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A new liquid crystal of considerable value for the separation of closely related solvents by gas chromatography

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The synthesis, characterisation and mesomorphic properties of a new chiral liquid crystal, (S)-5-(10-undecenyloxy)-2-[[[4-(2-methylbutoxy)phenyl]imino]methyl]phenol (UMBPIMP) are described. The phase transition temperatures of this mesogenic compound have been investigated by optical polarising microscopy, differential scanning calorimetry and inverse gas chromatography. The thermodynamics of UMBPIMP were investigated in order to understand its selectivity as a stationary phase in gas chromatography. Its liquid crystal selectivity was tested using the isomers *n*-butyl acetate, *tert*-butyl acetate and *iso*-butyl acetate, and the isomers *n*-butyl alcohol, *tert*-butyl alcohol and *iso*-butyl alcohol, as model chromatographic probes. The retention diagrams of the isomers were plotted between 30°C and 110°C using inverse gas chromatography. Using the specific retention volume, V_g^0, parameters such as the Flory–Huggins polymer–solvent interaction, χ_{12}^{∞}, and hard-core polymer–solvent interaction, χ_{12}^{*}, and exchange parameters such as effective energy, X_{eff}, enthalpy, X_{12} and entropy, Q_{12}, were determined for the solvents chosen.

Keywords: inverse gas chromatography; liquid crystal; phase transition temperature; thermodynamics; interaction parameter

1. Introduction

The liquid crystalline state is a unique state of matter, combining order and mobility. Thermotropic liquid crystals are compounds that show a degree of long-range correlation and order in the liquid phase which changes with temperature. A range of mesophases can form on melting the solid crystalline phase before an isotropic liquid is formed [1]. The introduction of a chiral tail within liquid crystalline compounds allows the preparation of materials which are of considerable technological interest, both for display and non-display applications [1–4]. In some applications, liquid crystals are dissolved or dispersed in a solvent, and it is therefore necessary to understand in depth the interactions between the liquid crystal and solvents for further exploitation of these applications.

Liquid crystals have found extensive use as the stationary phase in gas chromatography. Liquid crystalline stationary phases are useful for separating isomers having similar boiling points, which are very difficult to separate using classical stationary phases [5–10].

In the present study, the synthesis of (S)-5-(10-undecenyloxy)-2-[[[4-(2-methylbutoxy)phenyl]imino]methyl]-phenol (UMBPIMP) has been successfully achieved and the product characterised. Its phase transition properties were determined by differential scanning calorimetry (DSC), polarising microscopy and inverse gas chromatography (IGC). It was to be expected that UMBPIMP would perform successfully as the stationary phase in the chromatographic separation of isomers. Its selectivity in gas chromatography was assessed using *n*-butyl acetate, *tert*-butyl acetate and *iso*-butyl acetate, and *n*-butyl alcohol, *tert*-butyl alcohol and *iso*-butyl alcohol, respectively, at temperatures between 30°C and 110°C. In addition, the interaction and exchange parameters of UMBPIMP were determined in the isotropic phase region at temperatures between 85°C and 110°C, in which no thermal transition was encountered and peak shapes were sharp and symmetrical.

We have previously determined directly the exchange enthalpy and entropy parameters of poly (dimethyl siloxane), poly(methylhydrosiloxane-co-dimethyl siloxane) and poly(methyl methacrylate) with a range of solvents during earlier inverse gas chromatography measurements [11–15]. In these studies it was demonstrated that the parameters X_{12} and Q_{12} were comparable with those determined earlier by other techniques at lower polymer concentrations. Although IGC had been used earlier to investigate the interaction and exchange parameters of polymeric materials with various solvents [16–18], liquid crystals are a relatively new application, having previously been used only with a few LC–solvent pairs [19–22]. Shillcock and Price have reported the effective exchange energy parameters, X_{eff}, of both polymeric and low molecular weight liquid crystals with selected alphatic and aromatic hydrocarbon probes [23]. They concluded that solution behaviour is governed by rigid

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cyanobiphenyl mesogens rather than by the flexible end-groups of the liquid crystal molecule.

As far as is known, a study of the determination of the parameters X_{12} and Q_{12} in liquid crystal–solvent systems has not previously been reported. The exchange parameters in the equation of state are expected to be independent of temperature but should depend solely on the chemical structures of the stationary phase, i.e. the liquid crystal and solvent. It should thus become possible to design novel tailor-made liquid crystal dispersions for other morphological states at any temperature by using the exchange parameters, provided the equation of state theory is applicable to these systems. However, the use of equation of state theory in the design of novel liquid crystal–solvent system will require careful study.

2. Experimental

2.1 Materials and instrumentation

The characterisation of the compound UMBPIMP has been confirmed using a variety of spectroscopic data, e.g. ^{1}H–, ^{13}C–NMR (Varian Unity 500 and 400 spectrometers, in $CDCl_3$ solution) with tetramethylsilane as internal standard, UV–Vis (Agilent 8453, $CHCl_3$ solution), FTIR (Perkin Elmer, $CHCl_3$ solutions), and mass spectroscopy (AMD 402, electron impact, 70 eV).

Its mesomorphic properties were investigated using polarised light optical microscopy 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 Linkam TMS93 temperature controller. DSC thermograms were recorded on a Perkin–Elmer DSC–7, at a heating and cooling rate of 10 K min^{-1}.

n-Butyl acetate (nBAc), *tert*-butyl acetate (tBAc), *iso*-butyl acetate (iBAc), *n*-butyl alcohol (nBAl), *tert*-butyl alcohol (tBAl) and *iso*-butyl alcohol (iBAl) were obtained from Merck AG, as was the support material, Chromosorb–W (AW–DMCS-treated, 80/100 mesh). Silane-treated glass wool, used to plug the ends of the column, was obtained from Alltech Associates, Inc.

A Hewlett–Packard 6890 N gas chromatography unit with thermal conductivity detector was used to measure the retention time of the solvents. The column was constructed of stainless steel, 3.2 mm outside diameter and 1 m in length.

2.2 Synthesis of UMBPIMP

UMBPIMP was synthesised using a well-established procedure [24, 25], by *p*-toluenesulfonic acid (40 mg) catalysed condensation of 2-hydroxy-4-(10-undeceny loxy)benzaldehyde [26] (2.5 mmol) with (S)-4-(2-methylbutoxy)aniline [27] (3 mmol) in toluene (25 ml). The solution was refluxed for 5 h and the product purified by crystallisation from acetone/methanol.

UMBPIMP
Yield: 0.71 g (63%), yellow crystals.

^{1}H NMR: δ (ppm) = 13.90 (s; OH), 8.48 (s; HC=N), 7.23–7.19 (m; 3 arom. H), 6.91 (d; $J \approx 8.9$, 2 arom. H), 6.47–6.43 (m; 2 arom. H), 5.84–5.76 (m; =CH, alkenic 1 H), 5.00–4.91 (m; =CH$_{2,}$ alkenic 2 H), 3.97 (t; $J \approx 6.6$ Hz; OCH$_2$), 3.82–3.73 (2dd; $J \approx 8.9$ and $J \approx 6.5$ Hz each; OCH$_2$ of chiral alkyl chain), 2.05–2.01 (m, =CH–C$\underline{H}_2$), 1.88–1.80 (m; CH), 1.79–1.74 (m; CH$_2$), 1.59–1.24 (m; 7 CH$_2$), 1.01 (d; $J \approx 6.8$ Hz; CH$_3$), 0.94 (t; $J \approx 7.4$ Hz; CH$_3$).

^{13}C NMR: δ (ppm) = 163.78, 163.28, 158.18, 141.01, 113.09 (5s; 5 arom. C), 159.36 (d; H$\underline{C}$=N), 133.10, 121.89, 115.17, 107.41, 101.59 (5d; 7 arom. CH), 139.19 (d; =CH), 114.09 (t; =CH$_2$), 73.20, 68.19 (2t; 2 OCH$_2$), 34.71 (d; chiral CH), 33.76, 31.89, 29.45, 29.37, 29.30, 29.08, 29.06, 26.11, 25.95 (9t; 9 CH$_2$), 16.50, 11.28 (2q; 2 CH$_3$).

MS: *m*/*z* (%) = 451 (85) [M$^+$], 380 (20) [M$^+$ –C$_5$H$_{11}$], 229 (100) [M$^+$ –C$_{11}$H$_{21}$–C$_5$H$_{11}$].

UV–Vis: λ (nm) = 242.0, 286.0, 350.0

IR: γ = 3065 (CH$_2$=CH), 1617 (C=N).

2.3 Theory

The specific retention volume, V_g^0 is determined experimentally from IGC measurements as follows [28–32]:

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

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

Under IGC conditions, the Flory–Huggins interaction parameter, χ_{12}^{∞} is defined as

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

where R is the universal gas constant, p_1^0, B_{11} and V_1^0 are, respectively, the saturated vapor pressure, gaseous state second virial coefficient and molar volume of the solvent at temperature, T, and v_2 is the specific volume of the liquid crystal. According to the

Flory–Huggins theory, it may be assumed that the excess volume of mixing is zero and the volumes of the polymer segments and solvents in the lattice site are independent of temperature. Flory and co-workers [16–18], have proposed an equation of state with parameters defined in terms of the characteristics of a polymer and solvent and their binary mixtures in the polymer solution. The hard-core volume does not include excluded volume, and represents a more realistic size. Although it is very difficult to determine the binary reduced parameters, the equation becomes very simple under IGC conditions, since the solvent concentration is virtually zero. The volume terms in Equation (2) are thus replaced by temperature-independent hard-core volumes

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

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

Although the interaction parameter, χ, was introduced originally as an enthalpic parameter arising from the interaction energies between polymer segments and solvent, it is now defined as the residual partial molar Gibbs free energy, consisting of the sum of the enthalpic (χ_{h}) and entropic (χ_{s}) interaction parameters. Although the interaction parameters depend on concentration, by a power series of the volume fraction of polymer in solution, it is not necessary to take into account the concentration variations under IGC conditions, since the polymer fraction becomes unity.

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

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

where p_1^* is the characteristic pressure, $v_{1\mathrm{r}}$ and $v_{2\mathrm{r}}$ are the reduced volumes of solvent and liquid crystal, respectively, and $T_{1\mathrm{r}}$ is the reduced temperature of the solvent. The reduced quantities in the above equation are defined as follows:

$$v_r = \frac{V}{V^*}, \quad T_r = \frac{T}{T^*}, \quad p_r = \frac{p}{p^*}, \tag{5}$$

where V is the actual molar volume of the liquid at temperature, T (in K), and pressure, p. The characteristic molar volume, V^*, and characteristic pressure, p^*, of a pure component can be calculated directly from experimental values of molar volume, V, thermal expansion coefficient, α, and thermal pressure coefficient, γ, of the pure component, using the following equations :

$$v_{\mathrm{r}} = \left[\frac{(\alpha T/3)}{1+\alpha T}\right] + 1, \tag{6}$$

$$T_r = \frac{(v_r^{1/3} - 1)}{v^{4/3}}, \tag{7}$$

$$a = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_{p=0}, \tag{8}$$

$$p^* = \gamma T v_r^2, \tag{9}$$

$$\gamma = \left(\frac{\partial p}{\partial T}\right)_V. \tag{10}$$

The enthalpic part of the hard-core interaction parameter, χ_{h}^* can be obtained from the slope of the plot of χ_{12}^* versus $1/T$ [33]:

$$\chi_{\mathrm{h}}^{*} = [\partial\chi_{12}^{*}/\partial(1/T)]/T. \tag{11}$$

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

$$\begin{aligned} \chi_{\mathrm{h}}^{*} = &(p_1^{*}V_1^{*}/RT)[(v_{1\mathrm{r}}^{-1} - v_{2\mathrm{r}}^{-1}) \\ &+ (\alpha_2 T/v_{2\mathrm{r}})(T_{1\mathrm{r}} - T_{2\mathrm{r}})/T_{2\mathrm{r}}] \\ &+ V_1^{*}(1+\alpha_2\mathrm{T})\mathrm{X}_{12}/(\mathrm{v}_{2\mathrm{r}}\mathrm{RT}), \end{aligned} \tag{12}$$

where X_{12} is the exchange enthalpy parameter. X_{eff} combines the parameters X_{12} and Q_{12} as follows:

$$X_{\mathrm{eff}} = X_{12} - Tv_{2\mathrm{r}}Q_{12}. \tag{13}$$

In the equation of state theory [16–18], the exchange parameters X_{12} and Q_{12} are designed to quantify the magnitude of the enthalpy and entropy, respectively, required to exchange a polymer segment adjacent to another polymer segment with a solvent molecule. According to the theory, it may be assumed that their magnitude depends on the chemical structure of the polymer and solvent and is independent of temperature and concentration of the mixture. Once the variation of X_{12} and Q_{12} with chemical structure has been determined, it should be possible to design novel liquid crystal dispersions without preliminary experimental study.

3. Results and discussion

UMBPIMP has been synthesised by the *p*-toluenesulfonic acid-catalysed condensation of 2-hydroxy-4-(10-undecenyloxy)benzaldehyde [26] and (S)-4-(2-methylbutoxy)aniline [26] in toluene, and purified by recrystallisation from acetone/methanol. The product has been characterised by the normal spectroscopic methods (^{1}H–, ^{13}C–NMR, UV–Vis, IR and MS). The spectroscopic data of the UMBPIMP is consistent with its proposed structure (see Section 2).

The liquid crystalline properties of UMBPIMP have been investigated using polarised optical microscopy and DSC. The compound shows enantiotropic smectic mesophases, which are a short range of a smectic A phase with fan-shaped texture, and a chiral smectic C* phase with a fingerprint texture at lower temperatures. The transition temperatures and corresponding enthalpy values for this compound are shown in Figure 1. The typical texture of the smectic mesophases of UMBPIMP are given in Figure 2, and a DSC thermogram is illustrated in Figure 3.

The specific retention volume, V_g^0, of the two series of isomeric solvents on UMBPIMP was obtained from IGC measurements between 30°C and 110°C according to Equation (1). The percentage error in V_g^0 was calculated as less than ± 0.5 by using four or five successive measurements for each datum. The results are given in Figures 1 and 2. According to the retention diagram in Figure 4, Cr–SmC*, SmC*–SmA and SmA–Iso transitions for UMBPIMP are shown to be 62°C, 72°C and 75°C, respectively, in terms of the maximum points indicated in the majority of the plots. The compound exhibits a crystalline state at temperatures below A, SmC* at temperatures between A and B, SmA between B and C, and is fully molten at temperatures above C. Although the SmC*–SmA and SmA–Iso transition temperatures by IGC are generally lower than those obtained by DSC, the results are comparable. The higher transition temperatures can be attributed to the delayed heat transfer at the heating rate of 10°C min^{-1} during the DSC measurements. On the other hand, under IGC conditions the liquid crystal molecules have plenty of time to order themselves in the mesophase region. In addition, the orientation of the molecules might be made easier by the probe molecules diffusing into the liquid crystal mesophases. From Figure 4, it is seen that good separation can be obtained between the isomers over the entire temperature range.

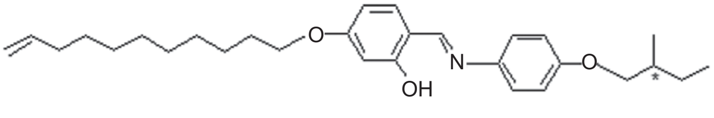
The study suggests that UMBPIMP is capable of separating the selected solvents at all temperatures above 62°C. It should also be noted that UMBPIMP was successful in separating iBAc and nBAl, which each have a boiling point of 118°C .

The thermodynamic parameters of the selected solvents with UMBPIMP were obtained from IGC measurements between 85°C and 110°C, at which thermodynamical equilibrium occurred.

The polymer–solvent interaction parameters, χ_{12}^{∞} and χ_{12}^{*}, determined using Equations (2) and (3), are summarised in Tables 1 and 2, respectively. The apparent standard errors in the values of χ_{12}^{∞} and χ_{12}* were less than ± 0.01. The values of χ_{12}^{∞} greater than 0.5 represent unfavourable liquid crystal–solvent interactions, whereas values lower than 0.5 indicate favourable interactions in liquid crystal solutions.

The values of the parameters suggest that all the solvents chosen were non-solvents for UMBPIMP. The trend of all the sets of data are similar, showing a decrease in the interaction parameter as the temperature increased. This indicates that the solvency increased with temperature.

The effective exchange energy parameters, X_{eff} in the equation of state theory were obtained from Equation (4) and results were given in Table 3. The magnitudes of X_{eff} are considerably higher in the case of aliphatic alcohols than those of aliphatic esters. Therefore, the higher values of X_{eff} indicate poor solubility. It was seen that X_{eff} of UMBPIMP in all solvents slightly decreased with temperature. The values of X_{eff} support the comments on χ_{12}^{∞}.



Compound	T/°C (ΔH/kJ mol^{-1})
UMBPIMP	Cr 62.0 (28.2) SmC* 76.6 (1.0) SmA 81.1 (1.9) Iso

Note: *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 transition enthalpies ΔH (kJ mol^{-1}) for UMBPIMP
Note. Cr: crystalline, Sm: smectic, Iso: isotropic phase.

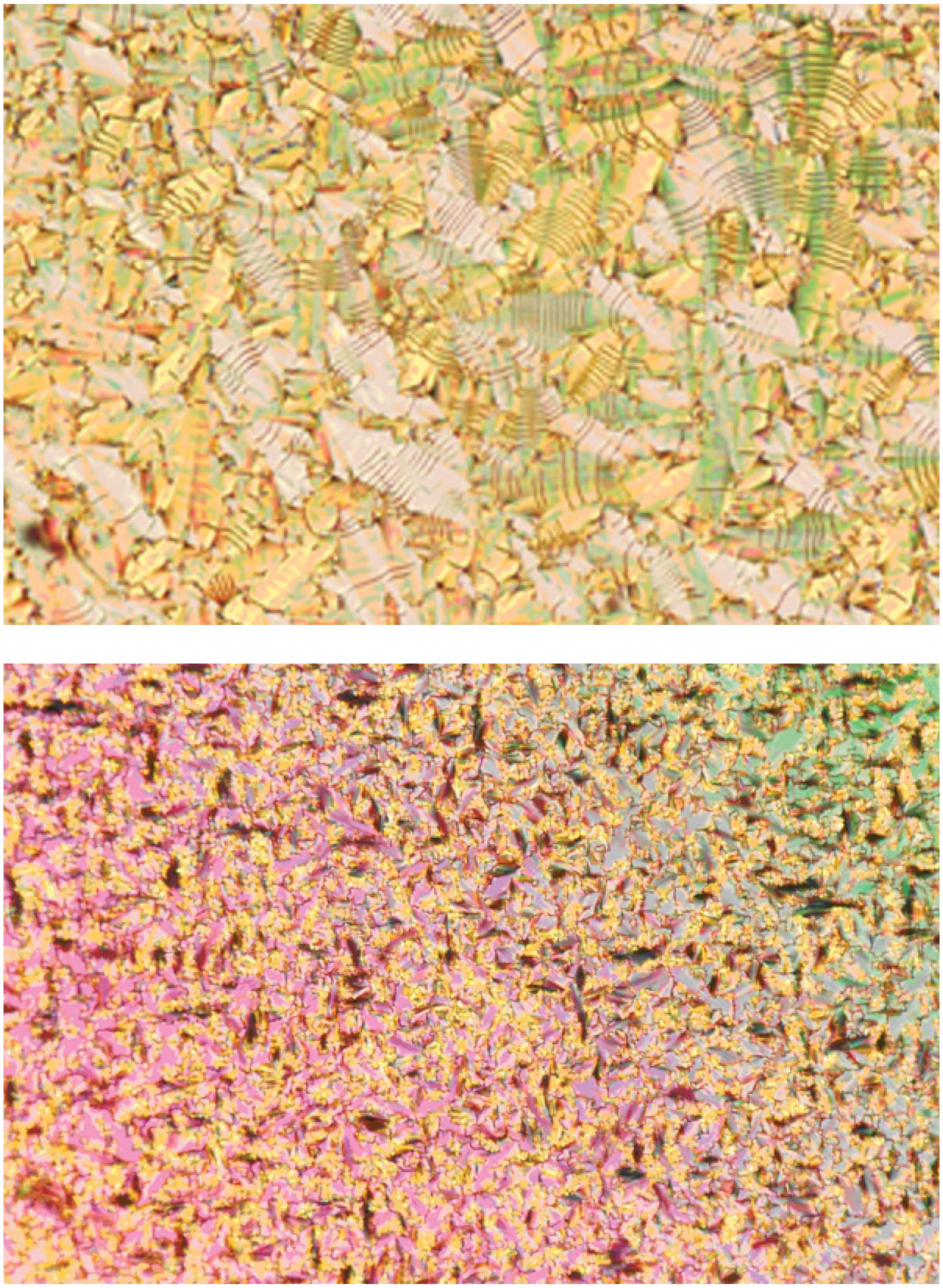


Figure 2. Polarised light optical photomicrograph of the mesophase of UMBPIMP as observed on cooling (a) the smectic C* phase at 72°C, and (b) the smectic A phase at 78°C.

The parameters X_{12} were obtained by means of Equation (12) using the values of χ_{h}^{*} found from the slope of the plots according to Equation (11). The parameters Q_{12} were then calculated from Equation (13). Results are provided in Tables 4 and 5, respectively. The apparent standard errors calculated for the values of X_{12} and Q_{12} are better than ±1. The parameters of enthalpy, X_{12}, and entropy, $Q_{12,}$ in the equation of state theory are assumed to be independent of temperature and composition of the mixture, but this has yet to be confirmed. In the present study, the values of the parameters X_{12} were found to be very close to one another for nBA and iBA (approx. 64) and somewhat higher for tBA (approx. 85). However,

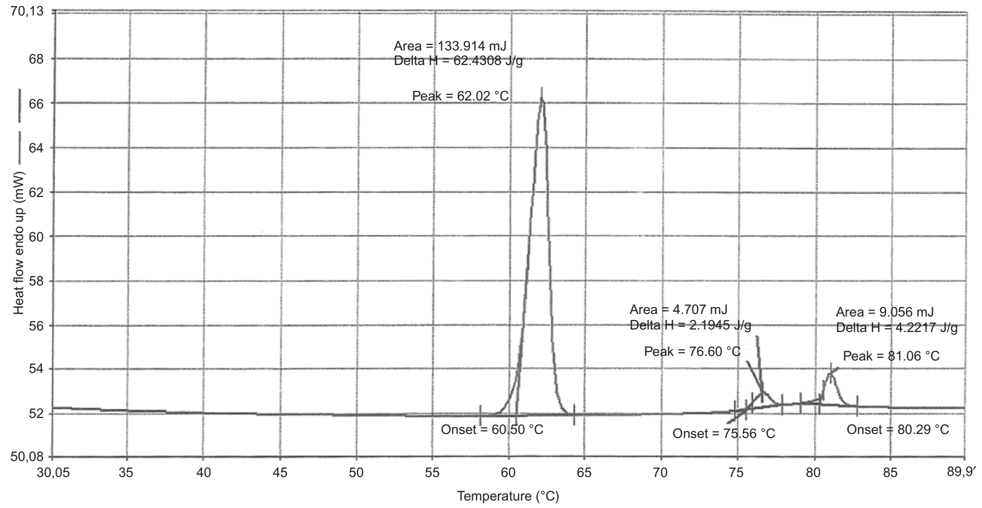


Figure 3. DSC scans of UMBPIMP during the second heating process.

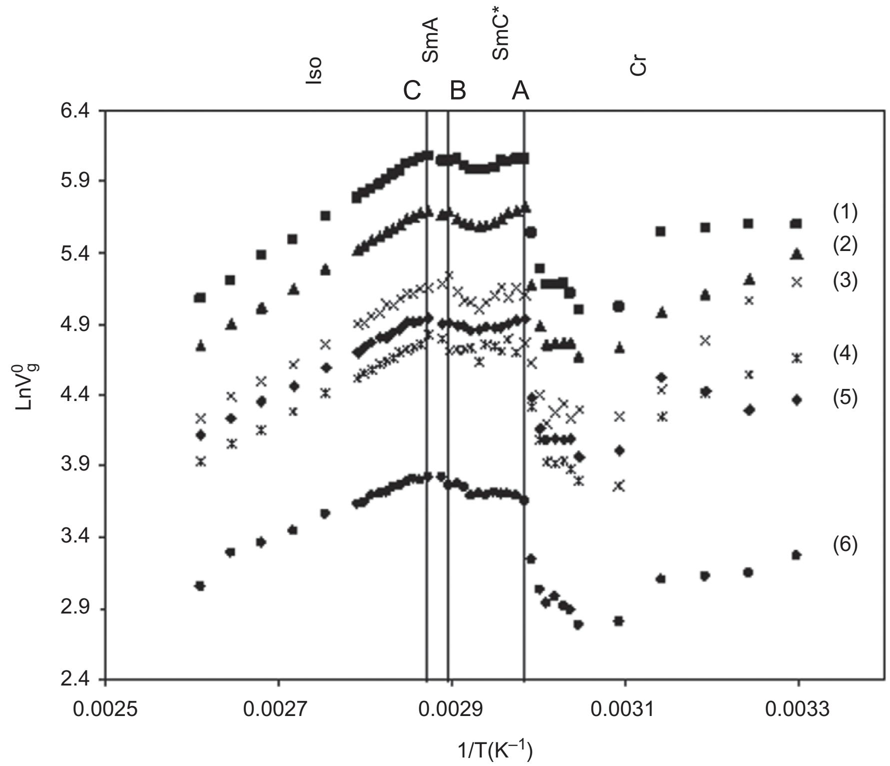


Figure 4. Variation in specific retention volumes of nBAc(1), iBAc(2), nBAl(3), iBAl(4), tBAc(5) and tBAl(6) with the reciprocal of absolute column temperature.

the X_{12} values are considerably higher for the alcohols (approx. 230). This suggests that the alcohol group considerably increases X_{12} in comparison to the acetate group. On the other hand, the *tert*-butyl group moderately increases X_{12} in comparison to *n*-butyl and *iso*-butyl groups. Their temperature dependence is almost negligible. The Q_{12} values of the alcohols are almost three times higher than those of the acetates, and they can be regarded as being independent of temperature. The *tert*-butyl group causes slightly higher Q_{12} values. This indicates that the values of X_{12} and Q_{12} are significantly influenced by the chemical nature of the probes.

Table 1. Flory–Huggins liquid crystal–solvent interaction parameters, χ_{12}^{∞}, for UMBPIMP with selected solvents at various column temperatures.

	χ_{12}^{∞}					
T **(°C)**	85	90	95	100	105	110
nBAc	0.74	0.68	0.66	0.60	0.61	0.58
iBAc	0.76	0.70	0.68	0.65	0.60	0.60
tBAc	0.81	0.78	0.70	0.65	0.62	0.63
nBAl	1.87	1.78	1.71	1.63	1.54	1.50
iBAl	1.83	1.74	1.66	1.60	1.52	1.47
tBAl	1.66	1.56	1.45	1.38	1.31	1.24

Table 2. Equation of state liquid crystal–solvent interaction parameters, χ_{12}^{*}, for UMBPIMP with selected solvents at various column temperatures.

	χ_{12}^{*}					
T **(°C)**	85	90	95	100	105	110
nBAc	0.83	0.79	0.77	0.71	0.72	0.70
iBAc	0.86	0.81	0.79	0.77	0.72	0.72
tBAc	0.93	0.90	0.83	0.78	0.76	0.78
nBAl	2.00	1.91	1.84	1.76	1.68	1.64
iBAl	1.84	1.74	1.66	1.60	1.51	1.46
tBAl	1.82	1.72	1.62	1.56	1.49	1.42

Table 3. The effective exchange energy parameters, X_{eff} (J cm^{-3}), for UMBPIMP for selected solvents.

	X_{eff}					
T **(°C)**	85	90	95	100	105	110
nBAc	13.4	11.8	11.0	8.7	8.9	7.7
iBAc	11.5	9.8	9.0	7.9	6.1	6.1
tBAc	13.0	12.4	9.8	7.9	6.8	7.1
nBAl	71.5	67.6	64.7	60.7	56.4	54.3
iBAl	80.0	77.1	74.0	71.6	68.5	67.0
tBAl	49.6	44.9	40.2	37.2	33.7	30.5

Table 4. The exchange enthalpy parameters, X_{12} (J cm^{-3}), for UMBPIMP with selected solvents at various column temperatures.

	X_{12}					
T **(°C)**	85	90	95	100	105	110
nBAc	64.5	64.6	64.9	65.1	65.5	65.9
iBAc	63.8	64.0	64.3	64.7	64.9	65.3
tBAc	85.6	84.8	85.6	86.3	86.9	87.5
nBAl	243.2	243.9	243.8	244.3	244.7	245.5
iBAl	208.3	207.4	206.4	205.0	204.1	203.2
tBAl	258.4	258.9	259.3	259.9	260.2	260.7

Table 5. The exchange entropy parameters, Q_{12} (J cm^{-3} K^{-1}), for UMBPIMP with selected solvents at various column temperatures.

	Q_{12}					
T **(°C)**	85	90	95	100	105	110
nBAc	0.12	0.12	0.12	0.13	0.13	0.13
iBAc	0.12	0.13	0.13	0.13	0.13	0.13
tBAc	0.17	0.17	0.17	0.18	0.18	0.18
nBAl	0.40	0.41	0.41	0.41	0.42	0.42
iBAl	0.30	0.30	0.30	0.30	0.30	0.30
tBAl	0.49	0.50	0.50	0.50	0.50	0.50

4. Conclusions

The synthesis and characterisation of the compound UMBPIMP are described. The phase behaviour of the enantiotropic liquid crystal has been investigated by PM, DSC and IGC. The transition temperatures of mesophases determined by IGC are somewhat lower than those obtained by DSC. The interaction parameters suggest that all the solvents selected were poor solvents for UMBPIMP. The magnitude of the parameters X_{12} (and Q_{12}) are close to one another within each isomeric group of acetates and alcohols, but there is considerable differerence between the two groups. The temperature dependence of the parameters X_{12} and Q_{12} was negligible for all the solvents considered. The present study confirms that UMBPIMP is a valuable tool for separating isomeric solvents, and in addition for separating solvents with identical boiling points such as iBAc and nBAl. These results imply that equation of state exchange parameters can be used, not only in the design of novel liquid crystal dispersions for displays, but also as analytical chromatography stationary phases for the separation of liquids of similar boiling points.

Acknowledgements

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