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THE STRUCTURE OF MESOPHASES OF BINARY AND MULTICOMPONENT MIXTURES OF SOME CHOLESTERIC LIQUID CRYSTALS

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Abstract We present the results of the study of binary and multicomponent mixtures of cholesteryl enanthate with cholesteryl nonanoate and cholesteryl formiate. The aim of the study is the preparation of the system with phase transition temperature close to room temperature. Phase diagrams of binary mixtures are formed on the basis of data obtained by the optical microscopy and DS calorimetry and the shift of phase transition points of order $30 - 50°$ with respect to initial components was established. In the case of three- and four-component mixtures, we have identified the presence of enantiomorphic phase transitions of smectic and cholesteric type respectively. X-ray diffraction data have enabled the characterization of the structure of smectic or cholesteric mesophase and the calculation of molecular parameters: apparent length of the molecules l and the average intermolecular distance (D).

INTRODUCTION

This work represents the continuation of our studies[1,2] of binary and multicomponent mixtures of cholesteric liquid crystals undertaken with the aim to obtain the systems with stable mesophase phase transitions and transition temperatures close to room temperature. Comparing the results of optical microscopy and differential scanning calorimetry (DSC) we have identified the type and the temperature of the phase transition and outlined the phase diagrams. X-ray diffraction data from

unoriented sample were the basis for extracting the information on the molecular arrangement (conformation and packing) as well as on the temperature dependence of the molecular parameters (average lateral distance D and apparent length of the molecules l). The calculation of short spacing d values and long spacing l values was performed using the modified Bragg law: $Kn\lambda = 2x \sin\theta$, where the constant K was assigned the values 1.117 and 1.229, respectively[3,4,5].

EXPERIMENTAL

Unoriented samples were investigated by the X-ray diffraction in a transmission geometry by means of a conventional powder diffractometer, Seifert V-14, CuK_α radiation at 0.154 nm, with an automatical high temperature kit Paar HTK-10.

DSC measurements were carried out with a Du Pont Instrumental Thermal Analyser 1090 910 DSC Pressure Cell. The calorimeter was calibrated with respect to an empty aluminium pan. Sample weight was 2-5 mg. Spectra registration was carried out in atmospheric pressure in an air atmosphere. The heating rate was $10^o/min$. Indium standards were employed for the enthalpy evaluation.

Optical study was performed using polarization microscope Carl Zeiss (Jena) in the transparent light with special additional facility for the controlled heating and cooling of the sample, Mettler FP 5.

RESULTS AND DISCUSSION

The first step were optical and DSC studies of pure substances: cholesteryl formiate, cholesteryl enanthate and cholesteryl nonanoate, which have shown good agreement with existing literature data[3]. After that we have studied their binary (50% - 50%) mixtures as well as three component mixture of cholesteryl enanthate (72.5%) with cholesteryl formiate (17.5%) and cholesteryl nonanoate (10%). In order to stabilize the mesomorphous phase transition we have added to this three component mixture cholesteryl chloride whose participation in the four component mixture was bellow

10%.

Pure substances of cholesteryl enanthate and cholesteryl formiate posses a monotropic phase transition of smectic and cholesteric type (93.1 and $84°C$) and cholesteric type ($54.1°C$), respectively. Cholesteryl nonanoate forms mesophase of cholesteric type ($70.4°C$) in the heating process, while during the cooling process it forms smectic, S_A phase ($67.2°C$).

Binary mixtures of cholesteryl formiate with cholesteryl enanthate or nonanoate form the mesophase of the cholesteric type stable at room temperature (Fig 1), while the binary mixture of cholesteryl enanthate with cholesteryl nonanoate does not show any significant shift of the phase transition temperature with respect to pure substances. In case of three- and four-component mixtures DSC diagrams show the presence of peaks at $44.6°C$ and $62.6°C$, and $63°C$ respectively, corresponding to the recrystallization of the sample into the solid phase, as confirmed by X-ray diffraction data taken at these temperatures. During the heating process at $95°C$ and during cooling at $83°C$, in the case of three-component mixture, we have identified

TABLE I Temperatures of phase transitions of pure cholesteryl esters and their mixtures (wt.%).

$T_S(°C)$		$T_{Ch}(°C)$		$T_I(°C)$	$T_{Cr}(°C)$
heating	cooling	heating	cooling	heating	cooling
			chol. formiate		
			54.1	95	
			chol. nonanoate		
	67.2	70.4		93.5	
			chol. enanthate		
	84		93.1	114	
		chol. formiate-chol. nonanoate (50-50%)			
		38.6	50.5	53.4	25
		chol. formiate-chol. enanthate (50-50%)			
61	48	72	73	80	32
		chol. enanthate-chol. nonanoate (50-50%)			
		84	90	93	82
	chol. enanthate-chol. formiate-chol. nonanoate (72.5-17.5-10%)				
	79	81	83	107	65
chol. enanthate-chol. formiate-chol. nonanoate-chol. chloride (69-16-7.5-7.5%)					
		79	79	89	47

the formation of the cholesteric blue phase which appears also for four-component mixture at $79°C$ and it is a reversible one. Phase transition temperatures of the substances studied are given in the Table I.

On the basis of these data, we have performed the study with X-ray diffraction method. Figure 2. shows the diffraction profiles of the binary (50% - 50%) mixture of cholesteryl formiate with cholesteryl nonanoate.

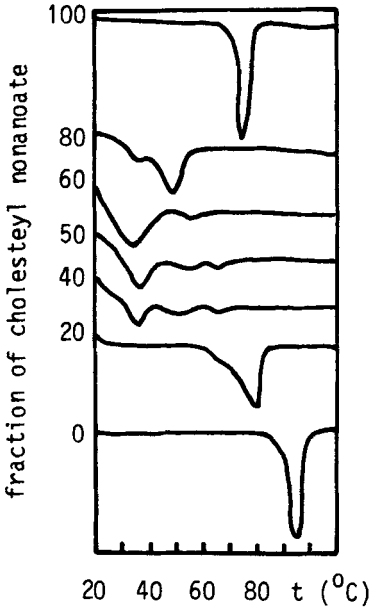

FIGURE 1 DSC curves in heating for cholesteryl nonanoate and cholesteryl formiate separately and in mixture.

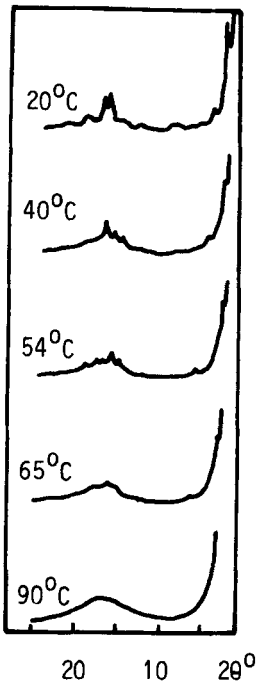

FIGURE 2 X-ray diffraction profiles of binary (50% - 50%) mixtures for cholesteryl formiate and cholesteryl nonanoate.

One can notice that low angle peak ($\theta = 3.5°$) corresponding to long spacing distance l moves towards higher angle values with increasing temperatures. The calculation of l values is performed using the modified Bragg law ($K = 1.229$) for binary and multicomponent mixtures (Tab. II). In the isotropic i.e. cholesteric phase one can

consider that l is approximately equal to the length of the molecule which decreases with temperature increase. In the smectic S_A phase one can consider l to represent the width of smectic layers[4,5]. X-ray diffraction profiles of the studied substances in the cholesteric phase are shown in Figure 3.

X-ray diffraction profiles of binary and multicomponent mixtures in the isotropic phase show the presence of a broad peak appearing in the range $\simeq 15 - 28^o$. The maximum of this diffuse peak for all studied compounds occurs for $2\theta = 17^o$ corresponding to short spacing $d \simeq 5.8\mathring{A}$, as calculated from the modified Bragg law. In the cholesteric and smectic phase it was established the shift of the maximum of the broad peak towards lower angle values. If one assumes that $d \simeq D$ i.e. the lateral interchain distance (or perpendicular distances between molecules) the increase of D values with temperature indicates the decrease of the density of molecular packing (Tab.II).

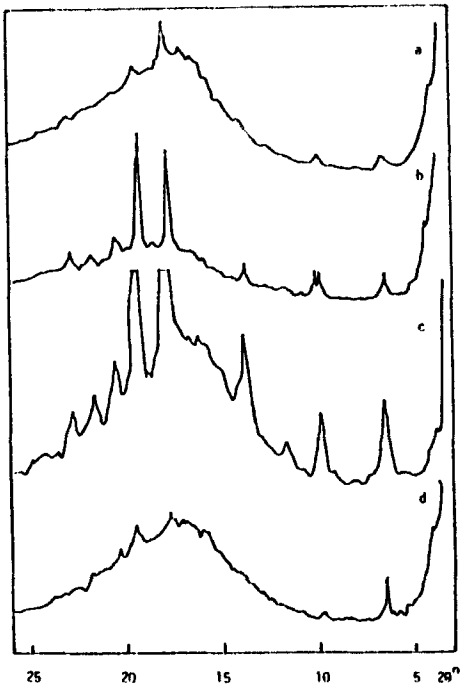

FIGURE 3. X-ray diffraction profiles of binary and multicomponent mixtures in cholesteryl phase. a) chol. enanthate-chol. formiate (50-50%); b) chol. enanthate-chol. nonanoate (50-50%); c) chol. enanthate-chol. formiate-chol.nonanoate (72.5-17.5-10%); d) chol. enanthate-chol. formiate-chol. nonanoate-chol. chloride (69-16-7.5-7.5%).

TABLE II Calculated l and d values of several phases of binary and multicomponent mixtures of cholesteryl esters.

$t(°C)$ heating	$t(°C)$ cooling	$2\theta(°)$	$d(Å)$	$2\theta(°)$	$l(Å)$	*Phase*
chol. enanthate-chol. formiate (50-50%)						
61		18	5.49			chol
67		17.8	5.55	4.05	26.78	chol
71		17.3	5.71	4.1	26.45	smectic
73		17.5	5.65	4.2	25.82	smectic
				3.9	27.81	
80		17	5.81			iso
	61	17.2	5.75	4	27.11	chol
	48	17.3	5.71	4.15	26.13	smectic
	32	17.5	5.65	4.0	27.11	chol
	24	18	5.49			chol
chol. enanthate-chol. nonanoate (50-50%)						
88		19	5.21	3.82	28.4	chol
				4.05	26.78	
91		18.8	5.26	4.1	26.45	chol
98		17	5.81			iso
	94	17.2	5.75	4.05	26.78	chol
				4.01	27.05	
				4.2	25.82	
	84	19	5.21	3.85	28.17	chol
				4.1	26.45	
chol. nonanoate-chol. formiate (50-50%)						
40		16.8	5.88	3.52	30.8	chol
54		16.5	5.99	3.45	31.43	chol
65		16.3	6.06	3.4	31.89	chol
90		16.2	6.10			chol
chol. enanthate-chol. formiate-chol. nonanoate (72.5-17.5-10%)						
81		18.8	5.26	4.0	27.11	chol
94		18	5.49	4.0	27.11	chol
101		17.5	5.65	3.9	27.81	chol
107		17	5.81			iso
	79	18	5.49	4.1	26.45	smectic
	67	17.8	5.55	4.05	26.78	smectic
chol. enanthate-chol. formiate-chol. nonanoate-chol. chloride (69-16-7.5-7.5%)						
87		18	5.49	4.45	24.3	chol
93		16.8	5.88			iso
	78	17.3	5.71	4.1	26.45	chol
	74	17.5	5.65	4.1	26.45	chol
	57	18	5.49	4.0	27.11	chol+cryst.

CONCLUSION

The results of the study of binary and multicomponent mixtures of cholesteryl liquid crystals have shown that the maximal shift of temperature of mesomorphous phase transition ($Cr \longrightarrow Ch$) is achieved for binary (50% - 50%) mixtures of cholesteryl formiate with cholesteryl nonanoate or enanthate. The studies of the binary (50% - 50%) mixture of cholesteryl enanthate with cholesteryl nonanoate do not show any significant shift of the phase transition temperature so we were not able to obtain the expected stability of mesomorphous phase transition at room temperature as in our previous studies [1,2] for three- and four-component mixtures. X-ray diffraction data have enabled the calculation of molecular parameters l and D. Their temperature dependence was established which agrees with literature data for similar systems.

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