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P. Adamski [a] & A. Dylik-gromiec [a]

[a] Institute of Physics, Technical University of Lódź, Lódź ui., Zwirki, 36, Poland

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A Determination of the Cholesteric Liquid Crystalline Temperature Range by Birefringence Measurements in an Abbe Refractometer

P. ADAMSKI and A. DYLIK-GROMIEC

Institute of Physics
Technical University of Łódź
Łódź ul. Zwirki 36. Poland

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Determination of a cholesteric liquid crystal's mesomorphic temperature range is of paramount importance in studying its physical properties. There are several methods for determining this temperature range, such as: nuclear magnetic resonance, differential thermal analysis, viscosity, optical rotation, dielectric constant and birefringence measurements.

We have worked out a new simple method for determining cholesteric liquid crystal temperature range by measuring its birefringence in an Abbe refractometer. For isotropic liquids, a single border line, dividing the field of vision, may be observed in the lunette of the refractometer. The image in the lunette is divided by two border lines with different intensity in the case of cholesteric liquid crystals. Each border line is related to the refractive index of light of the ordinary and extraordinary ray, respectively. The liquid crystal temperature range may be determined by measuring the temperature of appearance and disappearance of the second border line. Cholesteryl oleyl carbonate has been investigated by this method.

INTRODUCTION

Investigations on physicochemical properties of certain organic compounds undertaken many years ago uncovered a new state of matter which possesses an intermediate state between the solid state and the isotropic liquid. The liquid crystalline state has properties characteristic of both the solid state, and the isotropic liquid. The liquid crystalline state has greater order in the arrangement of its molecules than the isotropic liquid state, but less order in the solid state. Nowadays it is known that the liquid crystalline state may appear only in the case where compounds consist of long, rigid asymetric molecules, and therefore having a flat or elongated form. Brown[1] has stated that molecules of liquid crystal substances ought to be elongated and rigid due to large number of double bonds in the direction of the axis of elongation. Liquid crystalline properties often appear in substances with aromatic character. According to Brown's article, dipoles and polarizable groups in a molecule, are favourable to a liquid crystalline state also.

It has been remarked that large differences in the moment of inertia of a molecule cause certain limitations in its rotary motion. A definite molecular orientation in the liquid crystalline state may only occur when the molecules possess one rotational degree of freedom and all translational degrees of freedom as well. The above molecular orientation in a liquid crystal contributes to the its optical characteristics such as birefringence and optical rotation.

Furthermore, the possibility of translational motions of the molecules results in the appearance of a viscosity, an ability to form drops and a free surface, all of which are characteristic of liquids.

The structure and physical properties of liquid crystals has been the subject of many investigations. The temperature range in which this state occurs seems to be one of the most important parameters determining the liquid crystalline state. Knowing this parameter, we can undertake further investigations and provide a measure of practical utility of the investigated substances. This temperature range is usually defined as a difference between the melting point of the substance and a liquid crystal – liquid transition point. This range has beei measured by many different methods. Thermographic methods are of utmost importance.[2-11] Nuclear magnetic resonance NMR measurements[11-13] are remarkable too. Very good results were obtained by investigations of optical rotatory dispersion of liquid crystals[1] and the dependence of dielectric constant upon temperature[12]. Considerable viscosity changes with temperature have been observed in liquid crystals.[14-15] While studying natural[16-20] and induced[21] birefringence it is possible to obtain the required temperature range of liquid crystals.

The methods given above require difficult measurements as well as complicated and expensive apparatus. In this work a simple method is presented for determining the cholesteric liquid crystalline temperature range. This method makes use of refractometric measurements.

A SHORT CHARACTERISTIC OF KNOWN METHODS

Thermographic measurements are among the most efficient methods for phase transition investigations. The method consists of making use of the temperature dependence of the specific heat of the substance being investigated. The specific heat is more difficult to determine experimentally than is the temperature, because it requires the simultaneous measurement of the temperature increase and the quantity of heat provided. In the applied thermographical methods, therefore, one studies sample temperature as a function of heating time. One obtains from the resulting graph changes in the slope of the curve which is related to the specific heat of the tested substance.[6]

In practice, the most often used method is that of differential thermal analysis[9-11] i.e. investigations of the temperature difference between the heated sample and a selected standard which are simultaneously heated.

Recently, nuclear magnetic resonance has very often been applied for temperature range determination in liquid crystal substances[11-13]. Such measurements may be used only for substances having comparatively simple NMR spectra.

A measurement of the measomorphic temperature range has been also obtained from viscosity changes. The viscosity of liquid crystal does not decrease in a monotonic way with increasing temperature but attains extremal values in a suitable temperature range. It is supposed that the extremum is a result of the phase transition in the liquid crystal. Viscosity studies of this kind have been reported by Sakamoto[14] and Wysocki.[15] The method is very sensitive but it requires a large quantity of material and samples of extreme purity.

The liquid crystal interval was also determined by measuring the parallel and perpendicular dielectric constants and their change with temperature. That method was also described in detail.[21]

A determination of the mesophase temperature range has often been made by investigations of optical properties such as birefringence and optical rotation. These investigations have been possible only with oriented substances. A simple method of preparing oriented nematic crystals was given by Chatelain.[18] The method was based on melting the examined sample between two cover glasses which were rubbed with blotting paper in one direction. An optical axis obtained by this method coincides, probably, with the direction of rubbing.

Chatelain was also the first one who examined the birefringence of liquid crystals.[17,18] He measured the refractive indices for *p*-azoxyanisol at wavelength. $\lambda_1 = 5890$ Å and $\lambda_2 = 5460$ Å. The results were later confirmed by other authors.[20] The value of the refractive index for the ordinary ray, n_o, was considerable different from that of extraordinary ray, n_e. The difference gradually decreases while the temperature of the sample approaches the transition to the isotropic liquid. Chatelain measured n_o and n_e by a method based on the minimal deviation of a beam of light in a prism[19] and with the aid of Newton's rings.[17]

Microscopic observations of nematic and smectic liquids made by cross polarizers[1] have shown that these liquid crystals may behave as uniaxial crystals and possess negative birefringence. This property seems to be a consequence of the molecular order.

METHOD

In the present paper a liquid crystal temperature range is reported as determined by examination of refractive indices of a liquid crystal substance.

As is known, the refractive index of a liquid may be determined by an Abbe refractometer. The basis of the measurement is total internal reflection. The refractive index of the examined substance may be accurately determined (exact accurancy 10^{-4}) by measurements of the border angle.

A few drops of the examined liquid were put into a refractometer and enclosed between two termostatic prisms made of a glass possessing a relatively high refractive index ($n = 1.89$) compared to that of the measured liquid. A border line dividing the field of vision into dark and clear areas is observed in a lunette of the refractometer. The image for an isotropic liquid is shown in Figure 1a.

The measurement of refractive index by Abbe's refractometer consists of making the mentioned border line cut with the cross hairs. The refractive index values were read directly on the scale.

In the case of compounds having liquid crystalline properties, the sample should be melted between the prisms of refractometer; the measurements are then possible when the liquid crystalline phase has formed between them. When the liquid crystal is placed in the refractometer there results a characteristic pattern in the field of vision. For liquid crystals, besides the normal observed border line for isotropic liquid, there is also seen the less intense border line.

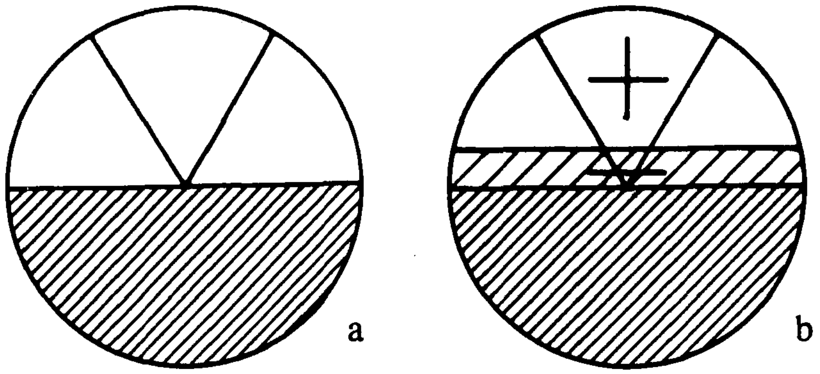

FIGURE 1 An image in the lunette of the refractometer: (a) isotropic liquid; (b) cholesteric liquid crystal.

Thus, the field of vision is devided into three parts: the shade area, the semi-shade area, and the clear area. The characteristic picture of the two border lines in the refractometer field for a liquid crystalline sample is shown in Figure 1b. Two border lines appear throughout an accurately determined temperature range for the given liquid crystal compound. The mentioned border lines of illumination have been observed only between melting point of the examined compound and liquid crystal-isotropic liquid transition temperature. Above the clearing temperature a picture seen in refractometer does not differ from the observed picture for ordinary liquids.

Refractive index investigations were carried out while the sample was being cooled because it seemed that the isotropic liquid-liquid crystal transition occurs faster than does the liquid crystal-isotropic liquid transition. From investigations with polarized light it has been verified that the light rays which form the mentioned border lines are linearly polarized. The planes of polarization of the rays are perpendicular to each other. Repeated results obtained that in manifold experiments for the same compounds suggest that the optical axes ought to be perpendicular to the orienting sheet. One would conclude from what has been said that the measured values ordinary and extraordinary refractive index seem to be maximal values.

RESULTS

A cholesteric substance, cholesteryl oleyl carbonate, was the subject of the investigation. This compound has liquid crystalline properties throughout the temperature range 22° - 29°C. A formula of cholesteryl oleyl carbonate is shown in Figure 2. The molecule has a rigid and flat structure caused by the presence of

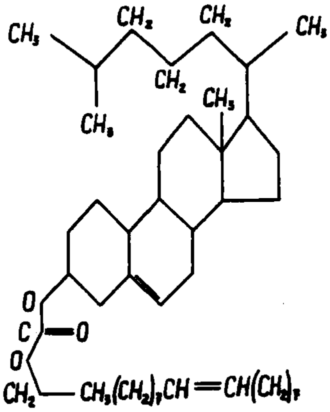

FIGURE 2 The formula of cholesteryl oleyl carbonate.

a condensed benzene ring system. Rotary motion around the axis perpendicular to the molecular long axis is the only possible spatial periodicity in the liquid crystalline state. Furthermore, if all molecules of that compound precess in a common direction, the energy of molecular interaction will be extremal. A free surface, arising after the compound melts, or a boundary surface (e.g. glass or mica plate) may be an additional deciding factor for the examined compounds molecular orientation.

As is known, liquid crystalline compounds can become ordered when formed in thin layers. This property has been utilized in this paper for the birefringence study of cholesteryl oleyl carbonate.

Refractive indices n_o and n_e differ in the second decimal place, and therefore their determination does not require precise apparatus. The following apparatus was used in the experiments: An Abbe refractometer for measuring refractive index to within values an accuracy ±0.0001, a Hoeppler's thermostat to maintain a sample temperature within ±0.1°C and a set of calibrated thermometers.

The temperature dependence of the refractive indices for cholesteryl oleyl carbonate is presented in Figure 3 and Table 1. The measurements for this com-

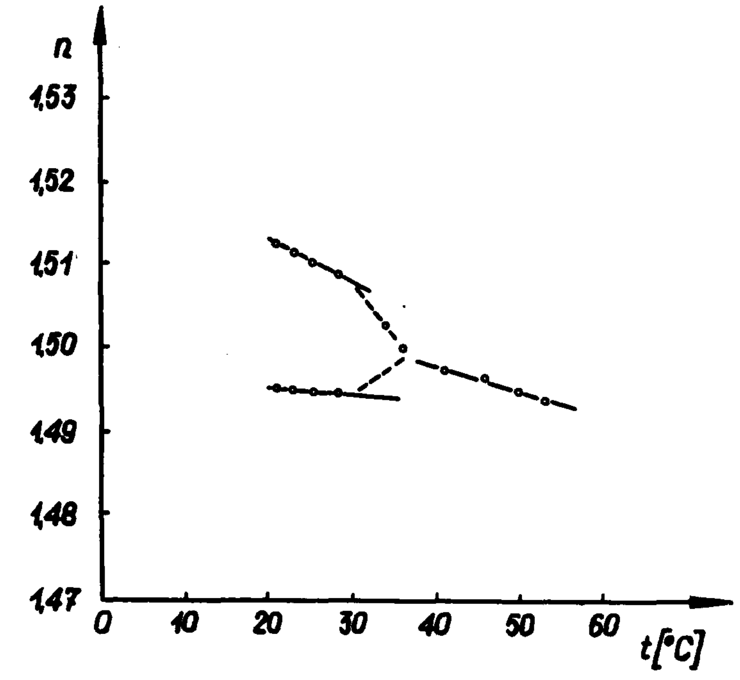

FIGURE 3 Refractive indices for white light of the ordinary and extraordinary ray as a function of temperature for cholesteryl oleyl carbonate.

TABLE I

Relationship between refractive indices of ordinary and extraordinary rays and temperature for cholesteryl oleyl carbonate

No.	Temperature	n_o	n_e	Δn
First Series				
1.	53.2	1.4938	–	–
2.	50.3	1.4949	–	–
3.	46.0	1.4966	–	–
4.	41.0	1.4971	–	–
5.	36.2	1.5000	–	–
6.	30.4	1.5029	–	–
7.	28.5	1.5089	1.4946	0.0143
8.	25.5	1.5101	1.4947	0.0154
9.	23.0	1.5115	1.4949	0.0166
10.	21.5	1.5126	1.4950	0.0176
Second Series				
1.	35.0	1.5009	–	–
2.	31.5	1.5014	–	–
3.	30.0	1.5026	–	–
4.	29.6	1.5069	1.4947	0.0122
5.	28.5	1.5080	1.4948	0.0132
6.	27.0	1.5089	1.4948	0.0141
7.	25.8	1.5099	1.4949	0.0150
8.	23.3	1.5115	1.4949	0.0166
9.	22.3	1.5123	1.4954	0.0169

pound were repeated many times for studied temperature range. Changes in the refractive index anisotropy with temperature are shown in Figure 4. The difference in refractive indexes was the greatest at the melting point. It decreases with increasing temperature until its disappearance at the transition temperature to the isotropic liquid.

Therefore, this method of determining the temperature range in which the compound has liquid crystal properties requires, measuring the temperatures at which two border lines appear in the refractometer field of vision and the temperature of disappearance for one of them.

Observations similar to those described above were obtained for the nematic substance *p*-azoxyanisol by Chatelain. He examined the temperature dependence of the refractive indices of this compound by use of Newton's rings[17] for light of known wavelength.

The Abbe refractometer used measures an average refractive index for white light. The method reported therefore, does not allow a dispersion study of the liquid crystal. In conclusion, this work reports a new technique which has proven successful, for determining the temperature range of cholesteric compounds.

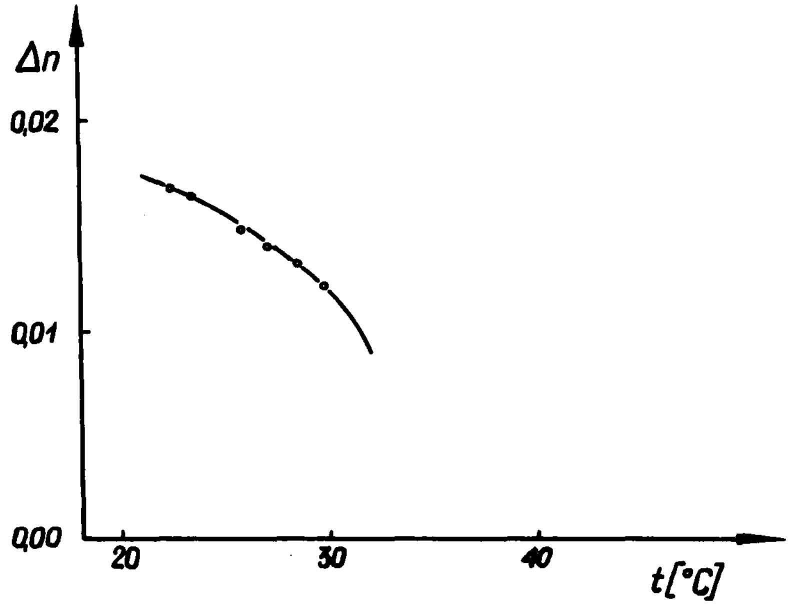

FIGURE 4 Difference between refractive indices of the ordinary and extraordinary ray for cholesteryl oleyl carbonate as a function of temperature. Measured for white light.

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