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EVALUATION OF LIQUID CRYSTAL SMECTIC MESOPHASES FOR GAS–LIQUID CHROMATOGRAPHIC SEPARATIONS

JEROME E. HAKY* and GARY M. MUSCHIK
Chemical Carcinogenesis Program, Frederick Cancer Research Center, Frederick, MD 21701 (U.S.A.)
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SUMMARY

The gas chromatographic properties of the smectic and nematic mesophases of four well-characterized liquid crystals are reported. Selectivity and resolution of anthracene and phenanthrene is greater at column temperatures corresponding to these liquid crystals' smectic A and smectic C phases than at those corresponding to their nematic phases. Peak broadening does not occur in the smectic A or smectic C phases, but is seen in the smectic B phase. Separations of six polycyclic aromatic hydrocarbons and four polychlorinated biphenyls on the liquid crystal columns are compared. The results indicate a continuity of the mechanism of solute separation in the smectic A, smectic C and nematic phases, and demonstrate that these phases are useful in gas chromatographic analyses.

INTRODUCTION

The use of liquid crystalline compounds as stationary phases in gas–liquid chromatography (GLC) is rapidly gaining in popularity[1,2]. They have been successfully used in the GLC analyses of a variety of compounds, including polycyclic aromatic hydrocarbons (PAHs)[3–7], steroid epimers[5,8] polychlorinated biphenyls[10] and methylnaphthalenes[11]. In most cases, liquid crystalline stationary phases have been effectively utilized only in their nematic mesophases. Only a few smectic stationary phases have been studied[4,12–17], and these have produced mixed results. Generally, when compounds having both nematic and smectic mesophases have been studied, it has been found that chromatographic selectivity is significantly worse in the compound's smectic mesophase than in its nematic, despite the lower column oven temperatures that correspond to the smectic structure of these phases. In spite of this, there have been a few successful GLC applications of the smectic mesophase, *e.g.* as GLC phases for the separation and analysis of substituted benzene isomers[12], PAHs[13], insect pheremones[14] and more recently, isomeric olefins[15].

The smectic mesophase exists in several types (identified by letter A, B, C etc.) which correspond to different degrees of order and molecular alignment. The successful application of some smectic liquid crystals in GLC separations suggests that at least some of these smectic types may have potential for use in GC. We have

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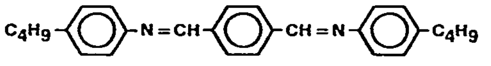
evaluated the GC properties of specific smectic phases of four well-characterized liquid crystals, and compared them with those of corresponding nematic phases.

EXPERIMENTAL

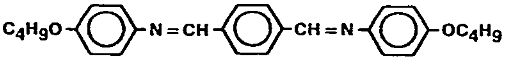
Materials

The liquid crystalline compounds were synthesized using published methods[18–21] and purified to give constant transition temperatures (Table I) which matched those previously reported[18–22]. Their structures are given below:

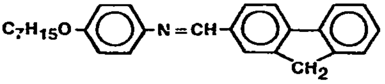


N,N′ terephthalylidene-bis-(4-*n*-butylaniline) (TBBA)[18,21]

N,N′ terephthalylidene-bis-(4-ethylaniline) (TBEA)[18]



N,N′ terephthalylidene-bis(4-*n*-butoxyaniline) (TBBOA)[20]



2(4-*n*-heptyloxybenzylideneamino)fluorene (HBAF)[19,22]

The PAHs were obtained from the International Hydrocarbon Bank (Ottawa, Canada) and the polychlorinated biphenyls from Analabs (North Haven, CT, U.S.A.).

Apparatus and procedure

Mesophase transition temperatures, enthalpies and entropies (Table I) were determined by differential scanning calorimetry with a Perkin-Elmer Model DSC-2 unit.

GC analyses were performed on a Hewlett-Packard Model 7610 gas chromatograph equipped with a flame-ionization detector. Columns packed with the TBBA, TBEA and TBBOA liquid crystals had the dimensions of 6 ft. × 2 mm I.D., while the column containing HBAF was 1 1/2 ft. × 2 mm I.D. Glass columns were used exclusively. The column packing was 2.5 wt. % of the liquid crystal on 100–120 mesh Chromosorb W HP. Chromatograms were on a 1-mV f.s. strip chart recorder using an electrometer setting of 16 × 10^2. Carrier gas flow (helium, 20 ml/min) was monitored by a calibrated Brooks 5840 Dual GC mass flow controller, while hydrogen and air flow-rates (40 and 500 ml/min, respectively) were measured by a soap bubble flow meter. Sample injection volumes were usually 1–2 μl using a Hamilton 701 N 10-μl syringe.

TABLE I

THERMODYNAMIC CONSTANTS OF THE COMPOUNDS STUDIED

T = transition temperature in °C; ΔH = enthalpy in kcal/mol; ΔS = entropy in cal/mol/°K. $C \rightarrow S_X$ = crystal to smectic mesophase; $S_X \rightarrow S_Y$ = smectic phase to next smectic phase; $S_Y \rightarrow N$ = smectic mesophase to nematic mesophase; $N \rightarrow I$ = nematic mesophase to isotropic liquid.

Compounds	*Transition*	T	ΔH	ΔS
TBBA	$C \rightarrow S_B$	112 (113.0)*	4.4	11.4
	$S_B \rightarrow S_C$	144 (144.1)*	0.81	1.9
	$S_C \rightarrow S_A$	172 (172.5)*	**	
	$S_A \rightarrow N$	198 (199.6)*	0.12	0.25
	$N \rightarrow I$	235 (236.5)*	0.18	0.35
TBEA	$C \rightarrow S_B$	126 (126)***	3.9	9.8
	$S_B \rightarrow N$	149 (149.7)***	2.6	6.2
	$N \rightarrow I$	248 (248)***	0.06	0.11
TBBOA	$C \rightarrow S_C$	191 (190.6)§	7.0	15.1
	$S_C \rightarrow N$	221 (221.2)§	**	
	$N \rightarrow I$	295 (295.5)§	0.50	0.88
HBAF	$C \rightarrow S_A$	121 (121.5)§§	4.1	10.4
	$S_A \rightarrow N$	159 (159)§§	0.19	0.44
	$N \rightarrow I$	191 (191)§§	0.29	0.62

* Ref. 21.

** Transition heat is small and diffuse.

*** Ref. 18.

§ Ref. 20.

§§ Ref. 22.

Calculations

Retention times for all solutes are corrected using benzene as the unretained solute. Partial molar enthalpies of solution (ΔH_S) were calculated from the slopes of the linear portions of the graphs of the logarithm of the retention time *vs.* the reciprocal absolute temperature according to the equation of Littlewood *et al.*[23] (slope $= \Delta H_S/R$). The separation factor, α, was determined by the ratio of corrected retention times ($\alpha = t'_{R2}/t'_{R1}$). Resolution was determined by the ratio of the distance between peak maxima and their average peak width at base, as $R = (t'_{R2} - t'_{R1})/0.5\,(W_2 - W_1)$.

RESULTS AND DISCUSSION

The four liquid crystalline compounds used in this study were carefully chosen so that proper evaluation of the GC properties of specific smectic phases could be made. Each of these compounds has at least one well-characterized smectic thermotropic region in addition to a nematic region, so that the GC properties of the smectic and nematic mesophases of each compound could be determined and compared.

Two three-ring PAHs, anthracene and phenanthrene, were used as solutes for the initial evaluation of the columns. Fig. 1 shows the behavior of the corrected retention time as a function of temperature for these two PAHs on the TBBA column. The discontinuity in the curves near the smectic B–smectic C transition temperature (144°C) is typical of the retention behavior of solutes near mesophase transition temperatures of liquid crystalline GLC phases[1,2,4]. However, no discontinuity in the curves occurs at the smectic C–smectic A or smectic A–nematic transition temperatures (172 and 198°C, respectively); points on the curves through the smectic C, smectic A and nematic temperature ranges fit straight lines with correlation coefficients greater than 0.99. The linearity of these curves in both the nematic and the two least-ordered smectic phases suggests a similarity in the solution properties of these thermotropic regions in GC analyses.

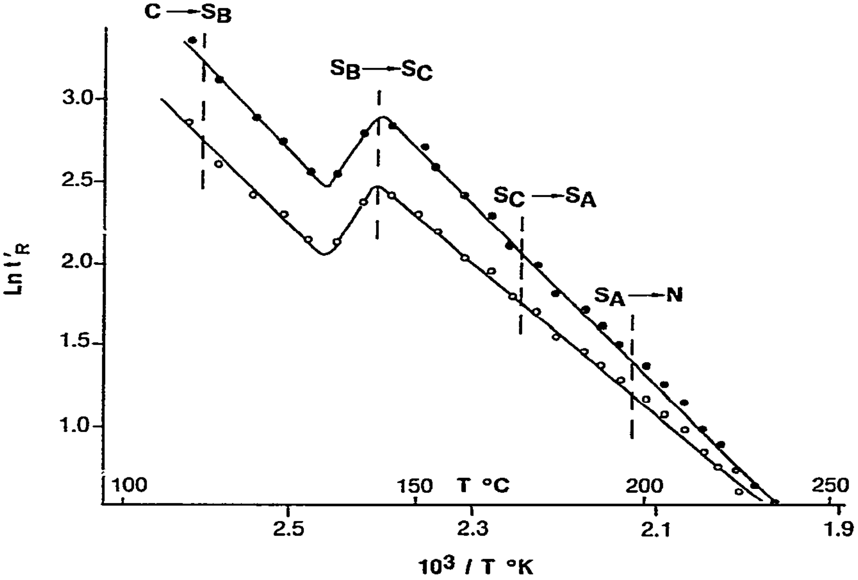


Fig. 1. Retention behavior of anthracene (upper curve) and phenanthrene (lower curve) on the TBBA column in the temperature range 110–240°C. Dashed lines indicate phase transition temperatures.

Partial molar enthalpies of solution (ΔH_1, ΔH_2) of the two PAHs for the various thermotropic regions of each column are listed in Table II. These enthalpies remain constant throughout the smectic C, smectic A, and nematic regions of TBBA, which indicates that the solution properties are constant. In contrast, the ΔH values vary somewhat between the smectic and nematic regions of the TBBOA and HBAF columns. In these two cases however, the difference in the enthalpies of solution for the two PAHs ($\Delta H_1 - \Delta H_2$) does not significantly change between the smectic and nematic mesophases, indicating similar enthalpic selectivity in these modifications. This similarity is reflected in the behavior of the separation factor, α, of the anthracene–phenanthrene system with temperature (Fig. 2). For each of these liquid crystal columns α continues to increase as the column temperature is lowered throughout the nematic, smectic A and smectic C thermotropic regions. Even higher values of α are obtained in the smectic B thermotropic regions of the TBBA and TBEA columns, (Fig. 2a) but these are accompanied by extensive peak broadening, causing substantial drops in resolution at temperatures corresponding to this modification (Fig. 3a). In the other two columns, which do not have a smectic B phase, such peak broadening is not observed until the crystalline state is reached (Figs. 3b, c).

TABLE II

PARTIAL MOLAR ENTHALPIES OF SOLUTION OF ANTHRACENE AND PHENANTHRENE

ΔH_1 = partial molar enthalpy of solution of phenanthracene in kcal/mole; ΔH_2 = partial molar enthalpy of solution of anthracene in kcal/mole.

Column	*Temp. range, °C (mesophase)**	ΔH_1	ΔH_2	$\Delta H_1 - \Delta H_2$
TBBA	145–225 (S_A, S_C, N)	− 9.4	−10.9	1.5
TBEA	145–230 (N)	−13.4	−14.1	0.7
TBBOA	195–220 (S_C)	− 6.5	− 7.5	1.0
	235–265 (N)	−10.2	−11.0	0.8
HBAF	125–145 (S_A)	−12.2	−13.2	1.0
	165–185 (N)	−11.3	−12.3	1.0

* Temperatures where the log retention time *vs.* reciprocal temperature curves are not linear have been omitted.

The transition temperature data in Table I indicates that there is a wide temperature range in which the smectic A and C phases of TBBA overlap the nematic phase of TBEA. Since these two compounds are homologs, and should have similar polarities and molecular alignment characteristics, this allows a direct comparison of the GC properties of smectic and nematic phases in this temperature range. Comparison of the separation factors (Fig. 2a) and resolution (Fig. 3a) of anthracene and phenanthrene in these columns clearly shows the superiority of the smectic A and smectic C phases of TBBA over the nematic mesophase of TBEA. Superiority of the TBBA over the TBEA column in this separation is also indicated by the partial molar enthalpies of solution of the two PAHs for the two columns (Table II). The difference in the ΔH_S values for anthracene and phenanthrene is significantly higher for the TBBA column (1.5 kcal/mole *vs.* 0.7 kcal/mole), indicating higher enthalpic selectivity.

Further comparison of the chromatographic behavior of the TBBA and TBEA columns was made by evaluating the degree of separation of a set of three-ring PAHs at 170°C for each of the two columns. Fig. 4 shows the separation, clearly demonstrating the superiority of the smectic TBBA column. Significantly, while the TBBA column separated all of the components of this mixture, the TBEA column did not resolve 9-methylanthracene and 2-methylanthracene. Relative retention times for a set of polychlorinated biphenyls are shown for the two columns in Table III. Both columns gave similar separation of these compounds, indicating equivalent selectivity of the nematic and smectic modifications in this case.

Relative retention times for the four polychlorinated biphenyls and six PAHs on all of the liquid crystal columns are shown in Tables III and IV, respectively. With column temperatures corresponding to either the smectic C or smectic A phases, and analysis time kept to less than 20 min, adequate separations of these compounds were obtained on all the liquid crystal columns, with the possible exception of the polychlorinated biphenyls on the TBBOA column. Under the conditions used, it appears that the TBBA column is the most versatile. It is significant, however, that good separations were obtained on the short (1 1/2 ft.) HBAF column in its smectic A phase.

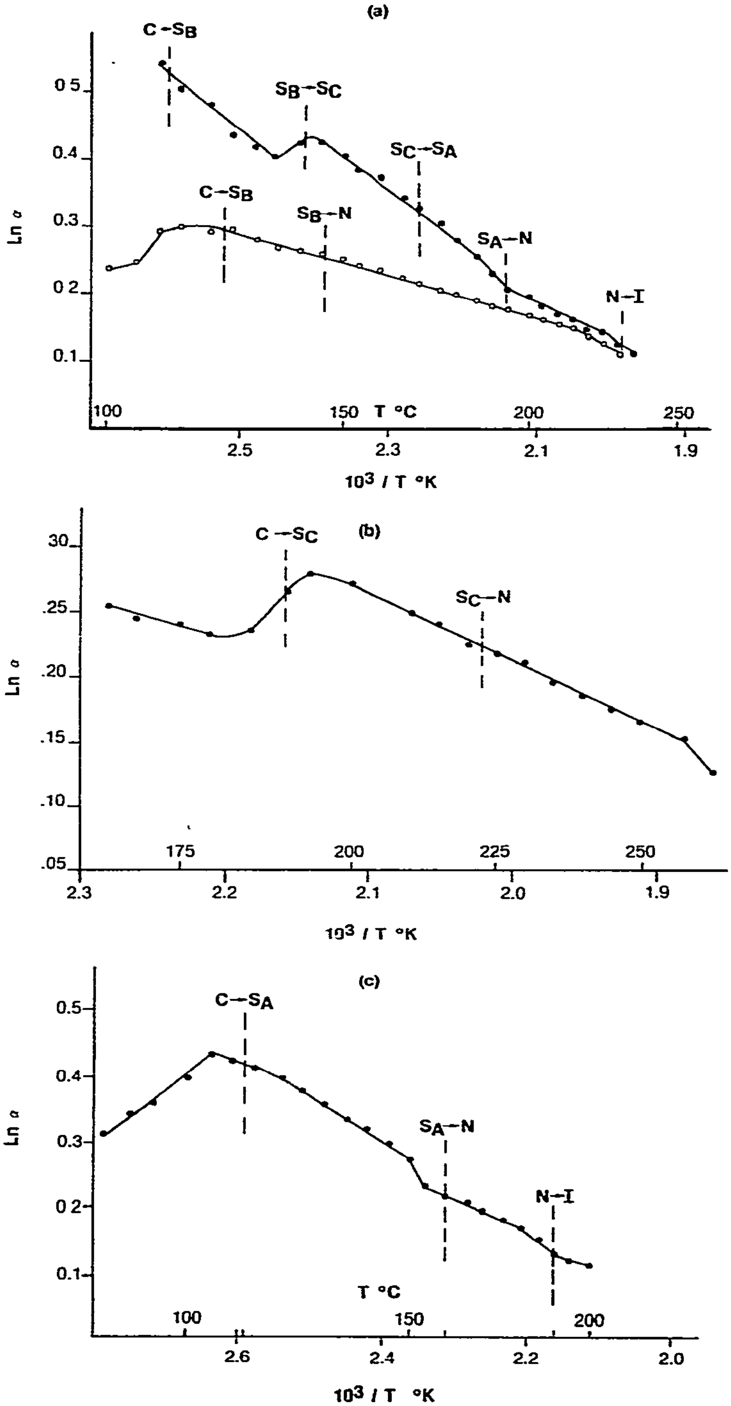


Fig. 2. Dependence of the separation factor (α) of anthracene-phenanthrene on column temperature. (a) TBBA (upper curve) and TBEA (lower curve) columns; (b) TBBOA column; (c) HBAF column.

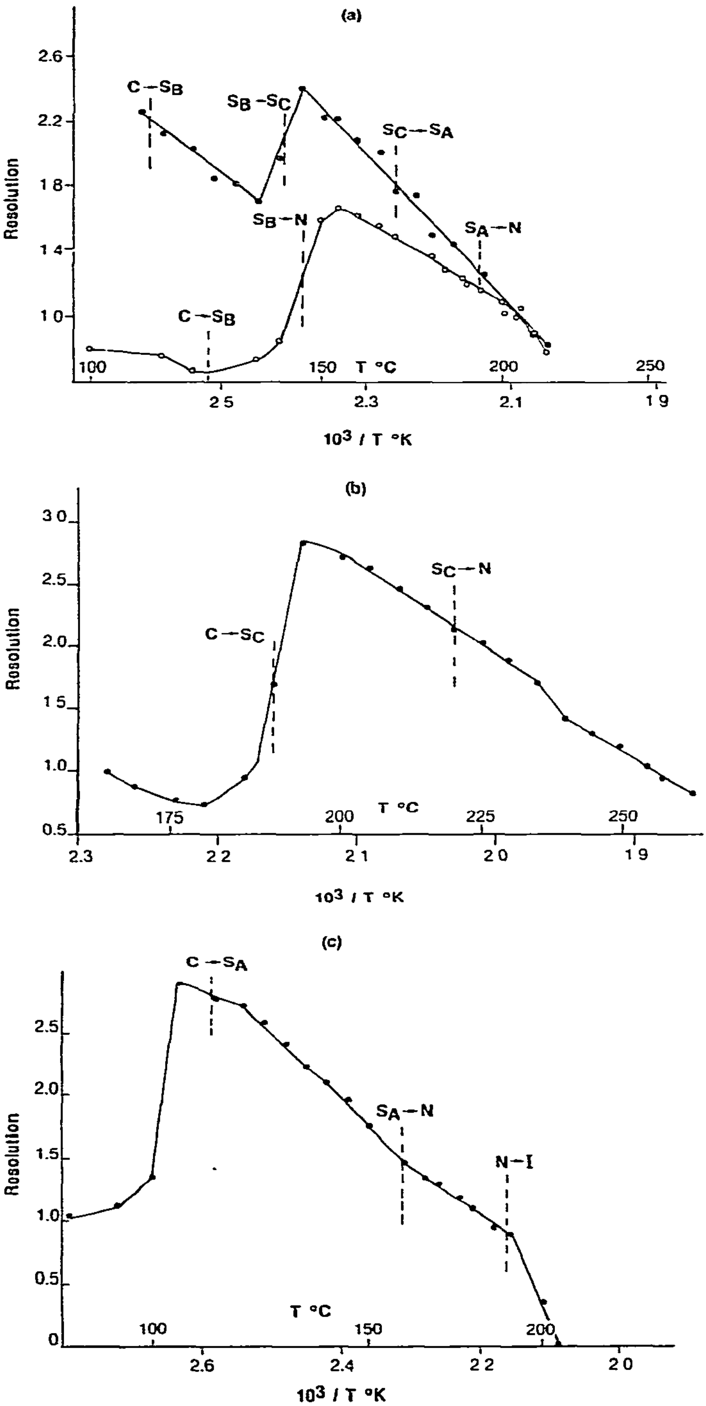


Fig. 3. Dependence of resolution of anthracene and phenanthrene on column temperature. (a) TBBA (upper curve) and TBEA (lower curve) columns; (b) TBBOA column; (c) HBAF column.

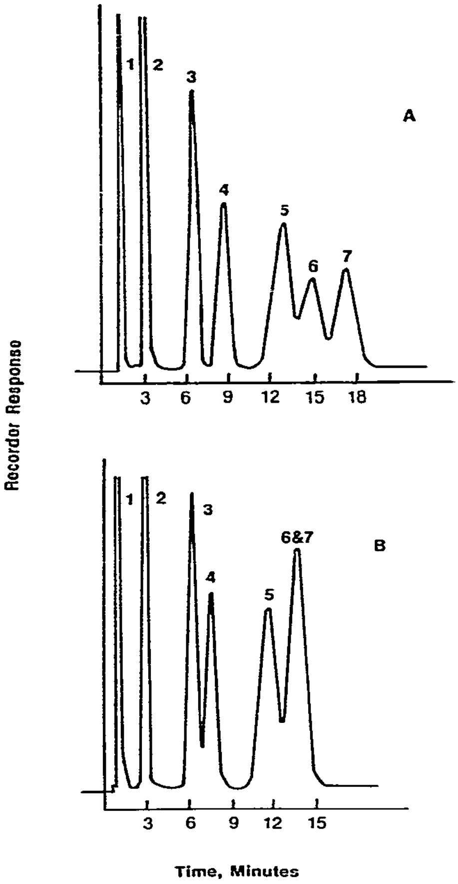


Fig. 4. Separation of three-ring PAHs on the TBBA (A) and TBEA (B) columns at 170°C. Peaks: 1 = solvent; 2 = fluorene; 3 = phenanthrene; 4 = anthracene; 5 = 1-methylphenanthrene; 6 = 9-methylanthracene; 7 = 2-methylanthracene.

TABLE III

RELATIVE RETENTION DATA OF FOUR POLYCHLORINATED BIPHENYLS ON DIFFERENT LIQUID CRYSTAL COLUMNS

TCB = tetrachlorobiphenyl.

Compound	*Relative retention*			
	TBBA at 190°C	*TBEA at 190°C*	*TBBOA at 200°C*	*HBAF at 130°C*
2,5,2′,5′-TCB	1.00	1.00	1.00	1.00
2,4,2′,4′-TCB	1.48	1.55	1.32	1.45
2,3,2′,3′-TCB	1.69	1.70	1.33	1.75
2,3,4,5-TCB	2.13	2.08	1.88	2.41

TABLE IV

RELATIVE RETENTION DATA OF SIX POLYAROMATIC HYDROCARBONS ON DIFFERENT LIQUID CRYSTAL COLUMNS

Compound	*Relative retention*			
	TBBA at 170°C	*TBEA at 170°C*	*TBBOA at 200°C*	*HBAF at 130°C*
Fluorene	1.00	1.00	1.00	1.00
Phenanthrene	2.79	2.92	2.41	1.72
Anthracene	3.83	3.71	3.14	2.49
1-Methylphenanthrene	5.87	6.05	4.50	4.28
9-Methylanthracene	6.85	7.43	5.10	5.22
2-Methylanthracene	8.05	7.43	5.74	5.88

As a result of the problems associated with the use of uncharacterized smectic mesophases in GC analyses in the past, it has been postulated that smectic mesophases offer greater resistance to solute penetration, resulting in inherently lower selectivity in GLC applications[4,17,24]. That this postulate is too sweeping is now indicated by our demonstration of the value of the smectic A and smectic C phases in such analyses, and their superiority over corresponding nematic modifications in certain cases. Moreover, the chromatographic superiority of the TBBA column over that of its ethyl homolog is inconsistent with the widely-held theory that in a homologous series, liquid crystals having the greater nematic temperature range and higher nematic–isotropic transition temperature will have higher chromatographic selectivity[4,25,26].

The enthalpies and entropies of transition (Table I) for the smectic A–nematic, smectic C–nematic and smectic C–smectic A transitions of the liquid crystals used in this study are considerably lower than corresponding values for the smectic B–smectic C, smectic B–nematic and crystal–smectic transitions. In the past, this type of thermodynamic data has been related to liquid crystal mesophase structure[27]. It now appears that such data can be related to GC properties as well. The lower thermodynamic values associated with transitions to smectic A, smectic C and nematic phases indicate a similarity in the structures of the liquid crystalline matrix for these modifications. The chromatographic data presented here indicate an analogous similarity in solution properties, allowing the smectic A and C modifications to be used as GLC phases with equal or greater selectivity than corresponding nematic mesophases.

A major problem still associated with liquid crystal GLC columns is their limited working temperature range, which results directly from the limited nematic temperature range of most liquid crystals. The GC value of the smectic A and C phases of liquid crystals demonstrated in this study indicates that lower column operating temperatures, and hence wider operating temperature ranges, may be achieved with no loss in selectivity through the careful selection and use of liquid crystals having these modifications.

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