

SUMMARY

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LIQUID CRYSTALS AND LIQUID CRYSTALLINE POLYMERS.

SYNTHESIS AND EVALUATION OF THEIR PROPERTIES.

PART - I

Following mesogenic homologous series and polymer system were synthesized and their mesogenic properties are studied.

- I. Homologous series with one or two amido central linkages.
 - (i) 1,3-bis(4'-n-alkoxy benzoyl) amino phenols.
 - (ii) 1,3,-bis(trans-4'-n-alkoxy cinnamoyl) amino phenols.
 - (iii) 3,3'-dimethoxy-4,4'-bis(trans-4-n-alkoxy cinnamoyl) benzidines.
- II. Mesogens with positive dielectric anisotropy.
 - (i) 4(4'-nitrobenzoyloxy)-3-methoxy benzylidene-4"-substituted anilines.
 - (ii) 4(4'-nitrobenzoyloxy)-3-methoxy benzylidene-2"-chloroaniline.
- III. Discotic Compounds.
 - (i) 1,3,5-Tri(trans-4'-n-alkoxy cinnamoyloxy) benzenes.
- IV. Mesogenic Polymers.
 - (i) Co-Polyester of 4-hydroxy benzoic acid and 2-hydroxy benzoic acid.
 - (ii) Polyesters from 3,3'-dimethoxy-4,4'-dihydroxy benzalazine.
 - (iii) Polyesters from various dihydroxy naphthalenes with 1,2-bis(4'-carboxy phenoxy) propane.

V. Textures of different phases

PART - II

Following mesogenic compounds were used as stationary phases in Gas Chromatography.

- (1) 4(4'-Nitrobenzoyloxy)-3-methoxy benzylidene-4"-anisidine.
- (2) Ethyl 4(4'-Nitrobenzoyloxy)-3-methoxy benzylidene-4"-benzoate.
- (3) Cholesteryl -p-nitrobenzoate.
- (4) 1,3,5-Tri(trans-4'-n-dodecyloxy cinnamoyloxy) benzene.
- (5) Co-polymer of 4-hydroxy benzoic acid and 2-hydroxy benzoic acid.
- (6) Co-polymer of 4-hydroxy benzoic acid and 2(4-hydroxy benzoyl) benzoic acid.

PART - I

I. Synthesis of homologous series with one or two amido central linkages.

Three homologous series were synthesized and their liquid crystalline properties were studied.

- (1) 1,3-bis(4'-n-alkoxy benzoyl) amino phenols.

Ten compounds were synthesized by changing the terminal alkoxy group. The central linkage has meta (1,3-) substitution which imparts non-linearity to the molecules. None of the members exhibit mesomorphism. The compounds have high tendency to crystallize from the melt hence super-cooling is not sufficient to induce even "monotropic phase".

- (2) 1,3-bis(trans-4'-n-alkoxy cinnamoyl) amino phenols.

Five members were synthesized to verify whether the series exhibits mesomorphism or not. All the five homologues are non-mesogenic.

- (3) 3,3'-dimethoxy-4,4'-bis(trans-4-n-alkoxy cinnamoyl) benzidines.

Ten members of the homologous series were synthesized and their mesomorphic properties were evaluated.

First member is non-mesogenic and starts decomposing from 260°C. n-Propoxy to octyloxy homologues exhibit nematic phases only. Smectic phase commences from decyloxy derivative. The nematic phase persists even upto the hexadecyloxy member. One of the homologues, octyloxy derivative exhibits one crystal-crystal transition. The plot of transition temperatures versus the number of carbon atoms in the alkoxy chain shows usual odd-even effect for the nematic-isotropic transition temperatures, where, even members fall on the upper nematic-isotropic transition temperatures curve. The smectic-nematic transition temperature curve does not merge with nematic-isotropic transition temperature even upto the last members of the series. The nematic-isotropic transition temperature curve exhibits descending tendency as the series is ascended. The smectic-nematic transition temperature curve rises to the maximum and then falls off.

II Mesogens with positive dielectric anisotropy :

- (1) 4(4'-nitrobenzoyloxy)-3-methoxy-4'-benzylidene substituted anilines.

Nine ester schiff bases were synthesized by changing terminal substituent at one end of the molecule. Out of nine compounds, unsubstituted member and fluoro, nitro and carboxy methyl substituted members are non-mesogenic. Alkoxy, alkyl, carboxy ethyl and chloro substituted compounds exhibit mesomorphism. Thus the study has provided mesogens with positive dielectric anisotropy and helped to understand the effect of different substituents on mesomorphism.

III. Discotic Compounds :

(1) 1,3,5-Tri(trans-4'-n-alkoxy cinnamoyloxy) benzenes.

Seven members from butoxy to octadecyloxy derivatives were synthesized. Discotic compounds exhibit nematic type of phase from octyloxy derivatives. Smectic type phase does not appear upto the last member of the series. The transition temperatures are plotted against the number of carbon atoms in the alkoxy chain. The nematic-isotropic transition temperature curve falls steeply upto hexyloxy derivatives and then rises a little.

IV Mesogenic Polymers :

(1) Co-polyesters of 4-hydroxy benzoic acid (P-HBA) and 2-hydroxybenzoic acid (O-HBA) :

A mesogenic co-polyester was synthesized by condensing *o*-hydroxy benzoic acid and *p*-hydroxy benzoic acid. The mesogenic co-polyester was

used as the liquid crystalline stationary phase for the GC study in the IInd part of the thesis.

(2) Polyesters from 3,3'-dimethoxy-4,4'-dihydroxy benzalazine.

Eight co-polyesters were prepared by varying the ratio of monomeric diacid chlorides and hydroquinone, keeping the azine ratio constant. All the polyesters of Adipoyl chloride were non-mesogenic showing that aliphatic fraction could not be conducive to mesomorphism, even with the introduction of p-phenylene unit in the molecule of the polymer unit.

One of the polyesters with isophthaloyl moiety exhibited mesomorphism. This indicates that polymeric systems are more complex. Non-mesomorphism of other members may be due to the small change in the ratio of monomers which are conducive to mesomorphism.

All the polyesters were characterized by elemental analysis, IR spectra and solution viscosity.

(3) Polyesters from various dihydroxy naphthalenes with 1,2-bis(4'-carboxy phenoxy) propane. Four polyesters were synthesized having odd-number of flexible spacers having, 2,7; 2,3; 1,5; and 1,4-substituted dihydroxy naphthalenes. All the polyesters were synthesized by solution condensation method and the polymers obtained were all non-mesogenic.

In the present system the acid moiety has odd number of flexible

spacer. It seems that due to the odd number of methylene units, none of the polymers of this class exhibited mesomorphism. Hence the study has indicated that even a small variation in the structure can eliminate mesomorphism from the system.

All the polyesters were characterized by IR spectra, elemental analysis and solution viscosity.

V. Textures of different phases :

All the liquid crystalline compounds were screened under polarizing microscope, provided with a hot stage for the exhibition of liquid crystalline properties. The various textures observed were ~~as~~ *under*:

(1) The cholesteric phase of cholesteryl p-nitrobenzoate exhibits plane textures.

(2) The smectic phase of 3,3'-dimethoxy-4,4'-bis(trans-4-n-dodecyloxy cinnamoyl) benzidine exhibit focal conic or fan shaped texture. They are mainly smectic A type.

(3) The nematic threaded texture with lines of discontinuity ~~is exhibited~~ *by* 3,3-dimethoxy-4,4'-bis(trans-4-n-hexyloxy cinnamoyl) benzidine.

The nematic ~~Schlieren~~ texture ~~is exhibited by 3,3-dimethoxy-4,4'-bis(trans-4-n-dodecyloxy cinnamoyl) benzidine.~~ *nematic phase is exhibited by* Marble texture of 1,3,5-tri(trans-4'-n-hexyloxy cinnamoyloxy) benzene.

PART - II

The gas chromatography study was carried out by using standard method reported in the literature for liquid crystalline stationary phases.

The study involves following steps :

- (a) Preparation of stationary phase on chromosorb W-NAW 60/80 mesh.
- (b) Column - 1.78 m length 44.5 mm ID.
- (c) Conditioning of column.
- (d) Probes.

The liquid crystalline compounds used as stationary phases are recorded in beginning.

Typical organic compounds of different classes like n-paraffins, isoparaffins, aromatics, cresols, phthalates etc. were investigated for GC behaviour on the liquid crystalline material coatings including polymeric liquid crystals and discotics.

The study was divided in different phases based on the techniques used and the parameters measured.

(I) Inverse gas chromatographic studies :

Para-xylene (p-x) and n-undecane ($n-C_{11}$) were selected as probe solutes for inverse GC studies as these are typical of aromatic and paraffinic compounds which represent important class of organic compounds. Further they have relatively low activity coefficient in the studied material which

suppresses gas-liquid interface adsorption effects. Specific retention volumes (V_g , mlg^{-1}) were determined. These values of $\log V_g$ was plotted as a function of inverse column temperature.

The solution effect is shown by the changes in slopes in the various regions of different phases, i.e. solid, mesophase and isotropic regions of the graph. The slope of curves for both solutes changes indicating phase transitions, but here sometimes pretransition is observed due to strong polar groups or surface adsorption of the solutes. A linear solute molecules shows a smaller disruptive effect on nematics than bulky, non-linear molecules because the former fits in more reality into the ordered "Lattice". The results indicate that inverse chromatographic technique can be used to determine phase changes of the liquid crystalline materials.

(II) Retention behaviour and thermodynamic parameter :

In gas-liquid chromatographs, the various molecular interactions between the solute and the solvent (stationary phase) determine the relative volatility or retention characteristics of the solute. These interactions could be due to the simple dispersion forces, and/or other forces like dipole-dipole inductions (Debye), hydrogen bonding, complex formation, charge transfer etc.. In case of liquid crystal mesophase, molecular ordering/orientation are also operative towards shape selectivity.

In the present study various parameters like activity coefficient at infinite dilution, partial molar heat of mixing, entropy and partial molal heat of solution are determined from the chromatographic results.

(a) The activity coefficient at infinite dilution γ^∞ :

γ^∞ was calculated and graph was obtained by plotting $\ln \gamma^\infty$ vs. $1000/T$. Following conclusions were drawn based on the graphs.

(i) Stationary phase LC PNV-1 :

γ^∞ for n-C₁₁ varies between 2.6 to 5.8, where as the same for p-xylene lies between 1 to 2. Thus p-xylene shows near ideal solubility, indicating compatibility with the stationary phase while n-C₁₁ is relatively less compatible.

(ii) LC Stationary phase PNVO-2 :

γ^∞ for n-C₁₁ lies between 0.9 to 1.6 showing near ideal compatibility. p-xylene, has more affinity ($\gamma^\infty < 1$) indicating presence of stronger interactions with the solvent.

(iii) LC Stationary phase Ch-PNB :

γ^∞ values for n-C₁₁ and p-xylene show positive deviation from Raoult's law and have γ^∞ values in the same order of magnitude. This compound (Ch-PNB) may not therefore show much selectivity for paraffinic/aromatic hydrocarbons.

(iv) LC Stationary phase 12-CPG :

γ^∞ values for n-C₁₁ and p-xylene are less than one (negative deviation). This means, 12-CPG has stronger interactions with both the solutes.

For the polymeric stationary phases, as molecular weight values were not obtainable the $\gamma^\infty M$ were determined. Following conclusions were drawn based on the results.

(1) LC Polymer stationary phase PO-HBA :

The values of $\gamma^{\infty} M$ are 2-3 times higher for n-C₁₁ than for p-xylene. This indicates higher affinity of p-xylene than n-C₁₁.

(2) LC Stationary phase CPh-2 :

The values of $\gamma^{\infty} M$ are more of the same order for n-C₁₁ and p-xylene till certain temperature ($\approx 180^{\circ}\text{C}$), but at higher temperatures, the solubility of p-xylene increases relatively.

(III) Partial molar excess enthalpies and entropies were calculated for the mesophase regions of the liquid crystalline compounds, viz. PNV-1, PNVO-2, Ch-PNB and 12-CPG. Following conclusions were drawn based on the results.

(1) PNV-1 shows positive and higher slopes in the nematic region than in the isotropic region. While in solid region slope is negative. Thus the partial molar heats of mixing are more endothermic in the mesophase region. Also values of \overline{H}^{∞} and \overline{S}^{∞} are both higher in case of p-xylene than for n-C₁₁.

(2) PNVO-2 for p-xylene there is no slope change in the solid-isotropic region as this compound is monotropic nematic. The substrate thus behaving like a solid and an isotropic liquid throughout the \overline{H}^{∞} and \overline{S}^{∞} values are also lower.

For the same compound the behaviour is different for n-C₁₁ and has two distinct branches in the crystalline-isotropy regions. Here the \overline{H}^{∞} and \overline{S}^{∞} values are also higher.

(3) Cholesteric liquid crystal, Ch-PNB exhibits for $n\text{-C}_{11}$ and p-xylene in the mesophase region two linear branches till certain temperatures, but slopes are positive. This shows that there are some intraphase changes taking place in the cholesteric regions.

(4) 12-CPG, for both solutes, $n\text{-C}_{11}$ and p-xylene the slopes are less than those in the isotropic region. Heats of mixing are less endothermic in the ordered mesophase. The $\overline{H_e^\infty}$ and $\overline{S_e^\infty}$ values for p-xylene and $n\text{-C}_{11}$ are in the same order of magnitude.

(IV) Analytical Applications :

The application study was carried out by using six liquid crystalline stationary phases exhibiting smectic, nematic, cholesteric and discotic phases to separate four mixtures incorporating aromatics, n-paraffins (lower and higher), xylenes (o, -m, -p) constituents.

In all, twenty four chromatograms were obtained. In the present study the results incorporated are for the best separation observed. All the liquid crystalline phase do not exhibit identical behaviour.

The study has provided detailed information regarding the behaviour of different liquid crystalline stationary phases and the individual solutes and the solute mixtures. The trend in the results indicate that capillary column coated by LC may provide more useful data. This literature will be taken up in the future programme.