

NEW ASPECTS OF THE POLYMORPHISM OF CYCLOHEXANE DISPERSED WITHIN AN EMULSIFYING MEDIUM

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Differential scanning calorimetry and X-ray diffraction experiments on the phase transformations of cyclohexane dispersed within an emulsifying medium (microsamples $1 \mu\text{m}^3$ in volume) are presented. The existence of a third metastable crystalline phase (denoted ϵ) besides the already-known phases (two stable phases, α and γ , and two metastable phases, β and δ) is demonstrated. Interpretations of the succession of transformations between these different phases and with the liquid phase, either upon cooling or upon heating, are given.

It is well known that liquids can supercool, crystallizing at a temperature $T < T_F$; T_F is melting temperature. The metastability breakdown (crystallization) displays an erratic character [1] and, if a great number of samples are cooled, their crystallizations occur over a temperature range $[T_0, T_e]$ with a most probable temperature T^* where they are the most numerous [2]. It has been shown that $\Delta T = T_F - T^*$, the degree of metastability, increases when the volume of the samples is decreased.

The largest degrees of metastability are found with microsamples about $1 \mu\text{m}^3$ in volume. Such microsamples can easily be obtained by dispersion of the liquid within an emulsifying medium. The advantage of studying an emulsion is that very small samples and, hence, larger ΔT values are obtained. Further, their great number permits a direct statistical study. In the opposite case, the study of macrosamples (a few mm^3 in volume) necessitates several experiments, whose results must be averaged.

Another phenomenon is possible for dispersed liquids: for certain substances, at the metastability breakdown, metastable crystalline phases appear, which can be

preserved for a sufficiently long time to be studied. After gallium [3], several molecular substances were reported [4, 5] to have metastable crystalline phases. Some of the exhibit several metastable phases.

In the particular case of cyclohexane, previous papers [4, 5] relating to X-ray diffraction and calorimetric measurements have shown that, besides the two well-known stable crystalline phases α and γ (α is the cubic phase, stable between $T_{F\alpha} = +6.5^\circ$ and $T_{F\gamma} = -87.0^\circ$; γ is the monoclinic phase stable below $T_{F\gamma} = -87.0^\circ$), two metastable crystalline phases, δ and β , exist. The β phase is detected between $T_{F\delta} = -113.0^\circ$ and $T_{F\beta} = -13.5^\circ$, at which the β crystals melt. The δ phase exists below $T_{F\delta} = -113.0^\circ$. In an RPE study, Szwarc [7] has shown that the temperature of -87.0° corresponds to the disappearance of free radicals previously formed as a consequence γ -radiation and to the accentuation of molecular diffusion motion in the crystal.

The aim of this paper is to present new experiments showing another metastable crystalline phase (denoted ϵ) exists, and to provide more information about the polymorphism of cyclohexane.

Experimental procedure

Cyclohexane (analytical grade) was dispersed, by a high-speed stirrer, within an emulsifying medium consisting of a mixture of glycerol and sorbitol with a few percent of sodium dodecylsulfate as a surfactant. The weight fraction of cyclohexane was 20–25%. The emulsion was not perfectly stable, since we observed that the droplet diameter increased when the dispersion was preserved at ambient temperature during a period of time t' , from a value less than 1 μm to about 2 μm during $t' \approx 7$ days. This small increase only slightly affected the temperatures of crystallization, but had an important effect on the quantities of the metastable phases, and we present results on freshly-prepared emulsion ($t' = 0$), which gives the most important quantity of metastable phase.

The transformations were detected by differential scanning calorimetry (Perkin-Elmer DSC 4 Calorimeter) and the crystalline phases were characterized in X-ray experiments with a Guinier-Simon camera which can be cooled down to -160° . The X-ray diffraction patterns were obtained throughout the entire heating process showing all phase transformations.

Results

1 Macrosamples (mm^3 range)

The volume of macrosamples (a few mm^3) corresponds with either the cell volume of the DSC Perkin-Elmer Calorimeter or the volume of the Lindemann tube for X-ray diffraction experiments:

Figure 1 presents DSC curves obtained upon cooling (rate 10 deg/min) and upon heating (rate 5 deg/min). Both curves confirm the existence of the two stable phases: the first one, denoted α (cubic) between $T_{F\gamma} = -87.0^\circ$ and $T_{F\alpha} = +6.5^\circ$, and the second one, denoted γ (monoclinic) below $T_{F\gamma} = -87.0^\circ$. Upon cooling, for both transformations (the liquid giving the α form and the transformation from the α to the γ form) the degrees of metastability are small (about 1–2 deg).

For X-ray diffraction analysis, the experimental procedure is different, since the cyclohexane inside the Lindemann tube is first rapidly quenched by a flow of liquid nitrogen directly over the sample, and the X-ray diffraction pattern is then recorded on reheating of the sample from -140° to -70° at a heating rate of 2 deg/hour. Figure 2 shows, besides the characteristic diffraction diagrams of the two forms (α for $T > -87^\circ$ and γ for $T < -87^\circ$), the coexistence at low temperature of a third phase with the γ form. This third phase was previously detected for the first time by Kahn et al. [8], who named it "cyclohexane III". This form III is metastable and is transformed irreversibly into the γ form at a temperature around -120° . All

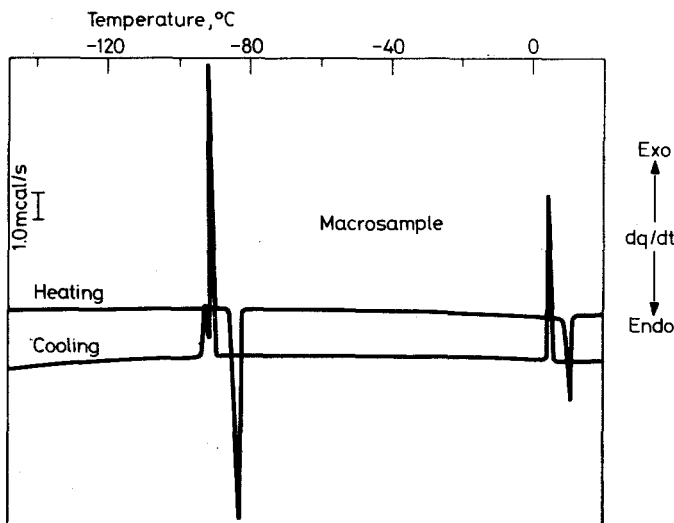


Fig. 1 Cooling and heating curves obtained with a macrosample (mm^3) of cyclohexane

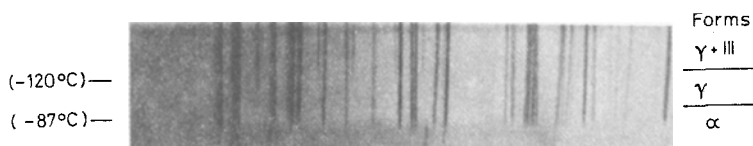


Fig. 2 Guinier-Simon diffraction experiment (heating pattern of a macrosample of cyclohexane)

attempts to achieve the same rapid quenching in the cell of the calorimeter failed; apart from the ones observed in Fig. 1, no transformation was detected in the DSC curves.

2) Microsamples (emulsion)

Figure 3 presents the curve obtained on a freshly prepared emulsion of cyclohexane at a cooling rate of 10 deg/min. Figure 4 depicts the corresponding immediate reheating at a heating rate of 5 deg/min. Both Figures show the glass transition of the emulsifying medium [4].

In Fig. 3, we can see two main temperature ranges of transformation, defined by the two temperatures $T_{\beta}^* = -70.0^{\circ}$ and $T_{\delta}^* = -147.0^{\circ}$. The heating curve (Fig. 4) reveals four peaks having the classical shape of those for first-order transformations. The corresponding temperatures are $T_{F\delta} = -113.5^{\circ}$, -87.5° , $T_{F\beta} = -13.5^{\circ}$ and $T_{F\alpha} = +6.5^{\circ}$.

These results seem to be the same as in the previous work of Dumas [4], who concluded that, besides the two stable crystalline phases, α and γ , two other metastable crystalline phases can be seen, β and δ . During the cooling, the liquid droplets crystallize at around T_{β}^* , giving the metastable β phase, and the metastable β droplets then transform at around T_{δ}^* into the second metastable

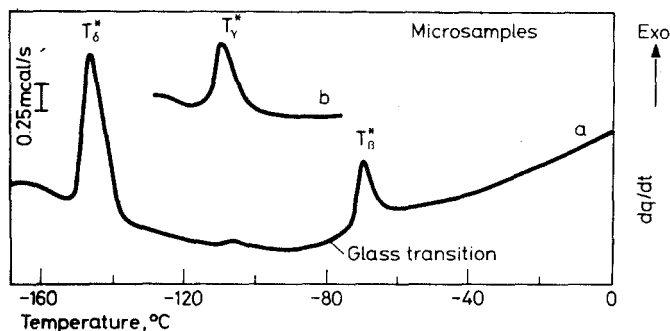


Fig. 3 Cooling curves (10 deg/min) of cyclohexane dispersed within an emulsion: a) full cooling; b) after appropriate thermal cycles (see text)

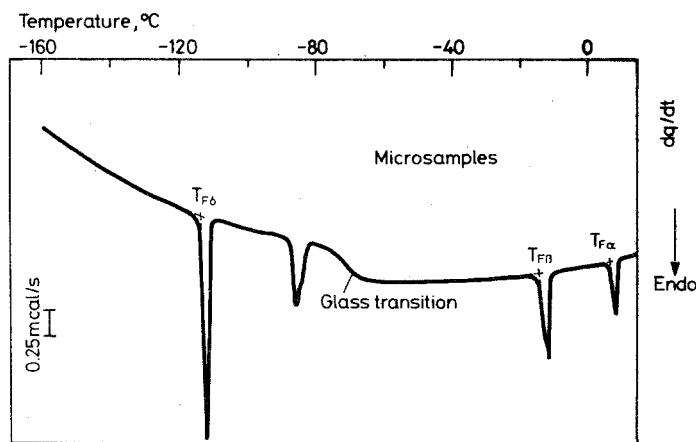


Fig. 4 Full heating (5 deg/min) curve of cyclohexane dispersed within an emulsion

phase, δ . Nevertheless, only a number of these δ droplets are preserved while the others δ droplets are transformed into the stable γ phase. Thus, at low temperatures, the emulsion contains two kinds of droplets: the metastable δ phase and the stable γ phase. Upon heating, the δ droplets are transformed at $T_{F\delta} = -113.5^\circ$ into the β phase, which melts at $T_{F\beta} = -13.5^\circ$. On the other hand, the γ droplets are transformed at -87.5° into the cubic α phase, which melts at $+6.5^\circ$. These explanations are consistent with the existence of four thermal peaks in the heating curve.

These assumptions to describe the succession of transformations were elaborated from different DSC experiments, in which the cooling or heating programs were stopped between appropriate thermal peaks and the following corresponding heating or cooling programs were then started; in this way, it is possible to analyse the areas of the thermal peaks, which are proportional to the quantity of droplets involved in the corresponding transformations [4]. The X-ray diffraction experiments performed by Bosio et al. [6] with a powder diffractometer [$\theta - 2\theta$] seemed to confirm this scheme for these transformations. A diffraction record obtained at -78° showed that the metastable β phase is different from the stable α phase. On the other hand, a diffraction record obtained at -158° showed the existence, in the emulsion of cyclohexane, of two phases, identified as the stable γ phase and the metastable phase III detected in macrosample experiments. The first conclusion of these authors was that the δ phase and phase III were the same.

To check this conclusion, we have now performed similar experiments with a diffraction technique, using the Guinier-Simon camera, which allows recording of the diffraction pattern not only at fixed temperatures as before, but continuously,



Fig. 5 Guinier-Simon diffraction experiment (heating pattern of cyclohexane as a microsample in an emulsion)

with variation of the temperature within the temperature range from -140° to -70° . The resulting heating diagram is given in Fig. 5. In contrast with expectations in the macrosample experiments, the diffraction in the macrosample experiments, the diffraction lines of cyclohexane III are found as in the previous experiments, but they do not disappear at -113° (as they ought to if $\text{III} \equiv \delta$), but at around -87° . However, a set of lines which vanish at -113° does exist, and at -113° we observe the appearance of the set of lines which does not exist for the macrosample and which are characteristic of the β phase. At around -87° , we also observe the appearance of a set of lines characteristic of the α phase, already found in the macrosample experiments (Fig. 2).

To explain these new results, we must now conclude that five crystalline phases exist in microsamples of cyclohexane. First, we found the two stable α and γ phases, which have already been observed in macrosamples. The high-temperature metastable phase is the β phase. At low temperature, two other metastable phases are detected. The first one, which is transformed at -113° , will be denoted the δ phase, but this phase is not the metastable phase III found with the quenched macrosample, in contrast with what was suggested in the past [6]. This δ phase is transformed into the β phase at -113° . On the other hand, the second phase, which is present at low temperature, has some diffraction lines situated at very similar diffraction angles to those of the previously found metastable phase III. This new metastable phase is transformed into the α phase at around -87° . Let us recall that the γ phase is transformed into the α phase at around the same temperature (-87°). To be consistent with our nomenclature, we denote this new phase as ε , with $\varepsilon \equiv \text{III}$.

Thus, Fig. 6 presents the succession of transformations in microsamples in either the cooling or the heating process.

Upon cooling, the liquid crystallizes into the crystalline β phase at around T_β^* . At around $T_\beta^* = -147^\circ$, the β phase is transformed into the metastable δ phase in all droplets [4]. Nevertheless, some δ droplets are transformed immediately into the metastable ε phase or into the stable γ phase. The transformation $\varepsilon \rightarrow \gamma$ is also

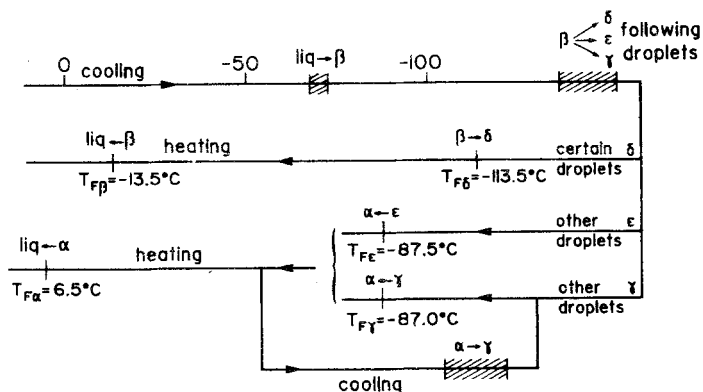


Fig. 6 Scheme for the phase transitions of emulsified cyclohexane either upon cooling or upon heating

possible. Hence, we can assume that, at low temperature after a cooling process, the following three phases are present in the emulsion $\gamma + \epsilon + \delta$.

Upon heating, the δ droplets are transformed at $T_{T\delta} = -113.5^\circ$ into the metastable β phase, this latter melting at -13.5° . The other droplets are transformed at $T_{F\epsilon} = -87.5^\circ$ into the α phase, and finally the γ droplets too are transformed into the α phase at around this temperature (-87°). This α phase melts at $+6.5^\circ$. Accordingly, two phenomena, the transformation $\epsilon \rightarrow \alpha$ and the transformation $\gamma \rightarrow \alpha$, take place at around -87° .

More accurate DSC experiments were performed to determine exactly the temperatures of these two transformations. Figure 7a shows the curve obtained at

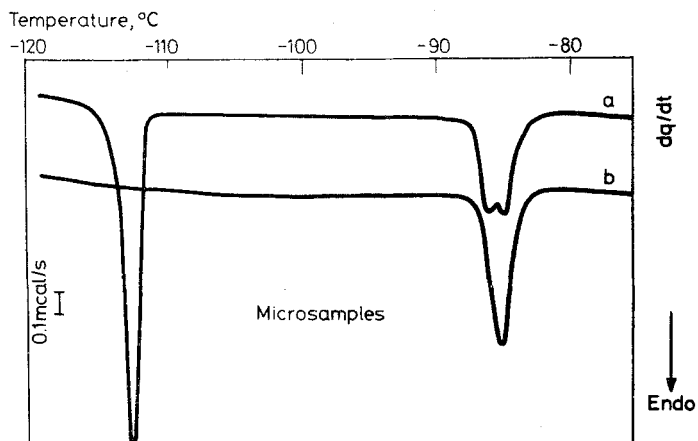


Fig. 7 Heating (2.5 deg/min) curve of cyclohexane dispersed within an emulsion: a) full heating (detail); b) after appropriate thermal cycles (see text)

around -87° a low heating rate (2.5 deg/min): the thermal peak does not have the usual shape of only one first-order transformation and appears to be the superposition of two thermal signals corresponding to two first-order transition at two close-lying temperatures. We can evaluate these temperatures, which correspond, respectively, to $T_{F\varepsilon} = -87.5^\circ$ (transformation $\varepsilon \rightarrow \alpha$) and to $T_{F\gamma} = -87.0^\circ$ (transformation $\gamma \rightarrow \alpha$).

To confirm that the DSC curve at around -87° really represents the superposition of two transformations and not a bad thermal signal due to the thermal conduction inside the sample, we carried out the following experiment. The heating was stopped before melting, at a temperature $T < T_{F\beta} < T_{F\alpha}$, and the following cooling was stopped at -130° , before the transformation $\beta \rightarrow \delta$ (at $T_\delta^* = -147^\circ$). In the corresponding curve (Figure 3b), we find only one transformation, at around $T_\gamma^* = -110.0^\circ$, giving the stable γ phase. Upon heating of this sample from -130.0° , no peak (Fig. 7b) is observed at $T_{F\delta} = -113.0^\circ$ (which is normal, because there was no presence of δ droplets giving the β phase), but a single thermal peak, characteristic of a first-order transformation, was observed at $T_{F\gamma} = -87.0^\circ$, i.e. at the same temperature as found for the transformation $\gamma \rightarrow \alpha$ in the case of the macrosample. The areas of the thermal peaks obtained at around -87° in the two heating experiments are practically the same. This experiment shows that:

- the β phase does not exist at -87° ;
- the same α phase appears in all droplets involved in either the transformation at $T_{F\varepsilon} = -87.5^\circ$ or the transformation at $T_{F\gamma} = -87.0^\circ$;
- during the following cooling, all α droplets are transformed into the γ phase at $T_\gamma^* = -110.0^\circ$, and immediate heating then gives only the $\gamma \rightarrow \alpha$ transformation (Fig. 6);

- thus, we can conclude that the peak at -87° in Fig. 7a is really the superposition of two peaks at two close temperatures (the experiment is reversible since, after heating up to ambient temperature and a cooling down to -170° , in the following cooling the curve of Fig. 7a is found again);

- the molar enthalpies of the transformations $\gamma \rightarrow \alpha$ [4] and $\varepsilon \rightarrow \alpha$ have the same value (the areas of the peaks in Fig. 7a and 7b are identical). This fact would explain why, in the macrosample experiment, the transformation $\varepsilon \rightarrow \gamma$ is detected by the X-ray diffraction technique but not by the DSC method, as mentioned above. The powder diffraction patterns of different phases observed with the Guinier-Simon camera are given in Table 1.

The reticular distances for the δ phase are different from those of the γ phase only for small angles of diffraction. These differences are enhanced by the geometry of the Guinier-Simon camera and are not visible with the diffractometer $[\theta - 2\theta]$ used

Table 1 Characteristic reticular distances d (Å) of different phases measured at appropriate temperatures (Guinier-Simon camera technique)

Macrosample experiments			Microsample experiments		
α (at -70 °C)	γ (at -90 °C)	III (at -150 °C)	δ (at -140 °C)	β (at -90 °C)	ϵ (at -140 °C)
4.90 (111)	5.39 (200)	4.45	5.26	5.41	5.05
4.28 (200)	4.90 ($\bar{1}\bar{1}\bar{1}$)	3.54	4.72	4.81	4.50
2.57 (113)	4.20 (111)	3.16	4.63	4.41	
2.47 (222)	3.90 (002)	2.79	4.38		4.00
	3.79 (202)	2.61	4.27		3.55
	3.48 ($\bar{1}\bar{1}2$)	2.47	3.76		3.33
	3.23 (020)		3.67		3.17
	2.97 (021)		3.46		2.79
	2.77 (220)		3.11		2.61
	2.67 (400)		2.63		
	2.65 (311/ $\bar{4}$ 02)				
	2.53 ($\bar{1}\bar{1}3$)				
	2.46 (022/221)				
	2.22 (113)				
	2.16 (312)				

by Bosio et al. [6]. On the other hand, continuous heating of the camera was necessary to prove the existence of five crystalline phases.

Conclusion

The polymorphism of cyclohexane dispersed within an emulsifying medium (microsamples $1 \mu\text{m}^3$ in volume) has been reviewed. An X-ray diffraction experiment different from that in previous work [6], and more accurate DSC experiments, have demonstrated the existence of five crystalline phases at atmospheric pressure, three of them being metastable. Upon heating, the metastable δ phase is transformed at -113° into the metastable β phase, which melts at -13.5° , whereas the metastable ϵ phase is transformed at -87.5° into the stable α phase, which melts at 6.5° . The ϵ phase can also be obtained from a macrosample (mm^3) quenched in liquid nitrogen. The transformations between the stable γ and α phases are the same as those detected for the macrosample. The appearance of metastable crystalline phases and the succession of transformations upon cooling or upon heating are due to the considerable undercooling obtained with these microsamples.

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Zusammenfassung — Neue Differential-Scanning-Kalorimetrie- und Röntgendiffraktionsexperimente an Phasenübergängen von in einem emulsionsbildendem Medium (Mikroproben von $1 \mu\text{m}^3$ Volumen) dispergierten Cyclohexans werden dargestellt. Neben den schon bekannten Phasen (zwei stabile Phasen α und γ sowie zwei metastabile Phasen β und δ) wird die Existenz einer dritten metastabilen Phase ε nachgewiesen. Ausserdem werden Interpretationen über die Reihenfolge der Übergänge zwischen diesen verschiedenen Phasen und der flüssigen Phase in Abhängigkeit von Abkühlen und Erwärmen gegeben.

Резюме — Представлены данные ДСК измерений и дифракции рентгеновских лучей по фазовому превращению циклогексана, диспергированного в среде эмульгатора. Наряду с уже известными фазами циклогексана (две стабильные фазы α и γ и две метастабильные фазы β и δ), установлено существование третьей метастабильной кристаллической фазы, обозначаемой ε . Приведены объяснения, касающиеся последовательности превращения между этими различными фазами, а также с жидкой фазой при нагревании или охлаждении.