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# Mixtures of *d*- and *l*-carvone. III. Thermodynamic properties of *l*-carvone

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## Abstract

In this study, the thermodynamic properties of *l*-carvone have been examined. DSC experiments and adiabatic calorimetry supplied complementary data on the complex polymorphic behaviour.

Heating a supercooled sample results in a glass transition at 171 K; next a crystallisation to metastable (II) material takes place, followed by a recrystallisation to stable (I) material, and finally, the melting of the sample. The polymorphic modifications II and I are monotropic forms.

The molar heat capacities of stable (I) *l*-cavone have been measured from 5 to 280 K. They show a reversible phase transition '$I\beta$ to $I\alpha$' between 190 and 215 K, which is an enantiotropic transition. The melting temperature of the $I\alpha$ phase is 249.5 K. The heat of melting is 11.73 kJ $mol^{-1}$.

The crystallisation behaviour of supercooled liquid to metastable (II) material has been studied under adiabatic conditions. The obtained curves of temperature against time may be of use in judging the kinetics of phase change at the beginning of the crystallisation process.

*Keywords:* Adiabatic calorimetry; Carvone; Crystallisation; DSC; Polymorphism

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## 1. Introduction

### 1.1. Investigating polymorphism

Organic compounds may often crystallise in different forms. The polymorphs differ with respect to physical properties, such as their melting point and solubility. Their

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existence frequently presents a serious problem in the pharmaceutical industries since physical properties are often used as criteria for quality control. Consequently, polymorphism is a phenomenon that needs to be thoroughly investigated.

The two types of polymorphism known are: enantiotropy and monotropy. Jacques et al. [1] gave a simplified description of them in the case that no vapour phase is present and the pressure is constant. Under these conditions, a system consisting of one component ($C = 1$) existing in two crystalline forms ($\Phi = 2$) is invariant ($v = C - \Phi + 1 = 0$ ). Therefore, the two polymorphs can be in equilibrium only at a single temperature $T_{co}$. In the case of enantiotropy, $T_{co}$ is lower than the melting points of both polymorphic forms. The transition of the two polymorphic modifications can occur reversibly at $T_{co}$. Upon heating of the sample this transition is endothermic [2,3]. In the case of monotropy, equilibrium coexistence does not occur ($T_{co}$ is either absent or above the melting points of the stable form ). The transition from the metstable to the stable crystal can take place at any temperature below the melting point of the metastable form. When this irreversible transition takes place, it is exothermic [2,3].

The thermodynamic behaviour of a sample upon heating is usually studied by means of DTA or DSC measurements. During the experiments, glass transitions, crystallisation and melting may occur. A disadvantage of differential thermal analysis, however, is the finite heating rate which may prevent thermodynamic equilibrium being reached. Moreover, some transitions display very weak energy effects and can hardly be detected. Adiabatic calorimetry is a powerful method to investigate the stability of a formed crystal and to measure very small heat effects or slow dynamics. In the adiabatic calorimeter, a sample is heated using the intermittent method. During each input period, energy is supplied. Then the sample and its container are kept under almost adiabatic conditions by keeping the surrounding shields at the same temperature. The thermal behaviour of the sample during the stabilisation periods is followed and indicates whether a change in thermodynamic state is taking place. Therefore, thermal analysis and adiabatic experiments can be used to obtain complementary data.

### 1.2. *Following crystallisation processes*

The kinetics of phase change under isothermal conditions has been described by Avrami [4–6]. Evans [7] used the original equations by Avrami to derive, among other things, the laws of expanding spheres in relation to the grain size of metals. A general overview of the Avrami equations in the context of polymer crystallisation has been given by Sperling [8]. The studies mentioned show that the volume of crystallised material can be described as

(i) ‘Seeded growth’, i.e. all nuclei developed at once before the sample was put at the optimal temperature for nucleation

$$V_{\mathrm{solid}}(t) = At^3 \tag{1}$$

where $V_{\mathrm{solid}}(t)$ is the volume of crystallised material at time $t$ after reaching the temperature where the crystallisation starts, and $A$ is the Avrami constant.

(ii) ‘Birth and spread’, i.e. the nuclei appear continually

$$V_{\mathrm{solid}}(t) = At^4 \tag{2}$$

In both cases it is assumed that the linear growth rate is constant. In the case of ‘birth and spread’, the number of nuclei is assumed to increase linearly with time. These equations are valid only for low degrees of crystallinity under isothermal conditions, i.e. in the initial stages of phase transformation.

For carvone, the optimal temperature range for nucleation and the optimal temperature range for crystallisation are separated. The substance is liquid at room temperature and can be supercooled to the glass phase. Experiments revealed that the nucleation rate is maximal at a temperature near the glass transition temperature. A sample can be cooled to the glass phase and afterwards put at a temperature at the beginning of the optimal range for crystallisation. During the crystallisation process, the nuclei present grow. We assume that the number of newly nucleating grains is negligible and the crystals are growing at a constant linear growth rate. The volume of crystallised material is thus expected to increase according to Eq. (1). Another possibility is to cool the liquid sample immediately down to a temperature at the beginning of the optimal temperature range for crystallisation. In this case, the sample does not pass the optimal temperature range for nucleation. Consequently, there will continually appear nuclei which immediately start to grow. This situation is described by Eq. (2). The volume increase of crystalline material in both types of crystallisation processes can be determined in an adiabatic calorimeter.

During true adiabatic measurements (with hardly any heat exchange with the environment), very small heat effects can be followed accurately for days, even at very low temperatures. When the sample is held under adiabatic conditions at the onset of an exothermic event, the total enthalpy of the vessel and its contents remains almost constant. The temperature of the system increases until the process is terminated. The obtained curve of temperature against time may be of use in investigating the crystallisation kinetics involved.

The amount of solid formed at a certain time can be deduced from the temperature at that moment using the equation

$$V_{\mathrm{solid}}(T) = \left(\frac{H_{\mathrm{liq}}(T) - H(T_0)}{H_{\mathrm{liq}}(T) - H_{\mathrm{sol}}(T)}\right) V_{\mathrm{total}} \tag{3}$$

where $H_{\mathrm{liq}}(T)$ is the enthalpy of the vessel filled with liquid and $H_{\mathrm{sol}}(T)$ is the enthalpy of the vessel filled with solid at temperature $T$. $V_{\mathrm{total}}$ is the total volume of solid after complete crystallisation. $H(T_0)$ is the enthalpy of the system at time $t = 0$ and temperature $T_0$. It is assumed that at $t = 0$ the amount of crystalline material can be neglected. The very small heat exchange with the environment causes a slight increase of the total enthalpy of the vessel and its contents with time. Consequently, $H(T_0)$ can be described by: $H_{\mathrm{liq}}(T_0) + \gamma t$.

For a small temperature range, the heat capacity of the vessel filled with liquid and when filled with solid are almost independent of temperature. This results in

$$V_{\mathrm{solid}}(T) = \left(\frac{\alpha(T - T_0) - \gamma t}{\Delta H + (\alpha - \beta)(T - T_0)}\right) V_{\mathrm{total}} \tag{4}$$

where $\alpha$ is the heat capacity of the vessel filled with liquid and $\beta$ is the heat capacity of the vessel filled with solid. $\Delta H$ is the enthalpy difference between the liquid and the solid phase at $T_0$.

Using Eq. (4), the measured temperature against time curve can be recalculated to a curve of $V_{\mathrm{solid}}$ against time. The system satisfies the conditions of the Avrami equations as long as the temperature increase is very small and the degree of crystallinity is low. This implies that the first part of the curve may be used to determine the type of crystallisation kinetics. In addition, almost the entire curve can be used to determine the growth rate as a function of temperature using only one experiment. When the crystallisation proceeds, the temperature starts of rise quickly and thus the growth rate increases. This is described by Van Miltenburg et al. [9] who applied the theory to a crystallisation curve of *l*-carvone.

### 1.3. Purpose

This study focuses on the thermodynamic properties of pure *l*-carvone. In a previous study [10], the temperature and enthalpy of fusion were determined by means of DSC measurements. In the present study the polymorphic behaviour is investigated using both DSC and adiabatic experiments. The transition temperatures and the types of polymorphs obtained are discussed.

The heat capacities of the stable phase have been measured from 5 to 280 K. The derived thermodynamic properties $S^0(T) - S^0(0)$ and $H^0(T) - H^0(0)$ are given.

The crystallisation and recrystallisation processes occurring in the sample under different conditions are investigated. The Avrami equations (1) and (2) are used to fit slow crystallisation curves obtained in the adiabatic calorimeter. The crystallisation kinetics at the beginning of the experiments are examined.

## 2. Experimental

### 2.1. Material

*l*-Carvone, liquid at room temperature, was obtained from E. Merck Nederland B.V. The product contained over 99% carvone. The optical rotation measured on a neat sample was $[\alpha]_D^{20} = -58.8°$.

### 2.2. Differential scanning calorimetry

The DSC measurments were performed on a DSC 120 from Seiko Instruments Inc. using a heating rate of 1.5 K $\mathrm{min}^{-1}$. The DSC apparatus was calibrated with adamantane and water. The weight of the DSC sample was 8.31 mg.

### 2.3. Adiabatic calorimetry

The adiabatic measurements were performed in an adiabatic calorimeter that has been described previously [11–13]. The intrinsic drift of the calorimeter approaches 15 mK $h^{-1}$, the internal precision is about 0.02% and the absolute accuracy is estimated to be 0.2%.The range of the temperatures at which adiabatic measurements can be performed is 5–420 K. The sample, weighing 7.81462 g, was sealed with helium gas as heat exchanger.

During the heating experiments performed between 5 and 30 K, the input periods were 100 s, and the stabilisation periods 120 s. In the temperature range 30–100 K, the input periods and the stabilisation periods were 600 s. From 100 K to room temperature, the input as well as the stabilisation periods were 800s.

## 3. Results and discussion

### 3.1. DSC experiments

### 3.1.1. DSC curve of a supercooled sample

The liquid sample in the DSC apparatus was supercooled to the glass phase and then heated from 150 K to room temperature. Fig. 1 shows the glass transition at 171 K, next a large crystallisation peak, followed by a recrystallisation, and finally, the melting of the sample at 247.7 K. The heat of melting was 11.55 kJ $mol^{-1}$. The crystallisation took place between 193 and 208 K and the heat of crystallisation was $-7.8$ kJ $mol^{-1}$. The sample recrystallised from metastable (II) to stable (I) crystalline material between 210 and 218 K, with a heat of transition of $-0.2$ kJ $mol^{-1}$.

### 3.1.2. DSC curve of a precrystallised sample

The liquid sample was supercooled to the glass phase and then heated to 230 K. This resulted in the glass transition, followed by the crystallisation to crystal phase II and

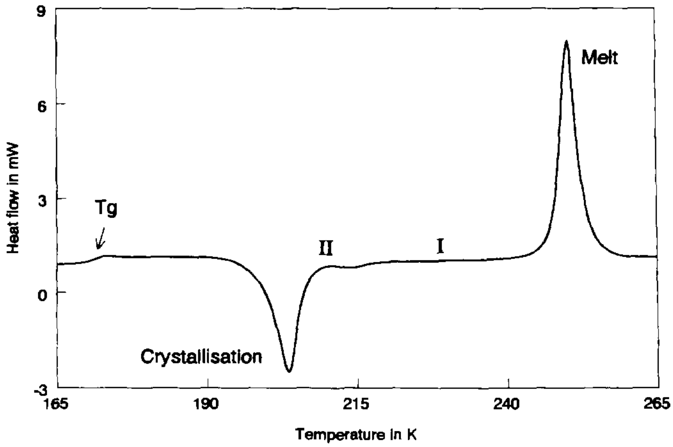

Fig. 1. DSC curve of a supercooled *l*-carvone sample showing the glass transition, a large crystallisation peak, followed by a recrystallisation, and finally, the melting of the sample.

finally the recrystallisation to crystal phase I. The stable (I) crystalline material was subsequently cooled down to 160 K. Thereafter it was heated to room temperature. This final heating experiment resulted in the DSC curve presented in Fig. 2a.

The exothermic transition from II to I, measured on the supercooled sample (see Fig. 1), is irreversible as it is not present in the DSC curve of the precrystallised sample in Fig. 2a. This implies that the metastable (II) and the stable (I) material are monotropic forms.

The enlargement of a part of the measurement curve, Fig. 2b, shows an endothermic event between 195 and 207 K. This effect is the transition of the I$\beta$ to the I$\alpha$ phase. The

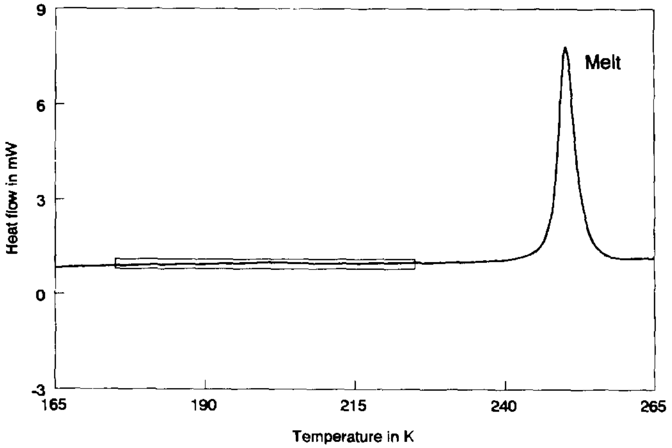

Fig. 2a. DSC curve of a precrystallised sample showing a small endothermic effect between 195 and 207 K, followed by the melting of the sample.

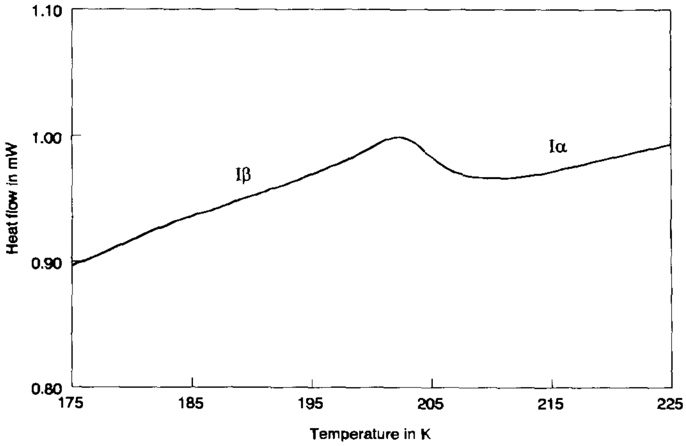

Fig. 2b. Enlargement of a part of the curve presented in Fig. 2a showing the small endothermic effect, which is the transition of the I$\beta$ to the I$\alpha$ phase.

heat involved is about 0.06 kJ mol$^{-1}$. The transition of the two polymorphic modifications is endothermic and thus a case of enantiotropism. This is confirmed by the reversibility of this transition, see Section 3.2.5.

### 3.2. Adiabatic measurements

### 3.2.1. Adiabatic calorimetry on a supercooled sample

A heating experiment in the adiabatic calorimeter on a supercooled sample resulted in the curve shown in Fig. 3. The sample passed the glass transition at 166 K, solidified between 179 and 225 K, and melted at 249.5 K.

The DSC experiment of a supercooled supercooled sample revealed that the solidification of carvone consists of a crystallisation followed by a recrystallisation. The solidification peak obtained from this adiabatic measurement, however, does not contain enough data points to distinguish the two exothermic effects as can be seen in Fig. 3. The total heat of solidification was about $-8.6$ kJ mol$^{-1}$.

The determined temperatures for both the glass transition and the melting of *l*-carvone are not exactly equal for the DSC apparatus and the adiabatic calorimeter. This is probably partially due to the fact that the DSC apparatus was calibrated only at 209 and 273 K. Another reason might be the influence of the relaxation of the glass and the correction for the impurities. The temperatures determined with the adiabatic calorimeter are believed to be very accurate.

### 3.2.2. Adiabatic calorimetry on a precrystallised sample

The sample in the adiabatic calorimeter was supercooled to the glass phase. Thereafter it was heated to 230 K, which implies that the sample passed the glass transition, crystallised to phase II, and recrystallised to phase I. Then the sample was

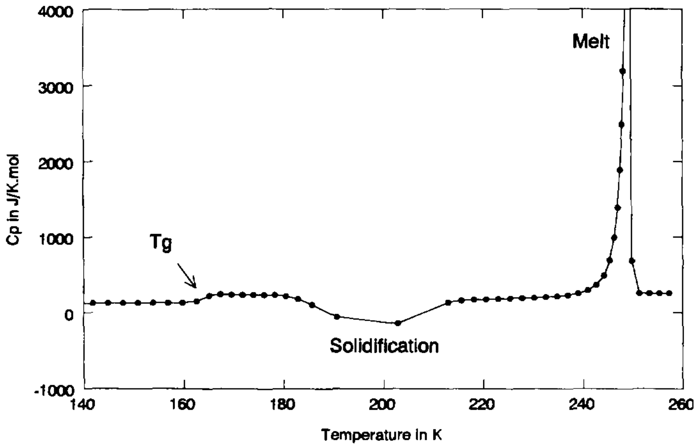

Fig. 3. Adiabatic calorimetry on a supercooled sample showing the glass transition, the solidification of the sample, and finally, the melting.

cooled down to 80 K. A heating experiment performed on this precrystallised sample resulted in curve 'a' in Fig. 4. The measurement curve shows the endothermic transition 'I$\beta$ to I$\alpha$' between 190 and 215 K. The sample melted at 249.5 K. The heat of melting was 11.73 kJ mol$^{-1}$.

### 3.2.3. *Crystallisation under adiabatic conditions after precooling to 179.5 K*

The liquid sample was supercooled to 179.5 K, which is at the beginning of the optimum temperature range for the crystallisation. The sample was then kept under adiabatic conditions. Fig. 5, curve A, shows the measured change in temperature against time. Due to the exothermic solidification process, the temperature rose from 197.5 to 199 K in 22 h. The curve of temperature against time was recalculated to a curve of $V_{\text{solid}}$ against time using Eq. (4) and the following experimentally determined values: $\alpha = 22.6\,\mathrm{J\,K^{-1}}$; $\beta = 18.2\,\mathrm{J\,K^{-1}}$; $\gamma = 9 \times 10^{-5}\,\mathrm{J\,s^{-1}}$; $T_0 = 179.52$ K; $\Delta H = 348.1$ J. The calculated amount of crystalline material at the beginning of the process is plotted in Fig. 6, curve A.

The conditions of the Avrami equations, discussed in the introduction, are satisfied during the first part of the crystallisation process. The sample did not pass the optimal temperature range for nucleation before the crystallisation experiment was started. Therefore, we expect Eq. (2) to be valid for the beginning of the crystallisation process.

The 378 data between $t = 0$ s and $t = 60000$ s ($V_{\text{solid}} = 7.1\%$ of $V_{\text{total}}$) were fitted using Eq. (2) resulting in: $A = 5.39 \times 10^{-21}\,\mathrm{cm^3\,sec^{-4}}$ and an $r2$ coefficient of determination $D = 0.9996$. This result strongly confirms the idea of a crystallisation process starting with 'birth and spread'. The curve found by this fitting procedure is presented in Fig. 6, curve Fit 'birth and spread'. As expected, a fitting procedure using Eq. (1), describing a case of 'seeded growth', resulted in a poor fit: $A = 2.83 \times 10^{-16}\,\mathrm{cm^3\,sec^{-3}}$ and an $r2$

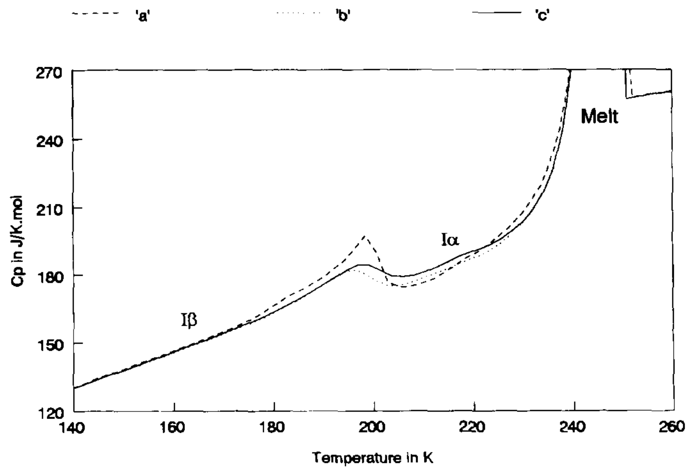

Fig. 4. The phase transition 'I$\beta$ to I$\alpha$' as determined with adiabatic calorimetry on stable (I) *l*-carvone. The thermal history of the sample is described in Section 3.2.2. for curve 'a', and in Sections 3.2.4. and 3.2.5. for curves 'b' and 'c', respectively.

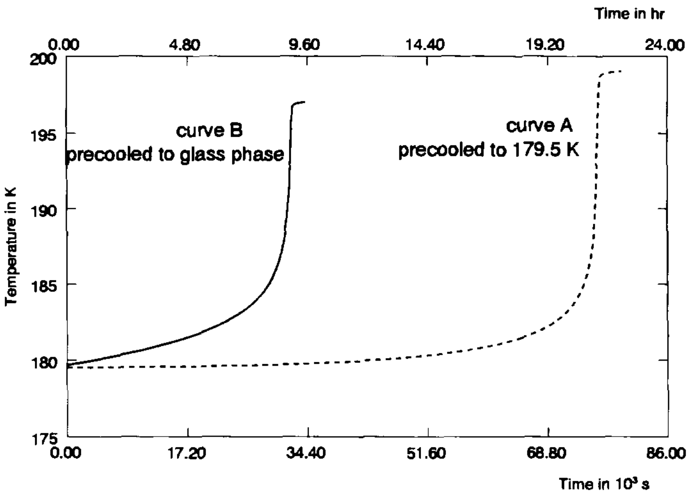

Fig. 5. Temperature increase during crystallisation processes under adiabatic conditions. Curve A presents the crystallisation of the sample cooled from room temperature down to 179.5 K. Curve B presents the crystallisation of the sample after passing the optimal temperature range for crystallisation.

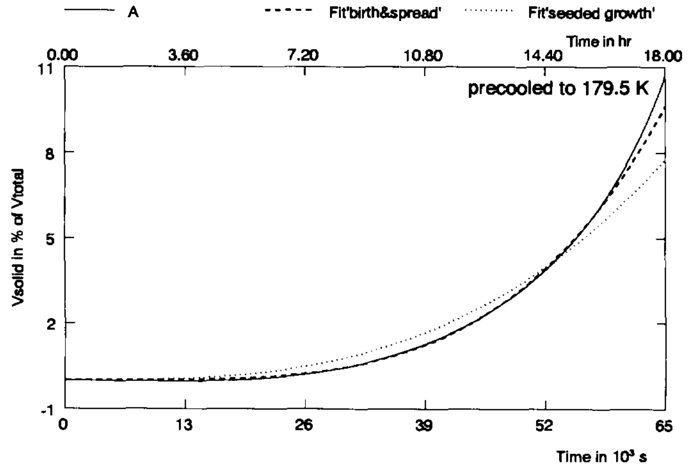

Fig. 6. Curve A shows the increase of crystallised material in the sample precooled to 179.5 K. The obtained Avrami fitting data are: $V_{\mathrm{solid}} = 5.39 \times 10^{-21} t^4 [100\% \, V_{\mathrm{total}}]$ for Fit 'birth and spread', and $V_{\mathrm{solid}} = 2.83 \times 10^{-16} t^3 [100\% V_{\mathrm{total}}]$.

coefficient of determination $D = 0.970$. This is shown in curve Fit 'seeded growth' in Fig. 6.

After the slow crystallisation, the sample was subjected to a heating experiment ranging from 200 K to room temperature. The sample showed an exothermic event between 202 and 225 K and melted at 249.5 K, see measurement data A in Fig. 7.

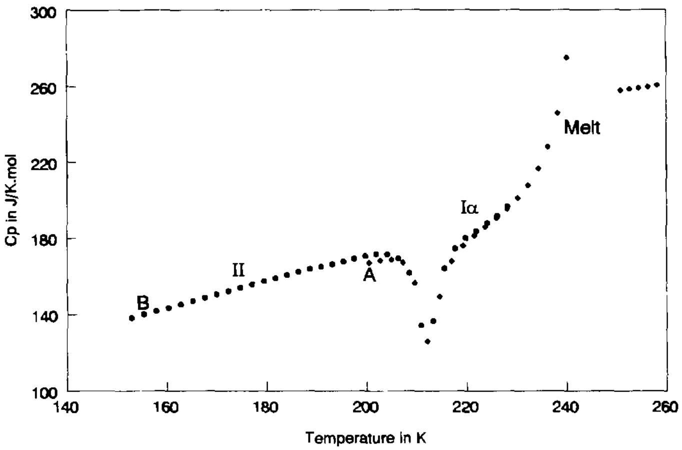

Fig. 7. Phase transition from metastable (II) to stable (I) *l*-carvone measured in the adiabatic calorimeter. The thermal history of the sample can be found in Sections 3.2.3. and 3.2.4. for the measurement data A and B, respectively.

Hence, the slow crystallisation experiment, which started with 'birth and spread', resulted in metastable crystalline material. This metastable material (II) recrystallised to stable material (I) when it was heated. The recrystallisation had a heat of transition of $-0.2$ kJ mol$^{-1}$.

### *3.2.4. Crystallisation under adiabatic conditions after precooling to the glass phase*

The liquid sample in the adiabatic calorimeter was supercooled to the glass phase and subsequently heated until the onset temperature of the crystallisation. Thereafter the sample was kept under adiabatic conditions. In Fig. 5, curve B, the change in temperature is given against time. The temperature rose from 179.7 to 197 K in 9 h due to the crystallisation. Then the intrinsic drift of the calorimeter was reached.

During the cooling as well as during the heating experiment, the sample passed the optimum temperature range for nucleation, which is expected to be below the optimum temperature range for crystallisation and above the glass transition temperature. The curve of temperature against time initiates with a slope comparable with the slope of curve A at 181 K ($t = 17$ h, $V_{\mathrm{solid}} = 8\% V_{\mathrm{total}}$). This implies that before the measurement started, about 8% of the sample had been crystallised, which is confirmed by the calculation of $V_{\mathrm{solid}}$ against time; during the experiment 91.5% of the sample crystallised. Consequently, this curve could not be used to examine the growth kinetics at the beginning of the crystallisation process.

After this slow crystallisation experiment, the sample was cooled to 150 K and then heated until 230 K. The measurement curve is presented in Fig. 7, measurement data B. It shows an exothermic event between 202 and 225 K, which is the phase transition of metastable (II) material to stable (I) material. Curve A and B in Fig. 7 show that this phase transition is easily reproducible.

### 3.2.5. *Reversibility of the transition Iα to Iβ*

The obtained crystalline material (I) was cooled from 230 to 150 K. Thereafter a heating experiment was performed to 230 K. Fig. 4, curve 'b', shows that the sample passed an endothermic event (the transition from Iβ to Iα) between 190 and 215 K. Comparison of curve 'a' and 'b' in Fig. 4 reveals that this transition is not easily reproducible.

Finally, the sample was cooled from 230 to 5 K and then heated to 280 K. The obtained measurement curve is presented in Fig. 4, curve 'c'. It shows the reversible phase transition 'Iβ to Iα' between 190 and 215 K, and the melting at 249.5 K. The

Table 1
Thermodynamic properties at selected temperatures for stable (I) *l*-carvone ($M = 150.22\,\mathrm{g\,mol^{-1}}$; $\Phi^0_m \overset{\mathrm{def}}{=} \Delta_0^T S^0_m - \Delta_0^T H^0_m/T$)

| $T$/K | $C^0_{p,m}$/J K$^{-1}$ mol$^{-1}$ | $\Delta S^0_m$/J K$^{-1}$ mol$^{-1}$ | $\Delta H^0_m$/J mol$^{-1}$ | $\Phi^0_m$/J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|
| 10 | 4.498 | 1.327 | 9.950 | 0.3320 |
| 20 | 17.22 | 7.995 | 113.70 | 2.310 |
| 30 | 30.70 | 17.57 | 354.34 | 5.755 |
| 40 | 43.34 | 28.16 | 725.80 | 10.02 |
| 50 | 54.42 | 39.04 | 1215 | 14.73 |
| 60 | 64.63 | 49.88 | 1812 | 19.69 |
| 70 | 73.99 | 60.56 | 2505 | 24.77 |
| 80 | 82.70 | 71.04 | 3292 | 29.90 |
| 90 | 90.97 | 81.27 | 4160 | 35.04 |
| 100 | 98.96 | 91.25 | 5108 | 40.16 |
| 110 | 107.07 | 101.07 | 6139 | 45.26 |
| 120 | 114.67 | 110.71 | 7248 | 50.31 |
| 130 | 122.24 | 120.19 | 8432 | 55.32 |
| 140 | 129.98 | 129.53 | 9694 | 60.29 |
| 150 | 137.85 | 138.77 | 11033 | 65.21 |
| 160 | 145.82 | 147.92 | 12451 | 70.10 |
| 170 | 154.22 | 157.01 | 13951 | 74.94 |
| 180 | 163.57 | 166.08 | 15539 | 79.75 |
| 190** | 175.82 | 175.24 | 17233 | 84.54 |
| 200** | 183.23 | 184.55 | 19049 | 89.31 |
| 210** | 181.03 | 193.34 | 20851 | 94.05 |
| 220 | 190.47 | 201.99 | 22709 | 98.76 |
| 230* | 199.10 | 210.64 | 24657 | 103.44 |
| 240* | 207.83 | 219.30 | 26691 | 108.09 |
| 249.5$^{s,*}$ | 216.12 | 227.53 | 28705 | 112.47 |
| 249.5$^{l,*}$ | 256.85 | 274.53 | 40433 | 112.47 |
| 250* | 257.04 | 275.04 | 40561 | 112.80 |
| 260* | 260.83 | 285.20 | 43150 | 119.23 |
| 270 | 264.16 | 295.10 | 45774 | 125.57 |
| 280 | 268.00 | 304.77 | 48433 | 131.80 |
| 290 | 272.85 | 314.26 | 51136 | 137.93 |

Key: *, extrapolated; s, solid; l, liquid; **, transition 'Iβ to Iα'.

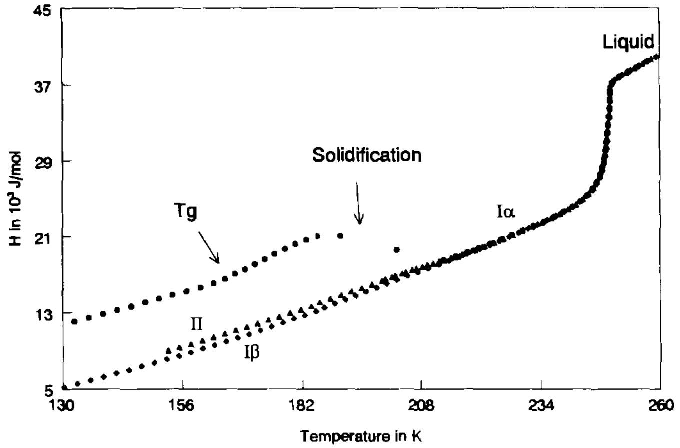

Fig. 8. Measured enthalpy paths of *l*-carvone during the experiments in the adiabatic calorimeter.

thermodynamic properties of the stable phase of *l*-carvone, from 5 to 280 K, are presented in Table 1.

## 4. Conclusion

In this study we focused on the thermodynamic properties of *l*-carvone. DSC experiments and adiabatic calorimetry supplied complementary data on its polymorphic behaviour and on the crystallisation and recrystallisation processes occurring in the sample under different conditions.

The DSC experiments revealed that the solidification takes place in two steps: first a crystallisation to metastable (II) material followed by a recrystallisation to stable (I) material. The different phases in which *l*-carvone can exist are summarised in Fig. 8. It presents the relative values of the enthalpy of the sample as determined with the adiabatic calorimeter. Heating a supercooled sample results in a glass transition at 171 K; next the sample crystallises to metastable (II) material. Heating of the resulting material causes a transition to the stable (I) phase between 202 and 225 K. The metastable (II) and the stable (I) material are monotropic forms. Stable *l*-carvone shows a reversible phase transition 'I$\beta$ to I$\alpha$' between 190 and 215 K: a case of enantiotropism. The melting temperature of I$\alpha$ is 249.5 K, with a heat of melting of 11.73 kJ mol$^{-1}$.

Using the adiabatic calorimeter, the crystallisation from supercooled liquid to metastable (II) material was followed under true adiabatic conditions. The start of the crystallisation process of a sample precooled from room temperature to 179.5 K proved to be a case of 'birth and spread'. The obtained data resulted in: $V_{\mathrm{solid}} = 5.39 \times 10^{-21} t^4$ [100% $V_{\mathrm{total}}$]. This equation is valid for the first 16 h of crystallisation during which 7% of the sample crystallised.

The crystallographic characteristics of the polymorphic modifications are currently being studied using X-ray diffractometry.

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