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Thermodynamics of Solutions with Liquid Crystal Solvents. VI. The Effect of Organic Solutes on the Selective Reflection of Visible Light by Cholesteric Mixtures†

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Abstract—Solute thermodynamic data have been obtained by gas–liquid chromatography for dilute solutions of a variety of organic solutes in cholesteric mixtures comprised of cholesteryl chloride, cholesteryl oleyl carbonate, and cholesteryl nonanoate. These data are analyzed in light of a previous study by J. L. Fergason on the same cholesteric mixtures and solutes, where shifts in the wavelength of maximum reflectance of the cholesteric solvents were induced by small amounts of solute. Correlations between the wavelength shifts and thermodynamic data are found for the chlorinated methanes. Non-random mixing may explain why correlations are not observed between the wavelength shifts and thermodynamic data for dissimilar solutes. A comparison of wavelength shift data normalized to equal mole fractions of dissolved solute reveals that hydrogen bonding, dipolar interactions, and small molecular size favor large shifts to longer wavelengths of reflected light.

1. Introduction

A recent study⁽¹⁾ has been made by Fergason on the shifts in the wavelength of maximum reflectance of cholesteric mixtures induced by small amounts of organic vapors. The mixtures he used selectively reflected green light at 18 °C. Thus, when some of the organic vapor (the solute) dissolved in the liquid crystal (the solvent), it was possible to detect either red or blue shifts, depending on how the solute affected the cholesteric structure. The reflectance measurements

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† Paper V in this series is Ref. 8.

were made by injecting increments of solute into an evacuated cell containing a cholesteric film and monitoring the wavelength change using a monochromator-photocell light system.

Mixtures of cholesteryl chloride (CCl) with cholesteryl oleyl carbonate (OCC) and cholesteryl nonanoate (CN) gave linear plots of wavelength of maximum reflectance (λ_{max}) *versus* the number of moles of injected solute.(1) Furthermore, the cell volume (15 liters) was large enough so that the number of moles of gaseous solute above the solution was approximately equal to the moles of injected solute. Fergason's results(1) suggested he was working with dilute solutions which obeyed Henry's law. To substantiate that the wavelength shifts resulted from bulk solution effects, Fergason(1) used thick films to show that the color changes not only occurred on the surface, but also in depth.

Different solutes induced different wavelength shifts in a given cholesteric mixture.(1) A thermodynamic investigation of the solute–solvent systems studied by Fergason could provide information which might explain why some solutes affect the cholesteric structure more than others. Therefore, a study was undertaken here using gas–liquid chromatography (GLC) to determine if a relationship exists between the wavelength shifts and the enthalpy or entropy changes that solutes undergo when dissolving in the cholesteric mixtures. In addition, the solute activity coefficients, which are quickly obtainable by GLC and valid for Henry's law region, can be used to normalize Fergason's response data to the liquid phase concentration of the solute in the liquid crystal. This normalized data can be used to assess how various solute properties affect the cholesteric structure.

2. Experimental

INSTRUMENTATION

A dual-column GLC apparatus, utilizing a Perkin–Elmer 880 flame ionization detector and a 25 liter water bath to maintain the column temperature, was employed. The bath temperature was easily controlled to within ±0.05° at near-ambient and sub-ambient temperatures. A Neslab PBC-2 immersion cooler and a Vycor 500 watt immersion heater were adjusted to give a bath temperature just below the desired temperature. The final adjustment to the desired temperature was accomplished with a Vycor 250 watt immersion heater operated through a Fisher transistor relay and thermoregulator. The temperature was read off a Brooklyn −35 to 25 °C thermometer. Hamilton injection ports (Model No. 86800), maintained at about 200 °C, were used. A Sargent–Welch Model SRG recorder was used to trace the sample elution.

Helium was used as the carrier gas. The column inlet pressure was regulated using a Negretti–Zambra precision pressure regulator (Model R/182), and was measured to ±0.05 p.s.i. with a calibrated USG pressure gauge (range, 0–30 p.s.i.). The outlet pressure was determined from barometric readings. The carrier gas flow rate was measured at room temperature with a soap-film flowmeter placed at the detector outlet. The flow rates (range, 30–100 ml min^{-1}) were chosen to give convenient elution times and reasonable column efficiencies.

THE SOLVENTS

The compositions by weight per cent of the two cholesteric mixtures used as liquid phases were (a) 24.0% CCl, 45.6% OCC, 30.4% CN and (b) 26.0% CCl, 44.4% OCC, 29.6% CN. A liquid phase comprised only of OCC was studied for purposes of comparison. The CCl and CN were obtained from Aldrich Chemical Co. and the OCC was obtained from ILIXCO,

The CCl was recrystallized three times in an equal volume mixture of isoamyl alcohol and methanol. The recrystallized CCl was determined by a differential scanning calorimetric procedure(2) to have a purity of 99.4%. The solid-isotropic transition temperature of CCl was determined by differential scanning calorimetry (DSC) to be 94.8 °C using a Perkin–Elmer DSC-1B unit. The CN, recrystallized twice in acetone, was found by DSC to have its crystal–cholesteric and cholesteric–isotropic transition temperatures at 78.3 and 92.0 °C, respectively. These transition temperatures correspond closely to those of high purity CN determined by changes in third harmonic generation intensities.(3) The OCC was purified by extracting impurities from the isotropic phase at about 50 °C with methanol until a DSC scan showed transition temperatures at 17°

and 34 °C. These correspond to the smectic–cholesteric and cholesteric–isotropic transitions. Dixon and Scala[(4)] found differential thermal analysis endotherms for OCC at 17.5 and 33 °C.

The Solutes

The organic solutes chosen for this study include the hydrocarbons, halocarbons, ketones, alcohols, and esters investigated by Fergason.[(1)] For each solute, the pure component physical properties needed in the calculation of the thermodynamic solution properties are available, or can be accurately estimated. Since the chromatograms of the solutes showed at most only trace impurities, they were used without further purification.

Infinite dilution activity coefficients and partial molar solution quantities were obtained for chloroform, carbon tetrachloride, dichloromethane, cyclohexane, benzene, cyclohexene, and *n*-hexane. Data were collected in the temperature range from 14 to 24 °C in 2° intervals. For the rest of the solutes, infinite dilution activity coefficients were determined at 18 °C in the 24% CCl mixture.

Preparation of Columns

Copper tubing ($\frac{1}{4}$ in. o.d.) was used for the columns. The packings were prepared by coating 60/80 or 80/100 mesh acid-washed, DMCS treated Chromosorb W (Johns-Manville) with the solvent compounds. This coating was accomplished using a Rinco rotoevaporator with either petroleum ether or dichloromethane as the solvent. The coated material was resieved to the appropriate mesh specification to assure that the uniformity of particle size was not destroyed in the coating process. The difference in weight before and after the packing addition was a measure of the amount of packing in the column. The amount of liquid crystal in the packing was determined gravimetrically by burning off the organic coating in a crucible. Column composition data are given in Table 1.

Measurement of Retention Times

Retention times were measured as the distance between the methane and solute peaks and converted to time using the recorder chart speed. In most cases, the solute samples injected with a Hamilton 10 μl syringe were so small that the retention times were

TABLE 1 Composition of Columns

Stationary liquid(a)	Liquid phase molecular weight(b)	Liquid phase weight %	Liquid phase (*g*)
26.0% CCl, 44.4% OCC, 29.6% CN	540.0	10.33	0.4005
24.0% CCl, 45.6% OCC, 30.4% CN	544.4	13.48	0.7439
OCC	681.1	14.21	0.7594
24.0% CCl, 45.6% OCC, 30.4% CN	544.4	16.20	0.3263
24.0% CCl, 45.6% OCC, 30.4% CN	544.4	16.20	0.8391

(a) Weight percentages are given.

(b) Number average molecular weights are given for the mixtures.

independent of sample size and the systems followed Henry's law. However, because of solid support effects exhibited by the alcohols, peak maximum retention times were extrapolated to zero sample size according to a previously described method.(5) The solvent loadings (10–16%) were high enough to give surface-to-volume ratios where surface effects at the gas–liquid crystal interface are usually negligible.(6,7) In a previous study of cholesteric liquid crystals and a cholesteric mixture,(8) surface effects were found to be negligible at both the solid support–liquid crystal and liquid crystal–carrier gas interfaces. In this study, solute specific retention volumes (at the same temperature) were independent of the solvent loading, indicating that the measured retention times resulted only from bulk solution behavior.

3. Results

Specific retention volumes ($V_g{}^0$) were calculated using the expression(9)

$$V_g{}^0 = 273.15(P_0 - P_w)t_r F_0 j / P_0 T_a g_1 \tag{1}$$

where P_0 is the column outlet pressure, P_w is the vapor pressure of water at the absolute ambient temperature T_a, t_r is the retention time, j is a compressibility factor, and g_1 is the mass of stationary liquid. For about two weeks of column use, the $V_g{}^0$ values were reproducible to within ± 1%. A significant change in the $V_g{}^0$ values after this time indicated decomposition of the cholesteric liquid phases, and, therefore, several columns were prepared in the course of this experimentation.

Solute activity coefficients at infinite dilution (γ_p) uncorrected for vapor phase non-ideality were computed using the expression(10)

$$\gamma_p = 1.704 \times 10^7 / M_1 p_2{}^0 V_g{}^0 \tag{2}$$

where M_1 is the solvent molecular weight and $p_2{}^0$ (mm Hg) is the vapor pressure of the pure solute. For the solvent mixtures, number average molecular weights were used. Solute vapor pressures were calculated using the Antoine equation and available constants(11) or by using the linear equations determined by least squares fits of $\log p_2{}^0$ vs. $1/T$ °K using data found in a compilation by Stull.(12)

Activity coefficients corrected for vapor phase non-ideality (γ_f) were determined from the expression[13]

$$\ln \gamma_f = \ln \gamma_p - p_2{}^0 \mathrm{B}_{22}/RT \tag{3}$$

where B_{22} is the second virial coefficient of the pure solute vapor at the absolute column temperature T. Second virial coefficients were calculated from the corresponding states equation of McGlashan and Potter[14,15]

$$\begin{aligned}\mathrm{B}_{22}/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 \\ - 0.0375(n_c - 1)(T_c/T)^{4.5}\end{aligned} \tag{4}$$

where T_c and V_c are the solute critical temperature (°K) and critical volume (ml mol^{-1}), and n_c is the effective carbon number. Critical constants were obtained from available compilations.[11,16,17] The effective carbon numbers of the halomethanes were determined by counting the carbon atom as one unit and each chlorine atom as one unit. The resulting carbon numbers gave B_{22} values which are very close to empirical values. For example, the B_{22} value we calculated for dichloromethane at 18 °C (-841 ml mol^{-1}) compares favorably to a value determined by an empirical equation[18] (-854 ml mol^{-1}).

The effective carbon numbers of the esters, ketones, and alcohols were determined by using experimental B_{22} values where available[19,20,21] to calculate the n_c values which fit Eq. (4). From these results, the effective carbon numbers of the esters, ketones, and alcohols were estimated, respectively, to be 10, 16, and 28. These relatively high n_c values (compared to hydrocarbons of nearly equal size) reflect associations and polar interactions in the gas phase.

The solute partial molar excess enthalpies ($\bar{H}_2{}^E$) and excess entropies ($\bar{S}_2{}^E$) at infinite dilution were determined from the slopes and intercepts of least squares linear fits for $\ln \gamma_f$ vs. $1/T$ °K sets of data according to the relationship[13]

$$\ln \gamma_f = \bar{H}_2{}^E/RT - \bar{S}_2{}^E/R. \tag{5}$$

Solute partial molar enthalpies and entropies are given in Tables 2, 3, and 4.

The responses of the cholesteric mixtures to solutes were reported by Fergason[1] as the change in the wavelength of maximum reflectance ($\Delta\lambda_{\max}$) per total moles of injected solute per liter of gas. As was pointed out in the introduction to this paper, the total moles of

Table 2 Solute Thermodynamic Quantities at Infinite Dilution in OCC at 22.0 °C

Solute	$\bar{H}_2^E$ (kcal mol^{-1})	$\bar{S}_2^E$ (cal °K^{-1} mol^{-1})	γ_f
chloroform	1.27 ±0.06	6.19 ±0.22	0.39
carbon tetrachloride	2.06 ±0.19	7.65 ±0.64	0.71
dichloromethane	2.01 ±0.41	8.05 ±1.37	0.54
cyclohexane	2.67 ±0.25	9.13 ±0.86	0.96
benzene	3.12 ±0.19	11.14 ±0.63	0.75
cyclohexene	3.02 ±0.18	10.70 ±0.61	0.79
n-hexane	1.98 ±0.04	6.31 ±0.12	1.22

Table 3 Solute Thermodynamic Quantities at Infinite Dilution in the 24.0% CCl Mixture at 18.0 °C

Solute	$\bar{H}_2^E$ (kcal mol^{-1})	$\bar{S}_2^E$ (cal °K^{-1} mol^{-1})
chloroform	0.39 ±0.05	2.44 ±0.17
carbon tetrachloride	1.41 ±0.05	4.88 ±0.18
dichloromethane	0.84 ±0.07	3.32 ±0.23
cyclohexane	1.66 ±0.09	5.21 ±0.29
benzene	1.43 ±0.06	4.89 ±0.21
cyclohexene	1.48 ±0.08	4.99 ±0.26
n-hexane	1.26 ±0.13	3.43 ±0.46

Table 4 Solute Thermodynamic Quantities at Infinite Dilution in the 26.0% CCl Mixture at 18.0 °C

Solute	$\bar{H}_2^E$ (kcal mol^{-1})	$\bar{S}_2^E$ (cal °K^{-1} mol^{-1})
chloroform	0.64 ±0.10	3.25 ±0.35
carbon tetrachloride	1.61 ±0.10	5.51 ±0.33
dichloromethane	1.61 ±0.18	5.91 ±0.60
cyclohexane	1.75 ±0.10	5.46 ±0.35
benzene	1.81 ±0.11	6.15 ±0.37
cyclohexene	1.69 ±0.09	5.66 ±0.32
n-hexane	1.40 ±0.19	3.85 ±0.66

injected solute is approximately equal to the moles of gaseous solute above the solution after equilibrium is achieved. Therefore, we are reporting Fergason's response data as $\Delta\lambda_{max}C_g^{-1}$ where C_g is the gas phase concentration in mol l^{-1}. For comparison with solute thermodynamic solution values, we normalized these responses to equal mole fractions of dissolved solute (X_2) by multiplying the responses by $\gamma_f p_2{}^0/RT$. This normalization factor was derived by combining the ideal gas relationship (assuming that deviations from gas phase ideality are very small at the very low pressures used by Fergason) with Raoult's law to give

$$n_g/VX_2 = \gamma_f p_2{}^0/RT \tag{6}$$

where n_g is the number of moles of gaseous solute and V is the cell volume.

The response data together with γ_f, $V_g{}^0$, and $p_2{}^0$ data are listed in Tables 5 and 6. Plots of λ_{max} vs. C_g are shown in Fig. 1 for chloroform, dichloromethane, and carbon tetrachloride in the 24.0% CCl mixture at 18.0 °C. Plots of λ_{max} vs. X_2 for the same solutes and

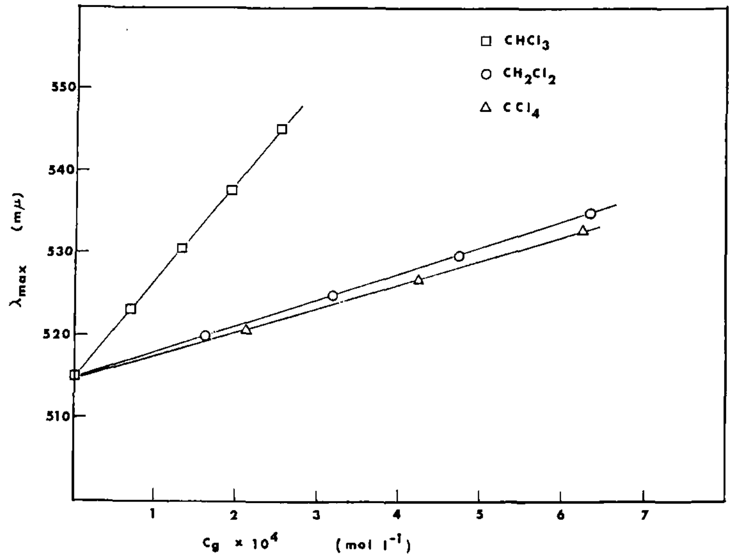

Figure 1. Wavelength of maximum reflectance (λ_{max}) vs. solute gas phase concentration (C_g) in the 24.0% CCl mixture at 18.0 °C. The plots are from Ref. 1, courtesy of J. L. Fergason.

TABLE 5 Solute Thermodynamic Quantities and Wavelength of Maximum Reflectance Data for the 24.0% CCl Mixture at 18.0 °C

Solute	$\Delta\lambda_{\max} C_g^{-1} \times 10^{-4}$ (a) (mμ l mol^{-1})	$\Delta\lambda_{\max} X_2^{-1}$ (mμ)	V_g^0 (ml g^{-1})	p_2^0 (mm Hg)	γ_f
Halomethanes					
chloroform	13.02	591.1	382.8	143.5	0.58
carbon tetrachloride	3.16	143.1	383.4	84.03	0.98
dichloromethane	3.50	503.3	121.7	327.5	0.80
Aromatics					
benzene	3.23	122.9	454.4	68.30	1.01
toluene	11.63	122.8	1637	19.27	1.00
o-xylene	39.47	94.7	7191	4.318	1.01
m-xylene	26.32	80.2	5665	5.346	1.04
p-xylene	22.22	63.7	6019	5.729	0.91
fluorobenzene	6.19	216.0	497.7	54.89	1.16
chlorobenzene	44.44	184.3	4161	7.683	0.98
Non-aromatic hydrocarbons					
cyclohexane	2.95	145.7	351.1	70.56	1.27
methylcyclohexane	4.54	109.7	717.0	32.33	1.36
cyclohexene	6.64	244.4	470.9	63.99	1.05
n-hexane	0.0	0.0	181.2	110.8	1.58
n-heptane	—	—	598.6	31.93	1.65
n-octane	—	—	1991	9.351	1.69
n-nonane	− 24.40 (b)	− 64.3 (b)	6529	2.767	1.74

Ketones					
acetone	1.12	331.1	59.38	161.0	3.34
2-butanone	4.85	449.1	188.5	71.71	2.35
2-pentanone	8.46	283.2	515.9	9.966	6.10
Alcohols					
methanol	0.96	559.3	29.84	83.71	12.64
ethanol	1.59	403.3	68.33	37.61	12.65
n-propanol	6.10	487.3	216.3	12.42	11.69
n-butanol	14.00	338.7	713.2	4.317	10.18
Esters					
methyl acetate	0.44	95.3	80.69	152.0	2.59
ethyl acetate	2.14	190.0	195.7	63.94	2.52
n-propyl acetate	4.62	134.0	596.4	21.78	2.42
isopropyl acetate	4.24	251.5	292.8	42.02	2.56
methyl propionate	2.62	182.2	249.7	57.56	2.19
ethyl propionate	4.20	126.6	574.1	24.17	2.27
methyl butyrate	6.21	155.5	690.7	21.42	2.12
methyl isobutyrate	4.17	184.1	392.5	33.87	2.37

(a) Reference 1.

(b) Reflectance data for *n*-nonane as a solute was not available for the 24.0% CCl mixture. The reflectance data reported in this table for *n*-nonane is for the 26.0% CCl mixture at 18.0°C and is assumed to be comparable to that of the 24.0% CCl mixture. Similar solutes like *n*-hexane and cyclohexane cause the same reflectance changes in the 26.0% CCl mixture as they did in the 24.0% CCl mixture.

Table 6 Solute Thermodynamic Quantities and Wavelenth of Maximum Reflectance Data for the 26.0% CCl Mixture at 18.0 °C

Solute	$\Delta\lambda_{\max} C_g^{-1} \times 10^{-4(a)}$ (mμ l mol^{-1})	$\Delta\lambda_{\max} X_2^{-1}$ (mμ)	V_g^0 (ml g^{-1})	γ_f
chloroform	17.50	812.0	378.0	0.59
carbon tetrachloride	4.74	219.5	378.0	1.00
dichloromethane	3.47	511.8	119.5	0.82
cyclohexane	2.96	151.8	340.7	1.32
benzene	5.16	199.2	452.7	1.03
n-hexane	0.0	0.0	177.8	1.62

(1) Reference 1.

solvent are shown in Fig. 2. Since the noise level in Fergason's apparatus is 0.01 mμ^1, as little as 10^{-5} mole fraction of a solute such as chloroform dissolved in the cholesteric mixtures should give a detectable color response.

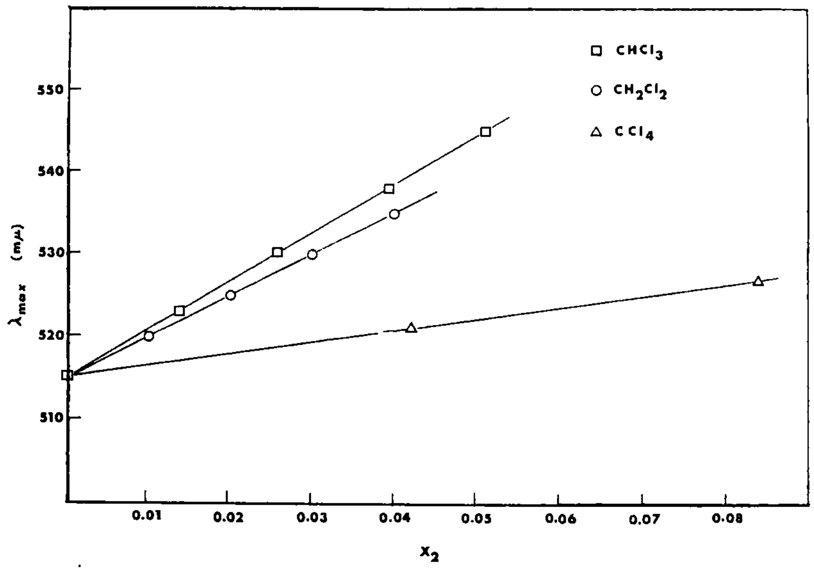

Figure 2. Wavelength of maximum reflectance ($\lambda_{\max}$) vs. solute liquid phase concentration (X_2) in the 24.0% CCl mixture at 18.0 °C.

4. Discussion

SOLUTE THERMODYNAMIC QUANTITIES

This discussion mainly involves the 24.0% CCl mixture in which we obtained our best solute thermodynamic data (as indicated by the relatively low standard deviations in the experimental $\bar{H}_2{}^E$ and $\bar{S}_2{}^E$ values). In this mixture, some correlations between the $\lambda_{\max}$ shifts and the solute thermodynamic quantities are observed. For the halomethanes, the relative $\bar{H}_2{}^E$ and $\bar{S}_2{}^E$ values suggest that the solute–solvent interaction energies follow the order: chloroform > dichloromethane > carbon tetrachloride. This follows the reasoning that a solute held more tightly by a solvent due to stronger interactions should have the least positive $\bar{H}_2{}^E$ and $\bar{S}_2{}^E$ values. The $\Delta\lambda_{\max} X_2^{-1}$ for the halomethanes also follow the trend: chloroform > dichloromethane > carbon tetrachloride. In this case, there appears to be a direct relationship between the solute–solvent interaction energies and the effect that a solute has on the cholesteric structure.

Interestingly, n-hexane has less positive $\bar{H}_2{}^E$ and $\bar{S}_2{}^E$ values than benzene, cyclohexane, cyclohexene, or carbon tetrachloride in the 24.0% CCl mixture but it induces no $\lambda_{\max}$ shift while the other solutes induce significant shifts. Possibly, n-hexane undergoes a significant decrease in internal energy on going into solution in the cholesteric mixture and this energy loss is included in the $\bar{H}_2{}^E$ and $\bar{S}_2{}^E$ values.

Previous results(7, 22) suggest that a flexible solute such as n-hexane should lose much of its conformational freedom to fit into an ordered liquid crystalline solvent before it can strongly interact with the solvent molecules.

There is no observed correlation between the $\Delta\lambda_{\max} X_2^{-1}$ and $\bar{H}_2{}^E$ or $\bar{S}_2{}^E$ for cyclohexane, cyclohexene, or benzene in the 24.0% CCl mixture. Since cyclohexane and cyclohexene are somewhat flexible, they could undergo an internal energy change but this effect should be small compared to a solute such as n-hexane. Also, since we were unable to assess the errors involved in Fergason's response data, we could not establish the interpretive limitations that result from those errors.

The reason we do not observe a general correlation between the $\Delta\lambda_{\max} X_2^{-1}$ values and thermodynamic data for the various solutes could be due to a non-random mixing process. In random mixing, the solute has an equal probability of being in contact with any part of the solvent molecule, but this is unlikely with the cholesteric solvents used in this study since they have both polar and non-polar character. When dissolved, a polar solute (e.g., dichloromethane) spends more time in contact with the polar portion of the solvent while a non-polar solute (e.g., cyclohexane) spends more time in contact with the non-polar portion. It is possible that the effect that a solute has on the cholesteric structure depends on its preferred location of contact with a solvent molecule.

EFFECT OF SOLUTE PROPERTIES ON WAVELENGTH SHIFTS

By comparing wavelength shift data normalized to the gas phase concentrations of the solutes, one can only conclude that low solute vapor pressures and good solubility in the cholesteric mixtures favor large $\lambda_{\max}$ shifts. However, other solute properties that favor large $\lambda_{\max}$ shifts can only be determined by using γ_f values (quickly obtainable by GLC) to normalize the wavelength shift data to equal amounts dissolved (i.e., equal solubility). Therefore, we compared $\Delta\lambda_{\max} X_2^{-1}$ values for a wide range of solutes to investigate which solute properties favor large $\lambda_{\max}$ shifts and which do not.

Dipolar effect. Solutes with sizeable permanent dipole moments give relatively large $\Delta\lambda_{\max} X_2^{-1}$ values. These include chloroform, dichloromethane, fluorobenzene, ketones, alcohols, and esters. Those solutes with larger dipole moments tend to give greater $\lambda_{\max}$ shifts. For example, ketones induce greater shifts than esters. The dipolar effect can also be seen for the xylene isomers where *m*- and *o*-xylene have relatively small permanent dipole moments and *p*-xylene has no permanent dipole moment. This is illustrated in Fig. 3 where $\Delta\lambda_{\max} X_2^{-1}$ values for the xylenes in the 24.0% CCl mixture are plotted against available dipole moments.(23) The ketones, alcohols, and esters have $\Delta\lambda_{\max} X_2^{-1}$ values in the 24.0% CCl mixture which vary in a zigzag manner with increasing alkyl chain length in a homologous series (Fig. 4). This could be attributed to variations, in an odd-even way, in the component of the dipole moment directed along the long axes of the solute molecules.

Hydrogen bonding. Of the solutes studied, those which form hydrogen bonds give the greatest $\Delta\lambda_{\max} X_2^{-1}$ values. These solutes

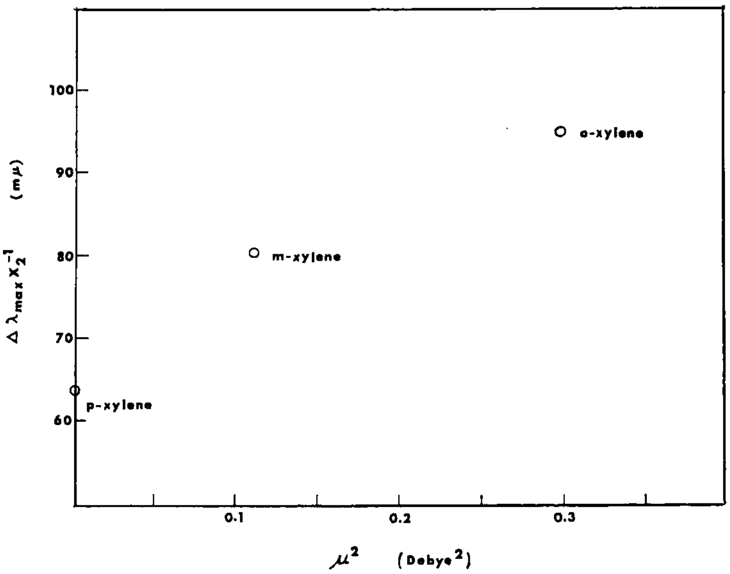

Figure 3. The shift in the wavelength of maximum reflectance per mole fraction of solute dissolved ($\Delta\lambda_{max}X_2^{-1}$) vs. dipole moment for *o*-, *m*-, and *p*-xylene in the 24.0% CCl mixture at 18.0 °C.

include chloroform, dichloromethane, and the alcohols. The dipole moments of these solutes also serve to increase the λ_{max} shifts.

Steric effect. An increase in the size or length of the solutes tends to decrease the $\Delta\lambda_{max}X_2^{-1}$ values. Thus, *p*-xylene probably has a lower $\Delta\lambda_{max}X_2^{-1}$ value than *m*-xylene or *o*-xylene because it is the longest of the three isomers in addition to it having no dipole moment. Even though chlorobenzene has a greater permanent dipole moment than fluorobenzene, fluorobenzene has a greater $\Delta\lambda_{max}X_2^{-1}$ value. It appears that the greater molecular size of chlorobenzene compared to fluorobenzene opposes its favorable dipolar effect. In Fig. 5, $\Delta\lambda_{max}X_2^{-1}$ values for the non-aromatic hydrocarbons in the 24.0% CCl mixture are plotted against $\ln\gamma_f$. Here we see a decreasing trend in $\Delta\lambda_{max}X_2^{-1}$ with increasing size and length.

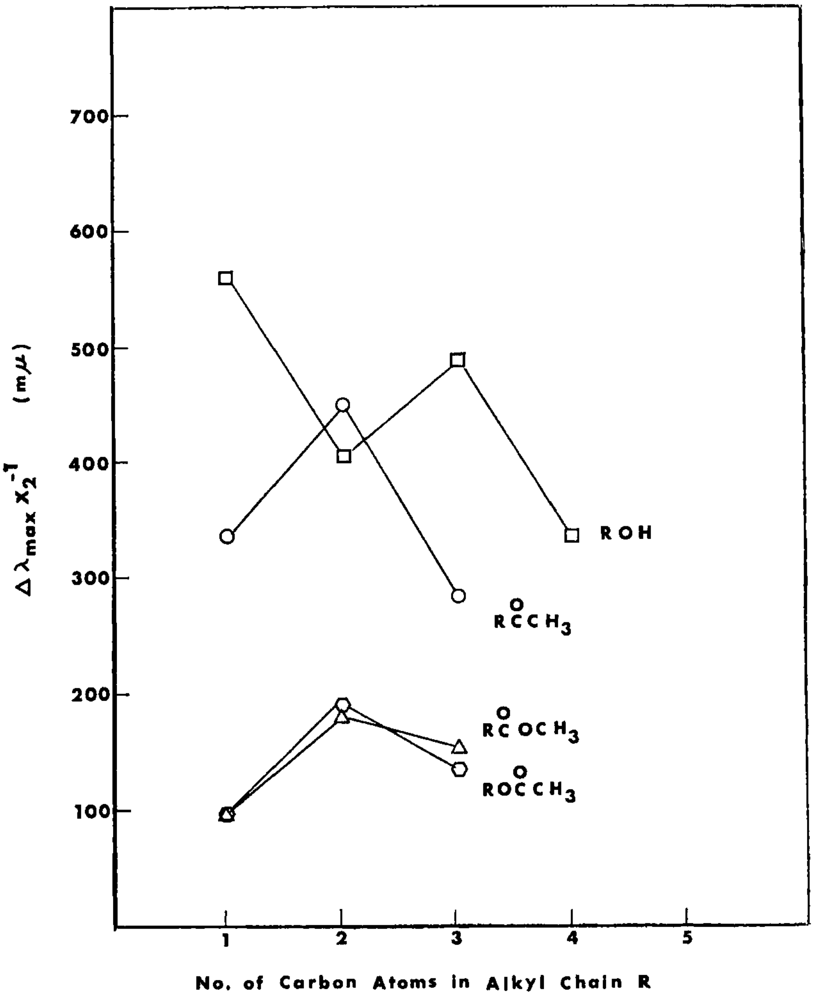

Figure 4. Shift in the wavelength of maximum reflectance per mole fraction of solute dissolved ($\Delta\lambda_{\max}X_2^{-1}$) vs. alkyl chain length for a homologous series of ketones, alcohols, and esters in the 24.0% CCl mixture at 18.0 °C.

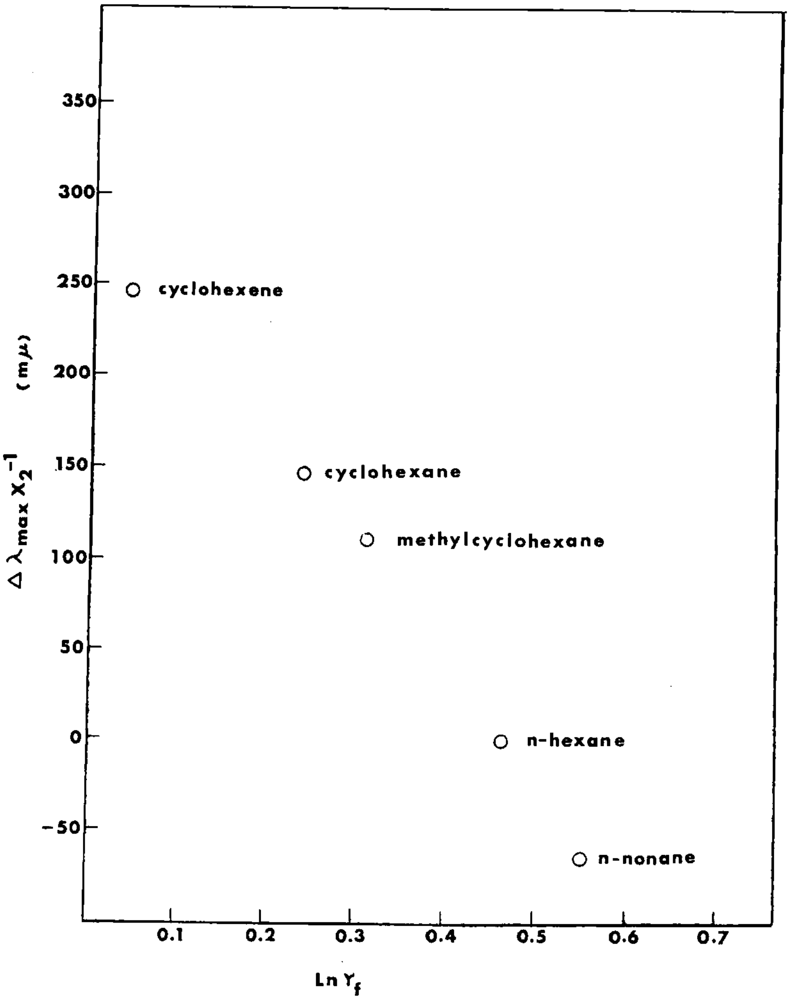

Figure 5. Shift in the wavelength of maximum reflectance per mole fraction of solute dissolved ($\Delta\lambda_{\text{max}}X_2^{-1}$) vs. natural logarithm of solute activity coefficients ($\ln\gamma_f$) for non-aromatic hydrocarbons in the 24.0% CCl mixture at 18 °C.

EFFECT OF SOLUTES ON THE CHOLESTERIC STRUCTURE

The pitch (distance of alignment) of the cholesteric structure is given by[24]

$$p = \frac{d}{\phi} \times 180^\circ = \frac{\lambda}{2} \qquad (7)$$

where p is the pitch, λ is the wavelength of scattered light, d is the plane spacing, and ϕ is the angle between adjacent planes in degrees. The effect of temperature on the wavelength of light selectively reflected by a cholesteric phase is explained by an increase in ϕ with increasing temperature.[24]

If the major effect of a solute on the cholesteric structure were in d, larger solute molecules should increase d more and cause a greater shift in $\lambda_{\max}$ to longer wavelengths. This is the opposite of what is observed. Therefore, we assume that the mechanism by which solutes effect the cholesteric phase is (like temperature) a change in ϕ.

Hydrogen bonding, dipolar effects, and small solute size favor red shifts. This is analogous to the effect of a decrease in temperature where ϕ is decreased. All of the solutes investigated in this study gave red shifts except for *n*-hexane which induced no shift and *n*-nonane, which induced a blue shift. Since *n*-nonane has no capacity to hydrogen bond or engage in dipolar interactions, its relatively large size and length promote a disturbing influence on the cholesteric structure analogous to that of an increase in temperature.

A very recent publication[25] indicates that the rotatory sense and pitch of cholesteric liquid crystals depend directly on the chain length in the 3β-carbon direction. This suggests that solute induced pitch changes result from structural perturbations in the packing at the 3β-carbon position. It is possible that the effect that polar solutes have on the cholesteric structure results from preferential interaction with the solvent molecules in the locality of the 3β-carbon position (e.g., at the polar carbonate functional group in OCC).

5. Conclusions

Correlations have been observed between $\Delta\lambda_{\max} X_2^{-1}$ values and thermodynamics of solution data for the chlorinated methanes.

Moreover, interesting observations have been made on the effect that various solute properties have on the cholesteric structure. Our results indicate that solute induced λ_{max} shifts merit further investigation. More reflectance and GLC studies should be made. The reflectance studies should include as many members of a homologous series of solutes as possible. For example, more definitive results could be obtained by including *n*-heptane and *n*-octane in the series of *n*-alkane solutes instead of just using *n*-hexane and *n*-nonane as was done by Fergason. At the very least, GLC studies should be made to obtain activity coefficients which can be used to normalize wavelength shift data to the liquid phase concentrations of the solutes.

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