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Liquid Crystals

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Use of inverse gas chromatography for the physicochemical characterisation of a new synthesised liquid crystal: (*S*)-5-(2-methylbutoxy)-2-{[(4-dodecyloxyphenyl)imino]methyl}phenol

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Use of inverse gas chromatography for the physicochemical characterisation of a new synthesised liquid crystal: (*S*)-5-(2-methylbutoxy)-2-{[(4-dodecyloxyphenyl)imino]methyl}phenol

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A new liquid crystalline compound, i.e. (*S*)-5-(2-methylbutoxy)-2-{[(4-dodecyloxyphenyl)imino]methyl}phenol (MBDOPIMP), was prepared and characterised. Phase transition temperatures of MBDOPIMP were determined by polarising optical microscopy and differential scanning calorimetry. Trace amounts of ethyl acetate, butyl acetate, isobutyl acetate, hexane, heptane, octane, nonane and decane were passed through a chromatographic column loaded with MBDOPIMP coated on Chromosorb W. The retention diagrams of the solvents on MBDOPIMP were plotted using specific retention volumes at temperatures between 105 and 125°C. Thermodynamic parameters, such as Flory–Huggins liquid–solvent interaction, χ_{12}^{∞}, equation-of-state liquid–solvent interaction, χ_{12}^{*}, effective exchange energy, X_{eff}, the exchange enthalpy, X_{12} and exchange entropy, Q_{12}, were determined for the liquid crystal–solvent systems. Subsequently, the partial molar heats of sorption, $\Delta\bar{H}_{1,\mathrm{sorp}}$ and mixing, $\Delta\bar{H}_1^{\infty}$, were determined from the slopes of the plots of the logarithm of the specific retention volume, ln V_g^0, versus $1/T$ and logarithm of the weight fraction activity coefficients, ln Ω_1^{∞}, versus $1/T$, respectively.

Keywords: inverse gas chromatography; liquid crystal–solvent interaction; thermodynamic interaction parameter

1. Introduction

Liquid crystals (LCs) have attracted much interest for many years due to use of these materials in numerous applications, such as display devices, optical and thermal sensors and stationary phases in chromatographic columns. Calamitic (rod-shaped) thermotropic liquid crystals exhibit several mesophases, which vary with temperature. A calamitic molecule consists of a rigid core with at least two aromatic rings, which are connected by linking groups and flexible terminal chains (*1*). Many studies have focused on the modification of molecular structure to obtain desired properties due to great importance of calamitic mesogens for technical applications. There are many examples of calamitic molecules synthesised to determine the effect of change of tail length on mesophase type and transition temperatures (*1–3*). In addition, the presence of a chiral tail connected to the rigid core can give rise to a significant change in the mesogenic behaviour of LCs (*4, 5*). By introducing a chiral moiety into LC molecules, unusual physical properties can also be obtained (*4–6*). Therefore, compounds containing chiral chains are also of increasing interest for the molecular design of LCs.

In recent years, inverse gas chromatography (IGC) has been used to investigate interactions between a LC and a solvent (*7–9*). IGC is an extension of conventional gas chromatography in which a solid material such as a liquid crystal to be investigated is immobilised within a column. Liquids of known properties are then injected into the column containing the sample. The retention times of these trace-amount liquids in the column are used to determine their interactions with the solid. The main thermodynamic parameters that provide valuable information for physico-chemical characterisation of a LC can be acquired relatively rapid and with good accuracy. The solubility data of a LC in some solvents might be required in design of novel applications in fields such as membranes and chemical sensors.

Recently, we suggested a new method of estimating an average exchange enthalpy, X_{12} and exchange entropy, Q_{12}, parameters for liquid crystal–solvent systems by IGC measurements (*10–14*). The parameters X_{12} and Q_{12} were determined by using a relationship given for the enthalpy interaction parameter in the equation of state theory, which is arranged for IGC conditions. This method has been used for only one liquid crystal–solvent pair until now (*15*). Thus, the method required many studies to confirm its reliability.

In this paper, the synthesis, characterisation and mesomorphic properties are reported of a salicylaldimine compound, (*S*)-5-(2-methylbutoxy)-2-{[(4-dodecyloxyphenyl)-imino]methyl}phenol (MBDOPIMP), that includes alkyloxy end chains, one of which is chiral. Some thermodynamic parameters of the LC were determined using the Flory–Huggins and equation-of-state theories in the temperature range

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105–125°C. The results are compared with data for anologues of MBDOPIMP.

2. Experimental

Materials and instrumentation

The characterisation of the MBDOPIMP was carried out using various spectroscopic techniques, i.e. ^{1}H and ^{13}C NMR (Varian Unity 500 and 400 spectrometers, in $CDCl_3$ solutions with tetramethylsilane as internal standard), UV–visible (Agilent 8453, $CHCl_3$ solutions), FT-IR (Perkin Elmer, $CHCl_3$ solutions) and MS (AMD 402, electron impact, 70 eV). Microanalyses were performed using a Leco CHNS-932 elemental analyser.

Mesomorphic properties were investigated using polarising optical microscopy (POM) and differential scanning calorimetry (DSC). Microscopy was performed on a Leitz Laborlux 12 Pol polarising microscope equipped with a Linkam THMS 600 hot stage and a Linkam TMS93 temperature controller. DSC thermograms were recorded on a Perkin-Elmer DSC-7, using heating and cooling rates of 10 K min^{-1}.

Ethyl acetate (EA), butyl acetate (BA), isobutyl acetate (IBA), hexane (Hx), heptane (Hp), octane (O), nonane (N) and decane (D) were obtained from Merck AG Inc. The support material, Chromosorb-W (AW-DMCS-treated, 80/100 mesh), was also supplied by Merck AG Inc. Silane-treated glass wool used to plug the ends of the column was obtained from Alltech Associates, Inc.

A Hewlett-Packard 6890 N gas chromatograph 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 1 m in length. Trace amount solvent was injected into the column with a 1 µl Hamilton syringe; 0.1 µl of solvent was taken into the syringe and flushed into the air. The resudial solvent was diluted five times by taking 1 µl of air into the syringe. At least three consecutive injections were made for each solvent at each column temperature. The flow rate of the carrier gas was kept almost constant at 4 cm^3 min^{-1}. Before the experiments, it was determined experimentally that the retention volume does not depend on the flow rate of the carrier gas below 6 cm^3 min^{-1}. The eluted peaks of studied solvents are sharp, symmetrical and reproducible above 3 cm^3 min^{-1} in the studied temperature range. The retention times were precise and reproducible to ± 0.001 min. The LC was coated onto the support by slow evaporation of chloroform while stirring the Chromosorb W in the LC solution. The proportion of the LC on the support was determined as 8.36% by calcination. Various authors like Galin and Rupprecht (*16*) have stated that specific retention volumes, V_g^0, are independent of the column loading at around 8% since the opposite effects of adsorption and non-equilibrium diffusion cancel each other around this column loading.

Synthesis of the MBDOPIMP

(*S*)-4-(2-methylbutoxy)-2-hydroxybenzaldehyde (*17*) (2.5 mmol), 4-dodecyloxyaniline (*18*) (3 mmol) and *p*-toluenesulfonic acid (40 mg) were dissolved in 25 ml of toluene. A Dean–Stark trap was adapted to the flask and the solution was boiled for 5 h under reflux. After cooling, a yellow precipitate was obtained. The precipitate was extracted with diethyl ether (3 × 100 × ml). The combined organic layers were washed with $NaHCO_3$ and NaCl and dried with anhydrous Na_2SO_4 before the diethyl ether was removed under reduced pressure. The crude product was purified by recrystallisation from acetone/methanol.

(*S*)-5-(2-Methylbutoxy)-2-{[(4-dodecyloxyphenyl) imino]methyl}phenol (MBDOPIMP) was obtained as yellow crystals. Yield: 0.99 g (85 %). ^{1}H NMR: δ 13.88 (s, OH), 8.47 (s, HC=N), 7.21–7.18 (m, 3 arom. H), 6.90 (d, $J \approx 8.9$ Hz, 2 aromatic H), 6.47–6.44 (m, 2 aromatic H), 3.95 (t, $J \approx 6.5$ Hz, OCH_2), 3.84, 3.75 (2dd, $J \approx 9.2$ Hz and $J \approx 6.5$ Hz each, OCH_2 of the chiral alkyl chain), 1.89–1.82 (m, chiral CH), 1.81–1.74 (m, CH_2), 1.60–1.21 (m, 10 CH_2), 1.00 (d, $J \approx 6.9$ Hz; CH_3), 0.94, 0.87 (2t, $J \approx 7.5$ Hz and $J \approx 6.9$ Hz, respectively, 2 CH_3). ^{13}C NMR: δ 163.57, 163.25, 157.85, 141.17, 113.04 (5s, 5 arom. C), 159.29 (d, HC=N), 132.95, 121.84, 115.12, 107.31, 101.62 (5d, 1, 2, 2, 1 and 1 arom. CH, respectively), 73.02, 68.39 (2t, 2 OCH_2), 34.68 (d, CH), 31.99, 29.74, 29.71, 29.67, 29.66, 29.48, 29.42, 29.37, 26.21, 26.13, 22.77 (11t, 11 CH_2), 16.58, 14.20, 11.38 (3q, 3 CH_3). MS: m/z (%) 467 (100) [M^+], 397 (14) [$M^+ -C_5H_{11}$], 229 (44) [$M^+ -C_5H_{11}-C_{12}H_{25}$]. UV–visible: λ (nm) 350.0. IR: $\gamma = 1625$ cm^{-1} (C=N). Elemental analysis: calculated for $C_{30}H_{45}NO_3$ (467.7), C 77.04, H 9.70, N 2.99; found C 77.18, H 9.49, N 3.28%.

Theory

The specific retention volume, V_g^0, is determined experimentally from IGC measurements via (*19–21*):

$$V_g^0 = \frac{Q(t_R - t_A)J273.2}{(T_r w)}, \qquad (1)$$

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

According to the Flory–Huggins and equation-of-state theories, respectively, interaction parameters χ_{12}^{∞} and χ_{12}^{*} are defined as:

$$\chi_{12}^{\infty} = \ln\left(\frac{273.2Rv_2}{p_1^0 V_g^0 V_1^0}\right) - \left(1 - \frac{V_1^0}{M_2 v_2}\right) - \frac{p_1^0\left(B_{11} - V_1^0\right)}{RT}, \tag{2}$$

where R is the universal gas constant, p_1^0, B_{11} and V_1^0 are the saturated vapour pressure, gaseous state second virial coefficient and molar volume of the solvent at temperature T, and v_2 is the specific volume of the LC, and

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

where v_2^* is specific hard-core volume of the LC and V_1^* is molar hard-core volume of the solvent.

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

$$RT\chi_{12}^{*} = p_1^* V_1^* \left\{ \begin{array}{l} 3T_{1\mathrm{r}} \ln\left[\left(v_{1\mathrm{r}}^{1/3} - 1\right)/\left(v_{2\mathrm{r}}^{1/3} - 1\right)\right] \\ + v_{1\mathrm{r}}^{-1} - v_{2\mathrm{r}}^{-1} + X_{\mathrm{eff}}/p_1^* v_{2\mathrm{r}} \end{array} \right\}, \tag{4}$$

where p_1^* is a characteristic pressure, $v_{1\mathrm{r}}$ and $v_{2\mathrm{r}}$ are the reduced volumes of the solvent and LC, respectively, and $T_{1\mathrm{r}}$ is the reduced temperature of the solvent.

The enthalpic interaction parameter, χ_{h}^*, can be obtained from the slope of the plot χ_{h}^* versus $1/T$ according to its definition (*10–15*)

$$\chi_{\mathrm{h}}^* = \left[\partial\chi_{12}^*/\partial(1/T)\right]/T. \tag{5}$$

According to the equation of state theory, χ_{h}^* is approximated under gas chromatographic conditions as

$$\chi_{\mathrm{h}}^* = \left(p_1^* V_1^*/RT\right) \left[\begin{array}{l} \left(v_{1\mathrm{r}}^{-1} - v_{2\mathrm{r}}^{-1}\right) \\ + (\alpha_2 T/v_{2\mathrm{r}})(T_{1\mathrm{r}} - T_{2\mathrm{r}})/T_{2\mathrm{r}} \end{array} \right] + V_1^*(1 + \alpha_2 T)X_{12}/(v_{2\mathrm{r}}RT), \tag{6}$$

where X_{12} is the exchange energy parameter. X_{eff} combines the parameters X_{12} and Q_{12} via:

$$X_{\mathrm{eff}} = X_{12} - Tv_{2\mathrm{r}}Q_{12}. \tag{7}$$

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

$$\Delta\bar{H}_{1,\mathrm{sorp}} = -R\left[\partial\left(\ln V_{\mathrm{g}}^0\right)/\partial(1/T)\right], \tag{8}$$

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 by

$$\Delta\bar{H}_1^{\infty} = R\left[\partial\left(\ln\Omega_1^{\infty}\right)/\partial(1/T)\right], \tag{9}$$

where Ω_1^{∞} is the weight fraction activity coefficient of solvents at infinite dilution, defined by

$$\ln\Omega_1^{\infty} = \ln\left(273.2R/V_{\mathrm{g}}^0 p_1^0 M_1\right) - p_1^0\left(B_{11} - V_1^0\right)/RT, \tag{10}$$

where M_1 is the molecular weight of the solvent.

The molar heat of vaporisation, ΔH_{v}, of the solvent is related to $\Delta\bar{H}_{1,\mathrm{sorp}}$ and $\Delta\bar{H}_1^{\infty}$ as follows:

$$\Delta H_{\mathrm{v}} = \Delta\bar{H}_1^{\infty} - \Delta\bar{H}_{1,\mathrm{sorp}}. \tag{11}$$

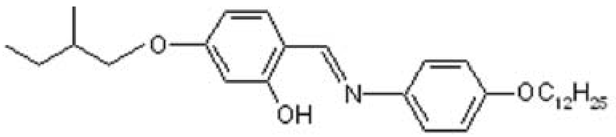
3. Results and discussion

The synthesis and mesomorphism of the new salicylaldimine compound, (*S*)-5-(2-methylbutoxy)-2-{[(4-dodecyloxyphenyl)imino]methyl}phenol (MBDOPIMP), are reported. The mesogenic salicylaldimine compound MBDOPIMP with a chiral alkyloxy tail was prepared in the usual way by *p*-toluenesulfonic acid-catalysed condensation of 4-dodecyloxyaniline with (*S*)-4-(2-methylbutoxy)-2-hydroxybenzaldehyde in toluene and purified by recrystallisation from acetone/methanol (*22*).

The structure of MBDOPIMP was characterised using various spectroscopic methods (^{1}H and ^{13}C NMR, UV–visible, IR and mass) and elemental analysis. The proposed structure is in full agreement with the spectroscopic data (see Section 2).

The liquid crystalline properties of the obtained salicylaldimine compound were investigated using POM and DSC. Compound MBDOPIMP exhibits an enantiotropic chiral smectic mesophase. The transition temperatures, corresponding enthalpy values (in parantheses) and mesophase types observed for this compound are shown in Figure 1.

The mesomorphic properties of the salicylaldimine compound MBDOPIMP are similar to those of the previously synthesised analogues (*2, 8, 9, 22*). The



Compound	T/°C (ΔH/kJ mol^{-1})^a
MBDOPIMP	Cr 68.2 (29.5) SmC* 94.4 (3.9) Iso

^{a}Perkin-Elmer DSC-7; heating rates 10 K min^{-1} for the melting and clearing process; the enthalpies are in parentheses.

Figure 1. Phase transition temperatures, T (°C), and enthalpies, ΔH (kJ mol^{-1}) of MBDOPIMP (Cr=crystalline, Sm=smectic phase, I=isotropic liquid).

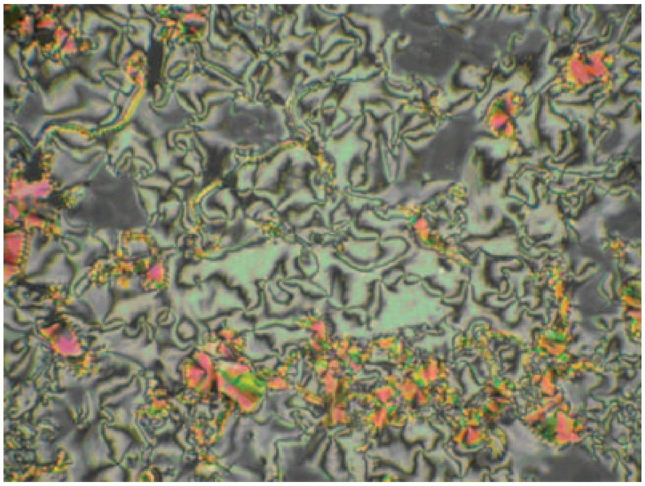


Figure 2. POM photomicrograph of the mesophase of MBDOPIMP as observed on cooling (schlieren texture of the SmC* phase at 76.5°C).

presence of a lateral hydroxy group, which can affect the rigidity and polarisability of the mesogenic core by intramolecular hydrogen bonding, gives rise to a significant stabilising effect for the salicylaldimines, as described in the literature (*23, 24*). On cooling from the isotropic liquid, compound MBDOPIMP exhibits an enantiotropic chiral smectic C (SmC*) mesophase, which was detected by a typical schlieren texture (see Figure 2). This schlieren texture is characterised by four-brush disclinations and hence it can be assigned as a tilted smectic phase. The crystal phase melting and SmC* phase clearing temperatures were determined to be around 68.2°C and 94.4°C, respectively (see Figure 3).

A comparison of the phase transition temperatures of MBDOPIMP with an analogue that includes an *n*-hexyloxy terminal chain instead of a *n*-dodecyloxy terminal chain shows that the alkyloxy chain length of the salicylaldimines influences the mesophase range (*9*). Depending on the effect of increasing

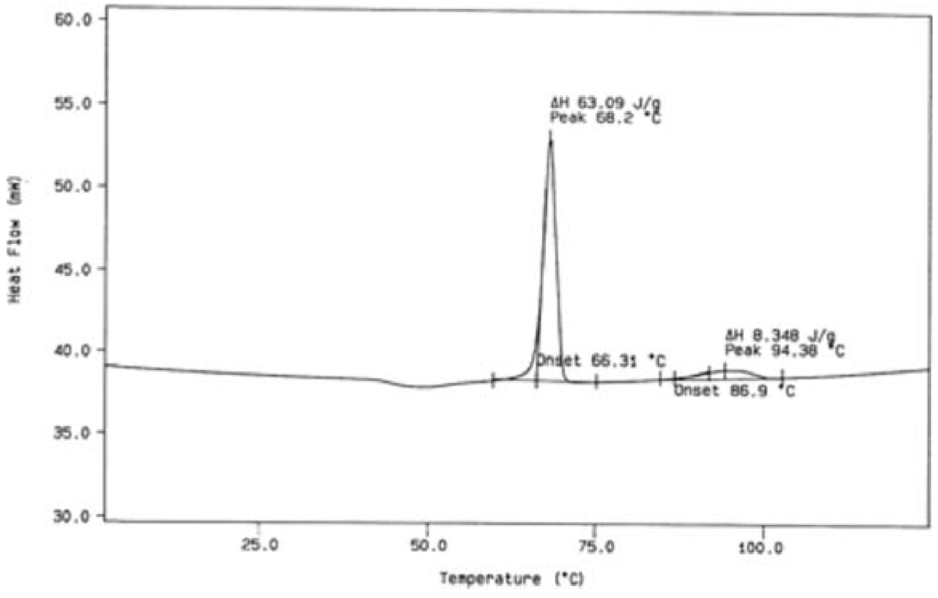


Figure 3. DSC scans of MBDOPIMP during the second heating process.

alkyloxy chain length, the clearing point of MBDOPIMP decreases, whereas the melting point increases. Enantiotropic chiral smectic phases are observed for these compounds (the phase sequence for the analogue with a hexyloxy chain is Cr 40.4°C SmX* 85.6°C SmC* 101.5°C I) (*9, 22*).

The specific retention volume, V_g^0, of the studied solvents on MBDOPIMP were obtained from IGC measurements between 105 and 125°C and using Equation (1). The results were shown in Figure 4.

All the plots are straight lines, indicating that no phase transition occurs in the studied temperature range, i.e. thermodynamical equilibrium exists. The percentage error in V_g^0 was calculated as less than ± 0.5 by using at least three successive measurements of each datum. The liquid–solvent interaction parameters, χ_{12}^{∞} and χ_{12}^{*}, were determined from Equations (2) and (3); the values of χ_{12}^{∞} and χ_{12}^{*} are given in Tables 1 and 2, respectively. The apparent standard errors in the values of χ_{12}^{∞} and χ_{12}^{*} were less than ± 0.01. Values of χ_{12}^{∞} greater than 0.5 represent unfavourable liquid crystal–solvent interactions, whereas values lower than 0.5 indicate favourable interactions in dilute liquid crystal solutions. The values of the obtained parameters suggest that all studied solvents are poor for the MBDOPIMP LC and that solvent quality is almost independent of temperature. Tables 1–2 also contain values for analogues of MBDOPIMP containing different alkyl chains, i.e. *n*-hexyl (*8*) at 95°C and *n*-hexyloxy (*9*) at 110–125°C, instead of the *n*-dodecyloxy chain attached to one of the side chains. The values of the parameters χ_{12}^{∞} and χ_{12}^{*} suggest that all the studied solvents are poor for MBDOPIMP. It appears that aliphatic esters are poorer, whereas alkanes are better solvents for MBDOPIMP than its analogues. This

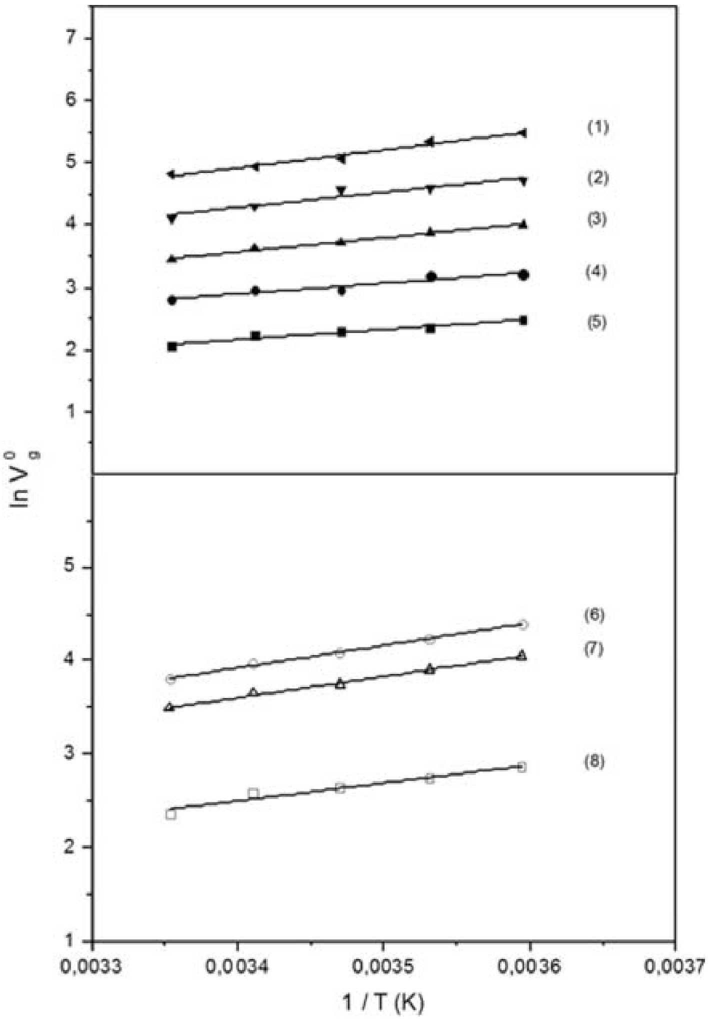


Figure 4. Variation of specific retention volumes of the Hx (1), Hp (2), O (3), N(4), D (5), EA (6), BA (7) and IBA (8) with the reciprocal of absolute column temperature.

Table 1. Comparison of the Flory–Huggins liquid crystal–solvent interaction parameters, χ_{12}^{∞}, of MBDOPIMP with solvents, as obtained in this study, with data reported in the literature for its analogues.

Solvent	105°C	110°C	115°C	120°C	125°C
EA	0.98	0.97	0.94	0.88	0.99
	0.79[a]	0.79[b]	0.77[b]	0.74[b]	0.72[b]
BA	0.68	0.68	0.67	0.64	0.66
		0.63[b]	0.61[b]	0.62[b]	0.62[b]
IBA	0.71	0.69	0.71	0.66	0.68
		0.66[b]	0.65[b]	0.63[b]	0.63[b]
Hx	0.98	0.99	0.94	0.89	0.96
Hp	0.97	0.86	0.95	0.82	0.86
O	0.89	0.86	0.87	0.82	0.86
		1.00[b]	0.99[b]	0.99[b]	0.96[b]
N	0.90	0.83	0.70	0.80	0.84
		1.03[b]	1.02[b]	1.00[b]	0.99[b]
D	0.84	0.79	0.88	0.83	0.79

[a] At 95°C, Ref. (*8*). [b] Ref. (*9*).

Table 2. Comparison of the equation-of-state liquid crystal–solvent interaction parameters, χ_{12}^{*}, of MBDOPIMP with solvents, as obtained in this study, with data reported in the literature for its analogues.

Solvent	105°C	110°C	115°C	120°C	125°C
EA	1.16	1.16	1.12	1.07	1.18
	0.94[a]	0.94[b]	0.92[b]	0.89[b]	0.88[b]
BA	0.80	0.80	0.80	0.77	0.80
		0.72[b]	0.70[b]	0.71[b]	0.71[b]
IBA	0.84	0.83	0.85	0.80	0.82
		0.75[b]	0.75[b]	0.73[b]	0.73[b]
Hx	1.15	1.16	1.12	1.07	1.15
Hp	1.10	1.00	1.09	0.97	1.00
O	1.00	0.97	0.99	0.95	0.99
		1.07[b]	1.06[b]	1.06[b]	1.04[b]
N	1.00	0.93	0.80	0.91	0.94
		1.09[b]	1.07[b]	1.06[b]	1.04[b]
D	0.92	0.87	0.96	0.92	0.88

[a] At 95°C, Ref. (*8*). [b] Ref. (*9*).

Table 3. Comparison of the effective exchange energy parameters, X_{eff} (J cm^{-3}) of MBDOPIMP with solvents, as obtained in this study, with data reported in the literature for its analogues.

Solvent	105°C	110°C	115°C	120°C	125°C
EA	24.8	24.5	22.9	20.2	26.3
	16.9[a]	16.8[b]	15.4[b]	13.9[b]	13.0[b]
BA	10.0	9.7	9.1	7.8	8.5
		7.6[b]	6.6[b]	6.8[b]	6.8[b]
IBA	7.9	7.1	7.4	5.5	6.0
		5.2[b]	4.9[b]	3.9[b]	3.9[b]
Hx	19.8	20.4	18.7	17.1	20.3
Hp	18.3	14.9	17.9	14.1	15.6
O	13.4	12.6	13.1	11.6	12.9
		16.8[b]	16.5[b]	16.5[b]	15.7[b]
N	12.2	10.5	7.3	10.1	11.2
		15.5[b]	15.1[b]	14.9[b]	14.4[b]
D	10.3	9.1	11.3	10.4	9.3

[a] At 95°C, Ref. (*8*). [b] Ref. (*9*).

suggests that the aliphatic character of the LC increases but that its polar character decreases with the length of its side chain.

The effective exchange energy parameters, X_{eff}, in the equation of state theory were obtained from Equation (4) and results are given in Table 3. The parameter X_{eff} was assumed to quantify the magnitude of the energy required to exchange a solute molecule close to another solute molecule with a solvent molecule. It appears that the parameter X_{eff} decreases with increasing chain length of *n*-alkanes and aliphatic character of esters. It can be stated that X_{eff} of MBDOPIMP in all solvents is almost independent on temperature.

The exchange parameters of enthalpy, X_{12}, and entropy, Q_{12}, in the equation of state theory are assumed to be independent on temperature and composition of the mixture but this situation is not yet confirmed. In this study, the parameters X_{12} were obtained by means of Equation (6) using the values of χ_{h}^{*} found from slopes of the plots according to Equation (5). Then, parameters Q_{12} were calculated from Equation (7). The results are shown in Tables 4–6. It appears that X_{12} is almost independent

Table 4. The enthalpic interaction parameter, χ_{h}^{*}, of MBDOPIMP with studied solvents at various column temperatures.

Solvent	105°C	110°C	115°C	120°C	125°C
EA	0.257	0.253	0.250	0.247	0.244
BA	0.353	0.348	0.343	0.339	0.335
IBA	0.439	0.434	0.428	0.423	0.417
Hx	0.644	0.635	0.627	0.619	0.611
Hp	1.842	1.818	1.794	1.772	1.749
O	0.381	0.376	0.371	0.366	0.362
N	1.098	1.084	1.070	1.057	1.043
D	0.345	0.340	0.336	0.332	0.328

Table 5. The exchange enthalpy parameters, X_{12} (J cm^{-3}), of MBDOPIMP with studied solvents at various column temperatures.

Solvent	105°C	110°C	115°C	120°C	125°C
EA	25.9	26.8	27.7	28.4	29.1
BA	18.4	18.9	19.5	20.0	20.5
IBA	21.1	21.8	22.4	22.9	23.5
Hx	30.3	31.6	32.3	32.9	33.3
Hp	56.8	57.0	57.3	57.4	57.5
O	15.7	16.1	16.4	16.8	17.1
N	29.5	29.6	29.7	29.8	29.9
D	11.4	11.6	11.7	11.9	12.0

Table 6. The exchange entropy parameters, Q_{12} ($\times 10^2$, $\mathrm{J\,cm^{-3}\,K^{-1}}$), of MBDOPIMP with studied solvents at various column temperatures.

Solvent	105°C	110°C	115°C	120°C	125°C
EA	0.26	0.51	1.04	1.76	0.58
BA	1.87	2.04	2.24	2.62	2.53
IBA	2.95	3.22	3.23	3.72	3.67
Hx	2.33	2.48	2.95	3.37	2.75
Hp	8.58	9.25	8.51	9.25	8.83
O	0.51	0.77	0.72	1.10	0.87
N	3.85	4.19	4.86	4.21	3.93
D	0.25	0.54	0.10	0.33	0.57

of temperature, whereas Q_{12} is slightly dependent on temperature.

$\Delta\bar{H}_{1,\mathrm{sorp}}$ and $\Delta\bar{H}_1^{\infty}$ were determined from the slopes of the linear plots exhibiting the variation of logarithms of specific retention volume, ln V_g^0 and weight fraction activity coefficient, ln Ω_1^{∞}, with $1/T$ (in Figure 5), respectively. ΔH_v was found by their subtraction and compared with the ΔH_v values calculated according to Watson's relationship (*25*) in Table 7. ΔH_v values obtained by IGC are comparable with those in the literature.

Table 7. The partial molar heat of sorption, $\Delta\bar{H}_{1,\mathrm{sorp}}$ ($\mathrm{kcal\,mol^{-1}}$), the partial molar heat of mixing, $\Delta\bar{H}_1^{\infty}$ ($\mathrm{kcal\,mol^{-1}}$), molar heat of vaporisation, ΔH_v ($\mathrm{kcal\,mol^{-1}}$) obtained using Equation (12) and experimental molar heat of vaporisation, ΔH_v ($\mathrm{kcal\,mol^{-1}}$) (*24*).

Solvent	$-\Delta\bar{H}_{1,\mathrm{sorp}}$	$\Delta\bar{H}_1^{\infty}$	ΔH_v	ΔH_v (*24*)
EA	6.9	0.2	7.1	7.7
BA	8.7	0.3	9.0	8.6
IBA	8.2	0.4	8.6	8.6
Hx	5.9	0.6	6.5	6.9
Hp	6.2	1.3	7.5	7.6
O	8.3	0.3	8.6	8.2
N	8.8	0.8	9.6	8.8
D	10.4	0.2	10.7	9.4

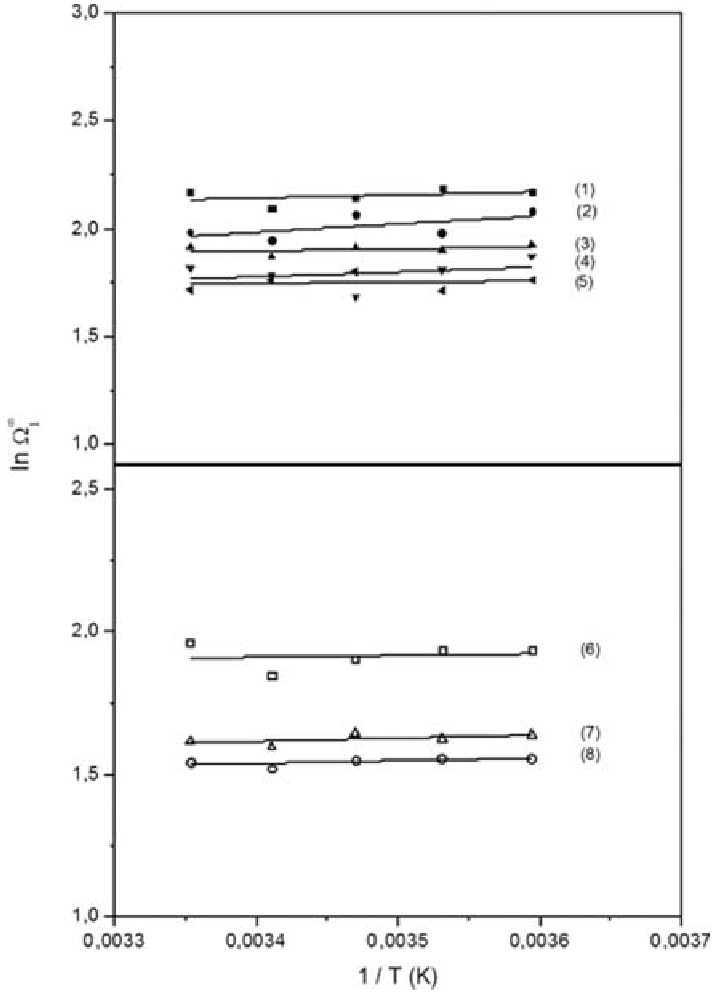


Figure 5. The logarithm of the weight fraction activity coefficients, $\ln \Omega_1^{\infty}$, of the D (1), N (2), O (3), Hp (4), Hx (5), BA (6), IBA (7) and EA (8) in MBDOPIMP as a function of temperature.

4. Conclusions

The synthesis and characterisation of the salicylaldimine compound MBDOPIMP is reported. The phase behaviour of MBDOPIMP was investigated by POM and DSC. The thermodynamic parameters obtained in this study at temperatures between 105 and 125°C were compared with those of its analogues obtained in earlier studies. It can be stated that aliphatic character of the LC increases but polar character decreases with the length of its side chain. This study suggests that all studied aliphatic hydrocarbons and acetates are poor solvents for MBDOPIMP between 105 and 125°C. It was found that the temperature dependence of X_{12} was negligible for all studied solvents. ΔH_v values obtained in this study were comparable with literature values.

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