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EFFECT OF AN ELECTRIC FIELD ON GAS CHROMATOGRAPHIC  
RETENTIONS BY LIQUID CRYSTALS\*

by

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## Abstract

Reversible changes in gas-chromatographic peak shape and retention time were produced by applying an electric field across a capillary column that employed a liquid crystal as a stationary phase. In general, applied potential caused peaks to be retained longer and to be more nearly symmetrical in shape. The behavior of a variety of substances has been studied over a range of temperatures.

The use of liquid crystals in gas chromatography has been reviewed by Kelker and Von Schivizhoffen (1). Using liquid crystals as stationary phases, Dewar and Schroeder (2,3) separated various disubstituted benzene derivatives. Schroeder et al. (4) showed that a mixture of nematic liquid crystals could be used to change relative retention times and, thereby, extend the useful temperature range in gas chromatography. Gas chromatographic behavior, including the thermodynamics of the interactions of solutes with various mesophases, has been studied (5-8). Discontinuities in plots of retention time vs. temperature have been used to determine the temperatures at which phase transitions occur in liquid crystals (9).

Numerous workers have investigated the effects of electric (10-20) and magnetic fields (21-22) on properties of liquid crystals. Those studies have shown that increased molecular order within a mesophase and phase transitions to more ordered phases can be induced by these fields, but none have dealt with chromatographic properties. Because the more highly ordered state should be more selective (2,8) as a stationary phase, the effects of alternating- and direct-current electric fields on the gas chromatographic behavior of a liquid-crystal stationary phase have been briefly explored.

### Experimental

#### Reagents

The liquid crystals, "product A" (a mixture of cinnamate esters shown by IR and NMR analysis to contain anisoate side chains) and cholesteryl myristate, were obtained from Vari-Light Corp., Cincinnati, Ohio. The exact composition of the nematic material

is unknown but is unimportant in this study; the important facts are that the material has a well defined nematic mesophase and that the mesophase exists over a broad temperature range, including room temperature. More detailed studies, such as the measurement of solution heats or the development of specific selectivities, will, however, require the absolute definition of the mesophase. The Vari-Light product A is also known to be easily oriented in an electric field in various nematic "display" devices.

Ethyl cinnamate was reagent grade from Eastman Organic Chemicals. Volatile chromatographic samples included chloroform, n-propanol and acetone ( J. T. Baker, reagent grade), diethyl ether (Mallinckrodt, analytical reagent), benzene (Mallinckrodt, spectrometric grade) and heptane (Matheson Coleman and Bell, chromoquality). All chemicals were used as received without further purification, except chromatographic samples, which were stored over 4A molecular sieves.

#### Apparatus.

Two chromatographic systems were used. Preliminary evaluation of the liquid phases was done using a chromatograph constructed from an oven salvaged from a F & M Model 770 preparative chromatograph and a Carle Model 100 Micro Detector system. A second system employed an Aerograph 660 gas chromatograph, modified to minimize the dead volume, and a flame-ionization detector operated at 180°C. A Honeywell Elektronik 19 recorder was used in all cases.

The 5 mm soft glass tubing used to make the capillary columns was rinsed with successive 5-ml portions of dichloromethane, methanol, and acetone. The tubing was then thoroughly dried before

being drawn on a glass-drawing machine (Hupe Apparatebau, Karlsruhe, Germany). While the straight capillary column was being drawn, 31 AWG (0.023 cm diameter) Chromel-A wire (Hoskins Mfg. Co., Detroit) was fed into the tubing. The columns were coated by the plug method using a micro-electrolytic cell described by Kaiser (23). The plugs, 50% by weight of liquid crystal in diethyl ether unless otherwise noted, were forced to move downward through the column at a rate of 2 ml/min. Then, using a flow rate of 0.3 ml/min of nitrogen, the columns were dried overnight at room temperature.

The outer electrodes for the straight capillary columns were made as follows. A thin paste consisting of a mixture of about 1.83 g powdered graphite (E.H. Sargent, technical grade), 0.80 g water soluble glue (Elmer's Glue-All, Borden Chemical Co., New York) and 2.9 g water was painted on the outer surface of the column using a small brush. The paste was allowed to dry about 2 hours. Then, to insure electrical continuity, the capillary column was wrapped with aluminum foil and, finally, with heat resistant tape (fiberglass type GV Temp-R-Tape, Connecticut Hard Rubber Co., New Haven). The resulting linear columns (0.6 mm i.d., 1.1 mm o.d. and 1.7 m long) were mounted on strips of wood and installed in the preparative chromatograph using 1.2 mm heat shrinkable Kynar tubing (Newark Electronics, Chicago) for connections to the splitter and to the detector. A short length of the central wire electrode (about 10 cm) was folded over the outside of the uncoated ends of the capillary prior to connection with the shrinkable tubing in such a manner as to provide a 5 cm lead for connection to the power supply.

To obtain greater accuracy and precision in retention-time measurements, longer columns were constructed in a similar manner except that they were coiled. After painting the graphite paste on the outer surface of each individual coil, the coils were collected together and wrapped as one unit with the aluminum foil and heat resistant tape. The resulting columns (0.6 mm i.d., 0.9 mm o.d. and 5.7 m long) used in the detailed studies, were installed in the Aerograph 660 system.

Static electric fields were maintained using a Beckman Duostat regulated power supply. Variable frequency sinusoidal electric fields were obtained using a Heathkit Model AG-10 sine-square signal generator. The signal was amplified to 300 V peak-to-peak using a push-pull operational amplifier configuration (Heathkit Model EUW-19B operational amplifier system).

A flow rate of 0.5 ml/min of helium was maintained through the linear columns in the preparative chromatograph, and flow rates of 0.16 or 0.08 ml/min of nitrogen were maintained through the coiled columns in the Aerograph 660 system. A 0.05 ul liquid sample was injected into a 100:1 Hamilton inlet splitter operated at 100°C using a 2.00 ul Pressure-Lok syringe (Precision Sampling Corp., Baton Rouge, Louisiana). The capacity ratio,  $k$ , was calculated in the usual way using air or methane as a "non-retained" reference peak to determine  $t_{\underline{n}}$ .

A DuPont 900 Thermal Analyzer was used to obtain the differential thermogram of Vari-Light A. Microscopic examination of this liquid crystal was performed using a Mettler hot stage between crossed polarizers.



## Results

### Differential Thermal Analysis and Microscopy:

Prior to construction of columns, the nematic range of Vari-Light A was determined. A 1 mg sample of the material was run in the thermal analyzer capillary melting-point cell from 0° to 85°C. The differential thermogram, Figure 1, shows that the endotherm due to the solid → mesophase transition begins at 32°C with a shoulder at 34°C and endothermal minimum at 36.2°C; the endotherm concludes at 39°C. The nematic mesophase shows a large pre-melting heat capacity change; this has been noted previously for similar materials (24). The premelting effect makes it impossible to determine accurately the onset of the mesophase → Isotropic liquid transition. Rapid endothermal processes appear to begin near 79°C. The characteristically sharp minimum of the endotherm occurs at 81.2°C and conversion to the isotropic liquid is complete by 82.5°C. On cooling the isotropic liquid, the nematic mesophase reforms at 80.9°C (supercooled by 0.3°C). The nematic mesophase does not form down to 20°C. The solid phase formation is supercooled to ~-10°C. On reheating, the thermogram was repeated in all essential details.

Microscopic examination, using a hot stage between crossed polarizers showed that the mesophase which formed between 36.2° and 81.2°C was indeed nematic. The characteristic dark nematic "threads" were in clear evidence against the bright background of depolarized (or rotated) light. Repeated heating up to 95°C under nitrogen did not result in any measurable depression of the nematic → isotropic liquid transition or broadening of the DTA endotherms. Thus, Vari-Light A appears to be thermally stable to decomposition up to 95°C.

Preliminary Chromatographic Experiments.

These were conducted using the shorter linear columns, which were easier to construct and install. Using Vari-Light A at 54°C and a flow rate such that the air peak required 1.17 min to elute, a potential of  $\pm$  400 V dc or more was found to produce the maximum increases in the capacity ratios of 20-40%. Furthermore, all peaks became narrower as shown in Figure 2.

Up to 400 V dc, the increase in retention time as a function of potential was linear. The change in each retention time,  $t_r$ , with potential was rapidly and reversibly attained when the potential was switched on or off. Furthermore, positive and negative potentials (the sign referring to the potential on the wire) appeared to be equally effective in increasing the capacity ratios.

In an effort to determine whether or not one particular location of the liquid (on the central wire or on the glass wall) had a greater influence on the contribution of the liquid phase, two experiments were done. In one, the coated wire was removed from the original capillary and placed in an uncoated capillary. In the second experiment, an uncoated wire was placed in the original capillary. Both systems showed nearly the same percentages of change in  $k$  with potential, and the increases were only about half of those observed when both surfaces were coated. For example, the percentage increases in  $k$  for heptane upon the application of a +500 V potential were as follows: both wall and wire coated, 25%; wall coated, 13%; and wire coated, 14%. In one experiment, neither the wall nor the wire was coated with liquid phase, and no changes in  $k$  with potential were

observed. It was concluded, therefore, that the surfaces contributed about equally to the changes in  $k$ .

The change in  $k$  as a function of potential for a given substance differed from column to column, suggesting that the level of liquid loading and/or the thickness of the glass were important. However, the absolute changes in retention time with potential were small, due to the shortness of the column and the small amount of liquid phase. To obtain larger absolute changes in retention time, longer coiled columns coated with 25%, 50%, and 75% solution of Vari-Light A were constructed. These data, being relatively more accurate and precise, were used to determine the effects on  $k$  of potential, temperature, loading, and frequency.

Before abandoning the shorter columns, two other stationary phases were examined so as to confirm the belief that the observed increases in retention times were a property of liquid crystals. One column was coated with ethyl cinnamate, which was not a liquid crystal, and it exhibited no change in capacity ratios upon application of a potential up to  $\pm 500$  V dc. ( $T = 54^{\circ}\text{C}$ ). In contrast, the second column material was a liquid crystal, cholesteryl myristate, and it exhibited changes in retention times with potential of 20-60% and 10-40% at  $76^{\circ}$  and  $86^{\circ}\text{C}$ , respectively, for the various samples.

#### Detailed Chromatographic Studies.

EFFECT OF POTENTIAL. As indicated earlier, not only did the retention times of the peaks increase with potential, but the peak shape became more nearly Gaussian and showed decreased tailing. Both effects improved the efficiency of a column. At zero potential,

diethyl ether and benzene were not completely resolved, whereas, at -500 V, base-line separation was achieved. (See Figure 2.)

Retention times for heptane and acetone, as functions of potential and temperature, are shown in Figure 3. Again, the retention times increased linearly with potential until a limiting threshold potential was reached, and the retention times at -500 V were, within experimental error, the same as for + 500 V. (See Table I) However, the threshold potentials were significantly smaller for the coiled columns than for the linear column, probably because of the smaller outside size of the capillary and the thinner wall each of which would require a smaller applied potential in order to attain a given potential gradient between the two electrodes. For example, the limiting threshold values for the applied potential at 54°C were 95 and 400 V for the coiled and linear columns, respectively.

The threshold potential decreased in absolute magnitude with increasing temperature. For example, values at 45°, 63° and 90°C for heptane were -92, -76 and -64 V, respectively. (See Figure 3) That trend is in agreement with the results of Wysocki and co-workers (14) who found, using mixtures of cholesteric liquid crystals, that the minimum potential required to induce a phase change decreased with increasing temperature. They attributed it to decreased viscosity.

**EFFECT OF FREQUENCY.** For heptane, a plot of the retention time at 54°C vs the frequency of a 300 V peak-to-peak sinusoidal signal is shown in Figure 4. For comparison the retention times were 1.77 and 2.27 min at 0 and -500 V dc, respectively. Both this figure and Figure 3 suggest that static fields at or above the threshold

potential ordered the mesophase while smaller potentials effected a proportionately smaller degree of ordering. Likewise, low frequency sinusoidal signals of potentials in the plateau region also achieved complete ordering. However, as the frequency was increased, the degree of ordering decreased smoothly until about 350 Hz above which it had no measurable effect.

**EFFECT OF TEMPERATURE.** The percentage increases in  $k$  upon the application of a -500 V potential, as a function of temperature are depicted for various substances, in Figure 5. To insure that the effect was not due to decomposition of the liquid phase and that it was reversible, the temperature was changed as follows:  $54^{\circ}$ ,  $72^{\circ}$ ,  $45^{\circ}$ ,  $63^{\circ}$ ,  $90^{\circ}$  and then  $54^{\circ}\text{C}$  again. Changes in  $k$  were smaller at higher temperatures, presumably owing to increased thermal motion. Significantly, changes in  $k$  were observed at  $90^{\circ}\text{C}$ , which is above the temperature of the nematic-isotropic transition of  $81^{\circ}\text{C}$ . Unfortunately, the retention times for  $n$ -propanol were always sample-size dependent and varied in an erratic manner.

**EFFECT OF LIQUID LOADING.** Columns coated with a 25% or a 50% solution of Vari-Light A resulted in smaller changes in  $k$  than those for a column loaded with a 75% solution. Representative changes at  $54^{\circ}\text{C}$  were 21%, 25% and 90% for acetone on going from 0 to -500 V using columns that had been coated with 25%, 50% and 75% solutions, respectively. Occasionally, however, a column coated with the 25% solution showed little or no effect of applied potential on the retention times. This was probably the result of insufficient loading, so the highest feasible loading should be used.

### Discussion

Use of an electric potential has resulted in improved resolution of chromatographic peaks because retention times increased and peak widths decreased. This effect is easily explained. In the absence of an electric field, the normal condition in the nematic mesophase is a swarming of molecules into regions of average, longitudinal order, i.e., molecules oriented with long axes parallel with no particular order between ends. These swarms orient on a surface so that the molecules are predominantly parallel to the surface. However, in an electric field, the swarms reorient with the long axes parallel to the electric field gradient (25,26). In the case of the gas chromatographic column, this would correspond to a change in orientation from wall-parallel to wall-vertical upon application of a field. In the wall-parallel configuration, the aromatic rings are exposed to the solute vapors; in the wall-vertical configuration, the aliphatic ends of the rod-like molecules are exposed. The effect of applying the field is to shift the nature of the stationary phase from a polar, aromatic one to an aliphatic, less polar one.

Since these aromatic molecules display an induced dipole in an electric field (27), interaction between field frequency and the molecules is to be expected. The direct-current or low frequency alternating-current field should give the most stable orientation.

In addition to orientation, another field effect reported for nematic liquid crystals (27) is "streaming." Swarms of molecules of the same orientation undergo a turbulent disturbance in the field

and are transported in the field gradient. This effect would make more of the viscous stationary phase accessible to the moving solute and, thereby, increase the apparent capacity of the stationary phase. Streaming would also tend to disorder the swarm alignment and, thus, decrease the selective effect of the field. Such behavior suggests that there may be an optimum voltage gradient at which the swarms are aligned but not undergoing a significant amount of streaming. Although we found a leveling-off rather than a maximum, these observations agree substantially with the effects seen in the gas chromatographic column.

The percentage increases in  $\underline{k}$ , shown in Table I, appeared to depend on a combination of molecular shape and dipole moment of the sample. Smaller or more nearly linear molecules may be retained longer because they fit more easily between the molecules of the nematic phase; in addition, those having significant dipole moments may interact more strongly with the ordered dipoles of the liquid crystals. The dipole moments (in Debye units) of the samples in the gaseous state are: benzene, 0; heptane, 0; chloroform, 1.02; diethyl ether, 1.15; n-propanol, 1.69; and acetone, 2.89. Diethyl ether and acetone, which are small and have large dipole moments showed the greatest increases in  $\underline{k}$ ; while heptane which is somewhat larger and chloroform which has only a small dipole moment showed smaller changes in  $\underline{k}$ . Benzene which is moderately large and has no dipole moment showed the smallest change in  $\underline{k}$ . n-Propanol which is primarily held up, to a large extent, by hydrogen bonding showed little or no effect due to change in polarity of the stationary phase.

An area worthy of future investigation is that involving separations of enantiomers. The fact that better resolution of enantiomers was achieved when a stationary liquid phase was allowed to solidify (28) suggests that the degree of ordering in the stationary phase may be important. If the optically active stationary phase were derivatized using a liquid crystal, increased ordering might be achieved by applying a potential rather than by lowering the temperature. Likewise, cooling the isotopic liquid to its mesophase or crystalline solid while applying a potential might cause the molecules to crystallize out into a more favorable geometry for resolution of enantiomers.

Another area that deserves exploration is the use of programmed potential. By applying a ramp potential it might be possible to achieve effects analogous to those obtained using a programmed temperature.



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TABLE I

Retention times and capacity ratios at  
potentials of 0, -500 and +500 V.<sup>1</sup>

Sample	Potential, V	$t_r^2$ , min	$t_r - t_n$ , min	$k$	Increase in $k$ , %
Diethyl ether	0	0.77	.15	0.24	-
Diethyl ether	-500	1.00	.38	0.61	150
Diethyl ether	+500	1.01	.39	0.63	160
Benzene	0	3.12	2.50	4.03	-
Benzene	-500	3.85	3.23	5.21	29.2
Benzene	+500	3.76	3.14	5.06	25.6
Acetone	0	1.03	0.41	0.66	-
Acetone	-500	1.43	0.81	1.31	98
Acetone	+500	1.40	0.78	1.26	90
Heptane	0	2.09	1.47	2.37	-
Heptane	-500	2.72	2.10	3.39	42.9
Heptane	+500	2.71	2.09	3.37	42.2
Chloroform	0	2.45	1.83	2.95	-
Chloroform	-500	3.04	2.42	3.90	32.2
Chloroform	+500	3.07	2.45	3.95	33.9
<u>n</u> -Propanol <sup>3</sup>	0	2.88	2.26	3.65	-
<u>n</u> -Propanol <sup>3</sup>	-500	3.30	2.68	4.32	18.6
<u>n</u> -Propanol <sup>3</sup>	+500	3.24	2.62	4.32	15.9

<sup>1</sup> Column 5.7 m long, coated using a 75% solution of Vari-Light A and operated at 54°C.

<sup>2</sup> Retention time for methane,  $t_n$ , was 0.62 min.

Retention times are sample size-dependent and erratic.

### Figure Captions

Figure 1. Differential thermogram of Vari-Light A, using a heating rate of  $5^{\circ}\text{C}/\text{min}$ . The upper and lower curves are for the heating and the cooling cycle, respectively.

Figure 2. Chromatogram at  $54^{\circ}\text{C}$  of diethyl ether-benzene mixture using a coiled capillary column coated with 50% solution of Vari-Light A.

Dashed line - potential 0 V

Solid line - potential - 500 V

Figure 3. Retention time as a function of potential for the same column and conditions as in Figure 2.

Dashed lines - heptane

Solid Lines - acetone

⊗  $45^{\circ}\text{C}$ , ○  $63^{\circ}\text{C}$ , ●  $90^{\circ}\text{C}$

Figure 4. Retention time at  $54^{\circ}\text{C}$  as a function of frequency for a peak-to-peak potential of 300 V applied to a coiled capillary column coated with a 75% solution of Vari-Light A.

Figure 5. Increase in capacity ratio as a function of temperature for an applied potential of -500 V on the same column as in Figure 2.

○ Ether

□ Chloroform

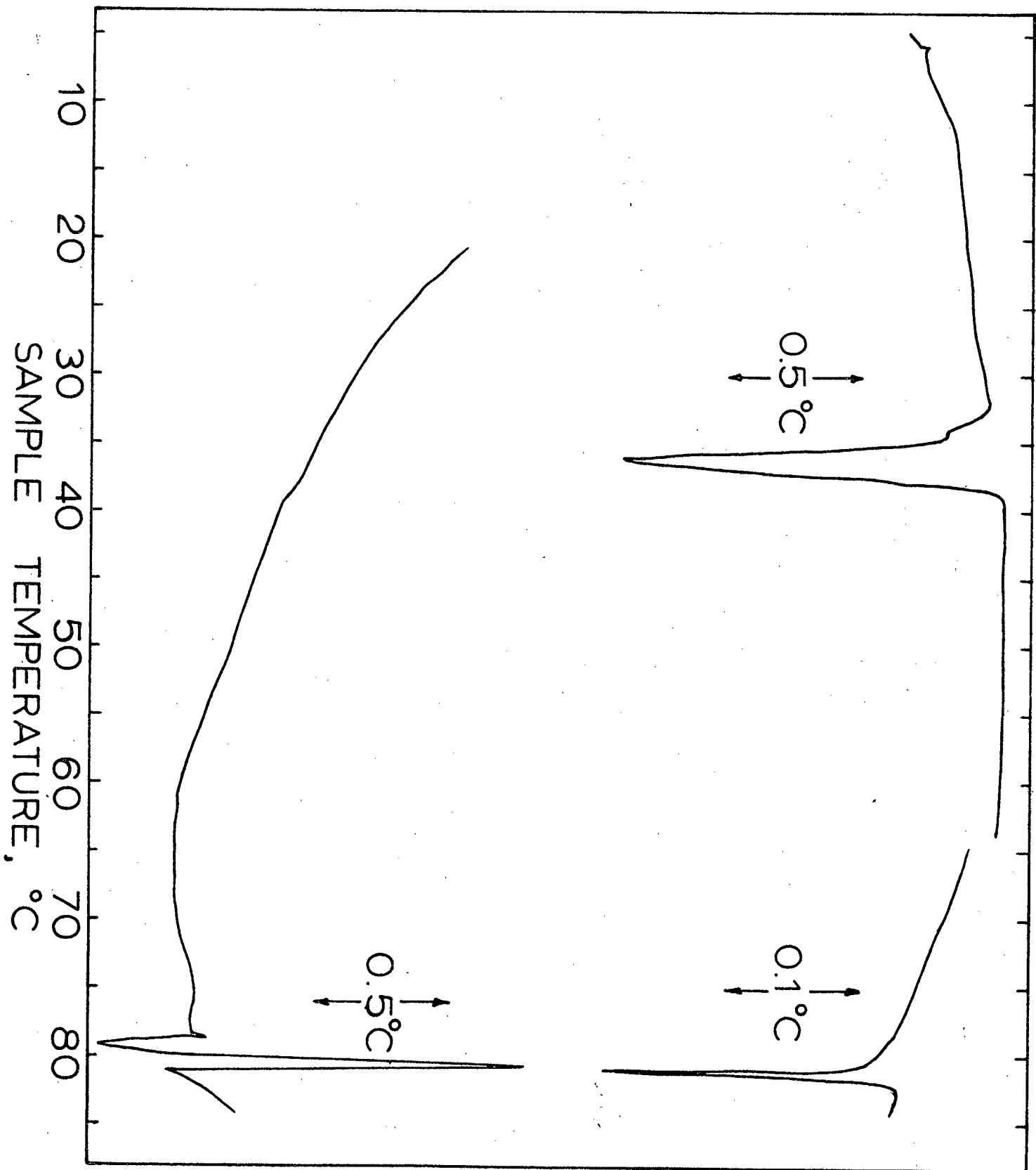
△ Benzene

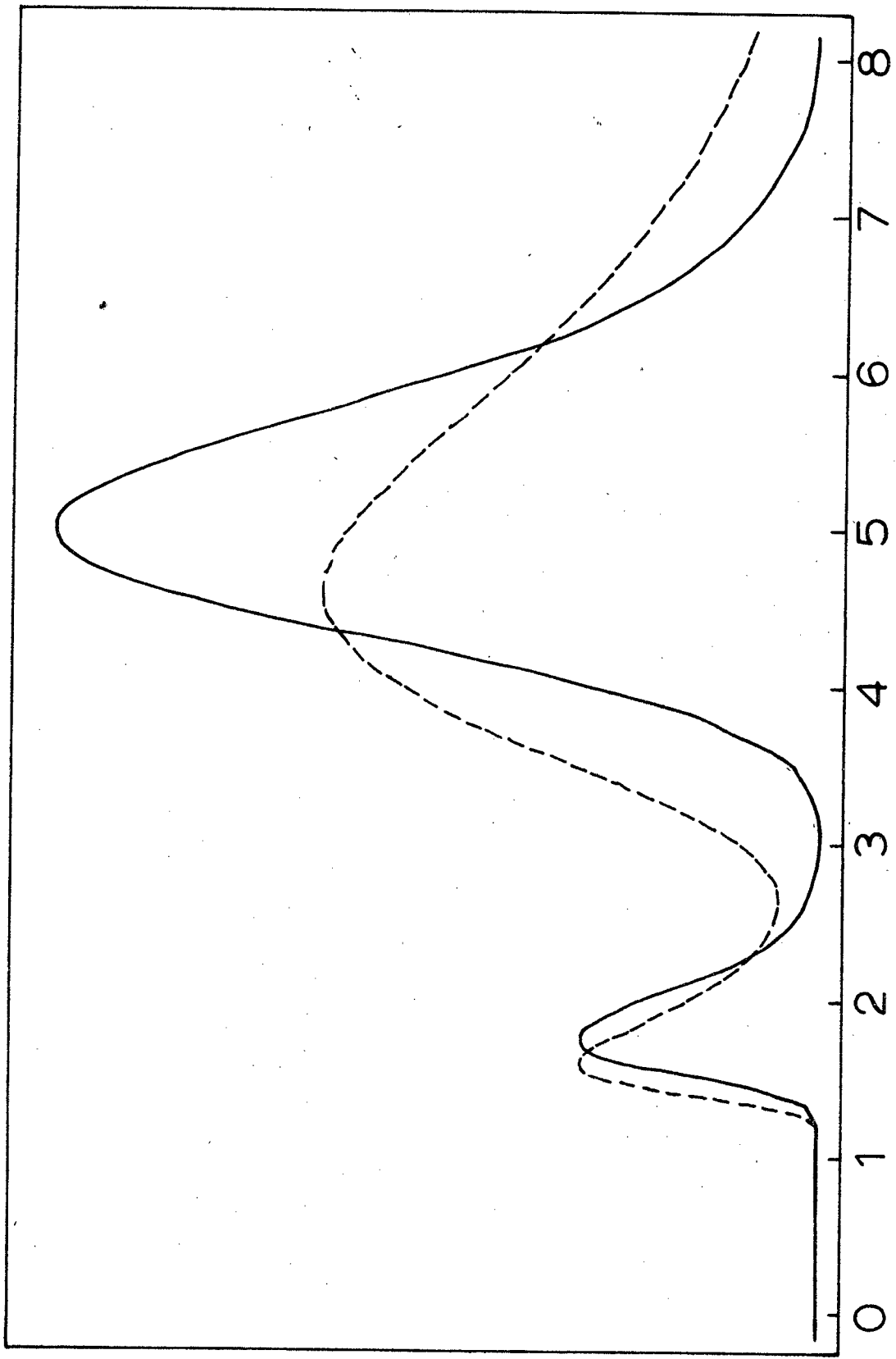
● Heptane

■ Acetone

▲ n-Propanol

DIFFERENTIAL TEMPERATURE, AS INDICATED  
← ENDOTHERMAL                      EXOTHERMAL →





DETECTOR RESPONSE

RETENTION TIME, MIN

