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A THERMODYNAMIC STUDY OF A LIQUID CRYSTAL AS A LIQUID PHASE IN GAS-LIQUID CHROMATOGRAPHY

I. A NEMATIC LIQUID CRYSTAL

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SUMMARY

The liquid crystal (*p*-ethoxyphenylazo)phenyl heptanoate (EPAPH) was found to be a suitable liquid phase for gas-liquid chromatography. Various thermodynamic properties have been calculated for solutes of several functionalities interacting with both the nematic and isotropic phases of EPAPH. The thermodynamic data and trends in values of activity coefficients for the solutes are discussed in relation to their structure and to the orientations of the liquid crystal.

INTRODUCTION

The existence of liquid crystals has been known for almost a century; however, their application to gas-liquid chromatography (GLC) is fairly recent. The distinct advantage of using liquid crystals as liquid phases in GLC is that in addition to the solvating power of the liquid phase, the solvent molecules have characteristic orientations when the solvent is heated to its mesomorphic region. Therefore, solvation and orientation effects of a liquid crystal as a liquid phase impart unique properties to the solvent.

If a material whose molecules are rod-shaped is dissolved in a liquid crystal, solute molecules will assume an orientation parallel with that of the solvent molecules. As the selectivity exhibited by many liquid phases is based on boiling point and specific solvent-solute interactions, the separation of positional isomers may be very difficult. The nematic mesophase of a number of liquid crystals offers specific affinity toward *para*-substituted benzenes and provides a solution to this problem.

The pioneering research on the use of liquid crystals as stationary phases in GLC primarily deals with the evaluation of nematogenic substances for use as liquid phases and the application of the nematic mesophase for the separation of positional isomers of xylene¹⁻⁵. Martire *et al.*⁶ used GLC to investigate thermodynamic aspects of dilute solutions involving liquid crystalline solvents and have studied solution

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effects of nematic, smectic and cholesteric textures using C₆-C₉ *n*-alkanes and xylenes as solutes. GLC is an attractive technique for investigating solvent properties, structure and solute behavior, because solvent-solute interactions occur at infinite dilution and neither disrupt nor destroy the long-range order of the liquid crystalline phase^{6,9}. NMR studies require much higher concentrations where liquid crystalline order can be altered⁷.

THERMODYNAMIC CONSIDERATIONS

The enthalpy of solution, $\Delta\bar{H}_2$, can be obtained from Littlewood *et al.*'s equation⁸:

$$\frac{d \ln V_g^0}{d(1/T)} = \frac{-\Delta\bar{H}_2}{R} \quad (1)$$

where V_g^0 is the specific retention volume, T (°K) is the column temperature and R is the universal gas constant (1.98 cal/mole · °K).

Solute activity coefficients at infinite dilution, γ_p can be determined from the expression¹⁰

$$\gamma_p = 1.70 \cdot 10^7 / M_1 P_2^0 V_g^0 \quad (2)$$

where M_1 and P_2^0 are the molecular weight of the solvent and the vapor pressure (mm Hg) of the pure solute vapor, respectively. Vapor pressures (P_2^0) can be estimated from the Antoine equation using the constants from Dreisbach's tabulation¹¹. Activity coefficients corrected for vapor-phase non-ideality, γ_f^∞ , can be calculated from the expression⁶

$$\ln \gamma_f^\infty = \ln \gamma_p - P_2^0 B_{22} / RT \quad (3)$$

in which B_{22} represents the second virial coefficient of the solute vapor. B_{22} values can be obtained from the corresponding equation of state of McGlashan and Potter¹²⁻¹⁵.

The thermodynamic relationship between the activity coefficient of a solute at infinite dilution (γ_f^∞) and its excess chemical potential (\bar{G}_2^E) is given by

$$\bar{G}_2^E = RT \ln \gamma_f^\infty \quad (4)$$

Making use of the relationship

$$\bar{G}_2^E = \bar{H}_2^E - T\bar{S}_2^E \quad (5)$$

eqn. 4 may be expressed as

$$\ln \gamma_f^\infty = \bar{H}_2^E / RT - \bar{S}_2^E / R \quad (6)$$

where \bar{H}_2^E and \bar{S}_2^E are the partial molar excess enthalpy and entropy at infinite dilution, respectively, and are determined from the slope and intercept of $\ln \gamma_f^\infty$ vs. $1/T$ sets of data.

With the reference state of the solute at infinite dilution in an ideal gaseous mixture⁶, $\Delta\bar{S}_2$ can be determined from the equation

$$\Delta\bar{S}_2 = -\Delta\bar{H}_2^{\text{vap.}}/T + \bar{S}_2^E \quad (7)$$

where $\Delta\bar{H}_2^{\text{vap.}}$ is the solute molar heat of vaporization. Alternatively, $\Delta\bar{H}_2$ can be determined from the expression

$$\Delta\bar{H}_2 = -\Delta\bar{H}_2^{\text{vap.}} + \bar{H}_2^E \quad (8)$$

The equation of Chow and Martire⁷:

$$\gamma_f^\infty = (1/z)(Q_u/Q_s)e^{-1} \quad (9)$$

where z = solute potential energy function and Q_u/Q_s represents the sum of the rotational and vibrational solute molecular partition functions, which account for the internal energy changes the solute experiences when transferred from the gaseous phase (g) to the solution phase (s), defines the activity coefficient at infinite dilution in terms of the three thermodynamic contributions to the solution process, namely, the potential, vibrational and rotational effects. As the solute translational energy change in the solution process can be assumed to be attributed to the potential energy of interaction on the real liquid mixture, a greater change in internal energy will increase γ_f^∞ and disfavor solution, while a greater change in translational energy will decrease γ_f^∞ and favor solution.

Eqn. 9 can also be written as

$$\Delta\bar{H}_2 = \Delta E_{\text{pot}} + \Delta E_{\text{r.v.}} - RT \quad (10)$$

where ΔE_{pot} and $\Delta E_{\text{r.v.}}$ refer to the translational and internal energy, respectively, of the solute undergoing solution.

In this investigation, the GLC behavior of various n -alkanes, aromatics and *cis-trans* isomers of 4-substituted cyclohexyl esters with a liquid crystalline liquid phase, (*p*-ethoxyphenylazo)phenyl heptanoate (EPAPH), was thermodynamically evaluated and compared in the nematic and isotropic phases of the crystal.

EXPERIMENTAL

Apparatus

The gas chromatograph employed was a Perkin-Elmer Model 900 equipped with dual hydrogen flame ionization detectors. Injection port and detector temperatures were maintained at 250°C. Column temperatures were read directly from the oven temperature control dial, and were accurate to $\pm 1/2^\circ\text{C}$. The hydrogen flow-rate was maintained at 30 ml/min throughout the study. Both helium (carrier gas) and air were passed through Type 5A molecular sieve moisture traps with flow-rates of 30 and 300 ml/min, respectively. Flow-rate measurements were made with a soap film flowmeter. A Leeds and Northrup 1-mV recorder was used to monitor elution with the chart speed established at 120 in./h.

Solvent

The liquid crystal (EPAPH) was obtained from Eastman-Kodak (Rochester, N.Y., U.S.A.). Liquid crystal transition temperatures were determined by a Perkin-Elmer DSC-1B differential scanning calorimeter. The temperature axis was calibrated with the following zone-refined materials of known Curie points: vanillin (80.0°C), acetanilide (114.3°C), and indium (156.5°C). Thermal decomposition data were obtained from a Perkin-Elmer TGS-1 thermobalance with a UU-1 temperature program control. The temperature axis was calibrated with the standards alumel (163°C) and nickel (354°C). A DSC profile of bulk EPAPH showed phase transitions at 60.1°C (solid–nematic) and at 120°C (nematic–isotropic). The phase transitions of EPAPH coated on solid support varied slightly from those of the bulk material, where the solid–nematic transition occurred at 60.2°C and the nematic–isotropic transition at 119.0°C.

Solutes

The solutes studied were *o*- and *p*-xylene, C₇–C₉ *n*-alkanes and four pairs of *cis*–*trans* 4-methylcyclohexyl alkanooates. All solutes except the 4-methylcyclohexyl alkanooates were of gas chromatographic reagent grade and were obtained from Matheson, Coleman & Bell (East Rutherford, N.J., U.S.A.). The 4-methylcyclohexyl alkanooates were synthesized according to the procedure outlined by Shriner *et al.*¹⁶. These solutes were chosen because they are readily available in high purity and can demonstrate the role of molecular geometry regarding solute–solvent interactions.

Preparation of columns

The stationary phase was prepared by coating 10% (w/w) of EPAPH on 80–100 mesh acid-washed Chromosorb W and packing it by vibration into 6-ft. sections of 1/8 in. O.D. aluminum tubing which had been previously rinsed with acetone and dried with a nitrogen flow. The columns were inserted into the gas chromatograph and conditioned overnight at 200°C.

Procedure

For each solute, retention volumes were measured in triplicate at 10°C intervals over the range 96–176°C. In the vicinity of 119°C (the nematic–isotropic transition temperature) retention volumes were determined at 1°C intervals in the range 115–123°C. Solutes were injected as vapors for the hydrocarbons studied with a microliter Hamilton syringe. A 0.1- μ l sample of the 4-substituted cyclohexyl esters was injected.

RESULTS AND DISCUSSION

The thermodynamic properties, enthalpy and entropy of solution and activity coefficients at infinite dilution are presented in Table I. The excess enthalpies and entropies of solution are listed in Table II for the solutes under consideration. In an isotropic solution process in GLC, a plot of $\log V''^0$ vs. $1/T$ (°K) is linear with the slope proportional to $\Delta\bar{H}_2$. Such plots obtained with liquid crystalline EPAPH as a liquid phase exhibited discontinuities and pronounced changes in slope at the nematic–isotropic transition temperature and indicate that solutes are entering an altered solvent environment at the transition temperature. The interaction of the solutes

TABLE I

THERMODYNAMIC QUANTITIES OF SOLUTES WITH EPAPH AS LIQUID PHASE

Units of ΔH_2 and ΔS_2 are kcal/mole and cal/mole·°K, respectively. N and I refer to the nematic and isotropic phases of EPAPH.

Solute	ΔH_2		ΔS_2		γ_f^∞	
	N	I	N	I	N(106°C)	I(121°C)
<i>n</i> -Heptane	-5.72	-6.17	-12.79	-12.31	0.977	0.628
<i>n</i> -Octane	-6.86	-7.83	-14.63	-14.39	1.917	1.018
<i>n</i> -Nonane	-7.49	-9.84	-17.54	-16.58	3.710	2.111
Benzene	-4.29	-6.62	-13.81	-12.67	0.333	0.228
Toluene	-5.22	-7.57	-15.59	-15.33	0.571	0.387
Ethylbenzene	-7.79	-8.35	-18.94	-18.32	0.956	0.658
<i>o</i> -Xylene	-5.53	-8.41	-19.37	-18.43	0.994	0.701
<i>p</i> -Xylene	-6.45	-8.67	-19.82	-18.66	0.891	0.643
<i>cis</i> -4-Methylcyclohexyl acetate	-5.26	-7.44	-24.22	-23.01	5.035	3.309
<i>trans</i> -4-Methylcyclohexyl acetate	-6.41	-8.28	-25.98	-24.09	4.263	2.769
<i>cis</i> -4-Methylcyclohexyl propionate	-6.07	-8.70	-26.53	-24.40	10.91	7.535
<i>trans</i> -4-Methylcyclohexyl propionate	-7.75	-9.65	-28.55	-25.04	9.390	5.810
<i>cis</i> -4-Methylcyclohexyl butyrate	-7.91	-10.08	-37.24	-30.51	615.75	315.5
<i>trans</i> -4-Methylcyclohexyl butyrate	-8.72	-11.30	-37.69	-31.55	447.15	231.1
<i>cis</i> -4-Methylcyclohexyl chloroacetate	—	-8.65	—	-29.22	—	7.745
<i>trans</i> -4-Methylcyclohexyl chloroacetate	—	-10.43	—	-29.92	—	5.680
<i>cis</i> -4-Methylcyclohexyl dichloroacetate	—	-8.98	—	-28.23	—	20.42
<i>trans</i> -4-Methylcyclohexyl dichloroacetate	—	-10.87	—	-29.15	—	7.520

with the nematic and isotropic phases of EPAPH will be discussed according to their functionality.

n-Alkanes

In the nematic phase of EPAPH, the ΔH_2 values follow the trend *n*-nonane > *n*-octane > *n*-heptane. The longer and more flexible molecules experience greater changes in rotational and vibrational motion upon dissolving in the anisotropic nematic environment. Also, because the longer molecules possess greater polarizabilities, stronger interaction with the solvent results by means of dispersion forces. Values of γ_f^∞ for the alkane molecules also increase with increasing chain length (Table I). As γ_f^∞ is directly dependent upon two competing effects which act in opposing directions (eqn. 9), the change in the vibrational and rotational motion of the solute more greatly influences the solution process than changes in the solute's translational motion. Greater entropy losses with increasing chain length are expected because greater changes in internal motion occur during the solution process.

TABLE II

PARTIAL MOLAR EXCESS ENTHALPIES AND ENTROPIES OF SOLUTION
 N and I represent the nematic and isotropic phases, respectively.

Solute	\bar{H}_2^E (kcal/mole)		\bar{S}_2^E (cal/mole $\cdot^\circ K$)	
	N	I	N	I
<i>n</i> -Heptane	3.19	2.26	9.44	6.76
<i>n</i> -Octane	3.90	2.74	8.97	5.87
<i>n</i> -Nonane	5.01	3.07	11.24	6.33
Benzene	3.24	2.46	8.95	6.86
Toluene	3.66	2.56	9.51	5.94
Ethylbenzene	4.77	3.89	7.78	4.61
<i>o</i> -Xylene	5.03	4.11	6.05	5.01
<i>p</i> -Xylene	4.98	4.08	7.50	4.99
<i>cis</i> -4-Methylcyclohexyl acetate	9.33	6.52	10.12	6.45
<i>trans</i> -4-Methylcyclohexyl acetate	7.81	5.50	8.36	5.37
<i>cis</i> -4-Methylcyclohexyl propionate	9.80	7.25	10.03	6.64
<i>trans</i> -4-Methylcyclohexyl propionate	8.41	6.51	8.01	6.08
<i>cis</i> -4-Methylcyclohexyl butyrate	13.64	10.71	11.13	7.36
<i>trans</i> -4-Methylcyclohexyl butyrate	12.77	9.66	10.31	6.32
<i>cis</i> -4-Methylcyclohexyl chloroacetate	—	5.96	—	4.68
<i>trans</i> -4-Methylcyclohexyl chloroacetate	—	5.51	—	3.97
<i>cis</i> -4-Methylcyclohexyl dichloroacetate	—	9.45	—	6.48
<i>trans</i> -4-Methylcyclohexyl dichloroacetate	—	6.73	—	5.56

With the isotropic phase of EPAPH one finds the same trend of increasing $\Delta\bar{H}_2$ and γ_f^∞ with increasing chain length. However, the values in the isotropic phase of EPAPH are larger than those in the nematic phase, indicating that a larger solute potential energy effect and smaller solute rotational and vibrational changes prevail in the isotropic state. Because solute-solvent interactions decrease with increasing temperature owing to increased thermal motion of the molecules and increased intermolecular separation, non-mesomorphic solutes are more compatible with the higher temperature isotropic state. Thus, as the solvent molecules attain a more isotropic distribution, solute geometry and orientation become less critical, that is, the solute need not lose as much rotational and vibrational motion to gain a strong potential energy of interaction. The above argument also explains the occurrence of smaller γ_f^∞ values for the isotropic state.

Aromatics

In the isotropic and nematic textures of EPAPH, $\Delta\bar{H}_2$ and γ_f^∞ data follow the pattern benzene < toluene < ethylbenzene. The thermodynamic interpretation of these results is similar to that presented in the previous section dealing with *n*-alkanes. An interesting result is the obvious decrease in $\Delta\bar{H}_2$ values with the aromatics as compared with the *n*-alkanes. As solution is favored by the least loss in entropy, as is the case with more rigid and rod-like aromatics, lower $\Delta\bar{H}_2$, $\Delta\bar{S}_2$ and γ_f^∞ values are observed. In the nematic texture of EPAPH, the heat of solution of *p*-xylene is greater than that of *o*-xylene. As these isomers are rigid, little vibrational energy loss is to be expected upon solution, and therefore thermodynamic values follow the expected trend of rotational energy losses. Although *o*-xylene is capable of some dipolar inter-

action with the solvent, *p*-xylene offers geometrically a more favorable position for dispersion interaction with the solvent. Solute entropy losses follow the same trend as $\Delta\bar{H}_2$ values.

Alkylcyclohexyl esters

This class of compounds was examined to observe solvent behavior with pairs of *cis*-*trans* isomers. Several conclusions can be made regarding the behavior of these solutes as the length of the ester substituent on the cyclohexyl ring increases by the incorporation of successive methylene groups. Enthalpies and activity coefficients follow the same trend observed with the *n*-alkanes within each separate set of *cis*- and *trans*-isomers. With every pair of isomers, the more linear *trans*-isomer has the higher $\Delta\bar{H}_2$ and lower γ_f^∞ values. The *trans*-isomer experienced the smaller entropy loss upon solution in both mesophases. The fact that the *trans*-isomer interacts to a greater extent with the liquid crystal than the *cis*-structure is verified by the elution order of the two isomers, in which the *trans*-isomer is eluted after the *cis*-isomer. This longer elution time is a result of the more linear structure of the molecule, *i.e.*, more rod-like and more spatially suitable for dispersive interaction, as both isomers have nearly identical boiling points and vapor pressures.

The chloro derivatives of the alkylcyclohexyl alkanates have larger $\Delta\bar{H}_2$ values than the corresponding unchlorinated species. In terms of the magnitude of thermodynamic values and elution times, *cis*-4-methylcyclohexyl propionate is comparable to *cis*-4-methylcyclohexyl chloroacetate. In the isotropic region, the difference in $\Delta\bar{H}_2$ values for a given chlorinated *cis*-*trans* pair is greater than the corresponding unchlorinated isomeric pair. One can assume that substitution within the ester group further enhances structural differences of the *cis*- and *trans*-isomers; that is, an enhancement in the linearity of the *trans*-isomer or a decrease in the linearity of the *cis*-isomer. Thermodynamic information for the chloro derivatives was unattainable in nematic phase owing to the occurrence of very broad elution curves below the transition temperature of 119°C. Unusually high activity coefficients were obtained with this class of compounds, especially when ester groups become long or bulky. Activity coefficients in the order of 100-1000 have been reported and accounted for by Martire¹⁷.

Table II reflects the fact that the partial molar enthalpy and entropy for a given solute are greater in the nematic region than in the isotropic phase. This difference corresponds to the enhanced difficulty in the dissolution of a solute in the more ordered nematic texture. The solution process is highly favored in the nematic phase as manifested by the correspondingly greater \bar{S}_2^E values but the process is controlled by the enthalpy effects; greater activity coefficients at infinite dilution are also observed in the nematic phase.

CONCLUSIONS

The molecular behavior of a number of solutes has been described in the anisotropic nematic phase utilizing thermodynamic data obtained from GLC measurements. It has been shown that the three solution effects (potential, vibrational and rotational) allow for consistent interpretation of solute enthalpies, activity coefficients and, indirectly, entropies of solution. The thermodynamic data illustrate that the

solutes chosen encounter molecular alteration of the liquid crystal at its transition temperature. We feel that studies of this nature can provide valuable supporting data for spectroscopic investigations of solute-solvent interactions.

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