Evidence for Polymorphism within the So-called “Blue Phase” of Cholesteric Esters.

I. Calorimetric and Microscopic Measurements

K. Bergmann and H. Stegemeyer
Lehrstuhl für Physikalische Chemie, Gesamthochschule Paderborn

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Calorimetric measurements as well as microscopic observations confirm the existence of two thermodynamically stable polymorphic forms of the so-called “blue phase” of cholesteryl nonanoate and myristate.

It is well known for a long time that various cholesteryl esters show violet-blue colours just below their clearing points, a phenomenon which usually is called “The Blue Phase” (BP) [1, 2]. Recently, the BP has been demonstrated by thermodynamic and optical measurements to be a stable phase in a very narrow temperature range of about 0.5 degrees [3—9].

The cholesteric → BP (ΔH_{CB}) and BP → isotropic (ΔH_{BI}) phase transitions have been re-investigated by means of differential scanning calorimetry (Perkin-Elmer DSC-2) for highly purified cholesteryl myristate (CM) and nonanoate (CN). To improve the resolution we used gold pans instead of aluminum pans.

From the thermograms (Fig. 1) transition-enthalpies ΔH_{BI} of 1.1 kJ mole⁻¹ for CM and 0.53 kJ mole⁻¹ for CN have been measured, whereas the respective values of ΔH_{CB} were found to be much smaller: within the range of accuracy 34 J mole⁻¹ for CM and 17 J mole⁻¹ for CN.

As a new result we have observed a third peak, almost hidden in the BP → isotropic peak in highly resolved thermograms, which is well reproducible although not completely separated. In both cases this effect has been found just 0.15 K below the clearing point. The change of enthalpy is estimated to be of the same order of magnitude as for ΔH_{CB}.

We attribute this additional enthalpy to a phase transition between two polymorphic “blue phase” states BP I → BP II. This suggestion is supported by the spectroscopic results given in [10].

Additional evidence for two polymorphic “BP” states originates from visual observations by means of polarizing microscopy. As in CM the selective reflection band λ_{R} [9] causing the well-known blue colour is positioned at the end of the visible wavelength region the transition BP I → BP II of the pure CM could not be observed by eye. Adding a nematogenic compound (p-pentylphenyl-2-chloro-4-(p-pentylbenzoyloxy)-benzoate, PCPB) λ_{R} is shifted to longer wavelengths [11]. In mixtures of CM with PCPB we have detected three phase transitions near the clearing point (Leitz Ortholux-Pol with Mettler heating stage FP 5). The resulting textures are summarized in Table 1.

Reprint requests to Prof. Dr. H. Stegemeyer, Lehrstuhl für Physikalische Chemie, Gesamthochschule Paderborn.

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Table 1. Phase transitions and textures of CM/PCPL, 42.37 mole-% CM.

<table>
<thead>
<tr>
<th></th>
<th>Cholesteric</th>
<th>BP I</th>
<th>BP II</th>
<th>Isotropic</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\theta/\degree C)</td>
<td>96.00</td>
<td>96.25</td>
<td>96.60</td>
<td></td>
</tr>
<tr>
<td>Heating</td>
<td>planar</td>
<td>“planar”</td>
<td>platelet(^a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(blue)</td>
<td>(green (\rightarrow) blue)</td>
<td>(green/blue)</td>
<td></td>
</tr>
<tr>
<td>Heating</td>
<td>focal-conic</td>
<td>platelet</td>
<td>platelet</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(green/yellow/red)</td>
<td>(green/blue)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cooling</td>
<td>focal-conic</td>
<td>super-(\leftarrow) platelet</td>
<td>platelet</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cooled</td>
<td>(green/yellow/red)</td>
<td></td>
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</tbody>
</table>

\(^a\) The platelet texture is of the same form as shown by Demus [12], Figure 158.

remain. This observation is of interest with respect to the results presented in [13].

Thus it has been demonstrated that BP I and BP II are thermodynamically stable phases with finite changes of enthalpy at defined transition temperatures; only the texture is influenced by the experimental conditions.

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