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On the polymorphism of solid cyclohexanol by adiabatic calorimetry and far infrared methods

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Résumé. — Nous avons utilisé la calorimétrie adiabatique et la spectroscopie dans l'infrarouge lointain afin de mieux comprendre le polymorphisme du cyclohexanol solide. Nous avons pu confirmer le système monotropique des phases II et III en nous basant sur les mesures calorimétriques effectuées entre 170 et 320 K et le bilan de l'entropie. Nous avons vérifié les conditions de croissance de chacune des phases et les réversibilités des transitions de phases. Nous avons trouvé deux façons d'atteindre la phase III dont une nécessite le passage par la phase intermédiaire métastable MS. A côté de l'observation de la transition entre phases III et II par méthodes infrarouges, la technique calorimétrique nous a aussi permis d'observer la même transition monotropique.

Abstract. — Adiabatic calorimetry and FIR spectroscopy were used to get a better understanding of the polymorphism of solid cyclohexanol. On the basis of calorimetric measurements performed in the temperature range from 170 K to 320 K and the entropy balance calculation, the monotropic set of phases II and III was confirmed. The conditions in which different phases can be grown and the reversibility of the particular phase transitions were checked. Two different ways for obtaining phase III, one passing through an intermediate metastable phase MS, were demonstrated by both methods. The influence of the thermal treatment on the apparent stability of phase III was discussed. In addition to the previously reported IR observation of the transition from phase III to II, the same monotropic transition was visualized in the calorimetric measurement.

1. Introduction.

Studies of the polymorphism of cyclohexanol were initiated in 1929, when Kelley [1] found two crystal phases in this substance using the calorimetric method. The most complete information on the polymorphism of solid cyclohexanol was given by Adachi et al. [2]; it was based on specific heat vs. temperature measurements in the temperature range of 14-320 K. They also gave a complete review of earlier papers on this subject. According to Adachi, cyclohexanol, below the melting point of $T_m = 299.05$ K, has two stable crystalline phases.
On heating, the low-temperature phase II transforms into phase I at a temperature $T_{II \rightarrow I} = 265.5$ K. Phase I is stable (i.e. has the lowest value of free energy) in the temperature range between $T_{II \rightarrow I}$ and $T_m$, but on cooling it can be easily supercooled and below the glassy type transition at $T_g \approx 150$ K it forms a glassy crystal with residual entropy of 4.72 J/mol K. In the low temperatures it is also possible to grow a crystalline phase III, metastable relative to phase II. At $T_{III \rightarrow I} = 244.8$ K phase III transforms into phase I. Although phase III is metastable in the whole temperature range, the authors did not observe a transformation of phase III into phase II.

Some time later Green and Griffith [3] on the basis of dielectric and visual observations reported three solid phases of cyclohexanol: a high-temperature rotational phase I, which is stable in the temperature range from $T_{II \rightarrow I} = 264.9$ K to the melting point $T_m = 298.2$ K, a crystalline phase II (1), stable in the temperature range from $T_{III \rightarrow II}$ estimated as being ca 210 K to $T_{II \rightarrow I}$, and a low-temperature phase III, stable below $T_{III \rightarrow II}$. Apart from that, they found the transition from phase III into phase I (i.e. the transition from overheated phase III to phase I) at $T_{III \rightarrow I} = 244$ K. They also observed the existence of an additional, low-temperature phase which they called «pre-II», metastable with regard to both phase II and phase III but more stable below ca 230 K than the supercooled phase I. Thus, the phase situation in solid cyclohexanol as given by Green and Griffith is quite different from that reported by Adachi et al., apart from the temperatures of respective phase transitions, which are in fairly good agreement. The essential difference between the two reported phase diagrams of cyclohexanol is seen most clearly in figure 1, where relevant free enthalpy schemes are sketched.

![Phase diagrams of cyclohexanol](image)

**Fig. 1.** — Phase diagrams of cyclohexanol postulated by Green [3] (left) and Adachi [2] (right).

The far infrared spectra of solid cyclohexanol studied by Ściesińska and Ściesiński [4] showed that phase III indeed transforms into phase II at a certain temperature range (e.g. at 238 K during ca 2 h) but the authors did not find that transition to be reversible. The authors also found that the supercooled phase I transforms at ca 200 K into phase III via an intermediate metastable phase MS, which probably corresponds to phase pre-II in [3]. The literature data quoted above as well as the later papers [5-9] do not give a definitive explanation of the nature of the particular solid phases of cyclohexanol. Phase I (with the symmetry Fm3m [7]) is undoubtedly a so-called plastic or ODIC (orientationally disordered) phase. This conclusion results from the broadening of the QNS peak [8], the low value of melting entropy (in agreement with Timmermans criterion [11]) and the values of $\varepsilon'$ and $\varepsilon''$ [12]. However, the nature of this plasticity remains unclear. Suggestions from IR

(1) In the original paper of Green and Griffith that phase was denoted phase III and the low-temperature phase was named phase II.
measurements concerning the ordering of molecules in phases II, III and MS [4, 13] need confirmation by, first of all, good diffraction measurement. Some new results obtained by means of neutron scattering were published recently [10].

The main aim of the present paper is to solve the controversy concerning the thermodynamic stability of particular phases. Specific heat measurements were performed mainly in order to observe the phase III to phase II transition and decide whether these phases form a monotropic [2] or an enantiotropic system as suggested in [3]. In addition we studied the reversibility of phase transitions in solid cyclohexanol, taking advantage of the distinct differences of far infrared spectra for particular phases. Generally, we applied the adiabatic calorimetry and IR spectroscopy as complementary methods to get more information on the polymorphism of the system studied.

2. Experimental.

The specific heat of cyclohexanol was measured in the temperature range of 170-320 K by means of the low-temperature automatized adiabatic calorimeter with platinum thermometer [14]. In the specific heat runs the standard amount of heat supplied resulted in a temperature rise of the sample of ca 2.5 K. The AC bridge used for the thermometer resistance measurements gave the sensitivity of the temperature measurement better than 10^-5 K. The time required to achieve thermal equilibrium was ca 2 h and in the vicinity of phase transitions it became much longer. The enthalpy of phase transitions was determined in separate runs. Apart from the classical adiabatic measurement, the calorimeter was also used in a dynamic mode. In that mode a constant heat flow from or to the sample was induced by proper adjustment of the adiabatic shield. Then the temperature of the sample as a function of time was recorded. Commercial cyclohexanol fractionally distilled was used in the experiment. The mass of the sample was 57.72 g, which is 0.5763 mol. The total volume of the sample holder was ca 80 cm³.

Far infrared spectra were measured using the Fourier Transform Spectrometer Digilab FTS-14 in the same conditions as described in [4]. The measurements were performed in the frequency range 100-500 cm⁻¹ with the resolution 2 cm⁻¹. The sample temperature was stabilized with an accuracy of ± 0.5 K. A temperature programmer was used in the growing of particular phases.

3. Results.

Figure 2 shows our experimental values of the molar specific heat of cyclohexanol (²). Smooth lines described by 3-rd order polynomials \( W(T) = A_0 + A_1 \times T + A_2 \times T^2 + A_3 \times T^3 \) were drawn for particular phases. The coefficients of the polynomials were obtained by a least squares fit to the experimental points lying outside the anomalies connected with the phase transitions. These coefficients are collected in table I. The specific heat values found in this paper for all phases are higher than those reported in [2] by 1.8 % on the average. The thermodynamic parameters of the phase transitions studied are given in table II, where the relevant values reported by Adachi et al. [2] are included for comparison. The enthalpy and entropy changes for the transitions were calculated assuming the transitions to be isothermal at the transition temperatures. The III → II transformation is formally treated here as if it were a reversible transition with the crossing of free energies of phases III and II. We discuss this point in section 4 and conclude that this is not the case.

(²) Numerical values for different runs are available from the authors on request.
Fig. 2. — The molar heat capacities of cyclohexanol.

Table I. — Coefficients of the polynomials for different phases.

<table>
<thead>
<tr>
<th></th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liq.</td>
<td>-2223.2606</td>
<td>22.0059895</td>
<td>-0.0691686793</td>
<td>0.0000763592</td>
</tr>
<tr>
<td>I</td>
<td>-383.66846</td>
<td>5.72531319</td>
<td>-0.0224958475</td>
<td>0.0000329227</td>
</tr>
<tr>
<td>II</td>
<td>-190.39713</td>
<td>3.55056518</td>
<td>-0.0157993632</td>
<td>0.0000270733</td>
</tr>
<tr>
<td>III</td>
<td>37.668636</td>
<td>0.17398209</td>
<td>0.0005704843</td>
<td>0.0000008149</td>
</tr>
</tbody>
</table>

Table II. — Thermodynamic parameters of the phase transitions studied.

<table>
<thead>
<tr>
<th></th>
<th>I $\rightarrow$ liq</th>
<th>II $\rightarrow$ I</th>
<th>III $\rightarrow$ I</th>
<th>III $\rightarrow$ II (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{tr}$ [K]</td>
<td>$297.92 \pm 0.02$ (299.05 $\pm$ 0.003)</td>
<td>$264.86 \pm 0.02$ (265.50 $\pm$ 0.01)</td>
<td>$244.5 \pm 0.1$ (244.8 $\pm$ 0.1)</td>
<td>$220.9 \pm 0.1$</td>
</tr>
<tr>
<td>$\Delta H$ [J/mol]</td>
<td>$1806 \pm 10$ (1782 $\pm$ 2)</td>
<td>$8662 \pm 40$ (8827 $\pm$ 10)</td>
<td>$8620 \pm 50$ (8640 $\pm$ 100)</td>
<td>$378.4 \pm 0.5$</td>
</tr>
<tr>
<td>$\Delta S$ [J/mol K]</td>
<td>$6.06 \pm 0.04$ (33.25 $\pm$ 0.04)</td>
<td>$32.70 \pm 0.15$ (35.29 $\pm$ 0.4)</td>
<td>$35.3 \pm 0.2$ (35.39 $\pm$ 0.4)</td>
<td>$1.713 \pm 0.01$</td>
</tr>
</tbody>
</table>

* See remark in section 4 of the text; values in parentheses from [2].
The thermal treatment of the sample by which different phases of cyclohexanol were obtained was based on the experience of [4] and is schematically shown in figure 3.

Fig. 3. — Diagram of the applied thermal treatment of the sample.

3.1 MELTING. — The phase I to liquid phase transition for the cyclohexanol sample studied in this paper took place at the temperature $T_m = 297.92 \pm 0.02$ K. From the fractional melting study (assuming no formation of a solid solution) the melting temperature of pure cyclohexanol was estimated to be $T_m^* = 298.27$ K and the degree of impurity of our sample to be of the order of 0.09 mol %. However, our $T_m$ is lower than the value given by Adachi by 0.76 K, which indicates that the degree of impurity of our sample must be higher than estimated. During the cooling of the liquid with constant heat flow from the sample the minimum cooling rate associated with freezing was found at $T = 293$ K, which indicates that a hysteresis of the phase I $\rightarrow$ liquid transition is significant.

3.2 PHASE III. — The initial procedure was to grow phase III from the supercooled phase I at a temperature of ca 200 K. The sample was cooled from room temperature to that point and then the cooling was stopped. The cooling rates used in far infrared measurements varied from 1 K/min to 6 K/min. At ca 200 K the sample transferred spontaneously during several hours into phase III via an intermediate metastable phase MS. Figure 4 shows an example of time evolution of the FIR spectra at the temperature of 198 K. The spectra correspond respectively to the initial pure phase I, mixture of phase I and MS, mixture of MS and III and the resulting pure phase III. It was found that the rates of transitions: phase I $\rightarrow$ MS and MS $\rightarrow$ phase III depend quite strongly on the temperature at which the cooling of phase I was stopped. The corresponding rates are the highest at ca 198 K and 213 K and are indicated in figure 3 by different thickness of lines.

The fact that the phase I to phase III transition takes place in two steps was also seen in the calorimetric measurements. The dependence of the rate of the sample temperature change vs. time, i.e. $dT/dt(t)$ at constant heat flow from the sample, exhibits two maxima (see Fig. 5). These maxima are caused by the release of enthalpy from the sample and they indicate that both transitions are exothermic.

Specific heat measurements for phase III were performed only up to ca 220 K because above that temperature phase III was loosing its stability. It was transforming to phase II. This fact was observed previously in FIR (see Fig. 3 in [4]) and IR measurements (Fig. 2 in [13]). This III $\rightarrow$ II transformation on increase of temperature was recently observed in the thermal conductivity measurement [9]. In our calorimetric measurements the instability of phase III manifested itself by anomalous behaviour of the sample temperature after each
energy input above 220 K. After attaining a temporary apparent equilibrium in the normal time of 2 h, the sample temperature started to decrease, although the sample was kept in adiabatic conditions. Figure 6 presents an example of this spontaneous cooling of the sample during the endothermic process. The duration of this process became much longer on lowering the initial temperature of the sample (e.g. ca 80 h for $T_{\text{initial}} = 222$ K). Therefore, in order to study the phase III to II transformation in the vicinity of 220 K an experimental series was performed in which subsequent amounts of heat ($Q \approx 78$ J) were supplied every 24 h, although this long time was still too short to obtain good thermal equilibrium. Figure 7 presents the results of this measurement in terms of $\Delta H/\Delta T(T)$. This measurement was used
Fig. 6. — Abnormal cooling effect due to the endothermic phase III to II transformation observed in thermal drift $dT/dt$ (continuous line and filled dots) and temperature (empty dots).

Fig. 7. — Results of the non-equilibrium measurement of the apparent heat capacity in the range of phase III to II transformation.

to calculate the enthalpy $\Delta H_{III \rightarrow II}$ needed to transform phase III to phase II isothermally at the temperature of the maximum of the curve in figure 7 i.e. at $T_{\text{max}} = 220.93$ K. The enthalpy value found in this way is $\Delta H = 378$ J/mol. However, the results presented do not enable us to determine whether the transition is reversible (enantiotropic system of phases III and II) or is not (monotropic set of phases). An attempt to observe the inverse transition, i.e. II $\rightarrow$ III, in spectroscopic measurements was a failure. To provoke this transition, a mixture of phases III and II was cooled to various temperatures below 220 K and FIR spectra were
recorded. No changes in the spectra were observed in reasonable time (several hours). This result may indicate an absence of reversibility but does not exclude it, because the phase II to III transition may be, for example, strongly hindered by kinetic factors.

As Adachi et al. did not observe the phase III to phase II transition but claimed that phase III transforms at 244.8 K directly into phase I, we also tried to observe that transition. In spectroscopic measurements phase III was heated from a temperature lower than 220 K to 248 K with the heating rate of 6 K/min and each time the spectrum recorded at 248 K indeed was the spectrum of phase I. It turns out, then, that with a heating rate high enough the sample can jump over the temperature range where it transforms into phase II. With our calorimeter such a high heating rate was not feasible. However, it was found that phase III may be obtained from the supercooled phase I also in another temperature range, different from that stated at the beginning of this section. That is to say, it can be grown at a temperature a little over 220 K. Spectroscopic measurements confirmed that the phase obtained in this way indeed is phase III and grows without an intermediate phase MS (see Fig. 8). The phase III grown in this way probably contains traces of phase I but no nuclei of phase II and it does not exhibit any tendency to transform into phase II. Thanks to that the calorimetric measurement could also be performed in the vicinity of the phase III to phase I transition. The transition temperature obtained, \( T_{\text{III} \rightarrow \text{I}} = 244.5 \pm 0.1 \) K, is in good agreement with the value given by Adachi et al. [2]. After the III \( \rightarrow \) I transition we did not observe the « sluggish exothermal transformation from crystal I to crystal II » reported in [2] and [5], because our phase I obtained at the III \( \rightarrow \) I transition was not contaminated by phase II nuclei. Under subsequent cooling and annealing at a lower temperature (e.g. at 170 K) phase III obtained in this second way would on slow heating tend to transfer to phase II again. A detailed analysis would require a separate and more systematic study. Nevertheless, a large separation in the temperature scale of the nucleation and growth processes of phase II is clear.

3.3 Phase II. — Phase II was always obtained via the phase III to phase II transition described above. Next it was cooled to 170 K and the routine specific heat runs were performed. In the cases when the newly obtained phase II was not cooled prior to the measurement, the heat capacity values were slightly lower (on average by ca 0.1 %). This may indicate that, after being obtained from phase III, phase II at first contains traces of phase III,

Fig. 8. — Time evolution of FIR spectra illustrating the direct transformation from supercooled phase I to phase III (at 223 K).
which disappear on cooling. It was found in calorimetric measurements that phase II transforms into phase I at $T_{II \rightarrow I} = 264.86 \pm 0.02$ K and no indication of instability of this phase was observed in the temperature range studied. As phase II was grown from phase III and not directly from phase I, we decided to study the reversibility of the $II \rightarrow I$ transition using the spectroscopic method. Phase II was partly transformed into I at 266 K and next the mixture was quickly cooled (6 K/min) to several degrees below $T_{II \rightarrow I}$. The time evolution of FIR spectra was then studied. Figure 9 presents an example of the evolution of the spectra for a mixture containing almost pure phase I transforming into II at 253 K. This result shows that the $II \rightarrow I$ transition is reversible. Nevertheless, all our varied attempts to get a similar result starting from pure phase I (not containing nuclei of phase II) failed. This means that the supercooled phase I has good stability in this temperature region. Thanks to this it was possible to measure specific heat for phase I beginning at a temperature of ca 240 K. Below this temperature phase I transformed into phase III.

Fig. 9. — FIR evidence of the reversibility of phase II to I transition; the spectrum of pure phase I (dashed line) is given for comparison.

4. Discussion.

In this section we discuss a problem already mentioned in the introduction, namely, whether phases III and II form an enantiotropic or a monotropic system. Basing on our results for the specific heat and thermodynamic parameters of the phase transitions we performed an enthalpy and entropy balance starting from a chosen equilibrium temperature in phase III (e.g. 220 K) and ending at a given temperature in phase I (e.g. 270 K). The enthalpy and entropy changes cannot depend on the way from the initial to the final equilibrium points. We did the calculations for two routes, namely A : phase III $\rightarrow$ phase I and B : phase III $\rightarrow$ phase II $\rightarrow$ phase I assuming that the III $\rightarrow$ II phase transition is reversible and its parameters are as given in table II. It turns out that the entropy change calculated on route A amounts to $63.83 \pm 0.3$ J/mol K and is by 2.5 J/mol K higher than that calculated on route B. As the observed transition temperature $T_{III \rightarrow II}$ may be higher than the actual one we repeated the calculations for lower $T_{III \rightarrow II}$ temperatures but the entropy balance still did not agree. Therefore, we conclude that the phase III to phase II transformation is irreversible and that it
involves the entropy production which is not included in the calculations. This result solves
the controversy between the older Adachi et al. [2] and Green and Griffith [3] papers in
favour of the monotropic phase II — phase III system postulated in [2]. Phase III is then
metastable with respect to phase II in the whole temperature range of existence of phase III.
This agrees with the fact that nobody has reported an observation of the inverse i.e. II → III
transition.

The temperature dependence of the reduced free enthalpy based on our experimental data
is shown in figure 10. As our measurements were not performed to low enough temperatures
the point for phase I at 290 K was taken from [2]. The MS phase is not included in figure 10
because it is not possible to make adiabatic calorimetric measurements for this phase on
account of the fast irreversible MS → III transformation. One could roughly place the free
enthalpy line above that of phase III with the reversible MS → I transition somewhere below
240 K. The direct MS → I transition was earlier observed by the far infrared method under
very fast heating conditions [4].

Fig. 10. — Experimental reduced free enthalpy of cyclohexanol (the fitting point for phase I at 290 K
from Adachi [2]).

5. Conclusions.

The monotropic system of phases II and III postulated by Adachi et al. was confirmed. Phase
III in the whole range of its existence is metastable with respect to phase II. Additionally to
the previously reported [4, 13] infrared observation of the irreversible phase III to II
transformation the same process was visualized calorimetrically, giving some hints about the
kinetics of the transition. The calorimetric evidence of the transition from the supercooled
phase I at ca 200 K to phase III via an intermediate MS phase is shown. An interesting feature
of phase III grown directly from supercooled I (without the intermediate MS phase) at
T > 220 K was noted : phase III grown in this way exhibits much more experimental stability
and does not show any tendency to transfer to phase II up to the III → I transition. A non-
obvious reversibility of the phase II to I transition was proved by FIR spectroscopy.
References

[8] DE MUL F. F. M., Molecular Motions in Cyclohexanol and Related Compounds Studied by Means