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Thermodynamics of Solutions with Liquid Crystal Solvents. IV. GLC Determination of the Degree of Order in a Nematic Mesophase†

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Abstract—Owing to thermal motion, molecular orientation is never entirely complete in a nematic mesophase. The commonly used methods of obtaining a measure of the extent of parallelism in this mesophase are ESR and NMR. Proposed here is a gas–liquid chromatography (GLC) approach for determining the degree of order, S.

Our working model regards the nematic phase as composed of a fraction of *completely* aligned molecules and a fraction of *completely* isotropic molecules. Further, solute molecules dissolved in the nematic state are assumed to distribute themselves between these two arrangements. Based on the assumptions of this " two phase " model and on exact thermodynamic arguments, a set of simultaneous equations is derived for evaluating S from GLC-determined solute infinite dilution activity coefficients and partial molar excess enthalpies.

From measurements on two nematogenic substances, *p*-azoxyanisole and 4, 4′-dihexoxyazoxybenzene, S values are obtained which are independent of the nature of the solute probe. The advantages and limitations of this method and the reason for the minor discrepancies between our S values and those determined from resonance experiments (ours are slightly lower) are discussed. The thermodynamic quantities corresponding to solution in completely aligned solvent are determined and discussed. The potential utility of this approach (e.g., studying order within the cholesteric mesophase) is also described.

Introduction

Owing to thermal motion, the molecular orientation in a nematic mesophase is never entirely complete. In recent years, NMR and

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ESR methods have been developed(1,2) and utilized(3–5) for determining the extent of parallelism in this mesophase. Common to both methods is the use of solute probes (paramagnetic in ESR) to generate spectra for interpretation. Analysis of anisotropic elements in the nematic phase spectrum (the dipolar coupling constants in NMR and the hyperfine coupling constants in ESR) and comparison with the isotropic liquid phase spectrum lead to an ordering factor, $S = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle$, which is an averaged measure of the alignment of the molecular long axes. For perfect parallelism $S = 1$, while for complete isotropy $S = 0$. The ordering factor is strongly temperature dependent, decreasing with rising temperature as the nematic–isotropic transition is approached. According to a recent survey(6) of existing results on a variety of nematogenic substances, S can range from about 0.8 to about 0.3.

Given the sensitivity of the anisotropic spectra to temperature, a major drawback to the NMR and ESR methods is the poor temperature control of the sample, especially at higher temperatures where thermal gradients are difficult to eliminate with existing instrument designs. Relative to ESR, NMR suffers additional deficiencies. Since ESR transitions are much more intense, smaller solute probe concentrations (approaching infinite dilution) can be used. With NMR the high probe concentration reduces the degree of alignment by perturbing the liquid crystal structure.(7) Therefore, S values obtained from NMR represent ordering factors for the particular solute-solvent system being studied at that temperature. Furthermore, the homogeneity of the magnetic field is more important in NMR which does not have the greater natural line widths of ESR.

An independent method for determining ordering parameters of liquid crystals was thought to be of interest. Accordingly, we propose a thermodynamic method based on interpretation of gas–liquid chromatography (GLC) measurement of infinite dilution solute activity coefficients and partial molar excess enthalpies. The GLC method has the advantages of simplicity of apparatus, excellent temperature control and true infinite dilution of the solute probe. As with the NMR and ESR methods, the determination of S must be based on a model.

Solution Model

Adopting a model first proposed by Frenkel,(8) and more recently utilized by others,(9,10) the nematic phase is considered to be composed of a fraction Y_a of *completely* aligned (anisotropic) molecules and a fraction Y_i of *completely* disordered (isotropic) molecules, where $Y_a + Y_i = 1$. The ordering factor S is identical to Y_a, for

$$S = Y_a \cdot \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle_a + Y_i \cdot \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle_i$$
$$= Y_a \cdot \tfrac{1}{2} \cdot 2 + Y_i \cdot \tfrac{1}{2} \cdot 0 = Y_a.$$

This model is essentially equivalent to the " swarm " or " cluster " model of the nematic phase, but its advocacy is not to be inferred by its use. It is in the same spirit as Eyring's significant structure theory of liquids,(11) which regards the thermodynamic functions of a liquid as composed of gas-like and solid-like contributions. Although it may not be an especially realistic picture of the nematic phase, it is, nevertheless, a useful working model.

The solute molecules, according to this model, distribute themselves between the two arrangements upon solution, a fraction X_a going into the anisotropic one and a fraction X_i going into the isotropic one (with $X_a + X_i = 1$). If we assume that one mole of solute is dissolved in n moles of solvent (where n is very large), the solute concentrations (in mole fraction units), C_a and C_i, in the anisotropic and isotropic parts of the solvent, respectively, are:

$$C_a = \frac{X_a}{nY_a} \tag{1}$$

$$C_i = \frac{X_i}{nY_i} \tag{2}$$

The solute chemical potential in each of these two " phases " can then be written as

$$\mu_a = \mu^0 + RT\ln\gamma_a C_a = \mu^0 + RT\ln\frac{\gamma_a X_a}{nY_a} \tag{3}$$

$$\mu_i = \mu^0 + RT\ln\gamma_i C_i = \mu^0 + RT\ln\frac{\gamma_i X_i}{nY_i} \tag{4}$$

where γ_a and γ_i are, respectively, the solute activity coefficients in the completely anisotropic and completely isotropic solvent arrangements. At equilibrium, the above chemical potentials are equal to each other and to the solute chemical potential (μ) in the solvent as a whole, i.e.,

$$\mu_a = \mu_i = \mu = \mu^0 + RT \ln \gamma \frac{1}{n} \tag{5}$$

where γ is the experimentally observed solute activity coefficient in the nematic phase.

From Eqs. (3), (4) and (5), we obtain

$$\gamma = X_a \gamma_a + X_i \gamma_i \tag{6}$$

and

$$\frac{1}{\gamma} = \frac{Y_a}{\gamma_a} + \frac{Y_i}{\gamma_i}. \tag{7}$$

Since enthalpy is a directly additive quantity, we have

$$\bar{H} = X_a \bar{H}_a + X_i \bar{H}_i \tag{8}$$

where $\bar{H}$ is the nematic phase solute partial molar excess enthalpy, and $\bar{H}_a$ and $\bar{H}_i$ are, respectively, the partial molar excess enthalpies of the solute in the *completely* anisotropic and *completely* isotropic solvent arrangements.

If GLC results are obtained for several solutes over a temperature range in both the nematic and isotropic liquid regions, and if one makes the reasonable assumption that the solute activity coefficient in the isotropic arrangement (γ_i) is the same just below and above the nematic–isotropic transition, then there are sufficient data to evaluate Y_a and its temperature dependence. In addition one can also determine and analyze the solute quantities γ_a and $\bar{H}_a$, which reflect the solute behavior in a *completely* aligned environment.

Determination of Nematic Ordering Parameters

We assume that, over the temperature range of the experiment, $\bar{H}_a$ and $\bar{H}_i$ are temperature independent, but allow for the possible temperature dependence of X_a and X_i (which, according to Eq. (8), would allow a temperature dependence to $\bar{H}$). However, to be consistent with the experimental observation(12) of a linear relationship between $\ln \gamma$ and T^{-1} in the nematic phase, $\bar{H}$, if it is not a constant, must be a linear function of temperature. Since

$$\ln \gamma = \frac{\bar{H}}{RT} - \frac{\bar{S}}{R} \tag{9}$$

(where $\bar{S}$ is the solute partial molar excess entropy in the nematic phase), then $\bar{H} = \bar{H}_0 + bT$ would yield a straight line relationship between ln γ and T^{-1} of slope $\bar{H}_0/R$, i.e.,

$$\ln \gamma = \frac{\bar{H}_0}{RT} - \frac{\bar{S} - b}{R}. \tag{10}$$

Thus, by allowing $\bar{H}$ to be temperature dependent, it is evident from Eqs. (6), (7) and (8) that there are now five unknowns at a given temperature of the nematic phase: X_a, Y_a, γ_a, $\bar{H}_a$ and b (γ_i can be determined by extrapolation of the experimental $\ln \gamma_i$ *vs.* T^{-1} plot into the nematic region). However, additional information can be gained from the temperature dependence of γ_a, i.e.,

$$\ln \gamma_a = \frac{\bar{H}_a}{RT} - \frac{\bar{S}_a}{R}. \tag{11}$$

Therefore, by considering three temperatures (T_1, T_2, T_3) the following eleven equations (with eleven unknowns) can be generated from Eqs. (6), (8) and (11):

$$\gamma_j = X_{a,j} \cdot \gamma_{a,j} + (1 - X_{a,j})\gamma_{i,j}, \quad j = 1, 2, 3 \tag{12}$$

$$\bar{H}_j = X_{a,j}\bar{H}_a + (1 - X_{a,j})\bar{H}_i, \quad j = 1, 2, 3 \tag{13}$$

$$\bar{H}_j = \bar{H}_0 + bT_j, \quad j = 1, 2, 3 \tag{14}$$

$$\ln \frac{\gamma_{a,j}}{\gamma_{a,1}} \Big/ \left(\frac{1}{T_j} - \frac{1}{T_1}\right) = \frac{\bar{H}_a}{R}, \quad j = 2, 3 \tag{15}$$

where the subscript j refers to the temperature condition. Once the γ_a values are obtained at T_1, T_2 and T_3, the Y_a's can be determined from Eq. (7).

Infinite dilution solute activity coefficients have been obtained by GLC for forty-two non-mesomorphic solutes (see Table 1) in the nematic and isotropic liquid regions of *p*-azoxyanisole (PAA) and 4,4′-dihexoxyazoxybenzene (DHAB).(12) From these values (γ and γ_i, respectively) and their temperature dependence (yielding $\bar{H}_0$ and $\bar{H}_i$, respectively), X_a, Y_a, γ_a, $\bar{H}_a$ and $\bar{S}_a$ were determined from Eqs. (7) and (11–15) at three equally spaced temperatures in the nematic region of each liquid crystal, through iterative solution by Newton's method. The results for Y_a and γ_a are listed in Table 2. Also, we have listed (Table 3) $\Delta\bar{H}_a^{\text{soln}}$ and $\Delta\bar{S}_a^{\text{soln}}$ (the solute partial molar enthalpy and entropy of solution in the *completely* aligned state) rather than $\bar{H}_a$ and $\bar{S}_a$ (the solute partial molar excess quantities) for reasons previously discussed.(12,13)

TABLE 1 Solute Components

Solute Number	Compound	Solute Number	Compound
1	*n*-heptane	22	*n*-1-decene
2	*n*-octane	23	*n*-1-undecene
3	*n*-nonane	24	1-chloropentane
4	2-methyloctane	25	1-chlorohexane
5	2,2-dimethylheptane	26	1-chloroheptane
6	3, 3-dimethylheptane	27	1-chlorooctane
7	4, 4-dimethylheptane	28	1-bromohexane
8	2,6-dimethylheptane	29	1-iodohexane
9	3-ethylheptane	30	*o*-xylene
10	3,3-diethylpentane	31	*m*-xylene
11	*n*-decane	32	*p*-xylene
12	*n*-undecane	33	*o*-dichlorobenzene
13	*n*-1-heptene	34	*m*-dichlorobenzene
14	*n*-1-octene	35	*p*-dichlorobenzene
15	*n*-cis-2-octene	36	*o*-chlorotoluene
16	*n*-trans-2-octene	37	*m*-chlorotoluene
17	*n*-cis-3-octene	38	*p*-chlorotoluene
18	*n*-trans-3-octene	39	*n*-butylbenzene
19	*n*-cis-4-octene	40	*iso*-butylbenzene
20	*n*-trans-4-octene	41	*sec*-butylbenzene
21	*n*-1-nonene	42	*tert*-butylbenzene

Discussion

Considering the uncertainty in the experimental data,(12) the Y_a values appear to be quite consistent and are independent of solute type. It is noteworthy that the average Y_a values obtained by the GLC method are somewhat lower than the S values obtained from ESR,(5) NMR(14) and other measurements(4) (see Fig. 1). The probable reason for the minor discrepancies is that our nematic ordering parameters are based on comparison to thermodynamic isotropic liquid values extrapolated into the nematic region, while the ESR and NMR S values are based on comparison with spectra where no anisotropic coupling characteristics are observed (some-

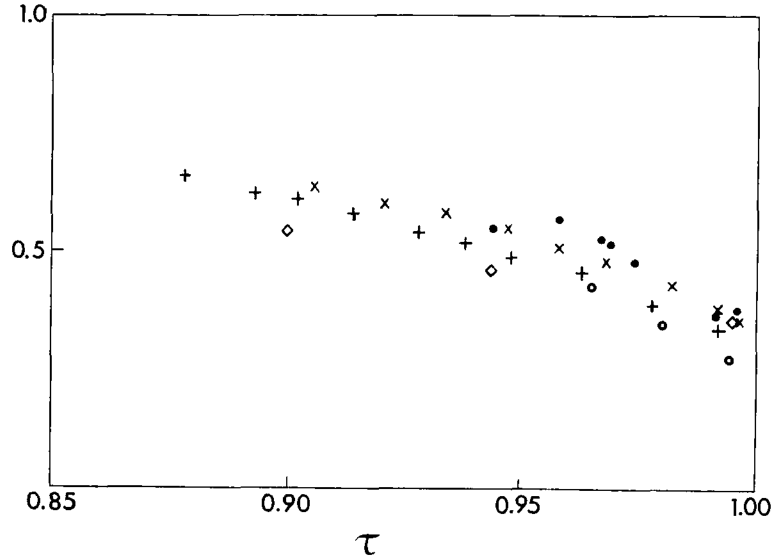

Figure 1. Nematic Ordering Parameter (S or Y_a) *versus* Reduced Temperature (τ).

PAA: ○, this study; ×, ESR results(5); ●, NMR results(14)

DHAB: ◇, this study; +, ESR results.(5)

The reduced temperature is defined as the ratio of the nematic phase temperature to the nematic–isotropic transition temperature.

where in the isotropic region). In short, the boundary conditions are different; our values being relative to an " isotropic " state at the same temperature at which the nematic state is being considered, and the resonance spectra values being relative to a higher temperature isotropic state. It should also be noted that S values can be obtained by NMR using *pure* liquid crystals,(14) and this would appear to be the approach of choice, given the previously mentioned difficulties with the solute probe technique.

It is observed that, when compared on a reduced temperature scale (see Fig. 1), the Y_a or S values for PAA are lower than those for DHAB. According to the statistical mechanical theories(4,15–17) of the nematic phase, the degree of order should be a function of three major factors: the molecular length-to-breadth ratio (favoring DHAB), the molecular flexibility (favoring PAA, the more rigid molecule), and the per segment lateral interaction energy(15) or the potential energy of interaction(4) (favoring PAA). This suggests

Table 2 Nematic Ordering Parameters (Y_a) and Solute Activity Coefficients in Completely Aligned Solvent (γ_a)

	PAA						DHAB					
	Y_a			γ_a			Y_a			γ_a		
Solute Number	392.2°	399.2°	405.2°	393.2°	399.2°	405.2°	361.2°	379.2°	399.2°	361.2°	379.2°	399.2°
1	0.39	0.34	0.29	24.8	23.4	22.1	0.59	0.53	0.46	4.61	3.90	3.30
2	0.40	0.34	0.29	30.7	28.8	27.0	0.54	0.47	0.39	5.71	4.78	3.99
3	0.40	0.34	0.28	36.2	33.8	31.6	0.54	0.47	0.38	6.67	5.54	4.61
4	0.41	0.35	0.29	38.4	35.5	32.9	0.55	0.47	0.38	6.23	5.13	4.23
5	0.45	0.38	0.31	58.5	53.6	49.2	0.58	0.52	0.45	6.98	5.71	4.66
6	0.46	0.39	0.31	55.4	50.6	46.3	0.58	0.51	0.43	6.90	5.62	4.57
7	0.47	0.40	0.32	56.4	51.4	47.0	0.58	0.51	0.43	7.30	5.93	4.81
8	0.45	0.38	0.30	62.0	57.0	52.5	—	—	—	—	—	—
9	0.46	0.38	0.30	55.0	50.5	46.1	0.59	0.53	0.46	6.27	5.09	4.13
10	0.48	0.41	0.32	50.4	45.6	41.5	0.60	0.54	0.47	5.66	4.56	3.66
11	0.41	0.35	0.28	43.1	40.1	37.3	0.54	0.45	0.34	8.24	6.79	5.59
12	0.43	0.37	0.30	49.6	46.3	43.4	0.53	0.45	0.35	8.16	6.56	5.27
13	0.40	0.33	0.26	25.2	23.7	22.3	0.55	0.45	0.33	5.63	4.86	4.20
14	0.40	0.33	0.26	27.9	26.1	24.5	0.55	0.44	0.31	6.79	5.80	4.96
15	0.43	0.35	0.27	34.7	32.3	30.2	0.55	0.45	0.33	6.47	5.57	4.80
16	0.41	0.33	0.25	32.0	29.9	28.0	0.55	0.49	0.41	4.57	3.87	3.28
17	0.41	0.35	0.28	30.0	28.2	26.6	0.53	0.44	0.33	6.04	5.15	4.38
18	0.41	0.35	0.28	30.2	28.4	26.7	0.54	0.45	0.33	6.35	5.49	4.74
19	0.44	0.36	0.28	37.2	34.7	32.4	0.55	0.48	0.40	5.18	4.37	3.68
20	0.41	0.35	0.28	30.7	28.9	27.3	0.55	0.48	0.39	5.28	4.53	3.88
21	0.42	0.35	0.28	31.5	29.5	27.6	0.54	0.45	0.35	5.99	4.98	4.14
22	0.43	0.36	0.29	34.9	32.9	31.0	0.54	0.46	0.36	6.62	5.45	4.48
23	0.42	0.36	0.29	37.9	35.4	33.2	0.54	0.45	0.34	7.67	6.24	5.07
24	0.38	0.33	0.27	9.65	9.20	8.79	0.52	0.43	0.33	3.63	3.04	2.54
25	0.41	0.34	0.27	12.9	12.3	11.8	0.53	0.44	0.34	3.90	3.22	2.66

26	0.41	0.35	0.27	14.7	14.1	13.5	0.54	0.44	0.33	4.39	3.63	3.00
27	0.42	0.36	0.29	16.2	15.5	14.8	0.54	0.45	0.33	4.77	3.91	3.21
28	0.40	0.34	0.27	12.5	11.8	11.3	0.53	0.45	0.34	3.92	3.21	2.64
29	0.43	0.36	0.28	14.2	13.5	12.8	0.54	0.44	0.31	4.62	3.78	3.09
30	0.39	0.33	0.26	8.63	8.22	7.83	0.52	0.42	0.31	3.06	2.57	2.16
31	0.40	0.33	0.26	9.38	8.94	8.54	0.52	0.43	0.33	2.89	2.42	2.03
32	0.37	0.31	0.24	8.04	7.72	7.41	0.50	0.41	0.30	2.84	2.40	2.03
33	0.42	0.34	0.27	7.10	6.80	6.51	0.53	0.42	0.28	3.15	2.58	2.10
34	0.42	0.34	0.25	7.98	7.64	7.31	0.53	0.43	0.30	3.06	2.51	2.06
35	0.38	0.30	0.22	6.46	6.24	6.04	0.52	0.41	0.28	2.89	2.40	1.99
36	0.41	0.34	0.26	8.58	8.17	7.79	0.53	0.45	0.35	2.73	2.26	1.86
37	0.39	0.33	0.26	7.75	7.39	7.06	0.55	0.42	0.27	3.75	3.14	2.63
38	0.35	0.30	0.23	6.18	5.94	5.73	0.50	0.42	0.32	2.45	2.06	1.74
39	0.43	0.36	0.28	14.5	13.7	13.0	0.55	0.45	0.33	4.63	3.79	3.10
40	0.44	0.36	0.27	18.5	17.3	16.2	0.54	0.45	0.34	4.49	3.65	2.98
41	0.45	0.38	0.29	17.4	16.3	15.3	0.56	0.47	0.35	5.05	4.08	3.30
42	0.47	0.39	0.30	18.8	17.6	16.5	0.56	0.47	0.37	4.58	3.72	3.03
Average:	0.42	0.35	0.28			Average:	0.54	0.46	0.36			
Stnd. Dev.:	±0.03	±0.02	±0.02			Stnd. Dev.:	±0.02	±0.03	±0.04			

Temperatures are in degrees Kelvin.

TABLE 3 Solute Partial Molar Enthalpies and Entropies of Solution in Completely Aligned Solvent

Solute Number	PAA		DHAB	
	$-\Delta\bar{H}_a^{\text{soln}}$	$-\Delta\bar{S}_a^{\text{soln}}$	$-\Delta\bar{H}_a^{\text{soln}}$	$-\Delta\bar{S}_a^{\text{soln}}$
1	4.04	16.4	4.96	15.7
2	4.84	18.8	5.86	18.6
3	5.66	21.3	6.89	21.6
4	4.97	19.6	6.45	20.3
5	3.88	17.6	5.71	18.5
6	3.93	17.6	5.87	18.9
7	3.78	17.3	5.74	18.7
8	4.25	18.7	—	—
9	4.20	18.3	6.21	19.6
10	3.72	17.0	5.83	18.4
11	6.62	23.9	7.90	24.7
12	7.97	27.6	8.64	26.5
13	3.69	15.5	5.09	16.6
14	4.65	18.1	6.05	19.4
15	4.38	17.9	6.11	19.5
16	4.52	18.1	5.85	18.1
17	4.75	18.5	5.83	18.6
18	4.70	18.4	6.06	19.4
19	4.30	17.8	5.65	17.8
20	4.89	18.9	5.91	18.6
21	4.69	21.0	6.74	21.0
22	7.13	24.8	7.68	23.6
23	7.87	26.8	8.61	26.3
24	5.08	17.1	5.16	15.8
25	6.15	20.4	6.07	18.3
26	7.27	23.5	7.14	21.4
27	8.28	26.2	8.11	24.1
28	6.70	21.7	6.73	20.1
29	7.51	24.0	7.42	22.2
30	6.51	20.5	6.69	19.5
31	6.40	20.4	6.49	18.9
32	6.62	20.7	6.54	19.0
33	8.06	24.0	7.68	22.1
34	7.72	23.4	7.39	21.3
35	8.32	24.5	7.63	21.9
36	7.31	22.5	6.99	20.1
37	7.48	22.7	7.28	21.5
38	7.79	23.1	7.21	20.5
39	7.75	24.6	7.91	23.5
40	6.46	21.9	7.24	21.7
41	6.69	22.3	7.17	21.7
42	6.39	21.7	7.14	21.4

Enthalpies are in Kcal./mole, entropies in cal./mole degree.

that particle shape (i.e., repulsive forces) may be the most important factor influencing the degree of order (which is not to say that the other factors are not also important). However, more experimental information (in particular, accurate nematic and isotropic liquid densities) is needed for testing the developing statistical theories of the nematic state and the nematic → isotropic transition. Since ordering parameters obtained from careful GLC or ESR measurements are direct and truly characteristic of pure nematic liquids, studies on a variety of nematogenic homologous series would provide much of the essential data for examining these theories.†

Furthermore, since it is felt that a realistic statistical theory must ultimately incorporate a realistic potential function, the accurate determination of ordering parameters takes on added importance. In a study confirmed by the present one, Luckhurst *et al.*(5) found that the nematic S values when plotted against reduced temperature τ (i.e., the nematic phase temperature divided by the nematic–isotropic transition temperature) did not fall on a universal curve, even for members of the same homologous series. This is contrary to the prediction using the Maier–Saupe(18) potential function (based on dispersion forces only) that nematic substances should have the same S values at similar τ values. More recently, Luckhurst(19) has found additional ESR evidence of the failure of an anisotropic distribution function based solely on dispersion forces. This suggests that a modified potential function (perhaps incorporating dipole–dipole, induction and repulsion forces(20)) should be sought and tested.

In the preceding paper of this series,(12) a molecular interpretation of solubility in nematogenic solvents was proposed. The interpretation was based on solute-to-solute comparisons of experimental activity coefficients and heats of solution. Listed in Tables 2 and 3 are the infinite dilution solute activity coefficients (γ_a) and partial

† The accuracy of ordering parameters obtained from GLC measurements is strongly dependent on the accuracy of the γ values. Therefore, it is important to choose proper solutes for each nematic liquid being studied to ensure maximum experimental accuracy. The considerations for such a selection are: (1) the solute retention volumes should be sufficiently large for accurate measurement, and (2) the vapor pressures and second virial coefficients must be accurately known over the experimental temperature range. It is not necessary to study a very large number of solutes; ten should suffice.

molar enthalpies ($\Delta \bar{H}_a^{\text{soln}}$) and entropies ($\Delta \bar{S}_a^{\text{soln}}$) of solution for the completely aligned ($Y_a = 1$) solvent as determined from our model.† Comparing the $\Delta \bar{H}_a^{\text{soln}}$ values to the corresponding experimental nematic phase values,(12) one finds that the former are considerably larger (more exothermic) than the latter. Since the γ_a values for all solutes are also much greater than the corresponding γ values, it can be concluded(12) that the larger $\Delta \bar{H}_a^{\text{soln}}$ values are primarily due to the greater loss of internal energy (rotational and vibrational) for solution in the completely aligned phase relative to the partially aligned phase. This is additional support for our initial premise(12) that the loss of solute rotational and vibrational motion (due to space restrictions imposed by the ordered solvent arrangement) is an important factor governing solubility in the nematic phase. Comparison of the $\Delta \bar{S}_a^{\text{soln}}$ values for the *n*-alkanes with sublimation entropies (i.e., ΔS (gas → solid)) for the pure *n*-alkanes(21) further suggests that in the completely aligned solvent the *n*-alkanes are nearly " solid-like " with respect to their rotational and vibrational motion (i.e., the preferred zig-zag conformation is dominant and rotation in the directions perpendicular to the molecular long axes is unlikely).

The generally lower γ_a values and more negative $\Delta \bar{H}_a^{\text{soln}}$ values for DHAB relative to PAA suggest that solute–solvent interactions are stronger with DHAB (which is expected to have a smaller cohesive energy density than PAA, hence offer less competition for the solute), while solute rotational-vibrational energy losses are greater with the more rigid PAA. Also, it had been noted previously(12) that there was a greater difference in the solvent behavior between the nematic and isotropic liquid phases for PAA. This is also reflected by the much larger X_a values (not tabulated here) for DHAB. In light of what has preceded, this could be an indication of one or both of the following: (1) a greater reduction in the cohesive energy density upon transition to the isotropic phase for PAA; (2) greater residual alignment in the isotropic phase for DHAB.(22)

Studies are presently being conducted on several cholesteryl

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† Utilizing the results in Tables 2 and 3, similar solute-to-solute comparisons can be carried out, leading to the same general conclusions as reached previously.(12)

esters. It is noteworthy that ESR and NMR experiments have failed to indicate any alignment with *pure* cholesteric phases, suggesting that any anisotropy is averaged to zero by the helical structure. It is possible for a high magnetic field to unwind the cholesteric structure and produce alignment; however, the induced structure would then be nematic. We anticipate that GLC studies on pure unperturbed cholesteric substances might provide ordering factors (i.e., the degree of alignment within a " layer ") where the resonance methods cannot.

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