

SOME THERMODYNAMIC INDICES DETERMINATION IN INDUCED
CHOLESTERIC LIQUID CRYSTALS

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ABSTRACT

Some thermodynamic parameters (phase transition temperatures, entropy and enthalpy changes) of liquid crystal systems (nematic liquid crystal-440 and optically active substances mixture) were studied. Two types of optically active additives were established: I type additives concentration increase results in monotonous decrease of ΔH and ΔS , while the maximum was observed with II type additives.

As for influence on temperature of transition to isotropic phase, here also two types of active additives were observed: mesogenous active additives have no effect on this temperature, while nonmesogenous ones contribute to its decrease.

Optically active substances are known to induce cholesteric structures in nematic liquid crystals (LC), these structures resulting from optically active substances (OAS) and LC molecular interaction [1]. It is the possibility to use them in information displaying devices that arouses interest in these systems. Phase transition thermodynamics study in such systems can provide a valuable information on liquid phase (mesophase) energetics, molecular degree of order and thermostability.

The present paper determines some thermodynamic indices (phase transitions temperature, entropy, and enthalpy changes) for nematic liquid crystals (alkoxyazoxy compounds/LC-440 mixture) - optically active substances (cholesterol ester of pelargonic acid, cholesterol chloride, tigogenincaprylate, L-menthyl-p-nitrobenzoate, di-L-menthyl-oxalate, L-menthyl-p-chlorobenzoate, p-nonyloxybenzylidene-p-amino-L-menthol benzoate) system. These compounds were synthesized by us.

Phase transitions thermodynamic indices both for basic substances and for LC-440 mixtures with the aforesaid OAS additives were studied using F. Paulic, I. Paulic, L. Erdei derivatograph, the device for thermogravimetric analysis. The studies were conducted under heating and cooling conditions at $0.5^{\circ}\text{C}/\text{min}$ temperature

increment and decrement respectively.

Two of OAS studied, cholesterol ester of pelargonic acid and cholesterol chloride, are mesogenous, i.e., capable to provide liquid crystal phase. Thermogravimetric analysis of cholesterol ester of pelargonic acid within 20-150°C temperature range indicated that (see Fig. 1a) two minima (80° and 90°C) and three maxima (85°, 70°, and 46°C) are formed at heating and cooling respectively, thus testifying to the various degrees of order in the structure of the given ester. It is in good correlation with literature data [2]. The first minimum on a heating thermogram corresponds to solid crystal → liquid crystal fusion (SC → LC) and the second one - to passing to isotropic liquid state (clearing point). In the case of cooling, however, the first, second and third maxima correspond to the appearance of specimen smectic liquid crystal phase, cholesteric and crystallization phases respectively. Fusion and clearing points are known to determine the temperature interval within which the mesophase is stable. For the given substance the mesophase existence at heating is determined by 10°C (90°-80°C) interval, while at cooling temperature range for mesophase existence is considerably wider -39°C (85°-46°C).

The attempt to find the characteristic clearing point within the same temperature range at cholesterol chloride heating proved to be unsuccessful (see Fig. 1b), while at cooling mesophase onset is observed at 65°C, its range being determined by temperature interval of 5°C (65°-60°C). Basic LC-440 mixture is fusing at the temperature lower than ambient. Therefore, phase transition from SC to LC state was not recorded by our device. Heating thermogram for this substance (see Fig. 1b) has one minimum (71°C) within the temperature range of 20-120°C which corresponds to LC transition to isotropic liquid state (IL) while at cooling mesophase onset is observed at temperature 60°C.

LC-440 mixtures with abovementioned OAS 1.5-12% additives were studied. These mixtures proved to be resistant to repeated thermal effects within 20-120°C temperature interval. This conclusion follows from gravimetric analysis (no sample weight variations and phase transition temperatures and heat reproducibility). Since fusing temperatures for the mixtures under study is lower than ambient, liquid crystal to isotropic liquid state transition was studied at heating, while mesophase onset - at cooling.

At heating and cooling all mixtures investigated have one minimum and one maximum on $\Delta T-T$ curves respectively.

In these mixtures (and similarly in basic mesogenous OAS) phase change temperatures at heating and cooling are not reproduced due to system metastability.

Two cases (see the table) were observed depending on the type of OAS concentration effect on clearing temperature (T_c): concentration increase in mesophase having OAS mixture almost doesn't influence initial LC-440 clearing temperature, whereas all OAS studied lacking the mesophase, decrease temperature of clearing; e.g. 3% L-menthyl-p-chlorobenzoate addition lowers clearing temperature on 10°C .

Two types of admixtures concentration effects on T_c in binary mixtures were previously reported in literature [3].

It should be noted, that the temperature interval of transition to isotropic state for pure LC-440 is less than 1°C , somewhat increasing in mixtures ($2-3^\circ\text{C}$).

Enthalpy and entropy difference changes (ΔH and ΔS respectively) under the effect of added OAS concentration were studied.

Fig. 2 shows ΔH -%OAS curves at heating. Obviously one can differentiate between two types of active components: I type components concentration increase leads to monotonic decrease of enthalpy difference (curves 1, 2, 3, 4). They differ considerably from each other in effect intensity. Thus, addition of 1.5% L-menthyl-p-nitrobenzoate decreases ΔH more than two times, while that of p-nonyloxybenzylidene -p-amino-L-mentholbenzoate leads to similar ΔH decrease at 6%.

Curves 5, 6, 7 are indicative of the II type OAS. They are characterized by a certain initial maximum, whereas even further significant OAS concentration increase (curves 6 and 7) has a little if any effect on ΔH .

Entropy changes data are listed in the table. At OAS concentration increase S tends to change in the way typical for ΔH change.

The existence of two types of OAS effects on ΔH and ΔS seems to be related to these substances structures and chemical nature.

REFERENCES

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3. V.De Jeye, Physical Features of Liquid Crystal Substances, Moscow, Mir, 1982.

№	MIXTURES UNDER STUDY	MIXTURE COMPOSITION, %	t° C		ΔH		ΔS 10 ³	
			Heating	cooling	Heating	Heating		
	LC - 440	100	71	66	0,1048	0,300		
1	<chem>Cc1ccc(cc1)C2=CC=CC=C2</chem> L-menthyl-p-nitrobenzoate	1,5	71	62	0,0386	0,11		
		3	68	59	0,0734	0,10		
		6	62		0,0273	0,08		
2	<chem>Cc1ccc(cc1)C2=CC=CC=C2</chem> L-menthyl-p-chlorobenzoate	1,5	68		0,0583	0,17		
		3	61		0,0548	0,16		
		6	54		0,0166	0,051		
3	<chem>Cc1ccc(cc1)C2=CC=CC=C2</chem> p-nonyloxybenzylidene-p-amino-L-menthol benzoate	1,5	69	66	0,0015	0,10		
		3	61	66	0,0060	0,17		
		6	60	65	0,0041	0,16		
		8	60	63	0,0013	0,1		
		12	68	65	0,0277	0,08		
4	<chem>Cc1ccc(cc1)C2=CC=CC=C2</chem> Di-L-menthyl oxalate	1,5	69		0,0688	0,2		
		3	67,5		0,0599	0,18		
		6	66,5		0,0548	0,16		
		8	65,5		0,0301	0,065		
5	<chem>Cc1ccc(cc1)C2=CC=CC=C2</chem> Tigogeninacprinate	1	69,5		0,1115	0,326		
		2	69,5		0,1125	0,318		
		3	63,5		0,1109	0,307		
		6	69,5		0,1006	0,29		
		8	68,5		0,0959	0,28		
		10	68,5		0,0675	0,206		
6	<chem>Cc1ccc(cc1)C2=CC=CC=C2</chem> cholesterol ester of pelargonic acid	1,5	72	68	0,1206	0,349		
		3	72	68	0,1198	0,348		
		6	72	68	0,1200	0,349		
		8	71,5	65	0,1215	0,352		
		10	71,5	65	0,0888	0,26		
		12	71,5	65	0,0811	0,24		
7	<chem>Cc1ccc(cc1)C2=CC=CC=C2</chem> cholesterol chloride	1,5	71,5	67	0,1055	0,306		
		3	71	67	0,1083	0,306		
		4	71	67	0,098	0,285		
		8	71	68	0,0801	0,233		
		10	71	68	0,083	0,241		
		12	71	68	0,086	0,23		

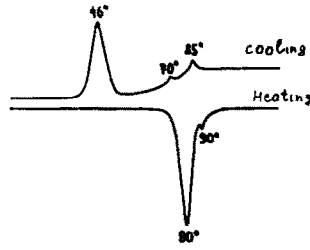


Fig.1a

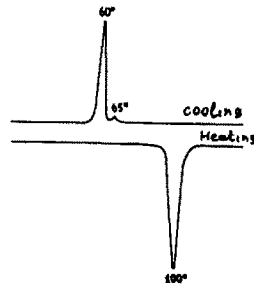


Fig.1b

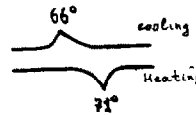


Fig.1c

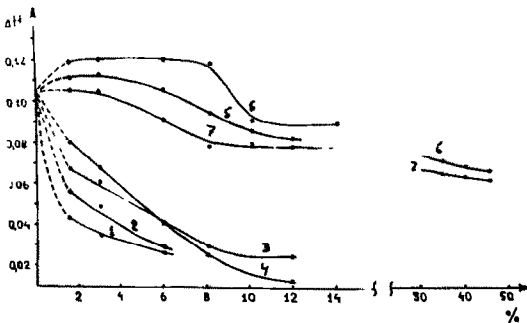


Fig.2