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Temperature Range and Optical Properties Investigations of Cholesteryl Oleyl Carbonate, Cholesteryl Nonanoate and Their Mixtures

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INTRODUCTION

Substance in the liquid crystal state possess physical properties, which belong to the solid state and to isotropic liquid. These properties are connected with the form and structure of molecules of these compounds. The liquid crystal state may appear only in the case of those organic compounds molecules which are straightly asymetric e.g. possess flat or elongated form. Three liquid crystal states may be separated in connection with their structure and arrangement; they are: the nematic, the smectic and the cholesteric states.

We shall limit our presentation to cholesteric liquid crystals. The cholesteric state may be produced by a compound possessing flat forms. This structure is united with the presence of condensed benzene rings.

The liquid crystal state of known organic compounds may only exist within a determined temperature range. This temperature range seems to be one of the most important parameters which permits one to undertake further investigations. This temperature range is usually defined as a difference between the melting point of the substance and a liquid crystal-liquid transition point.

Nowadays, many methods are available for measurement of this temperature range. These methods are: thermographic methods,[1-6] nuclear magnetic reso-

nance[7,8] and viscosity measurements,[9,10] investigations of optical rotatory dispersion[11] and dielectrical constant dependence on temperature.[7] Very good results were obtained by investigations of birefringence.[12-15]

In this work, a simple method for the determination of the cholesteric liquid crystal temperature range with the Abbe refractometer is presented.[16,17] In addition, the influence of the composition of known mixtures on thermogintude of the temperature ranges is defined.

EXPERIMENTAL PART

In present work cholesteric compounds are the subject of investigations. These are cholesteryl oleyl carbonate and cholesteryl nonanoate. Cholesteryl oleyl carbonate has liquid crystal properties in the temperature range 25–35°C. The temperature range of the liquid crystal state of cholesteryl nonanoate is 68–94°C. These substances are strongly birefringent. Their refractive indices are very sensitive to temperature. The liquid crystal temperature range of investigated compounds may be defined by the determination of liquid crystal refractive indices by use of the Abbe refractometer.[16,17] An image of the border line of total reflection in the plane of the cross hairs is formed. For isotropic liquid, it is noted that half of the field is dark and half is light.

Liquid crystals placed in the refractometer give a characteristic picture in the field of vision (Figure 1). In this case the field of vision is divided into three parts: the shaded area, the semishaded area and the clear area. Two border lines appeared for liquid crystal compounds only in a well-defined temperature range. The picture seen in the refractometer (above transition temperature from liquid crystal to isotropic liquid) did not differ from the observed picture for ordinary liquids.

Average refractive indices values of white light may be measured by the Abbe refractometer. The measurement of the refractive indices by the Abbe refracto-

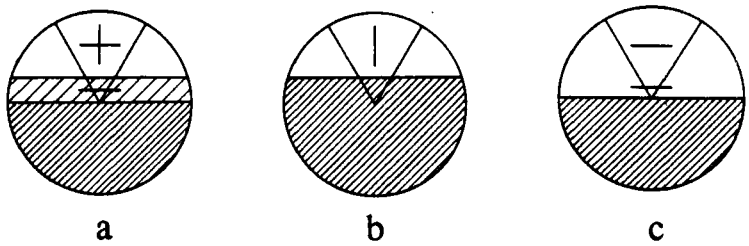

FIGURE 1 (a) Picture of field of vision of liquid crystals in Abbe refractometer. (b), (c) Picture of field of vision of liquid crystals looked at by the use of nicol prism.

meter consists in making the mentioned border lines cut with the crossed hairs. The refractive indices values were read directly on the scale. Exactness of the measurements is −0.0001. The differences in refractive indices values for ordinary and extraordinary ray are about 0.01. Hoeppler's thermostat allowed us to keep the sample temperature within the limits of ±0.1°C. Temperature was measured directly on the refractometer.

In our work the optical properties of cholesteryl oleyl carbonate, cholesteryl nonanoate and their mixtures were measured. The relationships between the refractive indices of ordinary and extraordinary rays and the temperature for these compounds and mixtures are recorded in Table 1 and Figure 2. In Figure 2 we can see that the relationships between refractive indices of cholesteric compounds and temperature are similar to those obtained by Chatelain [18] for *p*-azoxyanisole. It is known that these results were obtained by the use of Newton's ring methods.

Investigations of light polarization of liquid crystals have proved that light rays forming the mentioned border lines are linearly polarized. Polarization planes of these rays are perpendicular to each other. It was defined by observation of an image in the Abbe refractometer by the use of the nicol prism. Brightness changes in the individual's field of vision may be observed when the nicol prism

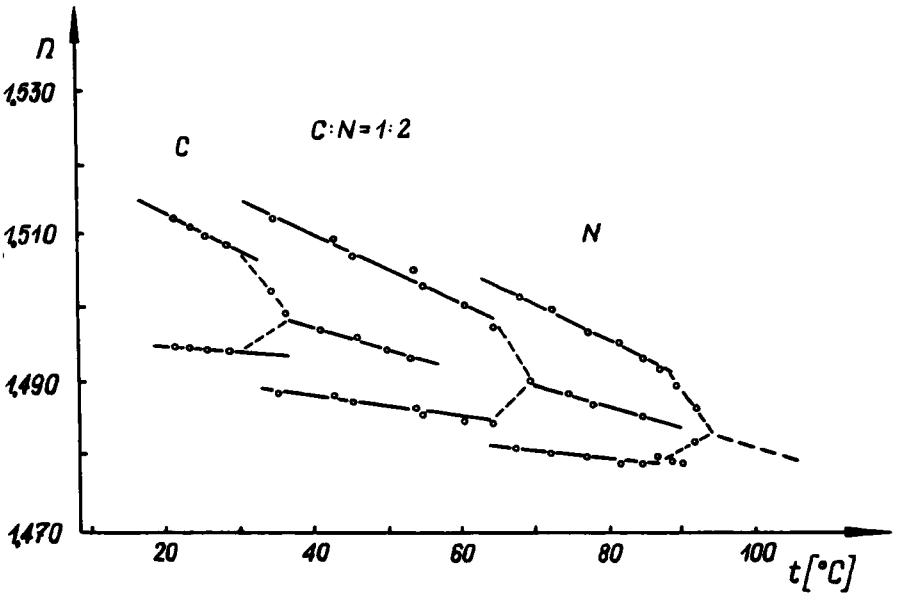

FIGURE 2 Relationship between light refractive indices of ordinary and extraordinary rays and temperature for cholesteryl oleyl carbonate C; cholesteryl nonanoate N; and their mixture C:N = 1.2.

TABLE I

Relationship between light refractive indices of ordinary and extraordinary rays and temperature for cholesteryl oleyl carbonate, cholesteryl nonanoate and their mixtures 1:1, 1:1.3, 1:1.5, 1:2.

Cholesteryl oleyl carbonate			Weight mixture 1 : 1 Cholesteryl oleyl carbonate and cholesteryl nonanoate tests		
Temp. (°C)	n_O	n_e	Temp. (°C)	n_O	n_e
50.3	1.4949		70.5	1.4904	
46.0	1.4966		65.3	1.4919	
41.0	1.4971		59.8	1.4941	
36.2	1.5000		56.6	1.5004	1.4880
30.4	1.5029		50.5	1.5036	1.4880
28.5	1.5089	1.4946	46.5	1.5050	1.4883
25.5	1.5101	1.4947	38.5	1.5088	1.4892
23.0	1.5115	1.4949	32.2	1.5113	1.4909
21.5	1.5126	1.4950	27.5	1.5148	1.4922
			23.0	1.5172	1.4934
			21.5	1.5189	1.4940
			21.7		1.4941
Weight mixture 1 : 1.3 cholesteryl oleyl carbonate and cholesteryl nonanoate			Weight mixture 1 : 1.5 cholesteryl oleyl carbonate and cholesteryl nonanoate		
Temp. (°C)	n_O	n_e	Temp. (°C)	n_O	n_e
69.4	1.4910		75.7	1.4891	
62.1	1.4939		68.2	1.4920	
55.5	1.4952		55.5	1.5002	1.4892
53.7	1.5029	1.4870	51.0	1.5033	1.4894
50.4	1.5048	1.4873	45.0	1.5062	1.4898
44.7	1.5062	1.4878	39.2	1.5092	1.4909
42.0	1.5089	1.4891	34.7	1.5118	1.4919
35.5	1.5110	1.4900	30.1	1.5142	1.4925
30.0	1.5144	1.4916	24.8	1.5162	1.4937
25.4	1.5171	1.4928	23.9		1.4941
25.3		1.4928			
Weight mixture 1 : 2 cholesteryl oleyl carbonate and cholesteryl nonanoate			Cholesteryl nonanoate		
Temp. (°C)	n_O	n_e	Temp. (°C)	n_O	n_e
78.4	1.4877		90.2	1.4861	1.4790
75.1	1.4889		87.0	1.4928	1.4790
69.8	1.4908		84.7	1.4938	1.4788
64.9	1.4980	1.4849	81.5	1.4955	1.4788
60.8	1.5010	1.4850	77.7	1.4973	1.4796
55.0	1.5038	1.4860	72.7	1.5000	1.4804
50.4	1.5060	1.4870	68.0	1.5018	1.4810
45.6	1.5081	1.4880	65.0		1.4814
40.3	1.5103	1.4890			
35.0	1.5128	1.4899			
30.4		1.4911			

was rotated. Results from many experiments on the same compounds and the same Δn values for may experiments suggest that the optical axes of the investigated liquid crystal substances ought to be perpendicular to the orientating sheet which is formed between the prisms of the refractometer. Different arrangements of the optical axis, parallel or sloped to this sheet, may give different Δn values. In the observed compounds extraordinary refractive indices values are lower than ordinary refrative indices values. Cholesteric liquid crystals are optically negative according to W. Gray.[19]

CONCLUSION

Investigations presented above show that the liquid crystal temperature range of cholesteric organic compounds and their mixtures may be defined by measuring the relationship of refractive indices with temperature. Liquid crystalline mixtures have temperature ranges of lying between the temperatures of the pure compounds. It was noticed that the temperature-range width is not proportional to the concentration of the mixtures.

It is evident that at the lower and upper temperature limits the increments in refractive indices, Δn, increases when the concentrations of the second component in the mixtures decrease. It may be connected with different molecular interactions in cholesteryl oleyl carbonate and cholesteryl nonanoate mixtures. It is possible that the unusual temperature range increase in mixtures in the liquid crystal state is connected with the possibility of rotatory motion of side chains in which single bonds exist.

Refractive indices values from repeated measurements of ordinary and extraorinary rays as a function of temperature in the range give proof that the optical axes of the liquid crystal sheet is perpendicular to the border of the sheet. In connection with this it has been said that the determined values of ordinary and extraordinary indices seem to be the maximal values.

Investigations of these mixtures measured after one month have shown that they are not durable. It seems that the reason for this instability may be a chemical decomposition of cholesteryl oleyl carbonate.

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