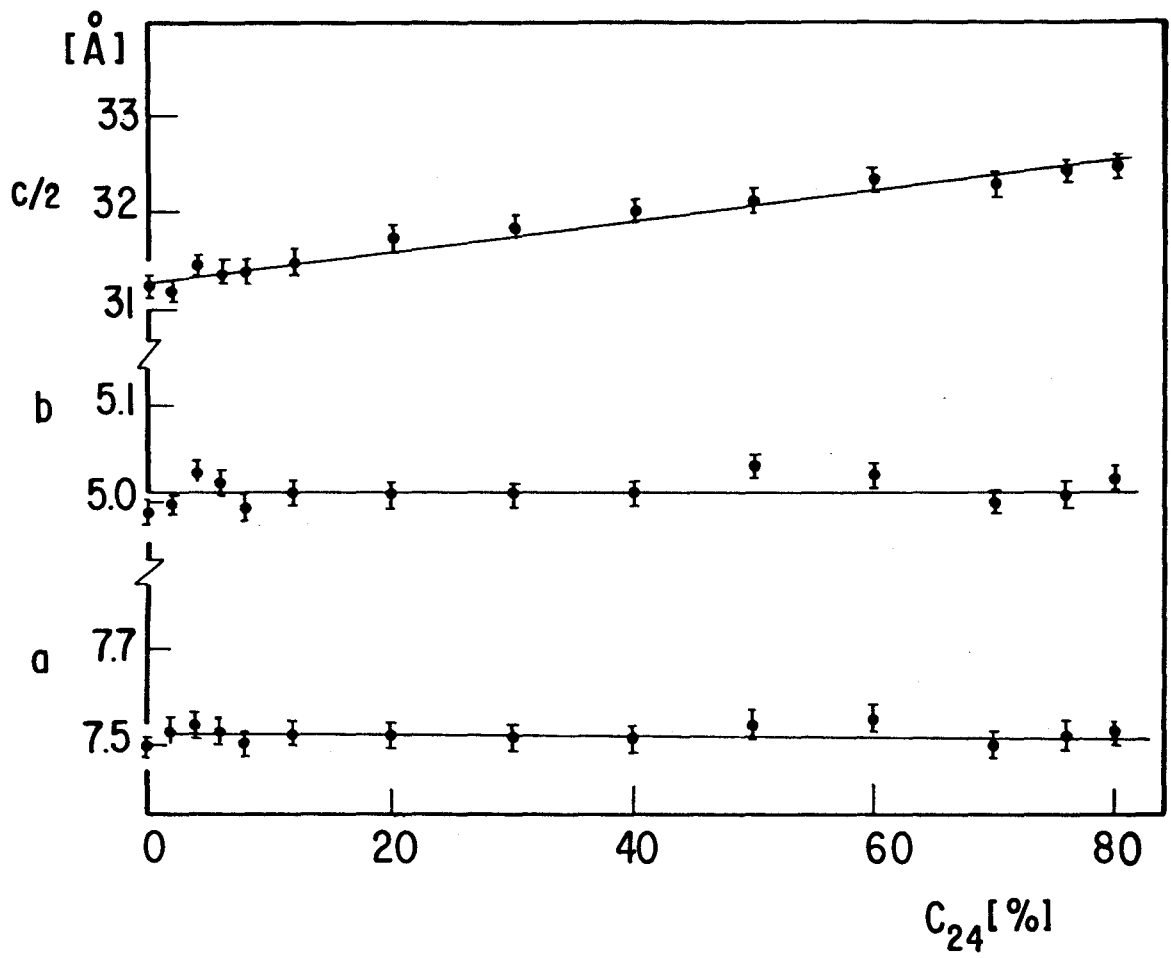


FIG. 3

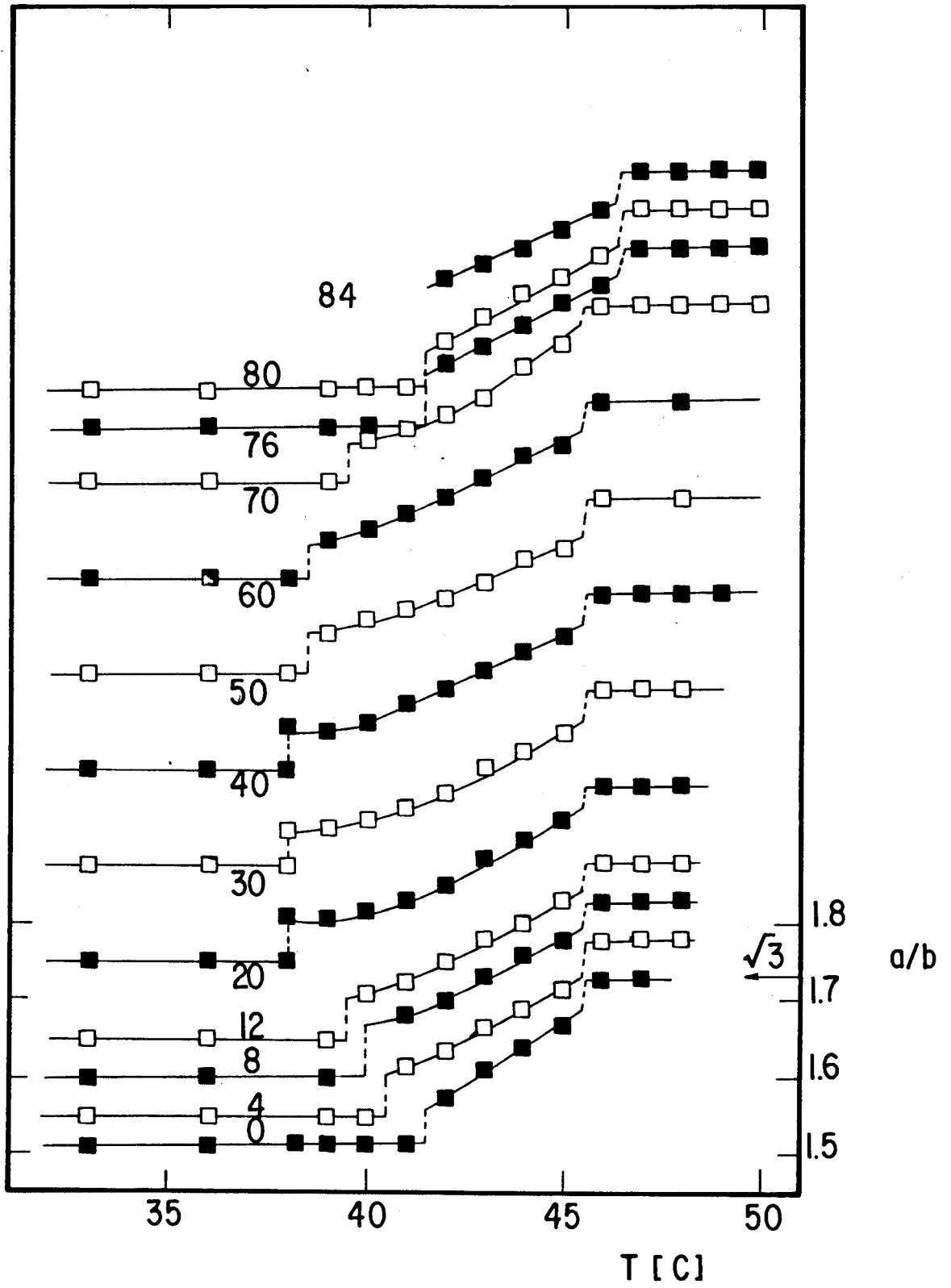


FIG.4

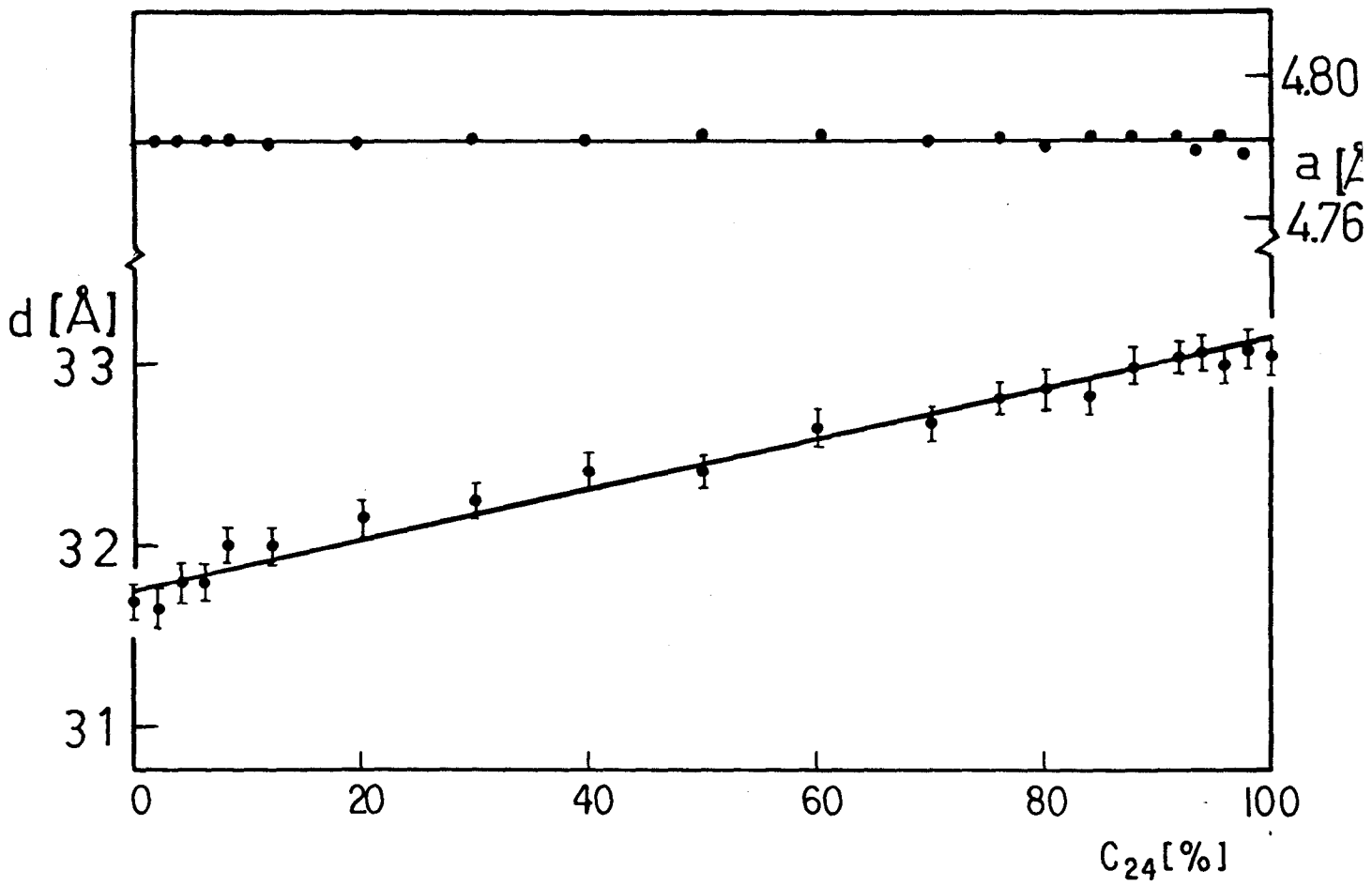


FIG.5