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# Effect of an Electric Field on the Gas-Chromatographic Properties of Cholesteric Liquid-Crystal Stationary Phases*

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## Abstract

Gas-chromatographic properties were determined using a homologous series of carboxylic acid esters of cholesterol as stationary phases and several homologous series of organic species, having different functional groups, as volatile solutes. In general, the capacity ratios for the various solutes increased upon application of an electric field. On a relative basis, the change with potential was larger for solutes having smaller capacity ratios, for solvents having a longer acyl chain length of the liquid crystal, and for a faster carrier-gas flow rate.

Recently, because of the unique structures of their mesophases, liquid crystals have received increasing attention as stationary phases in gas

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chromatography (*1–3*). The effect of an electric field on the gas-chromatographic properties of a nematic liquid crystal has been reported in a previous paper (*4*) which showed that low-frequency sinusoidal, as well as static, electric fields caused two effects. First, the capacity ratios for solutes increased. Second, the peaks became more symmetrical and less tailed. The latter is presumably due to a reorientation of the liquid crystal. It was assumed in the earlier gas-chromatographic research involving liquid crystals as stationary phases that the more rodlike molecules fitted into the voids present in the mesophase and, therefore, exhibited larger capacity ratios. It is now clear that the polarity and polarizability as well as the shape and size are important (*4*, *5*).

The purpose of the present study was to examine the effect of a static electric field on the gas-chromatographic properties of a homologous family of cholesteric liquid crystals. We were particularly interested in determining what effect the size of the alkyl substituent in the ester of cholesterol would have on the gas-chromatographic properties of different volatile species.

## EXPERIMENTAL

### Reagents

Cholesteryl propionate, cholesteryl hexanoate, cholesteryl octanoate, cholesteryl nonanoate, cholesteryl 10-undecenoate, cholesteryl laurate, and cholesteryl myristate were obtained from the Vari-Light Corp., Cincinnati, Ohio for use as the stationary phases. Volatile chromatographic samples included acetone, methyl ethyl ketone (J. T. Baker, reagent grade), *n*-hexane, cyclohexane (J. T. Baker, GC-spectrometric grade), diethyl ether (Mallinckrodt, analytical reagent), benzene (Mallinckrodt, spectrometric grade), 2-pentanone, *trans*-1,2-dichloroethylene, *cis*-1,2-dichloroethylene (Eastman Organic, practical grade), *n*-pentane (Phillips, practical grade), *n*-heptane, cyclopentane, 2-methylpentane (Matheson, Coleman and Bell, chromquality), 2,2-dimethylbutane, 2,3-dimethylbutane (Matheson, Coleman and Bell), and cycloheptane (Aldrich).

The carrier gas was 99.9% pure Airco nitrogen. Airco hydrogen and compressed air were used for the flame-ionization detector. Each of these gases was passed through traps of 4A molecular sieves before use. Chromatographic samples were stored over 4A molecular sieves, but all other chemicals were used as received.

## Apparatus

The chromatograph was an Aerograph Model 660, modified to minimize the dead volume and equipped with a flame-ionization detector operated at 180 °C.

The glass capillary columns, about 30 m × 0.6 mm i.d., were drawn and coated with about 2 ml of a 5-mole % solution of a liquid crystal in dichloromethane. To increase the level of loading, the plug was forced to move downward through the column at a rate of 2 cm/sec. All columns, except one coated with cholesteryl myristate, were constructed from soft glass. Columns of cholesteryl myristate were made from both soft glass and borosilicate glass.

The static electric fields were obtained as described previously (*4*).

## Procedures

The flow rate of nitrogen was adjusted so that methane took about 1.6 min to elute unless otherwise noted. Then, a 40-μl sample of vapor above the liquid sample was injected into a 100:1 Hamilton inlet splitter operated at 100 °C. For every volatile species the retention time was found to be independent of sample size by injecting 0.5 μl of liquid which produced a response about 40 times larger than the vapor, but had the same retention time. Retention times were obtained from the intersection of tangential lines drawn through the inflection points of the chromatograms. The capacity ratio $k$ was calculated in the usual manner using methane as a "nonretained" reference peak to determine $t_m$. Within experimental error, methane and ethane had the same retention times on all columns. This is an indication that methane was truly a good approximation to a nonretained peak. Capacity ratios were reproducible to ±1% or 0.01 units, which ever was larger, and were calculated from the average retention times of at least two determinations.

The cholesteric-isotropic transition temperatures for the liquid crystals were determined by setting the oven temperature $T$ of the chromatograph, allowing 10 min for equilibration and then injecting samples of $n$-heptane to determine its capacity ratio, both with and without the applied electric field. The oven temperature was observed to be constant within less than ±1 °C. The process was repeated in 5–10 °C increments, except near the transition point where the increments were 2–3 °C. The onset of the transition was indicated by a rapid increase in $k$ with $T$, and the completion of the transition was indicated by a maximum in the curves.

## RESULTS

### Transition Temperatures

Using *n*-heptane, the change in *k* with *T* for cholesteryl-10-undecenoate is depicted in Fig. 1. At 66°C *k* began to increase rapidly until it attained a maximum value at 78°C. Beyond 78°C *k* decreased, but at a slower rate. The rapid increase in *k* between 66 and 78°C is due (*6*) to the cholesteric-isotropic phase transition. Dewar and Schroeder (*7*) found a similar transition with *p*-azoxyanisole and attributed it to a decrease in free energy of solution of the sample on passing from the nematic mesophase to the isotropic liquid. It was important to determine the transition with an increasing, rather than a decreasing, temperature so as to avoid a supercooling effect such as that depicted in Fig. 1 by the dashed extension of the curve.

The gas chromatographic properties of each liquid crystal were then determined while operating the column at the temperature which produced the largest value of *k*. For example, the effect of potential on the retentions of the various solutes by cholesteryl-10-undecenoate was studied at 78°C (see Fig. 1). This point was chosen for two reasons. First, the point is reproducible. Fluctuations in oven temperature had a minimal effect on the retention time. Second, it is characteristic for each liquid crystal because it represents a state of "corresponding condition" (*8*).

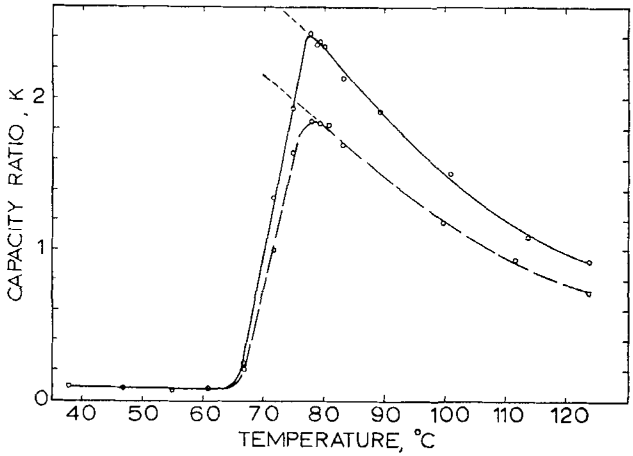

Fig. 1. Capacity ratio for *n*-heptane vs oven temperature for a column coated with cholesteryl-10-undecenoate: (- -) 0 V; (——) 500 V.

TABLE 1

Cholesteric-Isotropic Transitions of Liquid Crystals

| Liquid crystal | Transition temperature (°C) Chromatographic | Transition temperature (°C) Literature |
|---|---|---|
| Cholesteryl propionate | 87–97 | 116 [9] |
| Cholesteryl hexanoate | 94–103 | 101.5. [9] |
| Cholesteryl octanoate | 106–114 | 110 [9] |
| Cholesteryl nonanoate | 71–77.5 | 92 [9] |
| Cholesteryl 10-undecenoate | 66–78 | 95 [10] |
| Cholesteryl laurate | 75–83 | 93 [9] |
| Cholesteryl myristate | 60–79 | 86.5 [9] |
| Cholesteryl myristate[a] | 65–84 | 86.5 [9] |

[a] Column constructed from borosilicate glass; all others were constructed from soft glass.

The chromatographic cholesteric-isotropic transition temperatures for the different liquid crystals, together with some values found in the literature (*9*, *10*), are shown in Table 1. The literature values, except for cholesteryl hexanoate, lie on two curves when the cholesteric-isotropic transition temperatures are plotted vs acyl chain length. One curve is for the species which have an even number of atoms in the acyl chain, and the other where the atoms are odd in number. This type of behavior has also been observed in other families of liquid crystals (*11*). In general, the chromatographically determined transition temperatures were lower then the known values. Furthermore, the extent of depression of the transition point was not constant. These differences are not surprising since the transition points are known to depend on the nature of the surface, aging, thermal history, impurities, and sample thickness (*5*, *6*, *8*). The sample thickness would, in turn, depend on the viscosity and the wetting ability of the liquid phase.

## Effect of Electric Field on $k$

Application of a static electric field of 500 V (inner wire electrode, positive; outer graphite electrode, negative) caused the $k$ values to increase and the peak to become narrower and more nearly symmetrical in shape. Thus, qualitatively, cholesteric liquid crystals behaved in a manner much like the nematic liquid crystal reported earlier (*4*).

The capacity ratios with no electric field applied, $k_0$, with an electric field of 500 V applied, $k_{500}$, and the percentage increase in capacity ratio

TABLE 2

Gas-Chromatographic Data for a Variety of Volatile Solutes on Cholesteric Esters of a Series of Carbosylic Acids

| Sample | Propionate (97)[a] | | | Hexanoate (103)[a] | | | Octanoate (114)[a] | | |
|---|---|---|---|---|---|---|---|---|---|
| | $k_0$ | $k_{500}$ | % inc | $k_0$ | $k_{500}$ | % inc | $k_0$ | $k_{500}$ | % inc |
| Diethyl ether | 0.09 | 0.11 | 22±15 | 0.11 | 0.13 | 18±12 | 0.12 | 0.18 | 50±14 |
| Acetone | 0.11 | 0.11 | 0 | 0.13 | 0.13 | 0 | 0.14 | 0.16 | 14±9 |
| Methyl ethyl ketone | 0.37 | 0.44 | 19±3 | 0.35 | 0.41 | 17±4 | 0.39 | 0.49 | 26±3 |
| 2-Pentanone | — | — | — | 0.79 | 0.85 | 8±1 | 0.83 | 0.97 | 17±1 |
| *n*-Pentane | — | — | — | 0.09 | 0.11 | 22±14 | 0.12 | 0.18 | 50±14 |
| *n*-Hexane | — | — | — | 0.28 | 0.34 | 21±5 | 0.37 | 0.48 | 30±3 |
| *n*-Heptane | 0.86 | 0.90 | 5±1 | 0.79 | 0.89 | 13±1 | 0.92 | 1.10 | 20±1 |
| Cyclopentane | — | — | — | 0.20 | 0.27 | 35±7 | 0.29 | 0.38 | 31±5 |
| Cyclohexane | — | — | — | 0.57 | 0.69 | 21±2 | 0.70 | 0.93 | 33±5 |
| Cycloheptane | — | — | — | 2.08 | 2.30 | 10.6±0.5 | 2.53 | 2.71 | 7.1±0.5 |
| Benzene | 1.05 | 1.08 | 3±1 | 0.91 | 0.98 | 8±1 | 1.07 | 1.16 | 8±1 |
| *cis*-1,2-Dichloroethylene | 0.69 | 0.70 | 1±1 | 0.55 | 0.61 | 11±2 | 0.63 | 0.73 | 16±2 |
| *trans*-1,2-Dichloroethylene | 0.51 | 0.53 | 4±2 | 0.42 | 0.45 | 7±3 | 0.51 | 0.57 | 12±2 |

| Sample | Nonanoate (77.5)[a] | | | 10-Undecenote (78)[a] | | | Laurate (83)[a] | | |
|---|---|---|---|---|---|---|---|---|---|
| | $k_0$ | $k_{500}$ | % inc | $k_0$ | $k_{500}$ | % inc | $k_0$ | $k_{500}$ | % inc |
| Diethyl ether | 0.17 | 0.15 | −12±7 | 0.18 | 0.40 | 122±13 | 0.16 | 0.29 | 81±12 |
| Acetone | 0.15 | 0.15 | 0±7 | 0.20 | 0.42 | 110±10 | 0.17 | 0.33 | 94±12 |
| Methyl ethyl ketone | 0.61 | 0.59 | −3±2 | 0.70 | 1.12 | 60±3 | 0.54 | 0.80 | 48±3 |
| 2-Pentanone | — | — | — | — | — | — | 1.38 | 1.67 | 21±1 |
| *n*-Pentane | — | — | — | — | — | — | 0.15 | 0.31 | 107±14 |
| *n*-Hexane | — | — | — | — | — | — | 0.53 | 0.78 | 47±3 |
| *n*-Heptane | 2.04 | 2.02 | −1.0±0.5 | 1.81 | 2.33 | 29±1 | 1.60 | 1.90 | 19±1 |
| Cyclopentane | — | — | — | — | — | — | 0.35 | 0.62 | 77±5 |
| Cyclohexane | — | — | — | — | — | — | 1.02 | 1.51 | 48±1 |
| Cycloheptane | — | — | — | — | — | — | 4.26 | 4.84 | 13.6±0.3 |
| Benzene | 2.04 | 2.03 | 0±1 | 2.03 | 2.48 | 22±1 | 1.63 | 1.87 | 15±1 |
| *cis*-1,2-Dichloroethylene | 1.17 | 1.14 | −2.6±0.8 | 1.20 | 1.57 | 31±1 | 0.95 | 1.17 | 23±2 |
| *trans*-1,2-Dichloroethylene | 0.91 | 0.89 | −3±1 | 0.87 | 1.12 | 29±1 | 0.73 | 0.87 | 19±2 |

*(Continued)*

TABLE 2 (continued)

| Sample | Myristate (70)[a] | | | Myristate (Pyrex) (84)[a] | | |
|---|---|---|---|---|---|---|
| | $k_0$ | $k_{500}$ | % inc | $k_0$ | $k_{500}$ | % inc |
| Diethyl ether | 0.17 | 0.37 | 118 ± 13 | 0.18 | 0.40 | 22 ± 13 |
| Acetone | 0.15 | 0.31 | 107 ± 15 | 0.16 | 0.38 | 137 ± 16 |
| Methyl ethyl ketone | 0.61 | 0.95 | 56 ± 1 | 0.64 | 0.93 | 45 ± 3 |
| 2-Pentanone | 1.55 | 1.88 | 21 ± 1 | 1.51 | 1.91 | 27.2 ± 0.4 |
| *n*-Pentane | 0.17 | 0.34 | 100 ± 12 | 0.19 | 0.43 | 126 ± 13 |
| *n*-Hexane | 0.66 | 0.94 | 42 ± 3 | 0.65 | 1.03 | 59 ± 2 |
| *n*-Heptane | 2.03 | 2.39 | 17.7 ± 0.6 | 1.91 | 2.38 | 24.6 ± 0.7 |
| Cyclopentane | — | — | — | 0.44 | 0.87 | 98 ± 4 |
| Cyclohexane | — | — | — | 1.28 | 1.97 | 54 ± 1 |
| Cycloheptane | — | — | — | 5.18 | 6.08 | 17.4 ± 0.2 |
| Benzene | 1.98 | 2.30 | 16.2 ± 0.5 | 1.89 | 2.31 | 22.2 ± 0.7 |
| *cis*-1,2-Dichloroethylene | 1.09 | 1.36 | 25 ± 1 | 1.10 | 1.40 | 27 ± 1 |
| *trans*-1,2-Dichlorethylene | 0.88 | 1.05 | 19.3 ± 1.4 | 0.86 | 1.03 | 19.8 ± 1.4 |

[a] Temperature of column operation, °C.

upon application of the electric field for various solutes and liquid phases are shown in Table 2. The percentage increase in $k$ with potential was calculated as follows:

$$\% = 100(k_{500} - k_0)/k_0$$

All columns, except the one coated with cholesteryl nonanoate, showed larger capacity ratios for the various solutes when the electric field was applied than when it was not (i.e., $k_{500} > k_0$). Cholesteryl nonanoate showed either no increase in $k$ with potential or a small decrease.

A detailed examination of the $k$ values shown in Table 2 revealed some interesting trends. In general, the more volatile solutes, which had the smallest $k$ values, produced the greatest percentage increases in $k$ with potential. This behavior was also exhibited by the nematic liquid crystal reported previously (*4*) and was brought to our attention by McCrea and Annino (*12*).

The present study showed, however, that the dependence on $k$ of the percentage increase in $k$ was somewhat different for the different homologous families of solutes. The percentage increases in $k$ vs $k_0$ and vs $k_{500}$ for several solutes using the borosilicate column coated with cholesteryl myristate are shown in Fig. 2. The other solute and solvents showed similiar behavior except on the cholesteryl octanoate column where the line for cycloalkanes was nearly linear, rather than curved upward, and where the

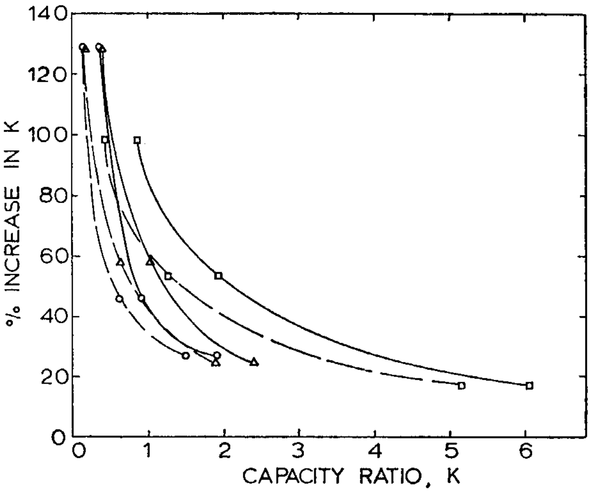

FIG. 2. Percentage increase in capacity ratio vs capacity ratio for a homologous series of solutes on a borosilicate glass column coated with cholesteryl myristate: (- -) 0 V; (——) 500 V; (○) ketones; (△) normal alkanes; (□) cycloalkanes.

line for methyl ketones curved slightly downward. However, the ketones on this column had very small *k* values and, thus, the uncertainties in the percentage increases in *k* were large.

## Effect of Solvent Chain-Length

The capacity ratios as a function of the acyl chain-length are shown in Fig. 3 for six representative solutes. The capacity ratios increased with chain length and lay on one of two curves depending on whether the acyl group contained an odd or even number of carbon atoms. For each solute, omitting the anomalous results for cholesteryl nonanoate, the curves for the liquid crystals which contained an odd number of carbon atoms in the acyl group lay above those that contained an even number. Also, the curves with the applied electric field lie above those without the electric field. Thus larger interaction is favored by the longer chains, especially those containing an odd number of carbon atoms, and by the applied potential.

Figure 3 shows that the *absolute* change in *k* with potential was largest for the species having the largest $k_0$ values; Fig. 2 shows that the *relative* change was largest for the species having the smallest $k_0$ values. Likewise,

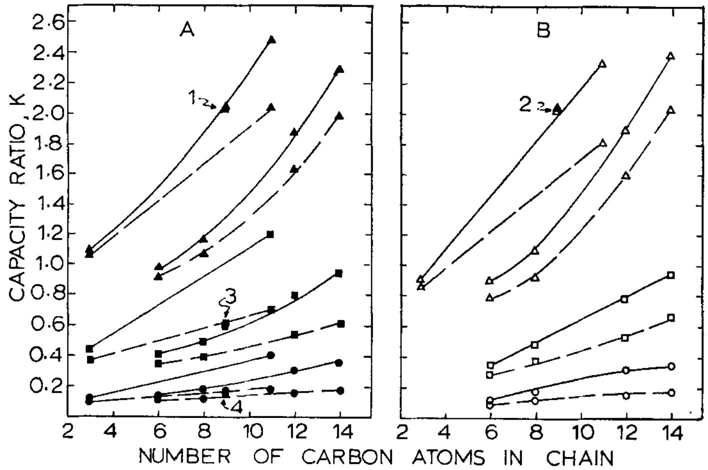

FIG. 3. Capacity ratio vs number of carbon atoms in the acyl chain of esters of cholesterol: (- -) 0 V; (——) 500 V. (A) (●) Diethyl ether; (■) methyl ethyl ketone; (▲) benzene. (B) (○) *n*-Pentane; (□) *n*-hexane; (△) *n*-heptane.

the relative increase in *k* was found to increase with acyl chain-length and to be larger for those solvents that contained an odd number of carbon atoms.

The only experimental data in Fig. 3 that do not lie within experimental error of the appropriate curves are those for cholesteryl nonanoate. For some of the solutes (e.g., benzene and *n*-heptane) the $k_{500}$ and $k_0$ both lay within experimental error of the curve with the electric field applied (see 1 and 2 in Fig. 3A and Fig. 3B, respectively) while those of others (e.g., methyl ethyl ketone and diethyl ether) lay on the curve corresponding to the data when the electric field was off (see 3 and 4 in Fig. 3A). The generally atypical behavior of cholesteryl nonanoate will be discussed later.

## Effect of Temperature

The $\log_{10} k$ values vs the reciprocal of the absolute temperature of column operation are shown in Fig. 4 for several representative solutes. This is not a conventional log $k$ vs $1/T$ plot because several different columns were used, and they were operated at different temperatures. In the present case the temperature of operation was dictated by the cholesteric-isotropic transition point (see Table 1). Nevertheless, the log $k$ vs $1/T$ curves appeared to have two linear portions that intersected at a minimum.

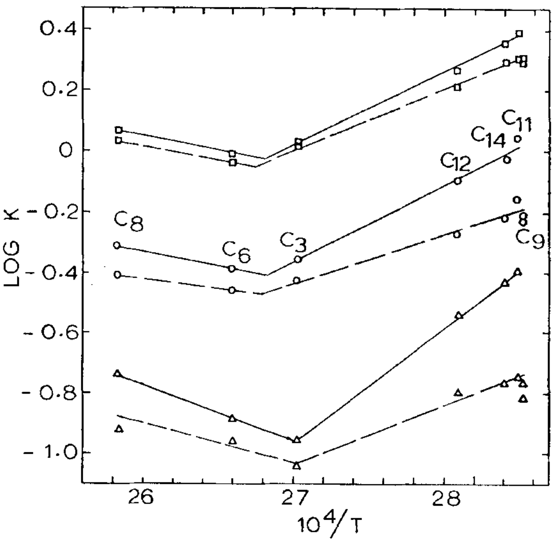

FIG. 4. Logarithm of the capacity ratio vs the reciprocal of the absolute temperature of the cholesteric-isotropic transition point of the liquid crystal stationary phase: (- -) 0 V; (——) 500 V; (△) diethyl ether; (○) methyl ethyl ketone; (□) benzene. The subscript on C corresponds to the number of carbon atoms in the acyl chain.

Although the experimental uncertainty is large, it appears that the minimum is different for each solute. For example, the reversals for benzene and diethyl ether are at $26.8 \times 10^{-4}$ and $27.0 \times 10^{-4}/°K$, respectively. Kelker and Von Schivizhoffen have reported a linear relationship (but no change in slope) between the logarithm of the specific retention volume and the reciprocal of the absolute temperature of clarification [states of corresponding condition (*11*)] for a family of closely related liquid crystals. An explanation for the change in slopes depicted in Fig. 4 is not known. Its interpretation is made more difficult by the fact that not only is the temperature changing but also the structure of the solvent. Again, the points on Fig. 4 that do not lie close to the curves are the ones resulting from the cholesteryl nonanoate column.

Graphs for several solutes of the percentage increase in *k* with potential vs $1/T$ are shown in Fig. 5. The divergence for the curves, with and without applied electric field, shown in Fig. 4 manifests itself in Fig. 5 as a "U"-shaped curve, producing larger percentage increases in *k* at either lower or higher temperatures. Again, the minima for the curves are at different

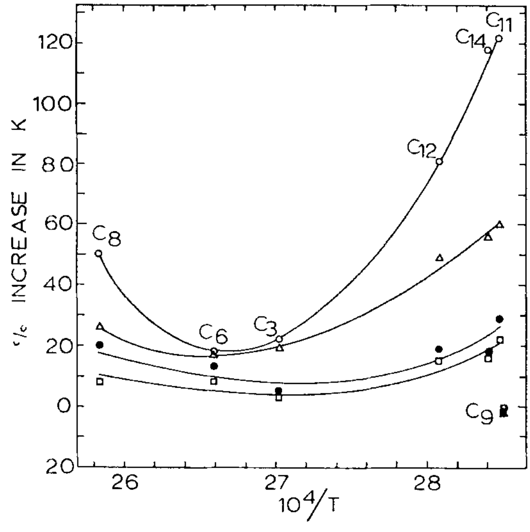

FIG. 5. Percentage increase in capacity ratio vs the reciprocal of the absolute temperature of the cholesteric-isotropic transition points of the liquid crystal stationary phases: (○) Diethyl ether; (△) methyl ethyl ketone; (●) heptane; (□) benzene. The subscript on C corresponds to the number of carbon atoms in the acyl chain.

points for different solutes. The atypical behavior of cholesteryl nonanoate is even more pronounced in this figure.

## Effects of Solute Structure

These effects will be presented in two ways: (a) as a function of boiling point and (b) as a function of carbon number. Both chain length and branching have been examined.

In Fig. 6A are plotted graphs of log *k* vs boiling point for one series of solutes, the cycloalkanes, in contact with different liquid-crystal stationary phases. In Fig. 6B are plotted log *k* vs boiling point for a variety of solutes on a single stationary phase, cholesteryl laurate. In general the lines were curved rather than straight. Specific interactions between the solutes and the oriented ester tails may account for these nonlinear curves (*6*). That idea is supported by the fact that the lines showed even more curvature when the electric field was applied and thus the liquid crystals were presumably more highly ordered. Specific interactions were further evidenced by the fact that the lines for ketones were concave downward while those for the

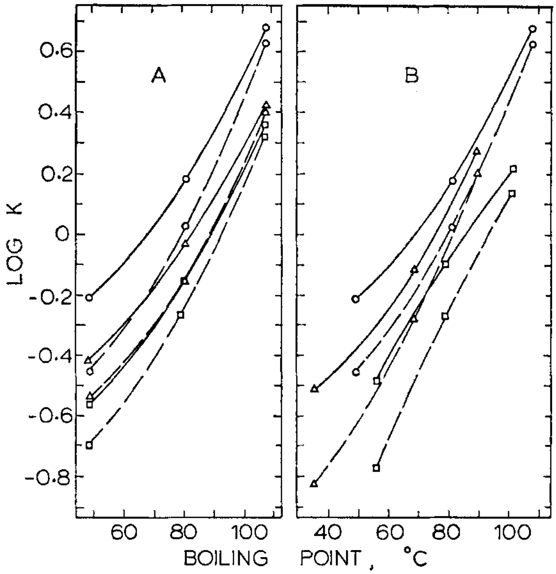

FIG. 6. Logarithm of $k$ vs the solute boiling point: (- -) 0 V; (——) 500 V. (A) Cycloalkanes on cholesteryl laurate (○), cholesteryl octanoate (△), and cholesteryl hexanoate (□). (B) Cycloalkanes (○), alkanes (△), and ketones (□) on cholesteryl laurate.

alkanes and cycloalkanes were concave upward (Fig. 6B). The curves with and without the electric field applied appear to be converging at higher boiling points.

For the columns depicted in Fig. 6B, the order of $k$ values for solutes of approximately equal boiling point was ketones, alkanes, and cyclic alkanes. That behavior suggests that the extent of interaction also increased in that order. The cholesteryl octanoate and cholesteryl hexanoate data behaved in the same way.

Plots of log $k$ vs the number of carbon atoms in the solute molecules were constructed for a variety of solutes and solvents. Again, the curves were smooth but nonlinear, an indication of specific interactions.

To study effects of molecular shape of the solute, capacity ratios of some isomeric hexanes were examined using a borosilicate column coated with cholesteryl myristate. The $k_0$ values for *n*-hexane, 2-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane were 0.56, 0.35, 0.27, and 0.14, while the $k_{500}$ values were 0.81, 0.59, 0.62, and 0.38, respectively. Their chromatographic behaviors were similar to those previously reported.

The more volatile species had the largest change in *k* with potential, and the plots of log *k* vs boiling point were nearly linear. Thus isomeric structural effects were of minimal importance.

In another study of molecular shape, the capacity ratios for the *cis*- and *trans*-1,2-dichloroethylenes were larger than expected on the basis of boiling point alone, indicating that the liquid crystals were highly selective toward these solutes. Also, in contrast to the other solutes, the more volatile species, the *trans* isomer, had a smaller relative change in *k* with potential.

## Effect of Flow Rate

Both $k_0$ and $k_{500}$ decreased with increasing carrier-gas flow rate. In Fig. 7, the $k_0$ and $k_{500}$ values for *n*-heptane on cholesteryl laurate are plotted vs the time to elute methane, a "nonretained peak." Other solutes

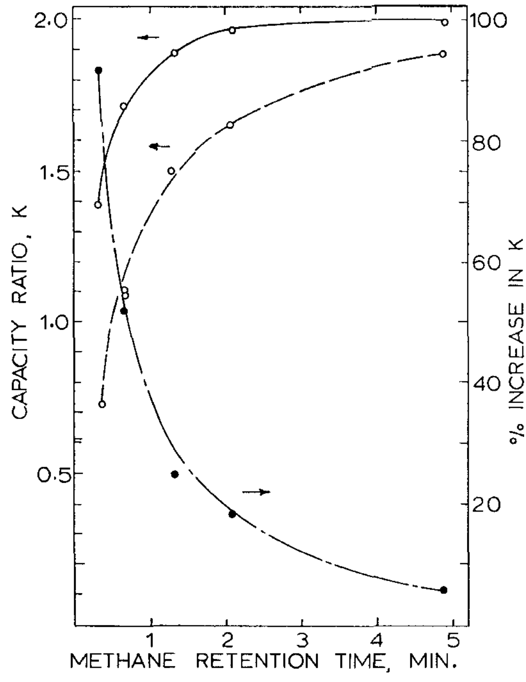

FIG. 7. Capacity ratio and percentage increase in the capacity ratio for *n*-heptane vs the retention time for methane using a column coated with cholesteryl laurate: (- -) 0 V; (——) 500 V; (— - —) percentage increase in *k*.

and solvents behaved similiarly. Likewise, the percentage change in $k$ with potential was a function of the flow rate. The percentage change in $k$ with potential decreased with decreasing flow rate (retention time for methane increasing). The results for *n*-heptane on cholesteryl laurate are also shown in Fig. 7.

The increase in $k$ as the retention time for methane increased is indicative of a nonequilibrium process. Therefore it is clear that the longer a given solute remained in the column, whether due to a slower flow rate or to lower volatility, the larger was the $k$ value and the smaller the percentage increase in $k$ upon application of the electric field.

## Effect of Column Material

In view of the fact that surface effects can influence, sometimes quite markedly, the behavior of liquid crystals, one column coated with cholesteryl myristate was made of borosilicate glass rather than of soft glass. The $k_0$, $k_{500}$, and percentage increase in $k$ with potential are shown in the last three columns of Table 2. In all cases, except for methyl ethyl ketone, the percentage change in $k$ was greater for the borosilicate glass column. This could be due to a larger $k_{500}$ on the hard glass column, a larger $k_0$ on the soft glass column, or a combination of both. Analysis of the data showed that both were important. For solutes having small $k$ values, $k_{500}$ was significantly larger on hard glass than on soft glass, whereas $k_0$ was almost the same. For example, $k_0$ values for *n*-pentane on soft and hard glass were 0.17 and 0.19, respectively, while $k_{500}$ values were 0.34 and 0.43. For solutes having larger $k$ values, $k_0$ was significantly larger on soft glass than on hard glass, while $k_{500}$ values were about equal. For example, $k_0$ values for benzene on soft and hard glass were 1.98 and 1.89, respectively, while $k_{500}$ values were 2.30 and 2.31.

The $k$ values for some of the soft glass columns, particularly those coated with cholesteryl propionoate and cholesteryl myristate, were usually somewhat smaller after the columns had been used for several days. For example, the $k_{500}$ value from *n*-heptane on cholesteryl myristate decreased from 2.48 to 2.39 after 3 days. In contrast, the $k$ values for cholesteryl myristate coated on borosilicate glass did not significantly change over a 3-week period. Similar differences between the stabilities of coatings on soft and hard glass have been reported (*13*) for the ureide of L-valine isopropyl ester when used as the stationary phase. Hence, esters may, in general, be more stable on borosilicate than on soft glass.

## DISCUSSION

Larger relative changes in capacity ratios with potential were obtained when solute solubility was low, but there was a leveling off at higher solubilities. These observations suggest that significant surface effects may be present (*12*) (see Table 2 and Fig. 2). However, Chow and Martire (*14*) have shown that, when the coating thickness of nematic liquid crystals was greater than 1000 Å on Chromosorb, surface effects were negligible at both the gas–liquid interface and the liquid crystal–solid interface compared to partition in the bulk liquid-crystal. Assuming that the liquid crystals were uniformly distributed on the surfaces in the capillary columns and that only half of the amount of liquid crystal dissolved in the plug used to coat each column was deposited on the glass surface, the coating thickness for our columns was on the order of $10^4$ Å. Hence the surface effects that appeared to be present in our columns may indicate that the surface was not uniformly coated. However, it is also possible that the results found by Chow and Martire (*14*) using nematic liquid crystals (4,4′-dimethoxyazoxybenzene and *p*-azoxyanisole) cannot be projected to cholesteric liquid crystals.

Because retention times were influenced by peak shape as well as by flow rate and volatility effects, moment analyses of the chromatograms are currently being conducted to determine the effects of these experimental variables. If the first moments are invariant upon application of an electric field, then the changes in *k* based upon peak maxima are only apparent ones that reflect peak distortion.

As discussed earlier, the maxima in the *k* vs *T* plots have been reported as the end of the cholesteric-isotropic transition (see Fig. 1 and Table 1). Reversible changes in the chromatographic properties were effected by the application of an electric field at the transition temperature as well as above it. This suggests that the liquid phase was not truly isotropic but still retained some degree of liquid crystallinity; possibly in the form of residual nuclei that could, upon application of an electric field, effect an ordering of the liquid crystal. These nuclei may exist in a nonequilibrium state. If this is true, then the extent of ordering brought about by the electric field may decrease with time as the system approaches equilibrium. For this reason the columns were prepared and their chromatographic properties determined as rapidly as experimentally possible. The changes in capacity ratio with time were small, indicating that equilibrium was achieved slowly.

As indicated earlier, the column coated with cholesteryl nonanoate consistently showed anamolous behavior in that the capacity ratios did not increase with potential nor did they lie on the curves for log $k$ vs $1/T$ or $k$ vs acyl carbon length.

Several columns of this liquid crystal were made to insure that its properties were truely related to the liquid crystal and not a consequence of a badly constructed column. They all behaved the same. Barrall et al. (*6*) also found unusual gas chromatographic properties using cholesteryl nonanoate as a stationary phase. This may be due to impurities or to an usual structure imparted to the liquid crystal, such as producing a "psuedo-cyclic" rather than a linear chain.

Cholesteryl-10-undecenoate was included in this study because initially it was believed to be the saturated rather than the unsaturated ester. However, the presence of unsaturation did not appear to effect its chromatographic properties relative to the saturated acyl chains.

## REFERENCES

*1.* P. J. Porcaro and P. Shubiak, *J. Chromatogr. Sci.*, *9*, 690 (1971).
*2.* D. G. Willey and G. H. Brown, *J. Phys. Chem.*, *76*, 99 (1972).
*3.* W. L. Zielinski, D. H. Freeman, D. E. Martire, and L. C. Chow, *Anal. Chem.*, *42*, 176 (1970).
*4.* P. J. Taylor, R. A. Culp, C. H. Lochmüller, L. B. Rogers, and E. M. Barrall II, *Separ. Sci.*, *6*, 841 (1971).
*5.* L. C. Chow and D. Martire, *J. Phys. Chem.*, *75*, 2005 (1971).
*6.* E. M. Barrall II, R. S. Porter, and J. F. Johnson, *J. Chromatogr.*, *21*, 392 (1966).
*7.* M. J. S. Dewar and J. P. Schroeder, *J. Amer. Chem. Soc.*, *86*, 5235 (1964).
*8.* H. Kelker and E. Von Schivizhoffen, in *Advances in Chromatography*, Vol. 6 (J. C. Giddings and R. A. Keller, eds.), Dekker, New York, 1968, pp. 247–297.
*9.* G. W. Gray, *J. Chem. Soc.*, *1956*, 3733.
*10.* Vari-Light Corporation, *Vari-Light High Purity Cholesterol Esters*, Cincinnati, Ohio 45242.
*11.* J. S. Dave and R. A. Vora, in *Liquid Crystals and Ordered Fluids* (J. F. Johnson and R. S. Porter, eds.), Plenum, New York, 1970, pp. 477–487.
*12.* P. F. McCrea and R. Annino, The Foxboro Company, Foxboro, Massachusetts 02035, Personal Communication, January 26, 1972.
*13.* J. A. Corbin and L. B. Rogers, *Anal. Chem.*, *42*, 974 (1970).
*14.* L. C. Chow and D. E. Martire, *J. Phys. Chem.*, *73*, 1127 (1969).

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