*Journal of Chromatography*, 556 (1991) 317–330
Elsevier Science Publishers B.V., Amsterdam

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# Thermodynamics of solution of non-mesomorphic solutes at infinite dilution in the smectic-A, nematic and isotropic phases of *p-n*-octyl-*p'*-cyanobiphenyl

## A gas–liquid chromatographic study

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ABSTRACT

From specific retention volumes measured at four temperatures in each of the three fluid phases of *p-n*-octyl-*p'*-cyanobiphenyl (8CB), infinite-dilution solute activity coefficients, partial molar excess enthalpies and entropies, and enthalpies and entropies of solution were determined for 21 solutes varying in molecular size, shape and flexibility. The reported results and their trends are discussed in terms of a previously proposed solution model. The results for 8CB are compared with those for the lower alkyl homologs in this liquid-crystalline solvent series, 5CB, 6CB and 7CB. The thermodynamic behavior within each of five solute groups is interpreted.

## INTRODUCTION

Gas–liquid chromatography (GLC) has become an established technique for the determination of reliable thermodynamic data for volatile solutes at "infinite dilution" in non-volatile solvents. In the Henry's law region, GLC has become the method of choice because of the speed and ease with which data can be obtained for a wide variety of solutes. As the solute diffusion rate in both the liquid and vapor phases is extremely fast, instantaneous equilibrium takes place at all points in the column. Accordingly, the dynamic equilibrium of GLC can be approximated by true static equilibrium. Two comprehensive studies (one undertaken in this laboratory [1] and one inter-laboratory [2]) comparing GLC and extrapolated static data have confirmed that inifinite-dilution solute activity coefficients accurate to better than ± 1% can be obtained by GLC.

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Of particular interest to the present authors is the reliability [3–5] and application of GLC [6–17] for the determination of thermodynamic properties of non-mesomorphic solutes in the mesophases and isotropic phase of liquid crystals. The purpose of these studies was to achieve a better understanding of the effect of solute characteristics (size, shape, flexibility, polarity and polarizability) on the solution process in ordered and disordered assemblies of rod-like molecules.

In this work, thermodynamic data were obtained by GLC for 21 non-mesomorphic solutes in the smectic-A ($S_A$), nematic (N) and isotropic (I) phases of *p-n*-octyl-*p'*-cyanobiphenyl (8CB). This study complements previous work on *p-n*-pentyl-*p'*-cyanobiphenyl (5CB) [6], *p-n*-hexyl-*p'*-cyanobiphenyl (6CB) [17] and *p-n*-heptyl-*p'*-cyanobiphenyl (7CB) [16], and forms part of a systematic study on the members of this important series [18]. Of the four liquid crystals listed, 8CB is the only one to exhibit the more ordered smectic-A mesophase. The data, which are examined in the light of an infinite-dilution solution model [7,9,19], are compared with previous results.

## EXPERIMENTAL

The liquid stationary phase was obtained in sealed ampoules from BDH (Poole, UK) and was used without purification. Its quoted purity of 99.5% was evident from its sharp crystal to smectic-A endotherm observed by differential scanning calorimetry (DSC) [20]. Shown in Table I are the observed transition temperatures and enthalpies ($\Delta H$) for 8CB [20]. The very small $\Delta H$ value obtained for the smectic-A to nematic ($S_A \rightarrow N$) transition indicates a very weakly first-order phase transition. Other investigators, using X-ray scattering and DSC [21] or high-precision calorimetry [22], have come to the conclusion that the $S_A \rightarrow N$ transition is virtually second order ($\Delta H \approx 0$).

8CB was coated on Johns-Manville 60–80 mesh, acid-washed and DMCS-treated Chromosorb W HP (Alltech, Deerfield, IL, USA). Details of the column preparation are given elsewhere [6,23]. The weight percentage of liquid phase in the packing (*i.e.*, the liquid phase loading) was determined by careful ashing [24] of three samples of about 1 g of packing, done before and after combustion of 8CB. The column used to obtain the thermodynamic data contained a loading of 11.50 ± 0.03%.

The 21 non-mesomorphic solutes chosen for this study (see Table II) exhibit a range of solute sizes, shapes and flexibilities. They were obtained from various standard sources and fall into five main categories: normal alkanes ($n$-$C_5$ to $n$-$C_9$), branched hexanes, branched heptanes, quasi-spherical molecules (3,3-diethylpentane

TABLE I

TRANSITION TEMPERATURES AND ENTHALPIES OF 8CB [20]

| Transition | $t$(°C) | $\Delta H$ (cal mol$^{-1}$) |
|---|---|---|
| Crystal → smectic A ($C \rightarrow S_A$) | 21.2 | 5900 ± 150 |
| Smectic A → nematic ($S_A \rightarrow N$) | 33.4 | 16 ± 2 |
| Nematic → isotropic ($N \rightarrow I$) | 40.6 | 187 ± 9 |

TABLE II

LIST OF SOLUTES

| Solute | Compound | Molecular weight | Boiling point (°C) |
|---|---|---|---|
| 1 | *n*-Pentane | 72.15 | 36.07 |
| 2 | *n*-Hexane | 86.18 | 68.74 |
| 3 | *n*-Heptane | 100.21 | 98.43 |
| 4 | *n*-Octane | 114.20 | 125.66 |
| 5 | *n*-Nonane | 128.26 | 150.80 |
| 6 | 2-Methylpentane | 86.17 | 60.27 |
| 7 | 3-Methylpentane | 86.17 | 63.28 |
| 8 | 2,2-Dimethylbutane | 86.17 | 49.74 |
| 9 | 2,3-Dimethylbutane | 86.17 | 57.99 |
| 10 | 2-Methylhexane | 100.21 | 90.05 |
| 11 | 3-Methylhexane | 100.21 | 91.85 |
| 12 | 3-Ethylpentane | 100.21 | 93.47 |
| 13 | 2,2-Dimethylpentane | 100.21 | 79.20 |
| 14 | 2,3-Dimethylpentane | 100.21 | 89.78 |
| 15 | 2,4-Dimethylpentane | 100.21 | 80.50 |
| 16 | 3,3-Dimethylpentane | 100.21 | 86.06 |
| 17 | 2,2,3-Trimethylbutane | 100.21 | 80.88 |
| 18 | Tetramethyltin | 178.84 | 78.0 |
| 19 | 3,3-Diethylpentane | 128.26 | 146.17 |
| 20 | Benzene | 78.12 | 80.11 |
| 21 | Toluene | 92.14 | 110.62 |

and tetramethyltin) and aromatics (benzene and toluene). All solutes were sufficiently volatile at the experimental temperatures and were used without further purification. Except for tetramethyltin, their required physical properties (molar volumes, saturated vapor pressure and second virial coefficients) were available or could be accurately determined [9].

A dual-column GLC apparatus, equipped with a Gow-Mac (Madison, NJ, USA) hot-wire thermal conductivity detector (Model 10-952) with AuW elements) in conjunction with a Gow-Mac bridge control and power supply (Model 40-001) and a well stirred and thermally regulated water-bath to maintain the column temperature to within ±0.03°C, was used. The column was installed and conditioned with a gentle flow of carrier gas (helium) for 24 h at 50°C. Before entering the column, the carrier gas was passed through a trap packed with 5A molecular sieve to adsorb moisture and contaminants. The carrier gas flow continued through a Negretti-Zambra (London, UK) precision pressure regulator (Model R/182) and finally to a Hamilton (Whittier, CA, USA) injection port (inlet part No. 86800, heated to about 200°C) and into the column. Inlet pressures were selected to give convenient elution times and reasonable column efficiency. The procedure followed to obtain accurate results is described elsewhere [6]. The use of internal standards showed that column bleeding and decomposition were negligible during the period of operation. Finally, all the usual, necessary steps were taken to ensure the attainment of the infinite-dilution condition [6] and the absence of interfacial effects [6,25].

## RESULTS

Specific retention volumes, $V_g^0$, [2,24] were obtained at four temperatures in each of the smectic-A (23.0, 25.5, 28.5 and 31.0°C), nematic (35.5, 36.5, 37.5 and 38.5°C) and isotropic (43.0, 45.5, 48.5 and 50.5°C) phases. By remaining at least 2.5°C below the smectic-A to nematic transition temperature and at least 2°C below the nematic to isotropic transition temperature, we ensured that the passage of the solute band through the column did not induce a phase transition [8,20]. The $V_g^0$ values reported in Tables III–V represent the average of three separate measurements for each point. The fugacity-corrected infinite-dilution solute activity coefficients, $\gamma_f^\infty$, were calculated from $V_g^0$ using the following equation [6]:

$$\ln(\gamma_f^\infty) = \ln(273.2R/M_1P_2^0V_g^0) - B_{22}P_2^0/RT \quad (1)$$

where $R$ is the gas constant, $M_1$ is the solvent molecular weight and $P_2^0$ and $B_{22}$ are the saturated vapor pressure and second virial coefficient, respectively, of the pure solute at the experimental temperature $T$. The vapor pressures were calculated from the Antoine equation, by use of the constants contained in Dreisbach's compilation [26]. The virial coefficients were calculated from the modified corresponding states equation of McGlashgan, Wormald and co-workers [27–29], using the critical constants from ref. 26. The resulting $\gamma_f^\infty$ values are reported in Tables VI–VIII. The

TABLE III

SOLUTE SPECIFIC RETENTION VOLUMES ($V_g^0$, ml g$^{-1}$) IN SMECTIC 8CB

| Solute No. | 23.0°C | 25.5°C | 28.5°C | 31.0°C |
|---|---|---|---|---|
| 1 | 37.76 | 35.03 | 32.28 | 30.23 |
| 2 | 118.8 | 108.5 | 96.37 | 89.34 |
| 3 | 364.5 | 327.9 | 287.5 | 260.9 |
| 4 | 1095 | 972.8 | 832.7 | 743.9 |
| 5 | 3307 | 2865 | 2409 | 2130 |
| 6 | 78.29 | 71.84 | 64.56 | 59.04 |
| 7 | 93.23 | 84.71 | 75.94 | 69.40 |
| 8 | 49.84 | 46.04 | 41.65 | 38.84 |
| 9 | 72.59 | 66.93 | 60.39 | 55.33 |
| 10 | 229.5 | 207.5 | 182.8 | 165.4 |
| 11 | 256.0 | 232.5 | 203.3 | 184.5 |
| 12 | 281.7 | 256.5 | 224.2 | 203.0 |
| 13 | 134.8 | 123.4 | 109.9 | 100.6 |
| 14 | 235.5 | 212.3 | 187.9 | 170.2 |
| 15 | 141.0 | 128.6 | 114.0 | 104.4 |
| 16 | 194.9 | 176.6 | 156.3 | 142.8 |
| 17 | 152.1 | 136.7 | 123.4 | 112.2 |
| 18 | 146.6 | 132.6 | 119.3 | 109.0 |
| 19 | 2116 | 1882 | 1604 | 1431 |
| 20 | 542.6 | 488.3 | 433.5 | 395.3 |
| 21 | 1787 | 1589 | 1377 | 1246 |

TABLE IV

SOLUTE SPECIFIC RETENTION VOLUMES ($V_g^0$, ml $g^{-1}$) IN NEMATIC 8CB

| Solute No. | 35.5°C | 36.5°C | 37.5°C | 38.5°C |
|---|---|---|---|---|
| 1 | 27.01 | 26.50 | 25.91 | 25.62 |
| 2 | 77.05 | 75.97 | 74.10 | 72.14 |
| 3 | 219.6 | 213.9 | 208.8 | 203.6 |
| 4 | 618.1 | 598.1 | 585.8 | 563.6 |
| 5 | 1741 | 1671 | 1624 | 1558 |
| 6 | 52.66 | 51.52 | 50.14 | 49.80 |
| 7 | 61.44 | 60.60 | 59.20 | 58.79 |
| 8 | 34.29 | 33.95 | 33.15 | 33.10 |
| 9 | 49.71 | 49.01 | 48.09 | 47.41 |
| 10 | 142.7 | 139.8 | 135.7 | 133.0 |
| 11 | 159.6 | 155.9 | 151.6 | 149.0 |
| 12 | 175.2 | 171.5 | 167.4 | 164.8 |
| 13 | 86.41 | 84.28 | 82.87 | 81.18 |
| 14 | 148.4 | 145.3 | 142.5 | 140.3 |
| 15 | 91.81 | 89.03 | 87.34 | 85.55 |
| 16 | 125.4 | 122.7 | 120.7 | 119.2 |
| 17 | 98.92 | 97.97 | 96.14 | 95.70 |
| 18 | 97.95 | 95.95 | 94.11 | 91.93 |
| 19 | 1237 | 1199 | 1178 | 1149 |
| 20 | 346.1 | 338.1 | 329.3 | 323.9 |
| 21 | 1078 | 1042 | 1011.6 | 984.5 |

TABLE V

SOLUTE SPECIFIC RETENTION VOLUMES ($V_g^0$, ml $g^{-1}$) IN ISOTROPIC 8CB

| Solute No. | 43.0°C | 45.5°C | 48.5°C | 50.5°C |
|---|---|---|---|---|
| 1 | 27.14 | 25.29 | 23.56 | 22.43 |
| 2 | 73.30 | 68.77 | 63.05 | 59.13 |
| 3 | 199.8 | 183.6 | 167.0 | 155.1 |
| 4 | 540.4 | 490.7 | 435.1 | 401.8 |
| 5 | 1451 | 1296 | 1131 | 1039.6 |
| 6 | 51.18 | 47.78 | 44.57 | 42.10 |
| 7 | 59.97 | 56.31 | 52.29 | 49.66 |
| 8 | 34.48 | 32.32 | 30.88 | 29.38 |
| 9 | 49.48 | 46.28 | 43.21 | 41.17 |
| 10 | 134.1 | 124.5 | 114.8 | 106.8 |
| 11 | 150.5 | 139.5 | 128.1 | 119.0 |
| 12 | 167.5 | 154.9 | 142.4 | 132.8 |
| 13 | 84.87 | 78.90 | 73.32 | 68.28 |
| 14 | 141.7 | 132.9 | 122.5 | 113.8 |
| 15 | 88.41 | 82.67 | 76.77 | 73.56 |
| 16 | 122.4 | 113.4 | 105.7 | 99.01 |
| 17 | 98.14 | 92.36 | 85.60 | 80.39 |
| 18 | 92.76 | 85.93 | 80.10 | 75.55 |
| 19 | 1131 | 1017 | 906.4 | 846.6 |
| 20 | 321.6 | 296.1 | 266.1 | 247.5 |
| 21 | 941.1 | 848.3 | 750.4 | 696.0 |

TABLE VI

SOLUTE ACTIVITY COEFFICIENTS ($\gamma_i^{\infty}$) IN SMECTIC 8CB

| Solute No. | 23.0°C | 25.5°C | 28.5°C | 31.0°C |
|---|---|---|---|---|
| 1 | 3.36 | 3.30 | 3.22 | 3.15 |
| 2 | 3.60 | 3.54 | 3.51 | 3.42 |
| 3 | 3.90 | 3.83 | 3.77 | 3.69 |
| 4 | 4.28 | 4.19 | 4.15 | 4.06 |
| 5 | 4.62 | 4.55 | 4.50 | 4.38 |
| 6 | 3.91 | 3.84 | 3.79 | 3.76 |
| 7 | 3.66 | 3.63 | 3.59 | 3.55 |
| 8 | 4.08 | 4.02 | 3.97 | 3.89 |
| 9 | 3.80 | 3.73 | 3.68 | 3.65 |
| 10 | 4.29 | 4.22 | 4.16 | 4.11 |
| 11 | 4.12 | 4.02 | 4.00 | 3.93 |
| 12 | 3.97 | 3.87 | 3.84 | 3.78 |
| 13 | 4.56 | 4.46 | 4.40 | 4.33 |
| 14 | 4.00 | 3.95 | 3.89 | 3.84 |
| 15 | 4.67 | 4.58 | 4.53 | 4.44 |
| 16 | 4.01 | 3.96 | 3.92 | 3.85 |
| 17 | 4.16 | 4.15 | 4.04 | 4.00 |
| 19 | 4.35 | 4.22 | 4.16 | 4.06 |
| 20 | 1.25 | 1.24 | 1.22 | 1.20 |
| 21 | 1.28 | 1.27 | 1.25 | 1.23 |

TABLE VII

SOLUTE ACTIVITY COEFFICIENTS ($\gamma_i^{\infty}$) IN NEMATIC 8CB

| Solute No. | 35.5°C | 36.5°C | 37.5°C | 38.5°C |
|---|---|---|---|---|
| 1 | 3.03 | 2.99 | 2.96 | 2.89 |
| 2 | 3.31 | 3.23 | 3.18 | 3.14 |
| 3 | 3.56 | 3.49 | 3.42 | 3.36 |
| 4 | 3.85 | 3.78 | 3.67 | 3.62 |
| 5 | 4.11 | 4.04 | 3.93 | 3.87 |
| 6 | 3.55 | 3.50 | 3.46 | 3.36 |
| 7 | 3.38 | 3.30 | 3.25 | 3.15 |
| 8 | 3.76 | 3.67 | 3.63 | 3.52 |
| 9 | 3.44 | 3.36 | 3.31 | 3.24 |
| 10 | 3.90 | 3.81 | 3.77 | 3.68 |
| 11 | 3.72 | 3.65 | 3.59 | 3.50 |
| 12 | 3.59 | 3.51 | 3.44 | 3.35 |
| 13 | 4.19 | 4.12 | 4.03 | 3.95 |
| 14 | 3.62 | 3.54 | 3.46 | 3.37 |
| 15 | 4.18 | 4.14 | 4.05 | 3.98 |
| 16 | 3.63 | 3.56 | 3.48 | 3.38 |
| 17 | 3.78 | 3.67 | 3.59 | 3.47 |
| 19 | 3.67 | 3.59 | 3.47 | 3.38 |
| 20 | 1.13 | 1.11 | 1.09 | 1.07 |
| 21 | 1.14 | 1.12 | 1.10 | 1.08 |

TABLE VIII

SOLUTE ACTIVITY COEFFICENTS ($\gamma_1^{\infty}$) IN ISOTROPIC 8CB

| Solute No. | 43.0°C | 45.5°C | 48.5°C | 50.5°C |
|---|---|---|---|---|
| 1 | 2.37 | 2.35 | 2.30 | 2.28 |
| 2 | 2.61 | 2.54 | 2.49 | 2.47 |
| 3 | 2.81 | 2.75 | 2.67 | 2.65 |
| 4 | 3.02 | 2.95 | 2.89 | 2.85 |
| 5 | 3.24 | 3.17 | 3.10 | 3.04 |
| 6 | 2.78 | 2.73 | 2.65 | 2.62 |
| 7 | 2.63 | 2.56 | 2.49 | 2.45 |
| 8 | 2.91 | 2.86 | 2.72 | 2.69 |
| 9 | 2.65 | 2.60 | 2.52 | 2.48 |
| 10 | 3.03 | 2.95 | 2.84 | 2.83 |
| 11 | 2.87 | 2.80 | 2.70 | 2.69 |
| 12 | 2.73 | 2.66 | 2.57 | 2.55 |
| 13 | 3.18 | 3.11 | 3.00 | 2.99 |
| 14 | 2.78 | 2.68 | 2.59 | 2.58 |
| 15 | 3.22 | 3.13 | 3.02 | 2.93 |
| 16 | 2.76 | 2.70 | 2.59 | 2.57 |
| 17 | 2.85 | 2.76 | 2.67 | 2.65 |
| 19 | 2.73 | 2.68 | 2.60 | 2.53 |
| 20 | 0.89 | 0.88 | 0.87 | 0.87 |
| 21 | 0.92 | 0.92 | 0.91 | 0.90 |

TABLE IX

SOLUTE PARTIAL MOLAR EXCESS ENTHALPIES ($\bar{H}^e$, kcal mol$^{-1}$)

| Solute | Smectic | Nematic | Isotropic |
|---|---|---|---|
| 1 | 1.43 ± 0.06 | 2.83 ± 0.25 | 1.07 ± 0.10 |
| 2 | 1.10 ± 0.16 | 3.18 ± 0.34 | 1.50 ± 0.18 |
| 3 | 1.21 ± 0.08 | 3.77 ± 0.04 | 1.66 ± 0.12 |
| 4 | 1.13 ± 0.12 | 4.08 ± 0.37 | 1.62 ± 0.07 |
| 5 | 1.14 ± 0.15 | 3.98 ± 0.28 | 1.67 ± 0.05 |
| 6 | 0.85 ± 0.07 | 3.33 ± 0.46 | 1.73 ± 0.12 |
| 7 | 0.66 ± 0.02 | 4.17 ± 0.33 | 1.93 ± 0.04 |
| 8 | 1.02 ± 0.09 | 4.06 ± 0.45 | 2.27 ± 0.25 |
| 9 | 0.90 ± 0.09 | 3.80 ± 0.11 | 1.83 ± 0.08 |
| 10 | 0.96 ± 0.06 | 3.58 ± 0.21 | 2.00 ± 0.21 |
| 11 | 0.97 ± 0.14 | 3.77 ± 0.22 | 1.84 ± 0.20 |
| 12 | 1.00 ± 0.16 | 4.32 ± 0.18 | 1.93 ± 0.16 |
| 13 | 1.14 ± 0.08 | 3.72 ± 0.16 | 1.75 ± 0.24 |
| 14 | 0.92 ± 0.01 | 4.46 ± 0.14 | 2.06 ± 0.29 |
| 15 | 1.09 ± 0.08 | 3.32 ± 0.28 | 2.62 ± 0.10 |
| 16 | 0.88 ± 0.07 | 4.56 ± 0.22 | 2.05 ± 0.20 |
| 17 | 0.94 ± 0.15 | 5.28 ± 0.28 | 2.07 ± 0.19 |
| 19 | 1.45 ± 0.15 | 5.48 ± 0.25 | 2.00 ± 0.16 |
| 20 | 0.98 ± 0.07 | 3.65 ± 0.21 | 0.71 ± 0.12 |
| 21 | 0.90 ± 0.10 | 3.17 ± 0.15 | 0.62 ± 0.06 |

infinite-dilution solute partial molar excess enthalpy ($\bar{H}^e$) and entropy $\bar{S}^e$) were determined from the usual thermodynamic relationship:

$$\ln(\gamma_f^\infty) = \bar{H}^e/RT - \bar{S}^e/R \tag{2}$$

Hence, a linear least-squares fit of ln ($\gamma_f^\infty$) as a function of $1/T$ gives $\bar{H}^e$ (from the slope) and $\bar{S}^e$ (from the intercept) (Tables IX and X). The high linear correlation coefficients (most of them in excess of 0.999) reflect the quality of the data. A typical plot of ln $\gamma_f^\infty$ *vs.* $1/T$ is shown in Fig. 1. It is important to point out that only a very small discontinuity in ln $\gamma_f^\infty$, if any, is observed at the $S_A \rightarrow N$ transition temperatue. This is the case for all the solutes studied and is consistent with the weakly first or second-order nature of the $S_A \rightarrow N$ transition.

The inifinite-dilution solute partial molar enthalpy and entropy of solution ($\Delta\bar{H}$ and $\Delta\bar{S}$) were obtained by means of the following equation [7,30]:

$$\ln(V_g^0) = -\Delta\bar{H}/RT + \Delta\bar{S}/R - \ln(M_1/273.2\ R) \tag{3}$$

A linear least-squares fit of ln $V_g^0$ *vs.* $1/T$ yields $\Delta\bar{H}$ (from the slope) and $\Delta\bar{S}$ (from the intercept) (Tables XI and XII). Virtually all of the linear correlation coefficients of the fits were in excess of 0.999.

TABLE X

SOLUTE PARTIAL MOLAR EXCESS ENTROPIES ($\bar{S}^e$, cal mol$^{-1}$ K$^{-1}$)

| Solute No. | Smectic | Nematic | Isotropic |
|---|---|---|---|
| 1 | 2.40 ± 0.18 | 6.95 ± 0.79 | 1.65 ± 0.30 |
| 2 | 1.16 ± 0.54 | 7.95 ± 1.09 | 2.85 ± 0.56 |
| 3 | 1.38 ± 0.25 | 9,70 ± 0.12 | 3.19 ± 0.39 |
| 4 | 0.92 ± 0.39 | 10.53 ± 1.18 | 2.94 ± 0.23 |
| 5 | 0.82 ± 0.50 | 10.07 ± 0.89 | 2.95 ± 0.14 |
| 6 | 0.17 ± 0.22 | 8.28 ± 1.48 | 3.45 ± 0.37 |
| 7 | 0.35 ± 0.07 | 11.08 ± 1.06 | 4.20 ± 0.13 |
| 8 | 0.64 ± 0.30 | 10.52 ± 1.44 | 5.05 ± 0.78 |
| 9 | 0.40 ± 0.30 | 9.85 ± 0.34 | 3.84 ± 0.24 |
| 10 | 0.35 ± 0.20 | 8.88 ± 0.69 | 4.14 ± 0.66 |
| 11 | 0.45 ± 0.46 | 9.61 ± 0.72 | 3.73 ± 0.63 |
| 12 | 0.63 ± 0.55 | 11.46 ± 0.58 | 4.12 ± 0.49 |
| 13 | 0.85 ± 0.27 | 9.22 ± 0.53 | 3.25 ± 0.75 |
| 14 | 0.35 ± 0.02 | 11.90 ± 0.44 | 4.49 ± 0.90 |
| 15 | 0.62 ± 0.27 | 7.92 ± 0.90 | 5.96 ± 0.31 |
| 16 | 0.21 ± 0.25 | 12.21 ± 0.70 | 4.46 ± 0.64 |
| 17 | 0.33 ± 0.49 | 14.46 ± 0.92 | 4.47 ± 0.59 |
| 19 | 1.97 ± 0.51 | 15.17 ± 0.80 | 4.34 ± 0.50 |
| 20 | 2.87 ± 0.24 | 11.57 ± 0.67 | 2.47 ± 0.36 |
| 21 | 2.54 ± 0.35 | 10.02 ± 0.49 | 2.13 ± 0.18 |

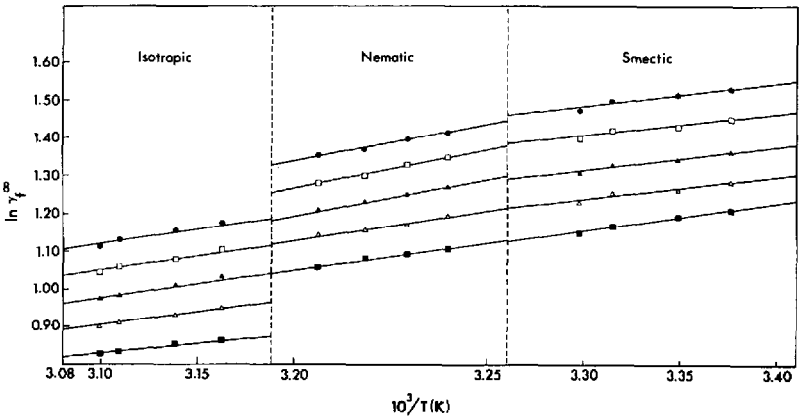


Fig. 1. Logarithm of the solute acitivity coefficient at infinite dilution ($\ln \gamma_f^\infty$) *versus* reciprocal temperature ($10^3/T$). ■ = *n*-Pentane; △ = *n*-hexane; ▲ = *n*-heptane; □ = *n*-octane; ● = *n*-nonane. Phase transition temperatures are indicated by dashed vertical lines.

TABLE XI

SOLUTE PARTIAL MOLAR ENTHALPIES OF SOLUTION ($\Delta\bar{H}$, kcal mol$^{-1}$)

| Solute No. | Smectic | Nematic | Isotropic |
|---|---|---|---|
| 1 | −4.97 ± 0.06 | −3.46 ± 0.25 | −5.13 ± 0.10 |
| 2 | −6.46 ± 0.17 | −4.25 ± 0.34 | −5.82 ± 0.17 |
| 3 | −7.53 ± 0.08 | −4.82 ± 0.04 | −6.80 ± 0.12 |
| 4 | −8.75 ± 0.12 | −5.69 ± 0.37 | −8.05 ± 0.07 |
| 5 | −9.91 ± 0.16 | −6.92 ± 0.28 | −9.07 ± 0.05 |
| 6 | −6.32 ± 0.06 | −3.72 ± 0.46 | −5.21 ± 0.12 |
| 7 | −6.60 ± 0.03 | −2.98 ± 0.33 | −5.10 ± 0.04 |
| 8 | −5.63 ± 0.09 | −2.48 ± 0.45 | −4.11 ± 0.33 |
| 9 | −6.08 ± 0.08 | −3.08 ± 0.10 | −4.94 ± 0.08 |
| 10 | −7.36 ± 0.06 | −4.61 ± 0.21 | −6.05 ± 0.21 |
| 11 | −7.41 ± 0.14 | −4.47 ± 0.23 | −6.27 ± 0.19 |
| 12 | −7.42 ± 0.16 | −3.95 ± 0.18 | −6.21 ± 0.15 |
| 13 | −6.61 ± 0.08 | −3.90 ± 0.17 | −5.76 ± 0.24 |
| 14 | −7.26 ± 0.01 | −3.59 ± 0.14 | −5.87 ± 0.28 |
| 15 | −6.78 ± 0.08 | −4.42 ± 0.28 | −5.00 ± 0.11 |
| 16 | −7.01 ± 0.08 | −3.21 ± 0.22 | −5.61 ± 0.20 |
| 17 | −6.71 ± 0.15 | −2.26 ± 0.29 | −5.36 ± 0.18 |
| 18 | −6.60 ± 0.08 | −4.01 ± 0.10 | −5.46 ± 0.16 |
| 19 | −8.85 ± 0.15 | −4.59 ± 0.25 | −7.87 ± 0.17 |
| 20 | −7.09 ± 0.08 | −4.30 ± 0.21 | −7.12 ± 0.11 |
| 21 | −8.20 ± 0.11 | −5.78 ± 0.15 | −8.21 ± 0.06 |

TABLE XII

SOLUTE PARTIAL MOLAR ENTROPIES OF SOLUTION, $\Delta\bar{S}$ (cal mol$^{-1}$ K$^{-1}$)

| Solute No. | Smectic | Nematic | Isotropic |
|---|---|---|---|
| 1 | −18.18 ± 0.21 | −13.30 ± 0.80 | −18.28 ± 0.32 |
| 2 | −20.95 ± 0.55 | −13.76 ± 1.08 | −18.49 ± 0.54 |
| 3 | −22.34 ± 0.27 | −13.54 ± 0.13 | −19.62 ± 0.37 |
| 4 | −24.25 ± 0.39 | −14.29 ± 1.18 | −21.57 ± 0.21 |
| 5 | −25.99 ± 0.53 | −16.21 ± 0.89 | −22.86 ± 0.16 |
| 6 | −21.31 ± 0.19 | −12.82 ± 1.49 | −17.30 ± 0.37 |
| 7 | −21.89 ± 0.09 | −10.09 ± 1.07 | −16.62 ± 0.11 |
| 8 | −19.87 ± 0.32 | −9.65 ± 1.45 | −14.61 ± 1.02 |
| 9 | −20.64 ± 0.27 | −10.84 ± 0.34 | −16.52 ± 0.25 |
| 10 | −22.68 ± 0.18 | −13.70 ± 0.69 | −18.04 ± 0.64 |
| 11 | −22.63 ± 0.45 | −13.02 ± 0.73 | −18.49 ± 0.61 |
| 12 | −22.45 ± 0.53 | −11.17 ± 0.59 | −18.11 ± 0.48 |
| 13 | −21.19 ± 0.26 | −12.42 ± 0.53 | −18.01 ± 0.74 |
| 14 | −22.30 ± 0.04 | −10.32 ± 0.45 | −17.35 ± 0.88 |
| 15 | −21.69 ± 0.27 | −13.97 ± 0.91 | −15.54 ± 0.33 |
| 16 | −21.81 ± 0.26 | −9.42 ± 0.71 | −16.81 ± 0.63 |
| 17 | −21.32 ± 0.50 | −6.82 ± 0.92 | −16.46 ± 0.57 |
| 18 | −21.01 ± 0.28 | −12.50 ± 0.31 | −16.89 ± 0.50 |
| 19 | −23.29 ± 0.50 | −9.35 ± 0.81 | −19.55 ± 0.54 |
| 20 | −20.07 ± 0.27 | −10.94 ± 0.68 | −19.67 ± 0.34 |
| 21 | −21.43 ± 0.37 | −13.50 ± 0.50 | −20.98 ± 0.20 |

## DISCUSSION

Although many trends have been identified and analyzed through extensive thermodynamic studies by GLC [6–17,31], a definitive molecular-level description of retention and selectivity in nematic liquid-crystalline phases is still lacking. In 1971, Chow and Martire [9] proposed an infinite-dilution solution model for the interpretation of thermodynamic results ($\gamma_f^\infty$, $\bar{H}^e$, $\bar{S}^e$, $\Delta\bar{H}$ and $\Delta\bar{S}$) from GLC. Although several workers have applied the model with some success [6–17] and it was later refined [19], the model remains semi-quantitative, at best. Clearly, additional systematic experimental studies (thermodynamic, spectroscopic and structural) and extension of a recent, promising, molecular theory based on a lattice model [32,33] are needed to further a more detailed understanding. Nevertheless, the refined solution model [6,7,9,19] can, at this stage, be reasonably used to discuss and analyze trends in the thermodynamic results.

We begin by comparing 5CB [6], 6CB [17], 7CB [16] and 8CB. The trends within each of five solute groups (*n*-alkanes, isomeric hexanes, heptanes, nonanes and the aromatic solutes) are then examined. Note that the discontinuities in ln $\gamma_f^\infty$ as a function of $1/T$ at the phase-transition temperatures (see Fig. 1) are discussed elsewhere [8,20].

### *General trends with 5CB, 6CB, 7CB and 8CB*

In both the isotropic and nematic phases, the general trends observed with 8CB

as the solvent are similar to those previously encountered with 5CB, 6CB and 7CB. The infinite-dilution solute activity coefficients exhibit positive deviations from Raoult's law ($\gamma_f^\infty > 1$), except for the aromatic solutes in the isotropic phase of 6CB, 7CB and 8CB, and all excess enthapies and excess entropies are positive. This indicates that, in general, the non-mesomorphic solutes are incompatible with both phases of these liquid-crystalline solvents.

Comparing the results for the nematic (N) and isotropic (I) phases, we note, without exception, the following trends in all four solvents:

(a) $(\Delta\bar{H})_I < (\Delta\bar{H})_N$ and $(\bar{H}^e)_I < (\bar{H}^e)_N$

(b) $(\Delta\bar{S})_I < (\Delta\bar{S})_N$ and $(\bar{S}^e)_I < (\bar{S}^e)_N$

(c) $(\gamma_f^\infty)_I < (\gamma_f^\infty)_N$

The small value of $\Delta H_{NI}$ (Table I) indicates that solvent–solvent interactions in the nematic phase are only slightly stronger than those in the isotropic phase. Therefore, trend (a) can only be interpreted as resulting from effectively stronger solute–solvent interactions in the isotropic phase. Trend (b) is less straightforward. In the nematic phase, rotational and conformational restrictions reduce solute entropy, while weaker solute–solvent interactions lead to an increase in solute (translational) entropy. Experiment shows that the latter prevails and the nematic phase is entropically favored. Trend (c) indicates that the lower solute excess Gibbs free energy in the isotropic phase is enthalpic in origin.

8CB is the only member of the series to exhibit a smectic phase. Let us compare the results for the different phases of 8CB. The trends are as follows:

(a) $(\Delta\bar{H})_{S_A} < (\Delta\bar{H})_I < (\Delta\bar{H})_N$ and $(\bar{H}^e)_{S_A} < (\bar{H}^e)_I < (\bar{H}^e)_N$

(b) $(\Delta\bar{S})_{S_A} < (\Delta\bar{S})_I < (\Delta\bar{S})_N$ and $(\bar{S}^e)_{S_A} < (\bar{S}^e)_I < (\bar{S}^e)_N$

(c) $(\gamma_f^\infty)_I < (\gamma_f^\infty)_N < (\gamma_f^\infty)_{S_A}$

In the light of our DSC measurements (Table I), solvent–solvent interactions are clearly not governing trend (a). The determining factor is the relative strength of solute–solvent interactions which are greater (more negative) in the smectic phase than in the other two phases. Strong solute–solvent interactions tend to restrict the solute's translational freedom and decrease its entropy. Further, the lack of long-range alignment of solvent molecules in the isotropic phase tends to increase solute entropy (through greater rotational and conformation freedom) relative to its smectic and nematic phase values. Again, the experimental results indicate that the first effect predominates and the nematic phase is found to be the most entropically favored. It is also the least favored in terms of enthalpy.

From (a) and (b) we conclude that the smaller $\gamma_f^\infty$ (the lower solute excess Gibss free energy) in the isotropic phase is caused by a more favorable enthalpy relative to the nematic phase and a more favorable entropy relative to the smectic phase, and the slightly smaller $\gamma_f^\infty$ in the nematic phase relative to the smectic phase is achieved through more favorable entropic effects.

In the following sections, we drop the subscript f in the activity coefficient notation and adopt the terminology with respect to $\Delta\bar{H}$ and $\Delta\bar{S}$ that larger refers to more negative values and smaller to less negative values.

*n-Alkanes (solutes 1–5)*

In the nematic phase, $\Delta\bar{H}$,$\Delta\bar{S}$ and $\gamma^{\infty}$ increase with increasing solute chain-length. This may be explained as follows: (a) as the solute chain length increases, the molecular polarizability increases, leading to stronger solute–solvent interactions (through dispersion forces) and larger $\Delta\bar{H}$ and $\Delta\bar{S}$ values; (b) with increasing solute chain length the solute-to-solvent size ratio increases and the combinatorial entropy contribution leads to larger $\Delta\bar{S}$ and less positive $\bar{S}^{e}$ values; and (c) a more elongated and more flexible molecule loses more rotational and conformational freedom on solvation, hence leading to larger $\Delta\bar{S}$ and more negative $\bar{S}^{e}$ values. The trend in $\gamma^{\infty}$ indicates that the enthalpy of solution increases less rapidly with increasing chain length than do the combined entropy of solution effects.

The same trends in $\gamma^{\infty}$, $\Delta\bar{H}$ and $\Delta\bar{S}$ are observed in the isotropic phase where rotational and conformational entropy losses are relatively small, and in the smectic phase where these losses are greater than in the nematic phase, thus making $(\Delta\bar{S})_{S_A}$ larger than $(\Delta\bar{S})_N$ (*i.e.*, more negative) for all *n*-alkanes.

*Isomeric hexanes (solutes 2 and 6–9)*

The hexanes vary in shape from that of the straight-chain and relatively flexible *n*-hexane to the more globular and conformationally more rigid 2,2-dimethylbutane. However, their $\gamma^{\infty}$, $\Delta\bar{H}$ and $\Delta\bar{S}$ values are too close to permit a clear interpretation. Nevertheless, when *n*-hexane is contrasted with 2,2- and 2,3-dimethylbutane, the trend observed is not unlike that encountered with the isomeric heptanes, which are discussed next.

*Isomeric heptanes (solutes 3 and 10–17)*

They vary widely in shape from that of the straight-chain and relatively flexible *n*-heptane to that of the more globular and conformationally more rigid 2,2,3-trimethylbutane. $\Delta\bar{H}$ and $\Delta\bar{S}$ tend to increase as the solute molecule becomes less branched because, as proposed [6,7,9,19], (a) rotational and conformational entropy losses increase, leading to larger $\Delta\bar{S}$ values, and (b) the effective strength of solute–solvent attractive interactions increases, leading to larger $\Delta\bar{H}$ and $\Delta\bar{S}$ values.

However, this effect is less marked in the isotropic phase and, even more so, in the smectic phase. The absence of a general trend in the $\gamma^{\infty}$ values of isomeric alkanes (which generally exceed those of their *n*-alkane counterparts) is due to a complex interplay between smaller $\Delta\bar{H}$ (tending to increase $\gamma^{\infty}$) and smaller $\Delta\bar{S}$ (tending to decrease $\gamma^{\infty}$) values resulting from increased branching. The absence of a general trend in the $\gamma^{\infty}$ suggests a subtle balance between enthalpy and entropy effects, which is difficult to interpret without a knowledge of the structure of the solution, the molecular conformations, etc.

The available data indicate that, for the same number of carbon atoms in the solute molecule, the branched alkane has, in general, a higher $\gamma^{\infty}$ value than the *n*-alkane. Exceptions to this rule, where the $\gamma^{\infty}$ values are comparable and/or the trend is reversed (7CB[16]), are encountered among solutes with centrally located

branches. For heptanes and hexanes at least, the more centrally located the branches are, the closer is the $\gamma^{\infty}$ value to that of the straight-chain isomer. Comparison of 2-methylhexane and 3-methylhexane shows a lower $\gamma^{\infty}$ value for the latter, *i.e.*, solute compatibility with the solvent increases as the branching is more centrally located. A similar trend is observed when 2,2-dimethylpentane and 3,3-dimethylpentane are contrasted.

*Isomeric nonanes (solutes 5 and 19)*

Two extremes in molecular structure were studied: *n*-nonane and the quasi-spherical 3,3-diethylphentane. The analysis proposed above also applies here. We simply note again that solution of the *n*-alkane is enthalpically favored (smaller $\bar{H}^{e}$ and larger $\Delta\bar{H}$) due to stronger effective solute–solvent interactions, but entropically unfavored (smaller $\bar{S}^{e}$ and larger $\Delta\bar{S}$) due to the conformational, rotational and enhanced translational entropy losses. In this case, however, the less favorable entropy prevails, and *n*-nonane has the higher $\gamma^{\infty}$ values.

*Aromatic solutes (solutes 20 and 21)*

For the three phases, the trends in $\Delta\bar{H}$ and $\Delta\bar{S}$ are toluene > benzene, while the $\gamma^{\infty}$ values are slightly higher for toluene. The $\Delta\bar{H}$ trend may be rationalized on the basis of molecular size and dispersion forces. The larger toluene molecule (with greater molecular polarizability) should have stronger solute–solvent interactions and, therefore, larger $\Delta\bar{H}$ values than the smaller benzene molecule. The trend in $\Delta\bar{S}$ follows both the trend in $\Delta\bar{H}$ (stronger interactions should result in greater translational entropy loss) and the trend expected from the combinatorial entropy ($\bar{S}^{e}$ increases and $\Delta\bar{S}$ decreases with decreasing solute size). The trend in $\gamma^{\infty}$ indicates that the enthalpy trend predominates, as was previously observed with 5CB, 6CB and 7CB.

Finally, comparing collectively the aromatic and aliphatic solutes, we observe that the latter have higher $\gamma^{\infty}$ values in all phases and solvents. This can be atrributed to more positive interchange energies (hence, less favorable enthalpies) and, in part, to the unfavorable conformational contribution of the more flexible alkanes.

## ACKNOWLEDGEMENTS

This material is based on work supported by the National Science Foundation under Grant CHE-8902735.

The authors are pleased to dedicate this paper to Professor Georges Guiochon on the occasion of his 60th birthday. We wish him continued health, happiness and productivity, and gratefully acknowledge the impact his generously shared insights and knowledge have had on our research.

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