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SOLID SUPPORT SURFACE EFFECTS ON THE CHROMATOGRAPHIC BEHAVIOR OF A LIQUID CRYSTAL STATIONARY PHASE

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SUMMARY

The present paper investigates the behavior of p-(p-ethoxyphenylazo)phenyl undecylenate (EPAPU) liquid crystal as a stationary phase coated on glass beads in gas chromatography under a variety of conditions. The columns studied were 0.69% and 0.10% (w/w) mesophase coated on neutral glass beads and 0.11% (w/w) on acid-treated beads. Unlike previous studies no hysteresis was found in the capacity ratio, k', and the plate height, H, as a function of the temperature. However, around the chromatographically observed melting point, k' and H varied with time at a given temperature. The same behavior was found around the solidification point. Surface orientation effects and the "swarm" model were used in trying to explain the above phenomena. When comparing EPAPU coated on acid-treated glass beads and on neutral beads different kinetics behavior (in terms of H) around the melting point was observed. The diffusion coefficients of p-xylene in EPAPU and activation energies in the nematic range were obtained. The lightly loaded columns gave very similar results which differed from the heavily loaded columns.

INTRODUCTION

Liquid crystals are now being used quite extensively in gas chromatography (GC) as selective stationary phases. They have long been used for the separation of various structural isomers, in particular for the separation of p- and m-substituted aromatics[1-14]. In addition, GC has become an important tool in studying the thermodynamic parameters of liquid crystal mesophases[9,15-23]. Several reviews have been devoted to the usage of liquid crystals in GC[24,25]. Recently, optically active smectic liquid crystals have been employed in GC for the resolution of various enantiomers[26-28]. However, up to this point, the chromatographic properties of liquid crystal mesophases have not been studied except by Rogers' group[29-31] as well as our own[32,33]. In particular, kinetics phenomena involving mass transfer in mesophases were rarely studied. With this lack of data in mind, it was decided to study the chromatographic mechanism in liquid crystals closely.

From our previous work, it became obvious that the surface on which the liquid crystal is coated can affect mass transfer properties in the latter phase. During initial studies using liquid crystals as the stationary phase coated on glass beads, p-

azoxyanisole (PAA) was used. However, reproducible data could not be obtained and it was discovered that PAA had an appreciable vapor pressure[34] and was not suitable as a stationary phase for GC. For that reason, the liquid crystal p-(p-ethoxyphenyl-azo)phenyl undecylenate (EPAPU) was employed since it showed no appreciable vapor pressure.

In our previous paper, initial studies were described on the behavior of EPAPU coated on glass beads. The probe molecules or solutes were p- and o-xylene. Glass beads were chosen as the solid support because their geometry is predictable, their surface is smooth and the distribution of a stationary phase on them is fairly well understood in terms of contact angles, surface tension, etc. Also, their chromato-graphic properties as solid supports have been very well defined and established[35]. In addition, glass tends to orient liquid crystal molecules. The nature of the orientation depends upon the prior treatment of the glass surface[36,37]. The glass beads used in that early study were cleaned and washed with the neutral solvent methylene chloride.

In the present study, the behavior of the mesophase on both neutral and acid-washed glass beads is studied. Here again, p-xylene is used as the solute. A closer look is taken at the behavior of the capacity ratio and plate height along with mass transport in the stationary phase.

EXPERIMENTAL

Apparatus

The gas chromatograph used for all the determinations was a modified Hewlett-Packard (Avondale, Pa., U.S.A.) Model 5750 research chromatograph. The modified heating system is described elsewhere[33].

The original injection block was disconnected and a new system installed. The new injection system consisted of a Seiscor (Tulsa, Okla., U.S.A.) Model VIII gas sampling valve, which was actuated by a selenoid valve. The selenoid valve was con-trolled by an automatic digital sequencer system[38]. Sample injections were done as described before[33].

Reagents

The reagents used and the purification of EPAPU were described before[33]. The glass beads were of soda-lime composition (60–70 mesh).

Procedure

Copper columns 200.0 cm long and of 1/4-in.-O.D. were used for all of the experiments. The glass beads were initially rinsed several times with methylene chloride and then dried overnight. One batch of the glass beads was placed in a three-necked flask and etched with gaseous hydrogen chloride at 350° for 56 h. The beads were then washed in concentrated hydrochloric acid, water, acetone and finally methylene chloride. Three batches of EPAPU coated on glass beads were prepared: 0.69% and 0.10% (w/w) on untreated beads and 0.11% (w/w) on the acid-treated glass beads. The weight percentages were determined by extracting 10-g samples with methylene chloride using Selas crucibles. The extractions were done on at least three different batches. The columns were dry-packed and conditioned overnight at 120°.

At least five runs were made at each temperature and velocity. Sixty minutes

were allowed between runs at different temperatures in order to achieve thermal equilibrium. The peak widths at half heights and retention times were obtained from the chromatograms. The peak widths were always greater than 1.00 cm.

The density of the EPAPU was determined using a 2-ml pycnometer. The volume of the pycnometer was first calculated at each temperature (70.0, 80.0, and 90.0°) by filling it with distilled water and calculating the volume based on the standard densities of water. The volume of the pycnometer at 100.0 and 110.0° was estimated from the previous three temperatures. The pycnometer was then dried thoroughly and filled with EPAPU. The density of the EPAPU was determined by measuring the amount of EPAPU in the pycnometer at each temperature and dividing by the previously calculated volumes. The estimated accuracy of the measurements is less than 0.5%.

RESULTS AND DISCUSSION

Effect of amount of EPAPU on plate height

The plate height can shed light on the kinetic processes which occur in the column. Previously[33] we obtained Van Deemter plots for three EPAPU loadings, on the untreated beads, at three different temperatures.

Three Van Deemter plots, shown in Fig. 1, were obtained here for the 0.11 % acid-treated column in which *p*-xylene was used as the solute. Each plot was at a different temperature, as indicated in the figure. The first two temperatures corresponded to the nematic range of the liquid crystal while the third temperature corresponded to the isotropic liquid.

The Van Deemter plot at 66.2° was obtained first, after which the plots at 88.3° and 111.2° were determined. These three temperatures are about the same as
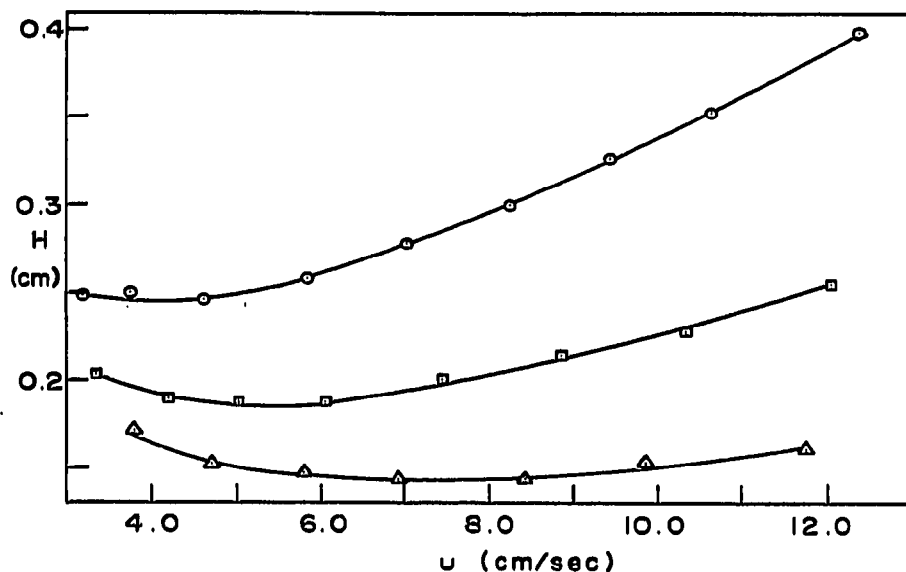

Fig. 1. HETP *vs.* carrier velocity. The circles, squares and triangles represent runs at 66.2°, 88.3°, and 111.2°, respectively.

those in Figs. 1–3 of ref. 33. (Erroneously we indicated in that reference that the Van Deemter plot at 66° corresponded to solid EPAPU.)

Several significant features should be mentioned. The plate height decreases for a given carrier gas velocity as the temperature increases. All of the peaks tailed slightly but the tailing decreased as the temperature was increased. In general, the plate heights were fairly high in the nematic and isotropic phases, indicating large resistance to mass transfer, perhaps in the liquid crystal. The best HETP value, obtained at 111.2°, was a mediocre 1.44 mm. It is of interest to mention here that normally in cases where the resistance to mass transfer in the liquid phase is predominating an increase in temperature can actually increase the plate height (*i.e.*, worse efficiency). The resistance to mass transfer C_s can be written as

$$C_s = q \frac{k' d_f^2}{(1 + k')^2 D_s} \qquad (1)$$

where k' is the capacity ratio, d_f is the stationary phase film thickness, D_s is the diffusion coefficient of the solute in that phase, and q is a geometric factor. As T increases D_s will increase while k' will decrease. The term $k'/(1 + k')^2$ has a maximum at $k' = 1$. Thus, although the increase in D_s will tend to improve the C_s term, the decrease in k' (provided the latter is greater than, but close to, unity) will more than negate the diffusion effect. In the present case it will be shown that C_s is the predominating contribution to the HETP but that the change in the diffusion is more important than the change in k'.

As before[33], the velocity at the Van Deemter minimum increased markedly as the temperature increased, doubling in value as the temperature increased from 66° to 111°. This behavior indicates that the resistance to mass transfer terms in the HETP decrease in magnitude as the temperature rises.

$\bar{u}_{min.}$, the velocity at the minimum of the Van Deemter plot, can be expressed as

$$\bar{u}_{min.} = \sqrt{\frac{B}{C_s + C_m}} \qquad (2)$$

where B is the solute molecular diffusion term and C_s and C_m are the resistance to mass transfer in the stationary and mobile phases, respectively. From eqn. 1 and the behavior depicted in Fig. 1, it can be summarized that $C_s + C_m$ most likely decreases with increasing temperature. This is consistent with the previous discussion regarding the importance of diffusion in the mesophase. The flatness of the HETP curves in Fig. 1, especially at 111.2°, is noteworthy, and it is in agreement with other works (*viz.* ref. 39 and refs. therein). In general, the three Van Deemter plots shown here are very similar to the 0.10 % untreated column[33]. The fact that the HETP plots at velocities higher than $\bar{u}_{min.}$ flatten with increasing T support the hypothesis of decreasing C_s and C_m terms.

Another reason for the high value of the HETP might be due to poor wetting of the glass by the EPAPU. We did not try to measure contact angles and surface tensions. It was felt that if such measurements were done on a glass slab the results may not be transferable to the glass beads because of impurities, etc. The laboratory is not equipped to study contact angles as a function of temperature. Since the liquid

crystal is polar, it should wet the glass quite well. The upcoming discussion will also show that different treatment of the beads does not change drastically the plate height values. Thus, although we realize that surface wetting problems might exist, we feel that most likely these are not important in the present study.

Temperature dependence of retention

In our initial study, using glass beads coated with EPAPU as the stationary phase, it was noticed that with the heavier loaded column, *i.e.* 0.69% mesophase, the HETP (H) had a temperature hysteresis while k' did not. Upon heating and then cooling, two different H values were obtained at the same temperature. With regard to our present study, the results for k' are shown in Figs. 2, 3, and 4. All of these plots are for the solute *p*-xylene with the carrier gas velocity maintained at 12.0 cm/sec, well above the Van Deemter minimum (except perhaps at the very high temperatures).
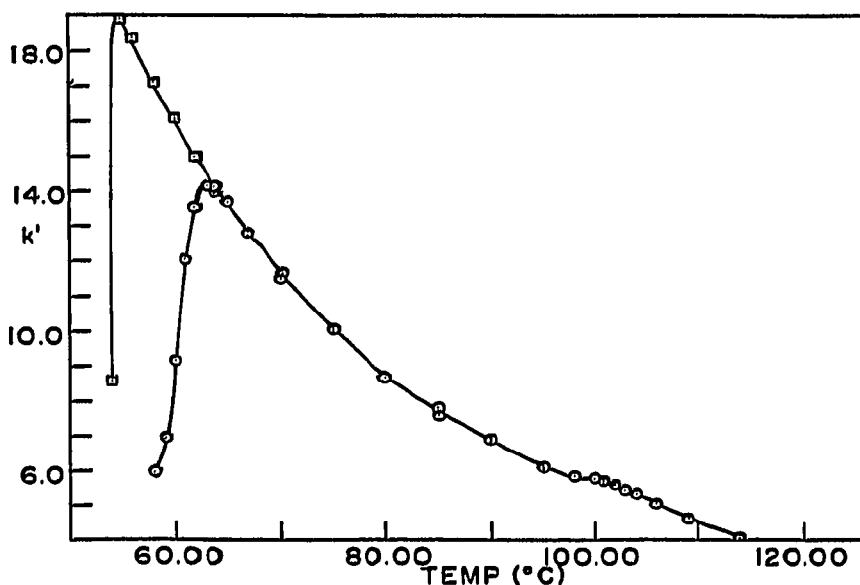

Fig. 2. Capacity ratio *vs.* temperature on the 0.69% column. The circles and squares represent the heating and cooling cycles, respectively. Identical points on both cycles are represented by circles only.

Fig. 2 shows the k' *versus T* plot for the 0.69% untreated column. The column was heated from 58° (EPAPU in its solid form) to 114° (EPAPU in its isotropic form). The column was then cooled down until the retention data indicated the solidification of the mesophase. Upon heating, the capacity ratio k' increased drastically between 60° and 64°. At 100° a curvature in the plot, indicative of phase change, is present. In the temperature range 64–114° heating and cooling yielded the same k' values. However, the liquid crystal can be "supercooled" to the temperature of 55°. Fig. 3 is for the 0.10% untreated column. The overall behavior of k' as a function of *T* is similar to that depicted in Fig. 2, except for the magnitude of k', which is smaller due to the lower amount of stationary phase. The clearing point is again at about 100°. The initial rise in k' is steepest between 60° and 62°. At this liquid loading the "supercooling" extended only to about 59°.
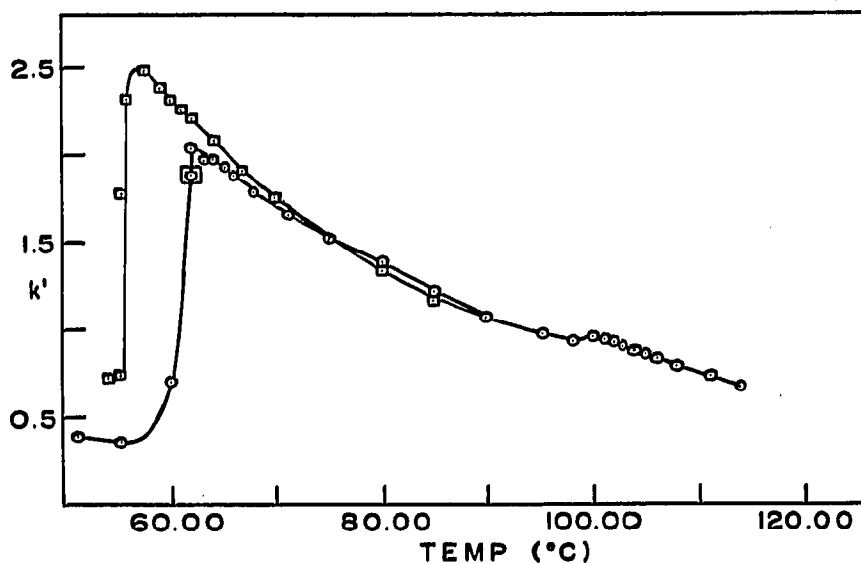
Fig. 3. Capacity ratio *vs.* temperature on the 0.10% column. The circles and squares represent the heating and cooling cycles, respectively. Identical points on both cycles are represented by circles only. Large squares represent points obtained after overnight equilibration at the same temperature as the last previous run.

Figs. 2 and 3 show several puzzling phenomena. The clearing point of EPAPU is at 107.5°. Yet, at both liquid loadings, the plots show 100° as the chromatographically observed transition point. The melting point of the liquid crystal studied here is at 62°. The k' plot for the 0.10% column peaked at about 62–63°, while the maximum capacity ratio on the 0.69% column, on the heating cycle, occurred at about 64°. In general, the melting range, in °C, of the EPAPU was larger on the latter column. It is instructive to mention here that Willey and Brown[22] have determined the melting point of EPAPU in bulk and as coated on Chromosorb W. In both cases, they found 62° as the melting temperature. Their reported clearing point was at 109°.

That the nematic to isotropic transition occurs at about 100° at both columns is most peculiar, and at this point, we can only speculate as to the reasons. It is well known that impurities can depress transition points (*viz.*, the recent work by Peterson and Martire[40]). Although the glass beads were thoroughly washed with methylene chloride, it is conceivable that some impurities from the glass or some sites on the glass surface affected the nematic to isotropic change. The effect of the solute probe (*p*-xylene) can, we feel, be neglected. The amount injected is much too small to cause a 7° change in the transition point. In addition, the solute, moving continuously in a narrow zone, does not have time to shift the transition point. Moreover, as will be shown shortly, on the acid-treated beads, the clearing point is at about 107°. The carrier gas, since undoubtedly it dissolves to some extent in the mesophase, can also alter the clearing point. However, in view of previous experiences and the results to be discussed shortly, we tend to feel that the effect of the carrier is minimal. It can also be postulated that as the temperature is increasing, the physical distribution of the liquid crystal on the glass bead changes. This effect would be most pronounced near the nematic-to-isotropic range and it is conceivable that the sudden change in

mesophase conformation will appear as a pseudo transition point. However, it is expected that such a mechanism would depend on the amount of the mesophase in the system. In this connection, the recent work of Serpinet[41] is most interesting. He found that the logarithm of the specific retention volume of heptane in an octadecanol stationary phase system is not a linear function of T above a certain loading of the liquid phase. There are two distinct breaks in the plot: one at the point of "highest compactness" and the second at the melting point of a "condensed phase" above the surface monolayer[41]. The temperatures of the two breaks in the curve are independent of the liquid phase loading above a certain amount. It is thus a possibility that the glass surface and the EPAPU interact in such a way as to give the liquid crystal in contact with the glass surfaces different properties than can be found in bulk EPAPU.

The actual effect of surface on the structure of the mesophase should also not be neglected. It is well known that liquid crystals can be oriented by glass surfaces (viz., refs. 36, 37, and 42–46). In general, however, and under normal conditions, the orientation will resist changes in the mesophase structure, and it would be thus expected that the clearing point will not be depressed due to surface effects. To the best of our knowledge, no study was made to determine the changes in transition point temperatures as a function of surface orientation. A recent study by Uchida et al.[36] indicates that on soda lime glass mesophases similar to EPAPU do not align. The recent review by Rajan and Picot[46], which includes many references to surface orientation, indicates that surface effects, when they exist, can orient the mesophase over long distances.

The behavior at the melting point is also intriguing. The 0.69 % column seems to indicate a melting point at 64°. Between 58° and 64° about six experimental points were taken on this column. The time between two consecutive temperature runs was 1 h so that it took about 6–7 h to increase the temperature from 58–64°. The rate of temperature increase was faster (less experimental points in a given temperature range) with the 0.10 % column. Although the time span between two consecutive temperatures was still 1 h, it seems that the faster rate of temperature increase gave a narrower melting range. Griffen and Porter[47], when studying binary systems of cholesteryl esters, found that the transition temperatures depended on the rate of cooling or heating. Unlike the present study, they found that the melting and clearing points increase with increasing heating rates. They did not give any rigorous explanation of this behavior. Several points should be made here: (a) The melting range is not very sharp on either column. (b) In the melting region, if a certain temperature was left overnight, the k' decreased noticeably (well below the experimental error) when measured at the same temperature the next day. An example is shown in Fig. 3 at 62°. This may be indicative of solidification of the mesophase. (c) As indicated, at faster rates of temperatures increase, the melting region narrows. This is also observed with the acid-treated 0.11 % column, as will be discussed shortly.

Again, the reasons for these phenomena might be due to several effects. The columns were conditioned at about 115–120° and then cooled to room temperature before studying the dependence of k' on T. In the process of cooling, the liquid crystal undoubtedly solidified on the glass surface with a higher degree of order than its initial distribution. It is possible that when the columns are heated again (in the k' versus T study), the melting of the EPAPU will begin with layers far from the glass surfaces, and that interaction with the surface will retard the melting of thin layers

immediately in contact with it. This will give rise to a wide range in melting temperature. In addition, the existence of a melt–solid region can explain the tendency of the melt to solidify upon remaining at a constant T. The above argument is consistent with the picture presented by Rajan and Picot[46].

With respect to the change in k' with time, it should be stressed that this occurred only in the melting and solidification regions. In the nematic range or around the clearing point, the k' values at a given temperature were, within experimental error (about 1–1.5%), constant (although it is possible that at the clearing point changes in k' were too small to notice). A recent paper by Chou and Carr[48] shows temperature dependence of d.c. conductivity of p-(n-nonyl)oxybenzoic acid (NOBA) when heated from the solid to the nematic range. However, only a slight temperature dependence was observed when cooling from the isotropic to the nematic range. They also show an hysteresis in the conductivity depending whether NOBA was cooled or heated. This is reminiscent of some of the HETP and k' behavior observed in our previous work[32,33]. Berman and coworkers[49], when studying nematic-to-smectic transitions, found that with 4-octyloxybenzylidene-4'-ethylaniline and 4-butyloxybenzylidene-4'-acetoaniline the orientation of the liquid crystals under the influence of a magnetic field (below a certain strength) is a function not only of the container surface geometry, but also of the rate of cooling. The faster the rate of cooling, the better was the molecular alignment. They seem to imply[49] that fast cooling can eliminate the surface effects of the container. It is possible that the present phenomenon is similar, i.e., quicker heating can perhaps overcome surface effects by melting the whole liquid crystal pools very fast. It is felt that melting and clearing behavior of thin films should be investigated more closely.

At this point another interesting fact can be brought out. Up to this point, the failure of the liquid crystal to crystallize when cooled to 62° from higher temperatures has been attributed to "supercooling". This seemed to be a reasonable assumption at the time since many pure organic substances have shown this. However, whenever the data were repeated, crystallization of the liquid crystal always occurred very close to one particular temperature for any particular column. A supercooling phenomena is usually not reproducible. Moreover, once crystallization of a supercooled liquid has begun, the solidification usually proceeds at a very fast rate until all of the material has crystallized. However, by looking at Table I, which represents data on an earlier column on which p-xylene was also being used as the solute with a carrier gas velocity of 10 cm/sec, it can be seen that here the crystallization process at 55° is slow. At the initial determination (time equals zero in Table I), after a 1-h

TABLE I

CHANGES IN k' AND H OF EPAPU AT 55° AS A FUNCTION OF TIME

Time (min)	k'	H (cm)
0	19.5	0.510
8	19.4	0.517
16	19.1	0.522
28	18.9	0.537
Overnight (14 h)	7.71	2.02

equilibration time at 55°, k' was 19.5. The next three successive measurements were done at about 8-min intervals and after 24 min k' was 18.9. After about 14 h (overnight) the k' value dropped to 7.71 (note the large increase in H after 14 h). It should be mentioned here that at 57° the capacity ratio was a constant (18.9) throughout the measurement time (about half an hour). Since crystallization represents a drastic change in the state of the liquid, and since here this change took a fairly long time, it is tempting to speculate that the present process of solidification is not via a "supercooled" liquid.

The fact that at around the melting point and the solidification region k' varies at a given temperature can be interpreted perhaps by the swarm hypothesis as discussed by Rajan and Picot[46]. Far from the surface, thermal Brownian motion will negate the surface-ordering effect. The swarm of liquid crystals can be randomly oriented (at any point in time). The existence of such oriented segments can tend to change the physical properties of the mesophase with time. These changes will be most pronounced when the viscosity of the liquid crystal is high, *i.e.*, melting and crystallization points. Much of this argument depends, of course, on the size of the liquid crystal pool at the contact points, since surface effect can extend up to 100 μm from the surface.

With the previous nformation in mind, and as a check of the arguments given, acid-treated glass beads were used as the supports. Fig. 4 shows the behavior of k' *versus* the temperature for *p*-xylene on the 0.11 % EPAPU acid-treated column. By treating the glass beads in this fashion, it was hoped that a rough surface could be obtained so that the liquid crystalline material could coat the beads in a more uniform manner instead of being concentrated at the contact points between them. It is well known that when material is coated on smooth glass spheres, most of the material
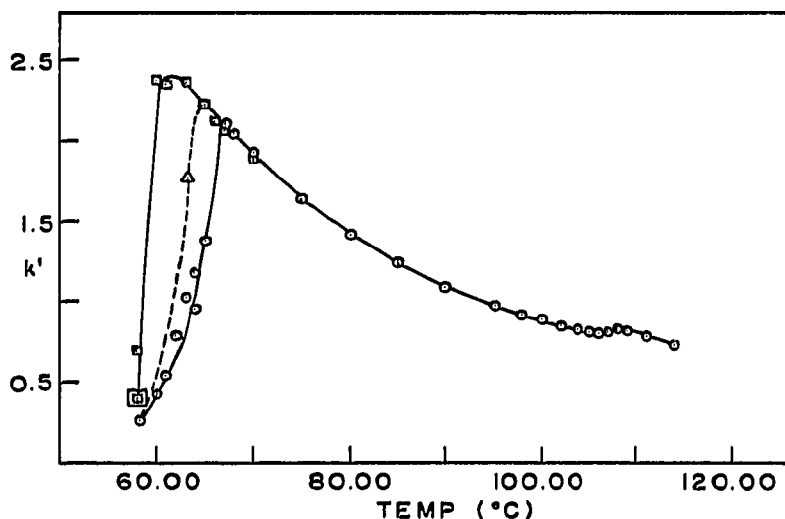

Fig. 4. Capacity ratio *vs.* temperature on the 0.11 % column. The circles and squares represent the heating and cooling cycles, respectively. Identical points on both cycles are represented by circles only. Large squares represent points obtained after overnight equilibration at the same temperature as the last previous run. The dotted line with triangles represent the repeated heating only data.

can be found at the contact points[50]. By etching the glass beads with concentrated acid, the alkali metal ions are leached out of the smooth surface, leaving a pitted surface. Exposed "active" sites (ions such as Ca^{2+} in soda-lime glass) can then "anchor" the coating substance to produce a uniform thin film of material. Much work has already been performed on this and the process is fairly well understood[51-57].

However, by comparing our acid-treated glass beads with the non-treated beads under a microscope, no visible difference in surface texture could be observed. Both sets of beads had shiny, smooth surfaces. Nonetheless, it was decided to pack a column with these beads to see if any differences could be detected.

At first glance, the capacity ratios in Fig. 4 appear to be very close to those for the 0.10% untreated glass bead column. However, the transition temperatures have changed by a considerable amount. The solid-to-nematic transition temperature now occurs between 66° and 68° and the range of melting, with slow heating rate, is wide, i.e. about 6-8°. The nematic-to-isotropic transition temperature has been shifted to about 108°. Since many active sites have been exposed on the glass sphere surfaces, these surfaces can exert a greater influence on the polar EPAPU molecules. The solid-to-nematic transition temperature has been increased to about 67°, a 5° increase in the observed bulk melting point. This could be due to the fact that indeed the "active" surface is holding the liquid crystal structure in its solid form until the increase in temperature can provide enough thermal energy to break up the solid and cause it to "melt" completely. The nematic-to-isotropic transition temperature has also been increased to about its normal transition temperature. Here again, the active surface can be causing the liquid crystalline structure to be maintained until sufficient thermal energy is available to cause the transition to occur. In the nematic and isotropic ranges, the cooling curve is essentially identical to the heating curve, in similarity with Figs. 2 and 3. In these ranges the k' values on the 0.11% treated and the 0.10% untreated columns were about the same. The liquid crystal solidified at about 60°. The data points of the solid line in this graph were collected over a period of five days, three days of increasing the temperature and two days for cooling. Again, a decrease in the value of k' at a given temperature with time was observed around the melting and recrystallization points, while the other repeated values of k' showed minimal deviations from each other.

Due to the fact that the solid-to-nematic transition temperature increased by such a large factor on the acid-treated column and to the fact that large deviations in k' seemed to always occur in this region, it was decided to repeat part of the data for the acid-treated glass bead column. These results are shown by the dashed lines in Fig. 4. One large discrepancy is immediately obvious. The solid-to-nematic transition has been decreased to approximately 65° while the rest of the data points agree quite well. The only difference between the two curves was the rate at which the data were collected. An hour was still allowed between successive points for thermal equilibrium to occur, however, the rate of heating was increased in the vicinity of the solid-to-nematic transition. It took about 3.5 h to reach the transition point in the repeated data while initially it took a substantially longer time (8 h on the first day and 2.5 h on the second day) to reach the transition point. If the surface was affecting the molecular orientation in the repeated series to the same extent as for the initial runs, the transition temperatures obtained should have been identical. However, since they were not identical, this suggests a decreased surface effect in the accelerated series.

Conceivably, in the case where "slow" heating was involved, the glass bead surface had time to fully interact with the entire amount of coated EPAPU. In the case where "fast" heating was involved, the liquid crystal did not have enough time to react or come into equilibrium with the surface. As the temperature was increased, the liquid crystal molecules farthest from the surface became less ordered and before the inner layer could "order" them the temperature was increased again. This is in agreement with the results previously discussed only here the surface effect, if indeed it is involved, is much more pronounced. Again this is similar to the observation of Berman et al.[49]. The temptation to employ the "swarm" theory to explain the results is great and it clearly indicates the necessity of further studying interfacial effects on transition temperature. The instability of k' at the crystallization point should also be noted.

Temperature dependence of HETP

The behavior of the plate height is shown in Figs. 5–7. All of the plots are for p-xylene, while maintaining the carrier gas velocity at 12.0 cm/sec. The temperature ranges are identical to those in Figs. 2–4.

From Fig. 5, it can be seen that the plate height first decreased rapidly as the temperature was increased. Once the EPAPU melted, the HETP curve flattened. As in Fig. 2, the solid-to-nematic transition temperature occurred between 62° and 64°. Only a small decrease in the HETP was observed as the temperature was further increased to about 100°. At approximately 101–102°, the HETP plot indicates a phase transition, i.e., nematic-to-isotropic. At this point, the HETP increased only slightly and then decreased slightly as the temperature was increased to 114°. Possible explanations were offered previously for the observed transition temperatures. As the temperature was decreased from 114° to approximately 65°, essentially the same curve was generated as when the column was heated. The EPAPU appeared to solidify at 55°,
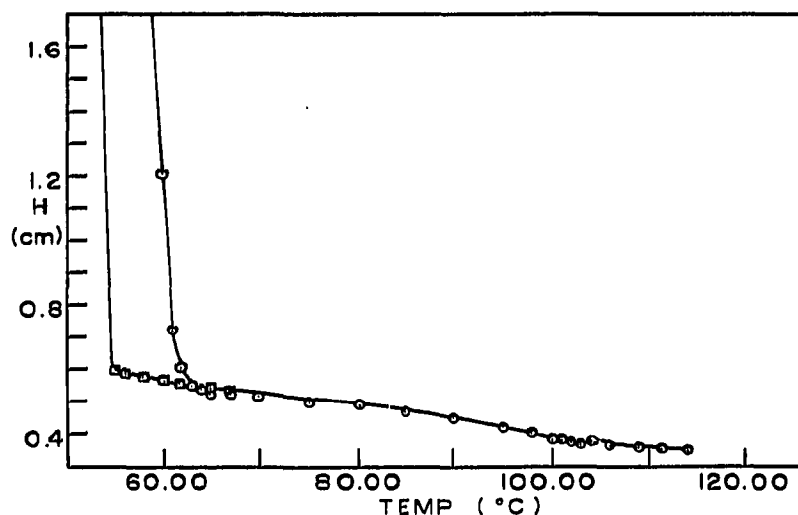

Fig. 5. HETP vs. temperature on the 0.69% column. The circles and squares represent the heating and cooling cycles, respectively. Identical points on both cycles are represented by circles only.

which is again as expected when compared to the data from the capacity ratio *versus* temperature plot for the 0.69% glass bead column.

Previous data obtained on the 0.69% column[33] showed a hysteresis in the HETP. In the cooling cycle, especially in the nematic region, the HETP was higher than in the heating cycle. This increase in the HETP was explained as due to surface effects. However, the time factor involved is substantially different for the two series. In the present study, it took 8 days to complete the HETP *versus* T study. In the previous work[33], it took 41 days with the instrument being turned off and on a number of times. As discussed, the results are time dependent. While small changes in the ordering of the mesophase in the nematic range may not change *k'* greatly, it affects the plate height to a greater extent via changes in viscosity and hence in the diffusion of the xylene in the liquid crystal. As shown, faster data collection does tend to decrease variance in the measured quantities.
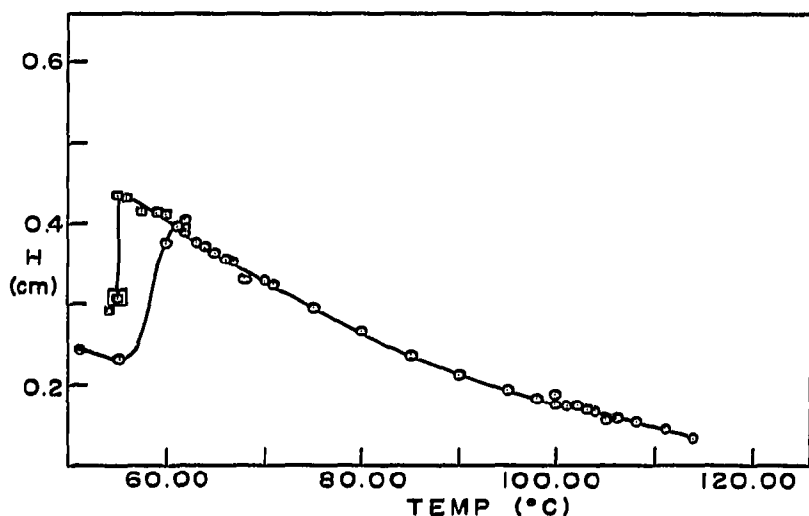

Fig. 6. HETP *vs.* temperature on the 0.10% column. The circles and squares represent the heating and cooling cycles, respectively. Identical points on both cycles are represented by circles only. Large squares represent points obtained after overnight equilibration at the same temperature as the last previous run.

Fig. 6 depicts the behavior of the HETP *versus* temperature for *p*-xylene on the 0.10% (w/w) EPAPU column. Since the glass beads in this column were treated similarly to the glass beads in the 0.69% EPAPU column, similar results should be achieved. It was noticed, however, that here, around the melting point, HETP increased rather than decreased. This difference in the behavior of the plate height is unclear to us. It is possible that, due to the difference in the amount of the liquid crystal in each columns, the physical distribution of the phase on the glass at the melting region will differ. Thus, in the highly loaded column, the EPAPU will redistribute itself so that the overall mass transfer will improve even though the liquid phase is viscous. With the 0.10% column, on the other hand, the mass transfer in the viscous liquid crystal does perhaps become the dominating factor. Rajan and Picot[46] mention

the fact that many measurements of mesophase properties are done with relatively thin films (100 μm), a fact which can influence the results. They recommend using larger sample sizes. It is possible that here the 0.69% column begins to show "bulk" behavior, while the 0.10% column is still dominated by surface effects. In order to elucidate this point, further studies on the EPAPU distribution on the glass beads is needed. The solid-to-nematic transition temperature occurred at 62° while the nematic-to-isotropic transition temperature was barely discernable at about 102–103°. Again, the heating and cooling curves were virtually identical in the isotropic and nematic ranges with no indication of hysteresis within experimental error. During the cooling cycle, the liquid crystal solidified at 55°. As with the k' study, it was found that during the heating cycle in the region of the solid-to-nematic transition, the HETP values changed whenever the column was left at the same temperature for a long period of time, such as overnight. In fact, the HETP always increased. No attempt was made in this study to see if the plate height would reach a constant value after a certain time. This facet of the research is now being examined. As speculated previously, the fact that around the melting point k' decreases and H increases might indicate a partial solidification of the EPAPU with time which can be explained by the swarm theory[46].

The instability of H at a given temperature is also observed, as indicated before, at the solidification point. At 55°, during the cooling cycle, the initial H was about 0.44 cm. When left overnight, the value at the same temperature was 0.31 cm. The previous HETP point at 56° did not show any change with time.

Fig. 7 shows the behavior of the HETP *versus* temperature for *p*-xylene on the 0.11% (w/w) acid-treated EPAPU column. The results differ significantly from the two previous HETP plots. As the column is heated from 58° to 66°, the HETP in-
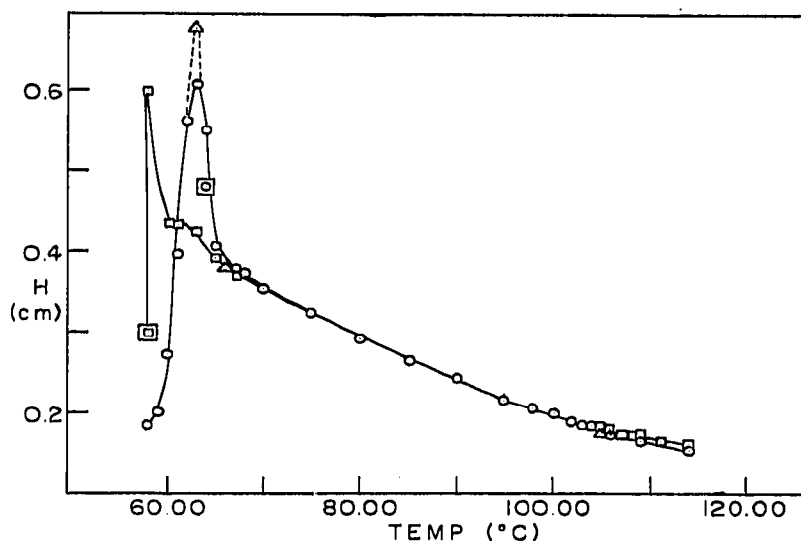

Fig. 7. HETP *vs.* temperature on the 0.11% column. The circles and squares represent the heating and cooling cycles, respectively. Identical points on both cycles are represented by circles only. Large squares represent points obtained after overnight equilibration at the same temperature as the last previous run. The dotted line with triangles represents the data of the repeated heating only.

creases to a sharp maximum value at 63° and then decreases again. However, in contrast to the k' plot (Fig. 4), the melting temperature did not shift as compared to the untreated columns. In fact, all three HETP plots show approximately the same solid-to-nematic transition temperature, somewhere between 62° and 64°. (The main differences between all the columns were in the magnitude of H.) Therefore, depending upon which plot is looked at, whether k' (Fig. 4) or HETP (Fig. 7), two different apparent transition temperatures are observed for the same column: 63° from the HETP plot or 67° from the k' plot. The reasons for the discrepancy are not yet clear to us. As the temperature was further increased to 114°, no discernable nematic-to-isotropic transition could be seen. However, while repeating the experiment, a barely observable transition at approximately 108° occurred.

As the temperature was decreased from 114° to 60°, the HETP increased steadily, until 59°. In fact, the cooling plot seems to approach a limiting value at 59°. However, cooling to 58° increases H drastically to 0.6 cm, giving again a sharp maximum. As the data were collected at 58°, it was noticed that H decreased slightly but consistently with time. After being left overnight at 58°, the HETP dropped to about 0.3 cm.

The fact that the behavior depicted in Figs. 4 and 7 is so different is extremely interesting. Since the capacity ratio has similar trends on the treated and non-treated beads, the thermodynamics of the systems might be similar. On the other hand, the behavior of the HETP plots can point to different kinetic processes on the two types of beads around the melting point. It is feasible that the acid-treated beads cause the liquid crystal to be much more viscous around the melting point, perhaps due to surface effects, so that while the partition coefficient may be close in magnitude to the 0.10% untreated column, the HETP is not.

To check the data, especially the maximum in H as T is increased, the experiment was repeated. Now, however, the beads were heated from 58° directly to 63° and then to 65°. Past 65° the rate of heating was as in the original run. From Fig. 7 it can be seen that unlike in the case of the k' studies, the rate of heating does not change the melting range.

The data in Fig. 7 show another anomaly. With the slow rate of heating the oven was left at 64° overnight. The H value was at first 0.48 cm while the value the next morning was 0.55 cm. The capacity ratio (in Fig. 4) was 1.18 and 0.967.

It is clear then that acid treating the beads alters the chromatographic behavior of the liquid crystal coated on them. Surface effects most likely play a major role.

Diffusion in EPAPU

In order to obtain a greater insight into what might be occurring in the 0.11% acid-treated column in comparison to the other two, it would be of interest to determine the diffusion of the solute, p-xylene, in the liquid crystal. Hawkes *et al.*[35] showed that, with glass beads at high carrier gas velocities, the resistance to mass transfer is due mainly to the stationary phase. They derived the following expression:

$$C_s = \frac{k' \, d_p^2}{120 \, D_s \, (1 + k')^2} \cdot \left(\frac{\% \, \varrho_g}{3m\varrho_s}\right)^{\frac{1}{3}} \tag{3}$$

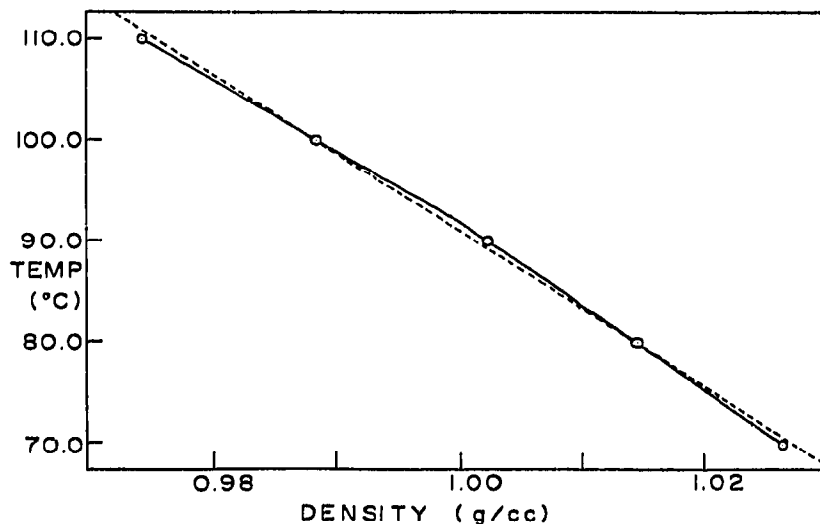where C_s is the resistance to mass transfer in the stationary phase, d_p is the glass bead

Fig. 8. EPAPU density vs. temperature. Dashed lines are densities at the nematic and isotropic ranges. The solid line is the least square fit for all points.

diameter, % is the percentage of liquid phase, ϱ_g is the density of the glass, ϱ_s is the density of the stationary phase, D_s is the diffusion coefficient of the solute in the stationary phase, and m is the mean number of contact points per bead (approximated to be 6.25). They found that for 60–70 mesh glass bead columns, the agreement between the theoretical and experimental values of C_s was excellent. Butler and Hawkes[58] further tested eqn. 3 in order to measure diffusion in long-chain solvents.
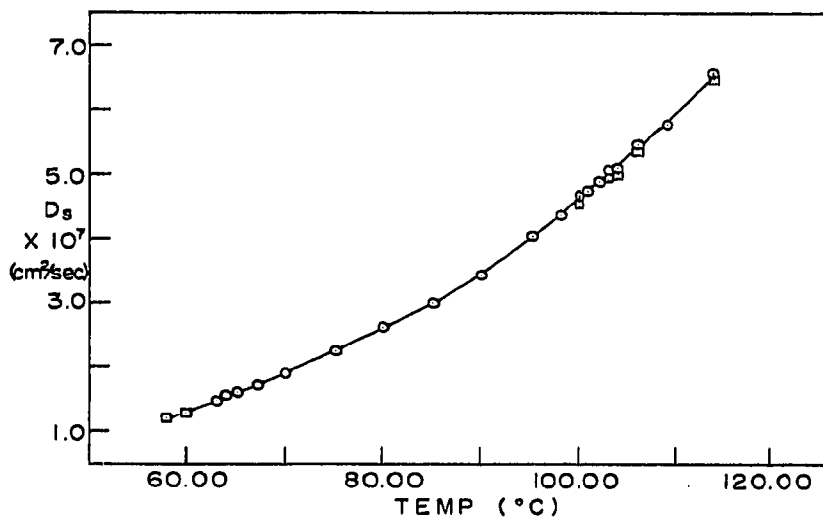

Fig. 9. Diffusion coefficient of p-xylene in EPAPU vs. temperature on the 0.69% column. The circles and squares represent the heating and cooling cycles, respectively. Identical points on both cycles are represented by circles only.

From Fig. 1 it can be seen that at 12 cm/sec the resistance to mass transfer term is large. Using the relationship[55]

$$C_m = \frac{\left[0.63 - 0.2\left(\frac{1}{1 + k'}\right)\right] d_p{}^2}{D_m} \qquad (4)$$

where D_m is the diffusion coefficient of the solute in the mobile phase, a calculation of the contribution of the resistance to mass transfer in the mobile phase, C_m, can be made. The diffusion coefficient of p-xylene in helium can be estimated according to a procedure given by Fuller *et al.*[59]. Typical values for D_m varied from 0.18 cm²/sec at 50° to 0.24 cm²/sec at 114°. The contribution of the C_m term to the total HETP is well below 0.5% and can be ignored. However, the molecular diffusion term, B, is significant and must, therefore, be subtracted from the total HETP to yield an accurate value for C_s. The molecular diffusion term can be expressed by the relationship

$$B = 2\gamma D_m/\bar{u} \qquad (5)$$

where γ represents an obstruction factor, which for 60–70 mesh glass bead columns can be approximated to be 0.60 (ref. 60).

In order to calculate D_s from eqn. 3, the densities of the liquid phase and of the glass beads are needed. For this study, the density of the EPAPU at various temperatures was determined and the results are shown in Fig. 8. A linear relationship obviously does not exist, however. Price and Wendorff[61] observed a similar relationship when they measured the density of PAA at various temperatures. They found a discontinuity in their data near the nematic-to-isotropic transition. For the purpose
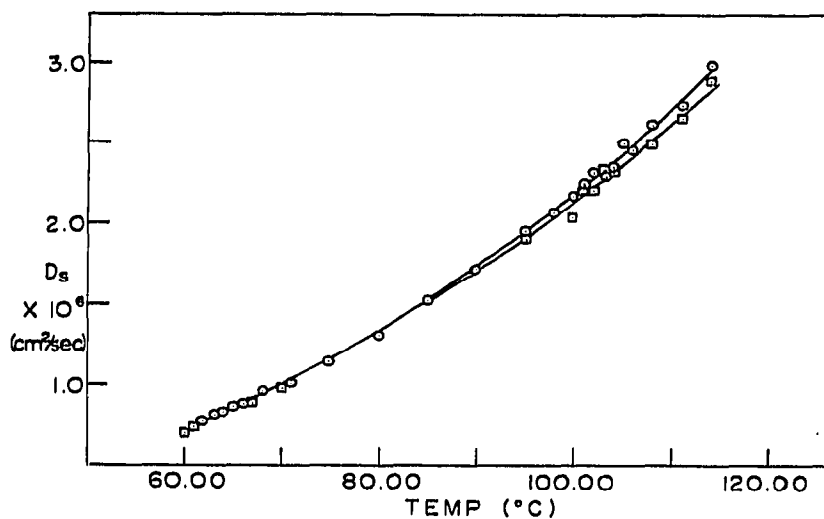

Fig. 10. Diffusion coefficient of p-xylene in EPAPU *vs.* temperature on the 0.10% column. The circles and squares represent the heating and cooling cycles, respectively. Identical points on both cycles are represented by circles only.

of this study, density measurements accurate to only three significant figures were required, therefore the two portions of the graph were least square fitted to a straight line and the densities were read directly from the graph.

At room temperature, the density of the glass beads was found to be 2.46 g/ml.

Once the molecular diffusion terms had been subtracted from the HETP values to get the C_s term, eqn. 3 was rearranged and solved for D_s, the diffusion coefficient of p-xylene in the EPAPU stationary phase. Figs. 9–11 illustrate the behavior of the diffusion coefficient, in the nematic and isotropic ranges, plotted against temperature. As can be seen from the graphs, the diffusion coefficients of Figs. 10 and 11 (0.10% and 0.11% columns) are nearly identical while the diffusion coefficients in the 0.69% column (Fig. 9) are an order of magnitude smaller. This may be indicative of the nature of the alignment of the liquid crystal molecules on the surface of the glass, since it has been shown that the diffusion of a solute molecule parallel and perpendicular to the long axis of the liquid crystal molecules is indeed different[62–70]. In fact, diffusion parallel to the liquid crystal molecules is usually greater than diffusion perpendicular to the molecules. Thus, the thinner film may have a larger number of regions which are parallel to the glass surface and in general be in a more ordered structure than the 0.69% column. Alternatively, with high loading the validity of eqns. 3 and 4 may break down.

Activation energies can be easily calculated from the dependence of the diffusion coefficient on the temperature. For the 0.11% treated column, the points at the sharp maximum were not taken into account. Activation energies were found for the nematic ranges only. The results are shown in Table II. Again, the 0.10% and 0.11% columns show nearly the same energies while the 0.69% column displays activation energies which are higher.

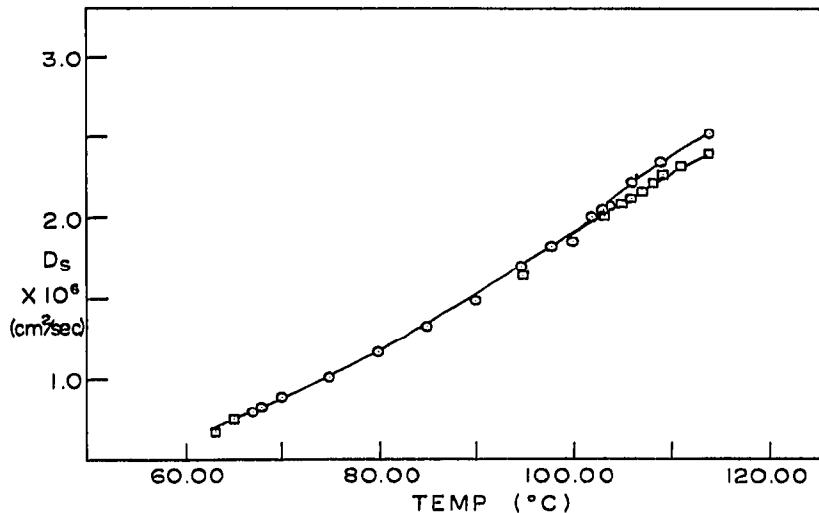The present study indicates the importance of the solid support in GC where

Fig. 11. Diffusion coefficient of p-xylene in EPAPU vs. temperature on the 0.11% column. The circles and squares represent the heating and cooling cycles, respectively. Identical points on both cycles are represented by circles only.

TABLE II

DIFFUSION ACTIVATION ENERGIES OF *p*-XYLENE IN EPAPU

Column	Activation energy (kcal/mole)	Correlation coefficient	Number of data points taken
0.10% –Heating	6.72	0.9993	15
–Cooling	6.82	0.9987	18
0.11% –Heating	6.59	0.9993	12
–Cooling	6.59	0.9987	13
Repeat–Heating	6.37	0.9990	11
0.69% –Heating	7.57	0.9997	16
–Cooling	7.77	0.9996	18

liquid crystals are used as stationary phases. The treatment of the support (that is, the previous history) affects the chromatographic behavior of the mesophase. It appears that surface effects are influential. Unfortunately, these effects are still not completely understood, although a pattern is beginning to emerge. Further work is now being carried out with glass beads of different composition, and initial results show marked difference from the present study.

The effect of the rate of heating on the apparent melting point and the time dependence of k' and H' around the melting and solidification points are most interesting since they do seem to implicate the surface of the support, especially with the 0.10% and 0.11% columns, in imposing a preferred orientation of the mesophases. It is possible to further speculate, and invoke the swarm model of liquid crystal to explain the slow recrystallization.

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