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LIQUID CRYSTALS AS STATIONARY PHASES IN GAS–LIQUID CHROMATOGRAPHY

IV. THERMODYNAMIC MEASUREMENTS ON BENZENE–DIHEXYLOXYAZOXYBENZENE, BENZENE–DIHEPTYLOXYAZOXYBENZENE, CARBON TETRACHLORIDE–DIHEXYLOXYAZOXYBENZENE AND CARBON TETRACHLORIDE–DIHEPTYLOXYAZOXYBENZENE SYSTEMS

J. F. BOCQUET and C. POMMIER*

Centre Scientifique et Polytechnique, Laboratoire de Chimie Physique, E.R.A. C.N.R.S. 456, 93430 Villetaneuse (France)

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SUMMARY

Distribution isotherms, phase diagrams and solute thermodynamic functions are determined for the systems benzene–dihexyloxyazoxybenzene (DHAB) or diheptyloxyazoxybenzene (PHAB) and carbon tetrachloride–DHAB or –PHAB using gas–liquid chromatography at finite concentrations. The influence of the sorption effect on the elution peak profiles is established. The dissolution processes in the mesophases are discussed.

INTRODUCTION

We have previously reported[1] that gas chromatographic (GC) studies at finite solute concentrations can provide useful information on the thermodynamic behaviour of solutes dissolved in a mesomorphic solvent. In particular, the interpretation of the anomalous peak profiles observed by elution on the mesomorphic phases allowed us to determine the phase diagrams in the systems decane–dihexyloxyazoxybenzene (DHAB) and decane–diheptyloxyazoxybenzene (PHAB)[2]. In such systems the retention of the solute is governed only by an isotherm effect. In the present paper, we shall extend this method to the study of more volatile solutes for which the sorption effect in the chromatographic process cannot be neglected. Then the thermodynamic properties of solutes with various molecular shapes, decane, benzene and carbon tetrachloride, will be discussed.

The experimental procedures have been described in a previous paper[2]. The solutes are pure compounds for chromatography.

ELUTION PEAK PROFILES: INFLUENCE OF THE SORPTION EFFECT

When a large sample of solute (carbon tetrachloride, benzene) is eluted on the

mesomorphic phases of DHAB and PHAB the observed chromatographic peaks are of two types: the first is similar to those previously reported with decane as solute[2] and is observed on the smectic phase of PHAB; the second is obtained on the nematic phases of DHAB and PHAB.

Fig. 1 shows the elution peaks for various amounts of carbon tetrachloride injected on the nematic phase of DHAB. The following observations can be made:

all peaks show a sharp front profile and a diffuse rear profile, except for small amounts of injected solute;

for sufficiently large samples there is a shoulder on the rear profile for a given value of gas phase concentration, C^G, this value decreasing as the column temperature is raised;
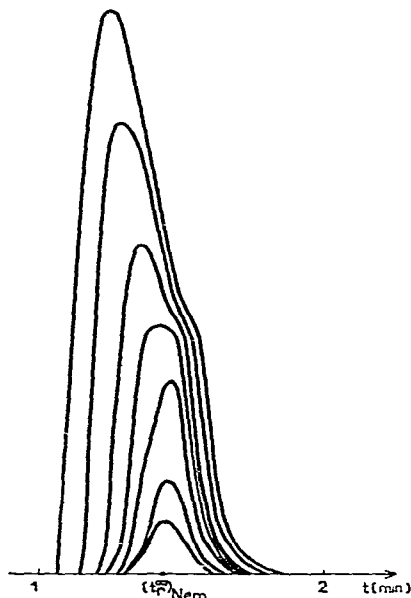
the diffuse rear fronts are not superposable.

Fig. 1. Elution peaks of CCl₄ on DHAB at 121.1°C. Volume of CCl₄ injected: 0.25; 0.5; 1; 2; 3; 5 and 7 μl.

When the column temperature is higher than the liquid crystal clarification temperature, T_c, the retention on the isotropic phase leads to peaks with diffuse rear profiles. So the behaviour of these solutes is quite different from those which have been reported with decane. However, the solute concentrations in the gas phase in these experiments are about ten times greater than those observed in the case of decane. Under these conditions, the sorption effect is probably important and can no longer be neglected.

A retention theory of gas chromatography at finite concentration has been proposed by several authors[3,4]. In classical systems, the experimental elution peak shape is the result of the competition between two major phenomena: the isotherm effect leading to a diffuse front profile in the case of an anti-Langmuir isotherm, and the sorption effect leading to a diffuse rear profile. As previously mentioned[2], the distribution isotherms for systems with liquid crystals as solvents are discontinuous:

for a given temperature below T_c, there is a gas phase concentration, C_t^G, in equilibrium with two liquid nematic and isotropic (or smectic) phases with concentrations C^N and C^I (or C^S). The competition between the isotherm and sorption effects is schematically shown in Fig. 2. For simplicity, we assume that there is no pressure gradient in the column and that the variations of the propagation rate of the solute due to the two effects are linear functions of the gas phase concentration, C^G (Fig. 2a, b). We shall consider four cases (a_1, a_2, a_3, b) corresponding to different relative importances of the sorption and isotherm effects in the two liquid phases on both sides of C_t^G.
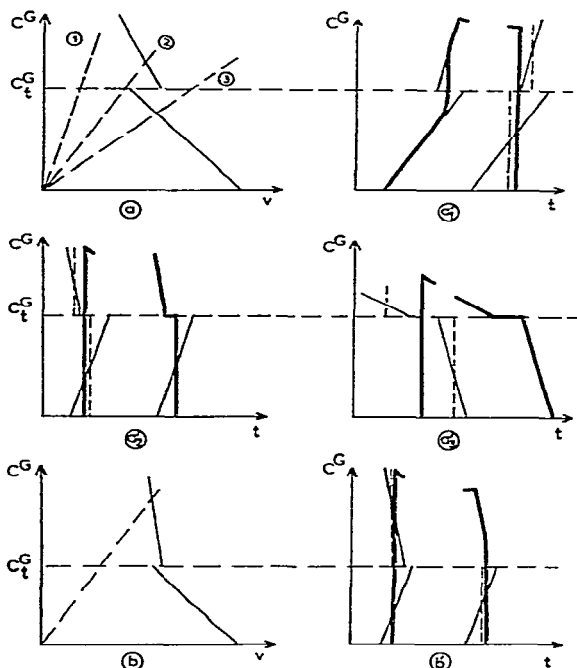

Fig. 2. Competition between sorption and isotherm effects. a, b: ———, Rate profile caused by isotherm effect; — — —, influence of the sorption effect. a₁′, a₂′, a₃′, b′, Resulting peak profiles.

In Fig. 2a₁ the isotherm effect for both the liquid phases is predominant. The front and rear profiles expected in this case are shown on Fig. 2a₁′ : a discontinuity appears on the front profile because a high concentration ($C^G > C_t^G$) cannot be eluted faster than a lower one. The rear profile is vertical because a high concentration ($C^G > C_t^G$) cannot be eluted slower than a lower one. This elution peak shape is similar to those observed with decane on DHAB and PHAB, and with benzene and carbon tetrachloride just below the smectic–nematic phase transition temperature of PHAB.

In Fig. 2a₂, the sorption effect is predominant only for $C^G > C_t^G$. The corresponding peak shape (Fig. 2a₂′) shows a sharp front profile and a shoulder on the rear profile at $C^G = C_t^G$. In Fig. 2a₃ the sorption effect is predominant for all C^G values. The peak shape is similar to the previous one except that for $C^G < C_t^G$ the rear profile

is diffuse. Other peak shapes can be generated according to the relative importance of the isotherm effects: for example, in Fig. 2b' the shoulder disappears, and there is only a single point on the rear profile.

The experimental peaks obtained when carbon tetrachloride and benzene are eluted on nematic phases of DHAB and PHAB (Fig. 1) can be compared with the profile in Fig. 2a$_2'$. For these systems, it will be possible to determine the distribution isotherms if one takes account of the sorption effect.

RESULTS

As shown in Fig. 1, the chromatographic peak profiles are not superposable for increasing amounts of injected solute. This can be explained by the influence of the finite injection time, the pressure increase at the column head caused by the injection and the diffusion phenomena in the gas phase. In order to correct for these effects, we have drawn the "right" rear profiles using the infinite dilution retention time and retention times of the finite concentration peak maxima. This procedure has been proposed by other authors[5] and we verified its results by step-and-pulse chromatographic measurements.

The retention time of a solute of mole fraction X in the gas phase has been related to the capacity ratio by the following expression which takes account of the sorption effect[4]

$$t_X = \frac{L[1 + K'(1 - X)]}{u} \bigg/ \exp \int_0^X \frac{K'\mathrm{d}X}{1 + K'(1 - X)} \tag{1}$$

where L is the column length and u is the carrier gas flow velocity. It is assumed that there is no pressure gradient in the column. We have used eqn. 1 with a mean value, $\bar{K}'$, of the capacity ratio and:

$$u = J_3^2 u_0 \tag{2}$$

In order to solve eqn. 1, we first calculate an approximate value of $\bar{K}'$ by

$$t_X = t_m[1 + \bar{K}'(1 - X)] \tag{3}$$

where t_m is the retention time of a non-retained solute. Use of the function $\bar{K}' = f(X)$ allows the determination of the exponential term in eqn. 1. A new $\bar{K}'$ value is then obtained from this equation and the calculation is repeated until values of $\bar{K}'$ constant within 0.5 % are obtained. The solute concentration in the liquid phase has been determined by integrating the function $\bar{K}' = f(X)$ and the distribution isotherms are drawn as $C^L = f(C^G)$ where C^G and C^L are expressed in grams of solute per cm^3 of gas phase and grams of solute per gram of liquid phase respectively.

Figs. 3 and 4 show typical isotherms on DHAB and PHAB: they are of the anti-Langmuir type and some are discontinuous. The limits of these discontinuities allow us to determine the phase diagrams of the studied systems. They are given in Figs. 5 and 6. For the system carbon tetrachloride–DHAB (Fig. 5a) the results are those obtained by Martire et al.[6] with a vacuum microbalance system. The agreement is quite good and this is a new confirmation of the validity of the chromatographic method proposed here.
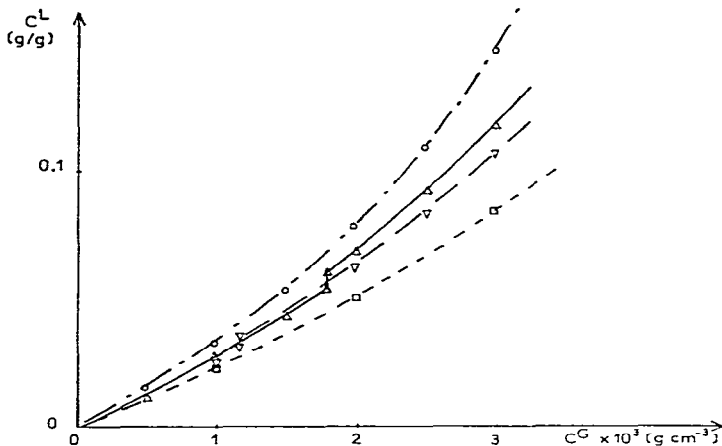
Fig. 3. Distribution isotherms for the system CCl_4–DHAB at 100°C ($\bigcirc$), 116°C ($\triangle$), 121.1°C ($\triangledown$) and 132.2°C ($\square$).
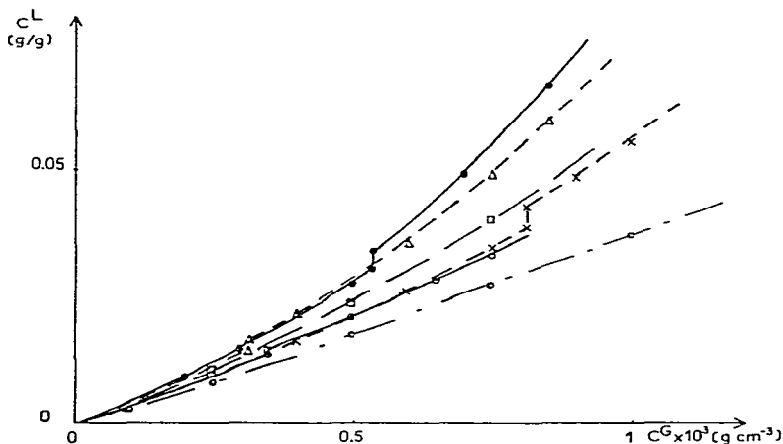

Fig. 4. Distribution isotherms for the system C_6H_6–PHAB at 82.7°C ($\bullet$), 87.7°C ($\triangle$), 97.9°C ($\square$), 109.9°C ($\times$), 118.3°C ($\bigcirc$) and 130.7°C ($\bullet$).

From the distribution isotherms, also determined are the solute activity coefficients, γ_2, using classical thermodynamic relations (eqn. 3 in ref. 2). The variations of these coefficients are shown in Figs. 7–10 and Table I gives selected values of the excess thermodynamic functions. These results demonstrate the pretransitional effects in DHAB and PHAB below the nematic–isotropic phase transition.

DISCUSSION

These results and those previously reported[2] allow a comparison of the solution behaviour of solutes with different molecular shapes, decane, benzene and carbon tetrachloride.
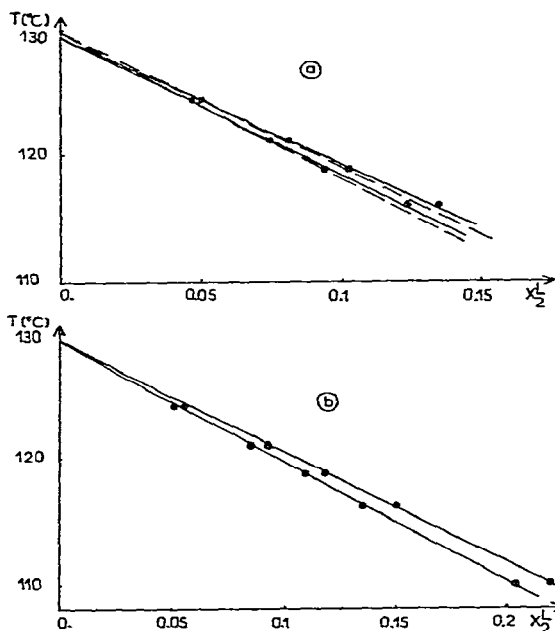
Fig. 5. Phase diagrams: a, CCl₄–DHAB; – – –, data from ref. 5; b, C₆H₆–DHAB.
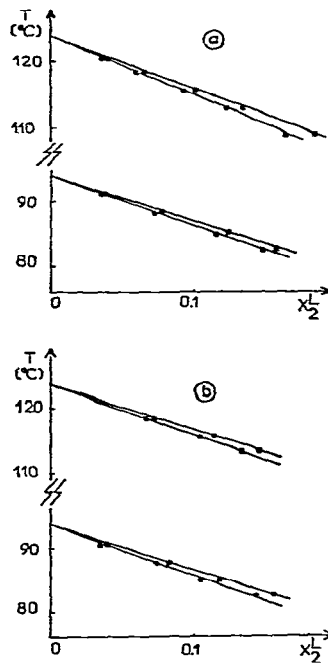
Fig. 6. Phase diagrams: a, CCl₄–PHAB; b, C₆H₆–PHAB.

Fig. 7. Activity coefficient of CCl₄ in DHAB for selected concentrations: 1, infinite dilution; 2, $C_2^{\ell} = 2.5 \cdot 10^{-2}$ g/g; 3, $C_2^{\ell} = 5 \cdot 10^{-2}$ g/g.

Phase diagrams

In all cases, the equilibrium curves can be approximated as straight lines. The absolute values of the slopes dT^*/dX_2 are reported in Table II ($T^* = T/T_c$, the reduced

Fig. 8. Activity coefficients of C_6H_6 in DHAB for selected concentrations: 1, infinite dilution; 2, $C_2^L = 1 \cdot 10^{-2}$ g/g; 3, $C_2^L = 2.5 \cdot 10^{-2}$ g/g; 4, $C_2^L = 5 \cdot 10^{-2}$ g/g.
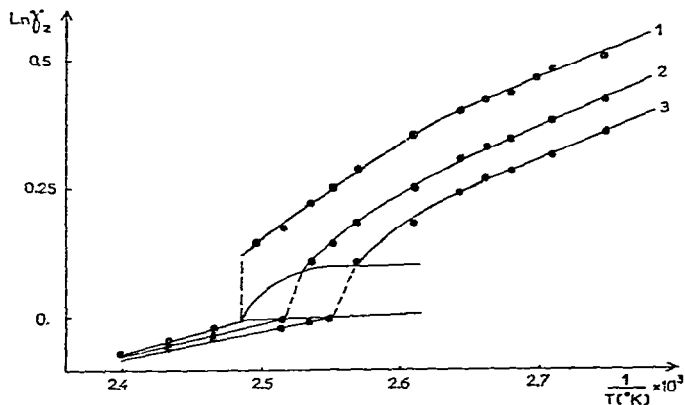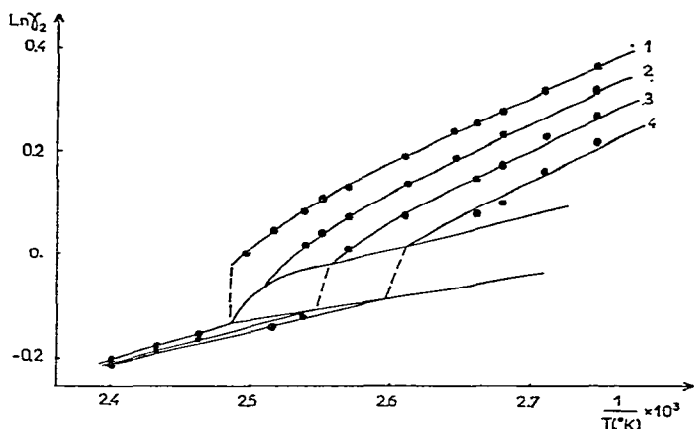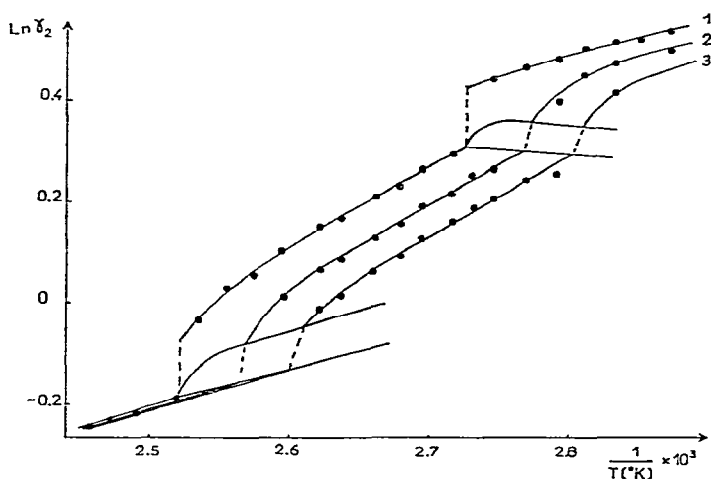

Fig. 9. Activity coefficients of CCl_4 in PHAB for selected concentrations: 1, infinite dilution; 2, $C_2^L = 3 \cdot 10^{-2}$ g/g; 3, $C_2^L = 6 \cdot 10^{-2}$ g/g.

temperature) and compared to the limiting slopes obtained from the classical thermo-dynamic relations[6]:

$$\beta_N = \left[\frac{dT^*}{dX_2^N} \right]^\infty = \frac{R}{\Delta S_t} \left[\frac{[\gamma_2^N]^\infty}{[\gamma_2^I]^\infty} - 1 \right] \tag{4}$$

$$\beta_I = \left[\frac{dT^*}{dX_2^I} \right]^\infty = \frac{R}{\Delta S_t} \left[1 - \frac{[\gamma_2^I]^\infty}{[\gamma_2^N]^\infty} \right] \tag{5}$$

Fig. 10. Activity coefficients of C_6H_6 in PHAB for selected concentrations: 1, infinite dilution; 2, $C_2^L = 1 \cdot 10^{-2}$ g/g; 3, $C_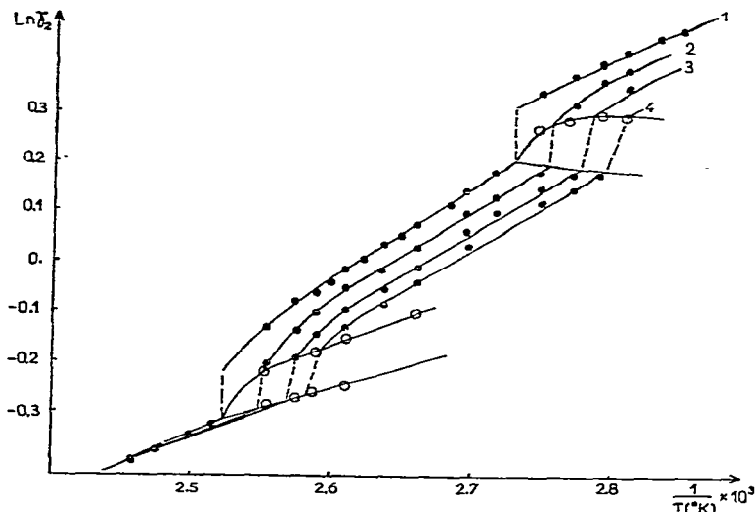2^L = 2 \cdot 10^{-2}$ g/g; 4, $C_2^L = 3 \cdot 10^{-2}$ g/g; ○, activity coefficients at the limits of the two-phase domain.

TABLE I

EXCESS THERMODYNAMIC FUNCTIONS OF CARBON TETRACHLORIDE AND BENZENE IN DHAB AND PHAB

$\bar{H}_2^e$ are in kcal mole^{-1}; $\bar{S}_2^e$ are in cal mole^{-1} °K^{-1}.

System	X_2^L	$(\bar{H}_2^e)^S$	$(\bar{S}_2^e)^S$	$(\bar{H}_2^e)^N$	$(\bar{S}_2^e)^N$	$(\bar{H}_2^e)^I$	$(\bar{S}_2^e)^I$
CCl₄-DHAB	Infinite dilution	—	—	2.38 ±0.07	5.51 ±0.19	1.58 ±0.05	3.94 ±0.13
	0.061	—	—	2.33 ±0.1	5.56 ±0.27	1.25 ±0.06	3.15 ±0.15
	0.115	—	—	2.14 ±0.1	5.17 ±0.27	1.03 ±0.06	2.63 ±0.15
C₆H₆-DHAB	Infinite dilution	—	—	2.49 ±0.08	6.11 ±0.21	1.59 ±0.06	4.21 ±0.15
	0.113	—	—	2.60 ±0.12	6.6 ±0.32	1.37 ±0.06	3.70 ±0.15
	0.203	—	—	2.6 ±0.15	6.72 ±0.4	1.30 ±0.07	3.55 ±0.17
C₆H₆-PHAB	Infinite dilution	2.13 ±0.05	5.14 ±0.14	3.47 ±0.06	9.1 ±0.15	2.51 ±0.05	6.96 ±0.13
	0.052	—	—	3.3 ±0.1	8.73 ±0.27	2.3 ±0.06	6.46 ±0.15
	0.098	—	—	3.30 ±0.12	8.8 ±0.33	2.18 ±0.06	6.17 ±0.15
CCl₄-PHAB	Infinite dilution	1.44 ±0.05	3.06 ±0.14	3.04 ±0.06	7.68 ±0.16	1.73 ±0.04	4.73 ±0.1
	0.077	—	—	3.18 ±0.10	8.20 ±0.26	1.7 ±0.04	4.66 ±0.1
	0.142	—	—	2.97 ±0.10	7.76 ±0.27	1.6 ±0.04	4.42 ±0.1

TABLE II

SLOPES OF THE EQUILIBRIUM LINES IN THE PHASE DIAGRAMS

β_S, β_N and β_I are defined as in eqns. 4 and 5.

System	Smectic–nematic				Nematic–isotropic			
	$\left[\dfrac{dT^*}{dX_2}\right]_S$	$\left[\dfrac{dT^*}{dX_2}\right]_N$	β_S	β_N	$\left[\dfrac{dT^*}{dX_2}\right]_N$	$\left[\dfrac{dT^*}{dX_2}\right]_I$	β_N	β_I
DHAB–C$_{10}$H$_{22}$*	—	—	—	—	0.315 ±0.003	0.261 ±0.006	0.30 ±0.04	0.26 ±0.03
DHAB–CCl$_4$	—	—	—	—	0.265 ±0.004	0.241 ±0.005	0.27 ±0.03	0.23 ±0.03
DHAB–C$_6$H$_6$	—	—	—	—	0.235 ±0.002	0.217 ±0.001	0.23 ±0.03	0.20 ±0.02
PHAB–C$_{10}$H$_{22}$*	0.305 ±0.005	0.269 ±0.004	0.23 ±0.03	0.20 ±0.03	0.226 ±0.003	0.210 ±0.002	0.22 ±0.03	0.20 ±0.02
PHAB–CCl$_4$	0.204 ±0.002	0.191 ±0.002	0.18 ±0.02	0.16 ±0.02	0.232 ±0.003	0.208 ±0.002	0.22 ±0.03	0.19 ±0.02
PHAB–C$_6$H$_6$	0.213 ±0.008	0.194 ±0.006	0.19 ±0.02	0.17 ±0.02	0.196 ±0.003	0.179 ±0.002	0.19 ±0.02	0.17 ±0.02

* From ref. 2.

Similar expressions for β_S and β_N can be written for the smectic–nematic transition. In these equations we used the transition entropies experimentally determined by calorimetry: $\Delta S_{N-I} = 1.06$ and 1.18 cal mole^{-1} °K^{-1} for DHAB and PHAB respectively; $\Delta S_{S-N} = 1.39$ cal mole^{-1} °K^{-1} for PHAB. The agreement between dT^*/dX_2 and β values is better for the nematic–isotropic phase transition. However, it is clear that small uncertainties (2%) in γ_2^∞ lead to large errors (near 15%) in the calculation of β from eqns. 4 and 5. Moreover, a precise measurement of ΔS_t is difficult because of the pretransition effect, if any.

When comparing dT^*/dX_2 values obtained with the three solutes, it is seen that decane is the most effective in destroying the order of the mesomorphic phases. However, if we express this ability in terms of the hard core volume fraction, dT^*/dV_2 increases in the order decane < benzene < carbon tetrachloride. For example, [dT^*/dV_2]$_N$ values are 0.7, 1.17 and 1.24 in the case of DHAB as solvent for decane, benzene and carbon tetrachloride respectively. Carbon tetrachloride, with a globular shape, is more effective than benzene in disrupting the order of the solution. For a given solute, [dT^*/dV_2]$_N$ decreases from DHAB to PHAB. This diminution is greater for decane than for the other solutes. This may be due to the fact that molecules of decane interact preferentially with aliphatic chains of the solvent, which are longer for PHAB than for DHAB. The ability to disrupt the order of the smectic mesophases (in terms of dT^*/dV_2) is less for decane than for the other solutes. However, it must be noted that, in the case of smectic phases, two types of dissolution sites are possible: inside or between the layers of solvent molecules.

Excess functions

In Table I we have given the $\bar{H}_2^c$ and $\bar{S}_2^c$ values, at infinite dilution and for various solute concentrations. They are all positive. Moreover, except in the isotropic

phase of PHAB and DHAB, γ_2 is always greater than unity. The dissolution of the solute is not favoured in these phases. From the relation

$$RT \ln \gamma_2 = \bar{H}_2^c - T\bar{S}_2^c \tag{6}$$

at constant temperature, an increase in γ_2 is the result of either an $\bar{H}_2^c$ increase (dominant enthalpic effect) or a $\bar{S}_2^c$ decrease (dominant entropic effect) or the combination of these two effects.

The transition from the isotropic phase into the nematic solution is governed by an enthalpic effect. In the nematic structure it can be considered that there are no preferential dissolution sites for the solute. So the positive excess molar entropy of the solute is due to the variation of its rotational and vibrational entropy; the order of the solvent favours some of these corresponding movements (*i.e.*, molecular rotations and vibrations), $(\bar{S}_2^c)^N > (\bar{S}_2^c)^I$. The $\bar{H}_2^c$ values are more positive in the nematic phase than in the isotropic one, that is the solute–solvent interactions are weaker in the ordered solution. These interactions are even less important in PHAB than in DHAB.

For the nematic–smectic transition, we observe a decrease in $\bar{H}_2^c$ and $\bar{S}_2^c$ and an increase in γ_2: the entropic effect is dominant. As smectic phases have been found less effective for gas–liquid chromatographic (GLC) separations than nematic ones[7], it is possible that the solute molecules are dissolved preferentially between the solvent layers. Moreover, the excess enthalpy and entropy are rather similar in smectic and isotropic phases. Then $\bar{S}_2^c$ contains contributions from both internal and configurational terms.

When comparing the behaviour of the three solutes, γ_2 for decane is larger in all phases (isotropic, nematic, smectic). Dissolution enthalpies (from the gas phase) are negative and more negative for decane. This means that this solute has more attractive interactions with the solvent molecules, essentially with the aliphatic chains.

An increase in the solute concentration causes a decrease of all the excess functions and it can be seen that the influence of X_2 is more important in the nematic phase than in the isotropic one. When increasing X_2, solute–solvent interactions are replaced by solute–solute interactions ($\bar{H}_2^c$ decreases) and the relative importance of the entropic term in γ_2 increases.

CONCLUSION

The above results show that the chromatographic method previously proposed[2] for studying thermodynamic properties of a solute dissolved in a mesomorphic phase and the phase diagram of the system can be extended to more volatile solutes for which sorption effects are no longer negligible.

Comparison of the excess functions of various solutes in the smectic, nematic and isotropic phases of liquid crystals allows a discussion of the dissolution processes. The conclusions which may be made are similar to those drawn by Martire and co-workers[3-10] from GLC experiments at infinite dilution in various mesomorphic solvents. Our $\bar{H}_2^c$ and $\bar{S}_2^c$ values are in good accordance with those given by these authors when available[11]. However, in every case, we observed a pretransition phenomenon in a temperature range (about 15°C) below the nematic–isotropic transition

point. This behaviour, previously mentioned by Kelker and Verhelst[12], has been clearly established, by measuring the specific retention volumes at many temperatures in this range.

On the other hand, the solute activity coefficient is related to molecular interactions which depend on the structural order of the mesophase[13]. So the γ_2 values can be correlated with the order of the solution. Such an approach has been proposed by Chow and Martire[14] in the case of infinite dilution. Our measurements will permit the determination of order in solution at finite concentration[15].

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