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THERMODYNAMIC CHARACTERIZATION OF BINARY LIQUID CRYSTAL MIXTURES

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abstract: The binary mixture of cholesteryl p-phenoxiphenil carbonate and cholesteryl *p*-phenoxiphenil tiocarbonate with different ratios has been characterized by differential scanning calorimetry (DSC) to determine the phase diagrams. A simple eutectic for this system was observed. The excess functions have been calculated by utilizing the computed activity coefficient data of the eutectic phase.

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Introduction

A lot of interest in liquid crystals came from their technological applications. One of the main properties of liquid crystals is their thermal stability and its knowledge is important because the upper limits of their applications may be governed by it.

Liquid crystal materials used in the display industry are usually multi-component eutectic mixtures. In view of the thermodynamic considerations, eutectic may be defined as the heterogeneous system consisting of two or more solidus phases which are in equilibrium with a single liquidus phase and for this correspond the lowest liquidus temperature in the binary solidus-liquidus diagram of state [1]. The eutectic phase cannot be chosen arbitrarily. Eutectic mixtures exhibit single step melting; whereas, non-eutectic mixtures exhibit two stage melting.

The present work is devoted to the thermodynamic characterization of cholesteryl *p*-phenoxiphenil carbonate, cholesteryl *p*-phenoxiphenil tiocarbonate and their binary mixtures.

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Experimental Section

Materials: Cholesteryl *p*-phenoxiphenil carbonate and cholesteryl *p*-phenoxiphenil tiocarbonate were obtained in organic chemistry laboratory at University of Pitesti and has been characterized spectral (IR, NMR) and thin-layer chromatography [2,3].

Sample preparation: Different ratios of both components were dissolved in acetone, mixed well and naturally evaporated for 24h.

Thermal analysis: Thermal properties of the sample were realised by differential scanning calorimetry (DSC Perkin Elmer) under a heating rate of 10 K/min over a temperature range (323–450) K. The apparatus was calibrated for temperature and enthalpy by melting high purity indium. The instrument was flushed with argon. Sample of 2 to 4 mg were transferred into aluminium crucibles which were sealed and weighted with the Partner XA balance with a precision of 10μg.

Results and discussions

The phase diagram of binary mixture obtained from measured DSC curves is shown in Fig. 1. The onset temperature at each first peak almost show constant value for the simple eutectic system and was taken as eutectic temperature. Since the onset temperature for the liquidus transition is difficult to be determined due to superimposed effect of the DSC curves, many authors [4,5] report the liquidus temperature as the peak temperature in the liquidus transition.

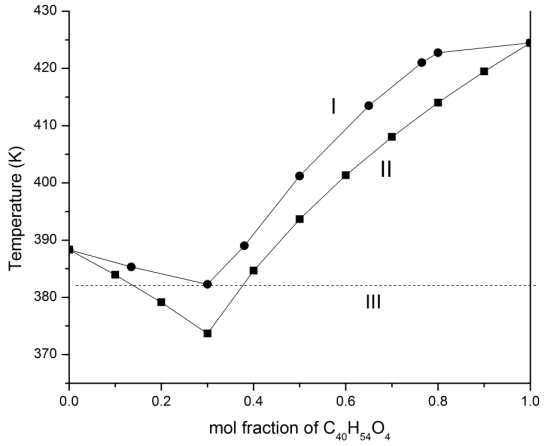
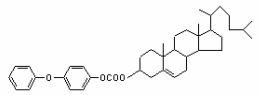
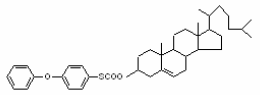


Fig. 1 *SLE phase diagram for studied system.*
I - liquidus curve; II – ideal curve; III – solidus temperature curve

The melting point of cholesteryl *p*-phenoxiphenil carbonate is 424.46 K and its decreases with addition of cholesteryl *p*-phenoxiphenil tiocarbonate and attains the minimum at 382.25 K when the mixture has 0.3 mole fraction of it.

The thermal properties of pure compounds obtained from DSC data are presented in Table 1.

Table 1 Chemical structures, melting points and heat of fusion for pure compounds

Compounds	Structure	Molecular weight (g/mol)	T_f (K)	$\Delta^f H$ (kJ/mol)
Cholesteryl p-phenoxiphenil carbonate $C_{40}H_{54}O_4$		598.67	424.46	31.253
Cholesteryl p-phenoxiphenil tiocarbonate $C_{40}H_{54}O_3S$		614.67	388.33	29.703

The enthalpy of mixing for binary mixture is given by equation:

$$\Delta^M H = \left(\Delta^f H\right)_{\text{exp}} - \sum_i \left(x_i \Delta^f H_i^o\right) \tag{1}$$

where $\left(\Delta^f H\right)_{\text{exp}}$ is the experimental value of enthalpy of fusion, x_i and $\Delta^f H_i^0$ are mole fraction and enthalpy of fusion of the component *i*.

The structure of binary mixtures depends on the sign and magnitude of enthalpy of mixing, therefore three types of structures are suggested [6]: quasieutectic for which $\Delta^M H > 0$; clustering of molecules in which $\Delta^M H < 0$, and molecular solutions, for which $\Delta^M H = 0$. The negative value of $\Delta^M H = -1.893$ kJ/mol, for the studied system suggest that there is clustering of molecules in the binary eutectic melt.

In order to know the nature of interactions between components forming eutectic, the excess free energy, G^E, and excess entropy, S^E, were calculated using the following equations [7]:

$$G^E = RT\left[x_1^l \ln \gamma_1^l + x_2^l \ln \gamma_2^l\right] \tag{2}$$

$$S^E = -R\left[x_1^l \ln \gamma_1^l + x_2^l \ln \gamma_2^l + x_1^l T\left(\frac{\partial \ln \gamma_1^l}{\partial T}\right)_P + x_2^l T\left(\frac{\partial \ln \gamma_2^l}{\partial T}\right)_P\right] \tag{3}$$

The activity coefficient of a component *i* present in the eutectic melt is given by:

$$-\ln x_i^l \gamma_i^l = \frac{\Delta^f H_i^0}{R}\left[\frac{1}{T} - \frac{1}{T_i^0}\right] \tag{4}$$

where x_i^l, γ_i^l, $\Delta^f H_i^0$ and T_i^0 are the mole fraction, activity coefficient, heat of fusion and the melting temperature of the component *i*, *R* is the gas constant and *T* is the liquidus temperature.

The values of excess free energy and excess entropy are graphically drawn in Fig. 2.

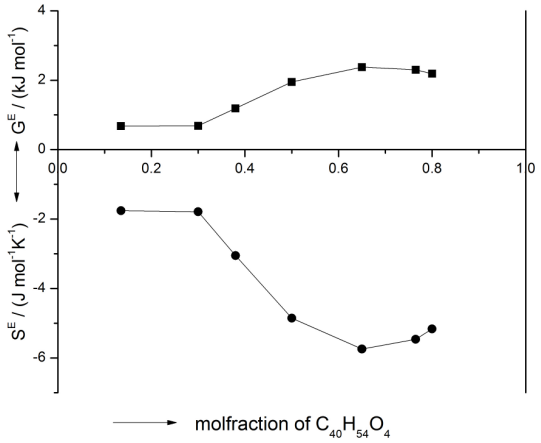


Fig. 2 *Excess functions G^E and S^E for cholesteryl p-phenoxiphenil carbonate + cholesteryl p-phenoxiphenil tiocarbonate system*

The positive value of excess free energy, G^E, suggests [8] that there is weak interaction among the components forming the eutectic melt, and strong association between like molecules.

Conclusions

The negative value of the enthalpy of mixing for the studied system, suggest that there is clustering of molecules in the binary eutectic melt.

The cholesteryl *p*-phenoxiphenil carbonate + cholesteryl *p*-phenoxiphenil tiocarbonate system is endothermic in nature, since G^E is positive and S^E is negative, indicating positive deviations of the system from its ideal behaviour.

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