

Thermal analysis of binary liquid crystals eutectic system cholesterol *p*-phenoxi phenyl carbamate–cholesterol *p*-biphenyl carbamate

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Abstract For a binary mixture of two liquid crystals, cholesterol *p*-phenoxi phenyl carbamate and cholesterol *p*-biphenyl carbamate, the solidus–liquidus equilibrium was investigated using differential scanning calorimetry (DSC) and the thermodynamic parameters were obtained. Simple eutectic point was observed for this system, situated approximately at the same temperature for all the studied compositions. This behavior is favored by grinding and is more evident in the composition 50:50. The excess functions G^E and S^E for the pre-, post-, and eutectic composition have been calculated using the phase diagram data. Comparing the experimental data with the existing theoretical data, the system deviation from the ideal behavior is observed. The structure of pure compounds was elucidated using FT-IR and hot-stage polarizing microscopy.

Keywords Liquid crystals · DSC · Phase diagram · Eutectic

Introduction

Cholesteric liquid crystals have many applications in advanced technologies such as direct measuring the temperature, displays, surface thermography and detection of atmosphere contamination, skin thermography, and cancer diagnosis.

To obtain mixtures with properties targeted for a specific application is necessary to characterize the pure liquid

crystal phase but is also important the characterization of mixtures of different molar fractions. For an adequate characterization of thermotropic liquid crystals, the thermal study is essential in general and differential scanning calorimetry and hot-stage polarizing microscopy in particular.

In these cases, although the measurement of solidus–liquidus equilibrium is very important, there is a little accumulation of these data, and the decisive measurement method is not established yet [1, 2].

Thermodynamic analysis of solidus–liquidus equilibrium data can yield important thermodynamic functions of binary mixtures in condensed phase [3–5].

In this paper, we present aspects regarding phase diagram, thermochemistry, and structure of binary mixtures of cholesterol *p*-phenoxi phenyl carbamate and cholesterol *p*-biphenyl carbamate.

Experimental

The substances under study were synthesized in the organic chemistry laboratory of University of Pitesti, were characterized from structural point of view, and kept in proper conditions [6, 7].

Mixtures of known concentration were prepared by weighing, grinding, and homogenized in normal laboratory conditions, room temperature, and atmospheric pressure.

The melting temperature and enthalpy of fusion of eutectic phases were determined by differential scanning calorimetry (Diamond DSC Perkin Elmer) under a heating/cooling rate of $10\text{ }^\circ\text{ min}^{-1}$ over a temperature range of (293.15–473.15) K in inert atmosphere (helium, 30 ml min^{-1} flow). At least three replicates of each measurement (pure compounds and mixtures) have been performed.

The apparatus was calibrated for temperature and enthalpy by melting high purity indium. Samples of

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2–4 mg were transferred into aluminum crucibles that were sealed and weighed with the Partner XA balance with a precision of 10 μg .

The FT-IR spectra were obtained using a Vertex 70-Bruker spectrophotometer with the following parameters: resolution 4 cm^{-1} ; spectral range (4,000–400) cm^{-1} ; beam splitter, KBr. Each sample has been dispersed in about 300 mg of anhydrous KBr, and the resulting powder was ground in an agate mortar.

The microstructure of pure compounds was recorded using a hot-stage polarizing microscope (Nikon 50i Pol microscope with a Linkam THMS 600 hot stage and a TMS 94 temperature controller) with a heating–cooling rate of 10 $^{\circ}\text{min}^{-1}$ over a temperature range of (293.15–473.15) K in normal laboratory conditions at atmospheric pressure, and interesting regions were photographed.

Results

Pure compounds

The thermal properties and structure of pure compounds are obtained from DSC data and are presented in Table 1 and Fig. 1, respectively.

The DSC diagram for compound **1** (heating stage, Fig. 7) shows that the melting point of this compound is 430.15 K, and in the cooling stage, there is no measurable effect, although by polarized light hot-stage microscopy can be seen the start of crystallization process at 343.15 K (Fig. 2).

The crystallization process was not observed in the DSC curve because this process takes place on a large domain of temperature and the thermal effect cannot be quantified.

In order to establish whether heating of compounds **1** and **2** involves structural changes [8], the FT-IR spectra were registered in both cases, before and after heating up to 473.15 K (Figs. 3, 4).

Before the thermal treatment, the characteristic vibration bands observed for compound **1** are $\nu_{\text{NH}} = 3,408 \text{ cm}^{-1}$, $\nu_{\text{C-O (sim)}} = 1,053 \text{ cm}^{-1}$, $\nu_{\text{C-O (asim)}} = 1,211 \text{ cm}^{-1}$, and $\nu_{\text{C=O}} = 1,737 \text{ cm}^{-1}$. The FT-IR spectrum obtained after heating–cooling cycle (straight line) shows disappearance of characteristic vibration band for secondary amine group, which indicates structural changes for compound **1**.

The DSC study for compound **2** (heating stage, Fig. 7) showed that the melting point of this compound is 446.43 K and presents an endothermic peak at 464.15 K, little revealed, with no measurable effect, that represents the transition of the liquid crystal to mesophase S_A , as also shown by polarized light hot-stage microscopy (Fig. 5).

In the DSC cooling curve of compound **2** can be seen an exothermic peak at 340.04 K, process that takes place on a temperature range of approximated 20 $^{\circ}$ and that suggests a slow crystallization process with a thermal effect of -10 kJ mol^{-1} .

The hot-stage polarizing microscopy experiment showed that, in the cooling stage, this compound crystallizes from mesophase S_A at 445.15 K, cooling stage (Fig. 6), process unnoticeable in the DSC curve due to the low thermal effect.

The characteristic vibration bands observed for compound **2**, before the thermal treatment, are $\nu_{\text{C-O(sim)}} = 1,055 \text{ cm}^{-1}$, $\nu_{\text{C-O(asim)}} = 1,266 \text{ cm}^{-1}$, $\nu_{\text{C=O}} = 1,759 \text{ cm}^{-1}$, and $\nu_{\text{C-O}} = 1,254 \text{ cm}^{-1}$. After the thermal treatment, the carboxyl group undergoes structural changes and in the spectrum (straight line) is observed a band for the hydroxyl group connected by hydrogen bonds ($3,300 \text{ cm}^{-1}$).

Binary mixture

Phase diagram

The DSC curves obtained for different compositions for compound **1** (cholesteril *p*-phenoxi phenyl carbamate) and compound **2** (cholesteril *p*-biphenyl carbamate) mixtures are shown in Fig. 7 and were registered using the temperature range (293.15–473.15) K and a heating–cooling rate of 10 $^{\circ}\text{min}^{-1}$. The onset temperature at each first peak almost shows constant value for the simple eutectic system. The eutectic temperature was taken as the onset temperature at the solidus transition, as was applied by most researchers [4, 9].

Since the onset temperature for the liquidus transition is difficult to be determined due to the superposition effect of the DSC curves, many authors [10, 11] report the liquidus temperature as the peak temperature in liquidus transition.

The mixing process is regarded as the ideal solution model, and the transition temperature of mixture is always lower than that of any of the pure compounds.

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

Denomination	Chemical formulae	Molecular mass/g mol ⁻¹	mp/K	$\Delta_{\text{fus}}H/\text{kJ mol}^{-1}$
Cholesteril <i>p</i> -phenoxi phenyl carbamate (compound 1)	C ₄₀ H ₅₃ NO ₃	597	431.94 ± 0.92	32.632 ± 0.588
Cholesteril <i>p</i> -biphenyl carbamate (compound 2)	C ₄₀ H ₅₂ O ₃	582	445.54 ± 0.82	26.982 ± 0.477

Fig. 1 Structural formulae for cholesterol *p*-phenoxy phenyl carbamate (A-compound 1) and cholesterol *p*-biphenyl carbamate (B-compound 2)

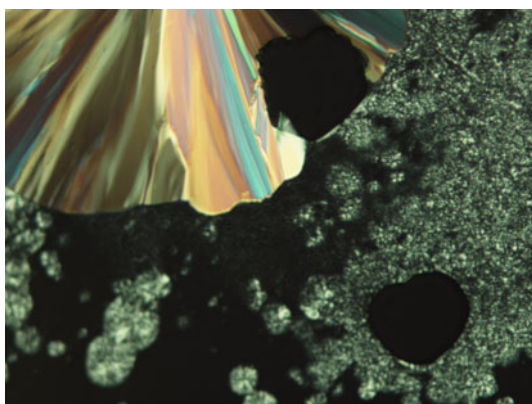
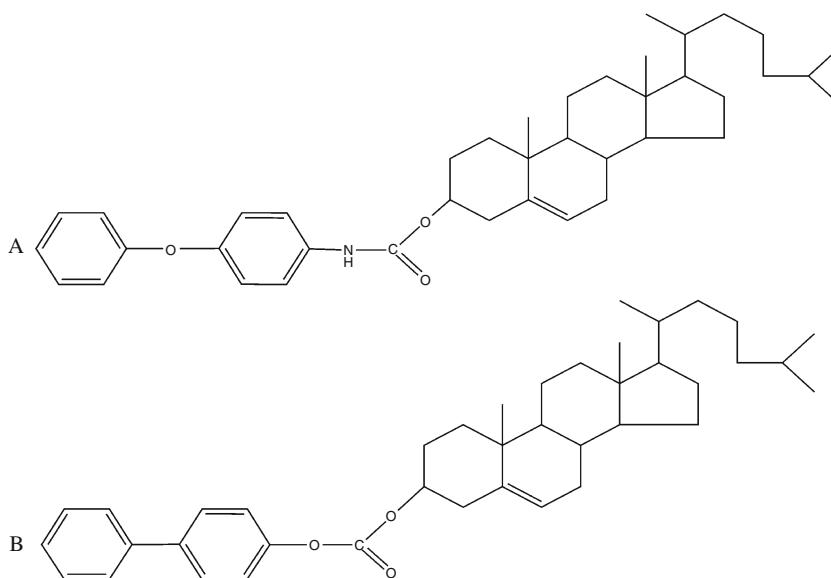


Fig. 2 Crystallization of compound 1 at 343.15 K

The eutectic transition temperature, for the binary mixture, can be calculated according to Schroder van Laar equation:

$$\ln x_i = -\frac{\Delta_{\text{fus}}H_i^0}{R} \left[\frac{1}{T} - \frac{1}{T_i^0} \right]$$

where x_i is the mole fraction of the components at the temperature T , R the gas constant, $\Delta_{\text{fus}}H_i^0$ the molar enthalpy of fusion of component i ($i = 1, 2$), and T_i^0 is the melting temperature of the pure component.

The phase diagram obtained from measured DSC curves is shown in Fig. 8 as temperature–composition plot.

The melting point of compound 2 is 446.43 K, and it decreases with addition of compound 1 and attains the minimum at 407.01 K at 0.5 mol fraction.

The phase diagram shows the deviation from the ideal behavior for the studied system for a mole fraction between 0 and 0.85 of compound 1 and for mole fraction higher than 0.85 the system inclines to ideal behavior.

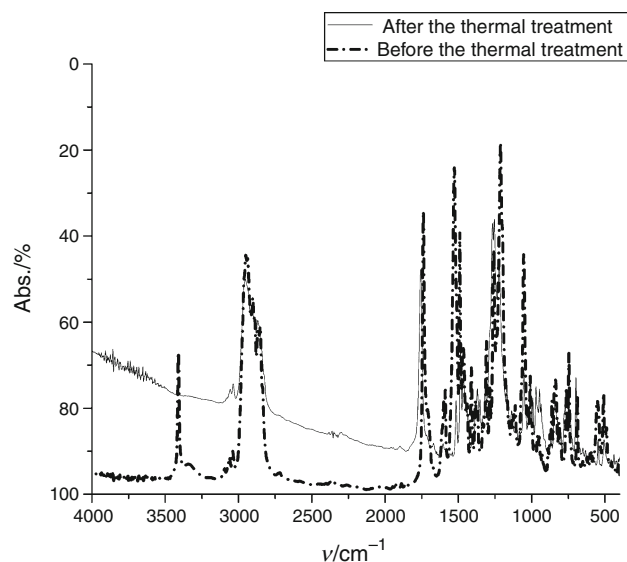


Fig. 3 FT-IR spectra for compound 1 (dash dot short dash line—before the thermal treatment, straight line—after heating to 473.15 K and cooling to room temperature)

Thermochemistry

If the eutectic mixture results from a simple mechanical mixture (no solvent) of two components not involving any type of association in the melt, the molar enthalpy of fusion can simply be calculated by the mixture law [12]:

$$(\Delta_{\text{fus}}H^0)_{\text{calc}} = x_1 \Delta_{\text{fus}}H_1^0 + x_2 \Delta_{\text{fus}}H_2^0$$

where x_i and $\Delta_{\text{fus}}H_i^0$ are the mole fraction and enthalpy of fusion of the component indicated by subscript, respectively.

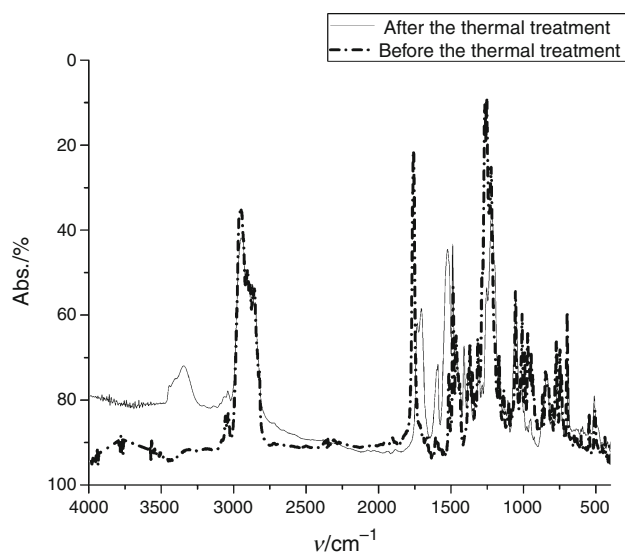


Fig. 4 FT-IR spectra for compound 2 (dash dot short dot line—before the thermal treatment, straight line—after heating to 473.15 K and cooling to room temperature)

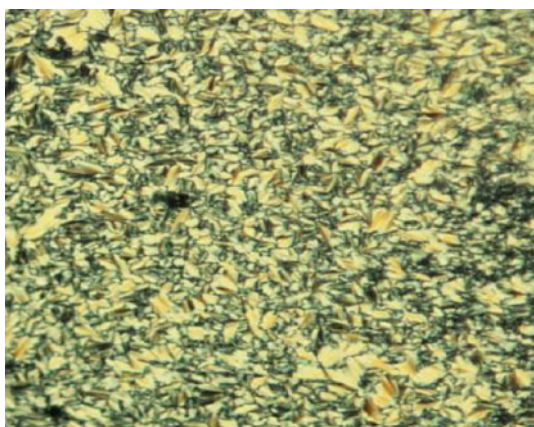


Fig. 5 Mesophase S_A of compound 2—464.15 K

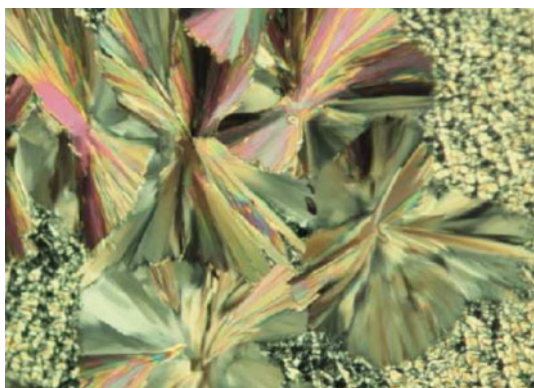


Fig. 6 Crystallization from mesophase S_A —445.15 K (compound 2)

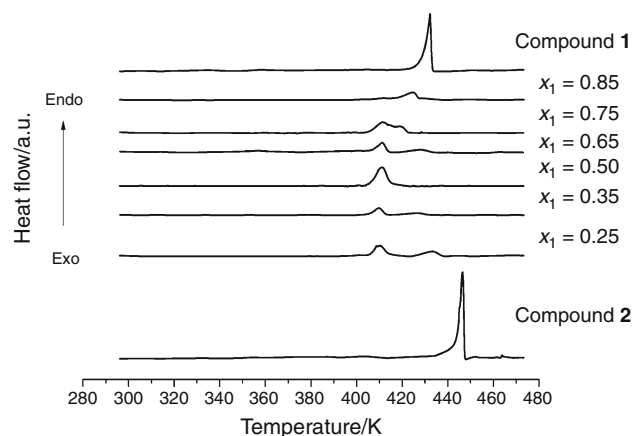


Fig. 7 DSC curves for cholesterol *p*-phenoxi phenyl carbamate and cholesterol *p*-biphenyl carbamate and their binary mixtures with variable composition

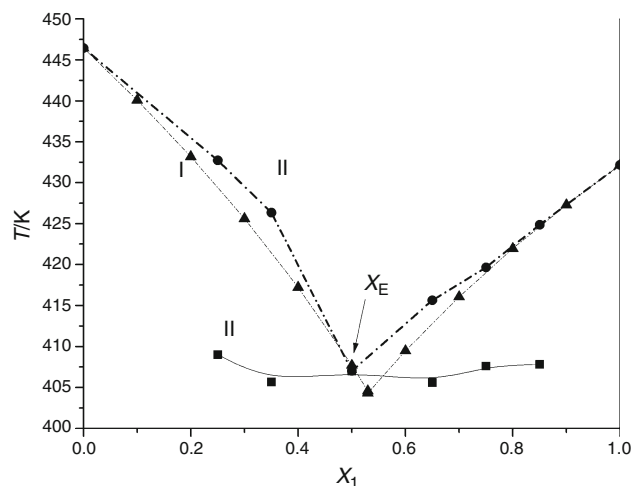


Fig. 8 Diagram of state for cholesterol *p*-phenoxi phenyl carbamate—cholesterol *p*-biphenyl carbamate system: *I* ideal temperatures curve, *II* liquidus temperatures curve and solidus temperatures curve—Eutectic composition, X_E

The characterization of eutectic melt is obtained using the value of mixing enthalpy, given by the following equation [13]:

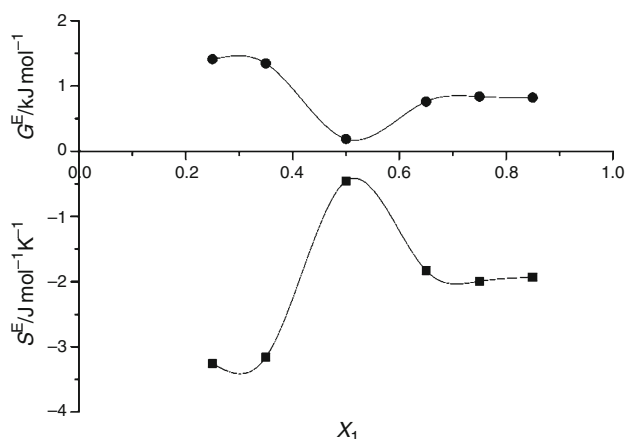
$$\Delta^M H = (\Delta_{\text{fus}} H^0)_{\text{exp}} - (\Delta_{\text{fus}} H^0)_{\text{calc}}$$

where $(\Delta_{\text{fus}} H^0)_{\text{exp}}$ represent the molar enthalpy of fusion determined from DSC experiments; $(\Delta_{\text{fus}} H^0)_{\text{calc}}$ represent the corresponding calculated value.

Thermochemical studies [12, 14, 15] suggest that the structure of the eutectic melt depends on the sign and magnitude of mixing enthalpy. There by three types of structure are suggested: quasi eutectic for which $\Delta^M H > 0$, clustering of molecules with $\Delta^M H < 0$, and molecular solutions with $\Delta^M H = 0$. The negative value of mixing enthalpy $\Delta^M H = -12.6 \text{ kJ mol}^{-1}$ for the binary mixture

Table 2 Activity coefficients and excess thermodynamic functions for the binary mixtures

x_1 (mole fraction)	Liquidus temperature/K	$\ln\gamma_1$	$\ln\gamma_2$	$G^E/\text{J mol}^{-1}$	$S^E/\text{J mol}^{-1}\text{K}^{-1}$
0.25	432.72	1.3979	0.0565	1409.90	-3.26
0.35	426.35	0.9238	0.0871	1346.78	-3.16
0.50	407.01	0.1234	-0.0136	185.78	-0.46
0.65	415.65	0.0644	0.5094	760.71	-1.83
0.75	419.66	0.0128	0.9208	836.67	-1.99
0.85	424.87	0.0041	1.5268	821.24	-1.93

**Fig. 9** Variation of excess functions with mole fraction composition for cholesterol *p*-phenoxy phenyl carbamate and cholesterol *p*-biphenyl carbamate system

suggests that in the binary eutectic melt clustering of molecules takes place. Therefore, the heat released during clustering of molecules leads to a decrease in mixing enthalpy for the real eutectic mixture. The combination of molecules through weak interactions supports the formation of clusters in the melt.

The deviation from ideal behavior can best be explained in terms of excess thermodynamic functions [16, 17]. These functions give more quantitative idea about the nature of molecular interactions and are expressed like difference between the thermodynamic functions of mixing for a real system at the same temperature and pressure [18].

In order to know the nature of interaction between the components forming the eutectic melt, the excess thermodynamic functions G^E and S^E of pre-, post-, and eutectic phase composition at the same liquidus temperature, T , at constant pressure, have been computed by using the following relations [19, 20]:

$$G^E = RT [x_1 \ln \gamma_1^I + x_2 \ln \gamma_2^I]$$

$$S^E = -R [x_1 \ln \gamma_1^I + x_2 \ln \gamma_2^I] - RT \left[x_1 \frac{\partial \ln \gamma_1^I}{\partial T} + x_2 \frac{\partial \ln \gamma_2^I}{\partial T} \right]$$

The values of activity coefficients and excess thermodynamic functions are showed in Table 2 and Fig. 9.

An insight analysis of the plot (Fig. 9) for excess thermodynamic functions indicates that the excess free energy of mixing, G^E , decreases on either side of the phase equilibrium curves and acquires minimal values at the eutectic composition, which is expected, since eutectic being the lowest liquidus temperature reached by the gradual addition of an eutectic phase into the other [13, 14].

This type of behavior is in accordance with the criteria of spontaneity according to which the mixing of eutectic phases of the system will progress only if every infinitesimal change in the composition is accompanied by a decrease in the Gibbs free energy. On the contrary, the excess entropy of mixing, S^E , shows a maximal value at the eutectic composition because the most probable distribution of the eutectic phase molecules occurs in a eutectic phase because of the coexistence of three phases: two solidus phases and a liquid phase in equilibrium at the eutectic liquidus temperature in the condensed phase.

Also, the excess Gibbs free energy, G^E , is positive on the whole range of composition, suggesting that there are weak interaction between the components forming the eutectic melt and strong interaction between similar components.

Conclusions

A few analytical and calculation methods were applied for the study of the binary mixture containing new cholesterol liquid crystals. The DSC measurements were taken for the pre-, post-, and eutectic composition. For the pure compounds, the FT-IR spectra were registered, before and after the thermal treatment, and the experiment indicates that the structure of these two compounds undergoes changes during the heating-cooling treatment. The hot-stage polarizing microscopy was carried out for the pure compounds on the same temperature range used for DSC.

Our results showed that no phase transition occurs for compound **1** although its structure is suitable for a liquid crystal behavior, but for compound **2**, mesophase S_A is observed. The DSC measurements indicate a simple eutectic point for the mixture, and this makes the binary

mixture suitable for different applications. Comparing the experimental phase diagram and the ideal phase diagram, the system deviation from the ideal behavior is observed, and for mole fraction higher than 0.85 of compound **1**, the system inclines to ideal behavior.

The negative value of mixing enthalpy for the cholesterol *p*-phenoxi phenyl carbamate and cholesterol *p*-biphenyl carbamate system suggests that in the binary eutectic melt, clustering of molecules takes place.

Since G^E is positive and S^E has negative values, the studied system is endothermic in nature with positive deviations from ideal behavior.

Considering the fact that liquid crystal applications are in general mixtures of at least two compounds, further studies will be necessary.

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