

# Gas–liquid chromatographic study of thermodynamics of solution of some alkanes on liquid crystal stationary phases

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(First received March 25th, 1993; revised manuscript received October 4th, 1993)

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## ABSTRACT

A gas–liquid chromatographic study of the interaction and elution characteristics of C<sub>5</sub>–C<sub>9</sub> normal, branched and cyclic alkanes using liquid crystalline stationary phases and at different column temperatures of 60–100°C for *p*-(*n*-hexyloxy)phenyl *p*'-methoxybenzoate and 90–150°C for *p*-pentyloxyphenyl *p*'-ethoxyazoxybenzoate as stationary phases is reported. Negligible surface effects at the liquid crystal–solid support interface were ensured using a high loading (20%, w/w) of liquid crystal stationary phase on 80–100-mesh Chromosorb W AW DMCS. The results are interpreted in terms of activity coefficients and related thermodynamic quantities.

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## INTRODUCTION

Gas–liquid chromatography (GLC) is an effective method for the investigation of the properties of solvents and the behaviour of solutes in liquid crystals. Martire *et al.* [1] established the feasibility of GLC for the thermodynamic investigation of liquid crystals using seven hydrocarbon solutes. Zielinski *et al.* [2] studied the GC and thermodynamics of divinylbenzene separations on 4,4'-dihexoxyazoxybenzene liquid crystal stationary phase. Chow and Martire [3] supported the concept of a two-phase (bulk gaseous phase and bulk liquid crystal phase) GLC partitioning process and hence of negligible surface effects at both the carrier gas–liquid crystal and liquid crystal–solid support interfaces, provided that a liquid crystal film thickness

of greater than 1000 Å is present. Later they studied the infinite dilution thermodynamic solution properties of non-mesomorphic solutes in nematogenic liquid crystals [4].

The activity coefficients of *n*-heptane dissolved in 4,4'-dihexyloxyazobenzene obtained from chromatographic measurements showed good agreement with the results obtained by statistical methods [5]. The values of the coefficients are different in particular phases of the liquid crystal [6,7]. Seifert and Kraus [8] investigated the solution behaviour of liquid crystal phases in capillary GC and correlated the partial molar free excess enthalpy differences at the transition temperatures with the heats of transition. Soják *et al.* [9] stated that liquid crystals as stationary phases in GC possess shape-selective separation properties for structural and geometrical isomers of hydrocarbons and the selectivity increases with the high separation efficiency of capillary columns. Soják and co-workers [10,11] investigated the separation of diastereomeric C<sub>8</sub>–C<sub>20</sub> alkanes using mesogenic stationary phases in a

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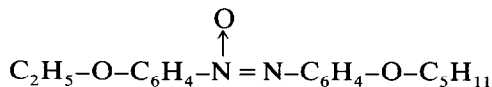
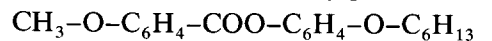
capillary GC column. A comparison of the retentions of the diastereomers on mesogenic and non-mesogenic phases showed the effect of mesophase diastereoselectivity.

Coca *et al.* [12] discussed the thermodynamic properties of 22 solutes at infinite dilution in the mesophases of 4,4'-bis(heptyloxy)azobenzene in relation to solute-solvent (liquid crystal) interactions as conditioned by the degree of order in the liquid crystal. Habboush *et al.* [13] dealt with the comparative GC behaviour of liquid crystal and polyester stationary phases at different column temperatures.

The aim of this investigation was to study the thermodynamics of solution in the two liquid crystalline stationary phases using C<sub>5</sub>-C<sub>9</sub> normal, branched and cyclic alkanes as model solutes and to correlate the measured thermodynamic quantities and structures of both the stationary phases and solutes.

## EXPERIMENTAL

*p*-(*n*-Hexyloxy)phenyl *p*'-methoxybenzoate and *p*-pentyloxyphenyl *p*'-ethoxyazoxybenzene were used as the stationary phases:



These phases were kindly prepared in Dr. G. Kraus's laboratory at Martin Luther University (Halle, Germany) for the purpose of thermodynamic studies. The transition temperatures and the purities of the two liquid crystals were determined by differential scanning calorimetry. The measurements yielded estimate purities of 99.7% for the former stationary phase and 99.8% for the latter.

All hydrocarbons and solvents were purchased from Fluka and BDH and Chromosorb from Johns-Manville.

Columns were made of stainless-steel tubing (6 ft. × 0.25 in I.D.; 1 ft. = 30.48 cm, 1 in. = 2.54

cm) and each column was packed with 20% (w/w) of stationary phase on 80–100-mesh Chromosorb W AW DMCS to ensure negligible surface effects on the liquid crystal–solid support and gas–liquid interfaces. Coating of the support was carried out as follows. An accurately known mass of the liquid crystal was dissolved in chloroform and added quantitatively to an accurately known mass of the support already wetted with chloroform in a fluted round-bottomed flask, followed by gradual solvent elimination through rotary vacuum evaporation. The dried coated stationary phase was transferred to a clean bottle and accurately weighed. The columns before packing were thoroughly washed with successive portions of acetone, methanol and diethyl ether. The mass of the loaded liquid crystal was calculated. The packing composition was checked by averaging the results for three separate Soxhlet solvent extractions carried out on a carefully weighed amount of fresh packing. The packed column was then conditioned in the gas chromatograph at a suitable temperature for 12 h with a nitrogen purge prior to use.

A Beckman GC-45 gas chromatograph equipped with a flame ionization detector was used with an optimum carrier gas (nitrogen) flow-rate of 30 ml min<sup>-1</sup> at NTP. Recording was done on Beckman Model 10 1-mV recorder. Temperature dependence was studied in the crystalline–nematic–isotropic regions at a minimum of six reasonably spaced temperatures.

Normal, branched and cyclic alkanes were used as sample components. The sample sizes ranged from 0.1 to 0.4 μl. Injections were made with a 1 μl Hamilton syringe. Each individual liquid sample and each mixture was run twice; no differences were found in the retention times when the compounds were injected individually or as a mixture, and the reproducibility was within 1%.

The solute peak retention times past the air peak were determined by taking the averages of at least four measurements obtained on two separate days. Also, early values were reproducible at the end of the experiment within the accuracy of the measurements of 1%. It was established that the solute retention times were independent of sample size, and hence that

operation was taking place in the Henry's law region (*i.e.*, infinite dilution). Further, it was found when an internal standard was used that the relative retention times were independent of the loading (15 and 20% were examined). This confirmed that solute adsorption on the solid support and the gas–liquid interface was negligible.

## RESULTS AND DISCUSSION

Specific retention volumes,  $V_g$ , were calculated from the corrected peak retention times and the column operating conditions by using the well known equation derived by Littlewood *et al.* [14]. Solute vapour pressures were calculated using Antoine's equations and constants [15]. The solute activity coefficients at infinite dilution,  $\gamma^\infty$ , were calculated for the two liquid crystal stationary phases in the temperature range 60–110°C on *p*-(*n*-hexyloxy)phenyl *p*'-methoxybenzoate and 90–150°C on *p*-pentyloxyphenyl *p*'-ethoxyazoxybenzene with 10°C increments from the following equation [16]:

$$\gamma^\infty = \frac{17.04 \cdot 10^7}{M_1 p_2^0 V_g} \quad (1)$$

where  $M_1$  is the molecular mass of the stationary phase and  $p_2^0$  is the vapour pressure of the pure solute vapour (mmHg; 1 mmHg = 133.322 Pa). The logarithms of the solute activity coefficients,  $\gamma^\infty$ , obtained were plotted against the reciprocal of the absolute column temperature (Figs. 1 and 2). The partial molar excess enthalpy,  $\Delta H_e^\infty$ , of mixing at infinite dilution were calculated from an equation formulated by Habboush and Al-Bazi [17] for the direct calculation of  $\Delta H_e^\infty$  from the specific retention volume and vapour pressure of a solute at two temperatures as follows:

$$\Delta H_e^\infty = 2.303R \cdot \frac{T_1 T_2}{T_2 - T_1} \cdot \log \left( \frac{p_2 V_g^{T_2}}{p_1 V_g^{T_1}} \right) \frac{T_1}{T_2} \quad (2)$$

The results are given in Table I. The excess partial molar free energy,  $\Delta G_e^\infty$ , and the partial molar excess entropy,  $\Delta S_e^\infty$ , of mixing at infinite dilution were calculated using the following equations:

TABLE I

EXCESS MOLAR ENTHALPY,  $\Delta H_e^\infty$ , (kcal/mol) AND ENTROPY,  $\Delta S_e^\infty$ , (cal/mol·K) OF ALKANES ON THE TWO LIQUID CRYSTAL STATIONARY PHASES

1 cal = 4.184 J.

No.	Compound	<i>p</i> -Pentyloxyphenyl <i>p</i> '-ethoxyazoxybenzene				<i>p</i> -( <i>n</i> -Hexyloxy)phenyl <i>p</i> '-methoxybenzoate			
		Mesophase		Isotropic		Mesophase		Isotropic	
		$\Delta H_e^\infty$	$\Delta S_e^\infty$	$\Delta H_e^\infty$	$\Delta S_e^\infty$	$\Delta H_e^\infty$	$\Delta S_e^\infty$	$\Delta H_e^\infty$	$\Delta S_e^\infty$
1	Pentane	9.17	24.87	2.88	6.62	4.35	13.30	2.40	6.50
2	Hexane	4.34	12.44	3.91	9.63	5.97	18.43	1.92	5.95
3	Heptane	4.20	12.46	3.84	9.87	4.93	15.70	1.09	3.70
4	Octane	4.65	13.94	4.14	10.88	4.64	15.05	3.80	11.15
5	Nonane	3.68	11.51	3.96	10.65	8.00	25.21	2.47	7.92
6	2,4-Dimethylpentane	4.97	14.37	2.23	5.75	2.71	9.22	2.31	6.91
7	2,3-Dimethylpentane	4.54	13.23	3.67	9.37	4.25	13.70	2.79	8.14
8	2,2,4-Trimethylpentane	4.71	13.96	3.80	9.87	4.44	14.51	2.96	8.83
9	2,4-Dimethylhexane	4.95	14.72	3.92	10.24	4.78	15.50	3.04	9.12
10	3-Methylheptane	4.66	13.95	3.02	8.10	5.20	16.69	3.54	10.43
11	Cyclopentane	3.82	10.57	4.05	9.59	4.48	13.62	1.30	3.56
12	Cyclohexane	4.31	12.32	3.10	7.66	4.96	15.38	1.08	3.27

TABLE II

EXCESS FREE ENERGY,  $\Delta G_e^\infty$  (cal/mol) OF ALKANES ON *p*-(*n*-HEXYLOXY)PHENYL *p*'-METHOXYBENZOATE AT DIFFERENT TEMPERATURES

No.	Compound	60°C	70°C	80°C	90°C	100°C	110°C
1	Pentane	268	210	133	77	22	-15
2	Hexane	428	354	279	227	182	154
3	Heptane	512	454	369	337	285	270
4	Octane	575	523	436	395	357	348
5	Nonane	649	647	556	548	486	460
6	2,4-Dimethylpentane	481	451	341	298	270	283
7	2,3-Dimethylpentane	499	449	350	295	243	207
8	2,2,4-Trimethylpentane	585	535	436	381	329	294
9	2,4-Dimethylhexane	592	538	432	392	358	322
10	3-Methylheptane	585	526	433	388	384	337
11	Cyclopentane	252	192	110	62	27	2
12	Cyclohexane	371	309	224	189	137	118

$$\Delta G_e^\infty = RT \ln \gamma^\infty \quad (3)$$

$$\Delta G_e^\infty = \Delta H_e^\infty - T \Delta S_e^\infty \quad (4)$$

$$\ln \gamma^\infty = \frac{\Delta H_e^\infty}{RT} - \frac{\Delta S_e^\infty}{R} \quad (5)$$

as given by Langer and Purnell [18]. The data are given in Tables II and III.

The values of the activity coefficients obtained are  $>1$  except for pentane on *p*'-pentyloxyphenyl *p*'-ethoxyazoxybenzene in the temperature range 120–150°C, which indicates a positive deviation from ideality. Inspection of the plots of  $\log \gamma^\infty$

versus  $1/T$  (Figs. 1 and 2) illustrates that at the transition temperatures both a discontinuity and a change in slope occur, indicating that the solute molecules experience a marked change in environment as they enter a new phase, *i.e.*, the interaction of solutes with the solvent in the mesophase region differs from the interaction in the isotropic liquid. Further, the activity coefficients of *n*-alkanes in the two stationary phases decrease in the order nonane  $>$  octane  $>$  heptane  $>$  hexane  $>$  pentane.

Inspection of the values of the partial molar excess free energy of mixing at infinite dilution,

TABLE III

EXCESS FREE ENERGY,  $\Delta G_e^\infty$  (cal/mol) OF ALKANES ON *p*-PENTYLOXYPHENYL *p*'-METHOXYAZOXYBENZENE AT DIFFERENT TEMPERATURES

No.	Compound	90°C	100°C	110°C	120°C	130°C	140°C	150°C
1	Pentane	154	105	46	-11	-68	-151	-194
2	Hexane	351	296	248	97	143	68	20
3	Heptane	494	446	402	355	297	230	186
4	Octane	608	546	512	459	418	350	307
5	Nonane	663	616	594	557	510	435	396
6	2,4-Dimethylpentane	459	392	347	292	225	146	117
7	2,3-Dimethylpentane	470	391	369	313	247	202	143
8	2,2,4-Trimethylpentane	556	497	455	400	335	274	232
9	2,4-Dimethylhexane	599	538	495	443	384	303	260
10	3-Methylheptane	602	543	506	455	400	320	288
11	Cyclopentane	168	114	68	12	-15	-93	-147
12	Cyclohexane	339	283	237	187	140	66	26

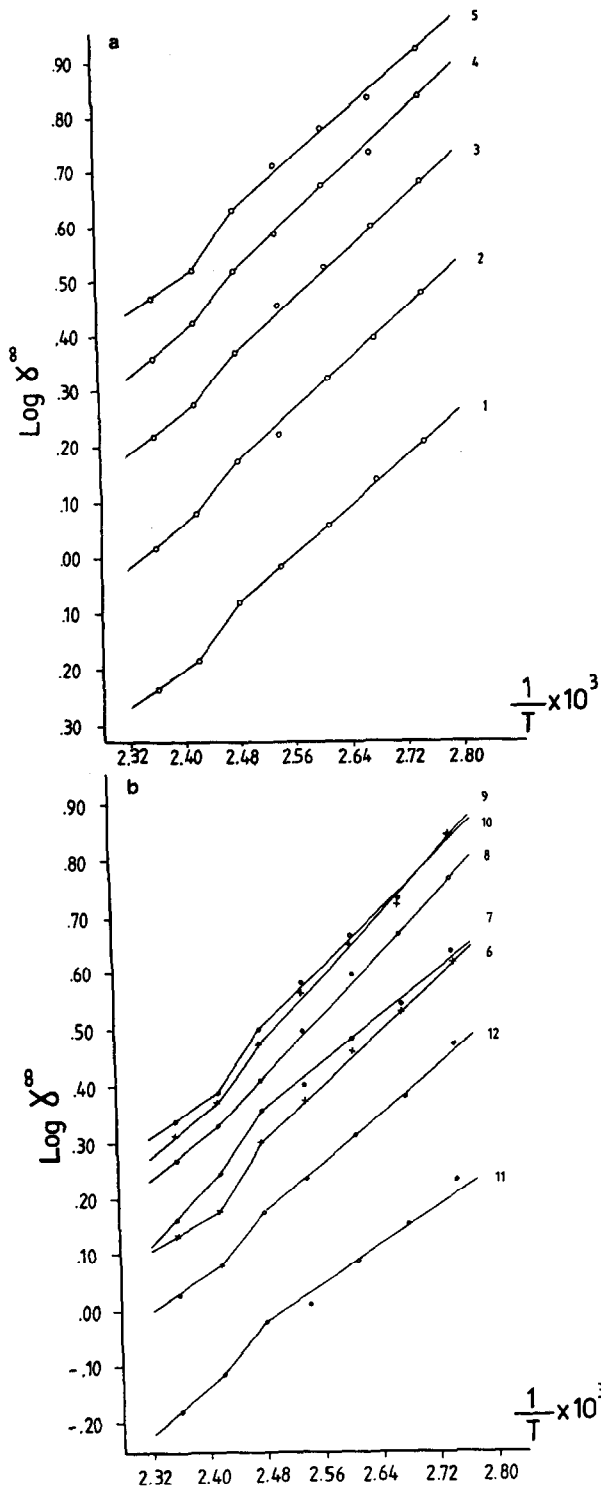


Fig. 1. (a) Plot logarithm of the activity coefficients of (a) *n*-alkanes and (b) branched and cyclic alkanes versus reciprocal of absolute temperature on *p*-pentyloxyphenyl *p*'-ethoxyazoxybenzene. The numbering is as in Table 1.

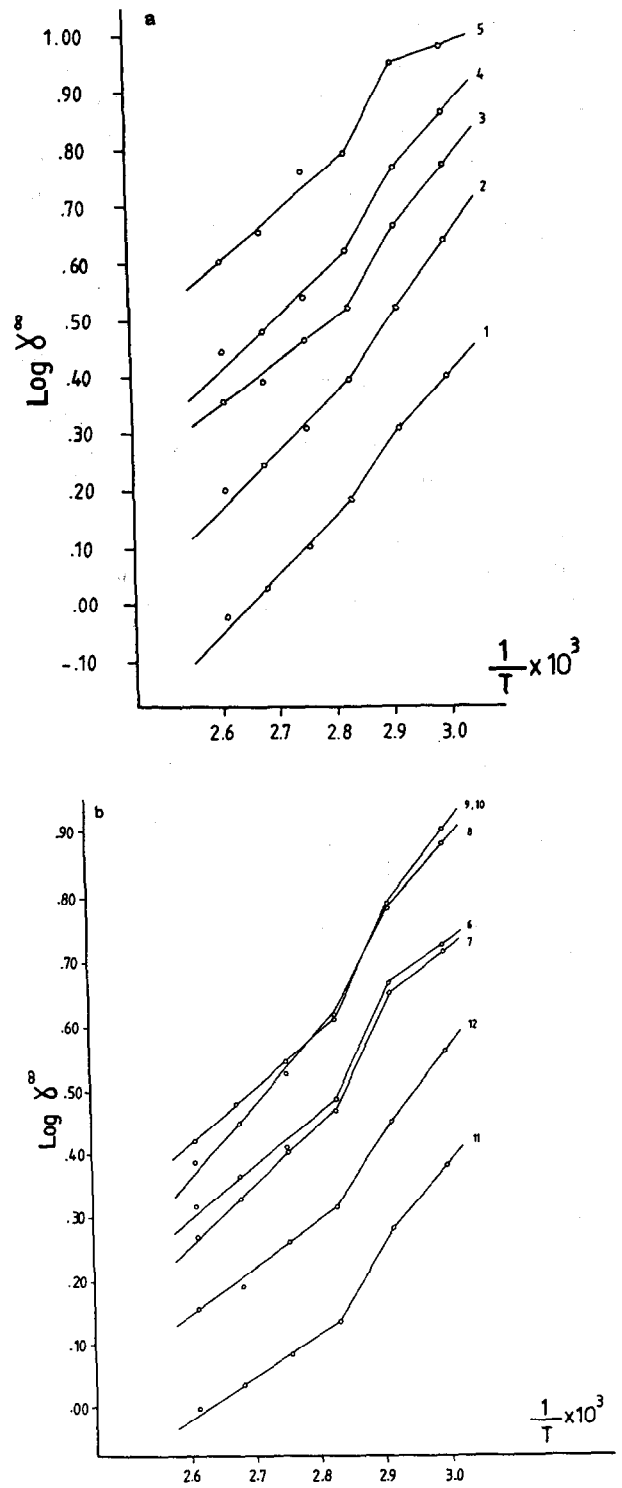


Fig. 2. (a) Plot of logarithm of the activity coefficients of (a) *n*-alkanes and (b) branched and cyclic alkanes versus reciprocal of absolute temperature on *p*-(*n*-hexyloxy)phenyl *p*'-methoxybenzoate. The numbering is as in Table 1.

$\Delta G_e^\infty$ , of paraffins in the two liquid crystalline stationary phases in Tables II and III reveals that free energy differences exist and are appreciable. The probable reason is that alkane molecules must “straighten out” and “stiffen up” to offer the maximum interaction cross-section to the rod-like liquid crystal molecules [1,2].

The results in Table I show that the excess molar enthalpies are positive in both phases, which indicates a strong endothermic mixing effect. It is also clear from Table I that the excess molar enthalpies in the mesophase region are greater than in the isotropic melt, which means that the solution process in an anisotropic liquid needs more energy because of the difficulty of dissolving molecules in a highly ordered structure [19–21].

It is also clear from Table I that the excess molar enthalpies,  $\Delta H_e^\infty$ , are accompanied by high positive entropies,  $\Delta S_e^\infty$ .

#### REFERENCES

- O.E. Martire, P.A. Blasco, P.F. Carone, L.C. Chow and H. Vicini, *J. Phys. Chem.*, 72 (1968) 3489.
- W.L. Zielinski, D.H. Freeman, D.E. Martire and L.C. Chow, *Anal. Chem.*, 42 (1970) 176.
- L.C. Chow and D.E. Martire, *J. Phys. Chem.*, 73 (1969) 1127.
- L.C. Chow and D.E. Martire, *J. Phys. Chem.*, 75 (1971) 2005.
- H.T. Peterson, D.E. Martire and W. Linder, *J. Phys. Chem.*, 76 (1972) 596.
- A.A. Jeknavorian, P. Barrett, A.C. Watterson and E.F. Barry, *J. Chromatogr.*, 107 (1975) 317.
- J.F. Bocquet and C. Pommier, *J. Chromatogr.*, 117 (1976) 315.
- K. Seifert and G. Kraus, *J. Chromatogr.*, 192 (1980) 97.
- L. Soják, G. Kraus, P. Farkaš and I. Ostrovský, *J. Chromatogr.*, 294 (1984) 155.
- L. Soják, I. Ostrovský, P. Farkaš and J. Janák, *J. Chromatogr.*, 356 (1986) 105.
- L. Soják, I. Ostrovský, G. Kraus and I.G. Andronikashvili, *J. Chromatogr.*, 436 (1988) 47.
- J. Coca, I. Melina and S.H. Langer, *Chromatographia*, 25 (1988) 825.
- A.E. Habboush, S.M. Farroha and A.Y. Kreishan, *J. High Resolut. Chromatogr.*, 14 (1991) 242.
- A.B. Littlewood, C.G. Phillips and D.T. Price, *J. Chem. Soc.*, (1955) 1480.
- R.R. Dreisbach, *Physical Properties of Chemical Compounds (Advances in Chemistry Series, No. 15)*, American Chemical Society, Washington, DC, 1955.
- D.E. Martire and L.Z. Pollara, *Adv. Chromatogr.*, 1 (1966) 335.
- A.E. Habboush and S.J.S. Al-Bazi, *J. Chromatogr. Sci.*, 16 (1978) 296.
- S.H. Langer and J.H. Purnell, *J. Phys. Chem.*, 67 (1963) 263.
- H. Kellar, *Fresenius' Z. Anal. Chem.*, 198 (1963) 254.
- H. Kelker and H. Winterscheidt, *Fresenius' Z. Anal. Chem.*, 220 (1966) 1.
- H. Keller and A. Verhelst, *J. Chromatogr. Sci.*, 7 (1969) 79.