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

II. A CHOLESTERIC LIQUID CRYSTAL*

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SUMMARY

Gas–liquid chromatography is utilized for the determination of thermodynamic solution parameters for various organic solutes at infinite dilution in the meso- and isotropic phases of cholesteryl palmitate. The thermodynamic data and trends in values of the activity coefficients for the solutes are discussed in relation to their structure and to the orientations of the liquid crystal.

INTRODUCTION

Light scattering and X-ray measurements have established that some organic compounds behave as ordered fluids within a well defined temperature region between the crystalline solid and isotropic liquid states. In particular, liquid molecular species of elongated structure in the presence of adequate forces of attraction will exhibit the formation of swarms of parallel-lying molecules. Such phases behave as uniaxial crystals with polarized light and are called liquid crystals. Upon heating a liquid crystal from its solid phase to the normal isotropic liquid, a direct solid to liquid transition does not occur; but rather it is possible to observe one or more stable intermediate phase transformations often referred to as mesophases.

The existence of liquid crystals has been known for almost a century; however, their application to gas chromatography (GC) is fairly recent. The distinct advantage of using liquid crystals as liquid phases in gas–liquid chromatography (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 mesomor-

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phic 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 to that of the solvent molecules. Since 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 separation of isomeric disubstituted benzenes on liquid crystalline stationary phases has been well documented[1–5] and, in the case of *meta–para* pairs, the *para* isomer is preferentially dissolved and retained. Kelker and von Schivizhoffen have published a review on the use of liquid crystals in GC[6]. Martire *et al.*[7], and Jeknavorian and Barry[8] have employed GLC to investigate thermodynamic parameters of dilute solutions involving nematic liquid crystalline solvents. GLC is an attractive technique for studying solution thermodynamics because solute–solvent interactions occur at infinite dilution where molecular ordering is not disrupted.

THERMODYNAMIC CONSIDERATIONS

Enthalpy of solution, $\Delta\bar{H}_2$, may be determined from the equation of Littlewood *et al.*[9], where V_g^0 is the specific retention volume, T represents the column

$$\frac{\mathrm{d}\ln V_g^0}{\mathrm{d}\,\frac{1}{T}} = -\frac{\Delta\bar{H}_2}{R} \tag{1}$$

temperature in °K, and R is the universal gas constant, 1.98 cal/mole °K.

Solute activity coefficients at infinite dilution, γ_p may be calculated from the expression[10]

$$\gamma_p = \frac{1.70 \times 10^7}{M_1 P_2^0 V_g^0} \tag{2}$$

where M_1 and P_2^0 refer to the molecular weight of the solvent and vapor pressure of pure solute vapor in mmHg, respectively. Vapor pressures (P_2^0) may be estimated from the Antoine equation using the constants from Dreisbach's tabulation[11]. Activity coefficients, corrected for vapor phase nonideality, γ_f^∞, can be obtained from the expression[7]

$$\ln\gamma_f^\infty = \ln\gamma_p - \frac{P_2^0 B_{22}}{RT} \tag{3}$$

in which B_{22} represents the second virial coefficient of the solute vapor. B_{22} values may be obtained from the corresponding equation of state of McGlashan and Potter[12].

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

$$\bar{G}_2^E = RT\ln\gamma_f^\infty \tag{4}$$

Making use of the relations

$$\bar{G}_2^{\mathrm{E}} = \bar{H}_2^{\mathrm{E}} - T\bar{S}_2^{\mathrm{E}} \tag{5}$$

eqn. 4 may be expressed as

$$\ln\gamma_f^{\infty} = \frac{\bar{H}_2^{\mathrm{E}}}{RT} - \frac{\bar{S}_2^{\mathrm{E}}}{R} \tag{6}$$

where $\bar{H}_2^{\mathrm{E}}$ and $\bar{S}_2^{\mathrm{E}}$ 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 mixture[7], $\Delta\bar{S}_2$ may be determined from the equation

$$\Delta\bar{S}_2 = \frac{-\Delta\bar{H}_2^{\mathrm{Vap.}}}{T} + \bar{S}_2^{\mathrm{E}} \tag{7}$$

where $\Delta\bar{H}_2^{\mathrm{Vap.}}$ is the solute molar heat of vaporization. Alternatively. $\Delta\bar{H}_2$ may be determined from the expression

$$\Delta\bar{H}_2 = \Delta\bar{H}_2^{\mathrm{Vap.}} + \bar{H}_2^{\mathrm{E}} \tag{8}$$

The equation of Chow and Martire[13]

$$\gamma_f^{\infty} = \frac{1}{z} \cdot \frac{Q_g}{Q_s} \cdot \mathrm{e}^{-1} \tag{9}$$

(where z = solute potential energy function and the term Q_g/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. Since the solute translational energy change in the solution process may 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. 8 may also be written as

$$\Delta\bar{H}_2 = \Delta E_{\mathrm{pot}} + \Delta E_{\mathrm{r.v.}} - RT \tag{10}$$

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

In this investigation, the GC behavior of various *n*-alkanes, aromatics and *cis–trans* isomers of 4-substituted cyclohexyl esters with a liquid crystalline liquid phase, cholesteryl palmitate, was thermodynamically evaluated in the smectic, cholesteric 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 and has been previously described[8]. 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 ±0.5 °C. 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 ml/min and 300 ml/min, respectively. Flow-rate measurements were determined 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, cholesteryl palmitate (CP), was obtained from Eastman-Kodak (Rochester, N.Y., U.S.A.). Liquid crystal transition temperatures were determined by a Perkin-Elmer DSC-1 B differential scanning calorimeter (DSC). 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 CP showed phase transitions at 77.6 °C (solid–smectic), at 82.4 °C (smectic–cholesteric), and at 147 °C (cholesteric–isotropic). The phase transitions of CP coated on solid support varied slightly from those of the bulk material, where the phase transitions occurred at 77.9, 81.8, and 146 °C, respectively.

Solutes

All solutes, except the 4-methylcyclohexyl alkanoates, were GC reagent grade and were obtained from Matheson, Coleman and Bell (East Rutherford, N.J., U.S.A.). The 4-methylcyclohexyl alkanoates were synthesized according to the procedure outlined by Shriner *et al.*[14]. These solutes were chosen because they are readily available in high purity and can demonstrate the role of molecular geometry regarding solute–solvent interaction.

Preparation of columns

The stationary phase was prepared by coating CP 10% by weight on 80–100 mesh, acid-washed, Chromosorb W and packed 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 76–176 °C. In the vicinity of mesophase transition temperatures retention volumes were determined at 1 °C intervals starting from 4 °C about the transition temperature. Solutes were injected as vapors for the hydrocarbons studied with a microliter Hamilton syringe. A 0.1-μl sample of the 4-substituted cyclohexyl esters was injected.

RESULTS AND DISCUSSION

The thermodynamic properties, enthalpy and entropy of solution are presented in Table I and activity coefficients at infinite dilution are found in Table II. Also, the excess enthalpies and entropies of solution for the solutes under consideration are listed in Table III. In an isotropic solution process in GLC, a plot of log V_g^0 *vs.* $1/T$ (°K) is linear with the slope proportional to $\Delta\bar{H}_2$. Such plots obtained with liquid crystalline CP as a liquid phase exhibited discontinuities and pronounced changes in slope at the smectic–cholesteric and cholesteric–isotropic transition temperatures and indicate that solutes are entering an altered solvent environment at the transition temperatures. The interaction of the solutes with the mesophases of CP will be discussed according to their functionality.

TABLE I

THERMODYNAMIC QUANTITIES OF SOLUTES WITH CP AS LIQUID PHASE

Sm, C and I refer to the smectic, cholesteric and isotropic phases of CP, respectively.

Solutes	$\Delta\bar{H}_2$ *(kcal/mole)*			$\Delta\bar{S}_2$ *(cal/mole-deg.)*		
	Sm	*C*	*I*	*Sm*	*C*	*I*
n-Heptane	−3.24	−5.94	−5.45	+19.23	−2.69	−9.78
n-Octane	−4.89	−9.83	−7.00	+23.76	−8.90	−11.04
n-Nonane	−5.16	−12.16	−8.27	+17.60	−14.71	−11.77
Benzene	−4.09	−6.20	−4.52	+24.77	−6.91	−15.68
Toluene	−4.79	−7.37	−5.10	+28.89	−7.47	−9.84
Ethylbenzene	−5.40	−9.17	−6.06	+23.45	−9.02	−11.55
o-Xylene	−5.43	−10.04	−7.64	+24.36	−8.78	−12.69
p-Xylene	−6.66	−10.47	−7.99	+23.33	−8.21	−12.98
m-Xylene	−6.15	−10.09	−7.95	+22.01	−8.15	−12.93
cis-4-Methylcyclohexyl acetate	—	−7.61	−7.70	—	−25.65	−21.97
trans-4-Methylcyclohexyl acetate	—	−7.83	−9.03	—	−25.71	−23.55
cis-4-Methylcyclohexyl propionate	—	−7.94	−8.46	—	−27.07	−23.45
trans-4-Methylcyclohexyl propionate	—	−7.60	−9.16	—	−25.84	−23.91
cis-4-Methylcyclohexyl butyrate	—	−6.67	−10.51	—	−35.21	−29.37
trans-4-Methylcyclohexyl butyrate	—	−7.87	−11.40	—	−35.62	−30.13
cis-4-Methylcyclohexyl chloroacetate	—	−7.68	−9.12	—	−25.47	−25.19
trans-4-Methylcyclohexyl chloroacetate	—	−7.65	−9.22	—	−26.16	−26.58
cis-4-Methylcyclohexyl dichloroacetate	—	—	−10.82	—	—	−27.19
trans-4-Methylcyclohexyl dichloroacetate	—	—	−11.60	—	—	−27.79

TABLE II

ACTIVITY COEFFICIENTS AT INFINITE DILUTION

Sm, C and I refer to the smectic, cholesteric and isotropic phases of CP, respectively.

Solute	γ_s^{∞}		
	Sm (80°C)	*C (85°C)*	*I (150°C)*
n-Heptane	0.840	0.750	0.260
n-Octane	1.500	1.420	0.483
n-Nonane	2.232	2.385	0.904
Benzene	0.342	0.343	0.136
Toluene	0.590	0.585	0.235
Ethylbenzene	0.830	0.830	0.418
o-Xylene	0.775	0.770	0.480
p-Xylene	0.750	0.770	0.413
m-Xylene	0.755	0.795	0.401
cis-4-Methylcyclohexyl acetate	—	8.060	2.537
trans-4-Methylcyclohexyl acetate	—	6.620	2.142
cis-4-Methylcyclohexyl propionate	—	10.64	4.374
trans-4-Methylcyclohexyl propionate	—	8.540	3.208
cis-4-Methylcyclohexyl butyrate	—	1193	117.8
trans-4-Methylcyclohexyl butyrate	—	609.7	98.85
cis-4-Methylcyclohexyl chloroacetate	—	41.71	8.110
trans-4-Methylcyclohexyl chloroacetate	—	37.74	6.025
cis-4-Methylcyclohexyl dichloroacetate	—	—	7.020
trans-4-Methylcyclohexyl dichloroacetate	—	—	6.170

TABLE III

PARTIAL MOLAR EXCESS ENTHALPIES AND ENTROPIES OF SOLUTION

Sm, C and I refer to the smectic, cholesteric and isotropic phases of CP, respectively.

Solutes	$\bar{H}_2^E$ *(kcal/mole)*			$\bar{S}_2^E$ *(cal/mole-deg.)*		
	Sm	*C*	*I*	*Sm*	*C*	*I*
n-Heptane	1.80	5.07	2.57	2.05	7.48	6.72
n-Octane	0.04	5.27	2.89	1.16	12.27	7.09
n-Nonane	−4.20	4.34	3.47	7.54	10.49	7.55
Benzene	−1.93	4.32	3.23	2.38	12.63	8.33
Toluene	−3.05	5.37	3.19	5.15	9.80	8.27
Ethylbenzene	1.12	6.84	3.17	2.14	10.21	8.66
o-Xylene	0.99	8.56	3.40	1.50	9.69	8.98
p-Xylene	−4.32	8.99	3.50	6.61	10.14	8.46
m-Xylene	−1.61	9.43	2.98	3.66	10.57	8.44
cis-4-Methylcyclohexyl acetate	—	6.69	5.92	—	6.34	5.47
trans-4-Methylcyclohexyl acetate	—	6.61	4.65	—	6.41	3.89
cis-4-Methylcyclohexyl propionate	—	6.69	6.61	—	6.06	5.76
trans-4-Methylcyclohexyl propionate	—	7.44	5.98	—	7.29	5.30
cis-4-Methylcyclohexyl butyrate	—	14.37	9.48	—	11.87	5.90
trans-4-Methylcyclohexyl butyrate	—	11.56	8.67	—	8.66	5.14
cis-4-Methylcyclohexyl chloroacetate	—	10.81	7.66	—	10.33	6.38
trans-4-Methylcyclohexyl chloroacetate	—	11.23	6.28	—	11.02	4.99
cis-4-Methylcyclohexyl dichloroacetate	—	—	6.69	—	—	5.21
trans-4-Methylcyclohexyl dichloroacetate	—	—	5.90	—	—	4.55

n-Alkanes

In the anisotropic phases of CP, the $\Delta \bar{H}_2$ values follow the trend: *n*-nonane > *n*-octane > *n*-heptane > *n*-hexane. The longer and more flexible molecules experience greater changes in rotational and vibrational motion upon dissolving in the anisotropic cholesteric 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). Since γ_f^∞ is directly dependent upon two competing effects which act in opposing directions (eqn. 9), the changes in the vibrational and rotational motions of the solute more greatly influence the solution process than changes in the solute's translational motion. Greater entropy losses with increasing chain length are usually expected because greater changes in internal motion occur during the solution process.

With the isotropic phase of CP 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 CP are smaller than those in the mesophases, indicating that a larger solute potential energy effect and smaller solute rotational and vibrational changes possibly prevail in the cholesteric texture.

Aromatics

In the isotropic and mesophases of CP, $\Delta \bar{H}_2$ 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 to the *n*-alkanes. Since solution is favored by the least loss in entropy, as is the case with more rigid and rod-like aromatics, low $\Delta \bar{H}_2$, $\Delta \bar{S}_2$, and γ_f^∞ are observed. In all the phases of CP, the heat of solution of *p*-xylene is greater than that of the other xylenes. Since these isomers are rigid, little vibrational energy loss is to be expected upon solution, therefore, thermodynamic values follow the expected trend of rotational energy loses. Though *o*- and *m*-xylene are capable of some dipolar interaction with the solvent, *p*-xylene offers geometrially a more favorable position for dispersion interaction with the solvent.

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^∞ value in the isotropic phase. The solution process in the cholesteric texture is quite complicated as Martire *et al.* have also reported[7]. 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*. This longer elution time is a resultant of the more linear structure of the molecule, *i.e.* more rodlike and more spatially suitable for dispersive interaction since both isomers have nearly identical boiling points and vapor pressures.

The chloro derivatives of the alkylcyclohexyl alkanoates have larger $\Delta \bar{H}_2$ values than the corresponding unchlorinated species. In terms of the magnitude of thermodynamic values and elution times, the *trans*-4-methylcyclohexyl propionate is comparable to the *trans*-4-methylcyclohexyl chloroacetate. 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 smectic phase due to the occurrence of very broad elution curves below the transition temperature of 78 °C. Unusually high activity coefficients were obtained with this class of compounds, especially when ester groups became long or bulky. Activity coefficients in the order of 100–1000 have been reported and accounted for by Martire[15].

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

From eqn. 10, the enthalpy of solution, ΔH_2^{soln}, is expressed in terms of two thermodynamic solution parameters: ΔE_{pot}, which represents the change in translational energy which a solute undergoes during the solution process, and $\Delta E_{r.v.}$, which represents the combined change in solute rotational and vibrational motions. Both solute energy changes act in opposite directions in influencing the magnitude of γ_f^∞. A linear relationship between ΔH_2^{soln} and ΔS_2^{soln} exists for homologous series of solutes in all phases of CP. Such linear correlations have been observed previously[6]. The liquid crystal solvent system employed in this investigation qualifies as one of Bell's[16] general catagories where the molecular size ratio of solute to solvent is very small, and the same type of intermolecular forces operate for a solute series. Correlations are more clearly manifested when solute molecules possess similar characteristics; this accounts for the separate correlations for each homologous series. The slopes and intercepts for the linear relationships between ΔH_2^{soln} and ΔS_2^{soln} for the isotropic and cholesteric phases of CP appear in Table IV.

Excess enthalpies, $\bar{H}_2^E$, presented in Table III, are larger on the cholesteric texture of CP than in the isotropic phase. Larger positive enthalpies in the anisotropic phases of CP are indicative of weaker specific solute–solvent interactions and occur

TABLE IV

SLOPES AND INTERCEPTS OF THE LINEAR CORRELATION BETWEEN ΔH_2^{soln} AND ΔS_2^{soln} FOR SEVERAL HOMOLOGOUS SERIES IN CP WHERE $\Delta H_2^{soln} = b + a\Delta S_2^{soln}$

	Isotropic		*Cholesteric*	
	a	*b*	*a*	*b*
Alkanes	0.71	−2.7	4.58	−0.55
Aromatics	0.52	−0.73	1.38	−3.17
o,m,p-Xylene	0.36	−2.60	−0.35	13.1

when solution components are energetically dissimilar, *i.e.* there is a greater tendency for solute–solvent interaction. This trend in the excess enthalpy values emphasizes the difficulty in dissolving solute molecules in a highly ordered structure. However, these positive excess enthalpies are accompanied by positive excess entropies. These counteracting excess enthalpy and entropy effects are responsible for the reasonable solubility exhibited by solute molecules in all phase of CP.

CONCLUSIONS

The molecular behavior of a number of solutes has been described in the anisotropic cholesteric phase utilizing thermodynamic data obtained from GLC measurements. 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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