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ACTIVATION ENERGIES FOR METASTABLE TO STABLE PHASE TRANSITION OF 4,4'-di-*n*-HEPTYLOXYAZOXYBENZENE

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Abstract

The paper studies metastable phases of 4,4'-di-*n*-heptyloxyazoxybenzene (liquid crystal substance) using adiabatic calorimetry. The process of transformation between metastable and stable phases is described quantitatively. The conclusion concerns activation energies for metastable phase to stable phase transition.

Keywords: activation energies, adiabatic calorimetry, liquid crystals, phase transition: metastable phase → stable phase

Introduction

Substances which in some temperature regions show liquid crystal properties are characterised by the existence of one or many metastable phases in the solid phase. As an example, let us take 4,4'-di-*n*-heptyloxyazoxybenzene (HOAB) constituting the subject of this work.

One of the methods useful for investigating of metastable phases is the adiabatic calorimetry used in [1], and its results form a basis for this work.

When cooling a sample from one of the liquid crystal phases or from the isotropic phase, a metastable phase can be reached. It can then transform to a more stable modification at a temperature depending on the type of substance and on its thermal history. The thermal effect connected with the process can be estimated as a self-heating effect in the adiabatic calorimeter. When passing from a metastable phase to a stable one, the temperature of the calorimetric vessel changes (increases) in time.

In order to pass from a metastable phase to a stable one, the sample needs to overcome the activation enthalpy ($\Delta H'$). In such a way molecules can pass over an energy barrier. The phase transition from a metastable phase to a stable one can occur after the passage over the energy barrier. One can write this down using the classical equation of an Arrhenius type presented in [2]:

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$$k=A\exp(-\Delta H'/RT) \tag{1}$$

where k – transition rate factor, A – transition constant, $\Delta H'$ – activation enthalpy.

The quantitative description of the process gives time constant τ connected with transition rate factor k as was shown in [3].

The main aim of this work has been to use the above method for HOAB in order to calculate activation enthalpy for the process in question (transition from metastable to stable modification).

As can be seen from (1), k *vs.* T dependence allows one to obtain $\Delta H'$, where k is connected with the time of transition from a metastable phase into a stable one, and particularly with τ (which denotes the time in which the temperature increase is equal to $1/e$ of all the temperature increase in the discussed phase transition, as it is clearly seen in the next chapters, e being the basis of natural logarithm). The problem how to obtain τ from experimental values was discussed in detail in [3] and also in [4]. In this work I use some values of τ shown in Table 1 of [3] and also a value of τ which was not presented in [3], i.e. for the temperature of 345.58 K.

Experimental

Some details connected with the adiabatic calorimeter used in the work are presented in [5]. The sample mass amounted to 50.76 g. The investigated sample was heated from low to high temperatures (corresponding to isotropic liquid) during measurements of the specific heat.

In order to get the metastable phase, the sample was cooled from the smectic, nematic, or isotropic phase by the direct thermal contact with the liquid nitrogen container. At the very beginning of the cooling process the cooling rate was ca 6 K min^{-1}, decreasing when cooling the calorimetric vessel to lowest temperatures which gives the average cooling rate equal to 2.6 K min^{-1}.

The obtained specific heat curve showing 3 enantiotropic phase transitions is shown in Fig. 1. Those phase transitions are not discussed in the article. The subject of our consideration is connected with monotropic transitions between two curves clearly seen in the solid-state region in Fig. 1. We can see the curve for metastable II and stable modification in the solid-state region of HOAB in the main part of Fig. 1. Additionally, in the upper left part of the Fig. 1, we can see the specific heat curve for the metastable phase I which is placed between those curves for the metastable I and stable modification. It is magnified from the main Fig. 1 in order to see better the curve for metastable phase I.

The mathematical description of the metastable to stable phase transition

To make clear our considerations let us recall some equations useful for obtaining τ.

A metastable phase and a stable phase are subsystems between which heat may exchange. The two phases are in the same space. The interaction between those sub-

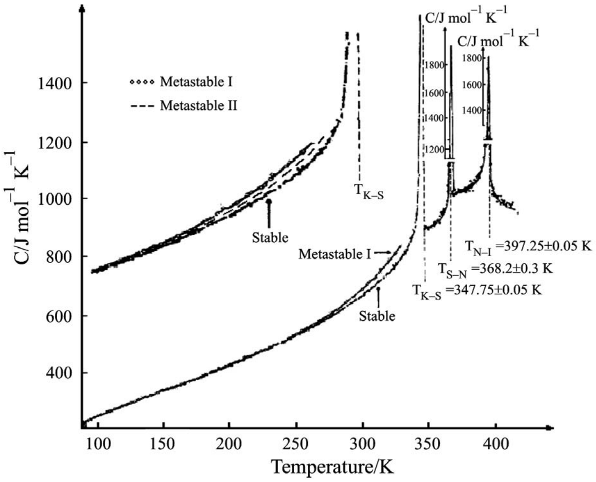

Fig. 1 Specific heat *vs*. temperature for HOAB

systems is described by a relaxation process. The system in which the relaxation process happens is isolated (it is in calorimetric vessel).

During the process an amount of the energy is transferred from one subsystem into the other. Therefore the change of entropy of the whole system in time dt is equal to:

$$\frac{\mathrm{d}S}{\mathrm{d}t}=\frac{1}{T'}\frac{\mathrm{d}U'}{\mathrm{d}t}+\frac{1}{T''}\frac{\mathrm{d}U''}{\mathrm{d}t} \tag{2}$$

where U' and T' stand for the one and U'' and T'' stand for the other subsystem.

From the law of the conservation of energy it follows:

$$\mathrm{d}U'+\mathrm{d}U''=0 \tag{3}$$

As a result of the fact that the system is isolated and the process metastable to stable phase is spontaneous, the rate of entropy increases and, consequently its source amounts to:

$$\frac{\mathrm{d}_{\mathrm{i}}S}{\mathrm{d}t}=\left(\frac{1}{T'}-\frac{1}{T''}\right)\left(\frac{\mathrm{d}U'}{\mathrm{d}t}\right)=\Delta\left(\frac{1}{T}\right)\left(\frac{\mathrm{d}U'}{\mathrm{d}t}\right) \tag{4}$$

Hence flux $J_\mathrm{u}=\mathrm{d}U'/\mathrm{d}T$ and impulse $X_\mathrm{u}=\Delta(1/T)$. If we remember that $J_\mathrm{u}=\sum_{\mathrm{k}=1}^{\mathrm{n}}L_{\mathrm{uk}}X_\mathrm{k}$ where L_uk are phenomenological factors, we can write for the relaxation process the phenomenological equation:

$$\frac{\mathrm{d}U'}{\mathrm{d}t}=(-L\,\Delta T)/T^2 \tag{5}$$

By introducing for dU' the equation:

$$\mathrm{d}U' = C\mathrm{d}T \tag{6}$$

where C means the specific heat of the first subsystem, we can write:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{L}{C}(\Delta T/T^2) \tag{7}$$

By denoting $-CT^2/L = \tau$, we get:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -(\Delta T)/\tau \tag{8}$$

Hence

$$\Delta T = B\exp(-t/\tau) \tag{9}$$

where B is a constant and is so called relaxation time. Therefore we can write the Eq. (8) in the following way:

$$T^{\infty} - T(t) = B\exp(-t/\tau) \tag{10}$$

where $T(t)$ means a temperature at a moment of transition, T^{∞} means the temperature after the transition, and t – time. After finding the logarithm of (10) we get

$$\ln(T^{\infty}) - T(t) = \mathrm{const.} - t/\tau \tag{11}$$

Results and discussion

The sample melted and then cooled to liquid nitrogen temperature was heated when measuring some specific heat values. In such a way the upper curve in Fig. 1 was obtained. At ca. 337 K a self-heating of the sample was observed, connected with metastable II to metastable I phase transition. It was found that after the transition at ca. 337 K is over and the sample has been heated, when measuring specific heat *vs.* temperature, another self-heating of the sample could be observed this time at ca. 344 K connected with metastable I to stable phase transition. After finishing the last heating the pure stable phase is received. For this phase the lowest specific heat curve in Fig. 1 was obtained. The earlier stage of self-heating at 337 K resulted in obtaining the phase depicted by specific heat curve that lies between the two mentioned above curves (metastable I).

Equation (11) was used to obtain τ for the above mentioned substance as it was shown in [3].

For HOAB the results shown in Table 1 were obtained for two metastable modifications present in the substance.

Looking at the results of this work (Table 1), one can see a dependence of τ on temperature, predicted by the Arrhenius equation, i.e. the higher the temperature, the greater the rate factor for the metastable phase I→metastable phase II transition and for the metastable II→stable phase transition. Taking into account the Arrhenius formula (1) and $k=1/\tau$, one can calculate $\Delta H'$ by drawing $\ln\tau$ *vs*. $1/T$. Activation enthalpy

ΔH’ obtained in such a way is equal to 242±33 kJ mol^{-1} for the metastable phase I→ metastable phase II transition, and 398±149 kJ mol^{-1} for the metastable phase II→ stable phase transition.

One could add that the energy difference between the mentioned phases could be easily estimated by multiplying ΔT (temperature increase) by the average heat capacity (in the region of the thermal increase) and by dividing that value by the sample mass. The result is equal to 2422 J mol^{-1} between metastable phase I and metastable phase II, and 1126 J mol^{-1} between metastable phase II and stable phase as stated in [3].

Table 1 Characteristic parameters for metastable phase to stable phase transition in HOAB

Transition	Average temperature of transition/K	τ/min
Metastable phase I→ metastable phase II	339.5	232±25
Metastable phase I→ metastable phase II	335.8	594±34
Metastable phase II→ stable phase	345.58	670±65
Metastable phase II→ stable phase	343.7	1357±133

The creation of metastable phases discussed in this work is similar to the analogous problem which was investigated in [6–9] for another liquid crystal substance, namely MBBA: N-(*p*-methoxybenzilidene)-*p*-butyl aniline. The MBBA molecule has a rod like character as HOAB one. For the case of MBBA it was also observed there that fast cooling of a sample in an isotropic or liquid crystal state can lead to the formation of a solid phase, in which conformation of the molecules is energetically less favored (metastable phase). A region of dielectric relaxation was found [8] in MBBA in the solid-state, for metastable phase only (in solid modifications of the substance). The dielectric relaxation (seen from the movement of dipole moment of the methoxy group) is connected with the conformational degrees of freedom of lateral tails. Hence, in the case of MBBA one could state that during formation of stable phase, the MBBA molecules change their conformation to a more favored as stated in [7–9]. In the process of formation of stable phase of MBBA, the external degrees of freedom can play a role as well.

It seems that in HOAB, which is the subject of this work, no conformational degrees of freedom (i.e. no internal degrees of freedom) play any role when passing from a metastable to the stable modification. However, the external degrees of freedom play an important and even a dominant role there. This results from the fact that for the two stable modifications of HOAB under investigation, no dielectric relaxation region (connected with a possible movement of lateral groups with dipole moments) was found in the metastable or stable modification of the sample [9]. A significantly higher degree of internal molecular mobility in the metastable modification was stated in MBBA only (for molecules with rather short lateral chains which is not the case for HOAB).

Hence although for some liquid crystal substances we obtain an experimental evidence of some metastable phases in solid-state temperature region, the transition from metastable phase to the stable one can have a complex nature:

1) It can be connected only with external degrees of freedom, as it was a case for HOAB
2) It can be also connected with some conformational degrees of freedom leading to more favored conformation of molecules.

Let us mention that the problem discussed in the work has been investigated by calorimetry for many substances. As an example one can show the article [10] – dealing activation energy of self-heating process studied by DSC or the article [11] dealing a problem of mesomorphism as it was a case in the work.

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