Bicomponent Mixtures of Cholesteryl Myristate and 4-*n*-Decyloxy Benzoic Acid: Future Prospects and Possible Use in Electronic Devices

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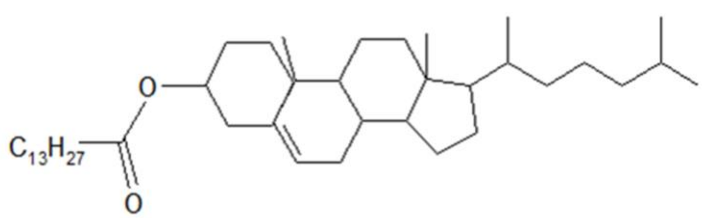
Liquid crystals (LCs) have been extensively investigated because they possess properties favorable to many technical applications related to electro-optical (E-O) displays, optical storage devices and non-linear optics [1-3]. Various applications need optimization of physical properties (for example dielectric anisotropic, operating temperature range and stability of the mesophases etc.) by preparing appropriate mixture because none of the LC material discovered till date has all the desired parameters from application point of view. The mixing of liquid crystals allows an adjustment of physical properties and occasionally can lead to induction, expression or suppression of meso phases. Many interactions, which are accountable for the formation of various liquid crystalline phases like Vander Walls forces, hydrogen bonds and electron donor-acceptor interaction in binary mixtures of rod-like LCs have been, reported [4]. Each of these forces, collectively or separately, may be responsible for an increase or decrease of the stability of various liquid crystalline phases or for creating new phases in the mixed systems. Usually such mixtures can be premeditated to have a large thermally stable liquid crystalline (usually nematic or smectic) range, together with optimized values for key material properties. Study of mixtures is important from the point of view of molecular interactions as well. For example a mixture of two cholesteric compounds with opposite optical activities give rise to materials of controllable and temperature sensitive pitch [5]. At a particular composition of cholesteric compounds with opposite optical activities exactly compensated nematic mixture is produced [6]. Mixtures of two non mesogenic compounds may give mesogenic compound [7], mixtures of nematogens may give smectics [8] and mixtures of smectogens may give nematics [9]. Mixtures of smectic C (SmC) and cholesteric (N*) phases may give chiral smectic C (SmC*) phase [10].The phenomenon of re-entrant nematic phases i.e. the reappearance of another nematic (N) phase after a smectic A phase (SmA) by lowering the temperature in rod-like LCs is common in mixtures [11, 12]. Wide varieties of frustrated smectic phases i.e. twist grain boundary (TGB) phases are also observed in mixtures [13-18]. Mixtures of a nematic (N) and a cholesteric (N*) phase adopts the cholesteric texture [19-20]. These mixtures often show blue phases and that too with increased temperature range [21-22]. Nematics and cholesterics are not thermodynamically distinct and therefore they are supposed to be infinitely miscible [23].

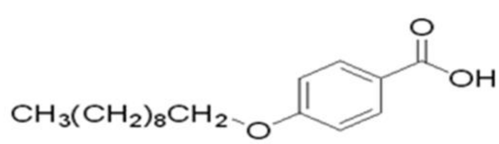
The binary system of cholesterics and nematics are characterized by the induction of extra helical twisting which is presumably due to peculiar features of interaction between molecules of different components [24]. Consequently binary system of Cholesteryl Pelargonate (cholesteric) and Nonyloxybenzoic Acid (nematic) gives rise to SmA* (now known as TGBA) phase [25-27]. Liquid crystals possessing nematic and/or smectic phases are most commonly used in production of LCDs due to their unique physical properties and wide temperature range. By applying an electric or magnetic field the orientation of the molecules can be driven in a predictable manner. This mechanism provides the basis for LCDs. The dielectric parameters of liquid crystals play an important role in the development of electro-optical devices. Frequency and temperature dependent dielectric studies of LCs mixture give information, not only about bulk properties, but also about molecular parameters, and their mutual association and rotation under an applied electric field. Pure grade samples of ChM and DOBA have been provided by the Institute of Physics, National Academy of Sciences of Ukraine, Kiev, Ukraine. Binary mixtures of different mol ratios were prepared by mixing the required amount of pure samples and were homogenized before taking the measurements by heating to a temperature several degrees above the transition to the isotropic phase, stirring/shaking, and finally cooling. The homogeneous nature of the mixtures was checked under a Polarized light microcopy (PLM) and the mixtures were used as such for the present study. The chemical structures of the individual compounds investigated in this work are shown in the **Figure 1**.

Figure 1(a)



Crystal (70.6° C) SmA (78.6° C) N* (84.0° C) Isotropic

Figure 1(b)



Crystal (87.0 ° C) SmC (114.0 °C) N (137.9 ° C) Isotropic

Figure 1: Chemical structures and phase transition temperatures of the liquid crystal materials (a) cholesteryl myristate (ChM) and (b) 4-*n*-decyloxy benzoic acid (DOBA) used for the preparation of the mixtures.

The different mol ratios of the binary mixtures of ChM and DOBA and their phase sequences and phase transition temperatures are shown in **Table 1**.

Table: 1 Phase sequences and their phase transition temperatures (in °C) for different mole percents of DOBA in heating mode. K, $K_1$and K_2 represents crystal, mixed crystal 1 (crystal + SmA), and mixed crystal 2 (crystal + SmC) respectively.

Systems (Mol %)	Phase sequences and their phase transition temperatures
0	K (70.6) SmA (78.6) N^* (84.0) I
9.7 (M_1)	K (55.5) K_1 (65.5) SmA (79.1) N^* (79.4) I
17.7 (M_2)	K (57.1) K_1 (62.2) SmA (77.6) N^* (78.9) I
30.0 (M_3)	K (48.5) K_1 (60.0) SmA (83.5) N^* (84.5) I
34.9 (M_4)	K_1 (64.5) SmA (89.9) N^* (94.7) I
56.6 (M_5)	K (63.8) K_1 (76.1) SmA (82.5) N^* (97.0) I
68.2 (M_6)	K (64.1) K_1 (79.6) SmA (85.5) N^* (99.0) I
79.9 (M_7)	K (60.8) K_2 (82.5) SmC (86.1) N^* (116.0) I
92.3 (M_8)	K_2 (87.7) SmC (101.6) N^* (128.7) I
95.5 (M_9)	K_2 (90.0) SmC (106.0) N^* (130.8) I
97.7 (M_{10})	K_2 (91.8) SmC (111.5) N^* (134.9) I
100	K (87.0) SmC (114.0) N (137.9) I

CONCLUSIONS SUMMARIZING THE ACHIEVEMENTS: Thermodynamical, optical and dielectric properties of the binary mixtures of Cholesteryl Myristate (having N^* and SmA phases) and 4-*n*-decyloxybenzoic acid (having N and SmC phases) have been carried out by the differential scanning calorimeter (DSC), polarized light microscopy (PLM) and impedance spectroscopy. Following points summarize the experimental results of the above compounds:

- Transition temperatures obtained at the scanning rate of 5 °C/ min have been used to prepare the phase diagram in the heating and cooling cycles for the individual compounds and their mixtures.

- In the variation of the transition temperatures of various mesophases with different scan rate, for the mixtures having DOBA concentrations 17.7 and 92.3 mol %, it has been established that, the slope of the lines for various phase transitions do not indicates the same steepness and also the tendency of the lines are not resembled to each other.

- In the binary system of ChM and DOBA, we have observed the phase diagram in heating and cooling cycles. The melting of the mixtures from the solid phase exhibits two peaks which merge with each other at the eutectic composition of 30 mol % of DOBA.

- The range of the SmA phase which is 8 °C in ChM, increases with mol % of DOBA and becomes maximum at the eutectic composition (~30 mol % concentration of DOBA). Above eutectic composition range of SmA phase is almost constant upto 68 mol % and disappears at ~ 80 mol % of DOBA. Thus around eutectic composition stability of the SmA phase is highest.

- Fan-shaped textures have been observed in the SmA phase and oily streaks in N* phase under the polarized optical microscope for the mixtures having DOBA concentrations 30.0 and 92.3 mol %, respectively.

- The dielectric permittivity in planar and homeotropic configurations in the isotropic liquid to crystal phase is almost constant with the frequency in the frequency range 1 Hz to 10 MHz for the mixtures having DOBA concentrations 30.0 and 92.3 mole %, implying that no dipolar relaxation phenomenon occurs in this frequency range.

- The individual compounds DOBA and ChM are having positive and negative dielectric anisotropy respectively. However, the mixtures having DOBA concentrations 30.0 and 92.3 mole % show low value of negative dielectric anisotropy.

FUTURE PROSPECTS: The various observed phases of liquid crystals mixtures are characterized not only by bulk properties viz. weak transition enthalpy, optical texture, dielectric permittivity and dielectric anisotropy etc. but also from the molecular parameters (existence of relaxation phenomenon etc.) for their mutual association and rotation under an applied electric field. Therefore, studies of the above parameters are important to understand the molecular dynamics and fundamental properties of observed phases vis-à-vis molecular design. Thermodynamic, optical texture and dielectric studies of the liquid crystalline mixtures gave temperature range, stability of the observed phases, optical textures, frequency and temperature dependent dielectric parameters.

Following lines are the future prospects of the bicomponent mixtures of liquid crystals Cholesteryl Myristate (ChM) and 4-n-Decyloxybenzoic Acid (DOBA):

- The pitch of the mixtures can be measured and correlate it with the dielectric parameters.

- Molecular ordering of the various observed phases of the studied mixtures will be further clarified by wide angle X-Ray Diffraction technique.

- Future scope in the field is to find the optical transmittance of the above studied mixtures which is also one of the important properties, that is very useful for determination of most crucial parameters of a display device, i.e. luminescence and contrast ratio.

POSSIBLE USE IN ELECTRONIC DEVICES: Liquid crystal materials for device applications are mostly mixtures, because no single compound fulfills all the criteria. Mixing many compounds enables us to adjust the properties such as temperature range, frequency range, electric permittivity etc. So the study of mixtures of liquid crystalline compounds is a subject of considerable interest for the application in electronic devices. Following lines can be the possible exercise of the bicomponent mixtures of liquid crystals Cholesteryl Myristate (ChM) and 4-n-Decyloxybenzoic Acid (DOBA) in electronic devices:

- Generally a smectic phase is induced in binary mixtures of nematogenic compounds, one having terminal polar group and other having terminal Nonpolar group. In some cases, however, induced smectic phases have been observed when both the compounds have strong polar end groups or both the compounds have weakly polar end groups. The reason for induction of smectic phase has been suggested due to charge-transfer interaction between the components of a binary mixture. However, other explanations have also been suggested. The formation of injected smectic phases can be a problem for mixtures used in electro-optical devices. However, existence of injected smectic phases at lower temperature may improve the performance of a device. Exactly, in our case we have observed the range of the SmA phase which is 8 °C in ChM which, increases with mole % of DOBA and becomes maximum at the eutectic composition (~30 mole % concentration of DOBA) and the existence of the SmA phase is from ~ 10.0 to 80.0 °C. Thus, SmA exist towards the lower temperature side and it is in the wide temperature range (~ 70.0 °C).Therefore, it can be implement in the production of display devices based on liquid crystal.

- We have observed, above eutectic composition range of SmA phase is almost constant upto 68 mole % and disappears at ~ 80 mole % of DOBA. Thus around eutectic composition stability of the SmA phase is highest. As a result, the mixtures around eutectic composition (~30 mole % concentration of DOBA) are most suitable for the optimization of other physical properties like frequency range, dielectric anisotropic etc. for which it can be apply in display technology and other devices.

- Chiral nematic (cholesteric) liquid crystals have ability to selectively reflect light with a wavelength equal to the pitch length. So if the pitch length is of the order of the wavelength of colored light then colored light will be reflected. Because the pitch is dependent upon temperature and pressure, the color reflected also is dependent upon temperature and pressure. Liquid crystals make it possible to accurately gauge temperature just by looking at the color of the thermometer. At high temperature, the pitch becomes wound up and short and hence the light reflected is blue but a lower temperature the pitch unwinds and becomes long which causes the reflection of red light. Hence, it can be used as temperature sensors. Although, at high pressure, pitch becomes long and vice versa, therefore, at different pressure it reflects light of different colour. Hence, it can also be used as pressure sensors. Therefore, the liquid crystal mixtures can be built as a device for desired temperature and pressure range.

❖ The dielectric studies provide useful information about molecular structure, molecular dynamics and phase transition behaviour, which is used as an input to its display applications The dielectric permittivity in planar and homeotropic configurations in the isotropic liquid to crystal phase is almost constant with the frequency in the frequency range 1 Hz to 10 MHz for the mixtures having DOBA concentrations 30.0 and 92.3 mole %, implying that no dipolar relaxation phenomenon occurs in this frequency range. Thus frequency range 1 Hz to 10 MHz is the usable frequency range for display purpose.

❖ Liquid crystals possessing nematic and/or smectic phases are most commonly used in production of LCDs due to their unique physical properties (low value of negative dielectric anisotropy etc.) and wide temperature range. As we have observed the individual compounds DOBA and ChM are having positive and negative dielectric anisotropy respectively. However, the mixtures having DOBA concentrations 30.0 and 92.3 mole % show low value of negative dielectric anisotropy. Therefore it is extremely beneficial in construction of LCDs.

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