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Note

Comparison of Bentone and liquid-crystal stationary phases for the gas chromatographic separation of isomers

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The usual stationary phases employed in gas-liquid chromatography (GLC) discriminate between samples on the basis of their boiling points (non-polar phases) or on differences in the degree of solute-stationary phase interactions (polar phases). It is therefore very difficult to separate positional isomers having similar boiling points and only very small differences in polarity. Bentone is a selective stationary phase owing its selectivity to the layered structure of the clay, molecules having structures which can easily be accommodated in the layers being readily absorbed. Elution of sample materials is difficult from untreated Bentones and it is customary to sacrifice some selectivity for ease of elution, swelling the clay by the incorporation of a conventional stationary phase.

Liquid crystals are substances which are intermediate between crystalline solids and isotropic liquids and possess sharp transition temperatures between mesophases. Linear molecules such as 4,4'-azoxyanisole will pass from a solid into a nematic mesophase where the ordered structure is retained in the liquid state. They will therefore behave towards solutes in a manner similar to Bentone 34, retaining linear molecules rather than the non-linear isomers. Liquid crystals can therefore be of great use for the separation of benzene positional isomers and for other materials differing mainly in molecular geometry. Kelker and Von Schivizhoffen¹ have extensively reviewed the application of liquid crystals to gas chromatography. Relatively strong deviations of activity coefficients from unity for *p*-substituted compounds on *p*-substituted mesophases have been observed leading to excellent selectivity for these isomers. Limitations of liquid-crystal phase selectivity lie in the fact that the anisotropy of the phase is at a maximum just above the crystal-nematic mesophase transition and decreases, with consequent decrease in isomer selectivity, with increasing temperature.

In order to compare the behaviour of this class of selective stationary phases the readily available liquid-crystal materials 4,4'-azoxyanisole (crystal-nematic 118°), 4,4'-azoxyphenetole (138°) and the eutectic mixture consisting of 57.5% of the former and 42.5% of the latter compound (98°) will be used as stationary phase 2° above their melting points. Comparison with a strictly non-polar conventional phase, Apiezon MH², and with a selective Bentone 34-Apiezone MH phase will be made in

terms of the Kovats retention indices³ of the isomers of xylene, chlorotoluene and methylanisole in order to determine whether the disadvantage of a very narrow temperature range is more than offset by improved resolution by liquid crystals over Bentone phases.

EXPERIMENTAL

The GLC apparatus used was a Pye Series 104 gas chromatograph, dual column, employing katharometer detectors. All retention times were measured using a stop-watch, dead times were obtained by injection of air samples. The columns were 2 m \times $\frac{1}{4}$ in. O.D. copper packed with 15% coatings of stationary phase on Chromosorb W AW DMCS (80–100 mesh) support. The five stationary phases employed were (i) Apiezon MH, (ii) Bentone 34–Apiezon MH (1:1), (iii) 4,4'-azoxyanisole, (iv) 4,4'-azoxyphenetole and (v) the eutectic mixture azoxyanisole–azoxyphenetole (57.5:42.5). The carrier gas was hydrogen with a flow-rate of 50 ml/min. Column temperatures in the range 100–160° were used with Apiezon MH and Bentone columns. Single column temperatures of 140, 120 and 100° were used for determinations of retention-index values of disubstituted benzenes on 4,4'-azoxyphenetole, 4,4'-azoxyanisole and the eutectic mixture, respectively.

RESULTS AND DISCUSSION

Differences in the Kovats retention index, *I*, are a measure of the separating power of a stationary phase in that if two substances have identical *I* values at a certain temperature, it will be impossible to separate them at that temperature, using the stationary phase, independent of the length of the column. The xylene results in Table I for Apiezon MH for instance, reveal that this stationary phase will not separate *m*- and *p*-isomers which will be eluted together before the *o*-isomer at any column temperature in the range 100–140°. This is a classical separation problem and one of the first to which Bentone 34 was applied as a selective stationary phase^{4–7}. In a more

TABLE I
RETENTION INDICES, *I*, OF XYLENE, CHLOROTOLUENE AND METHYLANISOLE ISOMERS

Stationary phase	Temperature (°C)	<i>I</i>								
		Xylene			Chlorotoluene			Methylanisole		
		<i>o</i>	<i>m</i>	<i>p</i>	<i>o</i>	<i>m</i>	<i>p</i>	<i>o</i>	<i>m</i>	<i>p</i>
Apiezon MH	100	911	888	886	983	985	986	1007	1022	1023
	120	917	893	891	987	989	990	1010	1024	1025
	140	923	898	896	991	993	994	1014	1027	1028
Bentone 34 Apiezon MH }	100	966	951	935	1073	1074	1070	1157	1200	1163
	120	974	958	943	1077	1078	1074	1163	1216	1168
	140	982	965	952	1080	1081	1077	1169	1235	1173
Liquid crystal eutectic	100	1107	1075	1085	1181	1205	1225	1228	1292	1316
	120	1140	1106	1107	1227	1251	1263	1313	1316	1370
	140	1086	1032	1053	1166	1166	1183	1243	1297	1308

recent study of this separation problem the best xylene separations were claimed on a column containing 7.5% Bentone 34 and 20% squalane⁸. Although a conventional stationary phase is necessary to swell the Bentone 34 it is known that some selectivity is lost, the magnitude of the loss being related to the amount of conventional phase. In this work the Bentone column contained 7.5% of this material swollen with an equal weight of Apiezone MH paraffinic grease so the selectivity could be expected to be high. The results in Table I show that a sufficiently long column packed with this material will resolve the xylene isomers, their elution order being *p*, *m*, *o*. The results on the liquid-crystal phases are quite different: *p*-azoxyphenetole will separate *m*- and *p*-isomers quite well whereas *p*-azoxyanisole gives no separation. The behaviour of the eutectic mixture is intermediate as might be expected. Ignoring temperature differences, the index values for the *m*- and *p*-xylenes on the eutectic are 1075 and 1084, respectively, calculated on the eutectic composition. This is very good agreement with the 1075 and 1085 values determined experimentally at 100°, the results showing that the eutectic mixture is a suitable stationary phase for this separation. The order of elution now being *m*, *p*, *o*. Kelker⁹ has described an excellent separation of benzene, toluene, ethylbenzene and the xylene isomers on 4,4'-azoxyphenetole.

Table I also shows the relative performances of the stationary phases for the separation of chlorotoluenes. Whereas Apiezon MH is quite unable to separate the *m*- and *p*-isomers (both have b.p. 162°) and a separation of the *o*-isomer is virtually impossible, the Bentone-column results indicate that a *m/p* separation would be extremely difficult and an *o/m* separation impossible on this phase. In this case liquid-crystal phases prove to be the solution to this difficult problem. Although 4,4'-azoxyphenetole will not resolve *o*- and *m*-chlorotoluenes, both 4,4'-azoxyanisole and the eutectic mixture are capable of complete isomer resolution, the elution order being *o*, *m*, *p*. Chiavari¹⁰ has previously reported the use of 2,6-naphthylene-bis(*p*-alkoxybenzoate) as a liquid-crystal phase suitable for the separation of *m*- and *p*-chlorotoluenes.

In Table I the methyl anisole data shows that the *o*-isomer will be eluted first and the *m*- and *p*-isomers will not be resolved by the Apiezon MH phase. Great difficulty in separating the *o*- and *p*-isomers on Bentone would be experienced with these isomers being eluted before the *m*-isomer. The behaviour of methylanisoles with liquid-crystal phases is quite different, the order of elution being *o*, *m*, *p*, with a relatively simple separation of the *o*-isomer and a more difficult separation of the *m/p* pair. Chiavari also investigated the behaviour of methylanisoles and decided that the 2,6-naphthylene-bis(*p*-alkoxybenzoate) phase was suitable for this isomer separation.

It would seem then that in terms of separating power, as measured by the differences in retention index values, liquid crystal phases such as those investigated here are marginally superior to Bentone phases. Their limitation is given by restriction to working temperatures a few degrees above their melting points where the anisotropy and consequently the selective retention of isomers is at a maximum. Whereas Bentone 34 will function from ambient temperatures to 180°, a range of liquid crystals of varying crystal-nematic mesophase transition temperatures are required to span the range. Such a range of materials are available, the eutectic mixture and the two azoxyethers described here span the range 100–140°. The 4-methoxycinnamic ester

of 4-hydroxy-4'-methoxy-azobenzene, with a transition temperature of 163° could be used at a column temperature of 165° and the terephthaldialdehyde-bis(4-ethoxyphenylimine) transition temperature of 196° would be useful at 200°, thereby spanning the general column-temperature working range in GLC.

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