

Physicochemical characterization of 5-Decyloxy-2-[[[4-Hexyloxyphenyl]Imino]Methyl]Phenol liquid crystal by inverse gas chromatography

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Trace amount of solvents such as benzene, toluene, ethylbenzene, n-propylbenzene, isopropylbenzene and chlorobenzene were passed through the gas chromatography column loaded with a new synthesized and characterized liquid crystal compound, 5-decyloxy-2-[[[4-hexyloxyphenyl]imino]methyl]phenol (DHOPIMP) which is coated on Chromosorb W. The retention diagrams of the solvents on the liquid crystal were plotted by means of specific retention volumes, V_g° at temperatures between 130 and 150 °C by inverse gas chromatography. The weight fraction activity coefficient at infinite dilution of the solvents, Ω_1^∞ , the liquid crystal-solvent interaction parameters of Flory-Huggins, χ_{12}^∞ , and equation of state, χ_{12}^* and effective exchange energy parameter, X_{eff} , were obtained. In addition, the partial molar heats of sorption, $\Delta\bar{H}_{1,\text{sorp}}$ and mixing, $\Delta\bar{H}_1^\infty$ were determined. Phase transition temperatures of DHOPIMP were determined by polarizing microscopy and differential scanning calorimetry.

(Received September 24, 2008; accepted November 27, 2008)

Keywords: Inverse gas chromatography, Liquid crystal, Phase transition temperature, Thermodynamics, Interaction parameter

1. Introduction

Mesogenic salicylaldimine compounds are very interesting materials for the physical investigations. The vast majority of compounds exhibiting liquid crystalline phases may be regarded as having a rigid molecular central group with one or two flexible terminal alkyl or alkoxy chains. Depending on the carbon number of the terminal alkoxy and/or alkyl groups in the salicylaldimine core, these materials display various liquid crystalline properties [1, 2].

Inverse gas chromatography (IGC) is widely used for characterization of polymers, polymer blends, surfactants, biopolymers, solid food and petroleum products, biological materials and liquid crystals [3-10]. In IGC method, the investigated nonvalite material such as a liquid crystal has been placed in the column and characterized using volatile solute probes. Liquids of known properties are then injected into the column containing the sample. The retention times of these trace amount liquids are used in determination of their interactions with the investigated nonvalite material in the column.

The objective of this work was to conduct a detailed study of the thermodynamic properties of 5-decyloxy-2-[[[4-hexyloxyphenyl]imino]methyl] phenol (DHOPIMP) which is a new synthesized liquid crystal with various solvents by IGC. First, the retention diagrams of some solvents on this liquid crystal compound were obtained over a temperature range from 130 to 150 °C, and then some thermodynamic parameters in the Flory-Huggins and

equation of state theories of the DHOPIMP were determined.

2. Experimental

2.1. Materials and instrumentation

The characterization of the liquid crystalline compound DHOPIMP synthesized here are based on various spectroscopic data, e.g., ^1H -, ^{13}C -NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in CDCl_3 solutions) with tetramethylsilane as internal standard, MS [AMD 402 (electron impact, 70 eV)].

Transition temperatures were measured using a Linkam THMS 600 hot stage and a Linkam TMS 93 temperature control unit in conjunction with a Leitz Laborlux 12 Pol polarizing microscope, and these were confirmed using differential scanning calorimetry (Mettler TA 3000/DSC-30 S with TA 72.5 software, heating and cooling rate: 10 K min^{-1}).

A Hewlett-Packard 6890 N gas chromatography with a thermal conductivity detector was used to measure the retention time of the solvents. The column was stainless steel tubing with 3.2 mm o.d. and 1m in length. Trace amount solvent was injected into the column with a 1 μL Hamilton syringe. At least five consecutive injections were made for each solvent at each column temperature. The flow rate of the carrier gas was kept almost constant at 4 $\text{cm}^3\text{min}^{-1}$.

All studied solvents and support material being Chromosorb-W (AW-DMCS-treated, 80/100 mesh) were supplied from Merck AG. Inc. Silane treated glass wool used to plug the ends of the column was obtained from Alltech Associates, Inc.

2.2. Synthesis of the liquid crystalline compound DHOPIMP

The compound 5-decyloxy-2-[[[4-hexyloxyphenyl]imino]methyl]phenol were prepared in the usual way [2,11,12] by a *p*-toluensulfonic acid (40 mg) catalyzed condensation of 4-decyloxy-2-hydrobenzaldehyde (5 mmol) with 4-hexyloxyaniline (6 mmol) in toluene (25 ml) and purified by crystallization from acetone/methanol. The DHOPIMP was characterized by various spectroscopic methods [12]. Only structurally relevant resonances are given, see below.

Yield: 1.61 g (71%) of yellow crystals. **¹H-NMR**: δ (ppm) = 13.84 (s; OH), 8.47 (s; HC=N), 7.23 (d; $J \approx 8.5$ Hz; 1 arom. H), 7.20 (d; $J \approx 8.5$ Hz; 2 arom. H), 6.90 (d; $J \approx 8.5$ Hz; 2 arom. H), 6.50 (d; $J \approx 2.7$ Hz; 1 arom. H), 6.46 (dd; $J \approx 8.5$ Hz, $J \approx 2.7$ Hz; 1 arom. H), 3.98, 3.95 (2t; $J \approx 6.5$ Hz; 2 OCH₂). **¹³C-NMR**: δ (ppm) = 163.82, 163.24, 157.97, 141.10, 113.05 (5s; 5 arom. C), 159.39 (d; HC=N), 133.10, 121.92, 115.14, 107.38, 101.57 (5d; 1, 2, 2, 1 and 1 arom. CH, respectively), 68.32, 68.19 (2t; 2 OCH₂). C₂₉H₄₃NO₃ (453.7); **MS (EI)**: m/z (%) = 453 (100) [M]⁺, 313 (18) [453-C₁₀H₂₀]; **MS (HR)**: m/z (%) = 453.3243 [M]⁺, Calc. 453.3244.

2.3. Theoretical Background on IGC

The specific retention volume, V_g^0 is determined experimentally from IGC measurements as follows [13-19].

$$V_g^0 = Q(t_R - t_A)J273.2/(T_r w) \quad (1)$$

where Q is carrier gas flow rate measured at the room temperature T_r ; t_R and t_A are retention times of the solvent and air, respectively; J is pressure correction factor, w is weight of liquid crystal in the column.

Ω_1^∞ is the weight fraction activity coefficient of solvent at infinite dilution, defined by the following equation,

$$\ln \Omega_1^\infty = \ln(273.2R/V_g^0 p_1^0 M_1) - p_1^0(B_{11} - V_1^0)/RT \quad (2)$$

where R is the universal gas constant; p_1^0 , B_{11} and V_1^0 are saturated vapor pressure, gaseous state second virial coefficient and molar volume of the solvent at temperature T ; M_1 is the molecular weight of solvent, respectively.

According to the theories of Flory-Huggins and equation of state interaction parameters, χ_{12}^∞ and χ_{12}^* are defined in the Eq.(3) and Eq.(4), respectively:

$$\chi_{12}^\infty = \ln\left(\frac{273.2Rv_2}{p_1^0 V_g^0 V_1^0}\right) - \left(1 - \frac{V_1^0}{M_2 v_2}\right) - \frac{p_1^0(B_{11} - V_1^0)}{RT} \quad (3)$$

$$\chi_{12}^* = \ln\left(\frac{273.2Rv_2^*}{p_1^0 V_g^0 V_1^*}\right) - \left(1 - \frac{V_1^*}{M_2 v_2^*}\right) - \frac{p_1^0(B_{11} - V_1^0)}{RT} \quad (4)$$

where v_2 is specific volume of the liquid crystal, M_2 is molecular weight of the liquid crystal, v_2^* is specific hard-core volume of the liquid crystal and v_1^* is molar hard-core volume of the solvent, respectively.

The effective exchange energy parameter, X_{eff} in the equation of state theory is defined as follows,

$$RT\chi_{12}^* = p_1^* V_1^* \{3T_{1r} \ln[(v_{1r}^{1/3} - 1)/(v_{2r}^{1/3} - 1)] + v_{1r}^{-1} - v_{2r}^{-1} + X_{\text{eff}}/p_1^* v_{2r}\} \quad (5)$$

where p_1^* is characteristic pressure of the solvent, v_{1r} and v_{2r} are reduced volume of the solvent and liquid crystal, respectively. T_{1r} is reduced temperature of the solvent.

The partial molar heat of sorption, $\Delta\bar{H}_{1,\text{sorp}}$, of the solvent sorbed by the LC is given as

$$\Delta\bar{H}_{1,\text{sorp}} = -R[\partial(\ln V_g^0)/\partial(1/T)] \quad (6)$$

where T is the column temperature in K. The partial molar heat of mixing, $\Delta\bar{H}_1^\infty$ at infinite dilution of the solvent is given as

$$\Delta\bar{H}_1^\infty = R[\partial(\ln \Omega_1^\infty)/\partial(1/T)] \quad (7)$$

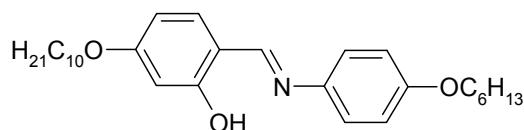
Molar heat of vaporization, ΔH_v , of the solvent is related to $\Delta\bar{H}_{1,\text{sorp}}$ and $\Delta\bar{H}_1^\infty$ as follows:

$$\Delta H_v = \Delta\bar{H}_1^\infty - \Delta\bar{H}_{1,\text{sorp}} \quad (8)$$

3. Results and discussion

The compound DHOPIMP was prepared in good yield under a nitrogen atmosphere and in two step process [12]. The DHOPIMP have been purified by several recrystallizations from acetone/methanol. The structure of DHOPIMP was characterized using various spectroscopic methods (¹H-, ¹³C-NMR and mass). The proposed molecular structure of compound DHOPIMP presented in Table 1 is in full agreement with these spectroscopic data (see Experimental Section).

Table 1. Phase transition temperatures ($^{\circ}\text{C}$) and enthalpies^a (kJ mol^{-1}) of the salicylaldimine compound DHOPIMP: Cr: crystalline, SmC: smectic C and Iso: isotropic mesophase.



Compound	Cr	SmC	Iso
DHOPIMP	• 69.3 (33.8)	• 123.2 (5.3)	•

^aThe enthalpies are in parentheses.

For the salicylaldimine DHOPIMP with two peripheral side chains, enantiotropic mesomorphic properties were observed. The investigations by polarizing microscopy (PM) and differential scanning calorimetry (DSC) show that it exhibits *smectic C* (*SmC*) mesophase. The transition temperatures and corresponding enthalpy values observed for the DHOPIMP is summarized in Table 1. On cooling of the compound DHOPIMP from isotropic phase smectic phase with broken fan-shaped and schlieren textures can be observed (see Fig. 1). For this compound the presence of the OH group increases the clearing point and the overall smectic range, because intramolecular hydrogen bonding gives rise to an increased coplanarity in the central part of the molecule [2, 20,21].

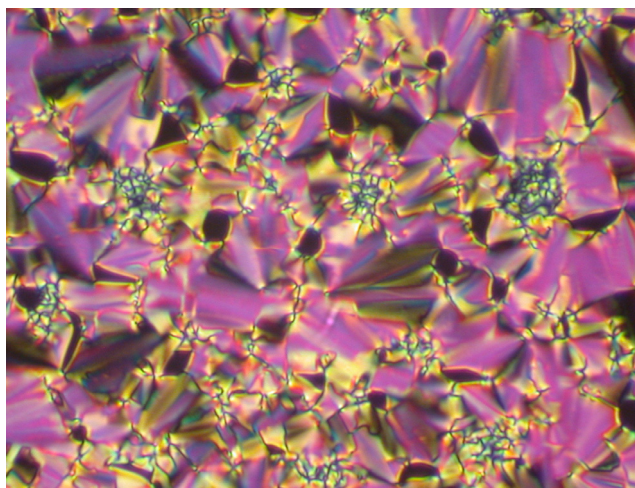


Fig. 1. Optical texture of smectic C phase of compound DHOPIMP observed at 95°C on cooling from isotropic phase.

The DHOPIMP shows similar mesomorphic properties with the previously synthesized analogs [2, 10,11]. During heating, the *crystal* – *Smectic C* phase transition occurs at 69.3°C and the *Smectic C* – *isotropic liquid* phase transition occurs at 123.2°C , in this case, the *Smectic C* mesophase exists in the temperature interval as 53.9°C . DSC scan can be seen in Fig. 2.

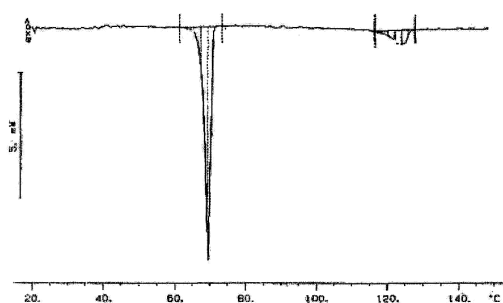


Fig. 2. DSC scan of compound DHOPIMP during the second heating process.

The specific retention volume, V_g^0 of the benzene (B), toluene (T), ethylbenzene (EB), n-propylbenzene (PB), isopropylbenzene (IPB) and chlorobenzene (CB) on the DHOPIMP were obtained from IGC measurements between 130 and 150°C using Eq.(1) because thermodynamical equilibrium occurred at this temperature range. The retention diagrams of the solvents on the liquid crystal were plotted in Fig. 3.

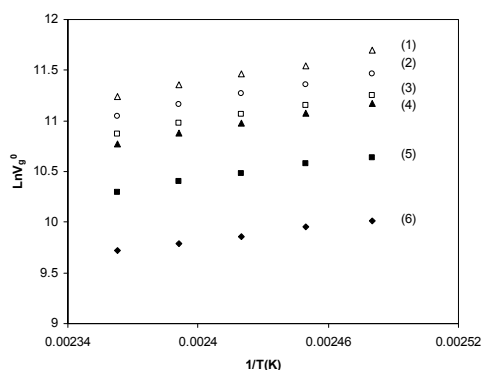


Fig. 3. The retention diagrams of PB(1), IPB(2), CB(3), EB(4), T(5) and B(6) on DHOPIMP.

According to Guillet, the solvent is good if the weight fraction activity coefficient of solvent at infinite dilution, Ω_1^{∞} is lower than 5 and poor if it is higher than 10. The values between 5 and 10 indicate moderately solubility. Ω_1^{∞} was determined from Eq.(2) and the values of Ω_1^{∞} are given in Table 2. The values of Ω_1^{∞} suggest that all studied solvents given in Table 2 are good for the DHOPIMP at the studied temperatures.

Table 2. The weight fraction activity coefficient at infinite dilution of the solvents, Ω_1^{∞} of DHOPIMP with studied solvents at various column temperatures.

t($^{\circ}\text{C}$)	B	T	EB	PB	IPB	CB
130	3.80	3.17	3.67	3.60	3.57	2.84
135	3.63	3.01	3.56	3.66	3.43	2.73
140	3.59	2.94	3.43	3.41	3.27	2.62
145	3.50	2.87	3.35	3.31	3.20	2.54
150	3.41	2.86	3.31	3.26	3.17	2.52

The polymer-solvent interaction parameters, χ_{12}^{∞} and χ_{12}^* were determined from Eq.(3) and Eq.(4) and the values of χ_{12}^{∞} and χ_{12}^* were given in Table 3 and Table 4, respectively. The values of χ_{12}^{∞} greater than 0.5 represent unfavourable liquid crystal-solvent interactions while the values lower than 0.5 indicate favourable interactions in dilute liquid crystal solutions. The values of the parameters suggest that all studied solvents are good solvents of the DHOPIMP. The trends of all sets of data are similar, showing a decrease of the interaction parameter as the temperature is increased. This indicates that the solvent quality increases with temperature.

Table 3. Flory-Huggins liquid crystal- solvent interaction parameters, χ_{12}^{∞} of DHOPIMP with studied solvents at various column temperatures.

t(°C)	B	T	EB	PB	IPB	CB
130	0.36	0.22	0.41	0.43	0.42	0.35
135	0.31	0.16	0.38	0.44	0.38	0.31
140	0.30	0.14	0.34	0.37	0.33	0.27
145	0.26	0.11	0.31	0.34	0.30	0.23
150	0.24	0.10	0.30	0.32	0.29	0.22

Table 4. Equation of state liquid crystal-solvent interaction parameters, χ_{12}^* of DHOPIMP with studied solvents at various column temperatures.

t(°C)	B	T	EB	PB	IPB	CB
130	0.52	0.35	0.52	0.53	0.53	0.46
135	0.47	0.29	0.48	0.54	0.48	0.42
140	0.45	0.26	0.44	0.46	0.43	0.37
145	0.42	0.23	0.42	0.43	0.40	0.34
150	0.39	0.22	0.40	0.41	0.39	0.32

The effective exchange energy parameters, X_{eff} in the equation of state theory were obtained from Eq.5 and results were given in Table 5. The higher values of X_{eff} indicate poor solubility while the lower values of X_{eff} indicate good solubility. The lower values of X_{eff} confirm the discussion concerning.

Table 5. The effective exchange energy parameters, X_{eff} (J/cm^3) of DHOPIMP with studied solvents at various column temperatures.

t(°C)	B	T	EB	PB	IPB	CB
130	3.88	-3.14	5.00	4.64	2.62	5.12
135	3.26	-4.05	5.13	6.48	2.88	4.68
140	4.29	-3.87	4.94	5.16	2.58	4.17
145	4.28	-4.09	5.19	5.21	3.00	3.75
150	4.18	-3.06	5.62	5.57	3.80	4.38

$\Delta\bar{H}_{1,\text{sorp}}$ and $\Delta\bar{H}_1^{\infty}$ were determined from the slope of the logarithm of specific retention volume, $\ln V_g^0$, versus $1/T$ plot (Eq.(6)) and from the slope of the logarithm of the

weight fraction activity coefficients, $\ln \Omega_1^{\infty}$ versus $1/T$ plot (Eq.(7)), respectively. ΔH_v was found by their subtraction from Eq.(8). According to the values of $\Delta\bar{H}_1^{\infty}$, the solubility of liquid crystal in B, T, EB, PB, IPB and CB are endothermic. In Table 6, ΔH_v values obtained were compared with the ΔH_v^{lit} values calculated according to Watson's relationship in Reference [22]. The values of ΔH_v obtained by IGC are in good agreement with the literature.

Table 6. The partial molar heat of sorption, $\Delta\bar{H}_{1,\text{sorp}}$ (kcal/mol), the partial molar heat of mixing, $\Delta\bar{H}_1^{\infty}$ (kcal/mol), molar heat of vaporization, ΔH_v (kcal/mol) obtained by Eq. 8 and molar heat of vaporization, ΔH_v^{lit} [22] (kcal/mol).

Solvents	$\Delta\bar{H}_1^{\infty}$	$-\Delta\bar{H}_{1,\text{sorp}}$	ΔH_v	$\Delta H_v^{\text{lit(22)}}$
B	1.7	5.0	6.7	7.3
T	1.7	5.8	7.5	7.9
EB	1.8	6.8	8.6	8.5
PB	2.0	7.4	9.4	9.1
IPB	2.0	7.0	9.0	9.0
CB	2.1	6.4	8.5	8.7

4. Conclusions

The liquid crystal DHOPIMP has been synthesized and characterized. The phase behaviour of DHOPIMP was investigated by PM and DSC. The parameters related to the interaction of the liquid crystal with some solvents were determined by IGC. The values of all parameters suggest that studied solvents in this study are good for DHOPIMP and solvent quality increases with temperature. These results suggest that an endothermic solubility behavior may exist between liquid crystal and studied solvents.

Acknowledgements

This research has been supported by Yildiz Technical University Scientific Research Projects Coordination Department.

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