

University Grants Commission
Minor Research Project (2007-2012)
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Project Title
A Study of Synthesis and Characterization of Liquid Crystalline Substances

Submitted
by
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c. Report of the work done: (Please attach a separate sheet)

Final Report of the work done on the Major/Minor Research Project.

(i) BRIEF OBJECTIVES OF THE PROJECT:

The Objective of the proposed project is to synthesize materials inductive to liquid crystal state, also to characterize magnetic properties of liquid crystal substances. It is proposed to carry out synthesis of homologues series of materials having favorable molecular geometry that may give rise to the formation of mesophase.

(ii) Methodology:

(a) Chemicals Utilized: All chemicals utilized were of Analytical grade.

(b) Equipment:

SR. NO.	NAME	SOURCE
1	Cyclone Mixer	CM101, Remi (India)
2	UV-Visible Spectrophotometer	UV-1800, Shimadzu (Japan)
3	HPLC System	LC-20AT, Prominence, Shimadzu (JAPAN)
4	FTIR	Nicolet 6700 Thermoscientific (USA)
5	Viscometer	LVT 230, Brookfield Dial Viscometer, Brookfield Engineering (USA)
6	Magnetic Stirrer	MS-500, Remi (India)
7	Orbital Shaking Incubator	Nova Pvt Industries Ltd. (India)
8	Stability Chamber	Thermoscientific Ltd.

9	Cooling Centrifuge	Remi (India)
10	Particle Size Analyzer	Zetasizer NS 90 &/or ZS 90, Malvern Instruments (UK)
11	Tecnai 220 (TEM)	Phillips, (Holand)
12	AVANS II	Bruker UK

(c) Selection of Methodology:

Preparation of p-n-alkoxy benzoic acids and p-n-alkoxy benzoyl chlorides will be carried out and from that azodye will be synthesized and further processed to obtain Azo-Ester linkage compounds homologues series which could have liquid crystalline properties.

(d) Synthesis:

In initial stage, we synthesized binary mixture by following steps.

(1) preparation of n-alkyl halides (from alcohol)

Synthesis of n- alkyl halides containing various number of Carbon atoms (C₁, C₂, C₃, C₄, C₅, C₆, C₇, C₈, C₁₀, C₁₂,) were synthesized by standard method From the corresponding alcohols and pure product were obtained.

(2) preparation of p-n alkoxy benzoic acids

Gray and jones, & Dave and vora have described the preparation of this acids following procedure was adopted base on these methods in this investigation. p-hydroxy benzoic acid (0.1 mole) corresponding alkyl halide (0.12mole) and KOH (0.25mole) were dissolved in 100ml methanol and reaction mixture was refluxed for three to four hours. 10% aqueous KOH solution (20ml) was added and refluxing continued for further two hours to hydrolyses any ester formed. The solutions was cooled and acidified with HCL to precipated .The corresponding alkoxy acids for the higher members the total refluxing period was extended to 7 to 8 hours. The alkoxy acids were crystallized from ethanol or acetic acid till they achieve constant melting points and transition temperatures.

Table: Preliminary Transition temp. of P-N Alkoxy benzoic acids

n-alkyl group	Transition temp ^o C		
	K-S Smectic	S-N Nematic	N-T Isotropic
Methyl	-	-	183.0
Ethyl	-	-	195.0
Propyl	-	143.0	152.0
Butyl	-	148.0	162.0
Pentyl	-	123.0	148.0
Hexyl	-	106.0	151.0
Heptyl	92.0	97.5	149.0
Octyl	103.0	106.0	146.0
Decyl	93.0	120.5	142.5
Dodecyl	97.0	132.5	136.0

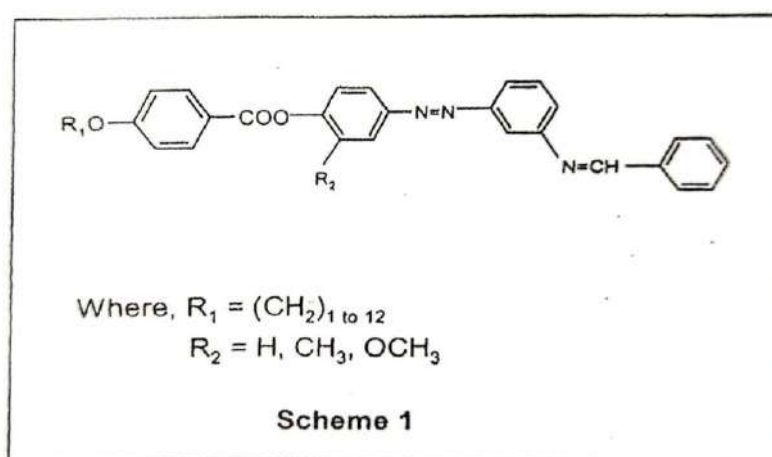
(3) preparation of p-n alkoxy benzoyl chlorides

p-n alkoxy benzoyl chlorides were prepared by heating the corresponding p-n alkoxy benzoic acids with freshly distilled thionyl chloride in water bath till evolution of hydrogen gas ceased. Excess of thionyl chloride was distilled off under reduced pressure using a water pump. The acid chlorides so left behind were directly used for further reaction without purification.

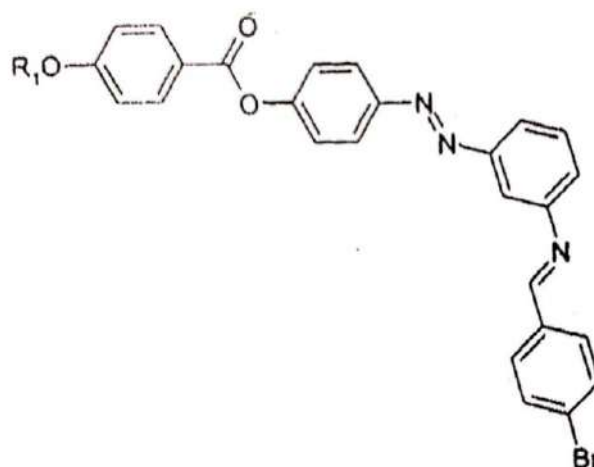
(4) preparation of 4 – (4' – n- alkoxy benzoyloxy)- phenyl azo-3''- benzylidene.

The mesomorphic characteristics of the homologues series are compared with geometrically identical homologous compound (fig.A)

Fig.



(A) 4-alkoxy-benzoic acid 4-{3-[(4-chloro-benzylidene)-aminol]-phenylazo}-phenyl ester Fig.



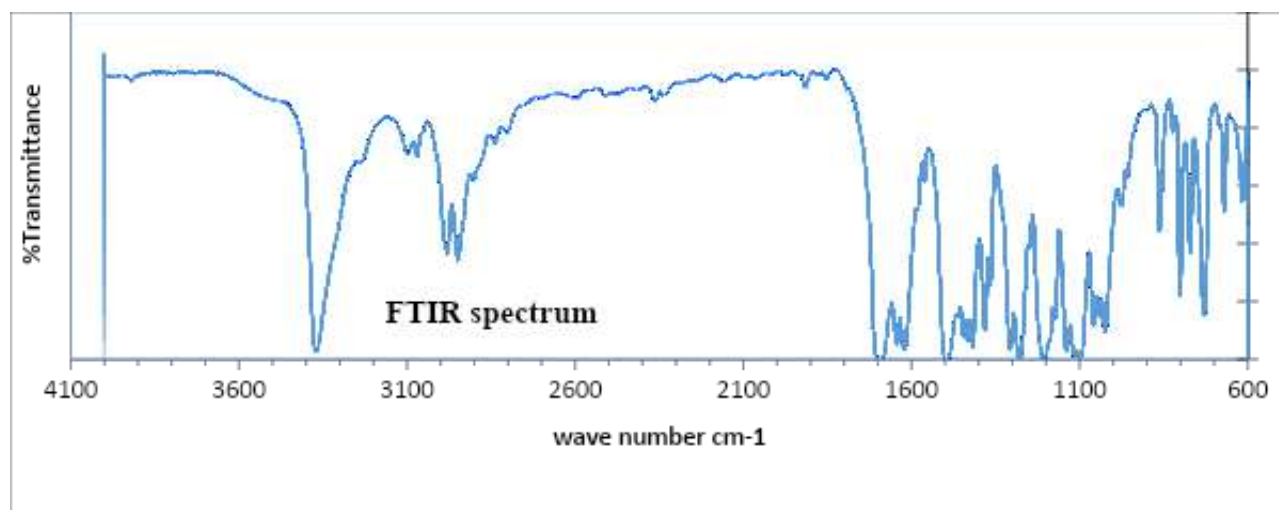
The homologous series possess fourth phenyl rings, linked through $-\text{COO}-$ and $-\text{N}=\text{N}-$ central Bridges, left n-alkoxy terminal group at the para position to $-\text{N}=\text{N}-$ unit at middle phenyl ring as common identical features .while they differ only by right functional terminal groups substituted at third phenyl ring. Therefor mesogenic behavior and degree of mesomorphism of the series under comparison is varied due to the variation of the forth phenyl ring only. The functional group are $-\text{Br}$ for series (4) respectively

(iv) Results & Discussion:

To Study the effect of different terminal group on mesomorphic properties of liquid crystalline compounds we have synthesized homologous series and confirmation obtained through elemental analysis

(1) Presence of Liquid Crystalline state and mesogens with IR Study

IR spectroscopy was conducted using a FTIR Spectrophotometer (NICOLET 6700, Thermo Scientific, USA). Spectrum was recorded in the wavelength region of $4000-400\text{ cm}^{-1}$. Liquid Crystals were mixed with KBr (potassium bromide-analytical grade, dehydrated) to avoid solid transition possibly inducing by extended grinding. The spectrum was scan at a resolution of 4 cm^{-1} .

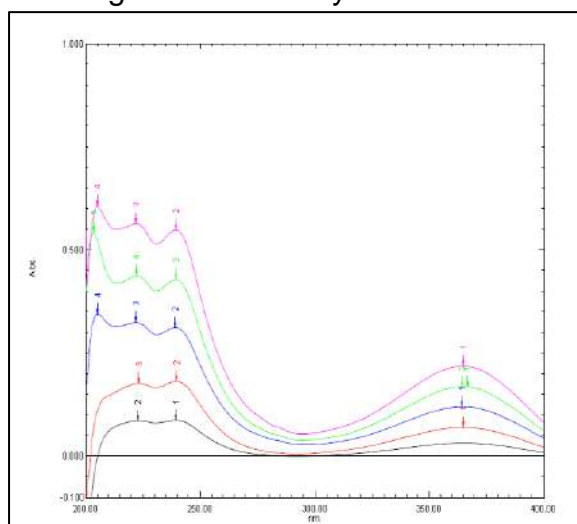


Major wave number noted:

SR	$\nu(\text{cm}^{-1})$
1	3370.79
2	3096.87
3	3069.66

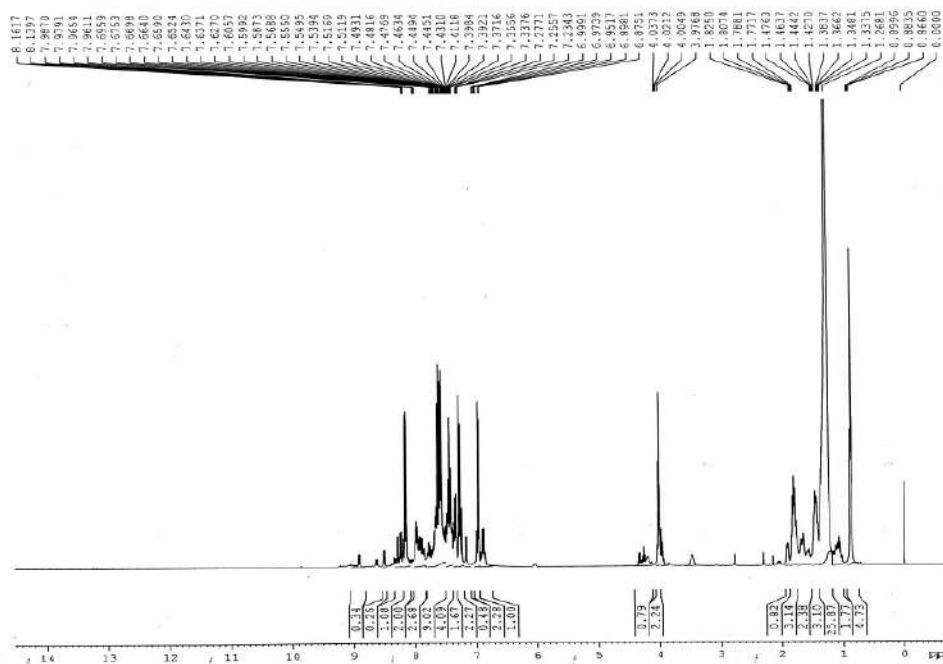
4	2980.11
5	2948.33
6	2838.15
7	1698.64
8	1643.45
9	1621
10	1496.32
11	1445.55
12	1417.48
13	1381.3
14	1364.06
15	1099
16	727
17	801
18	564
19	1205.39

(2) UV Spectrophotometric linearity: The compound with homologous series were also showing overall linearity determined and examined between 200nm to 400nm.



(3) Magnetic Properties and Identification

Compounds of Homologous series were subjected to $^1\text{H-NMR}$ spectral studies. $^1\text{H-NMR}$ spectra of representative compounds are shown in figure and chemical shifts are noted.



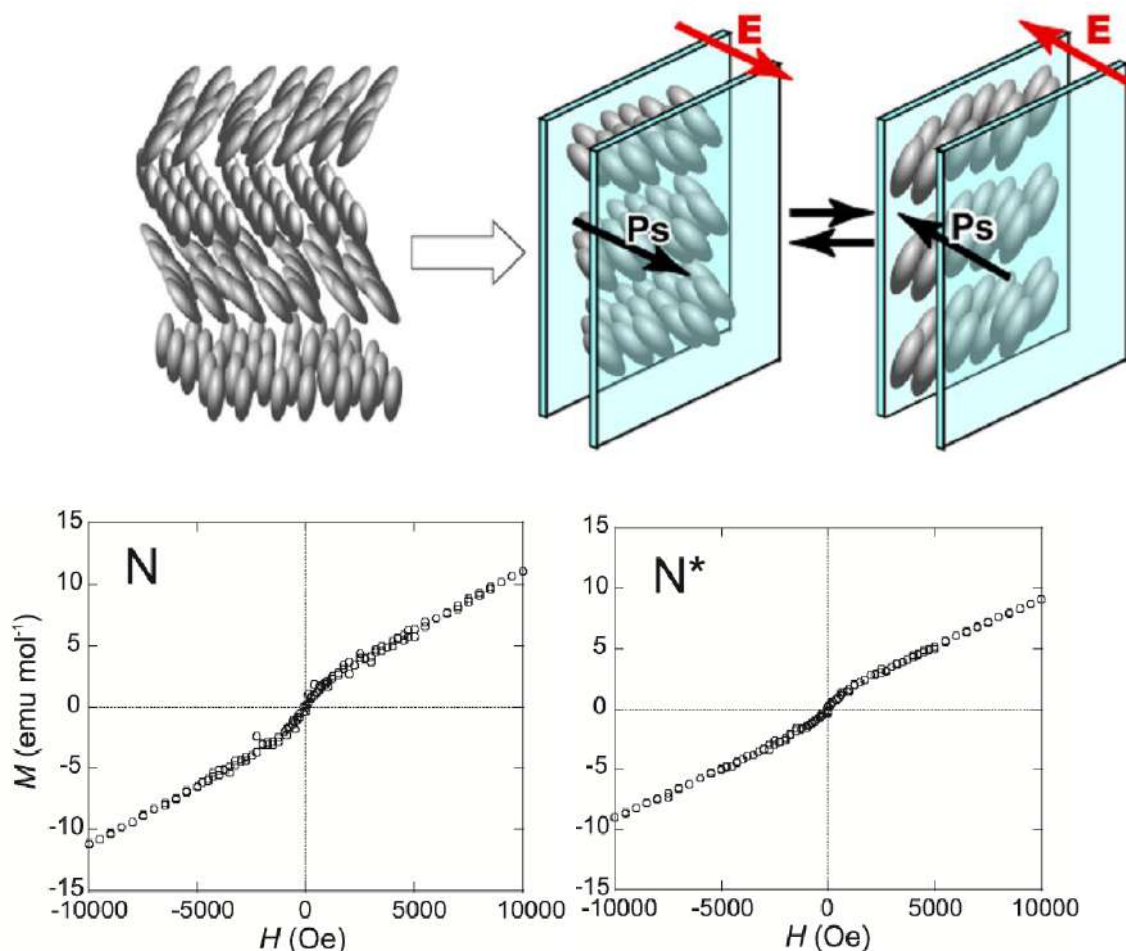
Phenyl multiplet	-CH ₃ Proton of aliphatic chain	-CH ₂ proton of aliphatic chain	-CH ₂ O Proton of alkoxy
6.80-8.28 (m)	0.85-0.89 (t)	1.25-1.85 (m)	4.00-4.05(t)
6.90-8.31 (m)	0.89-0.91 (t)	1.26-1.84 (m)	4.01-4.04(t)

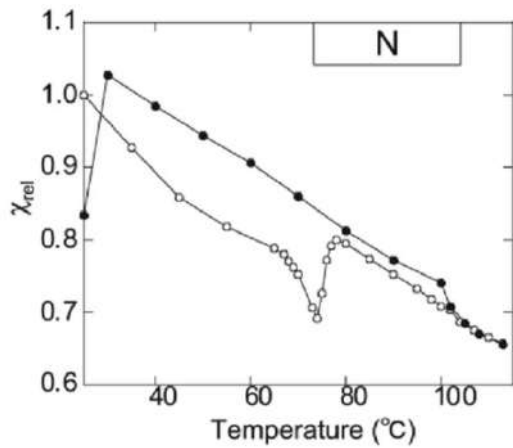
Since the magnetic properties such as $\Delta\chi$ – controlled molecular reorientation and magnetic interactions in all-organic magnetic LC Phases. It is known that rod-like metallomesogens with high viscosity are not always suited for the investigation on the alignment of LC molecules by magnetic fields. In contrast, LC compounds 12 with low viscosity, low phase transition temperature, and known principal g values of the NR moiety are considered to be a good spin-labeled candidate for the studies on the $\Delta\chi$ -controlled molecular orientation by weak magnetic fields. Therefore, to confirm that the magnetic-field-induced molecular alignment in the LC phases of 12 is $\Delta\chi$ diacontrolled, the $\Delta\chi$ para and $\Delta\chi$ dia values of 12 and the approximate magnitude of H_c for each LC phase of 12 were evaluated by EPR spectroscopy and SQUID magnetization measurement and by POM observation under variable magnetic fields, respectively (Uchida et al., 2009b).

First, the temperature-dependent $\Delta\chi$ para value of compound 12a (n=13) was calculated to be -1.7×10^{-6} emu mol⁻¹ at 300 K from the g-value obtained by EPR spectroscopy, while the temperature-independent $\Delta\chi$ dia value was calculated to be $+6.5 \times 10^{-5}$ emu mol⁻¹ from the experimental molar magnetic susceptibility of (\pm)-12a measured on a SQUID magnetometer. Thus, $|\Delta\chi_{\text{dia}}|$ has turned out to be 30 times larger than $|\Delta\chi_{\text{para}}|$; the molecular alignment of 12a by magnetic fields is definitely $\Delta\chi$ dia-controlled. Next, to identify the direction of molecular alignment in the bulk LC state under a weak magnetic field, the

temperature dependence of the experimental g-value (g_{exp}) of (\pm)-12a was measured at a magnetic field of 0.33 T by EPR spectroscopy. In the heating run, the g_{exp} of (\pm)-12a was constant at around 2.0065 in the crystalline state, then increased at the crystal-to-SmC phase transition, became constant at around 2.0068 in the SmC phase, then decreased abruptly to 2.0058 at the SmC-to-N phase transition, and finally returned to the level (\sim 2.0065) of the crystalline state in the isotropic phase. In the cooling run, the g_{exp} of (\pm)-12a was constant at around 2.0065 in the isotropic phase, then decreased at the Iso-to-N phase transition, became constant at around 2.0055 in the N phase, then increased to 2.0063 at the N-to-SmC phase transition, and finally increased to 2.0067 in the crystalline state.

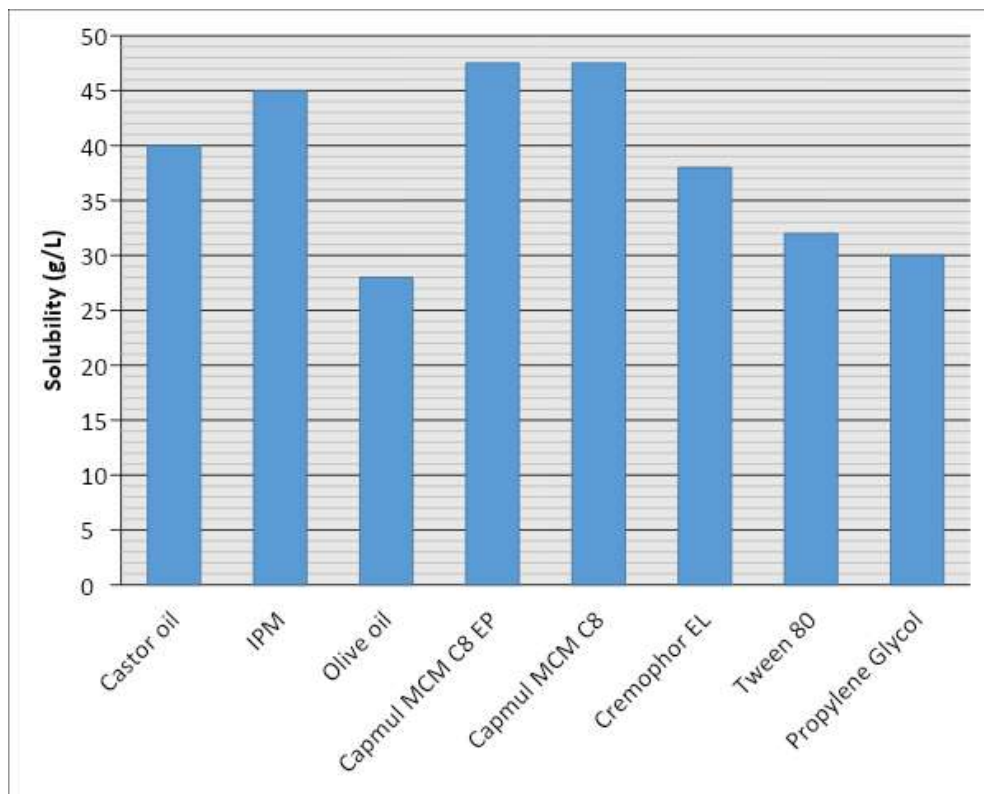
The natural Schlieren texture of the N phase gradually became dark with the increasing magnetic field until 0.5 T, resulting in the complete homeotropic orientation of molecules at 1.0 T, whereas the natural Schlieren texture of SmC phase of (\pm)-12a scarcely changed below 1.0 T, largely changed between 1.0 T and 1.5 T, and finished the change at less than 2.0 T to show another Schlieren texture, which is similar to the SmC Schlieren texture of (\pm)-12a observed under alternative homeotropic boundary conditions (Dierking, 2003). Accordingly, it has been concluded that the smectic layer planes became parallel to the glass plates at 2.0 T. Furthermore, no texture change was noted for N* and SmC* phase of (2S,5S)-12a below 5 T using the same experimental setup.





(4) Solubility Study in Different Oils, Surfactants & Cosurfactants:

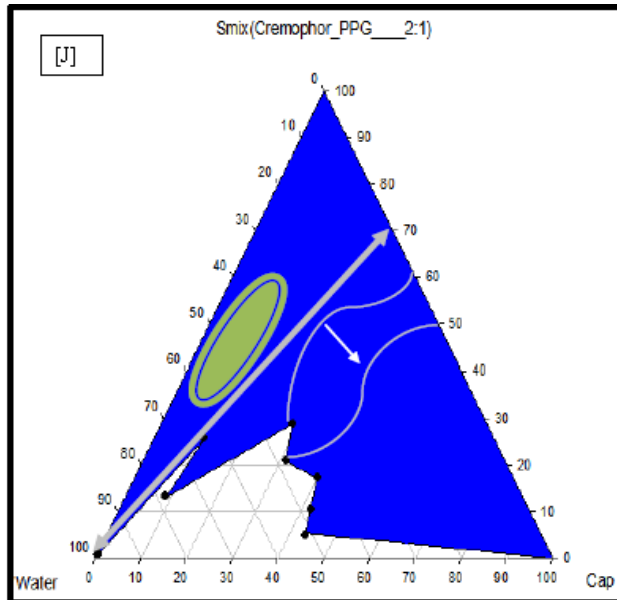
The solubility of crystalline phase was carried out by the incorporation of the 2ml of the different oils, surfactants and co-surfactants separately in screw capped plastic vial. These mixtures were vortexed for the 15 minutes and carefully observed for 72 hours at 24hours of interval after vortexing.



(a) Phase Diagram formation:

Surfactant was blended with cosurfactant in constant ratios (1:1, 2:1, 3:1). Aliquots of each surfactant and cosurfactant mixture (S_{mix}) were then mixed with oil at room temperature

(25°C). For each phase diagram, the ratio of oil to the Smix was varied from 9:1 to 1:9 as to get the maximum area in the ternary diagram. After equilibrium the samples were visually checked and determined for liquid crystalline phase. Phase Diagrams are used to construct and optimize the concentration of the Oil, Surfactant and Cosurfactant. The Plot Obtained here was chosen for the further preparation of the System.



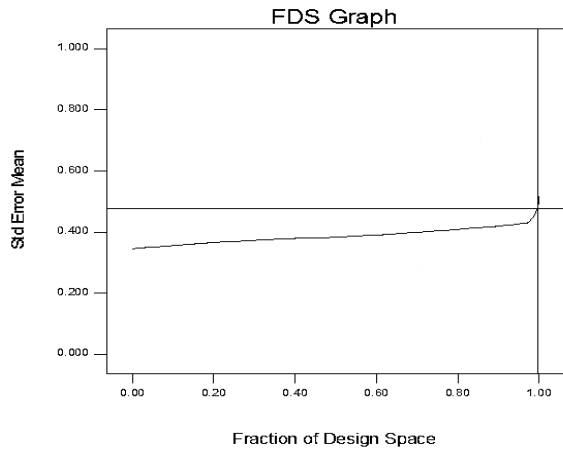
%Oil	%Smix	%Water
43.47826	4.830918	51.69082
41.88482	10.4712	47.64398
40	17.14286	42.85714
31.25	20.83333	47.91667
28.73563	28.73563	42.52874
8.791209	13.18681	78.02198
10.98901	25.64103	63.36996
0.19802	0.792079	99.0099
0.09901	0.891089	99.0099

(b) DOE Approach for Stable Liquid Crystal Formation:

The screening of the solution was based on the basis of the solubility and the suitability to the system. Azo-ester liquid crystal were further prepared with the use of DOE approach with size of droplet of liquid crystal, viscosity of the solution, zeta potential as dependent variable.

Type	3 ² Full Factorial Design
Number of Runs	9 x 3 = 27 Runs
Dependent Variables	3 (Liquid Crystal Size, Viscosity, Zeta Potential)
Independent Variables	2 (% Oil, % Smix)
Levels	-1, 0, +1.

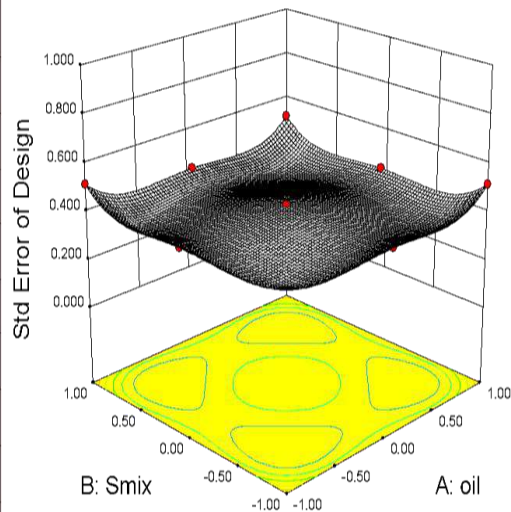
Fraction of Design Space was plotted to identify the Standard error of mean



Sr. No.	Parameter	Value
1	d "minimum detectable change in response"	1
2	s "standard deviation"	1
3	a "level of significance"	0.05

The Mixtures were taken according to below mentioned actual and coded value.

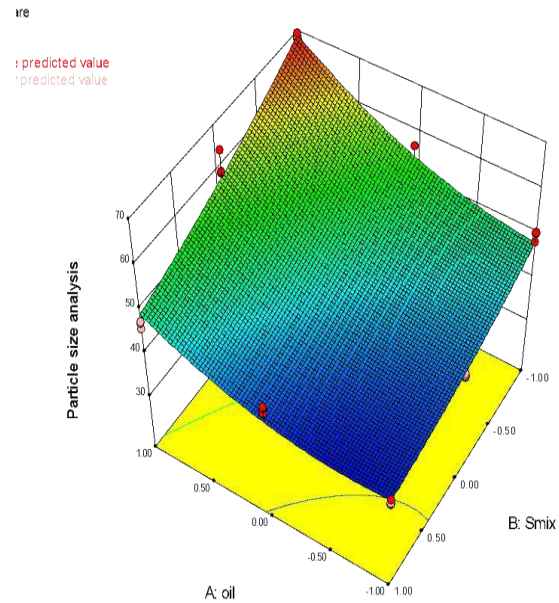
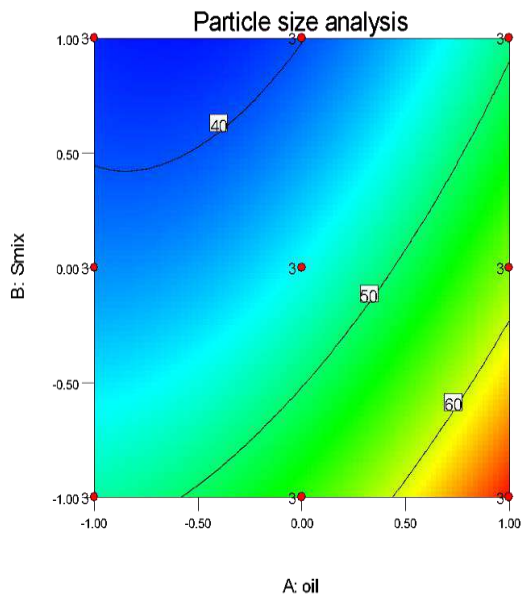
Test Runs	Actual Value		Coded Value	
	% Oil	% Smix	% Oil	% Smix
1	4	35	-1	-1
2	4	45	-1	0
3	4	55	-1	+1
4	6	35	0	-1
5	6	45	0	0
6	6	55	0	+1
7	8	35	+1	-1
8	8	45	+1	0
9	8	55	+1	+1



To ensure the 3^2 Full Factorial Design with statistically distributed for balancing standard error of design.

The contour and 3D surface plot for Particle size analysis, viscosity and zeta potential.

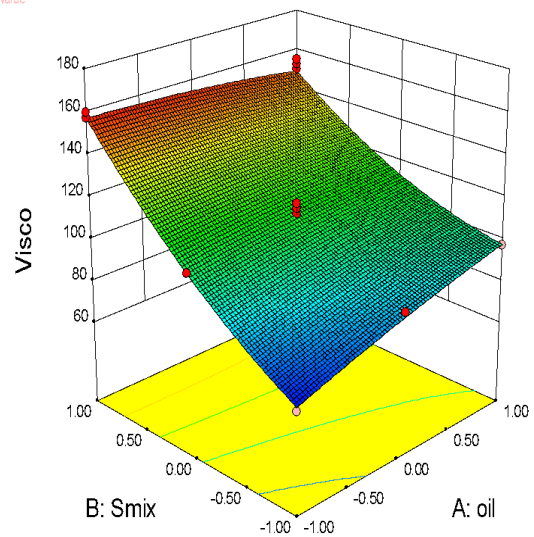
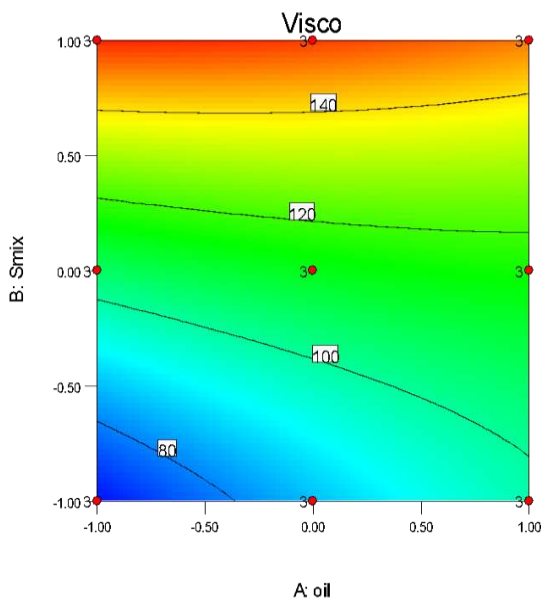
Particle Size Analysis Contour & 3D Surface Plot:



The above mentioned plot is matched for particle size with polynomial equation of quadratic model.

$$\text{Liquid Crystal Size} = 45.73 + \{7.88 \cdot \text{Oil} [p < 0.0001]\} - \{7.39 \cdot \text{Smix} [p < 0.0001]\} - \{2.52 \cdot \text{Oil} \cdot \text{Smix} [p = 0.0016]\} + \{4.01 \cdot \text{Oil}^2 [p = 0.0006]\} + \{1.57 \cdot \text{Smix}^2 [p = 0.1224]\}$$

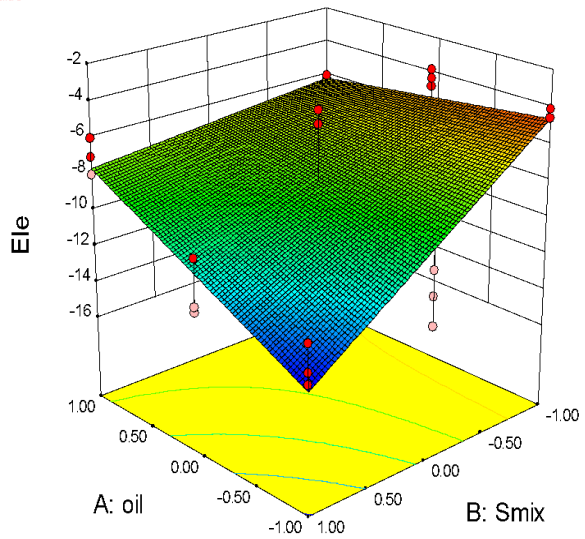
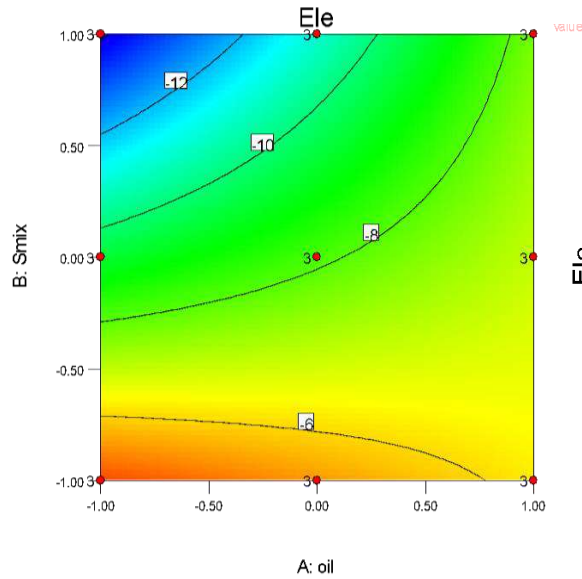
Viscosity Contour and 3D Surface Plot:



The above mentioned plot is matched for Viscosity with polynomial equation of quadratic model.

$$\text{Viscosity} = 112.15 + \{5.06 \cdot \text{Oil} [p < 0.0001]\} + \{34.86 \cdot \text{Smix} [p < 0.0001]\} - \{9.17 \cdot \text{Oil} \cdot \text{Smix} [p < 0.0001]\} - \{1.72 \cdot \text{Oil}^2 [p = 2244]\} + \{8.03 \cdot \text{Smix}^2 [p < 0.0001]\}$$

Zeta Potential Contour and 3D Plot:



The above mentioned plot is matched for Zeta Potential with polynomial equation of quadratic model.

$$\text{Zeta Potential} = -8.15 + \{1.23 \cdot \text{Oil} [p=0.0134]\} - \{2.75 \cdot \text{Smix} [p<0.0001]\} + \{2.01 \cdot \text{Oil} \cdot \text{Smix} [p=0.0017]\}$$

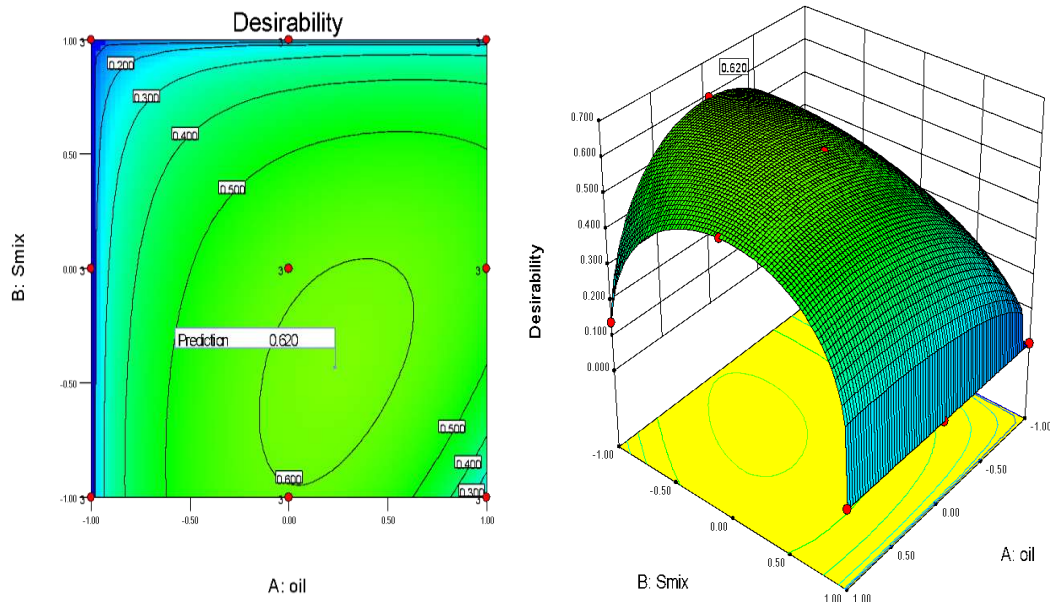
Check-point analysis was carried out for Viscosity and Particle size

Sr. No.	% Oil	%Smix	Droplet Size		Viscosity	
			P	O	P	O
1	-0.5	-0.5	46.2875	31.92	91.2873	95.5
2	+0.5	+0.5	46.75	24.95	131.514	130
3	+0.3	-0.9	42.4	42.5	148.73	147.5
Comparison of Data by Student's t- test						
4	p value		0.203		0.818	
5	Inference		Non-significant Difference		Non-significant Difference	

**Solution Suggested By
Design Expert 8.0.7.1, Stat Ease Inc., Minnesota, USA**

No.	Oil	Smix	Droplet Size	Viscosity	Zeta Potential	Desirability
1	0.23	-0.43	45.53	100.571	-6.871	0.620

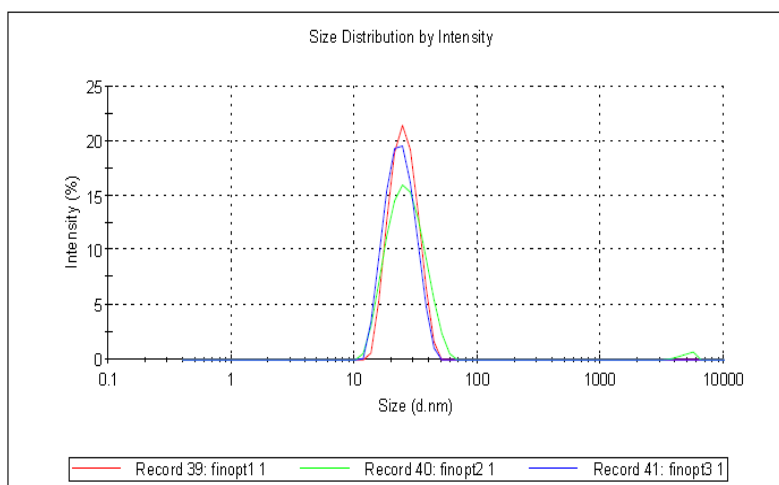
Contour and 3D Surface plot for Desirability



(5) Liquid Crystal Particle Size Determination:

The Liquid Crystals were prepared according to the Solution and outcome of Design of Experiments approach. The Characterization studies were carried out with different crystal size identification.

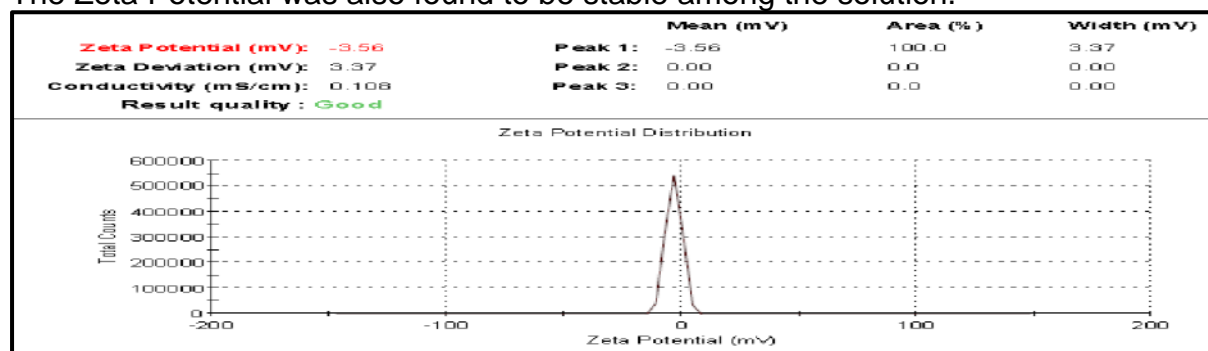
The size of Liquid Crystals identified with the help of Zetasizer (Malvern Instruments – USA) with Dynamic Light Scattering Technique. The range identified the size as 25.043 ± 0.586 d.nm as per below image.



Instrument	Technique	Particle Size
Zeta Sizer, Malvern Instruments, USA	Dynamic Light Scattering	25.043 ± 0.586 nm

(6) Zeta Potential Determination for static stability:

The Zeta Potential was also found to be stable among the solution.



(7) Texture Study determination:

The optical microscopy studies were carried out with polarizing microscope and observed using polarized light with crossed polarizer with sample in the thin film which was placed between the cover slip and glass slip. The compound of one of the series showed nematic phase at 80°C, 82°C & 84.6°C.

(v) Summary & Conclusion:

The homologous series is synthesized with p-n alkoxy benzoic acid and p-n alkoxy benzoyl chloride linkage with azo-ester compounds. Various mesogens were prepared and characterized thoroughly for the different mesomorphic correlation and magnetic properties. The initial identification with the help of FTIR spectroscopic correlation suggested the presence of various structural presence at different wave numbers. Also the homologous series showed the overall linearity in UV-Spectrophotometry. The liquid crystalline phase were identified for solubility with different oils, surfactant and co-surfactant which would give different mixture possibility for the liquid crystalline phase with the help of phase diagram. The phase diagram suggested that 23 % Oil mix, 43 % Smix shows highest solubility with stability for synthesized compound. The same were further taken for the synthesis with DOE 3² Full Factorial Design with variable of Particle size, Viscosity and Zeta Potential. Liquid Crystals which were prepared showed 25.053 ± 0.586 d.nm size in dynamic light scattering and zeta potential showed -3.56 mV. This along with texture study and magnetic study shows that unique properties were characterized and showed that metal-free formation of liquid crystals with very less particle size and very good particle stability. This Liquid Crystal Phase formulation showed nematic phase stability at different temperatures. The research is very nascent stage for the metal-free magnetic liquid crystalline phase and development in different microemulsion or gel or nanogel may open the strong opportunity of research.

Reference:

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Has the Minor Research Project Completed as per Proposal? --- YES

SIGNATURE OF THE PRINCIPAL INVESTIGATOR

SIGNATURE OF THE COINVESTIGATOR

REGISTRAR/PRINCIPAL