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Thermodynamic and Analytical Study at infinite dilution of Non- polar organics solution by IGC used Schiff Base Liquid crystal as stationary phase

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Abstract

This article describes the thermodynamic parameters and phase behaviour of a Schiff Base Liquid crystal , the mesogene was synthesized in the five chemical reactions and characterized by FTIR ,1H and 13C-NMR techniques. The mesomorphic properties were studied using differential scanning calorimetry (DSC) and polarizing optical microscopy (POM), The retention diagrams of n-alkanes on the stationary phase were plotted at temperatures in °C between 100 and 170 by inverse gas chromatography technique. The separation of n-alkanes was estimated using retention times in the infinite dilution region. The thermodynamic parameters of intermolecular interactions between the stationary phase and n-alkanes (free energy, enthalpy, and entropy) were calculated and the results were discussed.

Keywords: Stationary Phase; Schiff Base; IGC; n-Alkanes; Thermodynamic Parameters; Liquid crystals.

Nomenclature

LC. Liquid crystal ; IGC. Inverse gas chromatography, $T_{R'}$ .Retention time ; n_C .Carbon atoms number ; a, b. Constant; $Vg°$. Specific retention volume; J. Correction for gas compressibility; p_i .Inlet pressures; p_o .Outlet pressures ; T_C. Column temperature; D_s Carrier gas flow; Ws. Mass of stationary phase; γ^{∞}. Molar activity coefficient of the probe at infinite dilution; M_s. Molecular mass of the stationary phase P°. Vapor pressure of the pure gaseous; R .The ideal gas constant = 8.314 J/mol-K; ΔG. Gibbs free energy; ΔH. Enthalpy; ΔS. Entropy.

1. Introduction

Liquid crystals [1,2] are molecules that are intermediate phases between the crystal phase and the isotropic phase. These phases are called mesophases, and molecules that generate the mesogens. The existence of these phases has been demonstrated for the first time by Friedrich Reinitzer in 1888 [3].

Liquid crystals can be classified into two main categories: thermotropic liquid crystals [4], and lyotropic liquid crystals. These two types of liquid crystals are distinguished by the mechanisms that drive their self-organization, but they are also similar in many ways; most thermo tropic liquid crystals are rod-like molecules having a rigid core composed of two or more aromatic rings and one or more flexible terminal chains. Schiff base [5,6], also known as imines (CH=N), is a linking group used in connecting two core groups.

Schiff bases, which are the most popular class of theses carbonyl derivatives, carbocyclic and heterocyclic, have been reported as important materials in coordination chemistry [7,8], analytical chemistry [9,10] and liquid crystal science [11-17]. As, the molecular shape and structure of the organic molecules governs the mesomorphic properties, therefore efforts have been devoted to relate the changes in structure and shape of the molecule with the meosmorphic behavior. In this regard, the most derivatives of Schiff base have been synthesized earlier to study their mesomorphic properties [18-19].

Using liquid crystals as a stationary phase in inverse gas chromatography (IGC) was carried out particularly interstate analytical viewpoint [20-28]. On the other hand, several authors have determined the thermodynamic parameters. It was shown some years ago that measurements recorded under the correct conditions could give accurate equilibrium thermodynamic information. [29-33] the retention of a solvent or "probe" molecule in many different mesophases is recorded, and the measurement made effectively at infinite dilution of the probe. A range of thermodynamic parameters can then be calculated.

The aim of this investigation was to study the thermodynamics properties of non polar organics solution in the Schiff Base liquid crystal stationary phases using C13-C18, normal alkanes as model solutes and to correlate the measured thermodynamic quantities and structures of the stationary phase and solutes.

2. Materials and methods

All reagents were of the highest purity available, purchased from Fluka (Steinheim, Germany) and Prolabo VWR international and were used without further purification.

The FT-IR spectra were recorded with a Perkin Elmer FT-IR 1720x. The spectra are measured on KBr pellets.The number of bands wave is expressed in cm^{-1}.

Melting points (MP) were measured in a melting point capillary with a BUCHI Melting Point B-545 apparatus.

NMR spectra were recorded on Bruker Avance DPX spectrometer (300 MHz) using deuterated chloroform CDCl 3 for 1 H NMR and deuterated dimethyl sulfoxide DMSO-d6 as a solvent to 13 C to room temperature.The chemical shift values (δ) are expressed in ppm and coupling constants (J) in Hz The multiplicity of the signals is specified using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets).

DSC measurements were made under helium atmosphere using a device NETZSCH DSC 204F1 model equipped with an electronic computer TADS (thermal analysis data station) that allows to draw the baseline and calculate the equivalent enthalpy transitions with a heating rate of 20 ° C / min, the device was calibrated by the element indium (purity: 99.9%, melting point: 156.06 ° C, heat of fusion: 28.45 J / g).

The observation by POM was performed with a Zeiss Axioskop microscope equipped with a hot stage Linkam THMS 600 connected to Linkam TMS processor 93. The photograph was taken using a camera FUJIX Digital Camera HC-300Z.

2.1 Synthesis of the Liquid Crystal

The stationary phase used was liquid crystalline 1-[4-methoxy benzylidene amino]-4-[2-butylthio- 1, 3, 4-oxadiazole-5-yl] benzene.

Detailed procedures of synthesis the intermediates and the final liquid crystals were described In the Figure 1.

2.2 Chromatographic experiments

An Auto System XL Perkin Elmer gas chromatograph was used fitted with a capillary control unit and a split-split less manual injection port. This latter, and the flame ionization detector, were maintained at 250°C. Hydrogene was used as the mobile phase at a flow-rate of 1.4 ml min^{-1} and as the make-up gas to the detector. Oven temperatures of 100 to 170 °C were used, heating and cooling the various stationary phase capillaries at less than 2°C min^{-1} to avoid possible damage.

The columns used have dimensions of 30 m length and 0.25 mm internal diameter. The capillary was deactivated with polyethylene glycol (PEG) and conditioned during 8 h in the gas chromatograph oven from 100 to 170 °C with a heating rate of 2 °C min^{-1}. The impregnation of the stationary phase was carried out by the static method (using a carbon tetrachloride solution).

2.3 Solutes

Normal alkanes were uses as sample components. Injections were made with a 0,1 µl Hamilton syringe. Each individual liquid sample and each mixture was run twice; no differences were found in the retention times when the compounds were injected individually or as a mixture, and the reproducibility was within 1%.

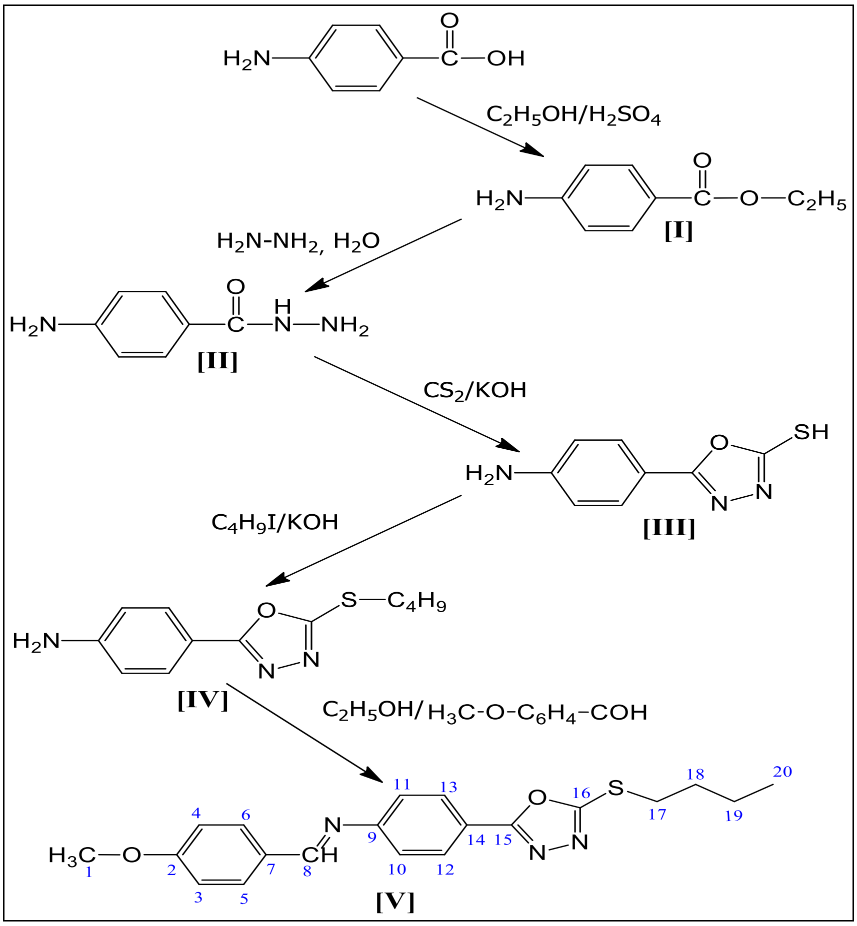

Figure 1. Synthetic scheme and structure of the liquid crystal.

3. Results and Discussions

3.1 Synthesis and Characterization of liquid crystal

The structure of liquid crystal (compound V) shown in Figure 1

The schiff base was obtained by the condensation reaction between 4-[5-(butylsulfanyl)-1,3,4-oxadiazol-2-yl] aniline and p-methoxy benzaldehyde.

Table1 brings together the physical characteristics of the prepared products: the melting point (MP) and yield (R) of each product.

Table 1. Physical properties of prepared products.

Product	Name	MP (°C)	Yield (%)
(I)	Ethyl-4-amino benzoate	89	88
(II)	4-aminobenzohydrazide	223	76
(III)	5-(4-aminophenyl)-1,3,4-oxadiazole-2-thiol	241	85
(IV)	4-[5-(butylsulfanyl)-1,3,4-oxadiazol-2-yl] aniline	115	80
(V) (LC)	1-(4-methoxy benzylidene amino)-4-(2-butylthio-1,3,4-oxadiazole-5-yl) benzene	119	87

Structural elucidation of compound LC was ascertained by using spectroscopic methods FTIR and NMR (Figure 2, Figure 3 and 4).

3.1.1. IR Spectroscopy

IR (KBr, cm^{-1}) (Figure 2): 3050–3098 (CH, aromatic), 2838–2956 (CH, aliphatic), 1506 (C═N, oxadiazole), 1600 (CH═N, imine), 1417, 1466, 1511 (C═C, aromatic), 1244(CH3─O), 1165 (C─O, oxadiazole).

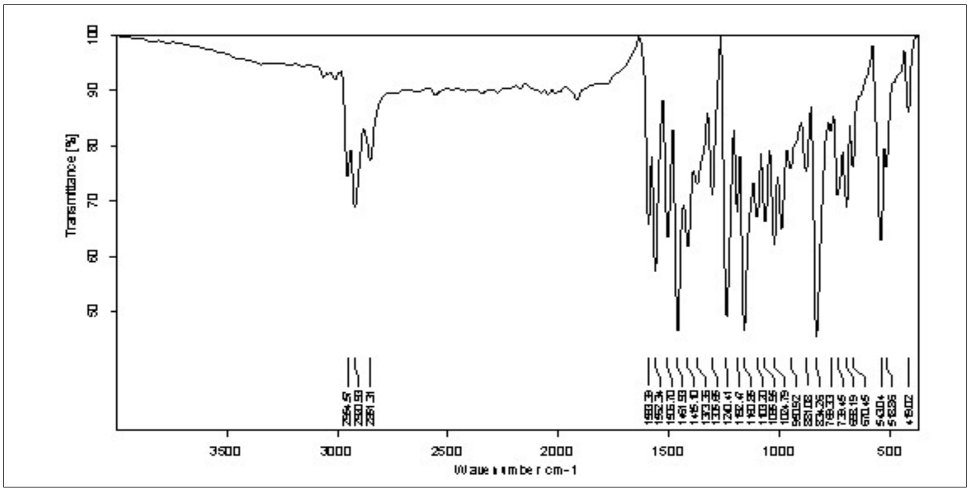

Figure 2. IR Spectrum of the liquid crystal.

Strong absorption bands appeared at 2838 and 2956 cm^{-1} in FTIR spectrum of LC indicates for aliphatic C-H in alkyl chain. A medium bands at 1417, 1466, 1511 cm^{-1} can be ascribed to C=C bonds of aromatic linking group. Absorption band emerged at 1506 cm^{-1} designates for C=N linking group.
An absorption band at 1165 cm-1 can be assigned to C-O stretching of oxadiazol.

3.1.2. ^{1}H and ^{13}C-NMR spectroscopy

^{1}H NMR (CDCL$_3$-d6, ppm) (Figure 3): 0.95-1.00 (t, 3H; *J* = 7.2 Hz; H-20), 1.26 (m, 2H; *J* = 7.2 Hz; H-19), 1.83 (qui, 2H; *J* = 7.2 Hz; H-18), 3.28 -3.33 (t, 2H; *J* = 7.6 Hz; H-17), 3.88 (s, 3H; H-1), 6.99-7.01 (d, 2H; *J* = 8.4 Hz; H-3, H-4), 7.26-7.29 (d, 2H; *J* = 8.4 Hz; H-5, H-6), 7.85-7.88 (d, 2H; *J* = 8.8 Hz; H-10, H-11), 8.00-8.03 (d, 2H; *J* = 8.4 Hz; H-12, H-13), 8.40 (s, 1H; H-8; imines).

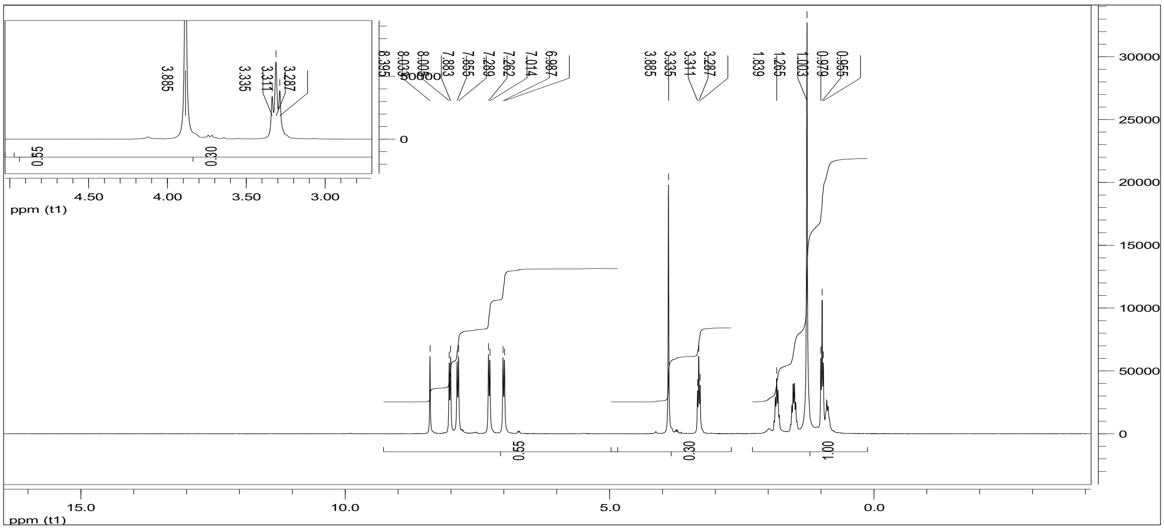

Figure 3: ^{1}H NMR Spectrum of the liquid crystal.

^{13}C NMR (DMSO-d6, ppm) (Figure 4): 13.51(1C; C-20), 21.76 (1C; C-19), 31.29 (1C; C-18), 31.92 (1C; C-17), 55.46 (1C; C-1), 114.30 (2C; C-3, C-4), 120.65 (2C; C-10, C-11), 121.55 (1C; C-14), 127.73 (2C; C-5, C-6), 128.84(1C; C-7), 130.86 (2C; C-12, C-13), 155.22 (1C; C-9), 160.72 (1C; C-8), 162.69 (1C; C-2), 163.62 (1C; C-16), 164.97 (1C; C-15).

3.1.3. Thermal and Optical Behavior

The relative thermogram in differential scanning calorimetry (DSC) and the nematic mesophase are shown in Figure 5 and Figure 6.

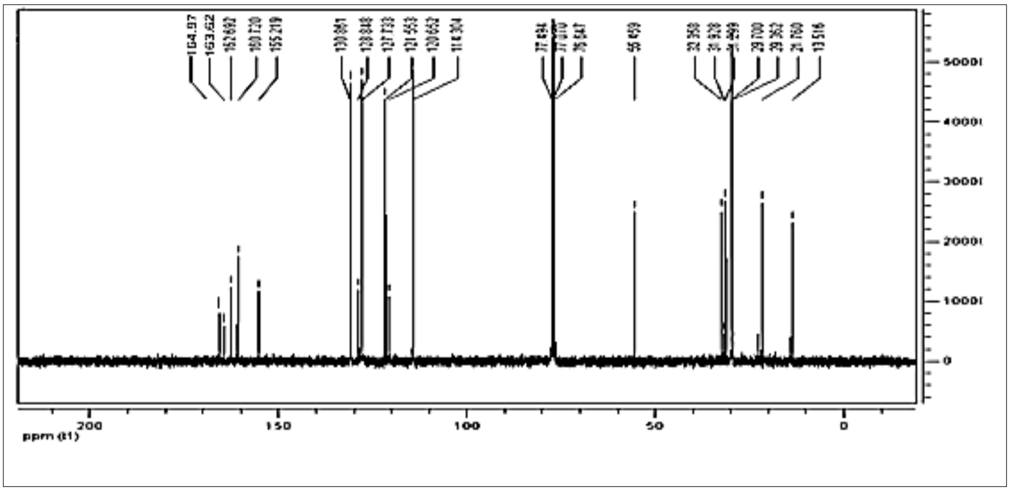

Figure 4: ^{13}C NMR Spectrum of the liquid crystal.

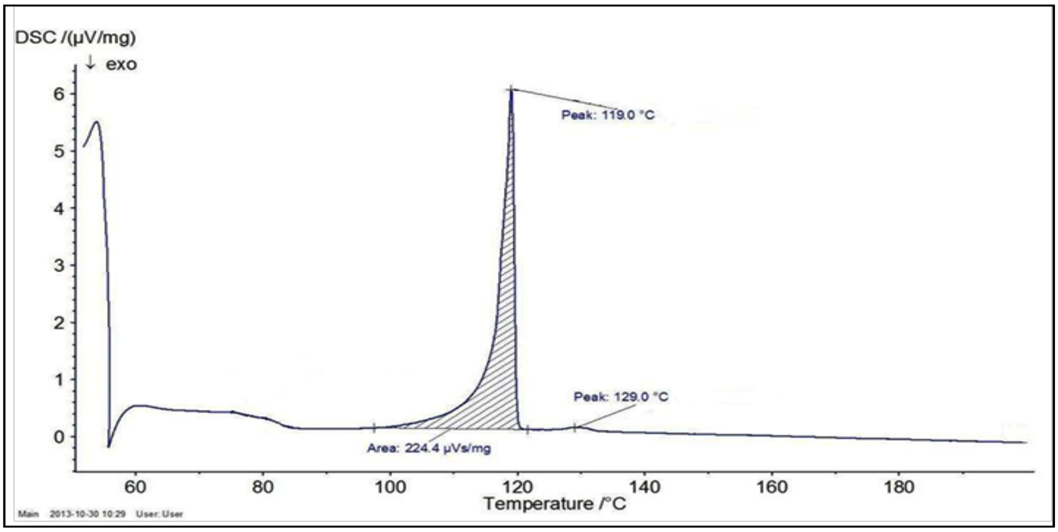

Figure 5: DSC thermograms of the liquid crystal.

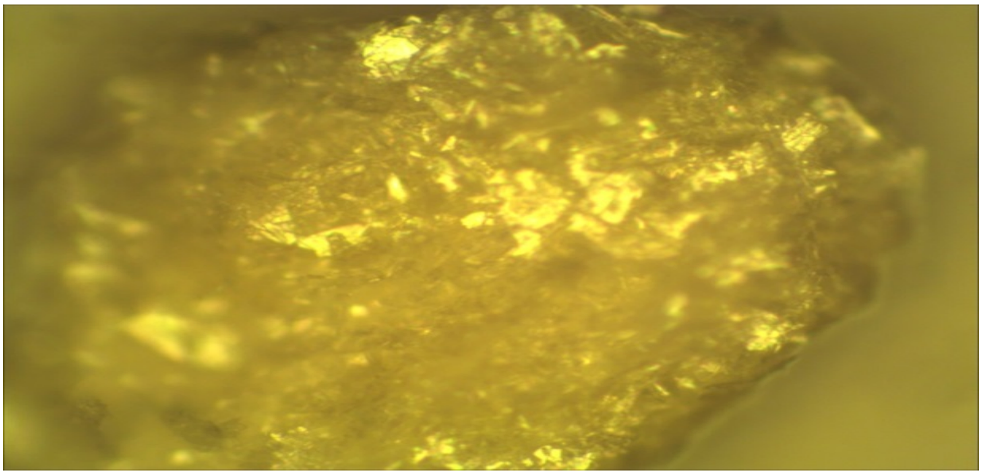

Figure 6: Optical photomicrographs of the liquid crystal (textures of nematic phase at 125°C, magnification x 200).

So the results obtained by measuring the DSC are as follows: transition temperature solid phase to nematic mesophase at 119 ° C .and the nematic mesophase to the isotropic phase at 129 °C.

The mesophases were identified by their textures observed by optical microscopy a marbled texture in the heating process as to identify the Nematic phase.

3.2 Analytical Study

The effectiveness of a column depends on the spreading of the peaks, and is measured for each compound by the number of theoretical plates N. The number of theoretical plates N of n-alkanes probe is listed in Table.2.

Table.2: The number of theoretical plates N of n-alkanes probe.

Phases	Temperature (°C)	N (plates . m^{-1})
Crystalline (Cr)	112	1567
Nematic (N)	125	1986
Isotrope (I)	155	1834

The numbers of theoretical plates calculated for the filled capillary column synthesized liquid crystal is comparable; superb selectivity and separation is observed in the nematic phase (figure 3).

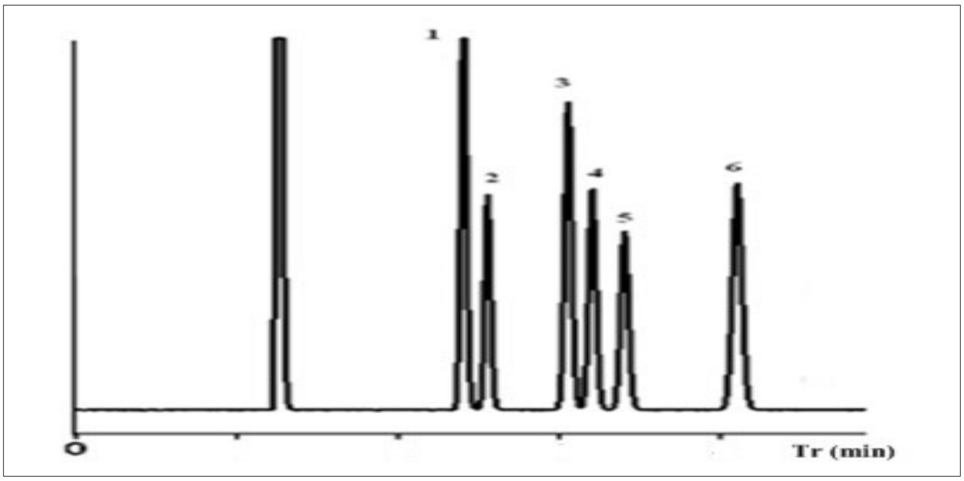

Figure 7: Separation of a mixture of n-alkanes to the nematic phase (at T = 125 ° C).
1-C13, 2-C14, 3-C15, 4-C16, 5-C17, 6-C18.

From values retention times shown in Figure 7, it shows that these retention times is proportional to the number of carbon atoms of alkanes; and is also noticed that our liquid crystalline phase has better separate the series of n-alkanes where the nematic phase showed better separation.

3.3 Thermal study by IGC

It consists of the study of variation of b Prametre according to the inverse of the temperature (Figure 8). The b parameter is the slope of the plot of the logarithm corrected retention times (T_R ') of a homologous series depending on the number of carbon atoms:

$$\mathrm{Log\,(TR')} = \mathrm{b.(n\,C)} + \mathrm{a} \qquad (1)$$

From the figure 8 we see two sharp breaks in the transition temperatures; and show all the n-alkanes retention bill decreases with increasing temperature.

3.4 Thermodynamic Study

It consists in the study of the variation of thermodynamic parameters (enthalpy and entropy and Gibbs free energies) with temperature.

From the infinite dilution activity coefficients at different temperatures, enthalpies and entropies and free energies of interaction [3] (Table 3) are determined by the following equations Eq 2 and Eq 3:

$$\mathrm{Ln}\,\gamma^{\infty} = \frac{\Delta H^{\infty}}{RT} - \frac{\Delta S^{\infty}}{R} \qquad (2)$$

$$\Delta G^{\infty} = RT\,\mathrm{Ln}\,\gamma^{\infty} \qquad (3)$$

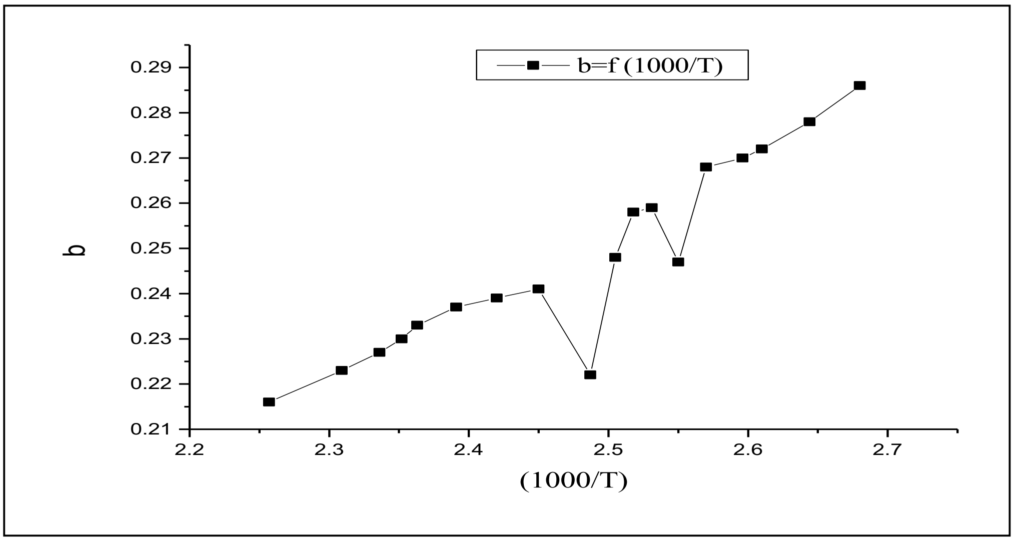

Figure 8: Evolution of slope b according to 1000 / T (K).

The infinite dilution activity coefficients γ^{∞} were calculated from corresponding values using Vg where ms is the molar mass of solvent and P °, saturation vapor pressure by the equation Eq .4 (Topphoff et al (1999)) [34, 35]:

$$\gamma^{\infty} = \frac{237{,}15\,R}{V_g\ m_s\ P^0} \qquad (4)$$

And plot the variation of ln γ^{∞} curves versus the inverse of temperature 1000 / T (Figure 9):

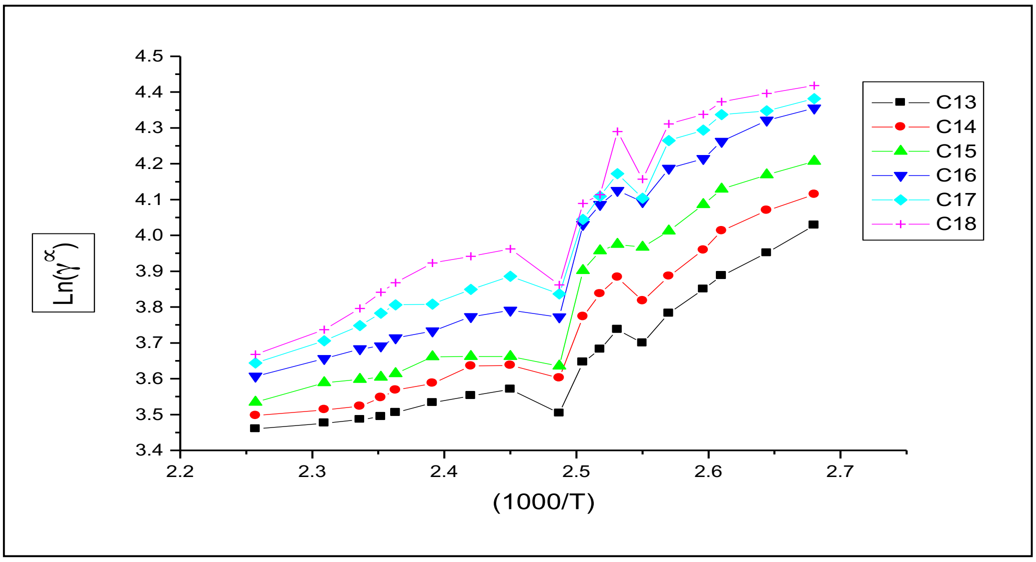

Figure 9: Evolution of ln γ^{∞} alkanes according to 1000 / T (K).

From the Figure 9, we show that the infinite dilution activity coefficients are proportional to the inverse temperature; transitions temperatures except where they relate to breakage**.**

The results of the enthalpy variation ΔH^{∞} and the entropy variation $\Delta S^{\infty,}$ free energies at infinite dilution are shown in Table 3 and Table 4.

From the results of Table 3, we see that the enthalpy values at infinite dilution are positive and larger in the nematic phase with other phases report; and the entropy of sondes- stationary phase system is even positive.

Table.3: Enthalpy variation and entropy variation at infinite dilution of the homologous series of alkanes studied for stationary phase.

Phase	**Isotrope**		**Nematic**		**Crystalline**	
n-Alkanes	**ΔH^{∞}**	**ΔS^{∞}**	**ΔH^{∞}**	**ΔS^{∞}**	**ΔH^{∞}**	**ΔS^{∞}**
C13	2.48	3.22	29.12	12.98	18.57	6.13
C14	2.66	3.25	35.32	17.55	17.26	5.66
C15	6.78	4.03	23.52	26.78	14.72	4.08
C16	7.74	2.49	30.20	22.50	12.66	3.40
C17	9.86	8.26	40.81	29.10	19.88	5.81
C18	11.03	6.01	64.17	28.73	24.55	4.51

Table 4. The free energies at infinite dilution of the homologous series of alkanes by the stationary phase at each temperature.

T	**ΔG^{∞} (kJ/mol)**					
(C°)	**C13**	**C14**	**C15**	**C16**	**C17**	**C18**
170	12.75	12.89	13.03	13.30	13.43	13.52
160	12.52	12.66	12.93	13.17	13.35	13.47
150	12.34	12.56	12.72	13.07	13.40	13.61
140	12.21	12.49	12.59	12.97	13.23	13.55
129	11.94	12.17	12.25	12.68	13.00	13.25
126	11.63	11.96	12.07	12.52	12.74	12.82
124	12.04	12.46	12.89	13.39	13.36	13.51
119	12.33	12.68	13.09	13.50	13.76	13.90
110	12.39	12.79	13.16	13.58	13.82	13.94
100	12.50	12.77	13.06	13.52	13.60	13.71

From the results of Table.4, the free energies values at infinite dilution is positive and is noted these values are proportional to the number of atoms of the probes.

The enthalpy values at infinite dilution ΔH^{∞} of (n-alkanes-stationary phase) system were found to possess positive values indicating an endothermic interaction process. It is also clear from Table 4 that the enthalpies in the mesophase region are greater than in the isotropic melt, which means that the solution process in an anisotropic liquid needs more energy because of the difficulty of dissolving molecules in a highly ordered structure.

The positive values of entropy ΔS^{∞} for the interaction of alkanes on the stationary phase indicates that the interaction species are more ordered on the surface, while the change in the free energy ΔG^{∞} values of alkanes on the liquid crystal was found to possess a positive values indicate and the interaction is non spontaneous.

Conclusions

In summary, we have reported the synthesis of Schiff-base LC was reported. The molecular structures of prepared compound were confirmed by NMR, FTIR and the thermal study by IGC confirmed the result of transitions temperatures of mesophase obtained by DSC and POM.

The specific interactions energies of the molecular probes with the LC. The change in the valeurs of enthalpy and entropy and free enthalpy of the n-alkanes probes-LC interaction depended also on the temperatures.

Moreover, the increase in the temperatures clearly influences the retention temps of the n-alkanes onto the LC, thus reflecting changes in the porous structure when the LC in temperatures transitions.

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