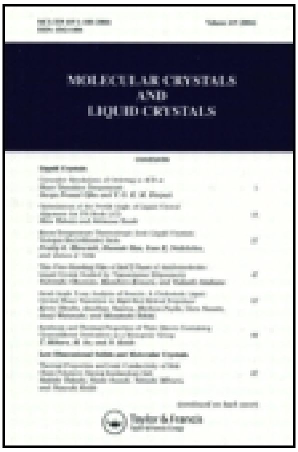

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Dimer Formation and its Reflection on the Self-Diffusion Coefficient

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The self-diffusion coefficients of nematic liquid crystals p-n-heptyloxybenzoic acid and p-n-nonyloxybenzoic acid have been measured depending on the temperature. The influence of the process of dimer formation on the self-diffusion was shown.

Keywords: Nematic liquid crystals, NMR, self-diffusion.

INTRODUCTION

The thermotropic liquid crystals are usually substances with elongated molecules containing two aromatic rings and at least one hydrocarbon chain. The hydrocarbon chain is flexible, it can exist in different conformations. The aromatic rings are rather rigid, they determine the elongated, solid part of the molecules. The compounds forming nematic liquid crystal phase often have a structure of the type shown in Figure 1, where X and Z are saturated hydrocarbon chains bound to the benzene rings either directly or by means of oxygen atoms, and Y is a relatively short atomic group binding both phenyl rings.

The interest in alkyloxybenzoic acids ($C_nH_{2n+1}O—C_6H_4—COOH$), object of this investigation, as compounds forming liquid crystal mesophases, described by Gray,[1] dates from more than twenty years ago. The first two members of this homologous series do not manifest liquid crystal properties upon heating or cooling. The nematic liquid crystal phase appears at $n = 3$ and the next three homologous members ($n = 4, 5, 6$) exhibit only a nematic phase. The heptyloxybenzoic acid ($n = 7$) (HOBA), octyloxy ($n = 8$) (OOBA), nonyloxy ($n = 9$) (NOBA), up to $n = 13$ form not only a nematic phase but also a smectic phase within a relatively narrow temperature range.

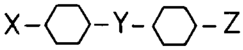

FIGURE 1 Typical graphic formula of liquid crystal.

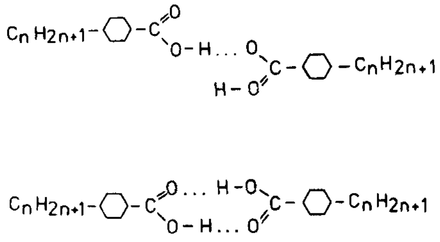

FIGURE 2 a) Open dimer; b) Close dimer.

The next members (from $n = 13$ to $n = 18$) show only a smectic liquid crystal phase. The presence of a carboxylic group (COOH) in the molecule of these substances presupposes the building of a hydrogen bond, formation of dimers.

Dimers and especially close dimers (Fig. 2b) structurally resemble the typical molecular conformation of liquid crystals – Figure 1. Such a configuration ensures a more stable arrangement of the molecules in the nematic and specially in the smectic liquid crystal phase.

The molecular characteristics – mobility, dimerization, conformation transition etc. – are directly connected with the relaxation NMR processes.[2–4] The molecular mobility (M) associated with the translational diffusion depends on the shape of the molecules or of the supramolecular aggregates (dimers). A direct method for determination of M is based on measurement of the transversal NMR relaxation in a gradient magnetic field.

MATERIALS AND METHODS

The p-n-heptyloxybenzoic acid (HOBA) and p-n-nonyloxybenzoic acid (NOBA) were investigated. They were kindly provided to us by the liquid crystal group from Halle Wittenberg.

The coefficient of longitudinal translational self-diffusion (D) was measured by the Carr-Purcell nuclear magnetic resonance spin echo method in a gradient H_0 field.[5] The measurements were performed depending on the temperature from 95 °C to 155 °C (HOBA-from 99 °C to 151 °C; NOBA-from 120 °C to 155 °C) by means of Brucker spectrometer at the Josef Stefan Institute in Ljubljana. All measured values were plotted on the drawing, and the temperature intervals were about 5 °C. There was aspiration for precise intervals of 5 °C, but the real obtained temperatures were shifted, because of a complicated temperature-controlled system.

RESULTS AND DISCUSSION

The corresponding values for the molecular mobility (M) were calculated according to the Einstein correlation

$$M = D/kT \tag{1}$$

(D-coefficient of self-diffusion, experimentally determined as described above; k-Boltzman constant, T-absolute temperature). The molecular mobility depending on the temperature was plotted on Figures 3a and 3b. The relative error in determining the magnitude in our case was of the order of 2.5%. On drawing 3 this means bars under 1 mm in size, that is why we use graphical presentation with a circlet.

The molecular theory[6,8] gives the molecular mobility as an exponential function of the reciprocal temperature:

$$M = M_0 \exp(-\Delta E/RT) \tag{2}$$

where ΔE is the activation energy, R the universal gas constant, and M_0 is a quantity which does not depend on temperature. This correlation is valid when the character of the intermolecular interaction is maintained unchanged, *i.e.*, neither the diffuse molecules nor the surrounding molecules undergo structural changes in the investigated temperature interval. On a semi-logarithmic graph this dependence should be presented by a straight line. But in our case the phenomenon appears to be more complicated.

The curves of HOBA (Fig. 3b) and NOBA (Fig. 3a) have a similar course. If we consider the course of the curves from isotropic to nematic phase it can be ascertained that the molecular mobility initially decreases with decrease of the temperature (Figure 3-A). Around the isotropic-nematic phase transition this course alters, the molecular mobility begins to increase abruptly (Fig. 3-B). New variation occurs by further decrease of the temperature in the nematic interval, the mobility begins to diminish again up to nematic-smectic phase transition (Fig. 3-C).

As we mentioned above, the substances of this homologous series can be presented as a mixture of three kinds of structural units: i) monomers – single molecules; ii) close dimers (Fig. 2b) – they have a pronounced elongated shape; iii) open dimers (Fig. 2a) – they do not have a compact form, both parts are bound more loosely, the constituent molecules keep a higher degree of freedom and their long axes can be orientated in different directions. Less probable threemers and larger molecular aggregates which possess more complicated conformations have similar characteristics.

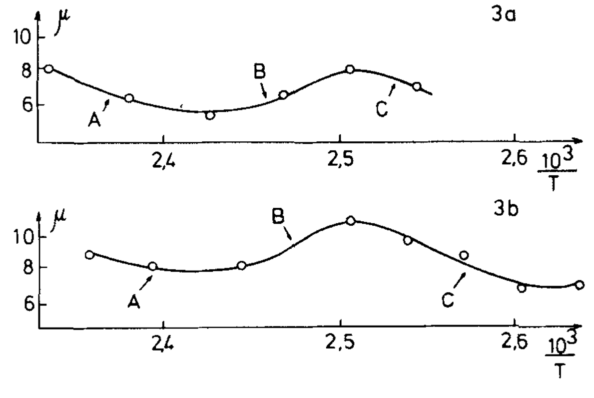

FIGURE 3 Molecular mobility (M) depending on the temperature for a) NOBA b) HOBA.

Let us consider the diffusion behaviour of the HOBA structure units. Obviously the monomers exhibit the greatest mobility. Their form is essentially elongated due to the presence of a C_7H_{15} group and they can be approximated as prolate ellipsoids with axes (a, b, c), $(c = b, a > b)$.

According to the theory of Lamb[7] the resistance force R_r surmounted by such an ellipsoid at its motion along the long axis a in the viscous medium depends on its eccentricity. We have calculated R_r according to Lamb[7] for a prolate ellipsoid with transversal axes b and c constant $(c = b = \text{const})$ and longitudinal axis a changing in frame from $a = b$ to $a = 10b$. The mobility M can be expressed and evaluated through the resistance force R_r. The mobility M was plotted as a function of the long axis a on Figure 4.

Due to stereochemical and structural considerations the ratio a_m (the long axis of monomer molecule) to b for monomer of HOBA could be expected to be within the range between 2 and 3.

Following the above mentioned structural consideration, we will approximate the close dimer (Fig. 2b), to an ellipsoid possessing the same transverse axes b and c and longitudinal axis a_d twice as long as the former. In this case the a_d to b ratio could be expected within the range between 4 and 6.

The decrease of the molecular mobility due to the formation of close dimers can be seen on Figure 4. The two values of M, M_m and M_d for two quantities of $a - a_m$ and a_d differing in factor 2 $(a_d = 2a_m)$ are compared. The ratio of these quantities $\chi = M_m/M_d$ was estimated. It was established that this ratio almost did not change – it depended slightly on a_m $(a_m = 2b, \chi = 1,33; a_m = 3b, \chi = 1,4)$. Consequently the formation of close dimers increases the molecular mobility of this conformation with factor – 1,4 irrespective of their eccentricity.

The open dimers during their motion in a viscous medium get a resistance force almost equal to the sum of the resistance forces of both monomer units because of the relatively unfolded configuration. Hence its mobility is approximately twice less than the mobility of monomers.

Therefore the consideration for the three main kinds of conformations suggests that the mobility of the close dimer is less than that of the monomer and larger than that of the open dimers.

In the isotropic phase area with temperature decrease the number of the dimers, initially open dimers, quickly grows. Their low mobility leads to a high decrease of the

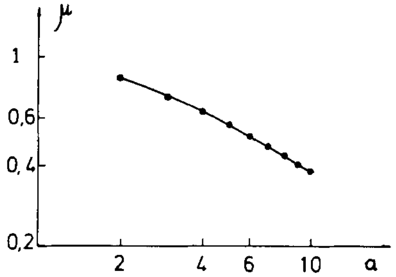

FIGURE 4 Molecular mobility (M) depending on the molecular longitudinal axis (a).

average mobility of the sample (Fig. 3). In the nematic phase area the mutually parallel arrangement of the molecules facilitates the formation of linear close dimers. The increase of their number at the expense of the open dimers gives rise to mobility growth of the sample. This process terminates in the nematic phase. With further decrease of the temperature the curve follows its exponential temperature behaviour tending to a theoretically expected temperature course (Eq. 2).

The same course of the curve for NOBA (Fig. 3a) allows similar treatment for the molecular association as by HOBA.

Other authors[9] draw analogous conclusions by the IR Spectroscopy method.

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