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Order Parameter in Nematic Solutions From GLC Measurements

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The order parameter of nematic solutions of $C_{10}H_{22}$, CCl_4, C_6H_6 in dihexyloxyazoxybenzene (DHAB) and diheptyloxyazoxybenzene (PHAB) have been determined from solute excess functions obtained by GLC. S values for various systems at various solute concentrations are compared and results are discussed in connection with those provided by conventional methods.

INTRODUCTION

Gas-liquid chromatography is a powerful analytical technique which has often been used for thermodynamical studies of solutions.[1] These studies are generally performed at infinite dilution of the solute in the stationary phase. GLC has been also extended at finite solute concentration in the scope of preparative applications and retention theory in these conditions has been proposed by several authors.[2] This theory supposes that there is no change in the solvent structure during the elution of the injected sample.

However, if the stationary phase is a partially ordered liquid crystal, the solute molecules may induce a modification of the mesophase order. So, if a given solute concentration (attainable by GLC technique) can completely disrupt the order of the mesophase and if the transition is first order, gas chromatographic experiments must allow the determination of a part of the solute-solvent phase diagram. Such diagrams, showing a two phase domain, have been recently obtained with $C_{10}H_{22}$, C_6H_6, CCl_4 as solutes and dihexyloxyazoxybenzene (DHAB) and diheptyloxyazoxybenzene (PHAB) as solvents.[3,4] For this last solvent, the smectic-nematic transition as well as the nematic-isotropic has been studied.

If we consider the two phase domain where the nematic and isotropic phases are in equilibrium, the orientational order parameter (defined as $S = \frac{1}{2}<3\cos^2\theta - 1>$) is zero for the isotropic phase and remains constant for the nematic phase for all solute concentrations at a given temperature, as shown by NMR measurements.[5]

In this paper, we used GLC results to determine the evolution of the orientational order parameter with temperature and solute concentration in the domain where the nematic solution exists alone. For that, we have extended to finite solute concentration the solution model proposed by MARTIRE at infinite dilution:[6] in this model the order parameter is determined from the thermodynamic functions of the solute, i.e. activity coefficient and partial molar enthalpy, all quantities attainable by GLC.

In a first part we shall develop the solution model and in a second one the results will be exposed and compared with values obtained by other experimental techniques such as NMR and ESR.

SOLUTION MODEL

We shall consider that a nematic solution with a solute molar fraction X_2^N, characterized by an orientational order parameter S is equivalent to a two phase system: one of these two phases is a perfectly ordered nematic phase A ($S = 1$) for which the solute molar fraction is X_2^A; the other one is an isotropic liquid I ($S = 0$) for which the solute molar fraction is X_2^I.

For a mixture of one mole of solute and N moles of solvent in the nematic state, we define NY^A and Z^A as the solvent and solute mole numbers respectively in the phase A. So, X_2^A and X_2^I can be expressed as:

$$X_2^A = \frac{Z^A}{NY^A + Z^A} \tag{1}$$

$$X_2^I = \frac{1 - Z^A}{N(1 - Y^A) + (1 - Z^A)} \tag{2}$$

The studied solutes are of different shapes and it is impossible to define an order coefficient for them.

So, we shall only write the order coefficient of the solvent in the solution according to the expression:

$$S = Y^A[\tfrac{1}{2}<3\cos^2\theta - 1>]^A + (1 - Y^A)[\tfrac{1}{2}<3\cos^2\theta - 1>]^I \tag{3}$$

$[\frac{1}{2}<3\cos^2\theta - 1>]^A$ is equal to 1, where as $[\frac{1}{2}<3\cos^2\theta - 1>]^I$ is zero. Then

$$S = Y^A \tag{4}$$

The order parameter of the solution is equal to the proportion of solvent molecules in the anisotropic phase A. The role of the solute is to disturb the solvent molecular order, and to act as a probe for the determination of the order of the solution.

Because the equivalence of the real nematic solution and the mixture of the two phases A and I in equilibrium, the solute chemical potential is the same in the 3 phases:

$$\mu_2^N = \mu_2^A = \mu_2^I \tag{5}$$

In the expression of the total enthalpy of the solution (mixture of the two phases A and I) the contribution of the solute is

$$(h)_{X_2^N} = Z^A(\bar{H}_2^A)_{X_2^A} + (1 - Z^A)(\bar{H}_2^I)_{X_2^I} \tag{6}$$

In this relation $(h)_{X_2^N}$ is a function of the temperature since the degree of order of the solution (and consequently X_2^A and X_2^I) varies with T.

The activity coefficient γ_2^N is related to the thermodynamic excess functions by

$$\text{Ln } \gamma_2^N = \frac{\bar{H}_2^N}{RT} - \frac{(\bar{S}_2^e)^N}{R} \tag{7}$$

Its evolution with temperature is given by the Gibbs-Helmholtz relation:

$$\left[\frac{\partial R \text{ Ln } \gamma_2^N}{\partial \dfrac{1}{T}}\right]_{X_2^N} = [\bar{H}_2^N]_{X_2^N} \tag{8}$$

The experiments show that in a range of about ten degrees below the transition temperature $(\partial R \text{ Ln } \gamma_2^N)/\partial(1/T)$ is not constant.

Out of this range, called pretransition domain, $\bar{H}_2^N$ is temperature independant, so that we cannot identify $(h)_{X_2^N}$ and $(\bar{H}_2^N)_{X_2^N}$.

Then, we shall consider that the relation between these two quantities is of the simple form:

$$(h)_{X_2^N} = (\bar{H}_2^N)_{X_2^N} + cT \tag{9}$$

This is the first hypothesis of the model. It will be verified comparing the results with those of the literature.

In the isotropic domain, the thermodynamic quantities $(\bar{H}_2^I)_{X_2^I}$ and $(\gamma_2^I)_{X_2^I}$ can be determined experimentally. We have shown[3,4] that $(\bar{H}_2^I)_{X_2^I}$ is temperature independant and that its variation with X_2^I can be expressed as

$$(\bar{H}_2^I)_{X_2^I} = (\bar{H}_2^I)_{X_2^I \to 0} + aX_2^I \tag{10}$$

The evolution of (γ_2^I) with X_2^I has been found linear:

$$(\gamma_2^I)_{T,X_2^I} = (\gamma_2^I)_{T,X_2^I \to 0} + d_T X_2^I \tag{11}$$

We shall consider that these properties will be preserved in the hypothetical isotropic phase I of the model. Furthermore, we shall assume that the thermodynamical functions of the solute in the anisotropic phase A have a similar behavior:

$$(\bar{H}_2^A)_{X_2^A} = (\bar{H}_2^A)_{X_2^A \to 0} + b X_2^A \tag{12}$$

$$(\gamma_2^A)_{T,X_2^A} = (\gamma_2^A)_{T,X_2^A \to 0} + e_T X_2^A \tag{13}$$

Thus, for three different temperatures $j = 1, 2, 3$ and a given solute molar fraction X_2^N, the following equations may be written:

$$(\gamma_2^N)_{j,X_2^N} \cdot X_2^N = (\gamma_2^I)_{j,(X_2^I)_j} \cdot \left(\frac{(1 - Z^A)}{N(1 - Y^A) + (1 - Z^A)} \right)_j$$

$$= (\gamma_2^A)_{j,(X_2^A)_j} \cdot \left(\frac{Z^A}{NY^A + Z^A} \right)_j \qquad j = 1, 2, 3 \tag{14}$$

$$\bar{H}_2^N + cT_j = (\bar{H}_2^A)_{(X_2^A)_j} (Z^A)_j + (\bar{H}_2^I)_{(X_2^I)_j} (1 - Z^A)_j \qquad j = 1, 2, 3 \tag{15}$$

$$\text{Ln} \frac{(\gamma_2^A)_{j,(X_2^A)_i}}{(\gamma_2^A)_{i,(X_2^A)_i}} = \frac{(\bar{H}_2^A)_{(X_2^A)_i}}{R} \left[\frac{1}{T_j} - \frac{1}{T_i} \right] \qquad \begin{matrix} j = 1, 2, 3 \\ i = 1, 2, 3 \\ i \neq j \end{matrix} \tag{16}$$

Equation (16) expresses the GIBBS-HELMHOLTZ law and can be written for three solute molar fractions and two temperatures j (6 equations).

The 15 equations (14–16) contain 15 unknowns which are: $(Z^A)_j$, $(Y^A)_j$, c, $(\bar{H}_2^A)_{X_2^A \to 0}$, b, $(\gamma_2^A)_{j,X_2^A \to 0}$, e_j. $(\bar{H}_2^A)_{(X_2^A)_j}$ may be calculated from Eq. (12) and $(\gamma_2^A)_{j,(X_2^A)_i}$ from Eq. (13).

This system has been solved in a temperature range where $(\partial R \text{ Ln } \gamma_2^N)/\partial(1/T)$ is constant. Inside the pretransition temperature range, the evolution of $(\gamma_2^A)_{X_2^A}$ will be assumed to be the same as out of this pretransition domain.

RESULTS

The evolution of the order parameter S versus the reduced temperature T^* ($T^* = T/T_{tr}$) for the studied systems is shown on Figure 1. The precision with which $\bar{H}_2^I$ and $\bar{H}_2^N$ are measured determine the error on the calculated S value. For solute infinite dilution, the errors made on these parameters are about 2%; this leads to an inaccuracy of about 5% on S. At finite concentration, the error on S can reach 9%.

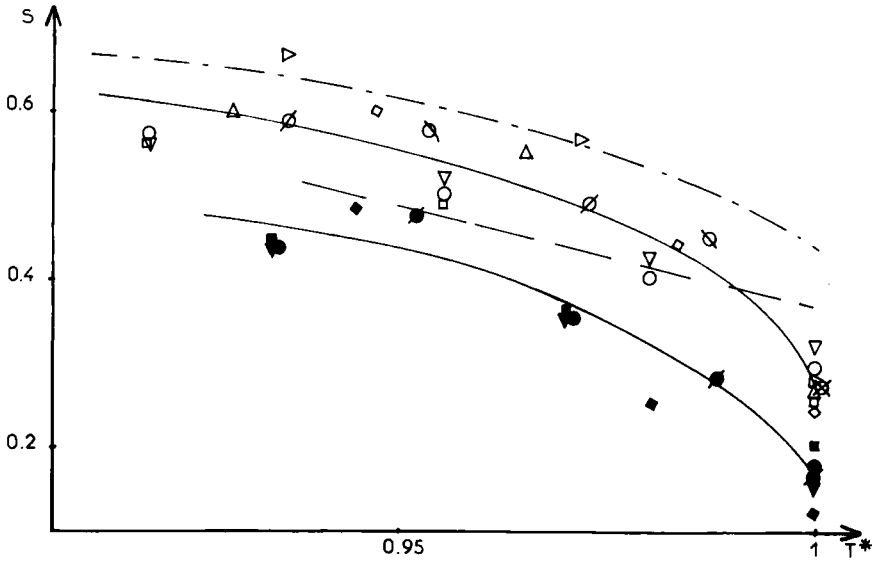

FIGURE 1 Evolution of the order coefficient S with reduced temperature T^*: DHAB—$C_{10}H_{22}$: (▽) infinite dilution, (△) $X_2^L = 2.710^{-2}$, (▷) $X_2^L = 5.310^{-2}$; DHAB—CCl_4: (○) infinite dilution, (⌀) $X_2^L = 6.110^{-2}$, (◇) $X_2^L = 0.1147$; DHAB—C_6H_6: (□) infinite dilution, (◇) $X_2^L = 0.1131$; PHAB—$C_{10}H_{22}$: (▼) infinite dilution; PHAB—CCl_4: (●) infinite dilution, (●) $X_2^L = 7.710^{-2}$; PHAB—C_6H_6: (■) infinite dilution, (◆) $X_2^L = 5.210^{-2}$. (-·-·-) Maier-Saupe; (---) Martire.[6]

In these conditions it can be noticed that on Figure 1, all points relative to the same solvent (for various solute nature and concentration) lie on a single curve. However the PHAB curve is below the DHAB one. On the same figure we have reported for comparison, the evolution of S deduced from the Maier and Saupe theory[7] and the results of Martire *et al.*[6] concerning DHAB using the same solution model but at infinite dilution of solute. These last results do not show pretransition phenomenon and the evolution of S is quasi-linear up to $T^* = 1$. This seems to be the consequence of the fact that these authors consider a linear variation of Ln γ_2^N versus $1/T$ in all the nematic range.[8]

In Table I, we have reported the values of the molar partial enthalpy and activity coefficient at infinite dilution for the real nematic and isotropic phases and for the anisotropic phase A. γ_2^A is greater than γ_2^N; $\bar{H}_2^A$ is lower than $\bar{H}_2^N$. This means that $\bar{S}_2^e$ is much lower in the phase A than in the nematic phase. So the dissolution of a solute in a perfectly ordered phase is essentially governed by the entropic term as previously mentioned by Martire.[6]

In Table II, we reported and compared our S values with those obtained by other authors using more "conventional" techniques. For DHAB the accordance is quite good in the studied temperature range. For PHAB, we observe a similar evolution but with lower values of S.

TABLE I

Order coefficients in DHAB and PHAB nematic phases; (a) Luckhurst;[12] (b) De Jeu.[13]

DHAB	Our results	(a)	(b)
$T^* = 1$	0.3	0.3	0.38
$T^* = 0.95$	0.54	0.5	0.56

PHAB	Our results	(a)	(b)
$T^* = 1$	0.17	0.24	0.36
$T^* = 0.95$	0.44	0.53	0.54

Using a statistical model, Dowell and Martire[9] have shown that the degree of order is a function of the following parameters:

—interaction energies between the "segments" of the molecule,
—length and flexibility of the terminal chains,
—length to breadth ratio.

When comparing DHAB and PHAB, dimensions and flexibilities are of the same order. On the other hand, interaction energies are rather similar since the nematic-isotropic transition enthalpies are very closed.[4,10] We should expect that, at a given reduced temperature, the order parameter be the same for these two compounds. However, our results show a significant difference. We cannot actually conclude on the origin of this difference: nature of the experimental technique and subsequent model, structure of the nematic phase of

TABLE II

Comparison of thermodynamic parameters of the solutes at infinite dilution in real nematic phase, and in isotropic and anisotropic phases model. (Partial enthalpies are in kcal.mole^{-1}).

	$(\bar{H}_2^N)^\infty$	$(\gamma_2^N)^\infty_{Tc}$	$(\bar{H}_2^I)^\infty$	$(\gamma_2^I)^\infty_{Tc}$	$(\bar{H}_2^A)^\infty$	$(\gamma_2^A)^\infty_{Tc}$
DHAB $C_{10}H_{22}$	3.1	2.93	2.5	2.52	3.0	4.27
DHAB CCl_4	2.4	1.13	1.5	0.99	2.1	1.73
DHAB C_6H_6	2.5	0.98	1.6	0.88	2.1	1.43
PHAB $C_{10}H_{22}$	4.4	2.22	3.0	1.98	3.8	4.19
PHAB CCl_4	3.0	0.93	1.7	0.83	2.6	1.84
PHAB C_6H_6	3.5	0.81	2.5	0.73	3.0	1.29

PHAB. Effectively, PHAB exhibits at lower temperature a smectic phase and a pseudo-strata structure has been proposed in the nematic state from X-ray measurements.[11] For such a structure in which two types of dissolution sites are possible the application of our model using activity coefficients (parameters taking account of solute solvent interactions) may be questionable. To conclude on this point it will be necessary to apply the method proposed here for the determination of order parameter in nematic solutions to a larger number of liquid crystals, some of them exhibiting, as PHAB, a smectic structure.

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