

CHAPTER V

Formulation of Several Multi Component Mixtures for VA Mode Application

5.1. Introduction:

A fast growing flat panel display industry constantly requires improved materials with optimum properties to manufacture high resolution Active Matrix Addressed Liquid Crystal Displays (AM-LCD's). Of the several Liquid Crystal Display (LCD) technologies that exists, Vertically Aligned (VA) mode applications [1-5] ranging from flat panel LCD devices [6] to high resolution projection micro-displays using Liquid Crystal on Silicon (LCoS) technology [7, 8] are based on Liquid Crystal (LC) materials with negative dielectric anisotropy [9-11]. Devices operating in the VA mode usually exhibit an excellent contrast [12] in combination with high speed switching [13-16]. This has created a greater demand for further development of new and improved liquid crystalline materials for application in vertically aligned (VA) mode LCDs. In VA mode, the liquid crystal molecules are usually aligned at right angles to the substrates, and in the presence of an electric field, they swing through 90° to lie parallel to the substrates.

In the last two decades, the use of organo-fluorine compounds has gained considerable importance both in the field of Liquid Crystal Display (LCDs) devices as well as in other technological applications [17]. It is well known that the introduction of fluorine atoms in liquid crystalline materials imparts interesting properties as compared to their hydrocarbon analogues [18]. Much attention is paid to fluorinated nematogens, because they often have

broad nematic mesophases range, low rotational viscosity and low conductivity [19]. Furthermore, the controlled choice of the molecular position of the fluorine atoms allows tailoring of the physical properties to approach appropriate dielectric anisotropies for commercial applications. An important class of materials satisfying the requirements of VA mode technology is the laterally fluorinated biphenyls and terphenyls [20].

The liquid crystal molecules have to satisfy a complicated interdependent set of material properties as far as their applicability in display devices is concerned. First of all, there must be a broad nematic mesophase range typically from -40°C to 100°C , to guarantee the so called “operating temperature” range of the LCD’s. Moreover, the materials should have large dielectric anisotropy ($\Delta\epsilon$) to decrease the operating voltage (V_{th}) and lower values of the bend elastic constant (K_{33}). For vertically aligned mode applications, liquid crystalline materials with lateral polar substituents which introduce a dipole moment perpendicular to the long axes of the molecule resulting in negative dielectric anisotropy is required. For VA mode applications, taking into account the cell gap ($d \approx 4\mu\text{m}$ in transmissive mode [21] and $1.5\mu\text{m}$ in reflective mode [22]) the birefringence values should be in the range of 0.1 to 0.15 [23]. Again, the switching time of an LCD is proportional to the rotational viscosity (γ_1) of the liquid crystal. To achieve at least 90% transition between two frames a switching time of 16msec (i.e. the time of one frame during which the voltage is sustained until the next refresh signal pulse arrives) is the basic requirement [24]. This necessitates development of improved LC materials with lower rotational viscosity. Since, no single liquid crystal compound can fulfill all the above-mentioned requirements; a mixture comprising of up to 10-15 components has to be formulated whose physical properties have to be optimized to fulfill the LCD manufacturer’s requirement. Therefore, from display point of view, preparation

of suitable multicomponent mixtures and a detailed investigation into the dielectric, visco-elastic and other physical properties are of utmost importance.

This chapter highlights the systematic development of multicomponent mixtures (mixtures **A-G**) from pure liquid crystalline compounds comprising of polar-fluorinated materials which combine the necessary polarity with chemical stability and adequate polarizability [25, 26]. 2, 3-difluorinated alkoxybenzene derivatives are suitable for preparation of VA mixtures because of their large negative dielectric anisotropy ($\Delta\epsilon \approx -6$). Terphenyl derivatives are also very promising candidates to improve the rotational viscosity ($\gamma_1 = 90\text{mPas}$) of the targeted mixtures having the birefringence Δn in the desired range of around 0.23 [27-29]. Starting from a simple three component system (mixtures **A-B**) several multi component mixtures (mixtures **C-G**) have been formulated from suitably selected pure components. The main aim of this work is to produce materials with wide temperature range, large negative dielectric anisotropy, low rotational viscosity and low to moderate values of the optical birefringence for their application in VA-LCD's. Furthermore, the material properties of a few mixtures have been modified by the addition of appropriate dopants to meet the target specifications of VA mode mixtures.

5.2. Formulation of multi component mixtures with negative dielectric anisotropy for VA mode application:

The chemical structures, transition temperatures of the pure components and the constituents of the mixtures (**A-G**) are listed in Table 5.1. The molar ratios and the eutectic points of the mixtures were calculated using the Schröder van Laar equation [30-33].

$$\ln x_k = -\frac{\Delta H_m^k}{R} \left(\frac{1}{T} - \frac{1}{T_m^k} \right) \quad (5.1)$$

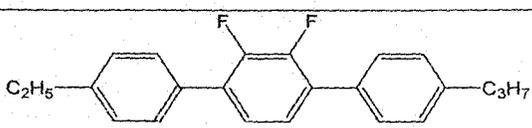
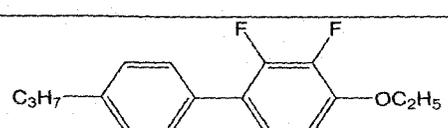
under the condition,

$$\sum_{k=1}^n x_k = 1 \quad (5.2)$$

where, x_k is the molar ratio of k-component; ΔH_m^k and T_m^k are the melting enthalpy (J.mol⁻¹) and the melting temperature values (in K) respectively and R is the universal gas constant (8.31 J.mol⁻¹.K⁻¹).

Mixtures **A** and **B** are two tri-component mixtures, consisting of two laterally fluorinated terphenyls (compounds **3** and **4**) and one bicyclohexane compound (compound **14** for mixture **A** and compound **15** for mixture **B** respectively). Mixture **C** is a five component mixture, comprising of three laterally fluorinated compounds (compounds **1**, **10** and **11**) along with a phenyl-cyclohexane compound (compound **12**) and a non-mesogenic compound (compound **13**) [34, 35]. Mixture **D** is a nine component base mixture essentially comprising of laterally fluorinated bi- and tri-phenyl compounds (**1-9**). Mixture **D** was further modified by the addition of laterally fluorinated tolane which were used as dopants (compounds **16** and **17**) resulting in the formulation of two ten component mixtures – mixture **E** and **F**.

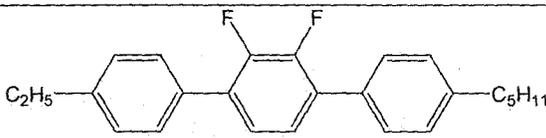
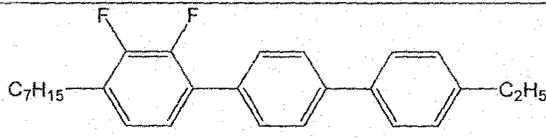
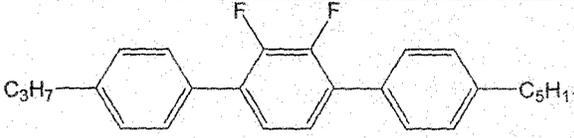
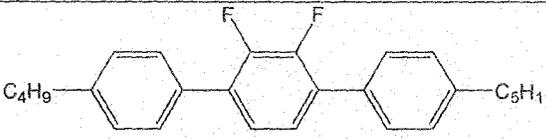
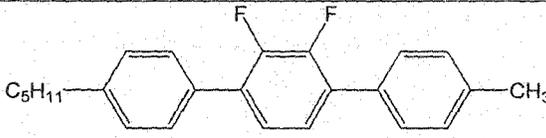
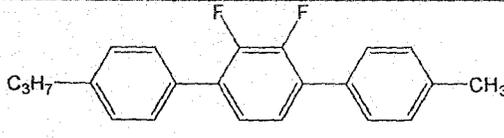
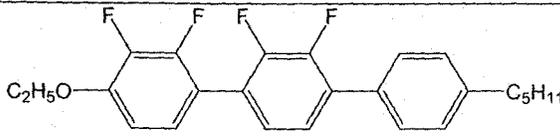
Table 5.1. Chemical structures of the pure components of the nematic liquid crystal mixtures **A-G**.

Sl. No.	Components	A	B	C	D	E	F	G
1	 Cr 72.7 N 114.5 Iso			+	+	+	+	+
2	 Cr 50.3 Iso ^a				+	+	+	+

^a indicates non-mesogenic compounds

+ indicates presence of the individual pure compound in the mixture

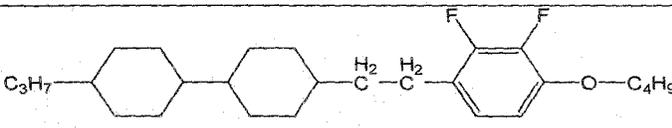
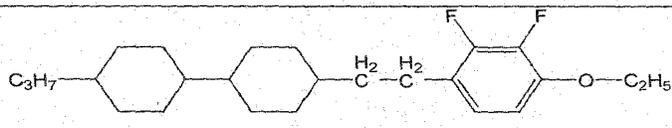
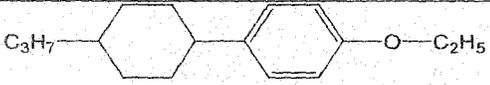
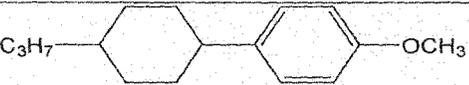
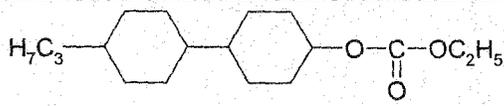
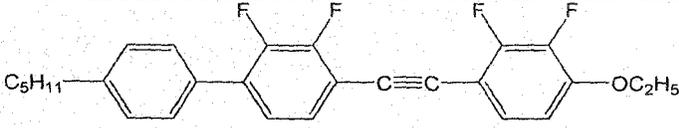
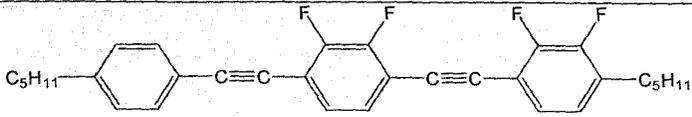
Table 5.1. 'contd. Chemical structures of the pure components of the nematic liquid crystal mixtures A-G.

Sl. No.	Components	A	B	C	D	E	F	G
3	 Cr 41.6 N 109.7 Iso	+	+		+	+	+	+
4	 Cr 67.1 SmB 75.2N 124.6 Iso				+	+	+	+
5	 Cr 54.6 N 123.1 Iso				+	+	+	+
6	 Cr 50.8 N 111.6 Iso	+	+		+	+	+	+
7	 Cr 74.2 N 128.1 Iso				+	+	+	+
8	 Cr 90.6 N 132.7 Iso				+	+	+	+
9	 Cr 93.3 N 122.9 Iso				+	+	+	+

^a indicates non-mesogenic compounds

+ indicates presence of the individual pure compound in the mixture

Table 5.1. 'contd. Chemical structures of the pure components of the nematic liquid crystal mixtures A-G.

Sl. No.	Components	A	B	C	D	E	F	G
10	 <p>N 109 SmB 162 Iso</p>			+				+
11	 <p>N 110 SmB 152 Iso</p>			+				+
12	 <p>N 37 Iso</p>			+				+
13	 <p>33 Iso^a</p>			+				+
14	 <p>N 80 SmB 86.4 Iso</p>	+						
15	 <p>Cr 60.8 N 72.8 Iso</p>		+					
16	 <p>Cr 75.4 N 195.15 Iso</p>					+		+
17	 <p>Cr 86.1 N 171.8 Iso</p>						+	+

^a indicates non-mesogenic compounds

+ indicates presence of the individual pure compound in the mixture

mixture E and mixture F respectively. Furthermore, a fifteen component mixture (mixture G) was also prepared which consists of eleven laterally fluorinated pure compounds (1-11), two phenyl cyclohexane compounds (12 and 13) and two laterally fluorinated tolane compounds 16 and 17 (Table 5.1).

5.2.1. Tri-component mixtures (mixture A and mixture B):

Initially, the phase diagram of the binary system comprising of compounds 3 and 4 (mixture A') was constructed and the eutectic point was determined. The physical properties of this mixture A' was then modified by the introduction of (i) compound 14 resulting in the formulation of the mixture A and (ii) compound 15 resulting in the formulation of the mixture B. The molar ratios of the individual compounds in the mixtures for the eutectic composition were theoretically estimated by solving the Schröder van Laar

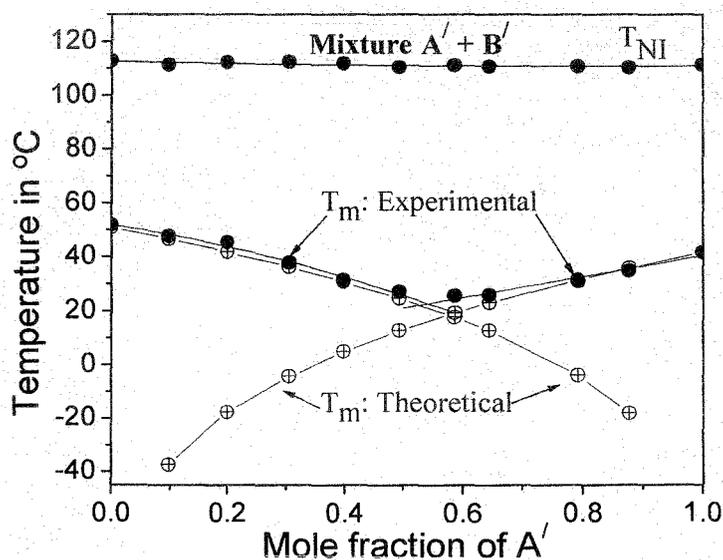


Figure 5.1. Phase Diagram of Mixture A'. From the experiment, $x_{\text{eutectic}} = 0.565$, $T_m = 22.5^\circ\text{C}$, $T_c = 110.9^\circ\text{C}$ and from the theory $x_{\text{eutectic}} = 0.575$, $T_m = 20.1^\circ\text{C}$, $T_c = 110.9^\circ\text{C}$, where T_m and T_c are the melting and the clearing temperatures respectively.

equation [30-33]. DSC measurements were done for both of these mixtures (A' and B') to confirm the formation of eutectic mixture and to obtain the transition temperatures and transition enthalpies.

The phase diagram of the A' system is shown in Figure 5.1. Also shown in Figure 5.1 are the theoretically calculated temperatures using the Schröder van Laar equations. The theoretically estimated eutectic point is at a concentration of 0.575 mole fraction of compound 3 with a clearing point at 110.9°C. The experimentally determined eutectic point was at 0.565 mole fraction of compound 3 with a clearing point at 110.9°C. It is observed from Figure 5.1 that the experimental eutectic point agrees quite well with the theoretically calculated value. DSC studies on the A' mixture at 0.565 concentration of compound 3 confirm the formation of eutectic mixture (Figure 5.2).

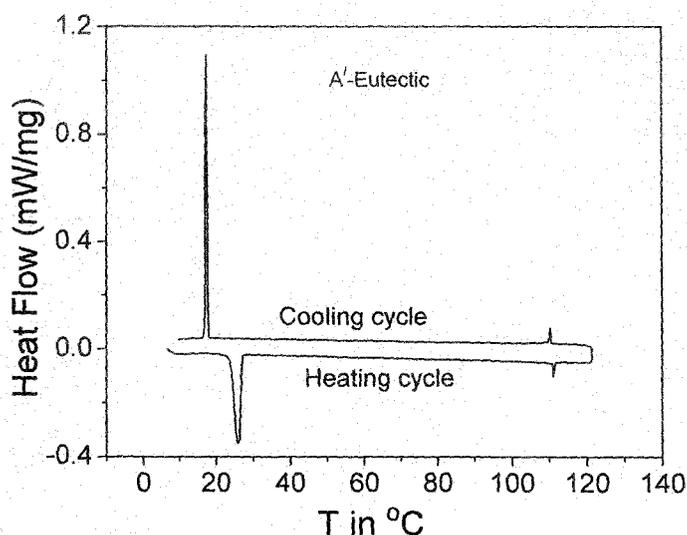


Figure 5.2. DSC scans of A' mixture at 0.565 concentrations of compound 3.

The formulation of the multi component mixtures was initiated from two simple three component systems. The eutectic composition for the tri-component mixtures (Mixture A and B) was estimated using theoretical calculations from the Schröder van Laar equation [30-33]. The mixtures were

prepared and Differential Scanning Calorimetric (DSC) studies were performed to test the formation of eutectic mixtures and also whether the calculated eutectic values are in agreement with the experimental eutectic points [34, 35]. DSC studies confirm the formation of the eutectic mixtures (Figure 5.3(a) - (b)). The results of the DSC measurements as well as the theoretically calculated eutectic points are listed in Table 5.2.

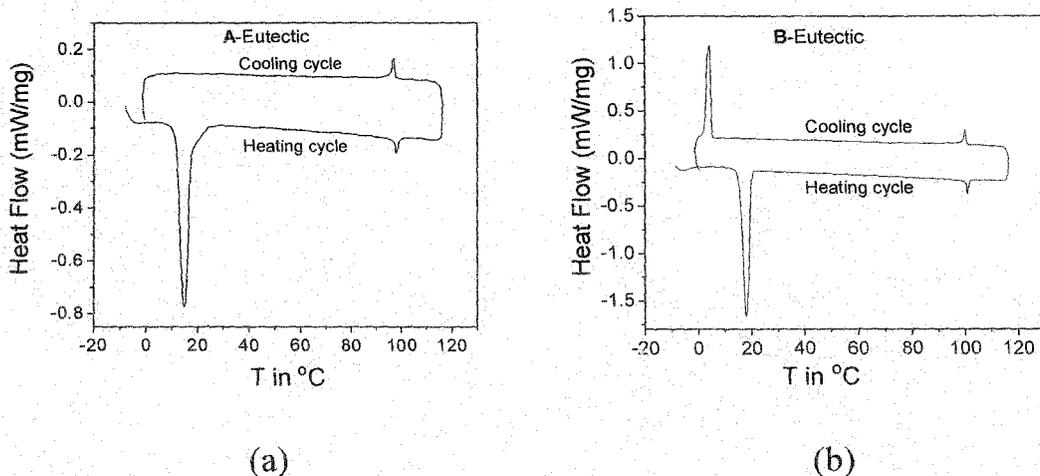


Figure 5.3. DSC scans of two eutectic mixtures (a) **A** and (b) **B** during heating and cooling.

Table 5.2. Comparison of the theoretical and experimental eutectic points.

Mixtures	Theoretical	Experimental
A	$T_m = 3.7^\circ\text{C}$ $T_c = 102.1^\circ\text{C}$	$T_m = 11.7^\circ\text{C}$ $\Delta H_m = 4.926$ kcal/mol $T_c = 97.5^\circ\text{C}$ $\Delta H_c = 0.138$ kcal/mol
B	$T_m = 12.4^\circ\text{C}$ $T_c = 104.6^\circ\text{C}$	$T_m = 15.4^\circ\text{C}$ $\Delta H_m = 3.778$ kcal/mol $T_c = 100.5^\circ\text{C}$ $\Delta H_c = 0.074$ kcal/mol

The experimental eutectic compositions of the bi and tri component systems were found to be within reasonable agreement with the theoretically calculated eutectic points. Moreover, the formation of these eutectic mixtures was not accompanied by the formation of inter molecular complexes. In order to improve the material properties further, it is required to formulate mixtures involving more components.

5.2.2. Five component mixture (mixture C):

Starting from two three component mixtures a multicomponent mixture comprising of five pure components (compounds **1**, **10-13** (Table 5.1)) has been formulated with the aim of achieving improved material parameters. Similar to tri-component mixtures **A** and **B** the molar ratios of the individual compounds were calculated by computing the CSL equations [30-33] for the five component system and the theoretical values of the melting and clearing temperatures were found to be -5.3°C and 80.9°C (experimental $T_{\text{NI}}=81.5^{\circ}\text{C}$) respectively at the eutectic point [36].

5.2.3. Nine and Ten component mixtures (mixtures D, E and F):

For further improving the material parameters and to get a broader nematic operating range a nine component base mixture (mixture **D**) comprising of compounds **1**, **3-9** was formulated. Similar to previous multicomponent mixtures, the molar ratios of the individual compounds were calculated by computing the CSL equations for the nine component system and the theoretical values of the melting and clearing temperatures were found to be -13.4°C and 105.9°C (experimental $T_{\text{NI}}=101.2^{\circ}\text{C}$) respectively at the eutectic point.

Dopants are very useful for modification of different mesomorphic properties of the base mixture. The nine component mixture had been modified into two ten component mixtures - mixture **E** and mixture **F**, by the addition of two laterally fluorinated tolane dopants, compound **16** and compound **17** (Table 5.1) respectively. The values of the melting and the clearing temperatures (theoretical) were found to be -14.8°C and 110.5°C (experimental $T_{\text{NI}}=108.4^{\circ}\text{C}$) for mixture **E** and -14.5°C and 107.4°C (experimental $T_{\text{NI}}=110.8^{\circ}\text{C}$) for mixture **F** respectively.

5.2.4. Fifteen component mixture (mixture G):

The goal of the work was to formulate a multicomponent mixture appropriate for VA mode display devices. In the pursuit of improving the rotational viscosity, birefringence and dielectric anisotropy, the fifteen component mixture (mixture G) was formulated consisting of eleven laterally fluorinated pure compounds (1-11), two phenyl cyclohexane compounds (12 and 13) and two laterally fluorinated tolane compounds (compounds 16 and 17). The theoretical melting and clearing temperatures were found to be -27.2°C and 96.0°C (experimental $T_{NI}=100.1^{\circ}\text{C}$) respectively at the eutectic point.

5.3. Summary and Conclusions:

Starting from a simple three component system (mixture A and B), several multicomponent mixtures for application in VA mode LCD's has been formulated. The molar ratios and the eutectic points of the mixtures were calculated using the Schröder van Laar equation. In each step effort was made to improve the material properties of the mixtures. With aim in view a five component mixture (mixture C) was prepared. For further improvement in the material properties, especially the rotational viscosity and relaxation time, mixture D, a nine component base mixture essentially comprising of laterally fluorinated bi- and tri- phenyl compounds (1-9) was prepared. Mixture D was further modified by the addition of laterally fluorinated tolane which were used as dopants (compound 16 and compound 17) resulting in the formulation of two ten component mixtures - mixture E and mixture F respectively. Moreover a fifteen component mixture (mixture G) was also prepared. The theoretically calculated values of the clearing temperatures of all the mixtures were found to be in close agreement with those determined from theory.

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