PART- II

II.1 INTRODUCTION

INTRODUCTION

II.1 LIQUID CRYSTALS IN GAS CHROMATOGRAPHY

Gas liquid partition chromatography is being practiced since 1952 (1). However, the use of liquid crystals as stationary phase in gas-liquid chromatography (GLC) was first reported during early sixties, almost simulataneously by Kelker (2,3) and Dewar and Schroeder (4). Application of gas chromatography in the study of liquid crystals is of great importance in modern chemical analysis and physico-chemical investigations, as can be seen from the wealth of publications on the subject (5-8). The topic was first reviewed by Kelker and Von Schivizhoffen (6); followed by Schroeder (7), and Janini (9) with up-to-date uses of liquid crystals for the separation of different classes of compounds.

Liquid crystals exhibit interesting solvent properties because of rod-like shape and the ordered arrangement of their molecules. These show long-range orientational order in which the rod-like molecules tend towards a mutually parallel alignment (6,7,9). This is beneficial as the solvents are separated on the basis of molecular shape in GLC using liquid crystals as the stationary phase. This unique solvent properties of liquid crystals were applied for the first time to the separation of positional isomers of various disubstituted benzenes (3).

The synthesis of new liquid crystal stationary phases with wide mesophase ranges and high phase transition temperatures has made it possible to separate compounds with high boiling temperature (10-13). Considerable experience has been gained with liquid crystalline stationary phases and a large number of compounds predominantly isomeric substituted benzenes have been separated using columns packed with liquid crystal substrates. The work of Kelker et al., (14) on the separation of anthracene-phenanthrene mixture using nematic stationary phases and the work of Kirk and Shaw (15) in which cholesteric stationary phases were used for the separation of steriod isomers are a few examples of separation of high molecular weight compounds on liquid crystalline stationary phases.

The high selectivity of liquid-crystalline stationary phases has enhanced the separation of polynuclear aromatic hydrocarbons (PAHS) as shown by Janini and co-workers (16-18) frequently in nanogram amounts. Their results and those of others have shown that high temperature liquid crystal can find practical application in the analysis of complex PAHS mixtures, PAH metabolites (19), steroid epimers (20) and bile acids (21). In addition other workers have employed high temperature liquid crystals for improved separation of optical isomers (22,23), geometric isomers of 3 to 5 rings of PAH (24), Polychlorinated biphenyls (25), Phenol ethers (26), isomeric olefins (27), aromatic marine pollutants (28), pharmaceuticals (29), polynuclear aza-heterocyclic air pollutants (30), PAH associated with combustion effluents (31) and in coal-tar pitch (32), as well as for the determination of carcinogens in cigarette smoke (18). Many problems, chiefly theoretical, involved in the analysis of PAHS on liquid crystal stationary phases remain, however unsolved. The group of liquid crystals used for this purpose so far is fairly small. It is not possible therefore to co-relate the separating properties of liquid crystal stationary phases with their chemical structure. Such data would allow one to plan the synthesis of new liquid crystal stationary phases possessing predetermined parameters.

The separation and identification of structural and positional isomers of mono, di- and tri- substituted alkylbenzenes have industrial importance. Retention indices (33,34,35) and a linear free energy relationship (36) have been used for structural determination of alkylbenzenes. Several workers have attmepted to separate alkylbenzenes using different commercially available stationary phases with columns of varying lengths and materials (37,38).

The separation of benzene, toluene, ethylbenzene and O-, m- and p- xylenes using a polar solid st. phase was carried out by Belyakova et al., (39). Di Corcia et al., (40) used carbopack C modified with 2,4,5,7-tetranitrofluorenone (TeNF) as a stationary phase to separate alkylbenzenes. There are several references (41-43) to the use of Bentone-34 in a modified form as a stationary phase giving improved resolution and separation but here too, the columns used are of considerable length (42) and the analysis time is long. Vernon and Khakoo (44) found liquid crystalline stationary phases to be superior to Bentone-34 and Maidachenko et al., (45) have patented the use of liquid crystal as a stationary phase for alkylbenzeneseparations.

Liquid crystalline stationary phases are particularly useful in separating close boiling positional isomers that have only small difference in polarity. Such isomers are very difficult to separate on conventional stationary phases. The reason that these compounds are well separated on liquid crystals is that the latter exhibit selective interaction with isomers of different molecular shapes. Most GLC studies reported so far have been carried out with the use of nematic liquid crystals. Except for a few compounds (46–48), another liquid crystalline phase, a smectic liquid crystal, has not been used for the GLC separation of positional isomers. This is because the separation factor in the temperature range of the stable smectic phase is worse than that in the nematic range inspite of the lower working temperature (6). Also disc-like liquid crystal stationary phases (8) have been reported for separation of mixtures of compounds as these have an ordered molecular structure analogous to that of rod-like liquid crystals (49). Disc-like liquid crystal stationary phases with wider ranges might have greater practical importance. At present, possibilities exists for studies on disc-like liquid crystals with a mesophase range of several dozen degrees (50).

II.1(A) GAS CHROMATOGRAPHY

(i) Introduction

In common practice gas chromatography is an analytical tool. it has an unparalleled potential in resolving components of a complex mixture. Recently gas chromatography is harnessed with equal faith for various analytical as well as non analytical applications (51), like in determination of thermodynamic and kinetic parameters involved in sorption processes (52), study of phase transitions (53,6), study of reaction kinetics (54) and determination of some properties of porous solids (55). Various advantages of GC are its high sensitivity (only a few mg sample generally being enough for analysis), high speed of analysis, excellent precision and accuracy, simplicity of instrumentation (with relatively low costs long life) and ease of operation of a gas chromatograph. Thus any sample that can be vapourised without thermal decomposition at the operating temperature, could be analysed by GC.

Born in 1952 (1), GLC has already attained adulthood. It is now a matured analytical technique based on scientific principles and is no more merely an art. To-day it finds applications in analyses of varied types - gases and pollutants, petroleum and petrochemicals, oils and fats, food and flavours, alcohol and beverages, drugs and vitamins, steriods and alkaloids, blood and serum, proteins and lipids, pesticides and fungicides, radioactive isotopes, elemental organic analysis and a number of miscellaneous materials.

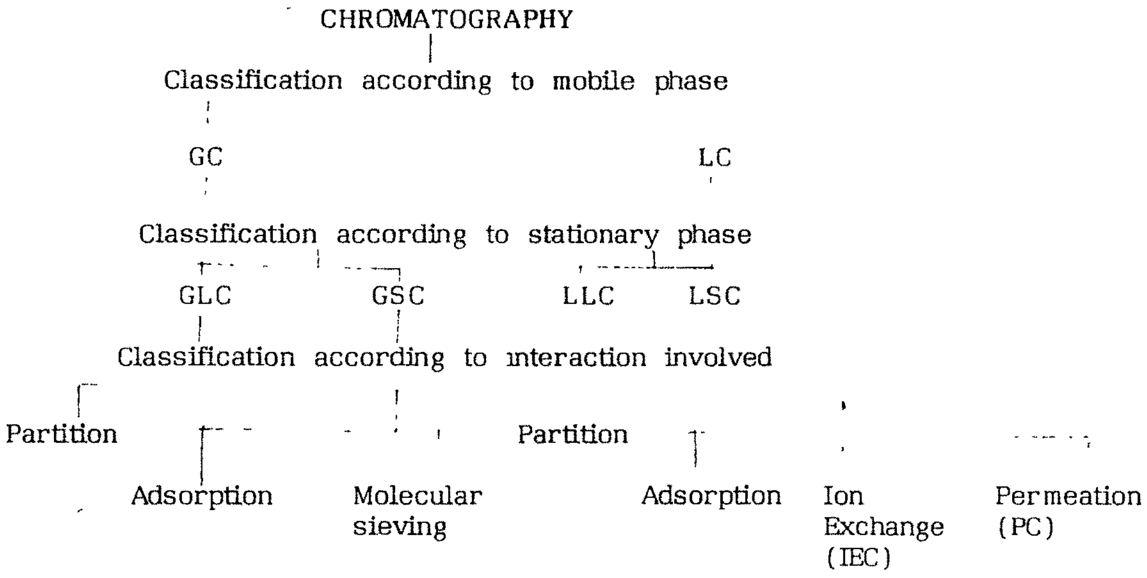
In the present studies the main objective has been to characterise newly developed liquid crystals and liquid crystalline polymers by gas chromatography through inverse GC studies, exploring solution thermodynamic parameters and generating GC retention data. Application of these liquid crystalline substrates for analytical ends viz., separation of organic mixtures of industrial significance has also been exploited.

(ii) Definition and Classification of Chromatography

"Chromatography is a physical process of separation in which the components to be separated are distributed between two phases - a stationary phase having large surface area (e.g. a porous solid) and a mobile phase (a gas or a liquid) moving in contact with the stationary phase" (56). This definition is similar to that put forward by Keulemans (57). In essence chromatographic process works on the principle of differential migration. The separation of the components of a mixture is achieved due to their differential migration produced under the influence of two forces, the driving force of a moving fluid and the resistive force of a stationary sorbent. Thus strain and Svec (58) define chromatography as a method of analysis in which the flow of solvent or gas promotes the separation of substances by different migration from a narrow initial zone in a porous sorptive medium.

Different forms of chromatography are named according to the physical state of mobile and stationary phases employed; then there may be further sub-classification according to the type of interaction between the solute and the stationary phase. Following chart shows this :

(G : Gas, S : Solid, L : Liquid, C : Chromatography)



Nomenclature based on the mode of employment is generally as follows :

Paper Chromatography	It is LLC wherein filter paper is used as support for stationary phase.
Column Chromatography	It is LSC wherein st. phase is taken in a glass column.
Thin Layer Chromatography	It is LSC wherein a thin layer of adsorbent coated on glass plate is used as stationary phase.

The chromatographic development with the mobile phase may be done in three ways :

Elution, Frontal Analysis or Displacement.

In elution technique a carrier fluid (eluent); which relatively inert towards the stationary phase, is kept flowing continuously and the sample is applied as a narrow band at the head of the stationary phase bed; the components of the sample are mutually resolved, but are in mixture with the carrier fluid. Actually it is this technique that is generally employed in GC. In frontal analysis the sample is continuously fed into the stationary phase where upon certain component of the sample are strongly sorbed (retained); the rest of the sample; thus; elutes out relatively purer till the sorbent bed is saturated with the sorbed components and through. In displacement technique, first the sample is sorbed on the stationary phase and then displaced by a fluid which has a stronger sorption (affinity) on the stationary phase than any of the sample components; thus the sample components, break through in the order of increasing affinity for the sorbent, the least sorbed coming out first.

iii Historical

Chromatographic separation dates back to 1850 when F.F. Runge, a German chemist used it to separate solution of various salts from a Spot, on filter paper. W. Ramsey employed this technique around 1905 for separating mixtures of gases and vapours. The term "chromatography" (meaning 'colour writing') was coined in 1906 by M. Tswell, a Russian biochemist. Tswell resolved plant pigments in the form of discrete coloured bands over calcium carbonate taken in a glass coloumn.

E. Heftmann has presented an interesting account on 'History of chromatography' (59). The history of gaschromatography has been described in good details by Ettre (60). Gas liquid chromatography ows its birth again to the origination of liquid-liquid chromatography (61), Nobel Laureate A.J.P. Martin, who together with A.F. James announced this new technique in 1952 (62). GLC was further developed with improved instrumentation and applications by N.H.Ray (1954) and B.N. Bradford, D.Harvey and P.E. Chalkley (1955). All these workers employed elution technique in GLC, which is common even today.

iv Principle of GC Separation

GC separation is accomplished in a tubular coloumn made of glass, metal, nylon or teflon. The column contains the stationary phase as sorbent. Solid adsorbents are packed in the form of fine size-graded powder whereas liquids are first coated over an inert, size-graded porous support and then packed into the column. A gas such as hydrogen, nitrogen , helium etc. serving as mobile phase, flows continuously through the column. It is called the carrier gas and serves to transport sample components in the column. The sample is introduced as a sharp plug of vapour at the carrier gas entrance end of the column. Here the components of the sample move under the influence of two forces-the driving force of the carrier gas and the retarding force due to selective sorption in the stationary phase. A component having strong affinity towards the stationary phase will move relatively slow compared to the one that has less affinity for the sorbent. Thus different components move with different speeds along the column of sufficient length and separation of sample components is thus achieved in GC as they arrive at the column end at different instants. A suitable detector is placed at the column outlet to detect the components eluting out of the column and the detector signal is recorded by a suitable recorder. Such a 'recorder trace' for any sample, which is a multitude of peak shapes on a common baseline, is called the 'chromatogram' of the sample.

v Basic Parameters and Relationships in GC

Since in the course of the present work various GC parameters have been extensively employed, it would be desirable to introduce them in brief. Referring to Fig. 1 , the various terms used are described as follows (57,63):

(1)	t_R	retention time, the time lapsed between sample introduction and the appearance of peak maxima.
(2)	t_M	retention time of a solute (usually air) that has no affinity for the stationary phase (gas holdup time).
(3)	t'_R	adjust retention time $(t_R - t_M)$
(4)	h	peak height
(5)	w	peak width at half height
(6)	W	peak width at base
(7)	L	column length
(8)	Ø	Column diameter (subscripts : i=internal & O=outer).
(9)	T_a	absolute ambient temprature.
(10)	T_c	absolute column temperature

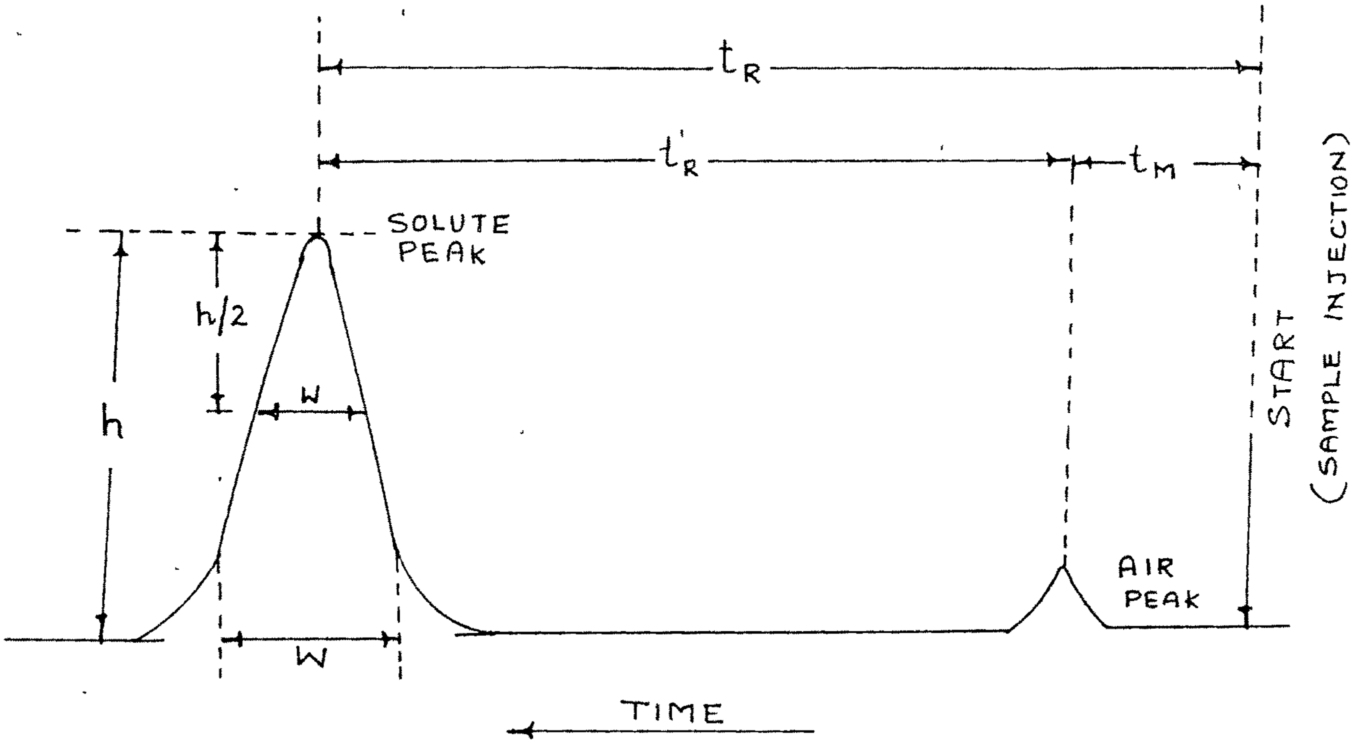


FIG 1. PEAK PARAMETERS

(11)	P	carrier gas pressure (subscripts : i=column inlet; & O=column outlet)
(12)	F_o	volume flow rate of carrier gas at column outlet measured by a soap film flowmeter.
	F_c	Volume flow rate of dry carrier gas at column outlet at column temperature
(13)	W_L	wt. of liquid phase in the column.
(14)	j	carrier gas compressibility correction factor $= \frac{3}{2} \times \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}$
(15)	V_R	retention volume of a solute = $t_R F_c$
(16)	V'_R	adjusted retention volume = $(t_R - t_M)F_c$
(17)	V^o_R	corrected retention volume = $V_R\ j$
(18)	V_N	net retention volume = $(t_R - t_M)\ F_c j$
(19)	V_g	specific retention volume $= (t_R - t_M)\ F_a j \times \frac{273}{T_a} \times \frac{1}{W_L} \times \frac{P_o - P_w}{P_o}$ where P_w = saturation water vapour pressure $F_a = \frac{F_o\ (P_o - P_w)}{P_o}$

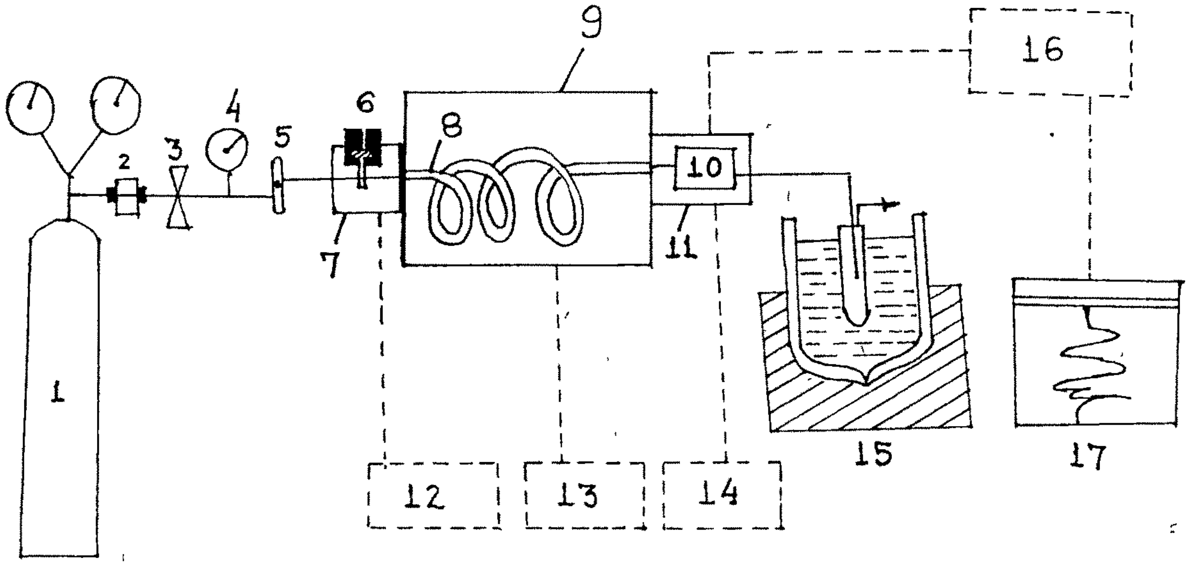
II. 1(B) Components of a Gas Chromatographic Setup

A schematic assembly of a GC system is as shown in Fig. 2 . Thus the main components of a GC setup are :

(i) <u>Carrier Gas</u>

The main purpose of carrier gas in GC is to transport sample components through the column. In chosing a proper carrier gas following considerations are taken into account :

SCHEMATIC OF A GC-SYSTEM



1 CARRIER GAS SOURCE

2. FILTER DRIER

3. PRESSURE CONTROL VALVE

4. PRESSURE GAUGE

5. FLOWMETER

6. SAMPLE INJECTION PORT

7. VAPOURISER HEATER

8 COLUMN

9 COLUMN OVEN

10. DETECTOR

11 DETECTOR OVEN

12, 13 AND 14.
-HEATER CONTROLS

15 FRACTION TRAP

16 DETECTOR ELECTRONICS

17 RECORDER

FIGURE. 2.

(1) It should be inert, i.e. it should not interact with sample, stationary phase or contacted hardware.

(2) It should be suitable for the detector which should respond to the sample analysed.

(3) It should give best column performance consistent with desired speed of analysis.

(4) It should be readily available in high purity.

(5) It should not cause the risk of fire or explosion hazard.

(6) It should be cheap.

The usual carrier gases used in GC are H_2, He, Ar and N_2. For thermal conductivity detector (TCD) either H_2 or He are used as carrier gas due to their higher thermal conductivities compared to that of sample components. For TCD the difference between thermal conductivity of sample components and that of the carrier gas should be as large as possible. Between H_2 and He the latter should be preferred for safety reasons, but H_2 is used due to being cheap and whenever He is not available.

With flame ionisation detector (FID) H_2 is used in producing a flame in the detector and hence should not be used in general as the carrier gas. Thus N_2, Ar or He could be used with FID. From theoritical consideration a high molecular weight gas (e.g. N_2 or Ar gives better resolution whereas a lighter gas (He) is preferable where rapid analysis is desired.

Electron Capture Detector (ECD) is generally operated with N_2 as carrier gas of purity better than 99.9 mole %.

The commonly employed source of carrier gas is a compressed gas cylinder, fixed with a pressure regulator, for reducing cylinder pressure to 0-10 kg/cm^2. Immediately after this, a filter drier is installed. Next there is a good needle valve for fine control of inlet pressure to the column and a pressure guage to read this pressure. Actual flow rate of carrier gas is measured at the column outlet with the help of soap bubble flow-meter shown in Figure 3

For hydrogen carrier gas, laboratory model electrolytic hydrogen generator's are also available - these produce hydrogen of purity better than 99.99% at flow rate of 200-300 ml/min and upto 60 psi pressure.

(ii) Sample Introduction System

A sample is introduced into the GC column in the form of a sharp plug through an injection port. The injection port contains a gas-tight self-sealing rubber septum through which the sample is injected with the help of a microlitre hypodermic syringe. Immediately after introduction, the sample is vapourised and flown into the column with minimum band broadening or back diffusion.

Liquid samples are generally introduced by hypodermic syringes in few μl quantities. Gases can also be injected by similar synringes which have gas tight (teflon tipped) plunger and are of larger capacity. The liquid syringe should be cleaned with suitable solvents and then dried using

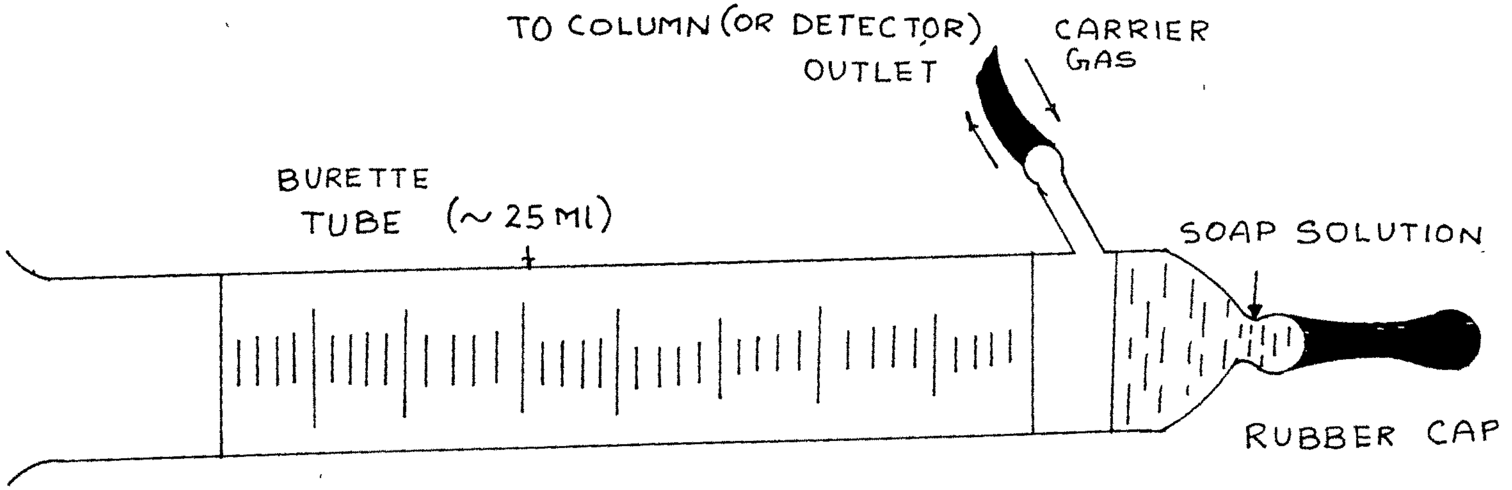


FIG 3. SOAP BUBBLE FLOWMETER

filteration flask (rubber stoppered with a hole to tightly hold the syringe) and filter pump. Occassional cleaning with chromic acid/soap solution may also be necessary to remove sludge like contaminants. To take sample in the syringe, the liquid is drawn in a few μl more than to be injected and flushed out. This is repeated at least once more. The liquid sample is pumped in and out a few times to expell any air bubble and drawn slowly a few μl more than required without any air bubble. The needle from the container is removed and wiped off with tissue paper. Holding it at the level of eyes, the desired volume is adjusted. The oozing out droplet is removed by touching with a tissue paper. The syringe is held only at the upper flange and not at the glass barrel. A little air plug is also drawn in. Now the needle is inserted into the injection Septum and the sample injected quickly.

(iii) Column

Column is said to be the heart of a GC system. Three types of analytical columns are used in GC : packed, open tubular, support coated open tubular (SCOT) and porous layer open tubular PLOT . They are discussed below.

(iv) Packed Column

These are prepared by packing metal or glass tubings with granular stationary phase. For GSC the columns are packed with size graded adsorbents or porous polymers. Charcoal, Alumina, Silica gel, and molecular sieves are the most commonly employed adsorbents. They are usually preferred in coarse mesh size 40/60 and are generally taken in 1/4 inch OD columns having length 2-4 metres. Various porous polymer beads are available in the market under the trade name Porapak, types P, P-S, Q, Q-S, R, S, N and T (Waters Associates Inc.) and Chromosorb types 101, 102, 103 etc. (Johns-Manville).

For GLC the packing is prepared by coating the liquid phase over a size-graded inert solid support. Following types of solid supports are generally available in the market. Celite 545 and Chromosorb (John-Manville, New York), Gas Chrom (Applied Science Lab. Inc. Pa.), Anakrom (Analabs Inc. Conn.), Celite (B.D.H., Eng.), Varaport 30 (Varian AG), Fluro Pak-80 (Fluoro-Carbon Co.) Kelf 6051 (Minnesota Mining and Manfg. Co.), Fuoroport T (Applied Science) and Tee-Six (Analab.), Glass beads, Microporous polyethylene, Porovina etc. are also used. These supports may also be thermally/chemically treated to modify the structure and/or enhance inertness the trade names are indicated accordingly.

(v) Liquid Phase

The main requirements in choosing a liquid for stationary phase are :

(1) It should be practically non-volatile and stable at the operating conditions.
(2) It should show selectivity for the components to be separated.
(3) It should have reasonable compatibility for the sample components.

(4) It should have low viscosity at the operating temperature and

(5) It should dissolve in a volatile solvent and should have wettability on support surface.

Liquid phases are generally classified in following groups.

(1) Non-polar: e.g. hexadecane, squalane, methyl silicone gum SE-30 etc.

(2) Polar : e.g. Dimethyl sulpholane, oxydipropionitrile, versamid-900 etc.

(3) Intermediate : e.g. Didecylphthalate, SE-52, DC-550 etc.

(4) Hydrogen bonding : e.g. Diglycerol, polypropylene glycol, tetra hydroxy ethylene diamine (THEED) etc.

(5) Specific : There are some stationary phases which interact with specific groups of solutes forming loose chemical complexes and are employed for specific separations only. For example :

(i) Saturated solution of $AgNO_3$ in ethyleneglycol, glycerol or triethylene glycol exhibits marked selectivity for olefins forming adducts with olefins. The olefins are, thus, retained much longer relative to paraffins which pass out quickly.

(b) Bentone-34 in conjuction with silicon oil is an important stationary phase used for resolution of C_8- aromatics (ethyl benzene -p,m- & O-xylenes); the selective nature of Bentone-34 is due to its layer structure.

(c) Tetra cyano ethyle penta erithritol (TCEPE) is super selective for aromatics. Here benzene elutes out after C_{10}-C_{13} saturated hydrocarbons.

(d) Liquid crystals are another type of phases that provide specific separations. They are described in Table A

TABLE - A

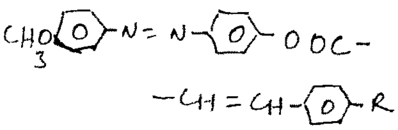
List of some Liquid Crystals used as stationary phases in GLC.

Sr. No.	Stationary Phase	Application
1.	P-azoxy anisol (PAA)	m,-p-xylene (2,3); m-,P-dialkyl benzenes (64) vapour pressure measurements (65), diethyl benzene, cresol, its methyl ethers and acetates, fluoro chloro benzene, fluorobromobenzene, fluroiodobenzene, fluroanisole, fluorobenzylchloride, flurobenzaldehyde, fluoronitrobenzene, dichlorobenzene, chlorotoluene, chloroaniline, chloromethylbenzoate, bromoanisole, dimethoxybenzene, diethoxybenzene, methyl methyl benzoate, methyl chloromethyl benzoate, methylnitrobenzoate, methylaniline, m-, p-di-i-propyl benzene (66)
2.	P-azoxy phenetole (PAP)	mono-, dimethyl naphthalenes (67), retention on solid PAP (68), eutectic mixtures (69,70), aromatic hydro carbon mixture (71).
3.	p,p'-dihexyloxy azoxy benzene	divinyl benzenes, thermodynamics (10).
4.	p,p'-di heptyloxy azoxy benzene and p-(p-ethoxyphenylazo)-phenylundecylenate.	n-alkanes, cyclohexane, benzene, xylenes (85).

Table - A ..contd..

5.	bis-(phenetidyl)-terephthaladehyde	n-hexadecane, methyl laurate, dimethylsebacate, O-xylene, O-, m- and p-cresol, O-, m- and p-dimethoxy benzene, O-, m- and p-dimethyl phthalate, O-m- and p-dibromobenzene etc. (14).
6.	4,4'-bis(benzylidene) benzidine.	(14).
7.	bis(p-methoxy benzylidene--trans-4,4' diamino-stilbene	(14).
8.	N,N'-bis(p-methoxybenzylidene)- α,α'-bi p-loluidine.	Separation of 2-6 ring polycyclic aromatic hydrocarbons including carcinogenic compounds (17,24), isomeric alkylnaphthalenes (28), androstanol and cholestanol epimers (20), isomeric benonaprofens (72) and azaheterocyclics (30).
9.	Esters of the type 	Aromatics (47).
10.	Esters of the type 	Aromatics (47).
11.	N,N'-bis(p-phenyl benzylidene)- α,α'-bi-p-toluidine and N,N'-bis-(p-hexyloxy benzylidene)--α,α'-bi-p-toluidine.	Polycyclic aromatic hydrocarbons including carcinogenic compounds and cigarette smoke (17,18).

Table - A ..contd..

12.	2,6-naphthalene-bis-(b-n-hexyloxybenzoate)	O-,m-, p-isomers of dichlorobenzene and dimethoxybenzene, m-,p-isomers or chlorotoluene, cresol methyl ethers, methyltoluate, methylacetophenone (73,74), 1 and 2 substituted naphthalenes (75).
13.	P-hexyloxy cinnamic acid derivatives of 2,5-diphenylpyrimidines.	Fatty acids, methylamisols, dimethylbenzenes chlorotuelenes, etc.. (77)
14.		Butyrylacetic acid ester, chlorobenzaldehydes, chloro benzotrichlorides etc. (78).
15.	(p-ethoxy phenylazo) phenyl crotonate	benefin, trifluralin (29).
16.	4-hydroxy-4'-methoxy azobenzene-4-methoxy cinnamate.	Oleic, elaidic and stearic acid separation, traces of 2-hydroxy naphthalene in 1-hydroxynaphthalene, o-,m-, p-methylphthalate, 1- and 2- ethyl naphthalenes.

vi. Column Oven

These are designed either for isothermal or programmed temperature operations. Their range of application is mostly from ambient to 400°C. A temperature programmer facilitates controlled increase of oven temperature during analysis. For good temperature programming, following requirements should be met :

(1) Dual column system : This compensates for bleeding of liquid phase from columns during increase of temperature.

(2) Separate heaters for injector (dual), column oven and detector system.

(3) Differential flow controllers : These help to maintain a constant flow rate of gas in the columns which otherwise decreases due to increase in temperature.

(4) A programmer with a range of programming rates, say 0.25°C to 25°C per minute.

(5) Low mass column oven for rapid heat transfer.

(6) Thin walled columns, preferably of stainless steel.

(7) Low liquid phase loading.

(8) Pure, dry carrier gas.

(9) Stable, nonbleeding injection septums.

(vii) Detector

Three types of dectors are in common usage, namely : TCD, FID & ECD. TCD filaments are made of platinum, tungsten or alloys of tungsten -rhenium as these have large temperature coefficient of resistance and are corrosion resistant. A TCD, in general, responds to all substances except the carrier gas. TCD is a concentration sensitive detector and its sensitivity depends on the type of carrier gas, filament current, detection block temperature and flow rate of the carrier gas. Increase in filament current increases response of TCD, but damage of filament can be there. So, with N_2 as carrier gas the safe upper limit of filament is 125-175 mA and with He/H_2 as carrier gas it is 300-350 mA. Also block temperature should be as low as possible for high sensitivities. The detector has to be heated enough to avoid condensation of eluted components. A precaution with TCD is that the carrier gas is made 'ON' first and then only the filament current/ detector block heater is switched on. Similarly, the carrier gas is turned 'Off' only after switching off the detector current and cooling down of the detector block. This avoids damage of the filaments and ensures long detector life.

In FID, a tiny flame of hydrogen is maintained at a capillary jet made of quartz, stainless steel or platinum, air or oxygen is introduced through a side by inlet for supporting the combustion. Column effluents are led into the flame wherein, ionisation of components may take place. An electrode system located close by picks up the ionisation current which is then amplified and suitably fed into a recorder. Thus, when no sample component is eluting, the recorder traces a steady base line. When a sample component elutes and passes through the flame, its molecules are ionised and the resulting ionisation current after amplification is fed to a suitable recorder that traces the corresponding curve. FID responds to almost all organic compounds. It is insensitive to following compounds :

Nobel gases, O_2, N_2, CO, CO_2, H_2O, Nitrogen oxides, NH_3, H_2S, SO_2, CS_2, COS, $SiCl_4$, $SiHCl_8$ and SiF_4.

For best FID performance, optimum flow rates of carrier gas H_2 and air/O_2 are to be used. Generally, 30 ml/min for carrier gas as well as H_2 and 300 ml/min for air is found to be most suitable. Unlike TCD, it is not concentration sensitive but is rather mass sensitive i.e. it gives response proportional to total mass of component (or carbons) entering the detector and is therefore independent of the carrier gas flow rate. This detector can be used upto 400°C.

ECD is a selective detector. It responds to only those compounds whose molecules have an affinity for electrons. e.g. Chlorinated compounds. It has very little response for hydrocarbons. The upper temperature limits are 200°C for tritium and 350°C for Ni^{63} detector. A short coming of this detector is that it has a very narrow linear range. This problem can, however, be solved by proper calibration and adjustment of sample size. For best operation, clean carrier gas and flow lines, use of filter drier, non-bleeding liquid phase and appropriately heated detector is used.

(viii) Recorder

The signal from a gas chromatograph is continuously recorded as a function of time, generally by a potentiometric recorder. A recorder of 1-10 mV full scale deflection ($\sim$10 inch) and 1 second or less response time is suitable. Variable chart speed between o.5-50 mm/min are employed.

The input signal is continuously balanced by a feed back signal employing a servo mechanism, a pen connected to this system moves proportionally along the width of the chart paper, thus recording the signal. The chart paper moves at a fixed speed along its length.

Before operating a recorder, its zero is adjusted with the input zero, otherwise the baseline would shift with changes in attenuation of the signal.

(ix) Integrator

It gives simultaneous measurement of areas under chromatographic peaks by mechanical/electronic means. Manual techniques for peak area measurement are time consuming, tedious and generally carry less precision. Thus integrator in a GC setup is always preferable. There are two types of integrator (i) Ball and Disc integrator (ii) Electronic integrator. The second gives high precision in peak area measurement but Ball and Disc integrator is fairly cheap.

II.I.(C) Properties of Liquid Crystals Significant for GC

With liquid crystals, it has been found that they should have different properties as solvents compared with conventional isotropic liquids.

Liquid crystals intended for use as stationary phases must meet different requirements than those designed for other uses, e.g. displays, There exist, however, commercial liquid crystals that can be applied both in mixtures used for displays and in gas chromatography (76).

From numerous investigations of isotropic liquids and solids with regard to their suitability as stationary phases, the following properties of substances have been found to be of decisive importance in their application to gas chromatography.

(i) Temperature range of liquid-crystalline phase (melting point, transition points, clarification point).

(ii) Vapour pressure, specific heat, density and coefficient of thermal expansion.

(iii) Surface tension, adhesive power on the carrier, texture of mesophase and their dependence on the interface, orientation effects.

(iv) Viscosity (and diffusion) properties.

(v) Behaviour in external fields.

(vi) Mixed phases : influence of mixture components on the transition points of mesophases, solubility of the solid substance in solvents.

(i) Temperature Range of the Liquid Crystalline Phase

Liquid crystalline stationary phases should have a high thermal stability. They should not decompose at the operating temperature.

Any consideration of the suitability of liquid crystalline phases for GC must place "selectivity" requirements. Selectivity is understood to mean only the solvent influences on the activity coefficients and their temperature dependence. To obtain short elution times, it is advantageous to use high operating temperatures. However, because inter molecular forces generally decrease with increasing temperature, one is forced to lower the temperature until the inter molecular forces are of sufficient magnitude to enhance selectivity. Therefore, a stationary phase should have a high temperature stability and melting point be as low as possible.

A mesophase ideally suited for use in GC would have a melting point at room temperature or lower and a clarification point as high as possible. In GC with temperature programming, use is made of liquid crystals with a wide mesophase range, low melting point and high clearing temperature (78,24).

The widest mesophase ranges occur in nematic liquid crystals and the latter are the type most often tested as stationary phases. The mesophase range can be extended by using mixtures of liquid crystals. Such mixtures when used as stationary phase often show better properties than their individual components. Good separation properties are shown by mixed liquid-crystalline stationary phases of entectic composition. One can also use liquid crystal mixtures obtained directly from isomers of azoxy compounds (6). The use of mixed liquid crystals increases the range of their applicability as stationary phases.

Mixed liquid crystalline stationary phases on supports show a strong tendency to become super cooled, so they can be used at temperatures below their melting points. The mesophase obtained at lowered temperature due to super cooling showes increased ordering, which leads to better separations. The tendency to become super cooled is not specific to mixed liquid-crystalline stationary phases, as in many instances super cooling has been observed for individual liquid crystals as well.

Commercially liquid crystals are also available as stationary phases for gas chromatography (79,80). In Poland liquid crystalline stationary phases are manufactured on a commercial scale by Chemipan (Warsaw) and marketed by POCH (Gliwice).

(ii) Vapour pressure, Density, Coefficient of Expansion and Specific heat of liquid crystalline phases.

Hardly any vapour-pressure measurements on liquid-crystalline phases have been made. From the measurements of Neumann (81), it is concluded that smectic range shows a remarkably smaller temperature dependence of vapour pressure compared to that in the isotropic region. The relative decrease in vapour pressure is a general property of liquid-crystalline phases which is an additional advantage in their use as a stationary phase.

While hardly any conclusions on the behaviour of the molecular order near the phase transition can be drawn from the Sparse V.P. data, a special kind of order is evident from some interesting effects is specific heat, coefficient of thermal expansion and density data.

(iii) Surface Tension, Adhesive Power, Liquid-Crystalline Texture and their dependence on the interface.

Practice has shown that liquid-crystalline phases are just as good as normal liquids for use on the usual gas-chromatographic support materials; good adhesion occurs. Also excellent adhesive layers are produced with cholesteric-phase mixtures of cholesteryl benzoate, -oleate, -chloride and -decanoate components on metallic bases, e.g. silver, copper and glass (cappiliary tube, glass beads of 0.1 mm diameter). Allowance must be made for distribution or texture differences in the melt, which can effect changes of specific retention volume in the region of the mesophase (6).

The nematic and smectic phases show the normal temperature effects of surface tension, i.e. it decreases linearly with increasing temperature and shows no specific characteristics on passing through the transition point. Brown and Shaw (82) have pointed to the work of Tamamushi (83), which describes surface tension by an equation of state in which static cohesive forces appear to be governed by the temperature-dependent and temperature-independent intermolecular forces. Interfaces have an unusually large influence on the texture of the liquid-crystalline phase. Between these interfaces, the phase is diffuse, due to anisotropic character of the molecules. In the nematic melts, the longitudinal axis of the molecules lies perpendicular to the glass surface only if the glass has previously been cleaned with acid (84). In contrast, they arrange themselves parallel to the surface with less well cleaned or alkaline-treated glass. Thus in the column, the liquid crystalline phase will assume the state it takes between glass surfaces.

For nematic phases this is "threaded" texture and for smectic phase it appears in the "focal-conic" texture. Also cholesteric phase appears in typical layer textures, thus indicating their dependence on the interface inter molecular forces involved in the different liquid crystalline texture.

(iv) Diffusion Coefficient

Nematic phase are thin liquids and although intrinsically viscous have viscosity values comparable to normal liquids, and often lower. Svedberg (85) showed that (in a magnetic field there is a distinct anisotropy of the diffusion observed. Otherwise little information exists on this. The solvating power of a column with a nematic stationary phase is not inferior to to comparable isotropic liquids. Cholesteric phases are very similar. Even for smectic phase the influence of the strongly pronounced viscosity of anisotropy and even greater viscosities may not be very great. Thus for such systems the resolving power does not change on exceeding the clearing point (86). The results of Dewar and Schröder (46), who separated m-xylenes with smectic phase of hexyloxyazoxybenzene (at a temp. of 75°C) also indicate HETP values in complete accord with normal values (e.g. 1.5 mm for a 7.6 m - long packed column).

The variation of η with $-\frac{1}{T}$ in the anisotropic region is distinguishable from the isotropic region. Just before reaching the clarification point, the viscosity increases sharply with temperatures passes through a sharp maximum and then decreases again practically linearly with $-\frac{1}{T}$ (6).

It may be indicated that before reaching the clarification point a slow decomposition of the order characteristic of the crystalline liquid has begun. This premature breakdown of structure may also be the reason of the specific volume and specific heat of liquid crystal melts show a similar temperature variation.

(v) Behaviour of Crystalline Liquids in External Fields.

Numerous methods and results deal with the behaviour of mesophases in electric or magnetic fields. This is due to the enormous size of the liquid crystal ~~and~~ swarms due to which an exchange effect with external fields occurs much more easily than for single molecules. Thus there is possibility of modifying solubility characteristics of liquid-crystalline phases by setting up magnetic or electric fields. Fredericks and Zolina have investigated the orientation effects of magnetic fields (87,88) while the influence of electric field was investigated by Naggiar (89), Moll and Ornstein, Muller (99) etc.

(vi) Liquid-Crystalline Mixed Phases.

It is significant that for the analytical application of GC to liquid crystal systems use of mixed phases can considerably extend the range of application of the method. But this does not improve "selectivity" of the nematogenic substances. While in cholesteric system, reverse was the case.

II.I.D Thermodynamic Aspects

(i) Thermodynamics of Solution with Liquid Crystal Stationary Phases.

GLC is particularly attractive method for investigating the thermodynamics of solution of nonmesomorphic solutes in liquid crystalline solvents. The method has been successfully applied for the investigation of the solution thermodynamics of nonmesmorphic solutes dissolved in nematic phases (2,3, 91,92), smectic phases (2, 93) and cholesteric phases (93-95). The advantages of the GLC method are :

1. Simplicity, Speed and accuracy with which a large number of systems can be investigated.
2. Availability of a range of easily controllable temperatures.
3. Compatibility of liquid crystals as GLC stationary phases.
4. The ability to work at infinite dilution where the solute molecules do not disrupt the long-range order of the mesophase.

Besides, the most significant advantage is highsensitivity and specificity of the sorption characteristics and the related retention parameters of the analysed substances, varying with the state of the liquid crystal phase : From the measured retention parameters, many thermodynamic quantities can be determined that characterize the liquid-crystalline stationary phase itself and the chromatographed substance liquid crystal system. The phenomen occuring in the transition are particularly interesting. They are related to the increase in the solubility of the chromatographed substance due to the decrease in the free energy of the solution on transition to a less ordered structure. The varied physico-chemical behaviour of liquid-crystalline phases compared with isotropic liquids leads to the conjecture that the special texture of liquid crystal leads to a specific solvent behaviour with respect to components of a gas phase. The behaviour depends upon the specific molecular interaction.

The activity coefficients of a substance dissolved in a liquid crystal obtained from chromatographic measurements show good agreement with the values obtained by static method (96). Once the specific retention volume (V_g) is determined, solute activity coefficient at infinite dilution (γ^{∞}) is readily calculated from the expression (97) :

$$\gamma^{\infty} = \frac{273\ R}{V_g M p^o} \qquad (1)$$

Where, M is the molecular weight of the liquid crystal, p^o is the vapour pressure of the pure solute at the temperature of the experiment, V_g is the solute specific retention volume and R the gas constant. V_g is obtained from GLC data within ± 1% by the well-known expression of Little wood et al., (98). The equation is given on page of this text. Activity coefficient corrected for vapour phase nonideality (γ_f^{∞}) could be determine from the relation (9)

$$\ln \gamma_f^{\infty} = \ln \gamma^{\infty} - \frac{p^o\ B_{22}}{RT} \qquad (2)$$

Where, B_{22} represents solute second virial coefficient. B_{22} values can be obtained from the corresponding states equation of Mc Glashan and Potter (99)

The enthaplies and entropies of various substances in liquid-crystalline stationary phases have been measured (10,95,91,100-103) utilizing the basic thermodynamic relation.

$$\overline{Ge}^{\infty} = RT \ln \gamma_f^{\infty} \qquad (3)$$

and the Gibbs expression

$$\overline{Ge}^{\infty} = \overline{He}^{\infty} - T\,\overline{S}_e^{\infty} \qquad (4)$$

we have

$$\ln \gamma_f^{\infty} = \frac{\overline{Ge}^{\infty}}{RT} = \frac{\overline{He}^{\infty}}{RT} - \frac{\overline{Se}^{\infty}}{R} \qquad (5)$$

Where, $\overline{Ge}^{\infty}$, $\overline{He}^{\infty}$ and $\overline{Se}^{\infty}$ are the solute partial molar excess free energy, enthalpy and entropy at infinite dilution respectively. $\overline{He}^{\infty}$ and $\overline{Se}^{\infty}$ can be determined from the slope and intercept of $\ln \gamma_f^{\infty}$ versus 1/T data.

Further more the partial molar enthalpy ($\Delta \overline{H}_2$) and entropy ($\Delta \overline{S}_2$) of solution accompanying the infinite dilution transfer of solute from the ideal gaseous mixture (solute plus carrier gas) to the real solution are given by the thermodynamic relations.

$$\Delta \overline{H}_2 = \overline{He}^{\infty} - \Delta \overline{H}_2 \text{ (vap.)} \qquad (6)$$

and

$$\Delta \overline{S}_2 = \overline{Se}^{\infty} - \frac{\Delta \overline{H}_2 \text{(vap.)}}{T} \qquad (7)$$

Where, $\Delta \overline{H}_2$ (vap.) is the solute molar heat of vaporization. $\Delta \overline{H}_2$ is also determined from the equation of Little Wood and co-workers (98).

$$\Delta \overline{H}_2 = -\frac{1}{R} \cdot \frac{d\,(\ln V_g)}{d\,(1/T)} \qquad (8)$$

$\Delta \overline{H}_2$ and $\Delta \overline{S}_2$ values provide information for comparing the solution behaviour of solute molecules. The chromatographically measured thermodynamic quantities provide information on the interaction of molecules with nematic liquid crystalline stationary phases in relation with those in isotropic state. (104).

Martire and co-workers have proposed (91) and subsequently refined (94,105) an infinite dilutin model for the molecular interpenetration of γ_f^∞, $\bar{H}_e^\infty$ and $\bar{S}_e^\infty$. According to this model solute activity coefficient is given by three independent contributions :

$$\gamma_f^\infty = \gamma^p \gamma^r \gamma^c \qquad (9)$$

where, solute non-ideality ($\gamma_f^\infty \neq 1$) results from

a. A potential energy contribution (γ^p) which depends on the strength of solute-solvent interactions.

b. A rotational contribution (γ^r) which depends on the extent of solute orientation by the ordered solvent environment.

c. A conformational contribution (γ^c) which depends on the extent of restriction of solute internal rotations by the ordered solvent environment.

Greater the strength of solute-solvent interactions, smaller is γ^p and consequently γ_f^∞ is also small. If in solutions certain rotational modes are completely lost or partially restricted, it results in $\gamma^r > 1$ and solubility is disfavoured. Also if in solutions certain solute conformations become less probable, it results in $\gamma^c > 1$ and solubility may reduce.

By chromatographic methods one can study the nature of interaction of inter molecules of two component liquid crystal mixtures (106) and measure the stability of hydrocarbon - liquid crystal complexes. It has been shown that a correlation exists between the properties of the smectic mesophase - dissolved substance system found chromatographically and those determined by IR methods (107).

By gas chromatography, making sometimes use of data measured calorimetrically, phase diagrams of liquid crystal-chromatographed substance systems have been determined (108-111). It has been found that the phase diagrams determined solely chromatographically or solely calorimetrically are in agreement (110). A knowledge of phase diagrams of such systems allow us to draw conclusions about the interaction of the liquid crystal molecules with a chromatographed substance and about the perturbation effect of the latter on the ordering of the liquid crystalline structure.

Liquid crystals are relatively poorer solvents than the corresponding isotropic liquids. Solution in the mesomorphic region is more endothermic (less negative $\Delta \overline{H}_2$ (solu.) values) than solution in the corresponding isotropic region, but the entropic contribution to the solution processacts in an opposite direction influencing the magnitude of the Gibbs energy of solution, resulting in larger (more negative) values for the Gibbs energy of solution in the isotropic liquid region (7,91). GLC studies could also provide information concerning nematic phase stability (112).

II.1' AIMS AND OBJECTIVES

AIMS AND OBJECTIVES

The use of liquid crystalline stationary phases for the separation of positional isomers is studied extensively. However, the efficiency of the liquid crystals depends on its geometry, phase and the transition temperatures. The use of discogen and mesogenic polymers in gas chromatography study is in its infant stage.

It was proposed to study the behaviour of classical liquid crystals, discogen and mesogenic polymers as stationary phases in gas chromatography. The evaluation of different parameters will throw light on the gas chromatographic behaviour of these stationary phases. The inverse gas chromatographic technique will be used to correlate transition temperatures obtained by thremo-optic methods. Separation of industrially important mixtures will be tried on LC stationary phases.

II.2 EXPERIMENTAL

EXPERIMENTAL

II.2 LIQUID CRYSTALS AND LIQUID CRYSTALLINE POLYMERS AS STATIONARY PHASES IN GAS CHROMATOGRAPHY

II.2.(A) Preparation of Stationary Phase

It was proposed to use liquid crystals and liquid crystalline polymers as stationary phases. The liquid crystals used for gas-chromatographic studies as stationary phases are listed in Table-1, along with their transition temperatures. The details of their synthesis is given in section-1.

The solid support used was chromosorb-W-NAW 60/80 mesh (Johns Man Ville, U.S.A.). Over this support, the substrate was coated from suitable solvent. The 10% coating of liquid crystalline material was prepared with one exception where it was 5%. Following procedure was followed:

A weighed amount (0.5-1.0 g) of the liquid crystalline substrate was dissolved in a suitable solvent taken in a round bottom flask. The solvent was benzene in case of liquid crystals and dimethyl formamide in the case of polymers. To this solution was added the weighed solid support slowly in small proportions. The quantity of solvent taken was just sufficient to make an uniform slurry. Subsequently the solvent was evaporated off in a Rotary Evaporator while blowing a gentle stream of nitrogen and/or keeping under slight vacuum by a water pump/and heating over a water bath. The latter was more necessary towards the end to drive off residual solvent, particularly in the case of DMF. However, care was taken to avoid attrition of particles on formation of lumps. The resulting free flowing powder was the coated stationary phase ready for filling in a GC-column.

II.2.B Column

Stainless steel column of 1.78 m length and 4.5 mm I.D. was used in all the experiments. First the column tubing was thoroughly cleaned by flushing with water and acetone in succession and then drying by passing hot air (by keeping the column in an oven). Following packing procedure was used.

One end of the column was plugged with clean galss wool. The column was kept vertical and at the open end (upper side) a small glass funnel was connected with the help of rubber tubing. Through the funnel the stationary phase (powder) was poured slowly while gently tapping the column with a piece of wood. Occassionally an electrical vibrator was also used to facilitate good packing. After no more stationary phase went into the column, the funnel was detached and this end was also plugged with glass wool. Weight of the stationary phase filled in the column was carefully measured and noted. Lastly, the column was suitably fitted in the gas chromatograph.

Table-2 gives the parameters of various columns prepared and employed in the present study.

(i) Conditioning the Column

This was accomplished in the oven of the gas chromatograph itself. One end of the column was connected to the injector side of the GC while the other end was not connected. Only a small stainless steel tubing was connected to this end and its other open end was brought out of the GC oven. Flow of nitrogen (carrier gas) was maintained in the column at approximately 50 ml/min. The oven temperature was kept at the highest temperature of application in these studies but at least 25°C lower than the decomposition temperature of the substrate the injector was also heated at 200-250°C. The conditioning was continued upto a minimum of 5 hours for each column. Thereafter the heating was switched off and column was cooled while keeping the nitrogen flow on.

II.2.C Apparatus

A Perkin-Elmer model F-30 gas chromatograph equipped with a thermal conductivity detector and with P.E. model 56 recorder was employed. Pressure gauge was incorporated at the column head to indicate inlet pressure (Pi). A soap bubble flowmeter was used to measure the flow rates of the carrier gas at the outlet of the detector. Samples were injected by a 10 µl liquid hypodermic syringe of Hamilton U.S.A. make.

Hydrogen gas of purity higher than 99.9% used as the carrier gas in these studies, supplied through an ethylene Hydrogen Generator (Milton Roy, U.S.A.). The flow rate of the carrier gas, measured at the detector outlet was kept 30 ml/min in all cases.

II.2.D Solute

Typical organic compounds of different classes viz. n-paraffins, iso-paraffins, aromatics, cresols, pthalates etc. were investigated for GC behaviour on the liquid crystals/polymer materials coated as stationary phases. These solutes were mostly pure grade with purity higher than 99%. They were injected into the GC-column with the help of Hamilton syringe in 2-5 ml quantity. The syringe was throughly cleaned first with a solvent, dried, flushed/rinsed a couple of times with the solute and then the measured quantity of the solute was quickly injected into the column. Care was taken that the solute is injected as a sharp plug of minimum or near zero band width, and that there was no leakage from the injection rubber septum. Solutes that were very viscous or solid at room temperature were dissolved in a suitable solvent that was injected into the gas chromatograph.

II.2.E Procedure

After connecting the column the carrier gas was made on, leaks tested with soap solution and accordingly set right. The flow rate was adjusted at 30 ml/min. Then the injector, detector and oven temperatures were set as given in Table-3. After stabilisation of the temperatures the flow rate of carrier gas was again checked and adjusted as necessary, to 30 mil/min.

The chart speed of the recorder was checked occassionally with a stop watch (the same was found to be okay).

The experiment was started after indication of the ready signal. Each solute was injected and the chromatogram traced at a suitable chart speed. Some air was also drawn in the syringe alongwith the solute so that air peak, indicating dead volume of the column, was also traced simulataneously. the retention distance was measured between the peak maximas for air and the solute. From this the adjusted retention time t_R' was calculated.

The barometric pressure was used to indicate the pressure at column outlet, measured by Aneroid barometer. The room temperature was also noted to determine saturation water vapour pressure existent in the flow meter.

TABLE - 1

LIQUID CRYSTALLINE COMPOUNDS STUDIED AS STATIONARY PHASES

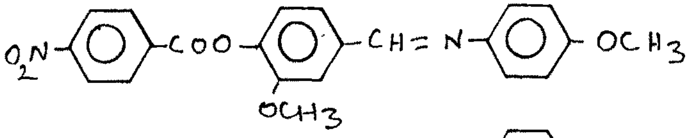
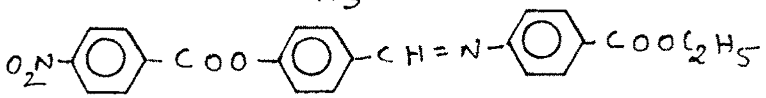
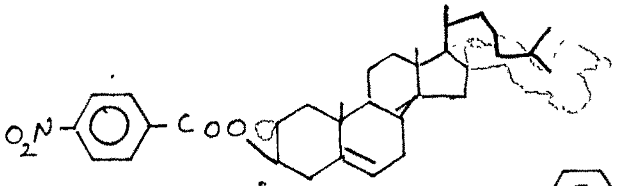
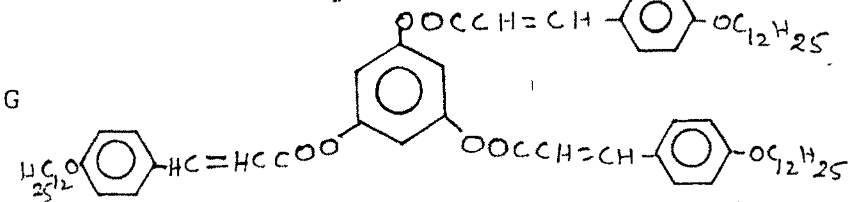
Phase No.	Code	Formula	Transition temperatures °C			
			Cholesteric	Smectic	Nematic	Isotropic
I.	PNV-1		-	-	168	205
II.	PNVO-2		-	-	(168)	182
III.	Ch-PNB		191.5	-	-	260 (D)
IV.	12-CPG		-	-	116	136
V.	PO-HBA	Co-Polymer of 4-Hydroxy benzoic acid and 2-hydroxy benzoic acid.	-	204	219	290 (P)
VI.	CPh-2	Co-Polymer of 4-hydroxy benzoic acid and 2(4-hydroxy benzoyl)Benzoic acid.	-	128	-	233

TABLE - 2

COLUMN PARAMETERS

Phase No.	Code	Length of S.S.Column (m)	Percentage of coating on solid support (Chromosorb W-NAW 60-80 mesh)	Total weight of packing (W_{S_P}) (gm)	Weight of liquid phase in the column (W_L) (gm)
I	PNV-1	1.78	10 %	8.6777	0.86777
II	PNVO-2	1.78	5 %	7.8698	0.39349
III	Ch-PNB	1.78	10 %	9.620	0.9620
IV	12-CPG	1.78	10 %	8.1699	0.81699
V	PO-HBA	1.78	10 %	8.4112	0.84112
VI	CPh-2	1.78	10 %	8.6032	0.86032

TABLE -3

GC PARAMETERS

Phase No.	Code	Oven Temperatures °C	Injector Temperatures °C	Dectector Temperatures °C	Flow rate (ml/min)	Inlet pressure Pi (mm)
I	PNV-1	140 to 210	250	300	30	990 to 210
II	PNVO-2	150 to 220	150	200	30	1003 to 1146
III	Ch-PNE	160 to 260	250	300	30	1018 to 1270
IV	2-CPG	80 to 150	150	200	30	948 to 1003
V	PO-HBA	145 to 260	250	300	30	997 to 1270
VI	CPh-2	100 to 245	250	300	30	958 to 1215

II.3 RESULTS AND DISCUSSION

II.3.A RESULT AND DISCUSSION

Table-1 lists the liquid crystalline compounds studied as stationary phases in the present work. These substrates encompass different mesophase types, wide transition temperature ranges as well as different chemical constitutions. The mesophase type and phase length of all the mesogens are recorded in table -4.

TABLE - 4

Phase Number	Code	Mesophase type	Phase length ΔT(°C)
I	PNV-1	Nematic	37
II	PNVO-2	Nematic (monotropy)	14
III	Ch-PNB	Cholesteric	68.5
IV	12-CPG	Nematic (Discotic)	20
V	PO-HBA	Smectic/Nematic (Polymeric)	15/71
VI	CPh-2	Smectic (Polymeric)	105

As reported earlier though many mesogens have been studied as stationary phases, the literature is scanty, (,8) for the liquid crystalline polymers and discotic mesogens. Naturally, these two types of mesogens were used as substrate with special interest.

(i) Solid support, % Loading and Probe solutes

Solute retention characteristics as well as its band-width (column efficiency) could be influenced by the activity of the solid support employed for impregantion of the LC stationary phase. Witkiewicz et al., (113) found Polsorb B NAW to be superior to polsorb B AW. Interaction between the support and the liquid crystal was reported to decrease in the order chromosorb W, chromosorb W AW and chromosorb W AW DMCS (102) whereas for chromosrb P it was NAW > AW > AW DMCS (114). Haky and Muschik (103) employed successfully chromosorb W HP. It is well known that chromosorb P is more surface active than chromosorb W (115). Based on these observation, chromosorb W NAW was chosen as solid support for the present investigations.

Solute retention on the stationary phase can also be modified due to adsorption effects on the gas-liquid interface (116). These effects are minimised by taking higher liquid loadings which also decrease support adsorption effect. Marciniak and Witkiewicz (114) report that for liquid crystal loadings above 5 % transition temperatures indicated by GC studies are comparable to those determined by thermo-optical method. In view of these, the liquid crystal loadings in the present studies were kept 10% except in one case when it was 5% (refer table-2).

Para-xylene and n-undecane were selected as probe solutes for inverse GC studies and for thermodynamic parameters determination. These solutes are typical of aromatics and paraffinic compounds which represent important class of organic compounds. Further, they have relatively low activity coefficients in the studied material which suppresses gas-liquid interface adsorption effects. This is also in line with reported work (93, 117, 118).

(ii) Inverse Gas Chromatographic Studies

Specific Retention Volumes (V_g, ml^{-1} $_g$) were determined as given by the equation :

$$V_g = (t_R - t_M) \times F_a \times j \times \frac{273}{T_a} \times \frac{1}{W_L} \times \frac{p_o - p_w}{p_o}$$

Log V_g was plotted as a function of inverse column temperature (expressed in K). As a matter of fact 1000/T values were considered instead of 1/T, so that values greater than 1 were obtained. Such plots for all the six stationary phases (I to VI), each plot for p-xylene as well as n-undecane (n-C_{11}), are shown in figures 4 through 9.

The characteristics of the plots obtained in the present study are discussed in detail in the following text.

I, PNV-1, Fig. 4
(K 168 N 205 I)

Starting from 140°C at which the substrate is in crystalline or solid phase, V_g decreases almost linearly as the temperature is increased upto 160°C. In solid phase, no solution effects are expected. Due to rise of temperature the solute vapour pressure increases causing reduction in

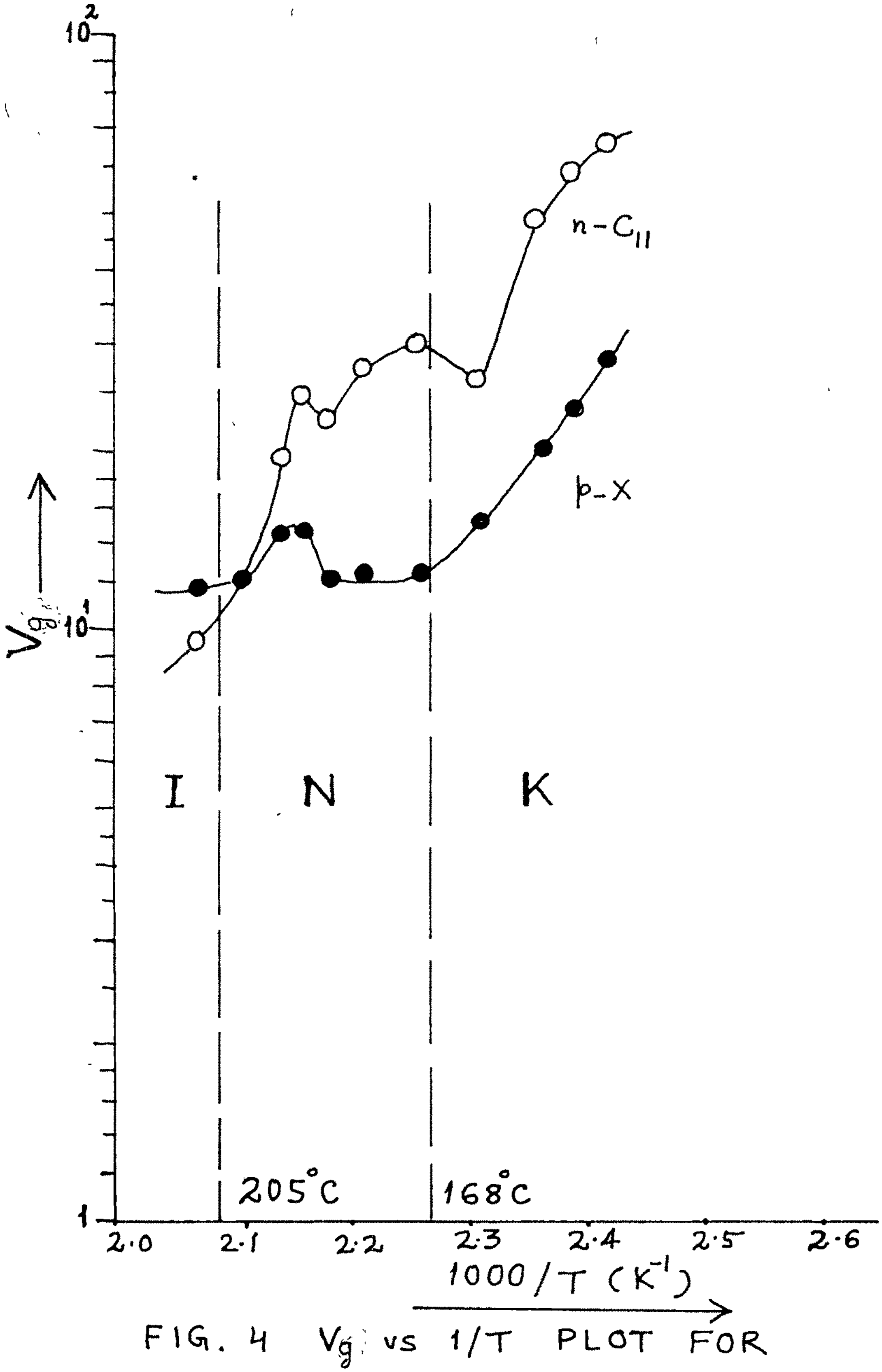


FIG. 4 V_g vs 1/T PLOT FOR PNV-1 LIQUID CRYSTAL in retention time. Since the solutes (n-C_{11} & p-x) do not have strong polar groups, surface adsorption also can not be expected. At 160°C, however in the case of n-C_{11} there is rise in V_g. This could be due to the setting-in of pre-transition of a few degrees before the melting point as reported by several workers (6,9,16). The effect is seen immediately on n-C_{11} which has less solubility (higher activity coefficient) compared to p-xylene where the effect is not visible.

At 170°C, the slope of curves for both solutes changes indicating phase transition. Against this, the phase transition obtained thermo-optically is 168°C which is in fair agreement with IGC (inverse gas chromatography) value. In the case of n-C_{11}, upto 195°C, the V_g value actually does not show rising trend (negative slope) but only a decrease of slope in the nematic region. The partition phenomenon is more apparent in the case of p-xylene in the nematic mesophase region where the V_g values are either steady or show a rise. This could be attributed to very high solubility of p-xylene in this phase.

The second phase transition is revealed by IGC curves after 195°C. The isotropic transition temperature for PNV-1 is 205°C. This correspondence is not very close; nevertheless it is fairly indicative considering the pre-clarification phenomenon reported earlier(6,97). It may be noted however, that the V_g decreases in the isotropic region for both n-C_{11} and p-xylene. A more vivid understanding of this phenomenon will be possible when thermodynamic parameters are discussed in the latter part of this text.

II, PNVO-2, Fig. 5
[K(168)N182I]

PNVO-2 exhibits monotropic nematic phase. Monotropic nematic phase is observed at 168°C when isotrpic liquid is cooled. Fig. 5 presents the change in V_g values when column temperatures are increased in stages of 10°C or 5°C starting from 150°C (Solid phase). It is noted that V_g decreases steadily with increase in temperature. There is no sharp change of slope indicative of phase transition. In going from crystalline to isotropic state, the increase in solute vapour pressure due to rise of temperature overwhelms the fall in activity coefficient. ($\gamma^{\infty} = \frac{273\ R}{V_g p^o M}$). Therefore V_g keeps on falling.

Naturally, on heating the solid compound (Fig.5) PNVO-2 will behave as any organic solid which on further heating gives liquid phase but not the ordered mesophase. Due to this reason the behaviour of the graph for PNVO-2 differs compared to other mesogens, as there is no phase transition.

III, Ch-PNB, Fig. 6
[K191.5 Ch260I (D)]

The first liquid crystal synthesised in 1888 was a cholesteric one-cholesteryl benzoate (119). Cholesteric liquid crystals have also been used in GC (15, 120). They are, however, reported to yield inferior GLC separations than the liquid crystals with nematic mesophase (6,7,9). In the present studies also one cholesteric liquid crystal (121), st. phase III, Ch-PNB, was included in order to have a comparative evaluation of its GC behaviour.

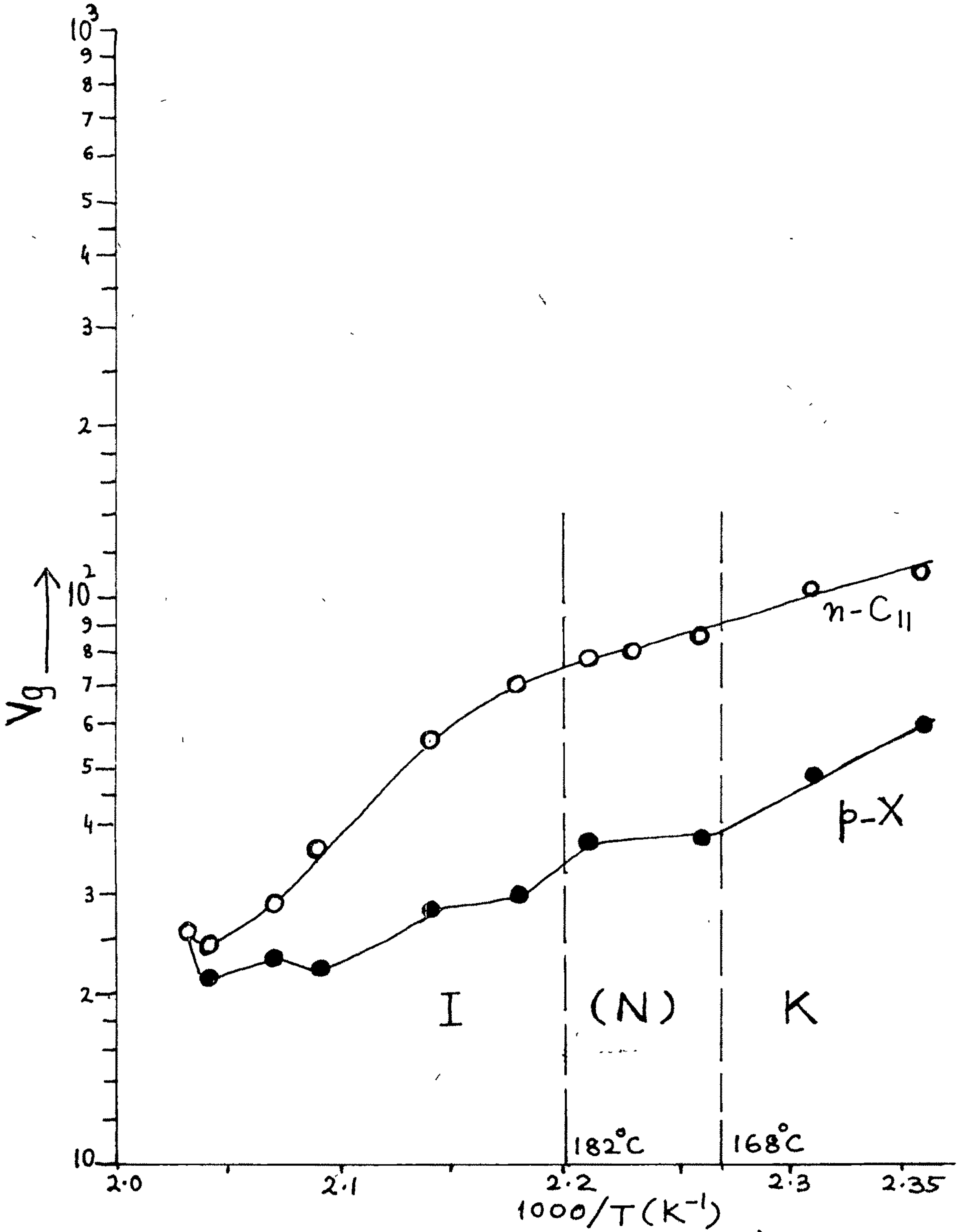


FIG. 5 Vg vs 1/T PLOT FOR PNVO-2 LIQUID CRYSTAL

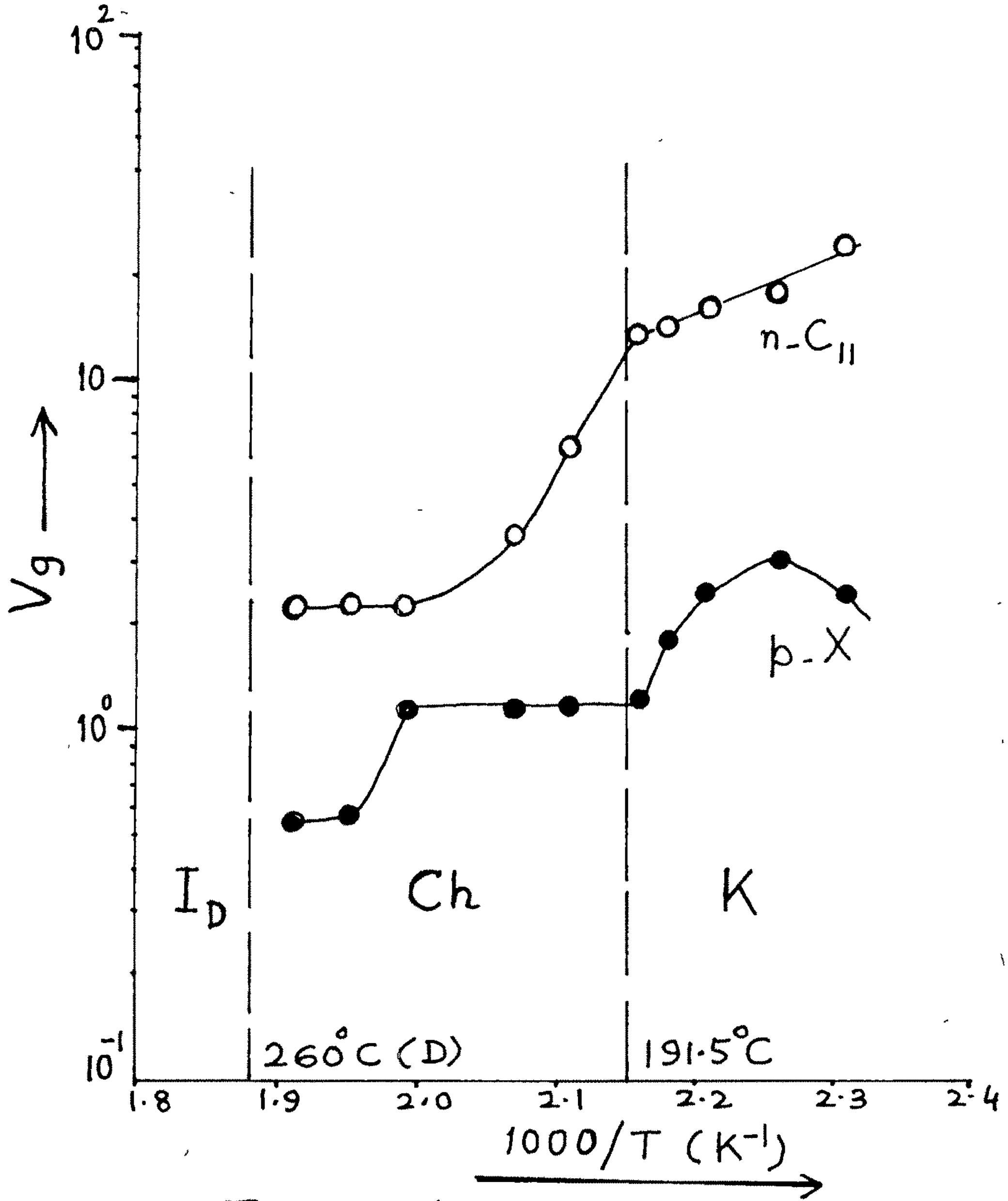


FIG. 6 Vg vs 1/T PLOT FOR Ch-PNB LIQUID CRYSTAL

The compound Ch-PNB, as examined thermo-optically, reveals the first transition from crystalline to cholesteric phase at 191.5°C and the second transition to isotropic liquid at 260°C. The compound, however, starts decomposing at 260°C. The GC studies were therefore, limited upto 250°C only.

Fig. 6 depicts the variation of log V_g with respect to inverse absolute temperature for p-xylene and n-C_{11} solutes on Ch-PNB. As the temperature rises from 170°C to 190°C, V_g for both solutes decreases almost linearly until first sharp change of slope occurs around 190°C. This closely compares with the thermo-optical transition of 191.5°C. Beyond 190°C, V_g remains almost constant upto 230°C in the case of p-xylene whereas for n-C_{11} it steadily falls upto this point. At higher temperatures, V_g for n-C_{11} becomes steady but the same for p-xylene falls and then remains same at 240°C and 250°C. This behaviour is not easily explained. One observation is apparent, however, that the partitioning effect dominates between 230-250°C in the case of both the solutes.

This typical behaviour of the cholesteric mesophase may be very interesting to exploit for GLC separations of unusual nature.

IV, 12-CPG, Fig. 7
(K 116 N 136 I)

12-CPG is a discotic liquid crystal in which the molecules of 1,3,5-tri(trans-n-dodecyloxy cinnamoyloxy) benzene are stacked one over other in columns with flat benzene rings forming the core. The first transition from solid to mesophase was noted at 116°C, whereas the clarification point was 136°C.

Variation of log V_g with 1/T is shown in figure 7 for n-C_{11} as well as p-xylene solutes. The curves display some interesting characteristics quite different from previous compounds i.e. I,II and III.

In the solid phase as the temperature increases from 80°C to 110°C the curves do not show steep slope indicating that the V_g values do not fall down much. Thus interaction of the solutes with even solid phase seems to take place. The first change of slope of the curves occur at 110°C (1000/T= 2.61). This temperature is 6°C less than the actual transition temperature. Therefore, as mentioned earlier, the transition phenomenon sets in before the melting point.

In the nematic phase the curves for both n-C_{11} and p-xylene become steep. This shows that with the increase in temperature the increase in vapour pressure offsets any increased affinity in the mesophase. Or there might not occur any increased affinity in this phase. The discotic mesophase allows the molecular discs to slip like pack of cards. This might result in loss of retention of solutes.

The second slope change of the curves is at 135°C which is very close to the actually measured clarification point (136°C). It may be noted that in the present case, though the slope changes are not very pronounced, yet they are very clear and marked.

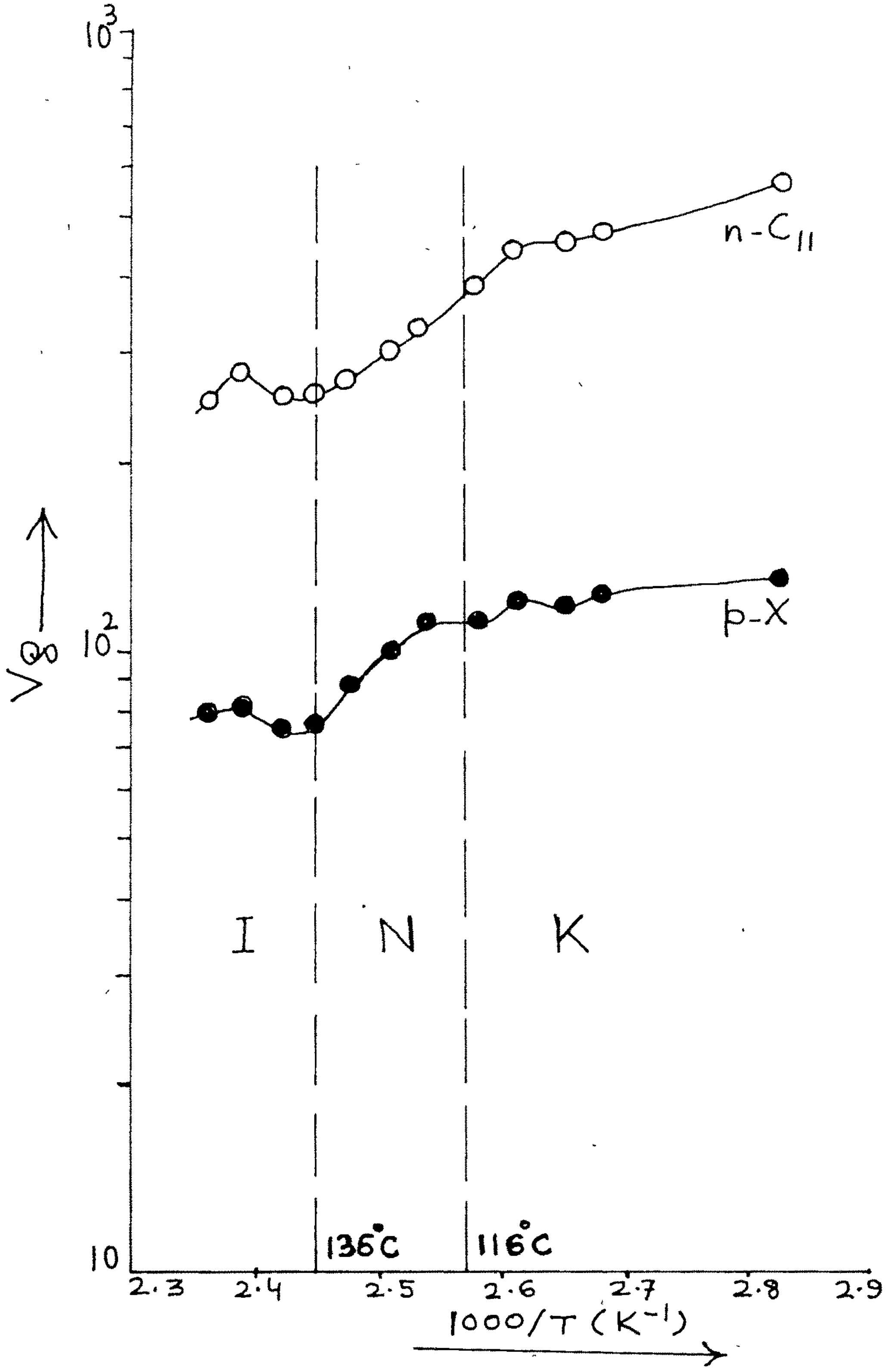


FIG. 7. V_g vs 1/T PLOT FOR 12-CPG LIQUIDCRYSTAL

In the isotropic liquid, again the solubility increases and the V_g's do not fall with increase in temperature. The study was, however, not pursued beyond 150°C.

One noteworthy characteristic in this case is that the behaviour of n-C_{11} and p-xylene, on log V_g vs 1000/T plot, is almost alike. This was not the case with previously studied compounds viz., I and III. This may be attributed to the difference in the orientation of molecules of discotic phases and mesophases of rod-like molecules.

V, PO-HBA, Fig. 8
(K 204 S 116 N 290 P)

PO-HBA is a co-polymer with solid-smectic, smectic-nematic and nematic-isotropic transitions at 204°C, 219°C and 290°C respectively. At 290°C, however, the material undergoes post-polymerisation. Therefore, the GC studies were kept limited upto 260°C only.

Fig. 8 exhibits the relationship between specific retention volume and temperature for n-C_{11} and p-xylene solutes. From 145°C to 200°C, the curve shows a change of slope indicating phase transition. Keeping in view the reported pretransition phenomenon, as was mentioned earlier in the text, this is very close to the thermo-optical transition temperature (204°C).

Upto about 210°C, the behaviour of both solutes, n-C_{11} and p-xylene, is almost similar. However, thereafter, the change in V_g with temperature is not smooth and the curves show several crests and troughs in the smectic

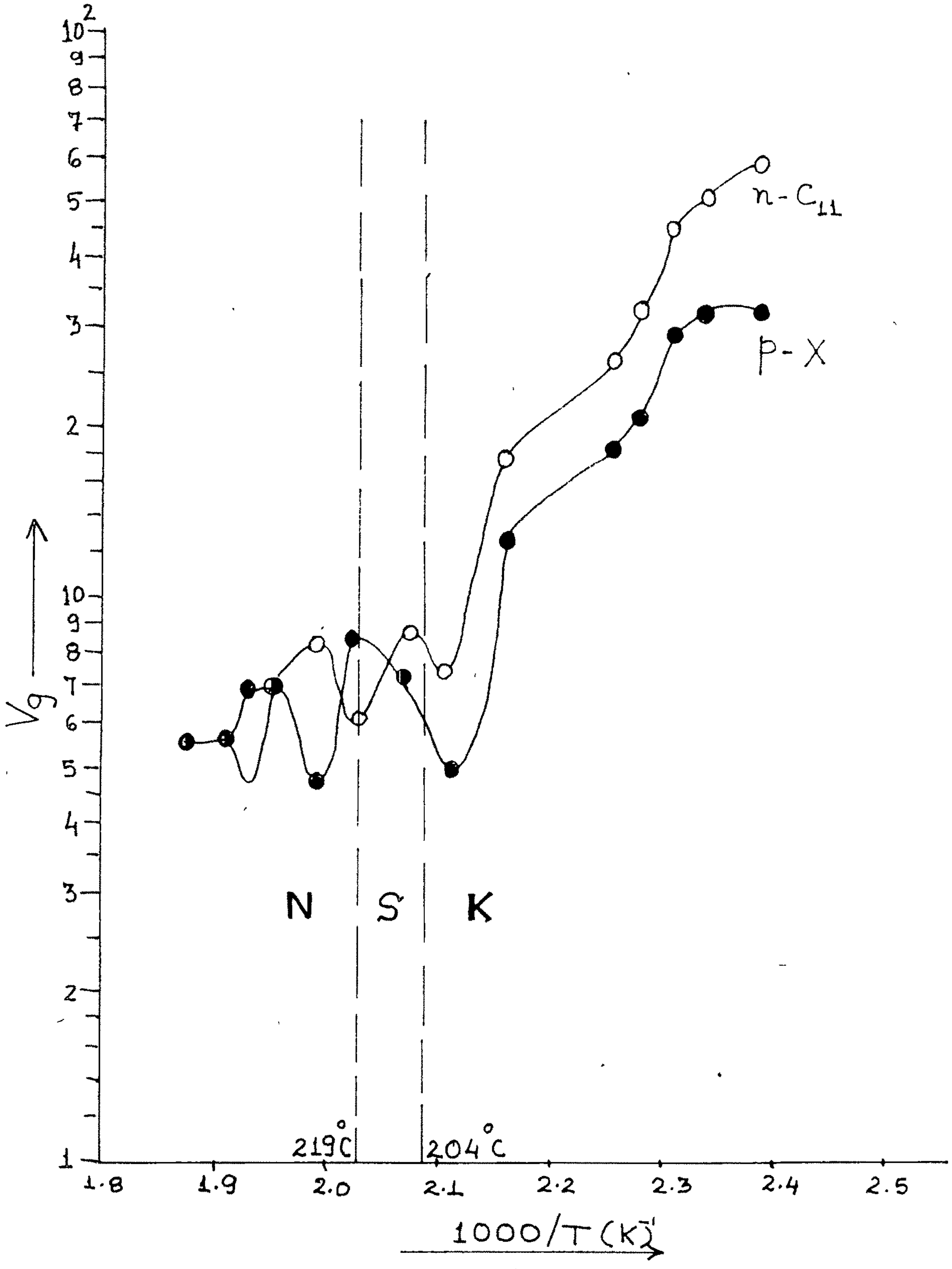


FIG. 8 V_g Vs 1/T PLOT FOR PO-HBA LC POLYMER and nematic regions. n-C_{11} and p-xylene, in this region, show opposite variations. There is a change of slope at 220°C for both solutes corresponding to smectic-nematic trnasition of 219°C, which is an excellent correspondence. But looking to the non-systematic pattern in these regions, we may consider only the average trend which shows that the solute retention ceases to fall rapidly with temperature rise in smectic/nematic regions.

It may be noted that polymer matrix consists of macromolecules of different sizes and the mesophase structure may not be as ordered as in the case of pure liquid crystalline compounds. Nevertheless the average retention behaviour may also yield significant analytical results. The analytical usefulness of such liquid crystals is apparent from the fact that it has a high temperature ($>$ 200°C) mesophase and has wide range (105°C).

VI, CPh-2, Fig. 9
(K 128 S 233 I)

CPh-2 is a co-polymer having solid-smectic and smectic-isotropic transitions at 128°C and 233°C respectively. There is no nematic phase region. It was thought interesting, therefore, to study the GC characteristics of this polymer which exhibits only smectic mesophase.

Fig. 9 represents the inverse gas-chromatogram for CPh-2 using n-C_{11} and p-xylene solutes. In the solid phase, both solutes show one maxima at 120°C. Near transition temperatures also distinct slope changes are observed showing good agreement with thermo-optical transition temperatures (130°C and 235°C against 128°C and 233°C respectively). However, in the

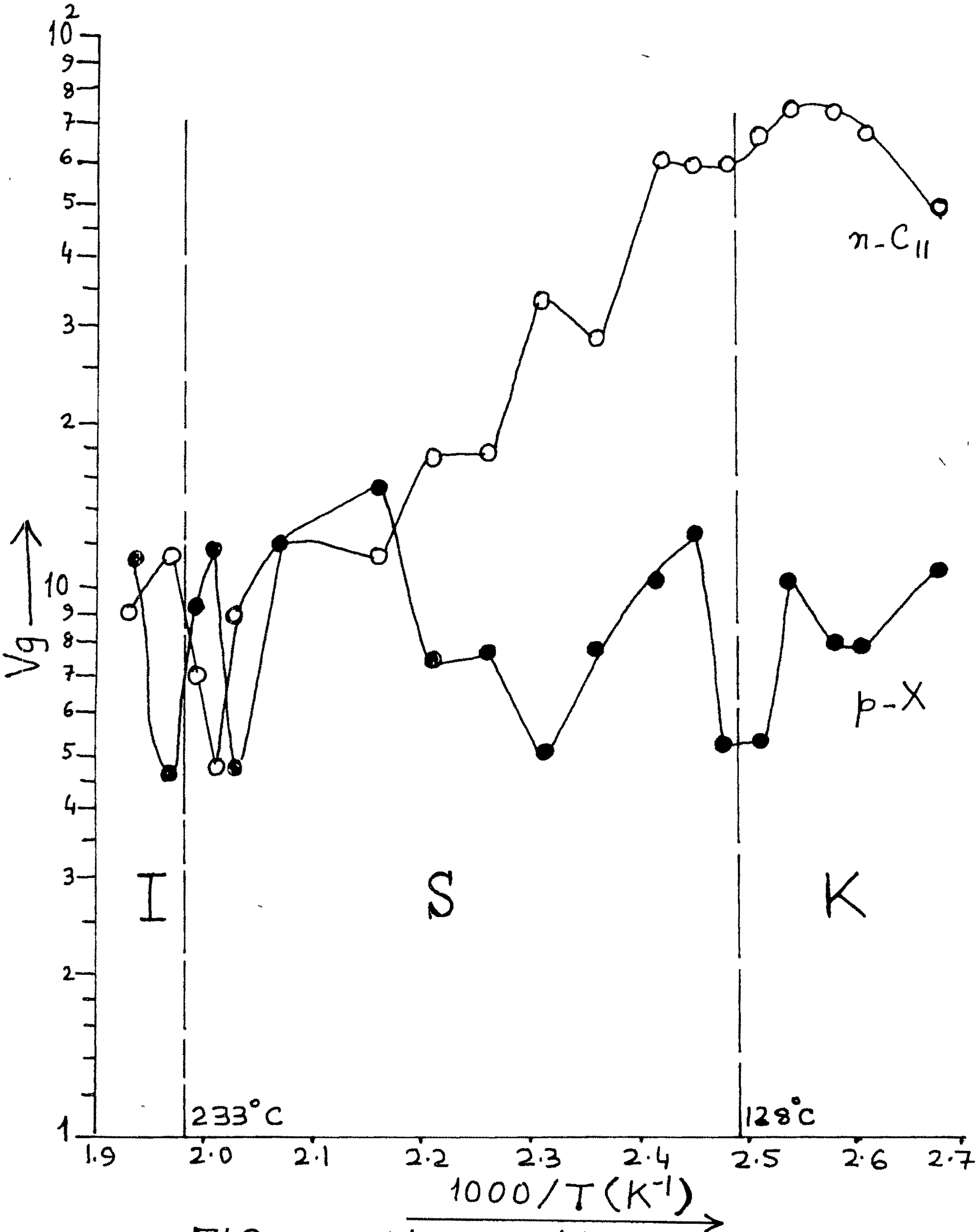


FIG. 9. Vg vs 1/T PLOT FOR CPh-2 LC POLYMER

smectic phase range, which is very wide (105°C), the curves for both solutes show several slope changes at common temperatures but in opposite directions. In addition few more changes are shown by each solute at different temperatures. Smectic phase could have eight sub-classes viz. smectic A to smectic H (9). Since these smectic sub-classes were not distinctly noticed on heating stage microscope for CPh-2, it may be difficult to attribute these slope changes to the presence of some smectic sub-classes in the smectic phase region of the polymer. For pure smectogenic compounds, Sakagami and Nakamizo (122) reported that smectic B - smectic C/smectic A change was strongly indicated on IGC curve but smectic C - smectic A changes was not seen.* Similar findings were reported by Haky and Muschik (103). In the present case the problem could be more complex due to the polymer matrix having a distribution of molecular sizes.

Due to the presence of so many slope changes in this case, it may be difficult to determine transition temperatures from IGC Curves. However analytical exploitation of this polymer could be certainly suggested in view of divergent behaviour of n-C_{11} and p-xylene.

Interest in liquid crystals as solvents stemmed from the orienting effect of the parallel molecular alignment in mesophases on dissolved molecules. Dave et al.,(46) reported that linear solute molecules show a smaller disruptive effect on nematics than bulky, non-linear molecules, because the former fits in more readily into the nematic "lattice" being oriented with their long axes parallel to those of the solvent molecules. Such behaviour suggests that nematic may display selectivity towards solutes on the basis of molecular shape, i.e. everything else being equal, a solute consisting

* (123)

of linear molecules should adapt sterically to the parallel alignment in the mesophase more readily than one with relatively bulky molecules and thus more soluble.

The study of mixed mesomorphism of Dave and Dewar (46), became the base for the use of liquid crystals as stationary phase in gas chromatography. Dave and Dewar observed that when a mesogen is mixed with the non-mesogen, the extent of the composition range over which liquid crystallinity is observed depends on the degree of similarity of the molecules of the non-liquid crystalline and liquid crystalline substances in shape, size, polarity of the end groups and polarizability. If the solute molecules are structurally compatible with the molecular arrangement of the mesophase, they should adjust to the parallel alignment of the mesophase and mixed liquid crystals should form over a wider composition range in the phase diagram; the most favourable condition for mixed liquid crystal formation would thus arise if the molecules of the non-mesogens are long and lath-shaped. Hence the IGC-curve for LCPS shows non-systematic pattern as polymer matrix consists of macromolecules of different sizes and hence mesophase structure may not be as ordered as in case of pure compounds.

(iii) Retention Behaviour and Thermodynamic Parameters

In gas-liquid chromatography, 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 simple dispersion forces and/or other forces like dipole-dipole, induction (Debye), hydrogen bonding, complex formation, charge transfer etc. In the case of liquid crystal mesophase, molecular ordering/orientations are also operative towards shape selectivity. It would be a very complex task to relate retention behaviour to all these molecular parameters. However such microscopic behaviour can be related to macroscopic thermodynamic quantities such as activity coefficient and heat of mixing. Current gas chromatographic theory is fairly developed based on above parameters (125).

Effort has been made in the present work to determine such parameters e.g. activity coefficients at infinite dilution, partial molar heat of mixing, entropy and partial molar heat of solution.

(1) Activity Coefficient (γ^{∞}) :

The activity coefficient at infinite dilution was determined by using following equation :

$$\gamma^{\infty} = \frac{273\ R}{V_g p^{\circ} M}$$

where, V_g = Specific retention volume

p° = Pure solute vapour pressure at the column temperature,

M = Molecular weight of the stationary phase.

R = Gas constant.

V_g was determined experimentally as described before in the text. M was calculated from the molecular formula of the liquid crystals. p° was computed from the Antoine Equation :

$$\log p^{\circ} = A - \frac{B}{t+C}$$

Where, t is the temperature in °C and A,B,C are constants whose values were taken from compilation of Boublic et al., (124).

In tables 5 thorugh 8 are given γ^{∞} values at different temperatures for n-C_{11} and p-xylene solutes for the four liquid crystalline stationary phases viz. PNV-1, PNVO-2, Ch-PNB and 12-CPG. Tables 5 through 9 also incorporates V_g and p^o values. Graphs are obtained by plotting $\ln \gamma^{\infty}$ vs. 1000/T (Fig. 10 to 13).

Variation of V_g can be discussed in terms of above mentioned equation wherein V_g is inversely proportional to the product of p^o and γ^{∞}. For ideal solution where Result's Law viz. $p_i = p^o{}_{xi}$ is obeyed, γ^{∞} should be unity since for real solution, $pi = \gamma^{\infty} p^o x_i$. If γ^{∞} is less than unity (negative deviation), higher solubility of the solute is indicated, however, if γ^{∞} is higher than unity (positive deviation) lower solubility of the solute than ideal behaviour may take place.

For PNV-1 stationary phase (Table 5), γ^{∞} for n-C_{11} varies between 2.6 to 5.8, whereas the same for p-xylene lies between 1 to 2. Thus, p-xylene shows near ideal solubility, indicating compatibility with the stationary phase. n-C_{11} which has higher γ^{∞} values is relatively less compatible.

The reference to Table 6 indicates that for PNVO-2, γ^{∞} for n-C_{11} lies between 0.9 to 1.6, showing near ideal compatibility of n-C_{11} in PNVO-2. p-xylene, however, has more affinity ($\gamma^{\infty} < 1$) indicating presence of stronger interaction.

The behaviour of cholesteric stationary phase Ch-PNB (Table-7) is a little different. Activity coefficients for both solutes, n-C_{11} and p-xylene, show positive deviation from Raoult's law and both are having γ^{∞} values in the same order of magnitude. This compound (Ch-PNB) may not, therefore, show much selectivity for paraffinic/aromatic hydrocarbons.

Table 8 for 12-CPG, which is a discotic compound, reveals γ^{∞} values for n-C_{11} as well as p-xylene less than one (negative deviation). This means, 12-CPG has stronger interactions with both the solutes, though the latter differs in nature.

The polymeric liquid crystals, unlike pure liquid crystalline compounds, have a distribution of molecular weights. Their average molecular weight could be expressed either as number averaged or as weight averaged and is determined by various physical methods. the accurate determination of average molecular weight may be rather difficult.

In the absence of exact molecular weights (M) of liquid crystal polymers, PO-HBA and CPh-2, it was not possible to compute γ^{∞} values. Therefore, as pointed out by Kelker and Schivizhoffen (6), the function $\gamma^{\infty}M$ was determined, instead, using the relation :

$$\gamma^{\infty}M = \frac{273\ R}{p^{o}V_{g}}$$

The values of $\gamma^{\infty}M$ alongwith specific retention volumes (V_g) for n-C_{11} and p-xylene on PO-HBA and CPh-2 at different temperatures are presented in table . 9.

On PO-HBA, the values of γ^{∞} M are 2-3 times higher for n-C_{11} than the same fo p-xylene. This indicates higher affinity of p-xylene than n-C_{11} in PO-HBA. This is not so in CPh-2. Upto 180°C in CPh-2, the γ^{∞} M values for n-C_{11} and p-xylene are generally in the same order. At higher temperatures, the solubility of p-xylene increases relatively. Thus, the behaviour of PO-HBA may be more selective.

In Figures 14 and 15, the γ^{∞} M function is plotted logarithmically against 1/T for the two polymeric substrates, separately for n-C_{11} and-xylene p-xylene solutes, covering the mesophase temperature ranges. These plots show rather scattered points but the regression trend is evident to be linear in both cases. The slopes and intercepts, however, are different in the two cases. Such linear plots are reported earlier (6) for isotropic range. In the present case, the temperatures cover the mesophase regions of the two polymeric liquid crystals.

(2) Partial Molar Thermodynamic Quantities :

Determination of activity coefficient at infinite dilution, γ^{∞} leads to several thermodynamic parameters viz., partial molar excess free energy, enthalpy and entropy at infinite dilution as given below :

$$\overline{Ge}^{\infty} = RT \ln \gamma^{\infty}$$

and since $\overline{Ge}^{\infty} = \overline{He}^{\infty} - T\,\overline{Se}^{\infty}$ (Gibb's expression),

$$\ln \gamma^{\infty} = \frac{\overline{Ge}^{\infty}}{RT} = \frac{\overline{He}^{\infty}}{RT} - \frac{\overline{Se}^{\infty}}{R}$$

TABLE - 5

Specific Retention Volumes (V_g), Solute Vapour Pressures (p^o) and Activity Coefficients at Infinite Dilution (γ^∞) for PNV-1 stationary phase at various temperature.

Sr. No.	Solute Temperature (°C)	n-Undecane V_g (ml/g)	 p^o (k Pa)	 γ^∞	p-Xylene V_g (ml/g)	 p^o (k Pa)	 γ^∞
01.	140	64.13	20.32	4.29	28.21	105.9	1.87
02.	145	58.72	23.98	3.97	23.05	120.6	2.01
03.	150	48.34	28.16	4.10	20.35	137.0	2.00
04.	160	25.20	38.31	5.79	15.12	174.9	2.11
05.	170	29.95	51.23	3.64	12.48	220.4	2.03
06.	180	27.13	67.43	3.05	12.33	274.6	1.65
07.	185	22.06	76.94	3.29	12.26	305.2	1.49
08.	190	24.33	87.47	2.63	14.60	338.4	1.14
09.	195	19.37	99.13	2.91	14.53	374.2	1.03
10.	200	12.01	112.0	4.15	12.01	412.8	1.13
11.	210	9.48	141.5	4.17	11.85	498.9	0.95

TABLE - 6

Specific Retention Volumes (V_g), Solute Vapour Pressure (p^o) and Activity Coefficients at Infinite Dilution (γ^∞) for PNVO-2 stationary phase at various temperatures.

Sr. No.	Solute	n-Undecane			p-Xylene		
	Temperature (°C)	V_g (ml/g)	p^o (k Pa)	γ^∞	V_g (ml/g)	p^o (k Pa)	γ^∞
01.	150	110.5	28.16	1.63	58.91	137.0	0.63
02.	160	100.7	38.31	1.31	48.14	174.9	0.61
03.	170	85.25	51.23	1.16	37.57	220.4	0.61
04.	175	78.94	58.88	1.09	35.88	246.4	0.57
05.	180	77.09	67.43	0.98	37.12	274.6	0.50
06.	185	69.52	76.94	0.95	29.80	305.2	0.56
07.	195	56.06	99.13	0.91	28.03	374.2	0.48
08.	205	35.92	126.1	1.12	22.11	454.3	0.50
09.	210	28.81	141.5	1.24	23.32	498.9	0.44
10.	215	24.51	158.5	1.30	21.78	546.6	0.43
11.	220	25.64	176.9	1.12	25.91	597.7	0.33

TABLE - 7

Specific Retention Volumes (V_g), Solute Vapour Pressure (p^o) and Activity Coefficients at Infinite Dilution (γ^∞) for Ch-PNB stationary phase at various temperatures.

Sr. No.	Solute	n-Undecane			p-Xylene		
	Tempe-rature (°C)	V_g (ml/g)	p^o (k Pa)	γ^∞	V_g (ml/g)	p^o (k Pa)	γ^∞
01.	160	25.26	38.31	4.38	2.53	174.9	9.60
02.	170	18.27	51.23	4.53	3.13	220.4	6.16
03.	180	16.07	67.43	3.92	2.47	274.6	6.25
04.	185	14.13	76.94	3.90	1.84	305.2	7.54
05.	190	10.37	87.47	4.68	1.22	338.4	10.28
06.	200	6.62	112.0	5.72	1.21	412.8	8.53
07.	210	3.56	141.5	8.41	1.19	498.9	7.16
08.	230	2.30	218.7	8.42	1.15	710.3	5.19
09.	240	2.27	267.8	6.99	0.57	837.8	8.93
10.	250	2.23	324.9	5.86	0.56	981.8	7.76

TABLE - 8

Specific Retention Volumes (V_g), Solute Vapour Pressure (p^o) and Activity Coefficients at Infinite Dilution (γ^∞) for 12-CPG stationary phase at various temperatures.

Sr. No.	Solute	n-Undecane			p-Xylene		
	Temperature (°C)	V_g (ml/g)	p^o (k Pa)	γ^∞	V_g (ml/g)	p^o (k Pa)	γ^∞
01.	80	565.2	1.72	2.19	128.7	15.61	1.06
02.	100	467.4	4.39	1.04	122.4	32.04	0.54
03.	105	449.6	5.44	0.87	116.6	37.82	0.48
04.	110	443.1	6.69	0.72	121.8	44.41	0.39
05.	115	386.8	8.17	0.67	110.5	51.89	0.37
06.	120	331.1	9.92	0.65	110.4	60.36	0.32
07.	125	308.0	11.97	0.58	98.96	69.89	0.31
08.	130	257.6	14.36	0.57	87.74	80.59	0.30
09.	135	256.7	17.12	0.48	76.47	92.54	0.30
10.	140	256.1	20.32	0.41	76.26	105.9	0.26
11.	145	276.6	23.98	0.32	81.35	120.6	0.22
12.	150	248.6	28.16	0.30	81.09	137.0	0.19

TABLE - 9

Specific Retention Volumes (V_g, ml g^{-1}) and $\gamma^{\infty}M$ (Product of Activity Coefficient at Infinite Dilution and Molecular Weight) values for Polymeric Liquid Crystal Stationary Phases at Various Temperatures.

Sr. No.	St. Phase	PO-HBA				CPh-2			
	Solute	n-C_{11}		p-Xylene		n-C_{11}		p-Xylene	
	Temp. (°C)	V_g	$\gamma^{\infty}M$	V_g	$\gamma^{\infty}M$	V_g	$\gamma^{\infty}M$	V_g	$\gamma^{\infty}M$
01.	110	-	-	-	-	65.74	5159	7.89	6473
02.	120	-	-	-	-	73.38	3116	10.48	3586
03.	130	-	-	-	-	57.25	2759	5.20	5413
04.	140	-	-	-	-	59.51	1876	10.35	2069
05.	150	-	-	-	-	28.23	2853	7.70	2150
06.	160	44.20	1340	28.60	453	33.04	1792	5.08	2553
07.	170	25.75	1720	18.03	571	17.62	2513	7.55	1363
08.	180	-	-	-	-	17.41	1932	7.46	1107
09.	190	17.57	1476	12.55	534	12.27	2113	14.72	455
10.	200	7.44	2722	4.96	1108	-	-	-	-
11.	210	8.56	1873	7.34	619	11.95	1341	11.95	381
12.	220	6.03	2126	8.44	450	9.43	1360	4.71	806
13.	230	8.30	1250	4.74	674	6.95	1492	9.27	345 45
14.	245	4.63	1659	6.94	360	9.05	849	11.32	221
15.	250	5.73	1218	5.73	403	-	-	-	-
16.	260	5.61	1034	5.61	354	-	-	-	-

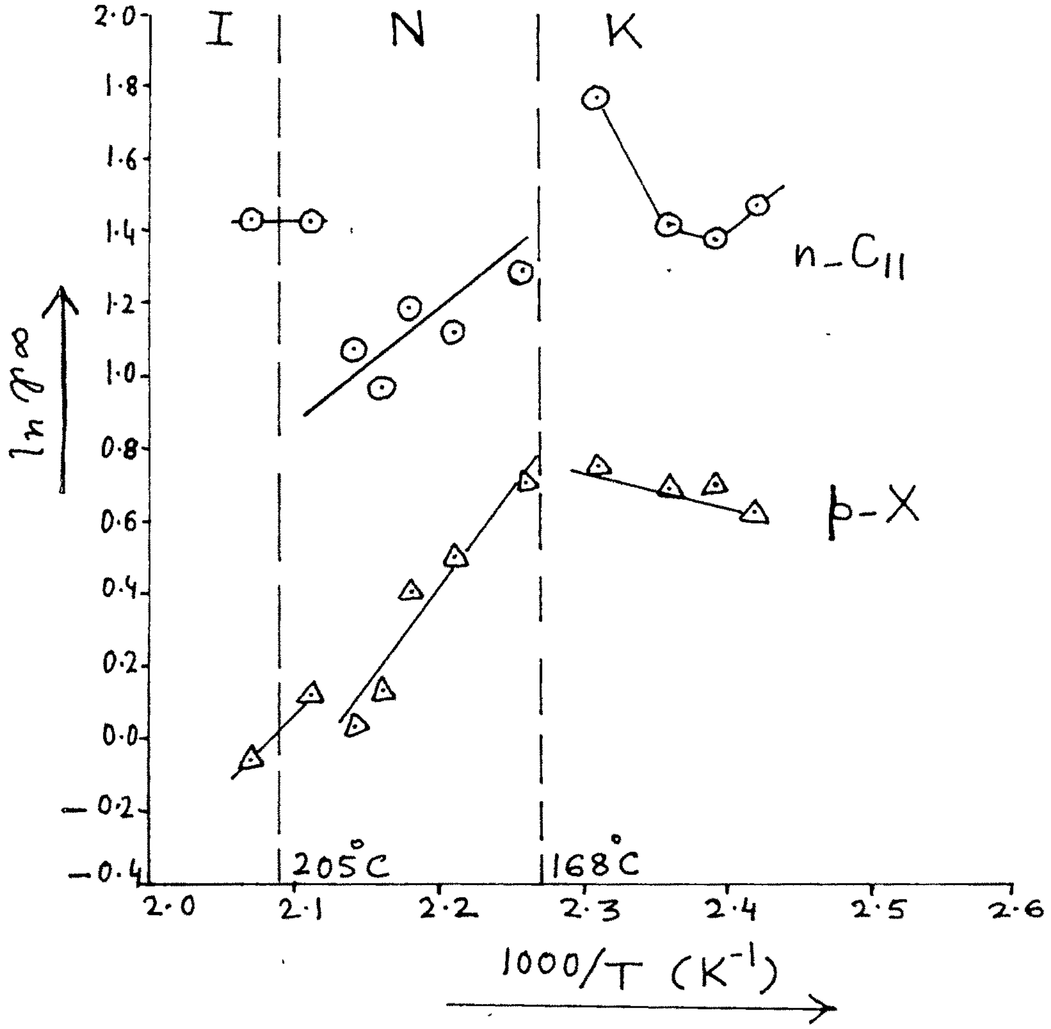


FIG. 10 $\ln\gamma^{\infty}$ vs $1/T$ PLOT FOR PNV-1 LIQUID CRYSTAL

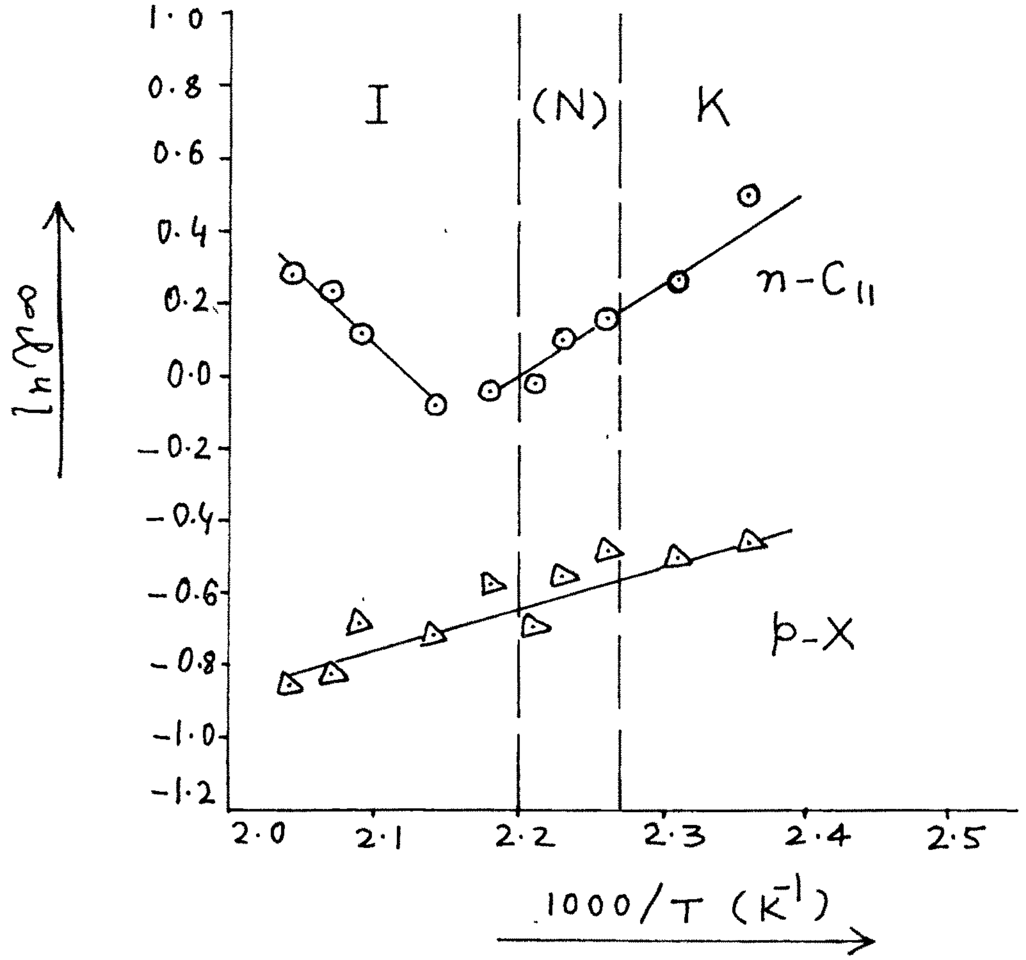


FIG. 11 $\ln\gamma^\infty$ vs 1/T PLOT FOR PNVO-2 LIQUID CRYSTAL

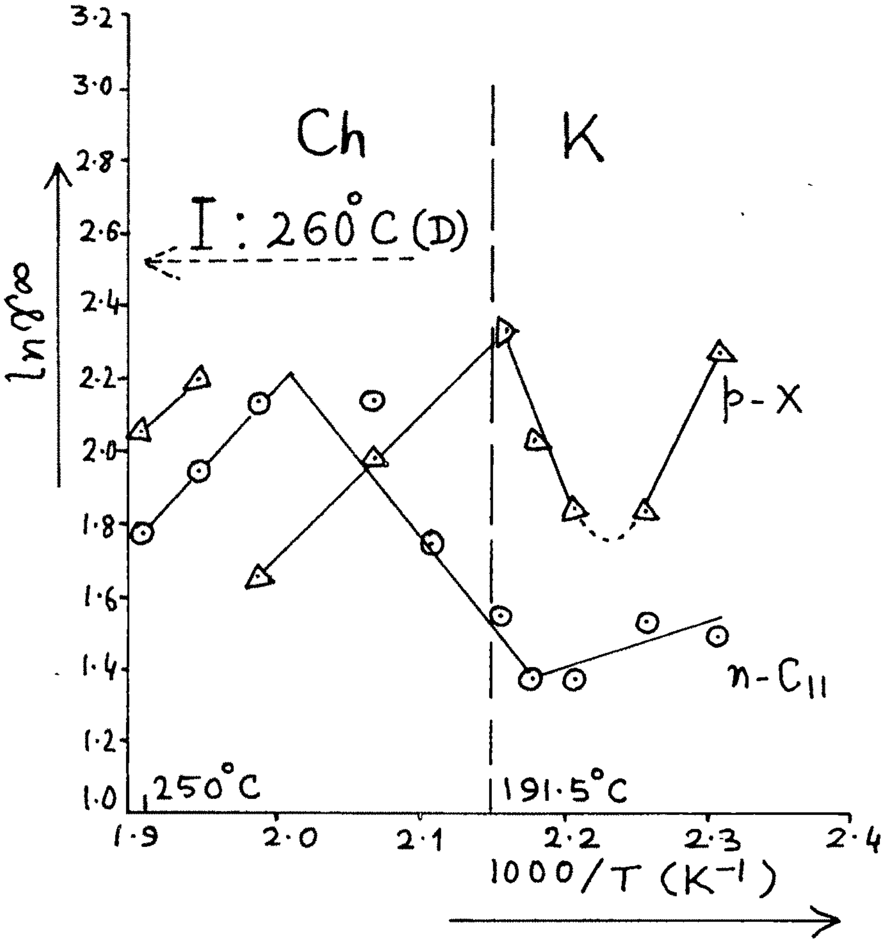


FIG. 12 $\ln\gamma^\infty$ vs 1/T PLOT FOR Ch-PNB LIQUID CRYSTAL

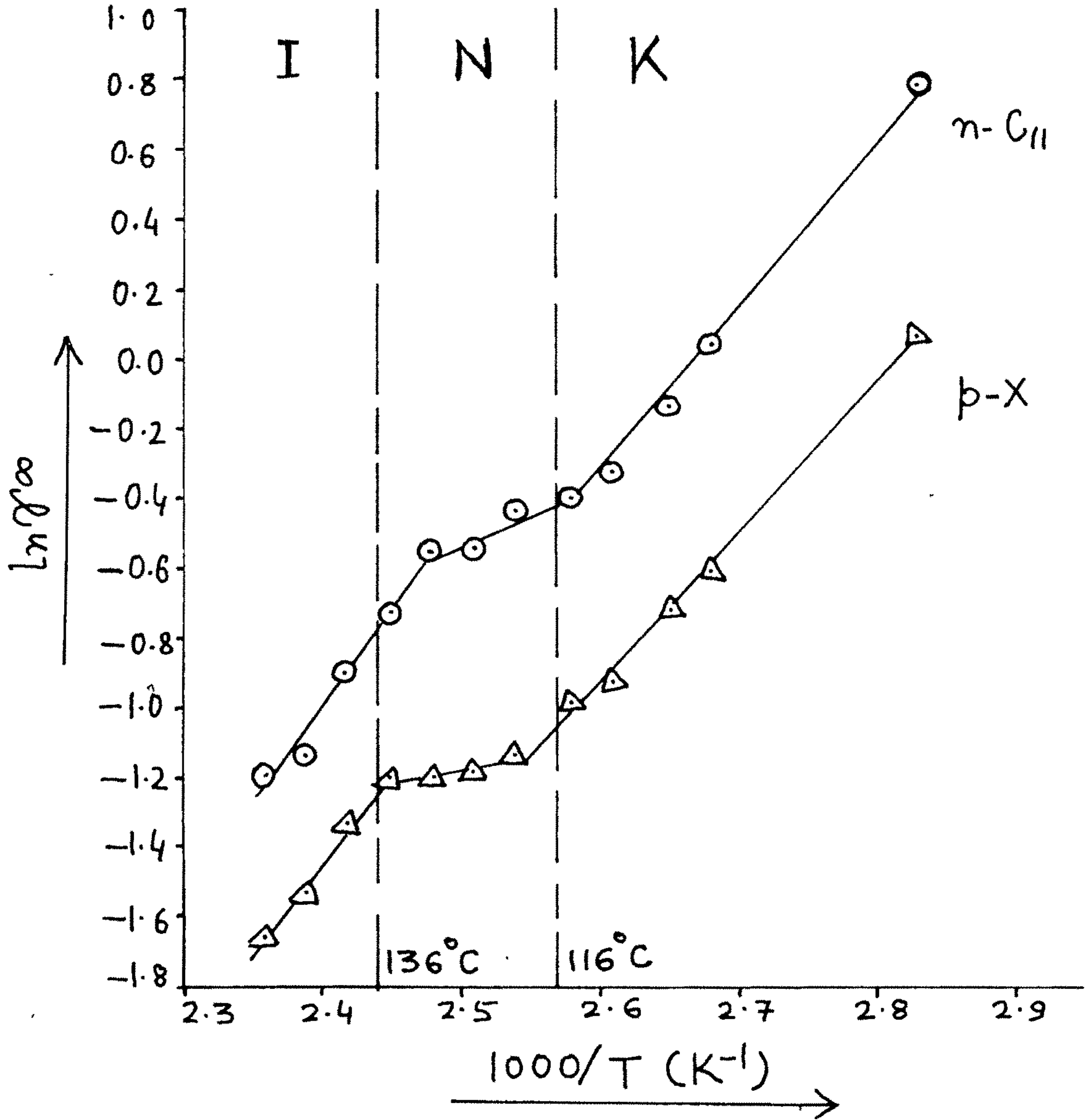


FIG. 13 $\ln \gamma^{\infty}$ VS $1/T$ PLOT FOR 12-CPG LIQUID CRYSTAL

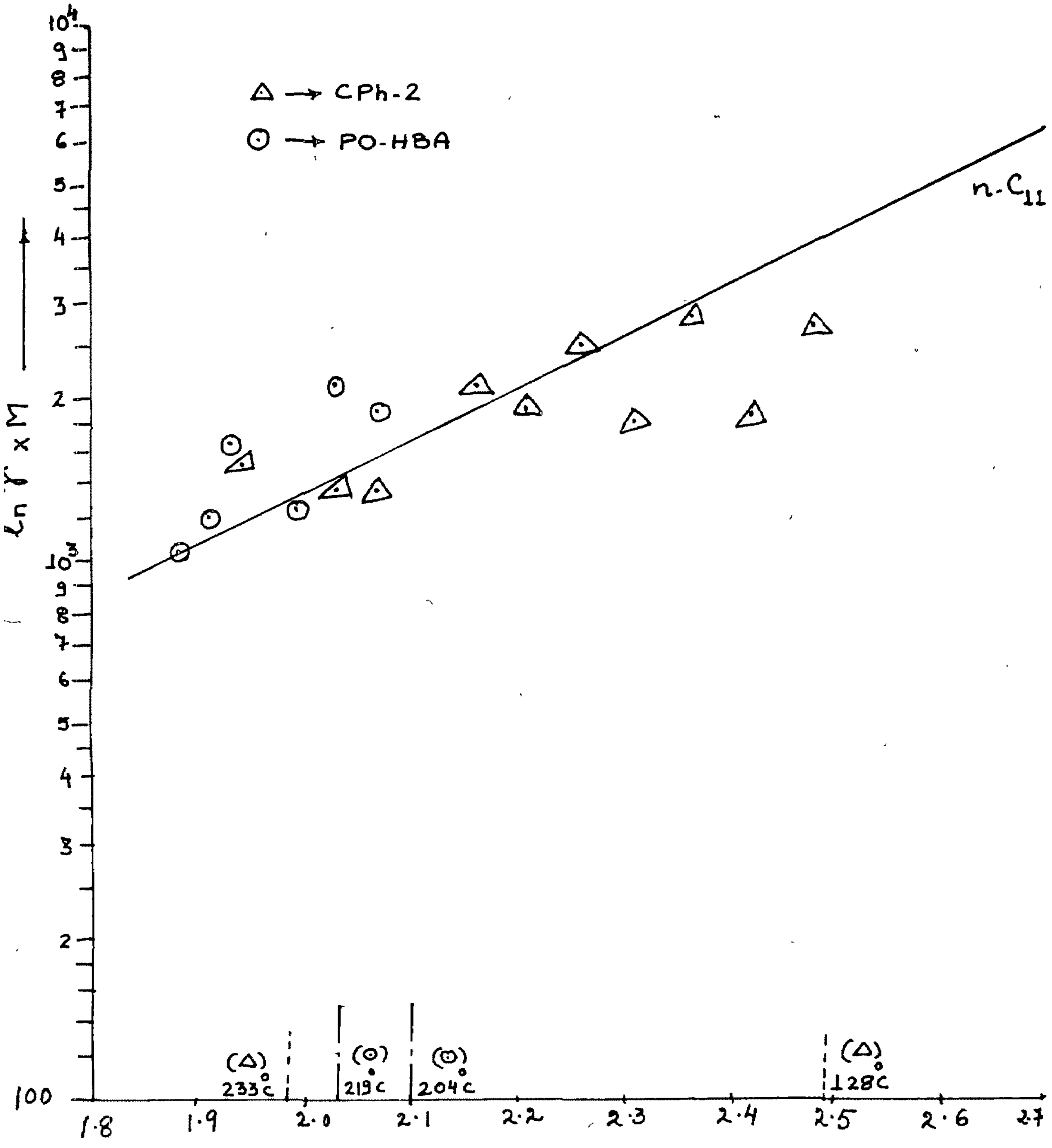


FIG. 14. ln $\gamma^{\infty} \times M$ Vs 1/T PLOT FOR n-C_{11} ON LIQUID CRYSTALLINE STATIONARY PHASES.

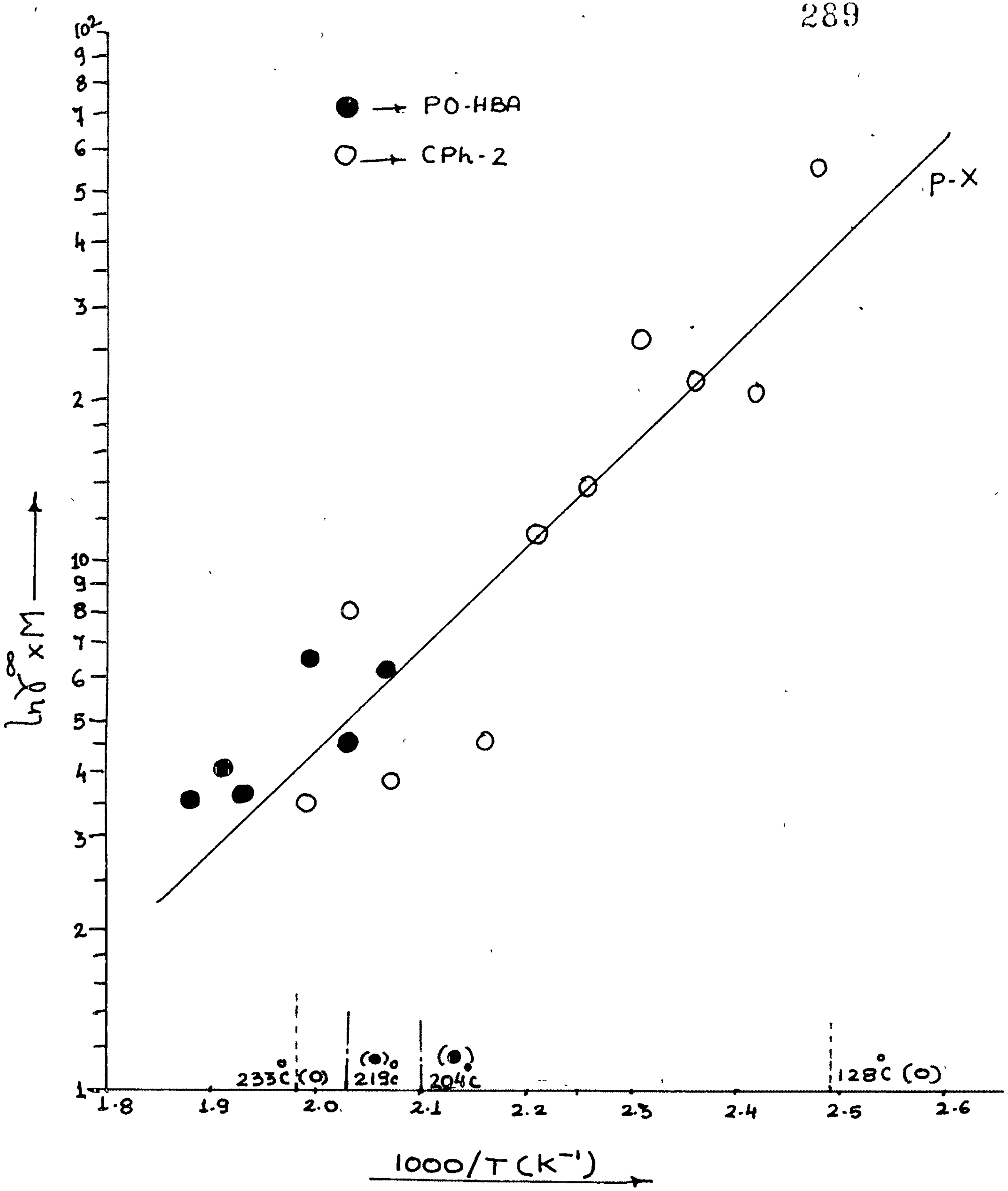


FIG. 15 $\ln \gamma^{\infty}_{xM}$ vs 1/T PLOT FOR PARA-XYLENE ON LIQUID CRYSTALLINE STATIONARY PHASES where $\overline{Ge}^{\infty}$, $\overline{He}^{\infty}$ and $\overline{Se}^{\infty}$ are the solute partial molar exess free energy, enthalpy and entropy at infinite dilution respectively.

Thus, ln γ^{∞} and 1/T are linearly related. By plotting ln against 1/T (in practice 1000/T), the slope (b) and intercept on ordinate axis (a) will give :

$$b = \frac{\partial(\ln \gamma^{\infty})}{\partial(1000/T)} = \frac{\overline{He}^{\infty}}{1000\,R}$$

OR

$$\overline{He}^{\infty} = b.\ 1000\,R$$

and,

$$a = \frac{-\overline{Se}^{\infty}}{R}$$

OR

$$\overline{Se}^{\infty} = -a\ .\ R$$

Graphs of ln γ^{∞} vs. 1000/T were plotted for the four liquid crystalline compounds viz., PNV-1, PNVO-2, Ch-PNB and 12-CPG. These are given in Figures 10 through 13 for n-C_{11} and p-xylene solutes.

Partial molar excess enthalpies and entropies have been calculated for the mesophase regions of the said four liquid crystals from ln γ^{∞} vs. 1/T study utilising above mentioned equations. The slopes and intercepts were obtained stastically by linear curve fitting using least squares method. The points considered included all those which showed linearity in the mesophase region. Thus, sometimes they belonged to regions just before the transition temperatures. This is quite consistent with the reported phenomena of pre-melting and pre-clarification point transitions. The values of $\overline{He}^{\infty}$ and $\overline{Se}^{\infty}$ are listed in table 10 for n-C_{11} and p-xylene solutes, the considered temperature ranges and the mesophases are also indicated for each liquid crystalline compound.

Figure 10 for PNV-1 shows positive and higher slopes in the nematic region than that in the isotropic region. The slopes in the solid phase are, in fact, negative. Thus, the partial molar heats of mixing are more endothermica in the mesophase region. Further, table 10 reveals that He and Se are both higher in the case of p-xylene than for n-C_{11}. It was seen earlier that activity coefficient of p-xylene were lower than that of n-C_{11}. These data indicate higher solubility of p-xylene.

The graph for PNVO-2, which shows monotropic nematic transition is given in Figure 11. As expected, for p-xylene, there is no slope change in the I regions, the substrate thus behaving like an isotropic liquid throughout. The $\overline{He}^{\infty}$ and $\overline{Se}^{\infty}$ values (table 10) are also substantially lower than the previous case. For n-C_{11}, the case is different. The plot (Fig. 11) has two distinct branches in crystalline and I regions with opposite slopes. The H and S values are also higher from table 10.

Cholesteric liquid crystal, Ch-PNB, displays strangely different characteristic for n-C_{11} solute as seen in figure 12. In the mesophase region itself there are two linear branches in the plot on the two sides of 230°C temperature, having opposite slopes. Two branches, separated by 230°C temperature are also evident for p-xylene solute, but the slopes

TABLE - 10

Partial Molar Excess Enthalpies and Entropies of Mixing of n-C_{11} and p-Xylene Solvents in Pure Liquid Crystalline Compounds.

LC Compound	Temperature Range (°C)	Mesophase	$\overline{He}^{\infty}$ (k J $mole^{-1}$)		$\overline{Se}^{\infty}$ (J $mole^{-1} dl\ g^{-1}$)	
			n-C_{11}	p-Xylene	n-C_{11}	p-Xylene
PNV -1	170 - 195	Nematic	16.63	44.05	27.0	93.5
PNVO - 2	160 - 185	Monotropy nematic	22.22	9.50	49.0	26.0
Ch-PNB	190 - 230	Cholesteric	-35.00	34.20	-88.4	54.4
	- 250	Cholesteric	27.11	-	38.1	-
	240 - 250	Cholesteric	-	21.10	-	38.5
12-CPG	115 - 135	Nematic (Discotic)	19.56	13.53	53.6	43.5

are both positive. This shows that before and after 230°C some intra-phase change takes place though the overall character remains cholesteric. Such phenomenon does not seen to have been reported earlier. It may be noted that the activity coefficients of both solutes show positive deviation (>1) and that the same for p-xylene are generally higher. Quantitative figures for $\overline{H}_e^\infty$ and $\overline{S}_e^\infty$ values are presented in table 10.

The behaviour of discotic liquid crystal, 12-CPG is shown in figure 13. For both solutes, n-C_{11} and p-xylene, the slopes are less than those in the isotropic region. This is contrary to the characteristic of PNV-1 (nematic). Heats of mixing are less endothermic in ordered mesophase. As was seen earlier, the activity coefficients of both the solutes show negative deviation i.e. are less than 1. The $\overline{He}^\infty$ and $\overline{Se}^\infty$ values for p-xylene and n-C_{11} are in the same order of magnitude as depicted in table 10.

From the above treatment for the four liquid crystals belonging to different mesophase classes, it is seen that distinctly different thermodynamic and retention characteristics are observed for p-xylene and n-C_{11} solutes. n-C_{11} is a long straight chain elastic molecule, whereas p-xylene is planer and rod-like rigid structure. The selection of these typical solutes, thus, has served the purpose of probing liquid crystals of different nature.

(iv) Analytical Application

For practical utilisation of a stationary phase in the separation of components of a mixture, it is necessary that the column should have high efficiency i.e. the solute bands should have high retention time and narrow band-width. This is achieved if the solute has sufficient solubility in the stationary phase and has high mass transfer coefficient between the stationary phase and the mobile (gas) phase. Such a characteristic is expressed in terms of number of theoritical plates (N) or height equivalent to a theoratical plate, HETP (H), as determined by following relationships :

$$N = 5.54 \left(\frac{t}{w} \right)^2$$

where t is the retention time of the peak and w is the peak width at half height of the peak.

Also,

$$H = \frac{L}{N}$$

where L is the length of the column, generally expressed in mm.

In useful packed columns the value of H should be as low as possible, generally it lies between 0.5 and 2 mm. H varies with flowrate of the carrier gas also and at an optimum flowrate H is minimum for a system. Low viscosity consistent with stability (no column bleed or phase degradation), high solubility and relative volatility for the solutes at the operating temperature are the requirements for a good column.

Table 11 lists HETP values on different studied liquid crystals for p-xylene and n-C_{11} (n-undecane) solutes. The values are determined at three temperatures corresponding to solid, mesophase and isotropic regions.

It may be noted from table 11 that the H values are always higher in the solid phase. This is quite obvious since very little or no partitioning may take place in the solid phase and the retention may be due to adsorption only.

It is also noted that the value of H is generally higher in the mesophase region than that in the isotropic phase. This is because in the mesophase region liquid crystalline ordering exists and viscosity may be higher causing slow mass-transfer of results compared to that in the pure liquid (isotropic) state. However, the significance of liquid crystals in GC separations, particularly for positional isomers, lies due to its shape-selectivity in the ordered mesophase region. Therefore, a good liquid crystalline stationary phase showed exhibit low H-value in the mesophase region also. Liquid crystals CPh-2 and 12-CPG show relatively better efficiency whereas PO-HBA is the worst. PNVO-2 shows monotropy, so its case is somewhat different. From this data, it may be suggested that these stationary phases may yield better results if total member of theoretical plates are increased e.g. in capillary columns.

It is also noted that the H-value in the mesophase region is generally higher for p-xylene than that of n-C_{11}. Again, this is due to the ordered structure of the mesophase and p-xylene being rod-like rigid molecule fits into it more strongly resisting mass-transfer into the gas phase.

TABLE - 11

Column Efficiency (HETP) in Various Liquid Crystalline Stationary Phases.

Sr. No.	St. Phase	Temp., °C	Phase	H. E. T. P. (mm) p-Xylene	$n\text{-}C_{11}$
01.	PNV-1	145	k	3.6	2.6
		170	N	3.7	3.5
		210	I	3.7	2.0
02.	PNVO-2	160	K	2.3	2.8
		175	K	2.2	2.2
		205	I	2.4	2.2
03.	Ch-PNB	180	K	2.7	5.4
		200	Ch	3.0	2.6
		250	Ch*	2.6	2.3
04.	12-CPG	110	K	2.7	1.9
		120	N	3.0	2.1
		145	I	2.9	1.8
05.	PO-HBA	155	K	55.3	33.5
		220	S	6.8	5.4
		250	N**	4.4	4.3
06.	CPh-2	110	K	3.2	4.8
		140	S	2.4	1.8
		235	I	10.6	3.2

* I - phase at 260°C, decomposes.

** I - phase at 290°C, post-polymerises.

For GC separation of two components, it is absolutely necessary that the relative volatility or separation factor, α , of these components should be different. Separation factor may also be expressed as the ratio of partition coefficients or specific retention volumes or as inverse ratio of the products of activity coefficient and vapour pressure of pure solutes :

$$\alpha_{1,2} = \frac{K_1}{K_2} = \frac{V_g(1)}{V_g(2)} = \frac{t'_{R(1)}}{t'_{R(2)}} = \frac{p_2^o \gamma_2^\infty}{p_1^o \gamma_1^\infty}$$

In table 12 a and 12 b separation factors of some organic compounds relative to p-xylene are compiled.

Among positional isomers, the separation of p-xylene and m-xylene is considered of much importance since both have nearly same boiling points and generally emerge simultaneously on polar as well as non-polar packed columns. Conventionally, they are resolved on Bentone-34 columns where the mechanism of separation is selective sorption on the surface of Bentone-34. p-Xylene emerges before m-xylene on such columns (boiling points of p & m xylenes being 138.3°C and 139.1°C respectively). Looking to the table 12a it is seen that, in the mesophase region, p-xylene emerges after m-xylene on PNV-1, Ch-PNB and CPh-2 columns. On PNVO-2, which exhibits monotropy nematic phase, m-xylene follows the p-xylene in solid and liquid phase. Strangely, p-xylene elutes after m-xylene in solid as well as isotropic regions, but in mesophase range the reverse happens. On PO-HBA also p-xylene elutes before m-xylene.

Selectivity for p & m cresols, though very little, is seen in the cases of PNVO-2 (179°C) and CPh-2 (138°C). Ch-PNB and PO-HBA do not

TABLE - 12 a

Separation Factor , (α) of different Liquid Crystals Stationary Phases in different phase regions.

Sr. No.	Solute	PNV - 1			PNVO- 2			Ch - PNB		12- CPG		
		145	175	210	160	179	200	181	201	100	119	140
01.	Benzene	0.20	0.24	0.32	0.11	0.38	0.15	0.125	0.50	0.14	0.19	0.21
02.	Toluene	0.45	0.44	0.60	0.44	0.62	0.46	0.38	0.50	0.40	0.46	0.51
03.	Ethyl benzene	0.82	0.81	0.77	1.00	0.90	0.85	0.75	0.67	0.84	0.924	0.91
04.	p-Xylene	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
05.	m-Xylene	0.97	0.96	0.97	1.11	1.09	1.08	1.00	0.83	0.98	1.01	0.97
06.	o-Xylene	1.30	1.24	1.26	1.56	1.24	1.92	1.25	0.83	1.17	1.29	1.25
07.	n-C_{11}	1.90	1.33	2.17						2.81	2.99	2.86
08.	n-C_{12}	-	2.37	3.09								
09.	n-C_{13}	-	4.59	4.91								
10.	n-C_{14}	-	8.96	8.00								
11.	p-Cresol				-	17.2	21.5	13.0	6.67			
12.	m-Cresol				28.9	20.4	23.4	13.5	6.67			
13.	o-Cresol				-	9.3	16.6	7.00	3.33			
14.	Naphthalene	-	9.33	16.2								
15.	DMT	-	8.44	-								
16.	DMI	-	6.52	-								

TABLE - 12 b

Sr. No.	Solute	PO-HBA		CPh - 2		
		175	252	118	138	243
01.	Benzene	0.23	0.29	0.40	0.25	0.50
02.	Toluene	0.46	0.57	0.60	0.50	0.75
03.	Ethyl Benzene	0.85	0.86	1.00	0.75	1.00
04.	p-Xylene	1.00	1.00	1.00	1.00	1.00
05.	m-Xylene	1.08	1.00	1.10	0.75	-
06.	o-Xylene	1.23	1.29	1.10	1.00	1.25
07.	n-C_{11}	1.31	1.14			
08.	n-C_{12}	2.69	1.71			
09.	n-C_{13}	5.15	2.43			
10.	n-C_{14}	-	3.71			
11.	n-C_{15}	-	3.71			
12.	n-C_{16}	-	6.00			
13.	n-C_{17}	-	11.7			
14.	n-C_{18}	-	14.8			
15.	DMI	-	49.1			
16.	DMT	-	53.7			
17.	Naphthalene	-	9.1			
18.	p-Cresol	-	10.3	22.0	9.75	61
19.	o-Cresol	-	8.6	12.4	22.5	21
20.	m-Cresol	-	10.3	21.6	10.5	61

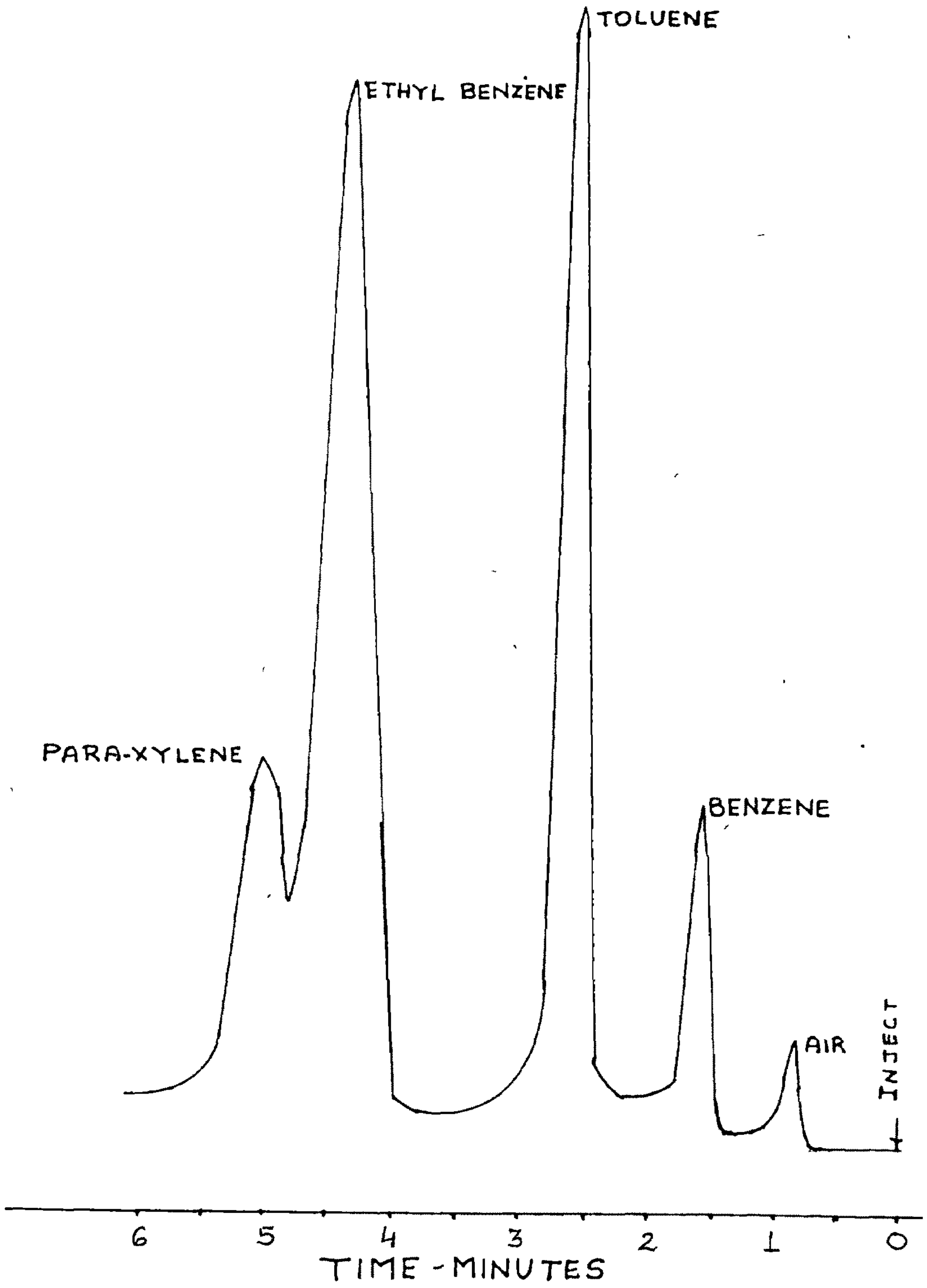
show selective separation factor. Selectivity for DMT/DMI separation is also seen in the case of PNV-1 (175°C) and PO-HBA (252°C).

In figures 16 through 20 are presented some typical separations for samples of industrial importance. Table 13, compares quantitative analysis on different liquid crystalline mesophases as well as on conventional (SE-30) stationary phase. It may be noted that in conventional analysis electronic integrator was used whereas other computations are based on h x w manual measurements. Thus the quantitative results are reasonally acceptable.

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) constituetns.

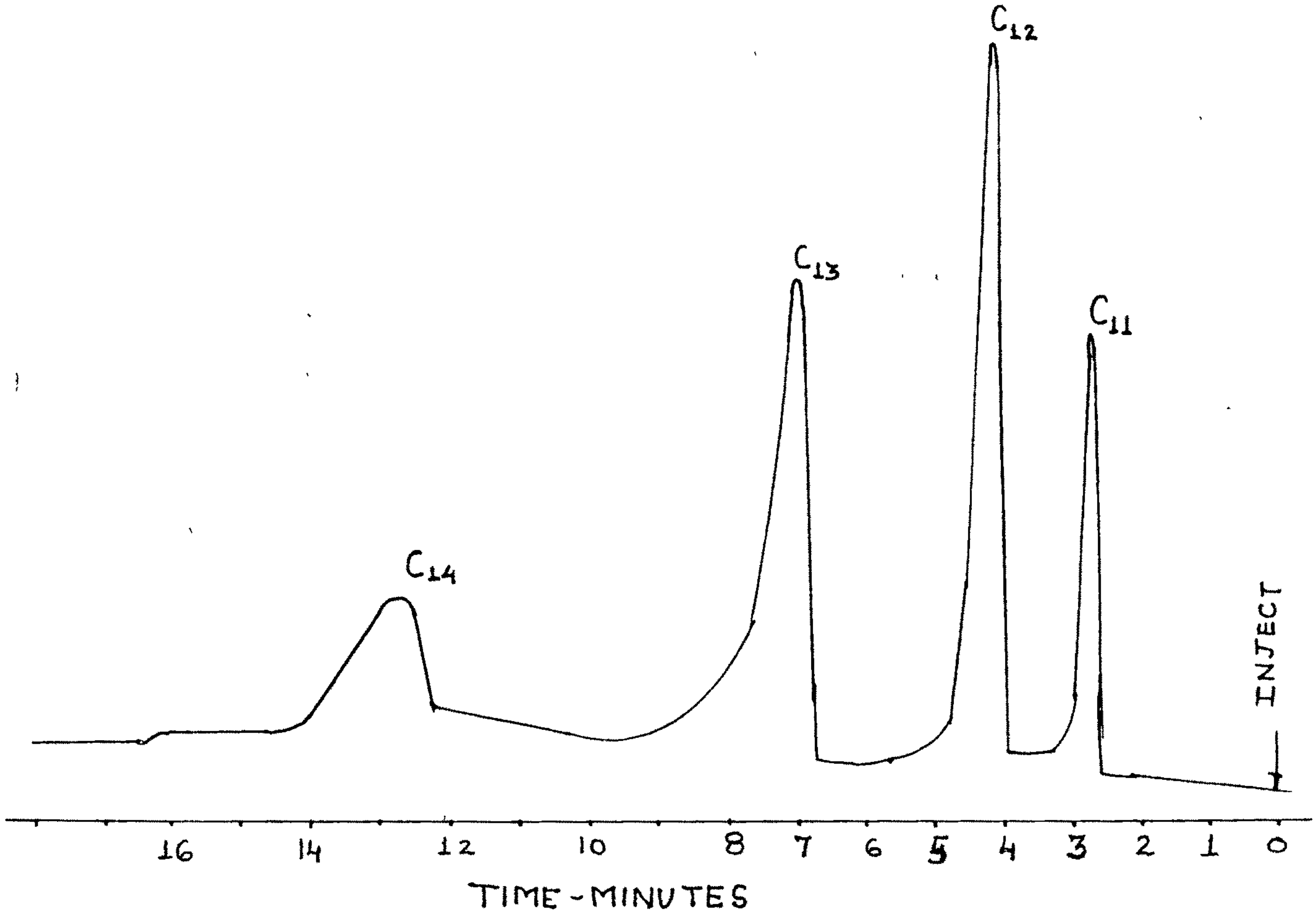
In all twenty four chromatogrames were obtained. In the present study the results incorporated are for the best separation observed. All the liquid crystalline phases do not exhibit identical behaviour.

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



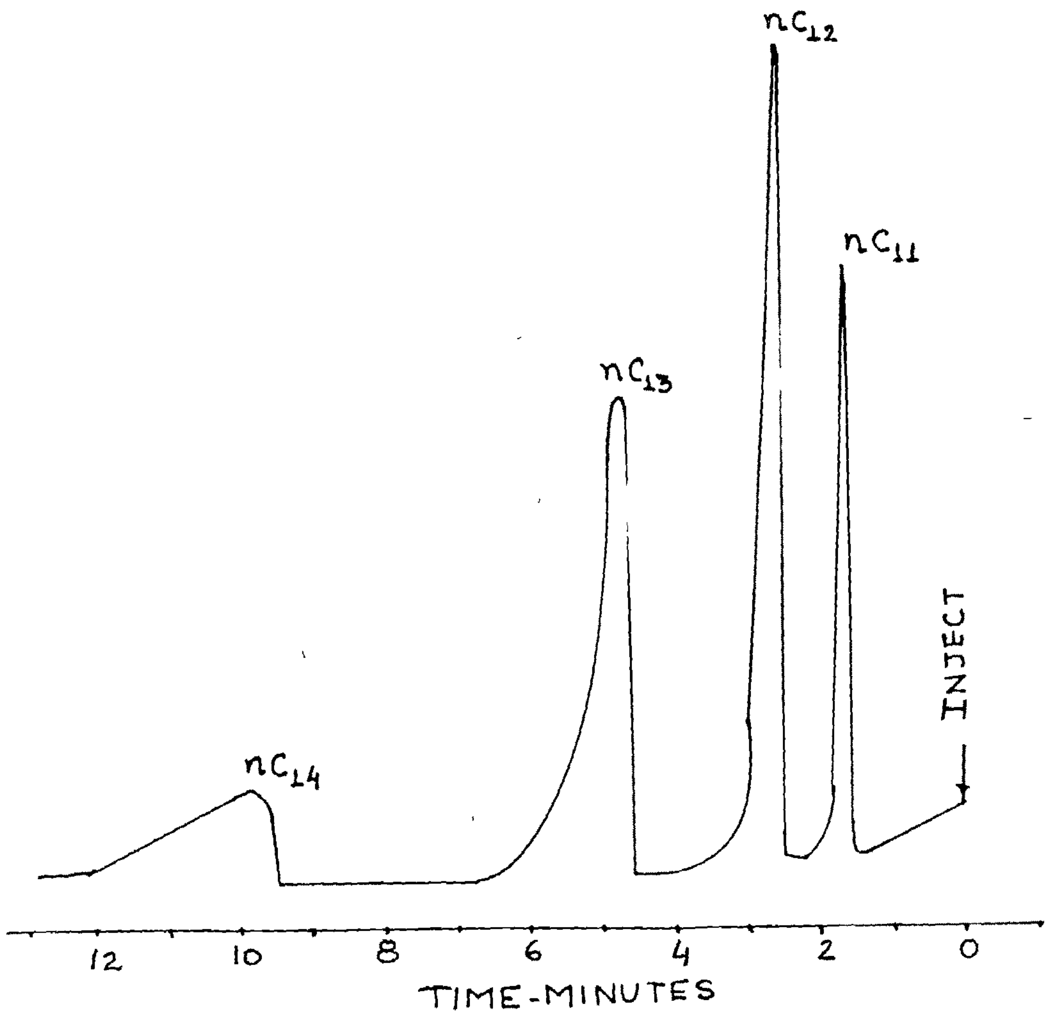
Chromatogram of Aroamtic mixture in the nematic phase (12-CPG at 119°C).

FIG 16



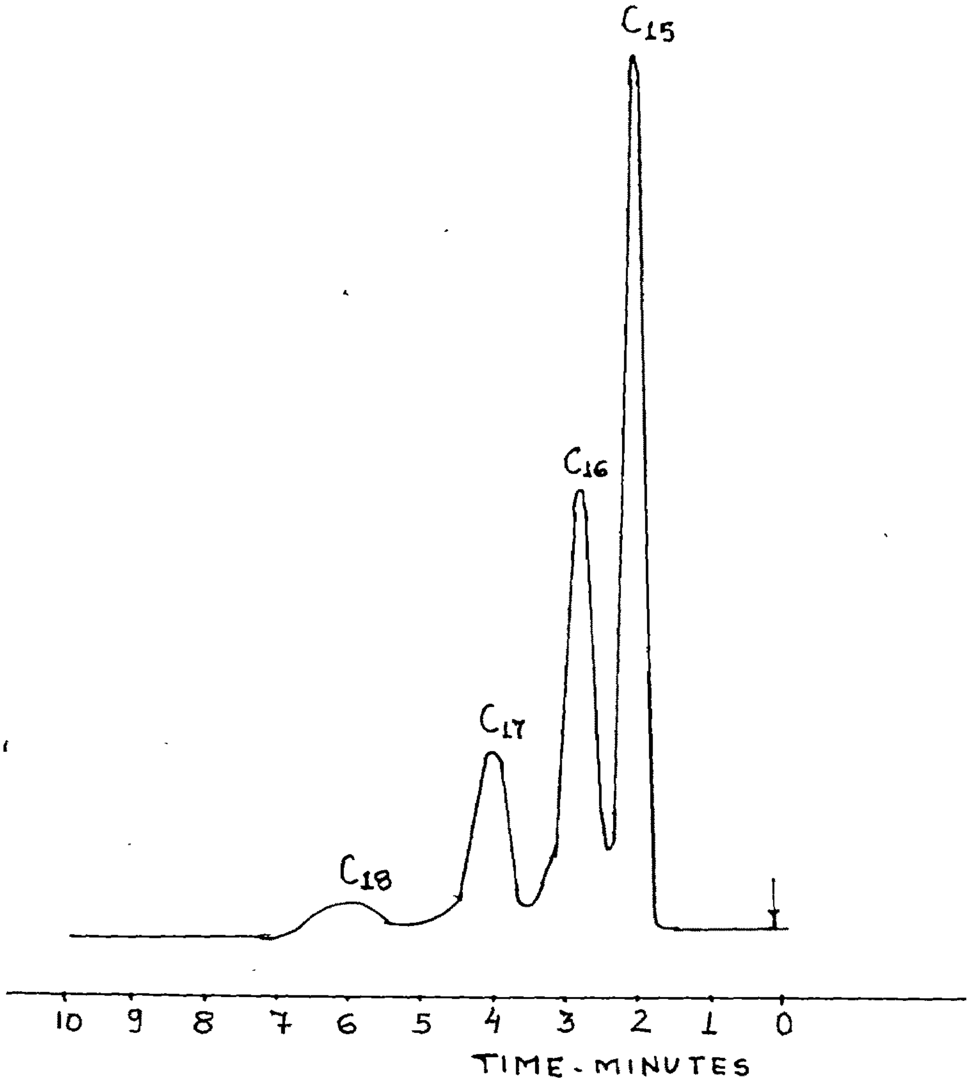
Chromatogram of noramal paraffins (n-C_{11} to n-C_{14}) in the Nematic phase (PNV-1 at 175°C).

FIG. 17



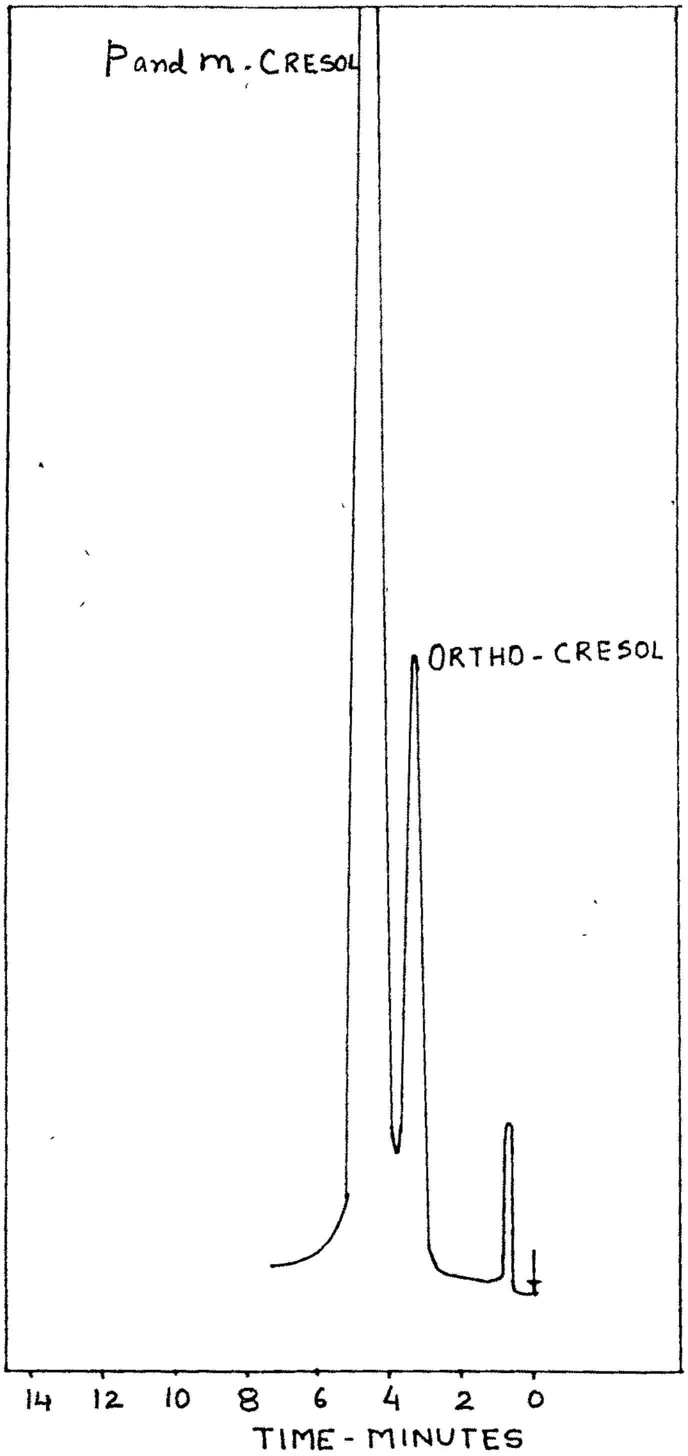
Chromatogram of normal paraffin (n-C_{11} to n-C_{14}) in the smectic phase (CPh-2 at 138°C).

FIG. 18



Chromatogram of higher normal paraffin mixture (n-C_{15} to n-C_{18}) on PO-HBA, nematic phase at 252°C.

FIG 19



Separation of Cresols on PO-HBA, nematic phase at 252°C.

FIG 20

TABLE - 13

Analysis of "Product Splitter Overhead Column sample"

(i.e. C_{11} - C_{15} n- Paraffins)

Component	% Weight (area ratios)			
	PNV-1	PNV-1	CPh-2	SE-30
	175°C (N)	210°C (I)	138°C (S)	180°C
n - C_{11}	12.37	12.73	14.06	13.6
n - C_{12}	32.02	34.50	36.25	34.6
n - C_{13}	36.03	36.15	34.29	34.8
n - C_{14}	19.58	16.62	15.40	15.7
n - C_{15}	traces	traces	traces	traces

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