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Thermodynamic Studies on Infinitely Dilute Solutions of Nonmesomorphic Solutes in Liquid Crystalline Solvents

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Infinite-dilution activity coefficients (γ_2^∞), partial molar excess enthalpies (H^E) and entropies (S^E), and partial molar enthalpies ($\Delta_{soln}H^\infty$) and entropies ($\Delta_{soln}S^\infty$) of solution, obtained using gas–liquid chromatography (GLC), are reported for hexane, *trans*-hex-3-ene, cyclohexane, *cis*-2-*trans*-4-hexadiene, *trans*-2-*trans*-4-hexadiene, and benzene in the nematic and isotropic phases of the liquid crystalline solvents *p*-(*n*-pentyloxy)-*p*′-cyanobiphenyl, *p*-(*n*-hexyloxy)-*p*′-cyanobiphenyl, *p*-(*n*-heptyloxy)-*p*′-cyanobiphenyl, and *p*-(*n*-octyloxy)-*p*′-cyanobiphenyl. General trends in the four solvents are identified. The results demonstrate the effects that the solute structure (shape, flexibility, and polarizability) and the length of the flexible alkyloxy tail on the solvent molecule have on the solution process.

Introduction

Gas–liquid chromatography (GLC) has become an established (*1*) technique for the determination of reliable thermodynamic data for volatile nonmesomorphic solutes at "infinite dilution" in the mesophase(s) and isotropic phase of liquid crystals. Two comprehensive studies (*1, 2*) comparing GLC and extrapolated static data have confirmed that infinite-dilution solute activity coefficients accurate to better than ±1% can be obtained by GLC. Such measurements provide information on the effect that solute structure (size, shape, flexibility, polarizability, and polarity) has on the solution process. Gas chromatographic separations that use liquid crystalline phases (*3*) rely on differences in structure among the components of the mixture. Furthermore, these results may be combined with the entropy change at the nematic-to-isotropic phase transition of the relevant pure nematogen to provide information (*4*) on the ability of the solute to disrupt the long-range orientational order in the nematic phase which in turn is needed to test statistical theories of binary mixtures (*5, 6*) and to assess the effect of potential additivies or impurities on nematic-phase stability.

The *p*-(*n*-alkyloxy)-*p*′-cyanobiphenyls (*7*) (ROCB) are commercially available in highly pure form, do not hydrolyze, and are photochemically unreactive. The use of internal standards showed that the bleeding and decomposition of these liquid crystalline phases from GLC columns were negligible during the period of operation. The liquid crystalline solvents used in this study are *p*-(*n*-pentyloxy)-*p*′-cyanobiphenyl, *p*-(*n*-hexyloxy)-*p*′-cyanobiphenyl, *p*-(*n*-heptyloxy)-*p*′-cyanobiphenyl, and *p*-(*n*-octyloxy)-*p*′-cyanobiphenyl. The solutes used (all with six carbon atoms) are hexane, *trans*-hex-3-ene, cyclohexane, *cis*-2-*trans*-4-hexadiene, *trans*-2-*trans*-4-hexadiene, and benzene. By systematically studying various categories of solutes with members of the ROCB homologous series of liquid crystals, the effects of both the solute structure and the length of the flexible tail on the solvent molecule on the solution process may be examined.

In this paper thermodynamic measurements are reported, at infinite dilution, for the above-mentioned solute/solvent systems. The general trends obtained were similar to those encountered with the *p*-(*n*-alkyl)-*p*′-cyanobiphenyl (*7*) (RCB) homologous series of liquid crystalline solvents (*8, 9*). Unlike the results for the nematic RCB's, the activity coefficients of solutes in the nematic ROCB's, extrapolated to (or interpolated at) a common temperature, did not show an odd–even effect.

Experimental Section

The (alkyloxy)cyanobiphenyl stationary phases were obtained from BDH chemicals with quoted purities in excess of 99.5 mass % and were used as supplied. Their high purity was evident from their sharp nematic-to-isotropic phase transitions (*5, 6*) at the temperatures given in Table 1. They were coated on a Johns-Manville 60–80-mesh acid-washed and DMCS-treated Chromosorb W. Details of the preparations of the columns are given elsewhere (*4*). Glass columns 1 m long with an outside diameter of 0.25 in. were used. The weight percentage of the liquid phase in each packing (i.e., the liquid-phase loading) was determined by careful ashing (*10*) of three samples of about 1 g of the bare support and of three samples of about 1 g of packing to correct for organic matter present in the support. The loadings of all columns used in this study were accurate to within ±0.04%. Preliminary measurements on the least and most retained solutes at a representative temperature in the nematic and isotropic phases of the four liquid crystalline stationary phases gave identical solute-specific retention volumes, V_g°, at loadings of about 9% and about 15%. The columns used to obtain the thermodynamic data had loadings around 12%.

The solutes (Table 1), obtained from Fluka, were highly pure and were used as supplied. All the solutes were sufficiently volatile at the experimental temperatures, and except for the critical constants of the hexadienes, their physical properties either were available (*12*) or could be computed (*13–15*).

A Perkin-Elmer Auto System gas chromatograph, modified (*8*) for accurate measurement of pressure at the column inlet was used. The temperature inside the oven of the gas chromatograph was constantly monitored during all runs using a chromel–alumel thermocouple, and the observed control of the column temperature was within ±0.03 °C. The procedure followed to obtain accurate retention volumes is described elsewhere (*4*). Adequate care was taken to ensure the attainment of the infinite dilution condition (*4, 10*). Interfacial effects (*4, 16*) were absent.

Results

Solute-specific retention volumes, V_g° (*4, 16*), were obtained at four temperatures in the nematic and isotropic phases of

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Table 1. List of Solutes and Solvents

	molar mass	bp/°C	T_{NI}/°C	$V_c{}^a \times 10^{22}$/cm^3	d^b/(J·g^{-1})	e^b/(J·g^{-1}·deg^{-1})
			Solutes			
hexane	86.12	68.74		6.11	92.06	0.1751
trans-hex-3-ene	84.16	67.08		5.97	93.17	0.1696
cyclohexane	84.16	80.74		5.14	98.33	0.1602
cis-2-*trans*-4-hexadiene	82.14	80.00			104.9	0.1816
trans-2-*trans*-4-hexadiene	82.14	80.00			104.9	0.1816
benzene	78.11	80.11		4.3	107.85	0.1711
			Solvents			
p-(*n*-pentyloxy)-*p*′-cyanobiphenyl	265.34		68			
p-(*n*-hexyloxy)-*p*′-cyanobiphenyl	279.37		75.5			
p-(*n*-heptyloxy)-*p*′-cyanobiphenyl	293.39		74			
p-(*n*-octyloxy)-*p*′-cyanobiphenyl	307.42		80			

[a] Critical molecular volume, calculated using critical volumes (cm^3/g) given in ref 12. [b] Reference 12 gives the parameters *d* and *e* for calculating $\Delta_{vap}H$ (J/g) at T (°C) from $\Delta_{vap}H = 4.1844(d - eT)$.

Table 2. Infinite-Dilution Solute Activity Coefficients, γ_2^∞, for each Solute at Four Temperatures (°C) (Given in Parantheses) in each of the Nematic and Isotropic Phases of the Four Liquid Crystals

solute	γ_2^∞ nematic phase				γ_2^∞ isotropic phase			
			p-(*n*-Pentyloxy)-*p*′-cyanobiphenyl					
	(51.84)	(53.99)	(58.94)	(65.19)	(70.60)	(74.66)	(79.13)	(84.21)
hexane	6.13	5.94	5.49	4.93	4.23	4.06	3.89	3.75
trans-hex-3-ene	4.94	4.88	4.52	4.11	3.62	3.49	3.36	3.22
cyclohexane	4.36	4.16	3.88	3.47	2.97	2.84	2.71	2.61
cis-2-*trans*-4-hexadiene	2.25	2.21	2.11	1.94	1.71	1.67	1.61	1.58
trans-2-*trans*-4-hexadiene	2.19	2.13	2.05	1.91	1.73	1.70	1.66	1.61
benzene	1.43	1.39	1.34	1.25	1.13	1.10	1.07	1.05
			p-(*n*-Hexyloxy)-*p*′-cyanobiphenyl					
	(60.11)	(64.19)	(68.20)	(72.35)	(78.20)	(81.40)	(84.51)	(87.52)
hexane	4.82	4.58	4.36	4.16	3.41	3.32	3.24	3.17
trans-hex-3-ene	4.11	3.91	3.73	3.55	2.88	2.83	2.78	2.72
cyclohexane	3.49	3.29	3.13	2.95	2.38	2.33	2.30	2.23
cis-2-*trans*-4-hexadiene	1.95	1.87	1.82	1.74	1.45	1.44	1.43	1.40
trans-2-*trans*-4-hexadiene	1.87	1.82	1.77	1.71	1.46	1.44	1.43	1.41
benzene	1.27	1.23	1.20	1.16	0.99	0.98	0.97	0.96
			p-(*n*-Heptyloxy)-*p*′-cyanobiphenyl					
	(57.33)	(61.17)	(65.25)	(69.28)	(76.56)	(79.62)	(82.45)	(84.94)
hexane	4.24	4.07	3.88	3.69	3.08	2.99	2.93	2.87
trans-hex-3-ene	3.68	3.55	3.38	3.21	2.66	2.60	2.55	2.50
cyclohexane	3.09	2.96	2.82	2.67	2.19	2.13	2.07	2.03
cis-2-*trans*-4-hexadiene	1.81	1.76	1.69	1.63	1.37	1.35	1.32	1.30
trans-2-*trans*-4-hexadiene	1.76	1.71	1.66	1.61	1.37	1.36	1.33	1.32
benzene	1.22	1.19	1.15	1.11	0.95	0.94	0.93	0.92
			p-(*n*-Octyloxy)-*p*′-cyanobiphenyl					
	(69.44)	(72.32)	(74.49)	(77.60)	(82.67)	(86.47)	(89.61)	(92.59)
hexane	3.51	3.37	3.26	3.11	2.64	2.55	2.46	2.39
trans-hex-3-ene	3.12	2.98	2.88	2.74	2.32	2.25	2.17	2.11
cyclohexane	2.58	2.46	2.37	2.24	1.89	1.81	1.75	1.70
cis-2-*trans*-4-hexadiene	1.64	1.56	1.51	1.45	1.24	1.21	1.18	1.15
trans-2-*trans*-4-hexadiene	1.60	1.54	1.49	1.43	1.24	1.21	1.19	1.16
benzene	1.14	1.09	1.06	1.01	0.88	0.86	0.84	0.82

the four liquid crystalline solvents studied. The V_g° values were obtained from the average of at least three separate measurements and agreed to within ±0.7%. No measurements were made in the neighborhood (within ±2.5 °C) of the nematic-to-isotropic transition temperature, T_{NI}, to avoid possible pre- or posttransitional effects inherent in the nematogen or the induction of a phase transition by the solute band (*5*, *6*).

The infinite-dilution solute activity coefficients, γ_2^∞, were calculated from V_g° using

$$\ln \gamma_2^\infty = \ln(273.2R/M_1P_2^\circ V_g^\circ) - B_{22}P_2^\circ/RT \qquad (1)$$

where M_1 is the solvent molar mass and P_2° and B_{22} are, respectively, the saturated vapor pressure and second virial coefficient of the pure solute at the experimental temperature T. The calculation is considered fully in ref 4. A propagation of error analysis showed that the γ_2^∞ values obtained by us are accurate to within ±1.2%. The γ_2^∞ values obtained are listed in Table 2. In addition γ_2^∞ values obtained at 74 °C from extrapolations (or interpolations) of linear least-squares fits of $\ln \gamma_2^\infty$ against $1/T$ in the nematic (γ_N*) and isotropic (γ_I*) phases of *p*-(*n*-pentyloxy)-*p*′-cyanobiphenyl, *p*-(*n*-hexyloxy)-*p*′-cyanobiphenyl, *p*-(*n*-heptyloxy)-*p*′-cyanobiphenyl, and *p*-(*n*-octyloxy)-*p*′-cyanobiphenyl are given in Tables 3 and 4, respectively. Since from thermodynamics

$$\ln \gamma_2^\infty = G^E/RT = H^E/RT - S^E/R \qquad (2)$$

infinite dilution partial molar excess enthalpies, H^E, and entropies, S^E, were obtained, respectively, from the slopes and intercepts of linear least-squares fits of $\ln \gamma_2^\infty$ as a function of T^{-1} and are reported along with their standard deviations in Tables 3 and 4. Representative plots of ln

Table 3. Infinite-Dilution Solute Partial Molar Excess Enthalpies, H^E, and Entropies, S^E, in Nematic (alkyloxy)cyanobiphenyls[a]

solute	H^E/(kJ·mol^{-1})	S^E/(J·mol^{-1}·K^{-1})	γ_N*	$-\Delta_{soln}H_N$*/(kJ·mol^{-1})	$-\Delta_{soln}S_N$*/(J·mol^{-1}·K^{-1})
		p-(*n*-Pentyloxy)-*p*′-cyanobiphenyl			
hexane	15.2 ± 0.2	31.7 ± 0.7	4.31	13.3	50.5
trans-hex-3-ene	14.1 ± 0.1	30.1 ± 0.2	3.62	14.3	51.7
cyclohexane	14.9 ± 0.7	33.6 ± 2.1	3.61	15.6	54.1
cis-2-*trans*-4-hexadiene	10.8 ± 0.8	26.5 ± 2.4	1.77	20.6	64.1
trans-2-*trans*-4-hexadiene	9.1 ± 0.5	21.5 ± 1.4	1.77	22.3	69.1
benzene	8.6 ± 0.5	23.5 ± 1.4	1.16	22.5	66.1
		p-(*n*-Hexyloxy)-*p*′-cyanobiphenyl			
hexane	11.7 ± 0.0	22.0 ± 0.1	4.08	16.8	60.2
trans-hex-3-ene	11.4 ± 0.1	22.5 ± 0.2	3.48	17.0	59.3
cyclohexane	13.1 ± 0.5	29.0 ± 1.5	2.89	17.4	58.7
cis-2-*trans*-4-hexadiene	8.7 ± 0.6	20.4 ± 1.8	1.72	22.7	70.2
trans-2-*trans*-4-hexadiene	7.0 ± 0.5	15.9 ± 1.5	1.69	24.4	74.7
benzene	6.9 ± 0.6	18.6 ± 1.6	1.15	24.2	71.0
		p-(*n*-Heptyloxy)-*p*′-cyanobiphenyl			
hexane	11.0 ± 0.4	21.2 ± 1.1	3.52	17.5	61.0
trans-hex-3-ene	10.8 ± 0.5	21.7 ± 1.4	3.06	17.6	60.1
cyclohexane	11.6 ± 0.4	25.6 ± 1.1	2.53	18.9	62.1
cis-2-*trans*-4-hexadiene	8.2 ± 0.4	19.8 ± 1.0	1.57	23.2	70.8
trans-2-*trans*-4-hexadiene	7.1 ± 0.4	16.6 ± 0.7	1.56	24.3	74.0
benzene	7.2 ± 0.2	20.2 ± 0.7	1.08	23.9	69.4
		p-(*n*-Octyloxy)-*p*′-cyanobiphenyl			
hexane	14.8 ± 0.5	32.8 ± 1.3	3.28	13.7	49.4
trans-hex-3-ene	15.7 ± 0.1	36.2 ± 0.3	2.90	12.7	45.6
cyclohexane	17.4 ± 0.1	42.8 ± 0.4	2.39	13.1	44.9
cis-2-*trans*-4-hexadiene	15.0 ± 0.3	39.6 ± 1.0	1.53	16.4	51.0
trans-2-*trans*-4-hexadiene	13.6 ± 0.0	35.7 ± 0.0	1.50	17.8	54.9
benzene	14.4 ± 0.2	41.0 ± 0.5	1.06	16.7	48.6

[a] The infinite-dilution solute activity coefficients, γ_N*, and partial molar enthalpies, $\Delta_{soln}H_N$*, and entropies, $\Delta_{soln}S_N$*, of solution are from extrapolations (or interpolations) of linear least-squares fits of ln γ_2^∞ against $1/T$ in the nematic phase to (or at) 74 °C.

γ_2^∞ as a function of T^{-1} are given in Figure 1. From H^E and S^E the infinite-dilution solute partial molar enthalpies, $\Delta_{soln}H^\infty$, and entropies, $\Delta_{soln}S^\infty$, of solution may be obtained, respectively, at the temperature of interest, from the relations

$$\Delta_{soln}H^\infty = H^E - \Delta_{vap}H \tag{3}$$

and

$$\Delta_{soln}S^\infty = S^E - \Delta_{vap}H/T \tag{4}$$

where $\Delta_{vap}H$ is the enthalpy of vaporization of the solute at the same temperature. The relation and parameters needed for $\Delta_{vap}H$ computation are available in ref 12. $\Delta_{soln}H^\infty$ and $\Delta_{soln}S^\infty$ at 74 °C in the nematic ($\Delta_{soln}H_N$* and $\Delta_{soln}S_N$*) and isotropic ($\Delta_{soln}H_I$* and $\Delta_{soln}S_I$*) phases of the four liquid crystals studied are given in Tables 3 and 4, respectively. Because $\Delta_{soln}H^\infty$ does not contain a solute–solute interaction term, it provides a relative measure of solute–solvent interaction strengths.

Discussion

The results (Tables 2–4) are examined in the light of an infinite-dilution solution model proposed by Chow and Martire (*17*) and later refined by Martire (*18*). They corroborate earlier studies on the RCB series of liquid crystals (*11*). Except for beznene in the isotropic phases of *p*-(*n*-hexyloxy)-*p*′-cyanobiphenyl, *p*-(*n*-heptyloxy)-*p*′-cyanobiphenyl, and *p*-(*n*-octyloxy)-*p*′-cyanobiphenyl, the infinite-dilution activity coefficients for the solutes exhibit positive deviations from Raoult's law ($\gamma_2^\infty > 1$). The partial molar excess enthalpies and excess entropies for all solutes in the nematic and isotropic phases of all solvents are positive. Nonmesomorphic solutes are therefore generally incompatible with both phases of these liquid crystalline solvents. On comparing the results for the four solvents, we find, without exception, the following trends:

$$(\Delta_{soln}H^\infty)_I < (\Delta_{soln}H^\infty)_N \quad \text{and} \quad (H^E)_I < (H^E)_N \tag{a}$$

$$(\Delta_{soln}S^\infty)_I < (\Delta_{soln}S^\infty)_N \quad \text{and} \quad (S^E)_I < (S^E)_N \tag{b}$$

$$(\gamma_2^\infty)_I < (\gamma_2^\infty)_N \tag{c}$$

where the subscripts I and N refer to the isotropic and nematic phases, respectively. Enthalpy changes at the nematic-to-isotropic transitions are small; thus, solvent–solvent interactions in the nematic phase are only slightly stronger than those in the isotropic phase. Therefore, trend a can only be attributed to effectively weaker solute–solvent interactions in the nematic phase. In the nematic phase rotational and conformational restrictions reduce solute entropy while weaker solute–solvent interactions lead to an increase in the solute (translational) entropy. Since the nematic phase is entropically favored (trend b), the latter effect must be prevalent. Trend c indicates that the lower solute excess Gibbs energy in the isotropic phase is enthalpic in origin.

trans-Hex-3-ene is more rigid and polarizable than hexane. An increase in rigidity leads to a weaker solute–solvent interaction (less negative $\Delta_{soln}H^\infty$ and $\Delta_{soln}S^\infty$ values) and tends to increase γ_2^∞. On the other hand, an increase in polarizability has the opposite effect. The lower γ_2^∞ value for *trans*-hex-3-ene relative to hexane indicates that the latter effect predominates. The same argument holds for the hexadienes and benzene which are progressively more rigid and polarizable, and the trend hexane > *trans*-hex-3-ene > hexadienes > benzene for the γ_2^∞ values is obtained (Figures 1 and 2). The effect of polarizability remains the overriding factor in the isotropic phase, and the above trend in the γ_2^∞ values holds even though rotational and conformational entropy losses upon solvation are smaller in the less orientationally ordered isotropic phase. On a scale of increasing rigidity in the

Table 4. Infinite-Dilution Solute Partial Molar Excess Enthalpies, H^E, and Entropies, S^E, in Isotropic (alkyloxy)cyanobiphenyls[a]

solute	H^E/(kJ·mol^{-1})	S^E/(J·mol^{-1}·K^{-1})	γ_I^*	$-\Delta_{soln}H_I^*$/(kJ·mol^{-1})	$-\Delta_{soln}S_I^*$/(J·mol^{-1}·K^{-1})
		p-(*n*-Pentyloxy)-*p*′-cyanobiphenyl			
hexane	9.3 ± 0.4	15.0 ± 1.2	4.10	19.2	67.2
trans-hex-3-ene	8.8 ± 0.3	14.9 ± 0.9	3.45	19.5	66.9
cyclohexane	9.9 ± 0.4	19.7 ± 1.0	2.86	20.6	68.0
cis-2-*trans*-4-hexadiene	6.4 ± 0.4	14.3 ± 1.2	1.68	25.0	76.3
trans-2-*trans*-4-hexadiene	5.6 ± 0.3	11.7 ± 0.9	1.69	25.8	78.9
benzene	5.2 ± 0.2	14.0 ± 0.7	1.11	25.9	75.6
		p-(*n*-Hexyloxy)-*p*′-cyanobiphenyl			
hexane	8.3 ± 0.1	13.5 ± 0.4	3.53	20.2	68.7
trans-hex-3-ene	6.5 ± 0.2	9.6 ± 0.5	2.96	21.9	72.2
cyclohexane	7.4 ± 0.6	13.8 ± 1.7	2.46	23.1	73.9
cis-2-*trans*-4-hexadiene	4.2 ± 0.6	8.9 ± 1.6	1.48	27.2	81.7
trans-2-*trans*-4-hexadiene	3.6 ± 0.5	7.2 ± 1.5	1.48	27.8	83.4
benzene	2.8 ± 0.7	8.1 ± 1.5	1.00	28.3	81.5
		p-(*n*-Heptyloxy)-*p*′-cyanobiphenyl			
hexane	8.9 ± 0.5	16.1 ± 1.3	3.15	19.6	66.1
trans-hex-3-ene	7.9 ± 0.0	14.5 ± 0.0	2.72	20.5	67.3
cyclohexane	9.6 ± 0.3	20.8 ± 0.8	2.24	20.9	66.9
cis-2-*trans*-4-hexadiene	6.2 ± 0.3	15.1 ± 0.9	1.39	25.2	75.5
trans-2-*trans*-4-hexadiene	5.2 ± 0.2	12.2 ± 0.5	1.39	26.2	78.4
benzene	4.1 ± 0.1	12.0 ± 0.4	0.96	27.2	77.6
		p-(*n*-Octyloxy)-*p*′-cyanobiphenyl			
hexane	10.9 ± 0.4	22.6 ± 1.1	2.90	17.6	59.6
trans-hex-3-ene	10.3 ± 0.5	21.9 ± 1.4	2.53	18.1	59.9
cyclohexane	11.5 ± 0.1	26.9 ± 0.3	2.08	19.0	60.8
cis-2-*trans*-4-hexadiene	7.7 ± 0.4	20.0 ± 1.0	1.32	23.7	70.6
trans-2-*trans*-4-hexadiene	7.4 ± 0.4	18.9 ± 1.0	1.33	24.0	71.7
benzene	6.9 ± 0.4	20.5 ± 1.1	0.93	24.2	69.1

[a] The infinite-dilution solute activity coefficients, γ_I^*, and partial molar enthalpies, $\Delta_{soln}H_I^*$, and entropies, $\Delta_{soln}S_I^*$, of solution are from extrapolations (or interpolations) of linear least-squares fits of ln γ_2^∞ against $1/T$ in the isotropic phase to (or at) 74 °C.

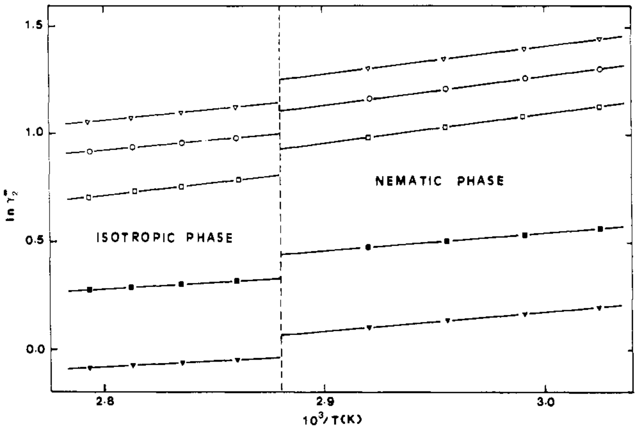

Figure 1. ln γ_2^∞ against $10^3/T$ for hexane (▽), *trans*-hex-3-ene (○), cyclohexane (□), *cis*-2-*trans*-4-hexadiene (■), and benzene (▼) in the nematic and isotropic phases of *p*-(*n*-heptyloxy)-*p*′-cyanobiphenyl. The phase transition temperature is indicated by the dashed vertical line.

direction hexane → *trans*-hex-3-ene → hexadienes → benzene, the rigidity of cyclohexane is slightly less than that of benzene while its polarizability is comparable to that of hexane. On the basis of the preceding argument, we would expect cyclohexane to have a γ_2^∞ value similar to that of hexane or slightly higher. The increased compatibility of cyclohexane with the liquid crystalline phases relative to hexane is probably due to its smaller size.

To examine the effect on the solution process of solvents of different structures having different nematic-to-isotropic transition temperatures and different temperature ranges for their nematic and isotropic phases, the data for both phases of each of these nematogens were extrapolated to (or interpolated at) a common temperature. A temperature of 74 °C was chosen. The symbols γ_N^*, $\Delta_{soln}H_N^*$, and $\Delta_{soln}S_N^*$ refer to the results from extrapolations (or interpolations) of linear least-squares fits of ln γ_2^∞ against $1/T$ in the nematic phase to (or at) 74 °C. These results are given in Table 3. γ_I^*, $\Delta_{soln}H_I^*$, and $\Delta_{soln}S_I^*$ are similarly defined for the isotropic phase and are given in Table 4. The trends outlined below and illustrated in Figure 2 are independent (between 64 and 84 °C) of the temperature to which (or at which) the extrapolation (or interpolation) is made.

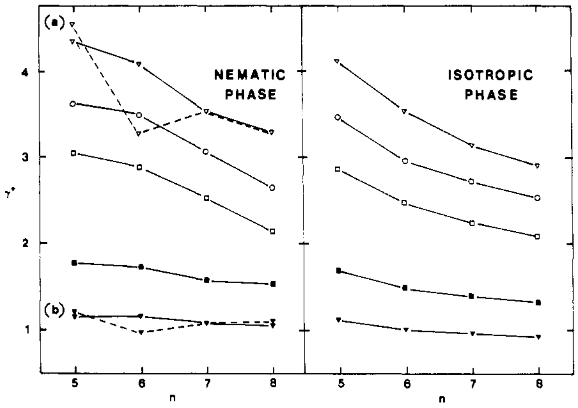

Figure 2. Solute activity coefficients from extrapolations to (or interpolations at) 74 °C in the nematic and isotropic phases against the number of carbon atoms, *n*, in the alkyloxy chain of the *p*-(*n*-alkyloxy)-*p*′-cyanobiphenyl, connected by continuous lines. The solutes are hexane (▽), *trans*-hex-3-ene (○), cyclohexane (□), *cis*-2-*trans*-4-hexadiene (■), and benzene (▼). The dashed lines a and b are for hexane (▽) and benzene (▼) in the nematic phases of the *p*-(*n*-alkyl)-*p*′-cyanobiphenyls.

Geneally, γ_N^* and γ_I^* decrease as the number of carbon atoms, *n*, in the alkyloxy tail of the solvent molecule increases from 5 to 8. This trend is similar to that previously encountered (*9*) for the RCB series of liquid crystals with the exception that the odd–even effect observed for the γ_N^* values in the RCB series, and attributed to the anisotropy of the polarizability of the RCB molecules, is suppressed for the γ_N^* values in the ROCB series. This is rationalized as follows. The additional oxygen atom on an alkyloxy tail would make its n correspond to $n + 1$ on an alkyl tail with the same number of carbon atoms. As a result one would expect the odd–even effect for the γ_N^* values in the ROCB's to be opposite that for the RCB's. Thus, for the same solute the γ_N^* values in *p*-(*n*-pentyl)-*p*′-cyanobiphenyl and *p*-(*n*-hexyl)-*p*′-cyanobiphenyl should be, respectively, higher and lower than the γ_N^* values in *p*-(*n*-pentyloxy)-*p*′-cyanobiphenyl and *p*-(*n*-hexyloxy)-*p*′-cyanobiphenyl. This is borne out by the experimental results for hexane and benzene in *p*-(*n*-pentyl)-*p*′-cyanobiphenyl and *p*-(*n*-hexyl)-*p*′-cyanobiphenyl (dashed lines a and b, respectively, in Figure 2) from ref 9. The suppression of the odd–even effect for the γ_N^* values in nematic ROCB's indicates that the dependence of the anisotropy of the polarizability of the ROCB molecule on the number of carbon atoms in the chain is appreciably diminished beyond $n = 6$. Support for this conclusion is provided by the near identity of the γ_N^* values in *p*-(*n*-heptyloxy)-*p*′-cyanobiphenyl and *p*-(*n*-heptyl)-*p*′-cyanobiphenyl and in *p*-(*n*-octyloxy)-*p*′-cyanobiphenyl and *p*-(*n*-octyl)-*p*′-cyanobiphenyl for hexane and benzene (Figure 2).

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