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PROPERTIES OF SINGLE AND MIXED LIQUID-CRYSTALLINE STATIONARY PHASES

I. SINGLE LIQUID-CRYSTALLINE STATIONARY PHASES

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SUMMARY

The polarities and selectivities of twelve liquid-crystalline stationary phases have been tested as well as their column efficiencies. The effect of these properties on the separating ability of the liquid-crystalline stationary phases with respect to disubstituted benzene isomers is discussed. The separating properties of the individual stationary phases have been predicted, and experimentally confirmed by carrying out separations of mixtures of isomers of disubstituted benzene derivatives.

INTRODUCTION

The use of liquid crystals as stationary phases has recently attracted great interest, and a large number of publications have dealt with analytical applications as well as with the physico-chemical and chromatographic properties of these stationary phases.

In this and the subsequent paper we now discuss the results of studies of the comparison of the properties of single and mixed liquid-crystalline stationary phases. First we consider the polarity, selectivity and efficiency of single phases, while in Part II the same properties of mixtures of those phases will be discussed. Separations of mixtures containing disubstituted benzene isomers have been carried out on selected phases. The chromatographic studies of pure compounds allowed us to draw conclusions about the character of the interactions between liquid crystals and substances dissolved in them, and to determine the relationship between the molecular structure of the liquid crystals and their separating properties.

EXPERIMENTAL

Stationary phases, columns and apparatus

Twelve stationary phases, synthesized at the Military Technical Academy, were selected. Their formulae and characteristics are given in Table I. The phase transition temperatures were determined with the help of a polarization microscope (Analytic Dresden) having a heated stage.

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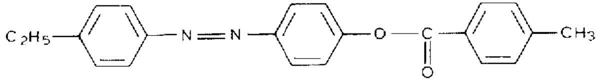
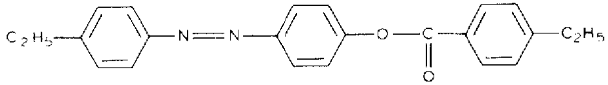
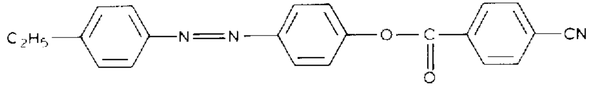
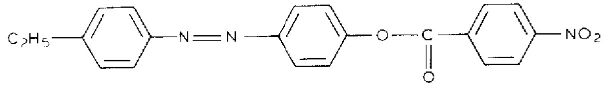
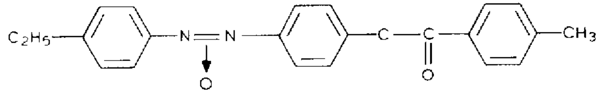
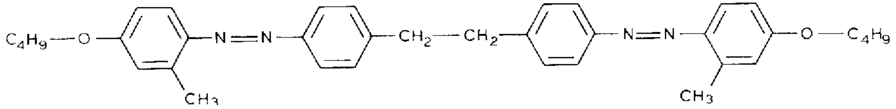
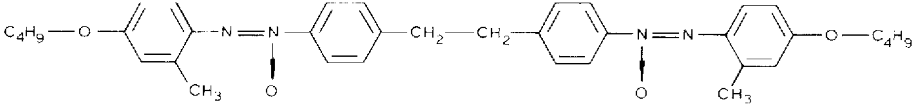
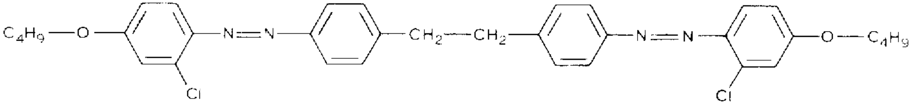
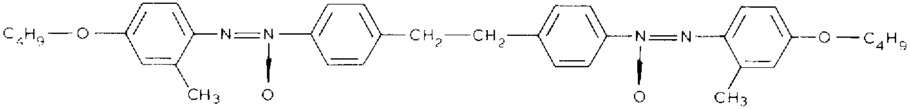
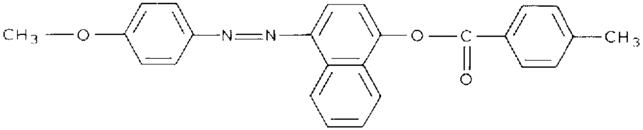
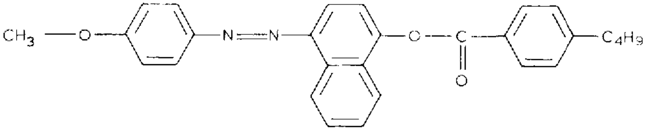
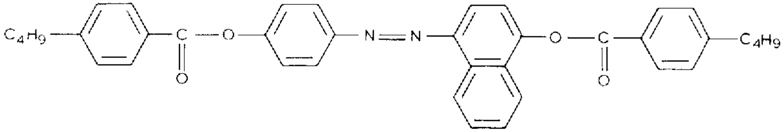
TABLE I

LIQUID CRYSTALS USED

Symbol	*Chemical formula*	*Temperatures (°K) of:*	
		Melting	*Clearing*
A_1		393	502
A_2		399	489
A_3		414	561
A_4		416	533
A_5		371	523
B_1		389 392*	502

B_2		431**	541
B_3		410	504
B_4		443	540***
C_1		441	476
C_2		399	463
C_3		417	566***

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* For more stable crystal form.

** Smectic in the range 431 441°K, nematic above 441°K.

*** Estimated on the basis of the phase diagrams.

The stationary phases were deposited (15%, w/w) on Chromosorb W NAW (particle size 0.15–0.20 mm) from methylene chloride solution by evaporation of the solvent.

The column efficiency was tested using a Pye Unicam GCV gas chromatograph; glass columns (2.1 m × 4 mm I.D.) were used.

The selectivity and polarity tests were carried out on a Chrom 42 gas chromatograph with metal columns (3.7 m × 3 mm I.D.). Separation tests were also carried out on this chromatograph, but with 3.1 m × 3 mm I.D. glass columns. The filled columns were heated at 440°K for about 2 h prior to the tests.

Polarity and selectivity

To determine the polarity of stationary phases, use was made of retention indices measured on those phases for standard test substances[1,2]: benzene; 1-butanol; 2-pentanone; 1-nitropropane; pyridine and *m*- and *p*-xylenes. Inclusion of the xylene isomers for determining the selectivity of liquid crystals towards molecules of different shapes was suggested in ref. 3. For measuring the retention indices the statistical method of Grobler and Balizs[4,5] was applied.

The measurements were carried out as follows. Each test substance (0.05 μl) was fed into the column and its retention time measured with a stop-watch. Before and after each measurement, the retention times of alkanes, from octane to undecane, in the form of mixture (0.1 μl), were determined. The measurements were repeated three times, enabling the retention indices to be determined with an error not greater than 0.5 units. The polarities of the phases were compared at 393°K. Of the phases whose melting temperatures are higher than 393°K, phases C_1 and C_3 are easily supercooled to this temperature. However, phases A_3, A_4 and B_2 are not supercooled at this temperature so the measurements were carried out at several higher temperatures from which the results were extrapolated to 393°K.

Beside the measurements of the retention indices of xylene isomers at 393°K, the selectivity of the phases with respect to molecules of different shapes was determined by two other methods. In the first use was made of an equation giving the dependence of the relative retention times of diethylbenzene isomers, chiefly *para* and *meta*, on the column temperature

$$\ln r_{p,m} = \frac{-\Delta H_{\mathrm{p}} + \Delta H_{\mathrm{m}}}{R} \cdot \frac{1}{T} + \frac{\Delta S_{\mathrm{p}} - \Delta S_{\mathrm{m}}}{R}$$

where $r_{p,m}$ is the relative retention of *p*- and *m*-diethylbenzene isomers, $-\Delta H_{\mathrm{p}} + \Delta H_{\mathrm{m}}$ and $\delta S_{\mathrm{p}} - \Delta S_{\mathrm{m}}$ are the differences in standard dissolution enthalpy and entropy of those isomers in the stationary phase and R is the gas constant. The second method is related to the first in that the same measurements are involved. It consists in the determination of differences in the retention indices of diethylbenzene isomers over a certain temperature range. The selection of those isomers was dictated by the temperature range in which the measurements were carried out and by the fact that the *meta* and *para* isomers differ in their boiling points, so they could be chromatographed together over a wide range of temperatures.

The retention indices of diethylbenzene isomers were determined using a mixture (0.5 μl) consisting of these isomers, three n-alkanes with retention times shorter than those of the isomers and one alkane with retention time longer. When the diethylbenzene isomers did not separate they were introduced separately into the column with suitable alkanes. The use of such a mixture and of 3.7-m columns made it possible to calculate on the basis of a single measurement the dead time, t_d, the separation ratio, $k = (t_R - t_d)/t_d$, the relative retention times, $r_{1,2}$, and the retention indices of the diethylbenzene isomers.

The dead time was found from

$$t_d = \frac{t_{R_{n+1}} t_{R_{n-1}} - t^2_{R_n}}{t_{R_{n+1}} + t_{R_{n-1}} - 2t_{R_n}}$$

where $t_{R_{n+1}}$, t_{R_n}, $t_{R_{n-1}}$ are the retention times of three successive alkanes[6]. The retention indices of diethylbenzene isomers were calculated by use of standard formulae, suitable corrections being introduced if the alkanes eluted before and after were not successive members of the homologous series[6].

The measurements were made in steps of 10°K during heating of the column from the melting point to about 440°K and during cooling of the column to 380°K provided the phase was supercooled at that temperature.

Measurement of the clearing enthalpy

Clearing enthalpies, from which entropies were calculated, were measured using a DuPont 910 differential scanning calorimeter with a temperature programming device and a DuPont 990 recorder. Pure aluminium trioxide was used as reference. The weights of all samples tested were close to 10 mg, with an accuracy of 0.02 mg. All measurements were taken during heating. The heating rate in the vicinity (± 15°K) of the clearing point was constant at 1°K/min. Three independent measurements were taken for each sample under isobaric conditions in a nitrogen atmosphere. The curves obtained were integrated graphically and converted into energy values. The devices were calibrated by use of the heats of melting of metals of high purity (indium and tin).

Column efficiency

For assessing the efficiency of columns, real plates[17] were measured according to Kaiser[7]. The tests were carried out for all columns at the same temperature of 418°K. Most of the phases tested have melting temperatures lower than 418°K, and phase C_1 supercools to that temperature. Although measurements were not carried out for the columns containing phases B_2 and B_4, it is be expected, on the basis of the results of measurements for phases A_1 and A_5, that these columns have equal or even higher efficiencies than those containing the corresponding azo compounds B_1 and B_3.

Mixtures (0.1 μl) of n-alkanes, from nonane to pentadecane, were used for determining the efficiency of columns. The retention times were measured with a stop-watch. The outlet velocity of the carrier gas was measured with a bubble flowmeter, the pressure at the column inlet with a mercury gauge and the atmospheric pressure with a barometer.

Assuming that the relationship $H = f(u)$ is described by the Van Deemter equation $H = A + \frac{B}{u} + Cu$, the coefficients of the latter were calculated by the least squares method. The linear flow velocity, u, was calculated from[8,9]

$$u = jf \cdot \frac{V}{a} \cdot \frac{T_{\text{col.}}}{T_{\text{flow}}},$$

where j,f are coefficients representing the pressure decrease along the column and the water vapour pressure in the flowmeter, respectively, V is the volume of carrier gas leaving the column per unit time under a pressure of 10^5 Pa and a is the volume of the gas phase per unit column length expressed as the ratio of dead volume to column length.

RESULTS AND DISCUSSION

Table II shows the McReynolds constants of the liquid-crystalline phases tested. This table also gives the natural logarithms of the relative retention times, b, for alkanes from octane to undecane, calculated from[4]

$$b = \ln \frac{t_{R_{n+1}} - t_{R_n}}{t_{R_n} - t_{R_{n-1}}}$$

TABLE II

POLARITY OF THE STATIONARY PHASES EXPRESSED AS THE DIFFERENCE IN RETENTION INDICES OF TEST SUBSTANCES

The retention indices on squalane were taken as 671 (benzene), 599 (1-butanol), 632 (2-pentanone), 667 (1-nitropropane) and 736 (pyridine)[10].

Phase	*$I = I_R$ (on the tested phase) $-$ I_R (on squalane)*					*Parameter characterizing the methylene group dissolution, b*
	Benzene, x	*1-Butanol, y*	*2-Pentanone, z*	*1-Nitropropane, u*	*Pyridine, s*	
A_1	138	259	228	313	274	0.614
A_2	131	249	223	299	280	0.617
A_3	213	337	297	419	367	0.577
A_4	223	319	310	412	438	0.576
A_5	167	292	259	352	317	0.600
B_1	132	216	203	260	283	0.604
B_2	160	254	231	313	300	0.588
B_3	153	226	212	270	283	0.607
C_1	187	311	281	382	345	0.595
C_2	167	267	256	354	327	0.615
C_3	166	245	220	318	287	0.596

where t_R is the non-corrected retention time for alkanes with n, $n + 1$ and $n - 1$ carbon atoms.

The values of the McReynolds constants x', y', z', u' and s' clearly reflect the changes of polarity of the stationary phases, since an increase in polarity of a given stationary phase produces not only an increase in retention of polar test substances but also a decrease in alkane retention. This is demonstrated by the magnitude of parameter b which is proportional to the energy of dissolution of one methylene group in the stationary phase. The fact that the increase in retention of the test substances and the decrease in alkane retention is decisive for the increase in the retention indices may sometimes render difficult the comparison of the phase polarities. This is particularly evident when the differences in the dispersion interaction energies of the phases with the substances dissolved in them are considerable. A solution to this problem was proposed in ref. 11. The procedure given there can be simplified, sufficient accuracy for comparative purposes being, however, preserved.

The natural logarithm of the mean relative retention time of alkanes from octane to undecane is proportional to the mean free dissolution energy per 100 units in the interval of 800–1100 retention index units. For the sake of simplicity it has been assumed that the amount of energy per 100 units is similar in the interval of 0–800 retention index units. Multiplying the retention indices of the test substances by $bRT/100$, we obtain the thermodynamic dissolution potentials for those substances (Table III). These values are exaggerated but the error is approximately equal for all phases.

Analysis of the values given in Tables II and III makes it possible to distinguish stationary phases differing only slightly in their molecular structures. The A_2 phase has one methyl group more in its molecule than the A_1, but that already produces a detectable increase in its dispersive capacity, $b_{A_2} > b_{A_1}$. An increase in the proportion of single C–C bonds in the molecule of the stationary phase causes a relative decrease in the number of bonds available for interaction with polar substances and in consequence leads to a lowering of the energy of interaction with those substances.

TABLE III

THERMODYNAMIC CHARACTERISTICS OF STATIONARY PHASES

Phase	*ΔG (kJ/mole)*				
	Benzene, X	*1-Butanol, Y*	*2-Pentanone, Z*	*1-Nitropropane, U*	*Pyridine, S*
A_1	16.2	17.2	17.3	19.7	20.3
A_2	16.1	17.1	17.3	19.5	20.5
A_3	16.7	17.6	17.5	20.5	20.8
A_4	16.8	17.3	17.7	20.3	22.1
A_5	16.4	17.5	17.5	20.0	20.7
B_1	15.9	16.2	16.6	18.4	20.0
B_2	15.9	16.4	16.6	18.9	19.9
B_3	16.3	16.3	16.7	18.6	20.2
C_1	16.6	17.7	17.7	20.4	21.0
C_2	16.6	17.1	17.5	19.9	21.1
C_3	16.3	16.4	16.6	19.2	19.9

The replacement of the methyl group by a strongly polar cyanate group increases the polarity of the stationary phase molecule, leading to lowered dispersive interactions, $b_{A_3} < b_{A_1}$, and increased interactions of other types. The dipole-orienting interactions increase the most, $U_{A_3} > U_{A_1}$, the basic properties, $S_{A_3} > S_{A_1}$, and interactions with the benzene ring π-electrons, $X_{A_3} > X_{A_1}$, increase, too. This increase is due to the increased proportion of conjugated bonds in the total number of bonds.

Phase C_1 differs from A_1 in that one benzene ring has been replaced by a naphthalene ring and the methylene group, $-CH_2-$, by oxygen, $-O-$. The significant differences in the retention indices of the test substance on those phases are due to the increased percentage of double bonds and the presence of the methoxy group. The latter group can yield weak hydrogen bonds and change the charge distribution in the benzene ring.

Double bonds account for 34% of all bonds in the C_1 phase molecules, 28% in C_2 and 23% in C_3. The differences in the interaction energies of these three phases with the test substances are closely related to the above percentages. The increased dispersive interaction energy in the case of phase C_2 as compared with C_1 is related to the increased length of the alkyl chain.

Least polar among the tested phases are those from group B, especially phase B_1 which reveals a similar dispersive energy to that of phase A_5, but the latter more readily dissolves polar substances owing to the higher proportion of conjugate bonds in the total number of bonds as well as the presence of carboxyl and azoxy groups. Oxidation of the azo compound to the azoxy form decreases the dispersive energy and increases the polarity of the molecule, as is seen from examples of compounds on phases A_1 and A_5 and B_1 and B_2.

The results obtained allow us to conclude that all the tested stationary phases can be classified as medium polar.

The molecular interactions in the systems considered are complicated. In the above discussion we have neglected the liquid-crystalline structure of the stationary phases. The existence of this structure is due to molecular interactions similar to those involved in the interactions discussed above, especially the dispersive ones. Also very important are short-range repulsive forces[12]. The highly anisotropic character of those forces justifies, however, separate treatment of the interactions directly related to the liquid-crystalline structure. The polar molecules of the test substances are oriented in a definite way with respect to that structure, affecting the magnitude of interactions tested using those substances. The present analysis makes it possible, however, to estimate the rôle of particular fragments, functional groups and bonds in the reactions of the investigated phases with the substances dissolved in them.

The measurement of the retention indices of the test substances makes it possible to detect even small changes in the molecular structure of the stationary phases. It should be realized, however, that the results may be affected by the non-covered portion of the support. The rôle of the support can be studied by comparing the retention indices obtained in the present work and those in ref. 13, where Chromosorb W AW DMCS was used as the support. It is also important that the carrier gas is suitably purified. If it contains oxygen, thermal decomposition of the stationary phase may take place, strongly affecting the retention indices of the test substances.

In the case of liquid-crystalline stationary phases the retention indices are af-

TABLE IV

COMPARISON OF THE RETENTION INDICES OF BENZENE (B), XYLENE (X) AND DIETHYLBENZENES (DEB)

Phase	$\Delta I_{p,m\text{-}DEB}$	$\Delta I_{p,m\text{-}X}$	$\Delta I_{p,m\text{-}DEB} - \Delta I_{p,m\text{-}X}$	$\frac{I_{m\text{-}X} - I_B}{2}$	$\frac{I_{p\text{-}X} - I_B}{2}$	$\frac{I_{m\text{-}DEB} - I_{m\text{-}X}}{2}$	$\frac{I_{p\text{-}DEB} - I_{p\text{-}X}}{2}$
A_1	45.8	18.2	27.6	104.7	113.8	67.1	80.9
A_2	40.7	15.2	25.5	107.8	115.4	68.9	81.6
A_3	50.9	21.1	29.0	106.5	117.0	60.0	75.0
A_4	41.1	15.1	26.0	108.5	116.0	58.6	71.6
A_5	48.1	20.2	29.8	104.5	114.6	63.1	77.1
B_1	49.5	21.5	28.3	105.6	116.3	63.2	77.4
B_3	38.4	17.3	21.2	103.7	112.4	60.7	71.3
C_1	49.5	16.8	32.7	98.8	107.2	63.3	79.6
C_2	33.0	11.6	21.4	101.8	107.6	70.2	80.9
C_3	43.6	18.9	24.7	102.3	111.8	63.5	75.8
Isotropic*	19.6	0	19.6	111.4	111.4	76.5	86.3

* Values taken from ref. 13.

fected not only by polarity but also by the ordering of the stationary phase structure. This is revealed by the retention indices of *m*- and *p*-xylenes, and more precisely, by the difference between the indices, $g = \Delta I_{p,m\text{-}X}$ (Table IV). In the case of conventional, non-liquid-crystalline stationary phases the elution order of the isomers (*para*, *meta*) is in accord with their boiling points, the difference between the retention indices usually increasing with increasing polarity of the stationary phase[14]. On liquid-crystalline stationary phases we observe the opposite order of elution, first *meta* and then *para*. This is due to the interaction related to the molecular structures of the chromatographed substance and the stationary phase.

The liquid-crystalline structure is the main although not the only factor affecting the value of *g*. It characterizes, to a certain degree, the selectivity of the stationary phase with respect to isomers. The dipole moment of *p*-xylene is zero, while for *m*-xylene it is 0.34 D. That is why the energy of induction interactions of *m*-xylene is greater than that of *p*-xylene. At the same time the methyl groups contribute to the formation by the xylene benzene ring of π-complexes with the molecules of the stationary phase, and that contribution may vary depending on the relative positions of those groups. The magnitude of *g* is a resultant of the effects of the liquid-crystalline structure and of the polarities of the stationary phase and the test substance. Solely on the basis of *g*, it is not possible therefore to estimate and order the stationary phases according to their selectivities for compounds whose molecules differ in shape; other interactions, such as induction, orientation or donor–acceptor, must be taken into account. It is not possible to separate these interactions as they all operate simultaneously.

If the tested phases are ordered according to the differences in retention indices of *p*- and *m*-xylenes, we obtain the following series: $B_1 > A_5 = B_2 > A_3 > C_3 > A_1 > B_3 > C_1 > A_2 > A_4 > C_2$. If, however, the phases are arranged according to the differences in retention indices of *p*- and *m*-diethylbenzenes, the above order changes to: $A_3 > B_1 > C_1 > B_2 = A_5 > A_1 > B_4 > C_3 > A_4 > A_2 > B_3 >$

C_2. To find the cause of the different orders we summarized the differences in retention indices of *p*- and *m*-xylenes and benzene ($I_{p\text{-X}} - I_B$, $I_{m\text{-X}} - I_B$) as well as the differences for the corresponding diethylbenzene and xylene isomers ($I_{p\text{-DEB}} - I_{p\text{-X}}$, $I_{m\text{-DEB}} - I_{m\text{-X}}$) (Table IV). In all cases the difference has been devided by 2, to enable estimation of the change in retention index per methyl group in xylenes and per ethyl group in diethylbenzenes. The values for the isotropic phase taken from ref. 13 are given for comparison.

On the basis of the values given in Table IV one can draw the following conclusions. Introduction of two methylene groups leads to an increase in the retention indices of xylenes by more than 100 units as compared with benzene. Substitution in the *para* position causes a greater increase in retention index than substitution in the *meta* position. It was not possible to determine why the increase in the xylene retention index is on some phases greater than that of benzene and on other phases smaller. This is undoubtedly the result of the varying polarity and selectivity of the tested phases with respect to compounds whose molecules differ in shape.

In the case of diethylbenzenes the increase in the retention index with regard to xylenes is less than 100 units per methylene group, being greater for the *meta* than for the *para* isomer. The retention indices on conventional phases vary in a similar manner[14,15], but the difference in the increase in retention indices for both isomers is greater than in the case of liquid-crystalline phases.

The differences between the increments in retention indices of *p*-diethylbenzene with respect to *p*-xylene, $I_{p\text{-DEB}} - I_{p\text{-X}}$ and *m*-diethylbenzene with respect to *m*-xylene, $I_{m\text{-DEB}} - I_{m\text{-X}}$, depend on the kind of stationary phase involved (Table IV). The major cause of this difference is the dispersive interaction energy, as is seen from the data in Table V, where the phases have been summarized according to their dispersive interaction energies characterized by parameter *b*.

There is good agreement between the order in which the dispersive interactions decrease and the retention indices increase. Distinct departures are visible only in the case of three phases, *viz.*, C_2 for *meta* isomers, C_1 for *para* isomers and B_3 for both isomers (see italicized values in Table V). As regards phases C_2 and C_1, the deviations are due to the effect of the liquid-crystalline structure; this results in C_2 having the lowest selectivity and phase C_1 the highest selectivity with respect to the diethylbenzene isomers. The considerable departure of phase B_3 is probably due not only to its low selectivity but also to another factor difficult to determine.

TABLE V

EFFECT OF DISPERSIVE INTERACTIONS, *b*, ON THE INCREASE OF THE RETENTION INDEX OF DIETHYLBENZENES WITH RESPECT TO XYLENES

Parameter	*Stationary phase*									
	A_2	C_2	A_1	B_3	B_1	A_5	C_3	C_1	A_3	A_4
b	0.617	0.615	0.614	0.607	0.604	0.600	0.596	0.595	0.577	0.576
$\frac{I_{m\text{-DEB}} - I_{m\text{-X}}}{2}$	68.9	*70.2*	67.1	*60.7*	63.2	63.1	63.5	63.3	60.0	58.6
$\frac{I_{p\text{-DEB}} - I_{p\text{-X}}}{2}$	81.6	80.9	80.9	*71.3*	77.4	77.1	75.8	*79.6*	75.0	71.6

TABLE VI

RETENTION INDICES, I, OF DIETHYLBENZENE ISOMERS ON THE TESTED PHASES AT 393°K AND COEFFICIENTS, $\partial I/\partial T$, CHARACTERIZING THE TEMPERATURE DEPENDENCE OF THE RETENTION INDEX

Phase	*meta*		*ortho*		*para*	
	I	$\partial I/\partial T$	I	$\partial I/\partial T$	I	$\partial I/\partial T$
A_1	1152.7	0.83	1171.2	0.93	1198.5	0.83
A_2	1155.0	0.69	1173.3	0.80	1195.7	0.71
A_3	1217.1	0.95	1244.3	1.03	1268.0	1.04
A_4	1227.7	0.86	1258.6	0.95	1268.8	0.93
A_5	1175.6	0.93	1198.5	1.02	1223.7	0.97
B_1	1141.3	0.82	1156.5	0.95	1190.8	0.77
B_2	1138.4	1.00	1155.0	1.09	1186.5	1.02
B_3	1152.6	0.79	1169.9	0.93	1191.0	0.84
B_4	1146.4	1.04	1169.4	1.07	1191.7	1.07
C_1	1181.9	1.09	1200.2	1.28	1251.4	1.01
C_2	1182.0	0.69	1202.0	0.92	1215.0	0.71
C_3	1170.5	0.82	1191.9	0.90	1214.1	0.86

Table VI lists the retention indices of *m*-, *p*- and *o*-diethylbenzenes at 120°C as well as the coefficients $\partial I/\partial T$ reflecting the dependence of the retention indices of those isomers on temperature. Analysis of these data allows us to conclude that the ability of the stationary phase to interact with the benzene ring is decisive for the absolute value of the diethylbenzene retention indices. The main factor responsible for the difference in retention indices of *p*- and *m*-diethylbenzenes is the interactions related to the liquid-crystalline structure, while other interactions related to the polarity of the given phase only have a small effect. An increase in polarity of the stationary phase results in an increase of retention, particularly of *m*-diethylbenzene.

The data in Table VI confirm that separation of the *m*- and *p*-diethylbenzene isomers is worse on the more polar phase if the phases show the same selectivity with respect to molecules of different shapes. The difference between the retention indices of *o*- and *m*-diethylbenzenes increases with increasing polarity of the stationary phase. The behaviour of diethylbenzene isomers is related to their dipole moments: *m*, 0.19 D; *p*, 0.15 D; *o*, 0.29 D. In some cases the effect of the liquid-crystalline structure may produce departures from the described regularities in behaviour.

From Table VI we see that there is a relationship between the rate of change of the retention index with temperature and the selectivity of the stationary phases. The rate of change with temperature is usually greater for more selective phases than for phases of lower selectivity with respect to diethylbenzene isomers. The greatest temperature dependence is revealed by the *o*-diethylbenzene retention index and the weakest by that of *p*-diethylbenzene.

The effective resolution of the column is determined by two factors: the column efficiency and the selectivity of the stationary phase for the compounds being separated. The same separation of the substances analysed can be achieved if the selectivity of the stationary phase is low but the column efficiency high or if the selectivity is high but the efficiency low. Sometimes, *e.g.*, in the case of phase A_3, the same factor is decisive for high selectivity and high mass transfer resistance in the liquid phase as that which leads to low column efficiency. It is reasonable therefore to consider simultaneously both factors controlling separation.

In Figs. 1-3 plots are given of the natural logarithm of the relative retention of diethylbenzene isomers *versus* the reciprocal of temperature. In Figs. 4-6 the real plate height is plotted *versus* the linear velocity of carrier gas. Table VII summarizes the coefficients of the equation determining the dependence of the natural logarithm of the relative retention time on the temperature reciprocal, while Table VIII lists the values of coefficient C characterizing the mass transfer resistance in the tested stationary phases. The remaining coefficients, in accordance with the measuring procedure assumed, are equal for all the tested columns, $A = 0$ and $B = 1.03$.

The relative retention time of diethylbenzene isomers was independent of whether the column was heated or cooled in the temperature range above the melting point. For the supercooled phase, the measurements at temperatures below the melting point were carried out during cooling of the column.

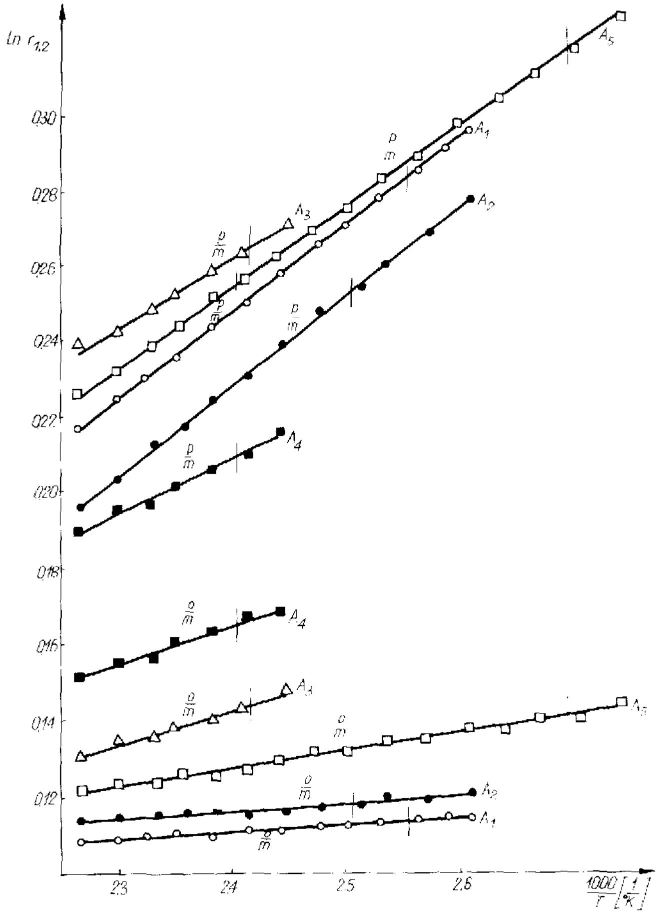

Fig. 1. Temperature dependence of the relative retention times of diethylbenzene isomers on group A phases.

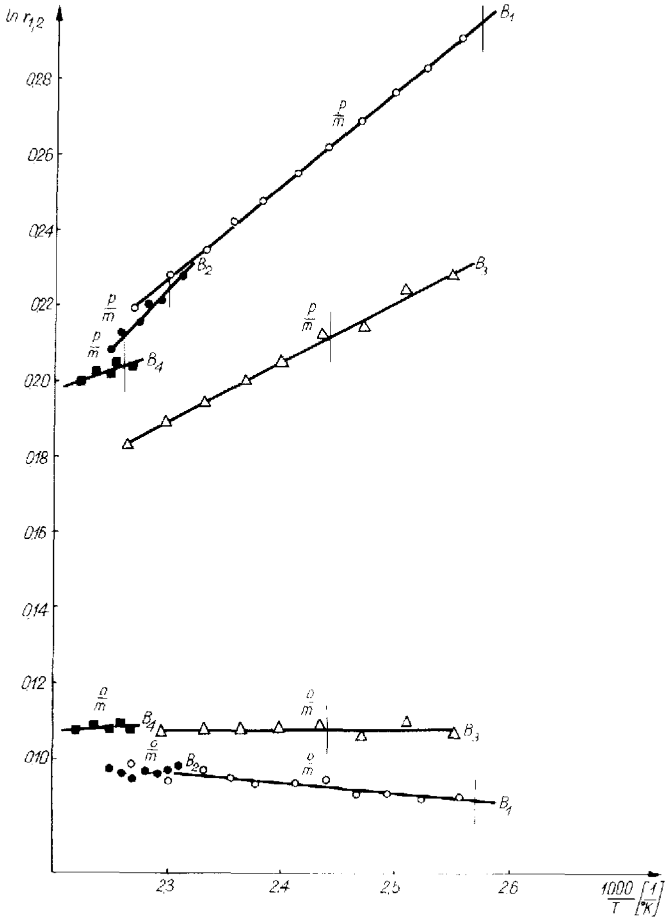

Fig. 2. Temperature dependence of the relative retention times of diethylbenzene isomers on group B phases.

The group C phases show the greatest tendency to supercooling. On a microscopic slide, compound C_3 can be supercooled even to ambient temperature. The compounds of group C can be used as stationary phases even at temperatures 40°K below the melting temperature. The supercooled mesophase shows high viscosity but this has little effect on the column efficiency. The A group phases can be supercooled by about 5–15°K. Group B phases, with the exception of B_3, do not supercool. This is probably due to their high molecular weight and low viscosity caused by the presence of the alkyl chain in the central part of the molecule.

Among the phases tested, the most selective with respect to disubstituted benzene isomers is phase A_3, however, the highest values of the relative retention times of these derivatives can be obtained on phase A_5 due to its low melting temperature. Phase A_5 is also characterized by the lowest mass transfer resistance in the liquid phase. The high selectivity and high mass transfer resistance of phase A_3 are probably due to the dimeric structure of the mesophase. Evidence in support of this is provided by the weaker dependence of the selectivity on temperature and the lower melting

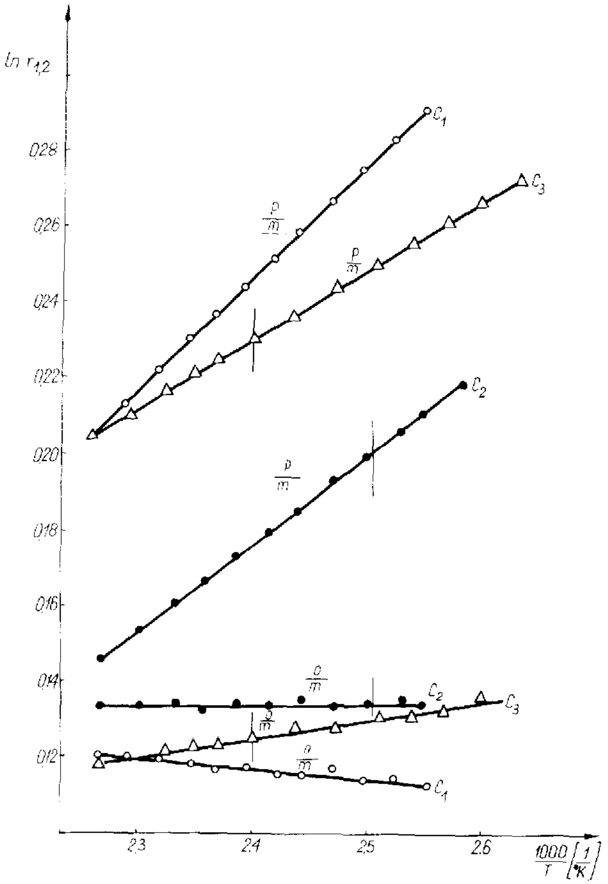

Fig. 3. Temperature dependence of the relative retention times of diethylbenzene isomers on group C phases.

enthalpy of this compound as compared with compounds A_1, A_2 and A_5. It is not clear, however, why the increase in mass transfer resistance, which is closely related to the increased viscosity, is not accompanied in this case by a tendency to supercool.

The replacement of a methyl group for a nitro group in the group A compounds significantly affects their selectivity towards disubstituted benzene derivatives. In this group, phase A_4 shows the lowest selectivity with respect to *m*- and *p*-diethylbenzenes and the highest one with respect to the *ortho* and *meta* isomers. The selectivity of the group A phases with respect to *m*- and *o*-diethylbenzenes varies approximately as their polarity. It may be concluded therefore that the separation of those isomers is strongly related to the polarity of the phases.

Phase B_2 matches phase A_3 as regards selectivity, but its disadvantage is the high melting point. Phase B_1 has a relatively low melting point and in the temperature range considered shows even better selectivity than phase A_5. Its higher molecular weight and lower vapour pressure as compared with phase A_5 may prove valuable in practical applications. On the other hand, phase A_5 has a lower melting point and a lower mass transfer resistance in the liquid phase.

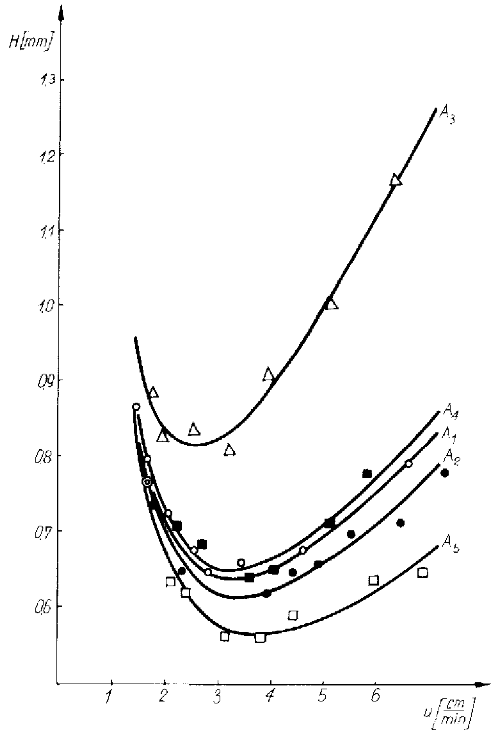

Fig. 4. Dependence of the real plate height on the carrier gas flow-rate for group A phases.

Replacement of a methyl group with chlorine in group B compounds results in a considerable decrease in selectivity with respect to disubstituted benzene derivatives. The selectivity of phase B_3 with respect to *m*- and *p*-diethylbenzenes is comparable with that of phase A_4, but the former has a lower melting point.

The oxidation of an azo compound to the azoxy form sometimes results in an increase in selectivity with respect to *p*- and *m*-diethylbenzenes, *e.g.*, in the cases of phases B_3 and B_4. A distinct improvement in the properties of the azoxy phase relative to the azo phase can be expected when a lowering of the melting point and a

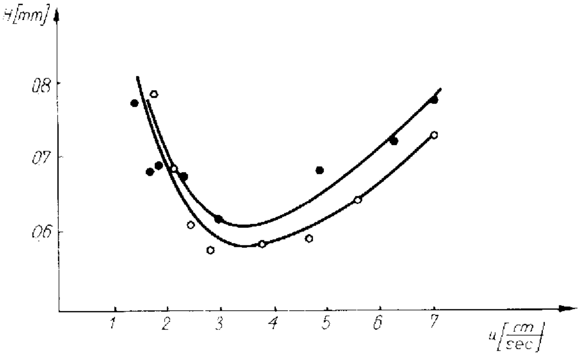

Fig. 5. Dependence of the real plate height on the carrier gas flow-rate for a phase from group B. ○ = Phase B_1; ● = phase B_3.

TABLE VII

COEFFICIENTS OF THE EQUATIONS CHARACTERIZING THE DEPENDENCE OF THE NATURAL LOGARITHM OF RELATIVE RETENTION TIMES OF DIETHYLBENZENES, $r_{1,2}$, AND ALKANES, $r_{n+1,n}$, ON THE RECIPROCAL OF TEMPERATURE

Phase	*p- and m-diethylbenzenes*		*o- and m-diethylbenzenes*		*Alkanes*	
	$\frac{-\Delta H_p + \Delta H_m}{R} \times 10^3$	$\frac{\Delta S_p - \Delta S_m}{R}$	$\frac{-\Delta H_o + \Delta H_m}{R} \times 10^3$	$\frac{\Delta S_o - \Delta S_m}{R}$	$\frac{-\Delta H_{n+1} + \Delta H_n}{R} \times 10^3$	$\frac{\Delta S_{n+1} + \Delta S_n}{R}$
A_1	0.235	−0.316	0.018	0.068	0.503	−0.671
A_2	0.241	−0.350	0.022	0.063	0.494	−0.645
A_3	0.187	−0.187	0.093	−0.080	0.540	−0.798
A_4	0.151	−0.153	0.098	−0.071	0.498	−0.697
A_5	0.219	−0.271	0.045	0.020	0.522	−0.732
B_1	0.254	−0.357	−0.027	0.157	0.520	−0.725
B_2	0.317	−0.503	0.096*		0.402	−0.442
B_3	0.164	−0.188	0.108*		0.456	−0.562
B_4	0.122	−0.072	0.107*		0.193	0.000
C_1	0.301	−0.476	−0.028	0.184	0.489	−0.658
C_2	0.231	−0.378	0.134*		0.483	−0.632
C_3	0.182	−0.206	0.048	0.010	0.504	−0.694

* The mean ln $r_{o,m}$ value when, because of the narrow temperature range, the relationship ln $r_{o,m}$ = f(T) could not be accurately determined.

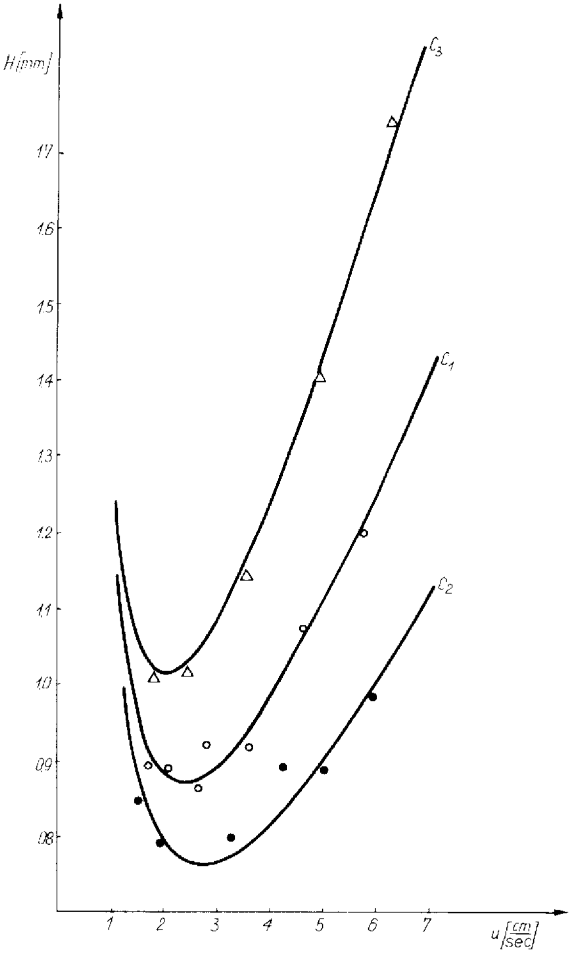

Fig. 6. Dependence of the real plate height on the carrier gas flow-rate for group C phases.

simultaneous decrease of the mass transfer in the liquid phase accompany oxidation, *e.g.*, in the cases of compounds A_1 and A_5.

Extension of the alkyl chain of a liquid-crystalline compound leads either to an increase or decrease in the melting point, but always produces a reduction in selectivity[16]. The presence of a longer alkyl chain in the molecule of phase C_2 is the cause of the low selectivity with respect to disubstituted benzene derivatives. This disadvantage is not compensated by the low mass transfer resistance in that phase as compared with the remaining compounds of group C. The high mass transfer resistance of phases C is related to the presence of the naphthalene ring in their molecules. The most advantageous properties in group C are revealed by phase C_1, which shows highest selectivity. Phase C_3 shows a low selectivity which is weakly dependent on temperature. The latter feature and the wide range of the mesophase make that compound useful as a single phase in separations conducted over a wide range of temperatures and at a low coverage of the support. The small amount of

TABLE VIII

MASS TRANSFER RESISTANCE, *C*, FOR SINGLE PHASES

	Phase									
	A_1	A_2	A_3	A_4	A_5	B_1	B_3	C_1	C_2	C_3
$C \times 10^{-2}$ (sec)	1.01	0.95	1.66	1.05	0.79	0.86	0.94	1.89	1.45	2.58

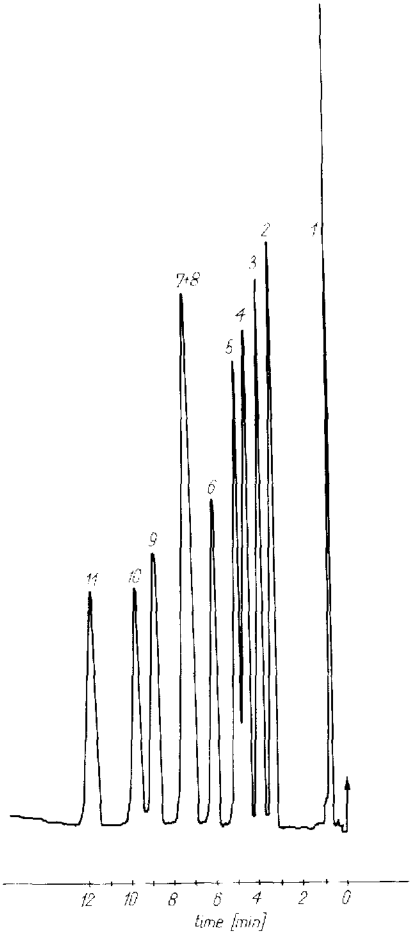

Fig. 7. Chromatogram of a mixture containing benzene (1), ethylbenzene (2), *m*-xylene (3), *p*-xylene (4), *o*-xylene (5), *m*-ethyltoluene (6), *p*-ethyltoluene (7), *o*-ethyltoluene (8), *m*-diethylbenzene (9), *o*-diethylbenzene (10) and *p*-diethylbenzene (11). The separation was carried out on a glass column (310 × 3 mm I.D.) containing 15% of phase B_1 on Chromosorb W NAW. The temperature of the injector was 493°K and that of the column 393°K; argon was the carrier gas with a flow-rate of 20 cm^3/min.

the phase on the support may to some extent neutralize the disadvantageous effect of the high mass transfer resistance of that phase.

In Table VIII are summarized the clearing entropies of compounds that do not decompose before clearing. When determining the thermal effects connected with clearing we did not allow for the pretransition effects which account for 10% of the clearing heat.

We can conclude that a relationship exist between clearing entropy and selectivity. However, in making predictions about the selectivity of a given stationary phase based upon the clearing entropy account should be taken of the number of degrees of freedom of the molecule related to its structure (especially length) and of the ordering in the isotropic liquid (degree of aggregation). For instance, the clearing entropy of phase A_3 is smaller than that of phase A_5 despite its higher selectivity, probably due to the existence of dimers in the isotropic liquid. Phase B_3 has a higher clearing entropy than A_5 and A_3, however, its selectivity is much lower, being related to the larger number of degrees of freedom of its molecules. However, if phases are compared that can be expected to have equal degrees of freedom and a isotropic liquid structure, *e.g.*, A_1 and A_2 or B_1 and B_3, there is a direct relationship between the clearing entropy and selectivity.

The above considerations predict that the best separations of disubstituted benzene isomers should be obtained on phases A_5 and B_1 and the poorest ones on phases C_2 and A_4. The tests carried out have confirmed those predictions. In Fig. 7 the separation of a mixture on phase B_1 is presented.

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