

Inverse gas chromatographic measurement of solubility parameters in liquid crystalline systems

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Abstract

Inverse gas chromatography, (IGC), has been used to measure interaction parameters in two low-molar-mass liquid crystals and a polymer substituted with the same mesogenic group. Solubility parameters have been calculated. The IGC method is shown to be applicable to this class of compounds and to give meaningful values over a range of temperatures. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Inverse gas chromatography (IGC), has proved to be a versatile and very useful technique for the measurement of thermodynamic parameters in a range of non-volatile materials such as polymers over a wide range of conditions [1–3]. In particular, it can provide a wealth of information on interactions between solvents and polymers in very concentrated polymer solutions since measurements are made effectively at infinite dilution where a small amount of solute is injected to “probe” the properties of the stationary phase. Knowledge of these interactions is of use in a range of applications such as inks, paints and surface coatings.

While acknowledging its limitations, the solubility parameter concept is still widely used in polymer

science to give a rough and ready approximation of solubility behaviour. The solubility parameter, δ , is the square-root of the cohesive energy density of a compound and thus is a measure of the strength of its intermolecular forces [4]. It is related to the enthalpy of vaporization, ΔH^{vap} and the molar volume, V_1° by

$$\delta_1 = \sqrt{\frac{\Delta H^{\text{vap}} - RT}{V_1^\circ}} \quad (1)$$

There are many methods for estimating δ but generally they are only applicable around room temperature. Extending the work of Bristow and Watson [5], Guillet and co-workers [6,7] demonstrated that IGC could usefully be applied to the measurements and would allow access to a wide range of temperatures.

In a non-volatile stationary phase, retention is governed by interaction with the probe. The Flory–Huggins model of solution thermodynamics uses an interaction parameter, χ , to characterise this. χ is

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readily calculable from IGC retention data [1]. While originally introduced to correlate the enthalpy of mixing in a solution, it is more correctly identified as a residual free energy term, accounting for all contributions to the Gibbs free energy other than combinatorial mixing. It thus has an entropic element and can be represented as

$$\chi = \chi_H + \chi_S \quad (2)$$

If we assume that χ_H is adequately described by regular solution theory and hence by the difference in solubility parameter between the probe and polymer, then it can readily be shown [6] that

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1^\circ} \right) = 2 \cdot \left(\frac{\delta_2}{RT} \right) \delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_S}{V_1^\circ} \right) \quad (3)$$

where χ_S is the residual entropy contribution and 1 and 2 refer to probe and polymer respectively. A plot of the left hand side against the probe solubility parameter, δ_1 , yields the polymer solubility parameter, δ_2 , from the gradient and the entropic contribution to the interaction parameter from the intercept. This approach, which was reviewed by Price [8], has been applied to a wide range of materials including polymers [9], pharmaceutical products [10], liquid crystals [11], organic pollutants [12] and biological materials [13]. It has also been used as a predictive tool in gas chromatography [14], reversed-phase HPLC [15,16], supercritical fluid [17] and electrokinetic [18] chromatographies.

Liquid crystal systems are gaining increasing use in dyes and surface coatings, as dispersions in polymers and also as chromatographic stationary phases [19–21]. The anisotropic molecular alignment in these materials has provided novel effects. Thus it was of interest to determine whether IGC derived solubility parameters could be measured and give useful information on these systems.

2. Experimental

The liquid crystals studied were 4-(*n*-hexyloxy)-4'-cyanobiphenyl (HCB), 4-(*n*-octyloxy)-4'-cyanobiphenyl (OCB), and a siloxane polymer substituted with the same mesogen, poly(dimethyl-co-methyl(4-cyanobiphenoxy)butyl siloxane) (PCMB),

which had 40 repeat units. For comparison with the liquid crystal polymer backbone, values were also recorded for a linear poly(dimethyl siloxane) (PDMS). They were all supplied by Merck (UK) with reported purities of 99.5+%. All probe solvents (Aldrich or Merck) were 99% pure or better. The probes used were *n*-alkanes (pentane–nonane), five isomeric heptanes, benzene, toluene, ethylbenzene and the three xylene isomers.

HCB has a nematic mesophase between 57 and 76 °C. OCB displays a nematic mesophase between 67 and 76 °C and also has a smectic-A mesophase between 55 and 67 °C. The polymer also has a smectic-A mesophase between –4 and 79 °C. Above these temperature ranges, all the compounds form isotropic liquids.

The methods and techniques used were entirely standard for thermodynamic measurements at infinite dilution by IGC. Full details have been published previously [22,23]. Briefly, the specific retention volumes, V_g° , for ~0.01 μ l injections of the probe vapours were measured at infinite dilution using nitrogen as the carrier gas and stationary phases consisting of 8–14% (w/w) of the liquid crystal coated onto acid washed, silanized Chromosorb P (100–120 mesh). Analysis of the results showed the V_g° to be accurate to $\pm 1.5\%$. In IGC measurements, there is the possibility that adsorption onto the support can contribute to retention. This was minimised by using a silanized support and previous work [22,23] has shown that there was no variation of retention volume with stationary phase loading in the range used here, indicating that surface adsorption effects are insignificant compared with bulk sorption. Additionally, there was no influence on the liquid crystalline properties.

3. Results and discussion

The specific retention volume, V_g° , was calculated [24] from the probe retention time, t_R , by

$$V_g^\circ = \frac{(t_R - t_M)F'J}{W} \quad (4)$$

where t_M is the retention time of the methane marker and W is the mass of stationary phase on the column. F' is the carrier gas flow-rate fully corrected to STP

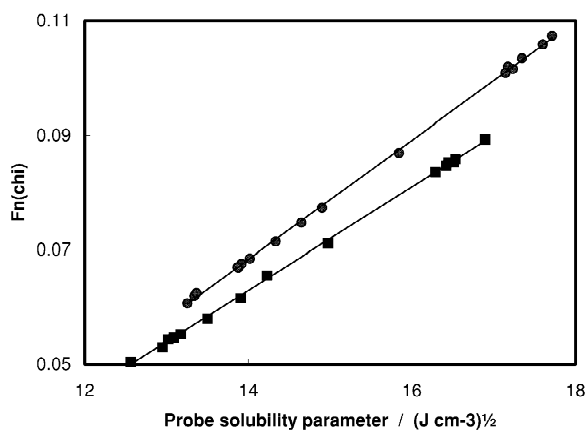


Fig. 1. Estimation of PDMS solubility parameter at 60 (●) and 90 °C (■). $F_n(\chi)$ is the function represented by the left-hand side of Eq. (3).

and J is the correction for gas compressibility in the column. Full details of these corrections are available in the literature [24].

The Flory–Huggins interaction parameter at infinite dilution, χ^∞ , can be calculated using

$$\chi^\infty = \ln \left(\frac{273.15R}{V_g^\circ p_1^\circ M_1} \right) - \left(\frac{p_1^\circ (B_{11} - V_1^\circ)}{RT} \right) - \left(1 - \frac{V_1^\circ}{V_2^\circ} \right) + \ln \left(\frac{M_1 V_2^\circ}{M_2 V_1^\circ} \right) \quad (5)$$

where B_{11} and p_1° are respectively the second virial coefficient and the saturated vapour pressure of the probe vapour at the column temperature T . M and V° represent the RMM and molar volume. These values were used in Eq. (3) along with probe solubility parameters calculated from literature data [25] to calculate values of δ_2 .

An illustration of the method applied to a linear polymer is shown for PDMS at two temperatures in Fig. 1. Excellent linear relations were obtained (correlation coefficient >0.9994) at both temperatures allowing a good estimate of δ_2 to be obtained. The values are given in Table 1.

Most literature values for solubility parameters have been reported at 25 °C. These were usually obtained by extrapolation of interaction parameter data from higher temperatures or, less commonly, by

Table 1
Solubility parameters, δ , and the dispersion, δ_d , and polar, δ_p , contributions at different temperatures, °C

| Phase | °C | δ | δ_d | δ_p | Phase | °C | δ | δ_d | δ_p |
|--------|------------|------------|------------|------------|--------|------------|------------|------------|------------|
| HCB N | 60.4 | 17.7 (0.3) | 15.5 | 8.5 | HCB I | 81.1 | 17.0 (0.3) | 14.8 | 8.4 |
| | 64.5 | 17.7 (0.3) | 15.9 | 7.8 | | 91.3 | 17.0 (0.3) | 14.7 | 8.5 |
| | 68.7 | 17.5 (0.3) | 15.4 | 8.3 | | 101.5 | 16.7 (0.3) | 14.2 | 8.8 |
| | 72.7 | 17.4 (0.3) | 15.1 | 8.6 | | 111.5 | 16.6 (0.3) | 13.6 | 9.5 |
| 58.0 | 17.6 (0.4) | 14.9 | 9.4 | OCB N | | 68.1 | 17.3 (0.4) | 14.8 | 9.0 |
| 61.1 | 17.5 (0.4) | 15.0 | 9.0 | | 70.4 | 17.1 (0.4) | 14.6 | 8.9 | |
| 64.1 | 17.4 (0.4) | 14.7 | 9.3 | | 72.9 | 17.1 (0.4) | 14.7 | 8.7 | |
| 65.6 | 17.3 (0.4) | 14.9 | 8.7 | | 74.8 | 17.2 (0.4) | 14.6 | 9.0 | |
| OCB I | 82.0 | 17.3 (0.3) | 14.4 | 9.5 | PMCB S | 50.0 | 17.1 (0.3) | 15.5 | 7.2 |
| | 85.1 | 17.1 (0.5) | 14.3 | 9.4 | | 54.6 | 17.2 (0.4) | 15.4 | 7.7 |
| | 90.3 | 16.9 (0.5) | 14.1 | 9.3 | | 59.7 | 16.7 (0.3) | 15.2 | 6.9 |
| | 95.4 | 16.6 (0.3) | 14.1 | 8.7 | | 64.3 | 16.8 (0.3) | 15.6 | 6.3 |
| PMCB I | 79.4 | 16.7 (0.3) | 14.7 | 7.9 | PDMS | 60.3 | 14.4 (0.1) | 13.6 | 4.7 |
| | 85.0 | 16.4 (0.3) | 14.6 | 7.5 | | 69.5 | 14.1 (0.1) | 13.4 | 4.4 |
| | 90.0 | 16.2 (0.3) | 14.3 | 7.6 | | 80.1 | 13.9 (0.1) | 13.1 | 4.6 |
| | 94.9 | 16.0 (0.3) | 14.2 | 7.4 | | 90.5 | 13.6 (0.1) | 13.5 | 1.6 |

Values in $(\text{J cm}^{-3})^{1/2}$ with standard deviations in parentheses.

direct measurement [26]. While the temperature dependence of the solubility parameter is considerably smaller than that of the interaction parameters, Fig. 1 shows that it is not insignificant. To obtain the temperature dependence of the solubility parameters for the systems studied here, values were measured at four temperatures in each phase and mesophase and the results fitted to an empirical relationship

$$\delta \text{ (J cm}^{-3}\text{)}^{1/2} = C - A T \text{ (}^\circ\text{C)} \quad (6)$$

where C and A are constants. The extrapolated value of PDMS at 25 °C of $15.2 \pm 0.2 \text{ (J cm}^{-3}\text{)}^{1/2}$ is in good agreement with the literature [27] values which range between 14.9 and 15.5 $\text{(J cm}^{-3}\text{)}^{1/2}$.

The solubility parameter plots for the liquid crystalline HCB are shown in Fig. 2. Two factors are immediately apparent; there is much less temperature dependence than with PDMS and the fit to a linear relation is not as good. Similar results were found for the other two liquid crystal compounds investigated. The reason for the latter observation is that the liquid crystals distinguish between the aromatic and aliphatic probe to a greater degree than PDMS. The aromatic probes will interact strongly with the aromatic biphenyl moieties in the liquid crystals. In addition, the solubility parameters will be slightly different in each mesophase.

Hansen [28] first suggested a development of the solubility parameter approach by considering the effect of polar interactions. He proposed that the

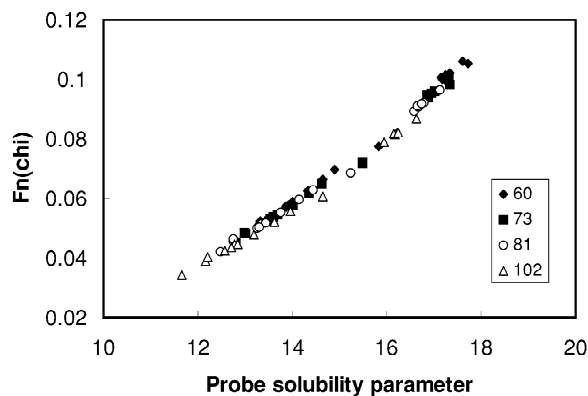


Fig. 2. Estimation of HCB solubility parameters at 60 and 73 °C in the nematic mesophase and 81 and 102 °C in the isotropic phase.

interaction energies could be considered as additive contributions from dispersion and polar interactions;

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (7)$$

where the subscripts d, p, h denote contributions from dispersion, polar, and hydrogen bonding energies, respectively. This approach has been employed in the analysis of the solubility parameters of GC stationary phases using the IGC technique [8,29]. Probes that interact only with dispersion intermolecular forces (i.e. the n -alkanes) should give a linear relation when plotted according to Eq. (3). However, probes that have other contributions to their retention will deviate from the line, the degree of deviation being a measure of the strength of the polar components. In the current work, none of the probes has a tendency to hydrogen bond so that only the first two terms of Eq. (7) will apply.

A typical plot is given in Fig. 3 for HCB and the difference between the two classes of probe is clear. The contributions to δ_2 for each of the compounds studied are shown in Table 1. In the liquid crystal phases of each of the systems, the polar contribution to the solubility parameter is quite constant, within the uncertainty of the method. There is significant difference between the three liquid crystals although not between the mesophases of each compound. The dispersion contribution generally decreases as the temperature is raised. This would be expected due to

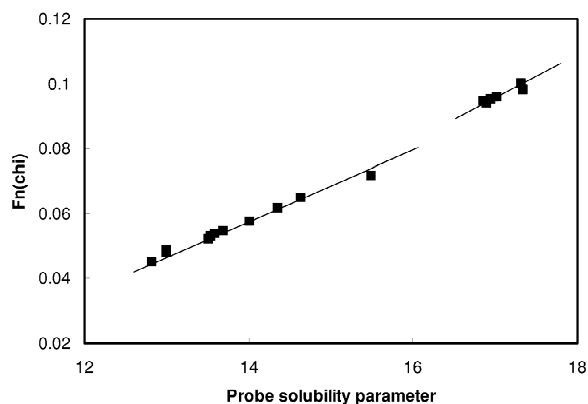


Fig. 3. Estimation of the contributions to HCB solubility parameter at 73 °C in the nematic mesophase. The lines indicate fits to the aliphatic probes [$\delta_1 < 16 \text{ (J cm}^{-3}\text{)}^{1/2}$] and aromatic probes [$\delta_1 > 16 \text{ (J cm}^{-3}\text{)}^{1/2}$].

the smaller effect thermal disruption of the molecules would have on more polar interactions. Also, PDMS exhibits considerably smaller polar contributions than the liquid crystal systems at all temperatures. The overall solubility parameter for PDMS varies between 13.5 and 14.5 (J cm^{-3})^{1/2} as the temperature decreases from 90 to 60 °C whereas the liquid crystal systems all exhibit higher values between 16.5 and 17.5 (J cm^{-3})^{1/2} more indicative of the aromatic fragments in the molecules. The results corroborate previous observations that PDMS favours aliphatic solvents whilst these liquid crystals favour aromatic solvents.

Values calculated from all the probes for each system are plotted as a function of temperature in Fig. 4. With the liquid crystal systems the solubility parameters could be fitted to a single linear relationship through all phases and mesophases without incurring significant too large an error. The regression equations for these were:

$$\text{HCB: } \delta_2 = 19.02 - 0.0225 T$$

$$\text{OCB: } \delta_2 = 18.76 - 0.0210 T$$

$$\text{PMCB: } \delta_2 = 18.27 - 0.0228 T$$

$$\text{PDMS: } \delta_2 = 15.92 - 0.0256 T$$

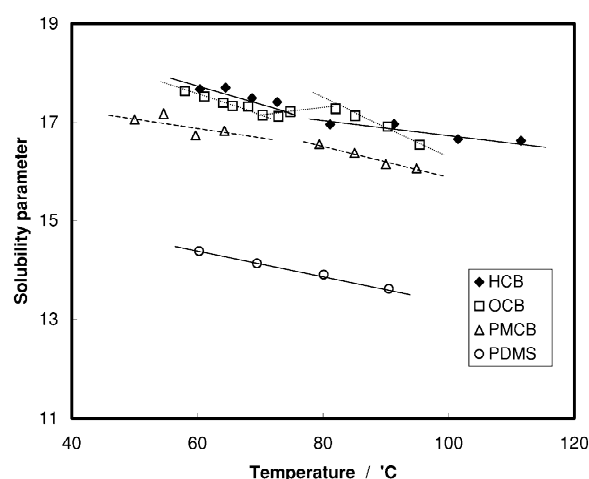


Fig. 4. Solubility parameters (J cm^{-3})^{1/2} as a function of temperature for PDMS, HCB, OCB and PMCB.

Table 2
Enthalpic χ^H and entropic χ^S contributions to the interaction parameter for hexane and benzene at different temperatures

| Phase | °C | Hexane | | Benzene | |
|--------|------|----------|----------|----------|----------|
| | | χ^H | χ^S | χ^H | χ^S |
| PDMS | 80.0 | 0.02 | 0.36 | 0.26 | 0.19 |
| PMCB S | 60.0 | 0.45 | 0.88 | 0.02 | 0.60 |
| PMCB I | 85.0 | 0.51 | 0.45 | 0.00 | 0.27 |
| HCB N | 66.0 | 0.74 | 0.91 | 0.00 | 0.65 |
| HCB I | 86.0 | 0.72 | 0.63 | 0.01 | 0.36 |
| OCB S | 58.0 | 0.68 | 1.02 | 0.00 | 0.67 |
| OCB N | 70.0 | 0.66 | 0.94 | 0.00 | 0.59 |
| OCB I | 85.0 | 0.78 | 0.61 | 0.02 | 0.29 |

However, closer inspection of Fig. 4 shows that there is a break in the lines at the mesophase transition temperatures. This parallels the behaviour of other thermodynamic properties although the relative differences between the different mesophases is smaller. The behaviour of the three liquid crystals is similar and distinct from that of PDMS suggesting that the major interactions are with the mesogen and the polymer backbone is relatively unimportant. The solubility parameter model is a crude description of solution behaviour and the validity of any conclusions drawn from the detail of the results should be viewed with caution. However, these results suggest that the enthalpic interactions in these cyanobiphenyls are very similar for both the low molar mass and polymeric liquid crystals materials.

Application of this model allows estimation of the enthalpic and entropic contributions to the interactions through Eq. (2). These are listed for two probes in Table 2 which clearly shows that this solubility parameter treatment predicts a significant contribution to the measured interaction parameter from entropic effects. The similarity of behaviour of the low-molar-mass and polymeric liquid crystals in contrast to PDMS and relative unimportance of the polymer backbone in determining the interactions is also further highlighted.

4. Conclusions

This work has shown that the IGC treatment of Guillet and co-workers can successfully be applied to liquid crystalline stationary phases. The retention

differences between the mesophases can be seen. Comparison of a polymeric liquid crystal with low-molar-mass analogues suggests that the retention behaviour is dominated by interaction with the mesogen and that the polymer backbone has only a minor modifying effect.

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