CHROM. 7689

THE BEHAVIOR OF p-(p-ETHOXYPHENYLAZO)PHENYL UNDECYLENATE (EPAPU) LIQUID CRYSTAL AS A CHROMATOGRAPHIC LIQUID PHASE COATED ON GLASS BEADS

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SUMMARY

The chromatographic behavior of liquid crystal stationary phases has almost never been studied. In the present paper, retention data, efficiency and mass transfer data were investigated using p-(p-ethoxyphenylazo)phenyl undecylenate (EPAPU) coated on glass beads. Glass beads were chosen as the support for several reasons: their geometry is known, they tend to orient liquid crystals, and diffusion coefficients can be studied when the liquid crystal is coated on them. The preliminary results obtained have shown the following. The resistance to mass transfer in EPAPU is rather large due to the viscosity of the liquid crystal. In general, as the column temperature increases the minimum velocity (in the Van Deemter sense) increases. HETP *versus* temperature results seem to indicate that the resistance to mass transfer of a solute in the nematic EPAPU depends on whether the column is being heated or cooled. At the same time, the capacity ratio is independent of temperature in the nematic range. Also, it was found that EPAPU can be supercooled when coated on glass beads.

INTRODUCTION

Liquid crystals are frequently employed in the separation of geometrical isomers. A fairly complete reference list on the usage of liquid crystals in gas chromatography (GC) was given in our previous paper[1], where the application of p-azoxyanisole (PAA) in capillary columns was described. Several other papers discussing mesophases in GC have since appeared[2,3]. A recent review of GC also mentions some of the workers who utilized liquid crystals[4].

With the exception of the work of Rogers' group[2,5] as well as our own[1], the chromatographic properties of mesophases have not been investigated, perhaps because most workers were interested only in specific separations. In particular, mass transfer phenomena were neglected. As mass transfer can indicate such diverse information as improvement of chromatographic systems and the structure of liquid crystals, it was decided to study this chromatographic mechanism closely. Our initial studies with PAA indicated that perhaps the column surfaces can influence the

properties of a mesophase. As the original work was carried out with capillaries, it was felt that more information could be gained by using columns packed with liquid crystal-coated glass beads. Initially, attempts with *p*-azoxyanisole and its homologues were tried. It turned out, however, that the dialkoxyazoxybenzenes have an appreciable vapor pressure and serious column bleeding occurred throughout the nematic range[6]. For that reason, the liquid phase *p*-(*p*-ethoxyphenylazo)phenyl undecylenate (EPAPU) was employed in this study.

It is well known[7] that liquid crystals can be oriented by surfaces. In chromatography, it is also well known that liquid crystals, whether coated on solid support or on capillary walls, can be "supercooled" far below their melting points. As the mesophase is deposited on the support in the form of a thin film, the effect of the surface can be important. Although Chow and Martine[8] did not find any difference in the melting points of one particular liquid crystal (PAA) on Chromosorb W, Chromosorb P and in the bulk form, while Willey and Brown[9] reported a slight depression of the clarification point of EPAPA coated on Chromosorb W, the influence of the support surface on the mesophase was not studied. Likewise, the effect of the amount of the mesophase on the support was not determined. This latter point can also indicate if surface effects are important.

In this paper, initial studies on the behavior of EPAPU on glass beads are described. The probe molecules (or solutes) were *p*- and *o*-xylene. Glass beads were chosen because their geometry is predictable, their surface smooth and the distribution of a stationary phase on them is fairly well understood (*i.e.*, contact angles, surface tension etc.). In addition, glass tends to orient liquid crystal molecules. The nature of the orientation depends upon the treatment of the glass surface[10]. The glass beads used in this study were cleaned and washed with a neutral solution. Future papers will describe the behavior of the mesophase on acid- and base-washed beads. We also report here some preliminary results on the effect of the amount of EPAPU, and mass transport coefficients in the stationary phase are discussed.

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 original heating controller was disconnected and a Fisher Scientific (Pittsburgh, Pa., U.S.A.) proportional temperature controller was used in its place. Temperatures at any point in the oven could be held to within $\pm 0.02°$. Temperature gradients were held to within $\pm 0.1°$. Temperatures were measured at three different points in the oven close to the column with copper–constantan thermocouples in conjunction with a Honeywell (Denver, Colo., U.S.A.). Model 2732 potentiometer

The injection system consisted of a Seiscor (Tulsa, Okla., U.S.A.) Model VIII gas sampling valve, which was actuated by a selenoid valve. Samples were injected by allowing the sample carrier gas (helium) to bubble through a liquid sample chamber, become saturated with the vapor of the liquid sample, and then pass through the sampling valve. The valve was thermostatted inside the oven while the sample chamber was located outside the oven.

The detector was a Beckman (Fullerton, Calif., U.S.A.) GC-4 flame ionization

detector (FID). The potential drop across the plates was 350 V, obtained from the power supply in the Hewlett-Packard chromatograph.

The signal from the detector was amplified by the Hewlett-Packard electrometer. The output from the electrometer was displayed on an Esterline-Angus (Indianapolis, Ind., U.S.A.) Model S-601-S Speedservo 5-in. strip-chart recorder.

Reagents

Commercially available helium was used as sample carrier and as the carrier gas. The *p*-(*p*-ethoxyphenylazo)phenyl undecylenate (EPAPU), which was purchased from Eeastman-Kodak (Rochester, N.Y., U.S.A.), was recrystallized very slowly from hot absolute methanol. Long, flat, thin crystals with a clear orange color resulted. These crystals were placed in an oven at 50° and allowed to dry overnight. The melting point of the EPAPU was 62° and the nematic-to-isotropic transition occurred at 107.5°. The glass beads were 60–70 mesh and were purchased from Analabs (North Haven, Conn., U.S.A.). The xylenes used were purchased from Eastman-Kodak. Natural gas was used as the unretained peak in all cases.

Procedure

Copper columns 200.0 cm long and of 1/4-in. diameter were used for all of the experiments. The glass beads were rinsed several times with methylene chloride and then dried overnight. Three batches of EPAPU-coated glass beads were prepared: 0.69, 0.27 and 0.10 % (w/w). These values were determined by extracting the mesophase repeatedly. The columns were then dry-packed and conditioned overnight at 120°. A small portion of the remaining coated solid support was put into a glass U-tube and immersed in an oil-bath[6]. Helium was passed through the tube and the temperature was raised to 120° to test the stability of the stationary phase. After 24 h, no visible bleeding of the stationary phase had occurred.

At least five runs were made at each temperature and velocity, while at least 60 min were allowed between runs at different temperatures in order to achieve thermal equilibration. The peak widths at half-heights and retention times were measured from the chromatograms by hand. All peak widths were always greater than 1.00 cm.

RESULTS AND DISCUSSION

Effect of amount of EPAPU on the plate height

In order to gain an insight into the chromatographic behavior of the mesophase, Van Deemter plots for *o*-xylene at three different temperatures were obtained on each liquid loading. The temperatures studied were 66, 88 and 111° (the exact temperatures are shown in the figures), corresponding to the solid phase, the nematic range and the isotropic liquid, respectively. The experiment started with the lowest temperature. Figs. 1–3 show the results graphically.

Several features are common to all three columns. (a) As the temperature increases, the plate height decreases. At 66°, the stationary phase is a solid and the chromatographic system is essentially gas–solid. Adsorption contributes significantly to the plate height. The peaks tailed but only slightly, and the tailing decreased with increasing temperature. (b) The plate heights at the Van Deemter minimum decreased with decreasing amounts of EPAPU in the column, irrespective of temperature. This
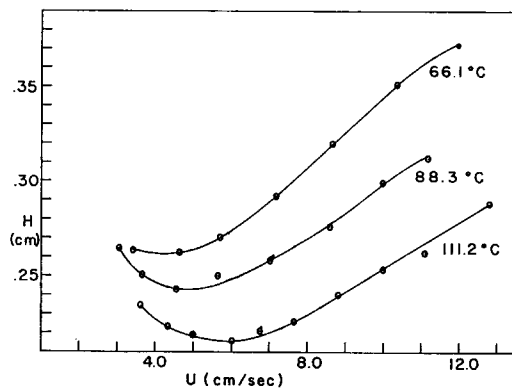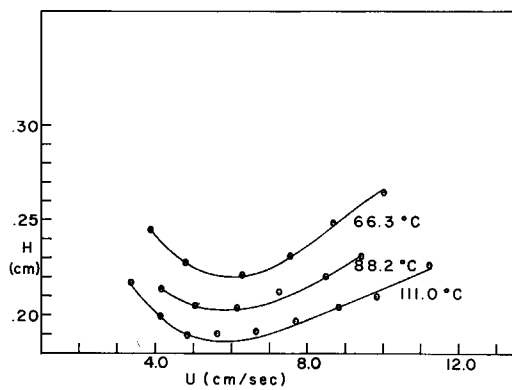
Fig. 1. *H versus U* for 0.69% EPAPU column.

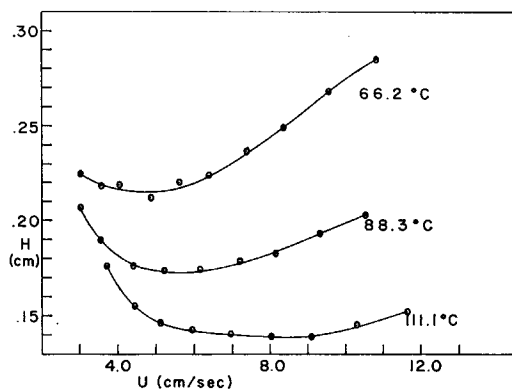Fig. 2. *H versus U* for 0.27% EPAPU column.

Fig. 3. *H versus U* for 0.10% EPAPU column.

is to be expected, as the resistance to mass transfer in the stationary phase is proportional to the amount of that phase. In general, however, the plate heights were high in the nematic and isotropic ranges, indicating the large resistance to mass transfer in the liquid crystal. The best HETP values, obtained with the 0.10% column at 111.1°, was a mediocre 0.138 cm. (c) Except for the 0.27% column, the minimum velocity, $U_{min.}$ (*i.e.*, the velocity at the Van Deemter minimum), increased markedly as the temperature increased. In fact, with the 0.10% column in going from 66 to 111°, the minimum velocity almost doubled. This is indicative of the importance of the mass transfer term. $U_{min.}$ can be expressed as

$$U_{min.} = \sqrt{\frac{B}{C_s + C_m}} \tag{1}$$

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. With PAA in the capillary column[1], $U_{min.}$ was observed to decrease with increasing temperatures. This was explained as the result of high viscosity of the mesophase. In the present work, however, this apparently is not the case, although the high HETP values still point to inferior mass transport in the stationary phase. A speculative explanation might lie in the "pooling" of the mesophase, both in the nematic and the isotropic ranges, at the beads' contact points. These stationary phase pools have the effect of providing a smaller surface area with which the solute molecules can come into contact. Even though the average depth of the pool is much larger than that of a thin and uniform film, the net effect of the pooling process may decrease the overall resistance to mass transfer. The flat HETP *versus U* plot of the 0.10% column at 111.1° is noteworthy. It was found previously that glass beads can indeed yield flat efficiency plots[11]. (d) The behavior of the 0.27% column is different from that of the other two columns. The minimum velocity is almost independent of the temperature; the reasons for this are not clear at this stage and further investigation using other columns with similar amounts of mesophase is now in progress. (e) The capacity ratios, k', of o-xylene on the three columns at the three temperatures are given in Table I. As expected, k' decreased with increasing temperature and decreasing percentage of the liquid crystal.

TABLE I

k' VALUES OF o-XYLENE ON COLUMNS PACKED WITH EPAPU-COATED GLASS BEADS AT THREE TEMPERATURES

EPAPU (%)	k'		
	66°	82°	111°
0.69	16.7	9.10	6.12
0.27	6.72	3.72	2.62
0.10	2.60	1.42	0.98

Temperature dependence of retention and HETP

In the previous study with capillary columns and PAA as a stationary phase, it was noticed that both k' and HETP (H) had a temperature hysteresis: upon heating
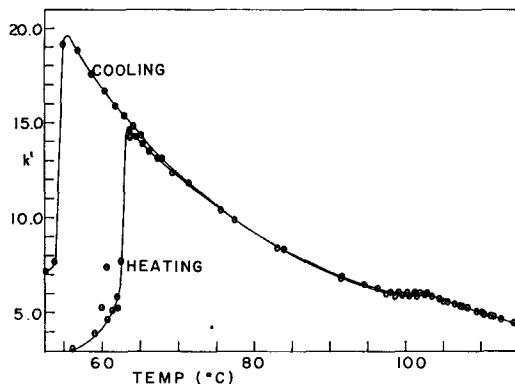
Fig. 4. Behavior of k' as a function of temperature for 0.69% EPAPU column. Solute: p-xylene. $U = 10$ cm/sec.

and then cooling, two different k' or H values were obtained at the same temperature. The results for the present system are shown in Fig. 4. The 0.69% column was first heated from 52 to 115°, well into the isotropic range. Then the temperature was decreased until the liquid crystal solidified (as judged by the retention data). For this study, the 0.69% column was used so that diffusion in the mesophase could be obtained. Although both o- and p-xylene were studied, only the data of the latter compounds are plotted. Fig. 4 indicates the following. As the EPAPU is heated, k' increased slowly. At 52.6°, k' was 3.97 while at 59.2° k' was 4.87 (this range is not shown in Fig. 4). Then k' began to increase more rapidly, changing from 4.87 at 59.2° to 17.5 at 63.7°. This, of course, is due to the fact that as the liquid phase melts partitioning of the solute takes place and the partition coefficient and k' increase. The expected melting point is 62°, yet the largest change in k' occurred between about 62 and 64°. As impurities tend to decrease the melting point, perhaps the glass surface influences the mesophase transition. The work of Willey and Brown[9] with EPAPU should be mentioned again. They found no difference in the melting point of bulk EPAPU and EPAPU coated on Chromosorb W.

It was also noticed that around the melting point, the physical nature of the liquid crystal at a given temperature varied with time. When the instrument was left overnight, k' values were taken in the evening and then the next morning; the latter value was always lower. For example, at 60.8°, a k' value of 7.42 was obtained in the evening compared with 4.62 the next morning. This phenomenon was observed only around the melting point and not in the nematic or isotropic phases. A possible explanation will be discussed shortly.

In the nematic and isotropic ranges, identical k' values, within experimental error, were obtained during the heating and cooling stages. Thus, in general, no hysteresis in k' as a function of temperature was found. Possible exceptions were around the clarification point and around the melting point where the "cooling" curve is slightly above the "heating" curve. The same effect was observed with o-xylene. The implication of the lack of hysteresis is significant. k' can be related to the activity coefficient of the solute in EPAPU. The activity coefficient in turn is indicative, implicitly, of the structures of the liquid crystal. Hence, on the whole, the k' data indicate

that EPAPU had the same structure during the heating and cooling cycles. As will be discussed shortly, the HETP study does not agree with the above.

The curvature in the plot around the clarification point is observed with most liquid crystals. Possible explanations for that phenomenon have been discussed by us elsewhere (ref. 1 and references therein).

A "supercooled" region was observed with EPAPU. The temperature range was about 7–10°. It is possible that the glass beads, by orienting the EPAPU molecules, were instrumental in the formation of the supercooled region. At this point, this is only speculation and our further studies with acid- and base-washed beads should help to clarify this observation. It is interesting to note that at 57°, on the cooling cycle, the k' values are 22.5 and 18.9 for o- and p-xylene, respectively; that is, the α (relative retention) value is 1.19. With common stationary phases, this α value does not present a difficult separation, requiring only about 650 plates for complete resolution. Here, however, owing to the high viscosity of the liquid crystal, the efficiency is much too low to achieve a complete resolution.
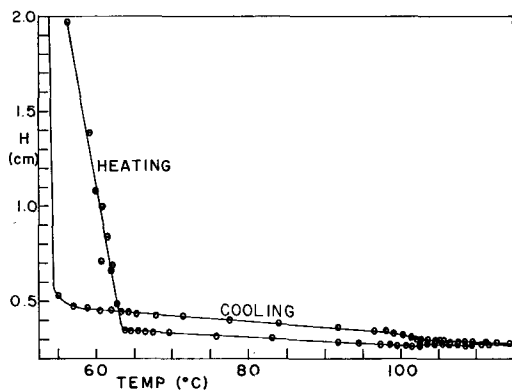

Fig. 5. Behavior of H as a function of temperature for 0.69 % EPAPU column. Solute: p-xylene. $U = 10$ cm/sec. The point on the cooling curves at 54° is outside the scale of the plot.

The behavior of the plate height with the temperature is shown in Fig. 5. Again, the solute was p-xylene and the column was the 0.69 % one. All measurements were made at an average carrier velocity of 10 cm/sec. Starting at 52.6°, the temperature was first increased, then, after reaching 115°, the column was cooled to 52.3°. At first, the plate height decreased rapidly as the temperature increased. Once the EPAPU melted, the HETP curve flattened. Only a small decrease was observed from about 64 to 102°. At 102°, as the mesopahse changed to the isotropic liquid the HETP increased slightly and then remained essentially constant up to the end of the heating cycle. The same results were obtained with o-xylene. It is interesting to note that the data for the HETP *versus* velocity plot (Fig. 1) were obtained first. Then the column was cooled and the temperature study was started. In order to check the consistency, we compared the H values in the temperature study obtained during the heating cycle with those in Fig. 1 at the three temperatures (at 10 cm/sec). The. results agreed to within 1 %. Thus, heating and cooling the column did not destroy the integrity of the EPAPU stationary phase.

As with the k' study, it was found that, during the heating cycle, in the region where the liquid crystal stationary phase begins to melt, the HETP values changed whenever the column was left at the same temperature for a long period of time, such as overnight. In fact, H increased. No attempt was made in this study to see if the plate height would reach a constant value after a certain time. The fact that around the melting point k' decreases and H increases might indicate partial solidification with time. The reasons for this are not yet clear.

Unlike the retention study, Fig. 5 clearly indicates hysteresis behavior. In the cooling cycle, especially in the nematic region, H was higher than in the heating cycle. This is interesting because, with PAA on capillary[1], H during the cooling cycle was lower. Moreover, in the present study, on the solid EPAPU the plate heights were much greater than the values in the liquid range. This was not true with the PAA on the capillary column. A possible explanation of the present behavior of high H on the solid EPAPU was given earlier when discussing the Van Deemter plots. With regard to the higher plate heights in the nematic range, the following can be postulated. The k' values are identical whether heating or cooling is carried out. The diffusion coefficients of the solute in the gas phase at any given temperature are the same whether the column is heated or cooled. Thus, most likely, the resistance to mass transfer term in the stationary phase is the term responsible for the behavior depicted in Fig. 5. It is possible that as the liquid phase was heated its surface tension properties changed so that when the column was cooled from the isotropic region through the nematic range the EPAPU distribution on the glass beads and the depth of the pools changed. However, the reproducibility of the plate height with temperature in the heating cycle and the constant k' values seem to indicate that this process did not occur. Most likely the increase in H is due to the increase in the diffusion coefficient of the solute in the EPAPU. Note that the divergence in the HETP values is greatest in the nematic range. It is possible that in going from the isotropic to the nematic range, the glass surface oriented the liquid crystal molecules to a greater extent than in the heating cycle, which would make the stationary phase more viscous at any given temperature. The solute will consequently have a smaller diffusion coefficient in the stationary phase, resulting in a larger HETP value. The supercooling phenomena evident in Fig. 5 might also be attributed to surface orientation.

It would be of interest to determine the diffusion of the solute in the liquid crystals. Hawkes et al.[12] showed that, with glass beads at high velocities, the resistance to mass transfer is due mainly to the stationary phase. They derived the following expression:

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

where C_s is the resistance to mass transfer in the stationary phase, d_p is the glass bead 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 (approximately 6.25)[12]. They found that for 60–70-mesh beads, the agreement in C_s values obtained from eqn. 2 and experimentally was excellent. Recently, Butler and Hawkes[13] used this expression to measure diffusion in long-chain solvents.

From Fig. 1, it can be seen that at 10 cm/sec the resistance to mass transfer term is large. Using the relationship[12]

$$C_m = \left[0.63 - 0.2 \left(\frac{1}{1 + k'}\right)\right] d_p^2/D_m \qquad (3)$$

where D_m is the diffusion coefficient of the solute in the mobile phase, it can be seen that the contribution of the resistance to mass transfer in the mobile phase, C_m, to H is very small. The molecular diffusion term contributes the most (about 10%) at high temperature or when the EPAPU is in its isotropic phase.

In order to calculate D_s using eqn. 2, the densities of the liquid phase and of the glass beads are needed. At room temperature, the density of the glass beads was found to be 2.46 cm³/g. The density of the EPAPU was not known and its temperature dependence was not reported previously. Furthermore, the effect of the glass surface on the density, if any, was not known. We therefore calculated the quantity $D_s\sqrt{(\varrho_s/\varrho_g)}$ as a function of temperature, and results are shown in Fig. 6. As the density of EPAPU probably decreases with increasing temperature, the trend depicted in Fig. 6 is due to the increase in the diffusion coefficient of p-xylene in the liquid crystal. Although we plan in the near future to determine the pure diffusion coefficient and activation energy, Fig. 6 still gives a qualitative picture of the behavior of D_s. It can be seen that in the cooling cycle the curve of $D_s\sqrt{(\varrho_s/\varrho_g)}$ is lower, thus indicating smaller diffusion coefficients. At and around the clarification point, the behavior of the plot is probably due to the non-linear temperature dependence of both the diffusion coefficient and the liquid density. It is known that around the clarification point the density changes sharply[14,15]. It is reasonable to assume that the density of EPAPU is about unity. Hence the quantity $\sqrt{(\varrho_s/\varrho_g)}$ is ca. 1.5–1.6. Consequently, the ordinate values in Fig. 6 are very close to the actual diffusion coefficients with the exception of the points in the nematic → isotropic region. The lower diffusion coefficient on the cooling cycle can indicate, as mentioned before, an orientation effect due to the glass surface.
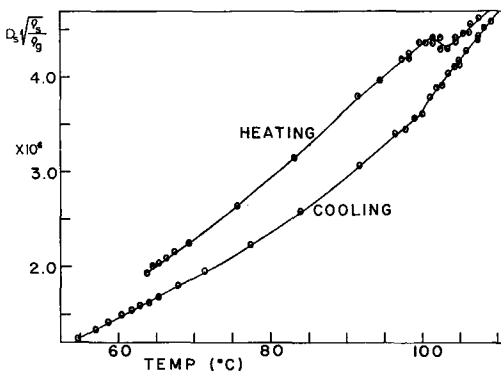

Fig. 6. Behavior of $D_s\sqrt{(\varrho_s/\varrho_g)}$ as a function of temperature. Conditions as in Fig. 5.

CONCLUSIONS

Initial studies with EPAPU on glass beads as stationary phase have shown some interesting and perhaps conflicting results; particularly noteworthy are the retention data and the HETP behavior. The variation of k' with temperature could lead one to believe that the liquid crystal structure, in the nematic range, remains the same during the heating and cooling cycles. The dependence of H on temperature, on the other hand, shows that the liquid crystal may undergo some changes during the two modes of operation. This contradiction should be investigated further.

At present, experiments are being carried out with glass beads whose surfaces have been treated in different manners, and with different amounts of stationary phases. We also intend to measure the density of EPAPU as a function of the temperature so that diffusion coefficients can be obtained directly and more accurately. This study should shed light on the distribution of EPAPU on glass beads, on the molecular structure of the liquid crystal and the effect of the glass surface in a much more reliable manner. The dependence of the diffusion coefficient on the amount of the liquid crystal can indicate if the glass beads surfaces do indeed effect the orientation, and to what extent.

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