

Investigation of the Phase Transition and Absorption Properties of Liquid Crystal Hexylcyanobiphenyl/Octylcyanobiphenyl Mixtures

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The hexylcyanobiphenyl (6CB) and octylcyanobiphenyl (8CB) mixtures have been investigated by means of differential scanning calorimeter and ultraviolet. Differential scanning calorimeter results indicate clearly the existence of four phase transitions in the 6CB/8CB mixtures. The phase diagram of mixture was obtained from differential scanning calorimeter and theoretical calculations. The experimental phase diagram is approximately similar to the calculated phase diagram. The phase transition temperatures of the 6CB/8CB mixtures rise with the heating rate between 2 °C/min and 10 °C/min. The activation energies were calculated for the phase transitions of 50 % 6CB and 50 % 8CB liquid crystal mixtures. UV experiments were carried out to characterize the absorptivity constants of liquid crystal and their mixtures. The molar absorptivity and maximum absorption wavelengths were measured in chloroform solution by UV spectrophotometry. The maximum absorption wavelength of the 6CB/8CB mixtures increases with decreasing percent weight of 8CB in 6CB, a result associated with the different lengths of the alkyl chain.

Key Words: Liquid crystal mixtures, Thermodynamic properties, Optical properties, Hexylcyanobiphenyl, Octylcyanobiphenyl.

INTRODUCTION

Liquid crystals (LCs) are substances that have properties between conventional liquid and solid crystal^{1,2}. The existence of liquid crystals has been known for more than a century. But in recent years, liquid crystal mixtures are of interest as novel materials for display applications ranging from flat panel displays to laser beam steering and optical switching³⁻⁷. This is because they offer a number of potential advantages over the well-established nematic devices as well as over a number of other competitors. Lots of liquid crystals in current display applications are eutectic mixtures of two or more mesogenic substances. A good example is E7, which is a mixture of four liquid crystals. Liquid crystal mixture E7, which has been widely used⁸⁻¹⁰, exhibits a nematic phase at room temperature.

Information on the phase behaviour of a liquid crystal sample, such as transition temperatures and enthalpies, can all be calculated from a single data run on differential scanning calorimeter (DSC) is one of the most widely used analytical instruments because of the ease with which it can provide large amounts of thermodynamic data. Invaluable qualitative and quantitative information about the liquid crystalline phases can be derived from the thermodynamic data at and in the vicinity of their phase transitions. The molecular structure phase stability relations can usually be understood from

detailed thermodynamic data. Transition temperatures, enthalpies and entropies are important quantities characterizing the materials. The difference in transition temperature between the melting and clearing points gives the range of stability of the liquid crystalline phases. The transition enthalpies and entropies between the phase transitions are related to the degree of internal order present in the system.

This work was designed for the development of liquid crystal mixtures. In order to design these processes, it is important to take a detailed knowledge of thermodynamic properties¹¹ of the nematic liquid crystal mixtures. We decided to study on mixtures of the nematogenic homologous *p*-(*n*-alkyl)-*p*'-cyanobiphenyl (*n*CB); where *n* is the number of carbons in the *n*-alkyl tails. 4-Hexyl-4'-cyanobiphenyl (6CB) and 4-octyl-4'-cyanobiphenyl (8CB) are two of the best known liquid crystalline substances. 6CB and 8CB, as well as other members of the *n*CB homologous series, are important for the technological applications due to the convenient temperature range of the nematic phase and good chemical stability¹². Important characteristics, such as the melting and clearing temperatures and their enthalpies¹³, can all be calculated from a single data run, of the 6CB and 8CB liquid crystals were carried out by Oweimreen *et al.*¹⁴ using an adiabatic scanning calorimeter. And also BDH Chemicals reported the electro-optical properties of these liquid crystals¹⁵. Information on the phase-transition

temperature and transition enthalpy of a pure liquid crystal allows one to estimate the effect of the mixture ratio (wt. %) on the emergence of a region in which the nematic and isotropic phases coexist. In this study, we have constructed the phase diagrams of 6CB/8CB liquid crystals mixtures. We have investigated the eutectic conditions and the phase structure of liquid crystal 6CB/8CB mixtures by using DSC and theoretical calculations.

The choice of adequate wavelength and the absorbance to use at the display technology is provided by UV experiments. In order to investigate the effect of alkyl chain length on the liquid crystal (LC) mixtures in chloroform solution, the spectral behaviours of 6CB, 8CB and their mixtures were, respectively measured by UV spectrometry.

EXPERIMENTAL

The liquid crystal materials 4-hexyl-4'-cyanobiphenyl (6CB) and 4-octyloxy-4'-cyanobiphenyl (8CB) were purchased from Sigma-Aldrich Corporation and were used without further purification: their phase transition temperatures were in substantial agreement with the data given in the Sigma-Aldrich catalogue. The structure formula of 6CB and 8CB nematic liquid crystals used in this study is shown in Fig. 1.

Thermal analysis: The thermodynamic properties of liquid crystals and their mixtures were investigated by a Perkin-Elmer differential scanning calorimeter (DSC-7) using continuous heating under a pure argon atmosphere. Before use, the DSC was calibrated with Indium (99.999 wt % pure In). Calibration is accomplished by running a standard material and comparing the experimental reliable temperature (melting point, clearing point) and enthalpy of transition to standard values. The experiments were carried out with scanning rate of 2, 5, 8 and 10 °C/min by means of DSC unit equipped with a data acquisition and analysis station.

The liquid crystals-mixture samples were stirred with an injector needle at temperatures below T_{CN} (Crystal to Nematic), T_{AN} (Smectic A to Nematic), T_{NI} (Nematic to Isotropic) and above T_{NI} , respectively, by heating on a hot stage. This process was made carefully twice about at 40 min. After that DSC samples were prepared in a thin aluminum pan, which was then placed on the stage of a piston-like sample crimper. The DSC was initially cooled to -20 °C and each sample was left in the sample pan for 2 min to ensure that thermal equilibrium was reached. Then the temperature was run from -20 °C to 70 °C above its reported¹⁵ clearing point and held at that temperatures for *ca.* 2-3 min to be sure of its complete transformation to the isotropic phase.

UV spectroscopy: While 6CB liquid crystal is a viscous liquid, 8CB is a little viscous liquid at room temperature. Solutions of mixtures within the concentration range 2.6×10^{-5}

and 3.7×10^{-5} M were prepared by weighting and dissolved in chloroform. The averaged molar mass of mixture was calculated by weighted sum of the individual molar masses (MM) of the liquid crystals and their molar fractions; the following compositions (w/w) were performed: 25 % of 6CB and 75 % of 8CB, 50 % of 6CB and 50 % of 8CB, 75 % of 6CB (MM = 263.38 g mol⁻¹) and 25 % of 8CB (MM = 291.43 g mol⁻¹). In order to ensure the good solubility of the liquid crystals in chloroform, at the concentrations studied, we made it possible to prepare uniform samples just by a magnetic stirrer at a temperature slightly above the transition temperatures T_{CA} and T_{CN} of binary liquid crystal mixtures. Absorption measurements were carried out in real time, in the wavelength interval of between 200 and 400 nm using a Perkin-Elmer Lambda 45 UV/VIS spectrophotometer. The spectra were recorded at room temperature using 1 cm quartz cuvette. The samples were separately placed in the spectrometer and another quartz cuvette was used as reference for transmission measurements. Before starting in transmission measurements, auto zero count was taken using two cuvettes.

RESULTS AND DISCUSSION

There are a number of reports about the phase transition behaviour of pure liquid crystal 6CB and 8CB. In this study, we have examined liquid crystal 6CB/8CB mixtures to assess the effect of the blends for display technology. Liquid crystal 6CB presents in the pure state the following transition temperature values given by Oweimreen and Morsy¹⁴ that the crystalline-nematic transition temperature $T_{CN} = 13.64$ °C and nematic-isotropic transition temperature $T_{NI} = 28.07$ °C. The pure 8CB presents phase transition temperatures: crystalline-smectic A transition temperature $T_{CA} = 19.74$ °C, smectic A-nematic transition temperature $T_{AN} = 29.07$ °C and nematic-isotropic transition temperature $T_{NI} = 39.07$ °C¹⁴.

Fig. 2 shows the DSC traces of pure liquid crystal 6CB and 8CB. As for pure 8CB, the stable mesophase sequence on heating from room temperature is: Crystalline (Cr)-Smectic A (SmA)-Nematic (N)-Isotropic (I), whereas for pure 6CB the SmA mesophase is absent being the mesophase sequence: Cr- N-I. The liquid crystals were assessed to be highly pure, because they showed sharp transition temperatures in good agreement with those literatures¹⁴⁻¹⁷. The DSC spectrals for 6CB/8CB mixtures obtained on heating across the smectic A-to-nematic and the nematic-to-isotropic transition temperatures are shown in Fig. 3.

The DSC traces of liquid crystals 6CB/8CB mixtures exhibit two or three endothermic peaks, indicating that structural transformation into isotropic phase takes places in steps. However, the DSC trace of 40 % 6CB + 60 % 8CB mixture exhibit an exothermic peak indicating melting. It can be seen

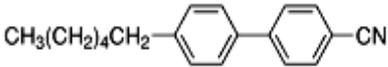
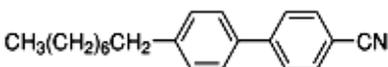
LC	Linear formula	Chemical structure	Molecular weight (g)
6CB	$\text{CH}_3(\text{CH}_2)_5\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CN}$		263.38
8CB	$\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CN}$		291.43

Fig. 1. Chemical structures of 4-hexyl-4'-cyanobiphenyl and 4-octyl-4'-cyanobiphenyl

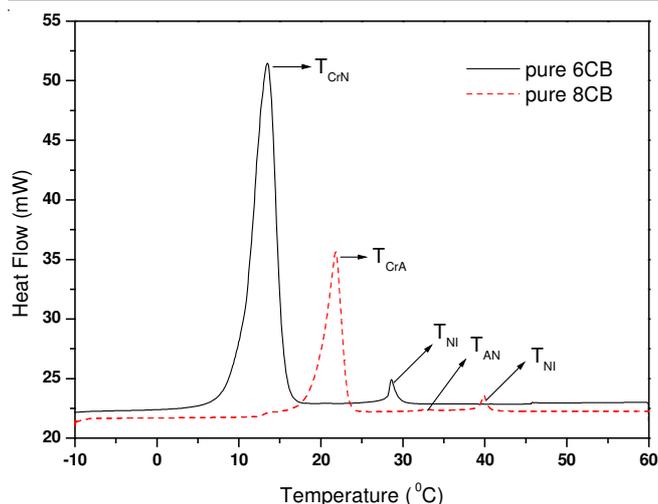


Fig. 2. DSC curves obtained during continuous heating of pure liquid crystal 6CB and 8CB

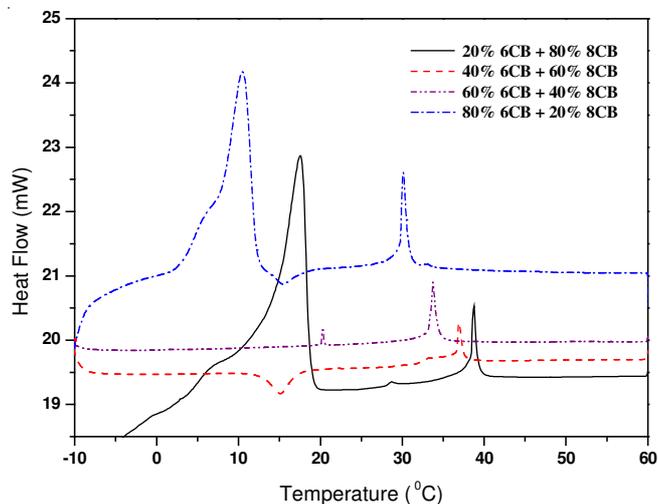


Fig. 3. DSC curves obtained during continuous heating of liquid crystal mixtures

that, phase transition temperatures T_{CrA} , T_{AN} and T_{NI} dependent on the ratio of mixtures (wt %). For example; T_{NI} temperature values increased from 30.15 to 38.75 °C with increasing wt % of 8CB from 20 % to 80 %. As seen in Fig. 3, we didn't obtain the crystalline-smectic A transition temperature (T_{CrA}) of 60 % 6CB + 40 % 8CB mixture because of it was near the eutectic mixture. The study revealed that the phase transition temperatures T_{AN} and T_{NI} of 6CB/ 8CB mixtures are between the transition temperatures of pure liquid crystal 6CB and 8CB to the corresponding mixture ratios.

Fig. 4 shows the phase diagram of the liquid crystal 6CB/ 8CB mixture system. The phase diagram was constructed from the results of DSC measurements and theoretical calculations¹⁸⁻²⁰. The symbols (or red dash lines) represent the transition temperatures *versus* liquid crystals concentration as obtained by DSC. As shown in Fig. 4, homogeneous nematic and isotropic phases can be observed for the whole concentration range of 6CB. Four distinct regions are clearly identified in this diagram. In the upper region, a single phase is obtained, where the 6CB/ 8CB mixture form an isotropic solution. The isotropization temperature (T_{NI}) of the blends decreases with the increase of

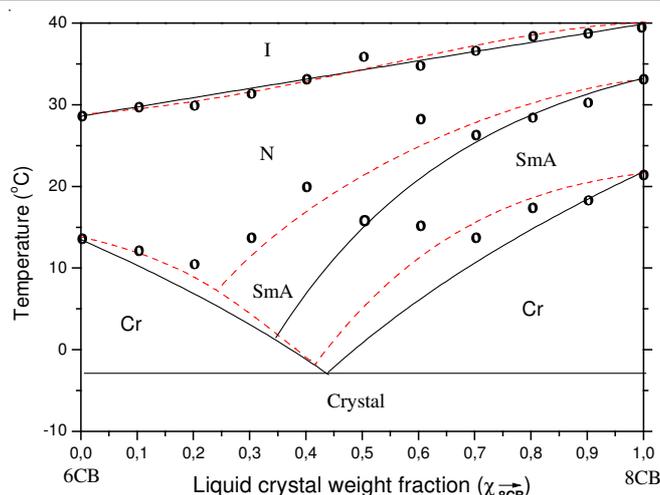


Fig. 4. Experimental (red dash lines) and calculated (solid lines) phase diagrams for the two-component system, 6CB + 8CB. The empty symbols represent the DSC measurements made in this work

6CB concentration. The diagram, calculated with Schröder van-Laar equation, exhibits a eutectic temperature at -2.84 °C. But the diagram, constructed with experimental results, exhibits a eutectic temperature at -1.71 °C. As seen in Fig. 4, the experimental nematic-isotropic phase transitions are very similar to theoretically drawing (solid lines) with Schröder van-Laar equation. On the other hand, the experimental SmA-N and Cr-N transitions are similar to the theoretical drawing. One can see a complete agreement between the two curves of mixture samples. So, The Schröder van-Laar equation is capable on liquid crystal 6CB/8CB mixtures, although the SmA phase transition occurs in 8CB. The N-I transitions of the experimental and calculated phase diagrams for the two-component system are in good agreement with those reported literatures²⁰⁻²² for a similar experiment. The experimental SmA-N and Cr-N transitions are approximately similar with literatures^{21,22} for a similar experiment, as determined from their continuous DSC results.

The phase transition temperatures (T_{CrA} , T_{CrN} , T_{AN} , T_{NI}) and enthalpies (ΔH_{CrA} , ΔH_{CrN} , ΔH_{AN} , ΔH_{NI}) are listed in Table-1. As seen in Table-1, the values of phase transition temperatures and enthalpies obtained in present experiment are approximately similar to the values reported in literatures¹⁴⁻¹⁷.

The phase transition temperature is dependent on heating rate. Fig. 5 shows the dependence of phase transition temperature on heating rate at 50 % 6CB and 50 % 8CB liquid crystal mixture. The obtained values can be used to estimate the associated phase transition activation energy by means of the Ozawa²³ and Kissinger²⁴ method. According to the Ozawa and Kissinger methods, the activation energy (EA) changes with temperature, or in other words, the environment of the rotating molecule changes with temperature. So, the value of activation energy can help us to speculate about the energy attributable to a molecular rotational mode. The activation energies, calculated by using Ozawa and Kissinger method, are listed in Table-2 for the phase transition peak temperatures T_{AN} and T_{NI} of 50 % 6CB and 50 % 8CB liquid crystal mixture, respectively. As seen in Table-2, the calculated values of the activation energy for the nematic-isotropic phase transition

TABLE-1
PHASE TRANSITION PEAK TEMPERATURES (T) AND ENTHALPIES (ΔH)
OF THE PURE LIQUID CRYSTALS AND THEIR MIXTURES

LC and mixture	T_{CrA} (°C)	ΔH_{CrA} (kJ/mol)	T_{CN} (°C)	ΔH_{CN} (kJ/mol)	T_{AN} (°C)	ΔH_{AN} (kJ/mol)	T_{NI} (°C)	ΔH_{NI} (kJ/mol)
6CB	–	–	13.49	22.57	–	–	28.61	0.29
80 % 6CB + 20 % 8CB	–	–	10.44	32.6	–	–	30.15	0.34
60 % 6CB + 40 % 8CB	–	–	–	–	20.27	0.04	33.27	0.22
40 % 6CB + 60 % 8CB	15.13	26.1	–	–	28.37	0.003	36.94	0.11
20 % 6CB + 80 % 8CB	17.53	37.5	–	–	28.77	0.004	38.75	0.24
8CB	21.8	22.15	–	–	32.83	0.002	39.9	0.25

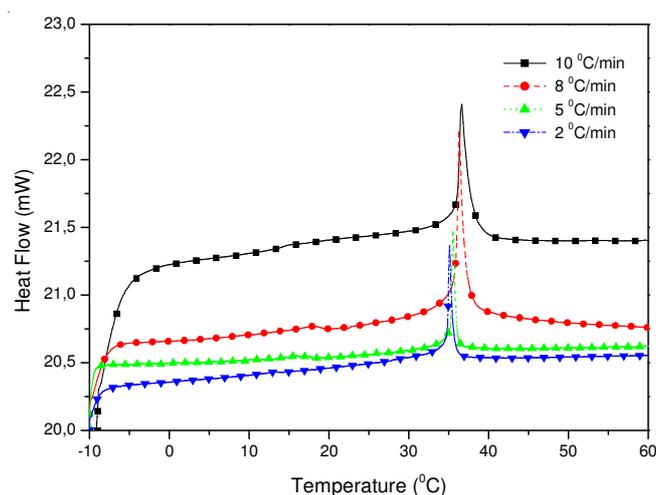


Fig. 5. DSC curves obtained during continuous heating of 50 % 6CB and 50 % 8CB liquid crystal mixture at different heating rates

TABLE-2
ACTIVATION ENERGIES E_A (kJ/mol) FOR
PHASE TRANSITIONS OF 50 % 6CB AND 50 %
8CB LIQUID CRYSTAL MIXTURE

Activation energy	Smectic A-nematic	Nematic-isotropic
Kissenger (kJ/mol)	212 ± 10	770 ± 10
Ozawa (kJ/mol)	206 ± 10	737 ± 10

were higher than the smectic A-nematic phase transition, indicating a relatively nematic liquid crystal structure. Here again, a good agreement exists between the two methods. A similar experiment was reported by Jadzyn *et al.*²⁵ for 6CB + 3CyP5 mixtures.

As seen in Fig. 5 and Table-3, the phase transition temperature values have clearly risen with increasing heating rate from 2 to 10 °C/min. While the peak heights are decreasing at the smectic A to nematic transitions, the peak heights are increasing at the nematic to isotropic transition by increasing heating rate from 2 to 10 °C/min. The smectic A to nematic transitions are much smaller than the nematic to isotropic transitions and sometimes hard to detect because they may be influenced by the nematic to isotropic transitions at high heating rates. As seen in Fig. 5, we couldn't observe the T_{CrA} phase transition at 2-10 °C/min heating rates because of near the eutectic temperature. The heating rate dependencies found for the phase transitions are in good agreement²⁶, but the peak heights for the nematic to isotropic transitions are not in good agreement with reported by Neuenfeld and Schick²⁷. We considered that the low heating rates may be needed to get the temperature sample to increase linearly with time. The heating rate dependence of

TABLE-3
PHASE TRANSITION PEAK TEMPERATURES T_{AN} ,
 T_{NI} OF 50 % 6CB AND 50 % 8CB LIQUID CRYSTAL
MIXTURE AS A FUNCTION OF HEATING RATES

Heating rate (β) (°C/min)	Smectic A-nematic (°C)	Nematic-isotropic (°C)
2	13.21	35.13
5	15.94	35.55
8	18.16	36.26
10	16.68	36.67

the peak shape of the liquid crystal mixture transitions is very complex. Therefore we recommend further investigations at phase transitions of liquid crystal mixtures by high sensitive calorimeters to detect the transition.

The absorbancies of the pure liquid crystal 6CB, 8CB and their mixtures were measured between 200 and 400 nm. Fig. 6 presents the obtained molar absorbance spectra within 240 and 400 nm. The 6CB and 8CB spectrum presents a maximum absorption wavelength located at 293 and 276 nm, respectively, in agreement with maximum absorption wavelength (λ_{max}) reported in literature^{26,28}, as well as similar liquid crystals. The spectra of liquid crystal mixtures also exhibited strong absorption bands between 293 and 276 nm, like pure 6CB and 8CB. The obtained values, according to the Beer law²⁹, ϵ (absorptivity), A (absorbance) and λ_{max} are listed in Table-4. The λ_{max} values increased from 281 to 290 nm, respectively, with increasing wt % of 6CB from 25 to 75 %, due to the presence of the same core length but different tail lengths. The UV spectrum presented in Fig. 6 shows negligible absorbance of mixtures at wavelengths higher than 340 nm, the wavelength of either the pulsed laser beam used in the liquid crystal deposition or the UV light used for curing sealant in liquid crystal devices³⁰. Irradiation at 340 nm caused a decrease of the $\pi \rightarrow \pi^*$ band intensity indicating the isomerization. We decided to consider the process successful when we could not observe any further change by comparing intensities of consecutive UV-visible spectra. All these features of 6CB/8CB mixtures are characteristic of liquid crystals molecules, due to $\pi \rightarrow \pi^*$ transition as found in single liquid crystals. Thus, these results in chloroform media seem to confirm the reported stability of mixtures to photo degradation³¹. One can choose the convenient wavelength and the respective molar absorptivities (ϵ) for the liquid crystals mixture assays.

Conclusion

The DSC curves that were used to determine the phase transition temperatures and enthalpies showed the existence of different phase transitions in liquid crystal 6CB/8CB

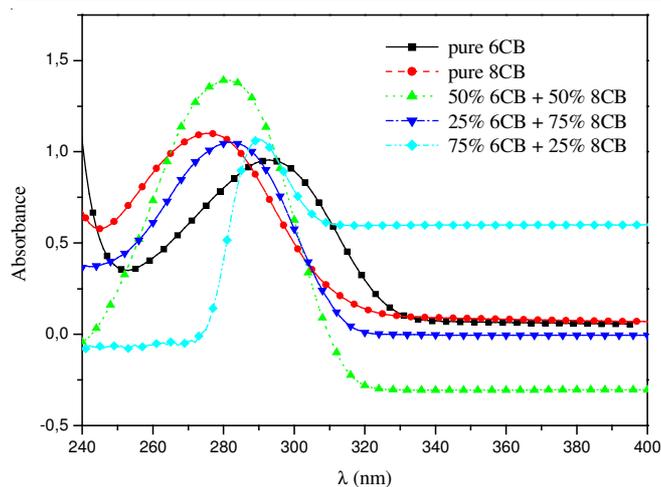


Fig. 6. UV traces of the pure liquid crystal 6CB, 8CB and their mixtures in chloroform

TABLE-4
ABSORBANCE (A), MOLAR ABSORPTIVITY (ϵ)
AND WAVELENGTH (λ_{\max}) OF THE PURE LIQUID
CRYSTAL 6CB, 8CB AND THEIR MIXTURES

LC and mixture	Absorbance	ϵ ($M^{-1}cm^{-1}$)	λ_{\max} (nm)
100 % 8CB	1.100	42.3×10^3	276
75 % 8CB + 25 % 6CB	1.050	32.4×10^3	281
50 % 8CB + 50 % 6CB	1.391	53.5×10^3	282
25 % 8CB + 75 % 6CB	1.069	38.2×10^3	290
100 % 6CB	0.954	25.8×10^3	293

mixtures during continuous heating. The phase diagram of the liquid crystal 6CB/8CB mixture system was established by the results of DSC measurements and theoretical calculations. The calculated and experimental phase diagram exhibited a eutectic temperature at -2.84 °C, -1.71 °C, respectively, that is not an important change and four distinct regions. The Schröder van-Laar equation was used on three phase transitions of binary mixtures for the first time. According to obtained values, the Schröder van-Laar equation can be used at binary mixtures that have got three phase transitions, like 6CB/8CB mixture. The activation energies of phase transitions were calculated by using Ozawa and Kissinger methods in this study for the first time. The calculated values of activation energies showed a good agreement between the two methods. The heating rate dependence of the peak shape of the liquid crystal mixture transitions was not determined very well. Further investigations on the heating rate dependence of liquid crystal 6CB/8CB mixtures could be carried out by high sensitive calorimeters to detect the phase transitions. The UV experiments showed that the properties of liquid crystal 6CB/8CB mixtures were characteristic of pure liquid crystal 6CB and 8CB molecules

in chloroform solution. The λ_{\max} values of 6CB/8CB mixtures increased by decreasing wt. % of 8CB in 6CB due to the alkyl chain length with H-aggregation.

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