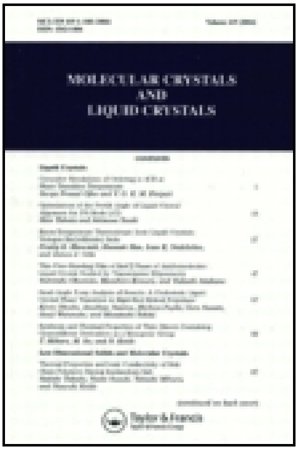

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Thermodynamics of Solutions with Liquid Crystals Solvents. VII. A Mixture of Cholesteryl Chloride and Cholesteryl Myristate

J. M. Schnur [a] [b] & D. E. Martire [a]

[a] Department of Chemistry, Georgetown University, Washington, D.C., 20007

[b] Naval Research Laboratory, Code 5513, Washington, D.C., 20375, U.S.A.

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Thermodynamics of Solutions with Liquid Crystals Solvents. VII. A Mixture of Cholesteryl Chloride and Cholesteryl Myristate

J. M. SCHNUR ‡ and D. E. MARTIRE

Department of Chemistry
Georgetown University
Washington, D.C. 20007

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Gas-liquid chromatography (glc) was used in a thermodynamic investigation of solubility in a 1.743:1.000 (weight:weight) mixture of cholesteryl chloride and cholesteryl myristate. This mixture exhibits a β cholesteric phase (increasing pitch with increasing temperature) at low temperatures, a "nematic point" at 42°C, and an α cholesteric phase (decreasing pitch with increasing temperature) up to 62°C, where a transition to the isotropic liquid takes place. Infinite dilution activity coefficients and partial molar enthalpies of solution were obtained for 16 diverse nonmesomorphic solutes in the β and α phases. The results are interpreted in terms of a statistical thermodynamic model[2] of solution in anisotropic solvents. Comparison of solubility behavior in the α and β phases suggests a pronounced difference in the molecular packing of the two phases. Evidence is presented that the $\beta \rightarrow \alpha$ transition may involve a higher order thermodynamic phase transition at the "nematic point".

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‡ Current address: Naval Research Laboratory, Code 5513, Washington D.C. 20375, U.S.A.

INTRODUCTION

The close relationship between nematic and cholesteric liquid crystals was first demonstrated by Friedel[1] in 1922, who was able to produce a nematic mesophase by mixing two cholesteric compounds of opposite helical screw sense. Such a compensated mixture has a "nematic point" (infinite helical pitch) at a temperature determined by the nature of the two compounds and their relative weights in the mixture.

Recently, Sackmann *et al.* reported[2] a nematic-like NMR spectrum at 40°C for benzene dissolved in a 1.9:1.0 by weight mixture of cholesteryl chloride (C) and cholesteryl myristate (M) and observed[3] a nematic point at 42°C for a 1.75:1.00 by weight mixture of C and M. More recently, Labes and co-workers[4-7] have studied the dielectric properties of, electric field effects on, dipole relaxation in, birefringence of, and optical rotatory dispersion of a 1.75:1.00 mixture of C and M over a temperature range. Except in the optical properties,[7] no discontinuities were found at the nematic point; however, a remarkable dip was observed at 42°C in the dielectric constant versus reciprocal temperature plot, suggestive of a higher than first order transition through this point. Furthermore, no observable enthalpy change is associated with this nematic "phase" at 42°C,[7,8] also suggesting that any possible phase transition would be higher order.

To further explore compensated mixtures, gas-liquid chromatography (glc) is used here in a thermodynamic investigation of solubility in a 1.743:1.000 (weight:weight) mixture of C and M. This mixture exhibits a β cholesteric phase (increasing pitch with increasing temperature) at low temperatures, a nematic point at 42°C, and an α cholesteric phase (decreasing pitch with increasing temperature) up to 62°C, where a first order transition to the isotropic liquid takes place. Through a previous study[8] with this mixture, it was established that surface effects (in a thermodynamic sense) are negligible at both the solid support-liquid crystal and liquid crystal-carrier gas interfaces in glc, hence, that the thermodynamic results from glc are indicative of *bulk* liquid crystal behavior only. The apparatus and procedure used to obtain the infinite dilution solute activity coefficient from glc have been described previously.[8-11] We report here only the notable differences in the apparatus and procedure, the salient features of our experiment, and the results.

EXPERIMENTAL

Liquid crystals

The source, purification procedure, and purity determination for C and M are given in Ref. 8. Estimated purities (from differential scanning calorimetry) are 99.5% for C and 99.2% for M.

Preparation of columns

Since the results of a previous study[8] indicated that a highly inert solid support which provides moderate surface area would be most suitable for this work, the only type of support used here was Johns-Manville 60-80 mesh, acid washed and DMCS-treated Chromosorb W. The support was coated with the liquid crystal mixture (1.743:1.000, C:M, weight:weight) using methylene chloride solvent and a rotary evaporator.[9] The exact weight percent of liquid crystal in the total packing material (dried coated support) was found to be 11.08.[8] The packed columns (made from 0.25-in. o.d. copper tubing) were conditioned under a gentle flow of helium for about 20 h at 80°C. Due to the slow decomposition of C, four separate columns had to be used during the course of this experiment. Data collected within about 150 h could be reproduced. The results from each successive column were checked against those of the previous column and were found to agree within ±1% in all cases.

TABLE 1

Solute Partial Molar Excess Enthalpies ($\bar{H}_2^e$), Excess Entropies ($\bar{S}_2^e$) and Heats of Solution ($\Delta\bar{H}_2^s$)[a]

	β Phase			α Phase		
Solute	$\bar{H}_2^e$	$\bar{S}_2^e$	$-\Delta\bar{H}_2^s$	$\bar{H}_2^e$	$\bar{S}_2^e$	$-\Delta\bar{H}_2^s$
n-heptane	0.55	0.35	8.03	5.49	15.91	2.90
n-octane	0.92	1.61	8.85	3.70	10.43	5.83
n-nonane	1.78	4.38	9.23	2.93	7.99	7.79
n-decane	0.63	0.87	11.38	5.12	14.68	8.90
2-methyloctane	0.55	0.52	9.92	6.92	20.22	3.29
2,2-dimethylheptane	0.22	-1.25	9.67	2.07	4.89	7.57
2,6-dimethylheptane	0.91	0.93	9.14	7.37	21.53	2.43
3,3-dimethylheptane	-3.73	−13.87	13.68	4.63	13.05	5.08
4,4-dimethylheptane	-0.19	-2.45	10.05	2.44	6.26	7.19
3-ethylheptane	1.24	2.51	9.17	4.86	13.98	5.30
3,3-diethylpentane	-1.58	-6.76	11.55	5.63	16.32	4.15
1-chloro-*n*-pentane	0.38	0.64	8.54	-7.69	-23.91	16.43
1-chloro-*n*-hexane	-1.58	-5.48	11.63	-2.80	- 8.89	12.63
1-chloro-*n*-heptane	-0.95	-3.48	12.14	1.22	3.46	9.70
1-bromo-*n*-pentane	1.52	4.52	8.82	-5.28	-16.53	14.80
1-iodo-*n*-pentane	1.28	3.90	9.25	-3.49	-10.83	13.78

[a] Units of $\bar{H}_2^e$ and $\Delta\bar{H}_2^s$ are kcal/mole and units of $\bar{S}_2^e$ are cal/mole deg. Typical uncertainties are 0.17 Kcal/mole for $\bar{H}_2^e$ and 0.38 cal/mole deg. for $\bar{S}_2^e$.

Solutes

A group of 16 non-mesomorphic solutes was chosen for this study (see Table 1). This group exhibits a range of molecular size, shape, polarity and polarizability. Most of these were included in a previous glc investigation of nematogens.[10] All solutes were used as obtained from the manufacturer. The chromatograms indicated no major impurities, and the minor impurities present were sufficiently removed from the main chromatographic peak to allow accurate retention time measurements.

Apparatus and procedure

The glc apparatus[8,9] and experimental procedure[9-11] used in obtaining our solute specific retention volumes (V_g^0) have been described previously. The V_g^0 values determined were found to be independent of sample size (for samples smaller than about 0.1 μ) and carrier gas flow rate.

RESULTS

Specific rentention volumes

V_g^0's were determined at four temperatures each in the β cholesteric phase (35.1°, 37.0°, 39.0°, 40.5°) and the α cholesteric phase (46.5°, 49.0°, 53.5°, 57°). The probable error in the measurement of V_g^0 is estimated to be 1.0%.[10]

Solute activity coefficients

The activity coefficients for the solutes at infinite dilution (γ_p^∞) were calculated from the expression[9,10]

$$\gamma_p^\infty = \frac{1.704 \times 10^7}{\bar{M}_1 P_2^0 V_g^0} \qquad (1)$$

where $\bar{M}_1$ is the number average molecular weight for the liquid crystal mixture (equal to 458.45) and P_2^0 is the saturated vapor pressure of the pure solute in torr. The vapor pressures (P_2^0) were determined as described previously.[10] Solute activity coefficients fully corrected for the non-ideality of the vapor phase (γ_f^∞) were obtained using the expression[9,10]

$$\ln \gamma_f^\infty = \ln \gamma_p^\infty - \frac{P_2^0 B_{22}}{RT} \qquad (2)$$

where B_{22}, the second virial coefficient of the pure solute vapor at T, can be readily evaluated as previously outlined.[10] The probable error in the determination of γ_f^∞ is estimated to be about 1.5%.[10] To minimize the amount of tabular data, the γ_f^∞ values are not listed here. However, they may be readily generated at the four experimental temperatures in each phase by utilizing Eq. (3) and the excess properties listed in Table 1.

Partial molar excess enthalpies and entropies, and partial molar enthalpies of solution

From solution thermodynamics we have

$$\ln \gamma_f^\infty = \frac{\bar{G}_2^e}{RT} = \frac{\bar{H}_2^e}{RT} - \frac{\bar{S}_2^e}{R} \tag{3}$$

where $\bar{G}_2^e$, $\bar{H}_2^e$ are, respectively, the infinite dilution solute partial molar excess free energy, enthalpy, and entropy. From the γ_f^∞ results, $\bar{H}_2^e$ and $\bar{S}_2^e$ were determined for each solute in the α and β "phases" of the solvent (liquid crystal) mixture through Eq. (3),[10] and are set out in Table 1. The infinite dilution solute partial molar enthalpies of solution $(\Delta\bar{H}_2^s)$ were determined from linear least-squares analysis of ln V_g^o as a function of reciprocal temperature, i.e.,

$$\frac{d \ln V_g^o}{d(1/T)} = \frac{-\Delta\bar{H}_2^s}{R} = \frac{\Delta H_2^{\text{vap}} - H_2^e}{R} \tag{4}$$

where ΔH_2^{vap} is the pure solute enthalpy of vaporization, a result which is readily derivable from Eq. (1). The $\Delta\bar{H}_2^s$ values are also listed in Table 1.

MODEL FOR INTERPRETING RESULTS

Following Chow and Martire,[10] one can derive the following expression from statistical thermodynamics:

$$\gamma_f^\infty = \left(\frac{Z_i}{Z_r}\right)_{\text{trans.}} \cdot \left(\frac{Q_i}{Q_r}\right)_{\text{rot.}} \cdot \left(\frac{Q_i}{Q_r}\right)_{\text{vibr.}}$$

$$= \left(\gamma_f^\infty\right)_{\text{trans.}} \cdot \left(\gamma_f^\infty\right)_{\text{rot.}} \cdot \left(\gamma_f^\infty\right)_{\text{vibr.}} \tag{5}$$

where the subscripts i and r refer to, respectively, an ideal solution and the real or actual solution. In Eq. (5), Z refers to the solute configurational molecular partition function (i.e., translational partition function), and $Q_{rot.}$ and $Q_{vibr.}$ are, respectively, the solute rotational and vibrational molecular partition functions. Equation (5) is derived by assuming that: (a) the product $P\bar{V}_2^e$, where P is the pressure and $\bar{V}_2^e$ is the solute partial molar excess volume is negligibly small; (b) the Flory-Huggins partial molar excess entropy[9] is negligibly small; (c) while the dissolved solute possibly affects the local structure of the solvent, the long range structure (if any) and the molecular energy states (on the average) are unaltered due to the infinite dilution condition of the solute; and, for convenience, (d) the translational, rotational and vibrational terms are separable. (Most likely, these terms are coupled, as will become evident.)

In an ideal solution, the solute-solvent segmental interaction energy is equal to the arithmetic mean of solute-solute and solvent-solvent segmental interaction energies,[9] and all energy terms are isotropic. In a real solution, solute-solvent interactions may be weaker or stronger than this arithmetic mean value and, in a nematic solvent, for example, anistropic solute-solvent forces may be operative. Accordingly, $(Z_i/Z_r)_{\text{trans.}}$ or $(\gamma_f^\infty)_{\text{trans.}}$ may be less than or greater than unity depending on the strength and anisotropy of solute-solvent interactions. In a given solvent (or in a given phase of a liquid crystal solvent), it is argued [10] that a measure of relative $(\gamma_f^\infty)_{\text{trans.}}$ values within a series of solutes should be the relative $\Delta\bar{H}_2^e$ values, i.e., stronger and, in a nematic phase, more anisotropic solute-solvent interactions lead to more negative $\Delta\bar{H}_2^e$ values and smaller $(\gamma_f^\infty)_{\text{trans.}}$ values, hence, to more negative (or less positive) deviations from Raoult's law. Thus, a more polarizable and rod-like molecule would be expected to have a smaller value of $(\gamma_f^\infty)_{\text{trans.}}$, and to be *energetically more favored* for solution in a nematic phase.

If the real solution is not an anisotropic medium, the segmental potential energy difference would be the only effect operative in Eq. (5), and γ_f^∞ would be equal to $(\gamma_f^\infty)_{\text{trans.}}$. This is the usual case in nonelectrolytic mixtures of equally-sized molecules.[9] On the other hand, if, in the real solution, the rotational motion of the solute molecule as a whole were to be restricted (e.g., due to an aligned nematic environment) relative to such motion in an ideal solution (free rotation assumed), the rotational partition function of such a hindered rotor should decrease. A straight-forward quantum mechanical derivation [12] of the partition function for a linear rotor, whose center is fixed in and whose rotational motion is hindered by a cylindrical box with infinite hard walls, would demonstrate that $(Q_i/Q_r)_{\text{rot.}}$ or $(\gamma_f^\infty)_{\text{rot.}}$ is always greater than or equal to unity. Thus, a more rod-like solute molecule would be expected to have a larger value of $(\gamma_f^\infty)_{\text{rot.}}$, and to be *rotationally less favored* for solution in a nematic phase. Furthermore, it can be shown that the hindered rotational frequencies are sufficiently low to lend themselves to classical treatment. Thus, the solute rotational energy (RT for a linear molecule) should be the same in both the ideal solution and the real solution, and the rotational free energy difference should be wholly entropic, i.e., $(\overline{H}_2^e)_{\text{rot.}} \approx (\overline{E}_2^e)_{\text{rot.}} = 0$, and $(\overline{G}_2^e)_{\text{rot.}} \approx (\overline{A}_2^e)_{\text{rot.}} = -T(S_2^e)_{\text{rot.}} = RT\ln(\gamma_f^\infty)_{\text{rot.}} = -R\overline{T}\ln(Q_r/Q_i)_{\text{rot.}}$.

Finally, consider the various possible vibrational modes of a polyatomic molecule: bond stretching, bond bendings and internal rotation (rotation about single bonds). The first two modes are high frequency and are "internal" modes in that the positional coordinates of the atoms undergo very small displacements about the equilibrium positions. As is usually done in solution thermodynamics,[13] we assume that these two modes are comparable in the ideal solution and the real solution, i.e., that they are environment independent. On the other hand, rotation about single bonds involves a major change in the positional coordinates of the atoms and this mode could very well be affected by the solvent environment.[13,14] Following Pitzer[15] and Seelig,[14] one can write the environmentally dependent portion of the internal rotational partition function, which we'll call $Q_{\text{conform.}}$, as follows:[12]

$$Q_{\text{conform}} = \sum_{i=1}^{i=N} e^{-a_i/RT} \tag{6}$$

where N is the total number of possible conformations of the molecule (equal to 3^{n-3} for n-alkanes, where n is the number of carbon atoms) and a_i is the energy of the i^{th} conformation relative to the lowest energy (and most probable) conformation (the fully extended or zig-zag conformation for n-alkanes). The terms a_i are determined by the internal molecular structure alone for a gaseous system, but can be affected by the environment in a condensed system.[14] For example, n-hexane has 27 possible conformations. The energy difference between the two lowest energy forms is about 500 calories in the gas phase and the pure liquid phase, leading to an appreciable population of higher conformational energy states.[14-16] In the pure solid phase the close molecular packing makes the a_i values effectively infinite for all conformations relative to the zig-zag conformation, which is observed to be the only one present.[16] In a smectic liquid crystal, an effective value of about 1450 calories has been estimated[14] as the energy difference between the two lowest energy conformers in n-alkyl chains. Thus, in the latter two cases the aligned close packing of the environment leads to: (a) greater a_i values (relative to isotropic phases) in Eq. (6), (b) a lower population of the higher energy and less linear conformations (relative to the zig-zag one), and (c) smaller values of $Q_{\text{conform.}}$. Similar considerations can be applied to alkyl chains in a nematic environment, leading to differences of the order of 600 calories between the two lowest energy conformers.[12] Recent laser Raman studies on the alkoxyazoxy benzene homologous series[17] lend support to the concept of progressive alkyl chain shortening (implied by the progressive reduction of a_i values) as one proceeds from the solid, to the smectic, to the nematic, and to the isotropic liquid phase.

Accordingly, Eq. (5) is rewritten as follows:

$$\begin{aligned}\gamma_f^\infty &= \left(\frac{Z_i}{Z_r}\right)_{\text{trans.}} \cdot \left(\frac{Q_i}{Q_r}\right)_{\text{rot.}} \cdot \left(\frac{Q_i}{Q_r}\right)_{\text{conform.}} \\ &= \left(\gamma_f^\infty\right)_{\text{trans.}} \cdot \left(\gamma_f^\infty\right)_{\text{rot.}} \cdot \left(\gamma_f^\infty\right)_{\text{conform.}}\end{aligned} \qquad (7)$$

where all terms now directly represent molecular modes which depend on the atomic coordinates and are environmentally dependent. One would expect that $(Q_i/Q_r)_{\text{conform.}}$ or $(\gamma_f^\infty)_{\text{conform.}}$ should always be greater than unity in an environment which restricts conformational freedom relative to such freedom in an isotropic state. With *n*-alkane solutes, it follows that a longer chain alkane should have a larger $(\gamma_f^\infty)_{\text{conform.}}$ and be *conformationally less favored* for solution in a liquid crystal environment.[10,12,14,18] It can also be shown[12,14] that the $Q_{\text{conform.}}$ are only slightly temperature dependent. Thus the conformational free energy difference between a real solution and an ideal solution should be largely entropic, i.e., $(\bar{H}_2^e)_{\text{conform.}} \approx (\bar{E}_2^e)_{\text{conform.}} \approx 0$, and $(\bar{G}_2^e)_{\text{conform.}} \approx (\bar{A}_2^e)_{\text{conform.}} \approx -T(\bar{S}_2^e)_{\text{conform.}} \approx RT\ln(\gamma_f^\infty)_{\text{conform.}} \approx -RT\ln(Q_r/Q_i)_{\text{conform.}}$. Taken together with similar findings for the rotational modes, this implies that the solute partial molar enthalpy of solution (see Eq. 4) is predominantly "translational" in origin and is indeed a valid measure of relative solute-solvent interaction energies, as previously assumed.[10]

The above concepts, in a less detailed form, were invoked by Chow and Martire,[10] and Willey and Brown,[18] to rationalize the the thermodynamic solution behavior of nonmesomorphic solutes in nematogenic liquid crystals. They also form a useful basis for interpreting the results given in Table 1.

DISCUSSION

Given the lack of any detailed information about the structure of the α and β cholesteric phases of this mixture, the best that can be done at this point is to present a self-consistent interpretation of our thermodynamic results, based on the foregoing model and on currently available physical information.[2-7].

The solute activity coefficients (γ_f^∞) in both the α and β phases are much smaller than those observed in nematic mesophases.[10,18] Since the $\Delta\bar{H}_2^s$ values are greater (more negative) than the corresponding nematic values, this would indicate that the $(\gamma_f^\infty)_{\text{trans.}}$ values are smaller. This could be due to stronger solute-solvent interactions and/or weaker solvent-solvent interactions, either of which would lead to a more favorable (more negative or less positive) interchange energy for solution.[9] The lower γ_f^∞ values observed here may also be due in part to lesser rotational and/or conformational restrictions of solute molecules (see Eq. (7)).

n-Alkanes

For nematic solutions it was observed[10] that both γ_f^∞ and $-\Delta H_2^S$ increased with increasing alkyl chain length. It was argued[10] that a longer alkane, having a larger molecular polarizability and and length-to-breadth ratio, interacted more strongly with the aligned nematic environment (thus producing smaller (γ_f^∞) trans. values), but that this effect was more than compensated for by the concurrent loss of rotational and conformational freedom imposed by the nematic environment, resulting in a larger $(\gamma_f^\infty)_{\text{rot.}} \cdot (\gamma_f^\infty)_{\text{comform}}$ product and, hence, a larger net γ_f^∞ value. It was assumed that the zigzag conformation became more exclusively preferred in the nematic phase relative to an unperturbed distribution of conformations (as in the gas phase). While it may be reasonable to assume that a non-mesomorphic solute might become rotationally and conformationally restricted upon solution in the cholesteric mixture, there is no specific structural reason to except the the zigzag conformation will always be the most preferred. In fact, any redistribution of the conformational population which favors any one conformation at the expense of all the others could also lead to smaller $Q_{\text{conform.}}$ and larger $(\gamma_f^\infty)_{\text{conform.}}$ values.

In the α and β phases the heats of solution increase (i.e. become more negative) with increasing alkane carbon number, as in nematic solutions. This should produce a trend of decreasing $(\gamma_f^\infty)_{\text{trans.}}$ with increasing carbon number. However, the countersolubility effects (rotational and conformational) obviously have no trend with increasing carbon number because no clear trends in the net γ_f^∞ values are discernible in either phase. Rotational and/or conformational changes upon solution are thus indicated, but their nature and extent are impossible to infer. However, the heats of solution are greater in the β phase than in the α phase, indicating lower $(\gamma_f^\infty)_{\text{trans.}}$ values and stronger solute–solvent and/or weaker solvent–solvent interactions in the β phase. Given that the net γ_f^∞ values are larger in the β phase, this would seem to indicate that there are more pronounced solute rotational and/or conformational restrictions in the β phase (see Eq. (7)). A solvent environment which produces stronger solute– solvent interactions would be consistent with the enhanced restrictions.

Isomeric nonanes

The nonanes form an interesting group in that their shapes vary widely from that of straight chain (n-nonane) to that of a quasi-sphere (3,3 diethylpentane). However, as was the case for the *n*-alkanes, there is no correlation between γ_f^∞ and $-\Delta\bar{H}_2^s$ in either phase. It is apparent that the interplay between the translational and rotational/conformational effects is more subtle here than with nematic solvents.[10] However, it is also clear, as with nematic solvents, that when "flexible" moleculs are involved there is no simple correlation between molecular shape and the thermodynamic solution properties. The comparison between the β and α phases described for the *n*-alkanes also applies to the isomeric nonanes (see Table 1).

Chloroalkanes

In the β phase, the choroalkanes follow the trend of increasing $|\Delta\bar{H}_2^s|$ with increasing carbon number (with no clear trend in γ_f^∞), as was observed with *n*-alkanes. However, upon entering the α phase of the mixture, chloropentane exhibits a remarkable increase of about 8 kcal. in $|\Delta\bar{H}_2^s|$, while the value for chlorohexane increases by 1 kcal. and that for chloroheptane *decreases* by about 2.5 kcal. Clearly, the α phase through, perhaps, a combination of dipolar interaction[4,6] and favorable molecular packing, displays a high energetic affinity for chloropentane. However, although chloropentane has the lowest activity coefficient at the low temperature end of the α phase, the unfavorable rotational/conformational effect causes it to have the highest γ_f^∞ value at the high temperature end.

Halopentanes

In the β phase $|\Delta\bar{H}_2^s|$ follows the trend iodo–>bromo–>chloro–, i.e., it increases with increasing solute molecular polarizability. The fact that the γ_f^∞ values follow the reverse trend indicates that the potential energy effect dominates and, possibly, that the rotational/conformational effect is comparable for all three solutes. In the α phase, all halopentanes show the substantial increase in $|\Delta\bar{H}_2^s|$ noted previously for chloropentane. There is apparently some combination of polarity and the ability to pack favorably in the α phase that is unique to the halopentanes. (The pure paraffins, on the other hand, seem to energetically accommodate themselves better to the β phase.)

CONCLUSIONS

As with nematic solvents, it is apparent that solute nonideality in this cholesteric mixture is not governed by the translational or potential energy effect alone, i.e., the nonmesomorphic solute experiences restriction of its rotational and/or conformational freedom upon solution. However, a less satisfactory interpretation of the thermodynamic solution data was presented here than for nematic mesophases. This was due to both the lack of specific knowledge about the structure of the mixture and the absence in most cases of clear-cut trends in our data. Nevertheless, it would be safe to state that the solute "probes" studied clearly experienced different solvent environments in the α and β phases. For all solutes, for example, marked differences existed between the solute partial molar heats of solution in the two phases.

Possibly the most important aspect of this study is the light it sheds on the question of a phase transition when the mixture passes through the "nematic" point on going from the β to the α phase upon heating. Thus far, no heat of transition has been observed, indicating that any such phase transition would be higher order than first. However, the transition could very well be weakly first order involving, for example, tens of calories, a heat which would be observable only with more sensitive calorimeters. Assuming, for the time being, that the transition is not first order, let us review the evidence for a higher order transition. First, while there is no discontinuity in the dielectric constant at the "nematic" point, there is a dip reminiscent of a lambda transition.[4] Secondly, the type of solute probe behavior reported here (i.e., the discontinuity in the $|\Delta \overline{H}_2^S|$ value at the "nematic" point) not only has been observed for first order transitions, but has also been found (by glc, as well) for second order glass transitions in polymers.[19,20]

It has been suggested to us that the β phase may not be cholesteric, but rather a "twisted" smectic *C* phase.[21] If that is indeed the case, the optically active smectic *C* to α cholesteric transition could still be second order. According to the Landau rules, as extended by de Gennes,[22] either a first or second order transition of this type would be possible.

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References

1. Friedel, M. G., *Ann. Phys. (Paris)* 18, 273 (1922).
2. Sackmann, E., Meiboom, S. and Snyder, L. C., *J. Amer. Chem. Soc.* 89, 5981 (1967).
3. Sackmann, E., Meiboom, S., Snyder, L. C., Meixner, A. E. and Dietz, R. E., *J. Amer. Chem. Soc.* 90, 3567 (1968).
4. Baessler, M and Labes, M. M., *J. Chem. Phys.* 51, 1846 (1969).
5. Baessler, H., Laronge, T. R. and Labes, M. M., *J. Chem. Phys.* 51, 3213 (1969).
6. Baessler, H., Beard, R . B. and Labes, M. M., *J. Chem. Phys.* 52, 2292 (1970).
7. Teucher, I. Ko, K. and Labes, M. M., *J. Chem. Phys.* 56, 3308 (1972).
8. Schnur, J. M. and Martire, D. E., *Anal. Chem* 43, 1201 (1971).

9. Tewari, Y. B., Martire, D. E. and Sheridan, J. P., *J. Phys. Chem.* 74, 2345 (1970).
10. Chow, L. C. and Martire, D. E., *J. Phys. Chem.* 75, 2005 (1971).
11. Willey, D. G. and Martire, D. E., *Mol. Cryst. and Liq. Cryst.* 18, 55 (1972); paper VI in this series.
12. Martire, D.E. Mol. Cryst. Liq. Cryst., in press.
13. Hijmans, J. and Holleman, Th., *Adv. Chem. Phys.* 16, 223 (1969).
14. Seelig, J., *J. Amer. Chem. Soc.* 92, 3881 (1970); 93, 5017 (1971).
15. Pitzer, K. S., *J. Chem. Phys.* 8, 711 (1940).
16. Mizushima, S., *Structure of Molecules and Internal Rotation*, Academic Press, New York, N.Y., 1954.
17. Schnur, J. M., *Phys. Rev. Letters* 29, 1141 (1972).
18. Willey, D. G. and Brown, G. H., *J. Phys. Chem.* 76, 99(1972).
19. Smidsrød, O. and Guillet, J. E. *Macromolecules* 2, 272 (1969).
20. Lavoie, A. and Guillet, J. E., *Macromolecules* 2, 444 (1969).
21. Fergason, J. L., private communication.
22. de Gennes, P. G., Mol. Cryst. Liq. Cryst., 21, 49 (1973).