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PROPERTIES OF SINGLE AND MIXED LIQUID-CRYSTALLINE STATIONARY PHASES

II. MIXED LIQUID-CRYSTALLINE STATIONARY PHASES

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SUMMARY

The properties of binary and ternary mixed liquid-crystalline stationary phases of eutectic composition have been tested. The experimental results are compared with theoretical ones obtained by assuming that the properties of the component phases are additive. It has been found that the selectivity of the mixed phases can be predicted at any temperature if the properties of the single phases are known. At the melting temperature the selectivity of the mixed phases is usually higher than that of the single phases. The efficiencies of columns with mixed phases are usually higher than expected from the additivity principle. Separations of mixtures of disubstituted benzene derivatives obtained on the mixed phases are comparable to those obtained using capillary columns with liquid-crystalline stationary phases.

INTRODUCTION

Early in the development of gas chromatography, when the number of known highly selective stationary phases was small, various methods of improving the separation of complex mixtures were used:

(1) Columns consisting of sections packed with materials having different properties¹

(2) Mixed packings: the individual stationary phases were separately deposited on supports which were then mixed in the required proportions²

(3) Mixed phases: stationary phases of different properties were deposited in suitable amounts on the same support³. A modification of this method is to use phases with a quasi-stationary component. The polarity of such phases can be varied continuously in the course of the chromatographic process since one of the components of the mixture is not deposited on the support but fed to the column with the carrier gas⁴. If layers of stationary phases of different polarities are successively deposited, packings whose polarity can be varied by varying carrier gas flow-rate can be obtained⁵.

Today, even though there exist many stationary phases covering the whole

range of polarities, including highly selective ones, it is sometimes necessary to make use of the above methods, among other reasons to limit the excessive number of phases in use⁶. The properties of the mixed phases are often better than those of the single components.

Several publications have described the properties of mixed liquid-crystalline stationary phases⁷⁻¹⁵. However, systematic investigations and comparative studies of mixed and single phases are lacking. Therefore in the present work we have studied the polarity, selectivity and efficiency of mixed phases, in the same manner as was done for single phases in Part I⁶. We also found it useful to check whether it is possible to predict the properties of mixed liquid-crystalline stationary phases from the known properties of the single phases.

We decided to conduct the investigations using eutectic mixtures of stationary phases since they have the widest range of the mesophase. The methods available so far for determining the eutectic composition of mixtures of liquid crystals, and which give reliable results, are laborious and consume large amounts of materials. Other methods, which are less laborious and do not require such large quantities only give satisfactory results if the simplifying assumptions made are strictly fulfilled. In view of these disadvantages, new methods have been developed, and are described in refs. 17 and 18.

EXPERIMENTAL

Three groups of mixed liquid-crystalline stationary phases were selected. The first group includes binary mixtures of eutectic composition in which compound A₅ is the main component (notation as in Part I⁶). This compound has the lowest melting point of the tested phases and the highest selectivity at that temperature, so mixtures including this phase were expected to exhibit good separating properties.

The second group includes binary mixtures containing compound A₃. This compound has a melting point intermediate between those of the other compounds and exhibits high selectivity, in fact the highest in the tested temperature range towards compounds of different molecular shapes. It was mixed with other compounds to yield simple eutectics. Of all the compounds tested it had the smallest enthalpy of melting and yielded eutectics with low melting points.

The third group includes ternary mixtures. Such mixtures, not investigated hitherto, were examined in order to determine whether eutectics with more than two components may be utilized in gas chromatography. The interactions in ternary systems are complex and therefore an explanation of all the observed phenomena, *e.g.*, the deviations from predicted properties, may be difficult. In order to elucidate the interactions and components which are decisive for the properties of the ternary phase, we also tested binary eutectics composed of the components of the ternary ones. The mixtures are summarized in Table I.

The testing procedure applied to the mixed phases was the same as that for the single phases¹⁶. In some cases the temperature range in which the selectivity was studied was extended towards lower temperatures by use of diethylbenzenes.

To convert the mole fractions of the components into volume fractions, we measured the molar volumes of the tested compounds. For this purpose a 5-cm³ pycnometer was filled at ambient temperature with the substance in the solid state.

TABLE I
CHARACTERISTICS OF THE EUTECTIC STATIONARY PHASES

Component	Molar fraction	Melting point ($^{\circ}\text{K}$)	Clearing point ($^{\circ}\text{K}$)
A ₃	0.356		
A ₅	0.644	366	536
A ₄	0.276		
A ₅	0.724	366	535
A ₅	0.794		
C ₃	0.206	362	535*
A ₅	0.913		
B ₂	0.087	370	525*
A ₅	0.950		
B ₄	0.050	370	524*
A ₃	0.596		
A ₄	0.404	393	552
A ₃	0.484		
B ₁	0.516	375	517
A ₃	0.719		
B ₂	0.281	396	553
A ₃	0.600		
B ₃	0.400	390	529
A ₃	0.802		
B ₄	0.198	401	555*
A ₃	0.717		
C ₁	0.283	396	534
A ₃	0.502		
C ₂	0.498	377	542
A ₃	0.655		
C ₃	0.345	386	563*
A ₃	0.21		
A ₅	0.65	355	537*
C ₃	0.14		
A ₁	0.815		
C ₁	0.185	385	496
A ₁	0.687		
C ₃	0.313	376	530
C ₁	0.341		
C ₃	0.659	402	543
A ₁	0.615		
C ₁	0.116	374	522
C ₃	0.269		
A ₂	0.801		
C ₁	0.199	391	489

* Calculated from melting points of components.

(Continued on p. 164)

TABLE I (continued)

Component	Molar fraction	Melting point ($^{\circ}\text{K}$)	Clearing point ($^{\circ}\text{K}$)
A ₂	0.641	381	509
A ₄	0.359		
A ₄	0.651	399	515
C ₁	0.349		
A ₂	0.547	376	504
A ₄	0.314		
C ₁	0.139		
A ₁	0.803	384	510
B ₂	0.197		
B ₂	0.537	414	550*
C ₁	0.463		
A ₁	0.712	379	505
B ₂	0.147		
C ₁	0.141		
B ₂	0.303	403	558*
C ₃	0.697		
A ₁	0.625	371	527
B ₂	0.096		
C ₃	0.279		

* Calculated from the melting points of the components.

Then, after melting the contents, further portions of the compound were added until the pycnometer was completely filled. It was then placed in the thermostat of the gas chromatograph and heated for 1.5 h at 418 $^{\circ}\text{K}$. For the final 15 min it was sealed with a stopper. Immediately before taking the pycnometer out of the thermostat, the excess liquid was removed from it. After cooling, the remaining solidified substance was wiped off the surface and the pycnometer was weighed and the molar volume calculated.

Compound C₁ does not supercool when present in large volumes, so three measurements were made in the temperature range 440–470 $^{\circ}\text{K}$ and the molar volume was found at 418 $^{\circ}\text{K}$ by extrapolation.

We did not measure the molar volume of compounds B₂ and B₄ since they do not supercool down to 418 $^{\circ}\text{K}$ and decompose at higher temperatures. In the calculations it has been assumed that the molar volumes of these compounds are the same as those of the corresponding azo compounds. This is justified by the results obtained for compounds A₁ (azo compound) and A₅ (azoxy compound), which differ only slightly. The measured molar volumes (cm³) are: A₁, 322.5; A₂, 339.0; A₃, 316.3; A₄, 318.8; A₅, 322.0; B₁, 548.5; B₃, 540.8; C₁, 344.1; C₂, 360.8; C₃, 536.

RESULTS AND DISCUSSION

Fig. 1 shows the dependence of the capacity ratio of *p*-diethylbenzenes on the column temperature as well as the relative retention of *p*- and *o*-diethylbenzene versus

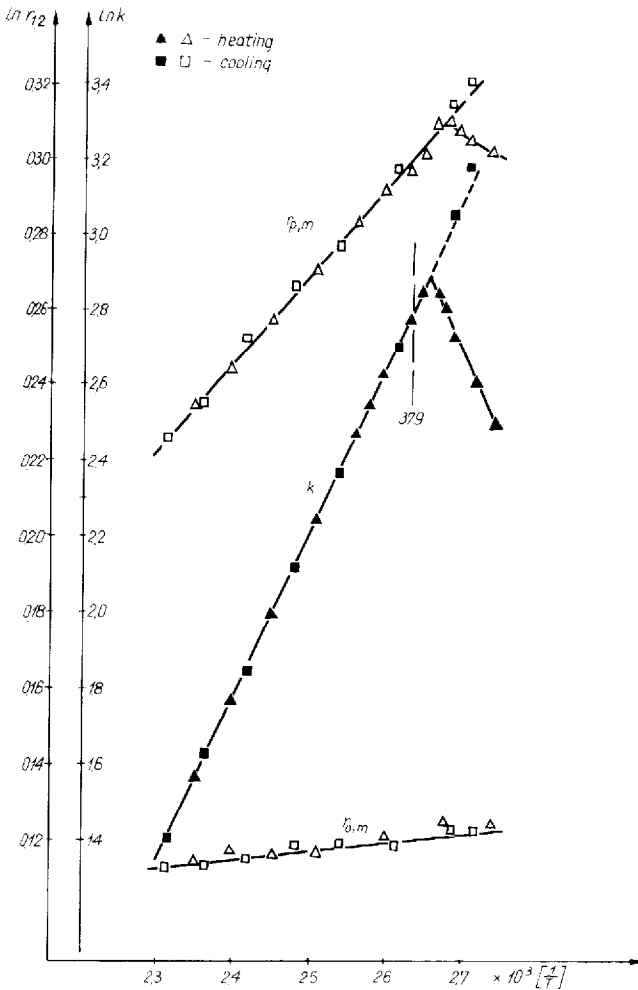


Fig. 1. The temperature dependence of the capacity ratio of *p*-diethylbenzene and the relative retention times of diethylbenzene isomers on the $A_1 + B_2 + C_1$ ternary phase.

m-diethylbenzene for a ternary mixture. The curves obtained are similar to those found for single liquid-crystalline phases. In the neighbourhood of the melting point there is a sharp increase of the capacity ratio and relative retention time, while in the mesophase range the logarithm of these quantities decreases linearly with the reciprocal of temperature. Similar relationships were obtained for the other multicomponent liquid-crystalline mixtures, thus confirming the existence of an eutectic system on the support and that the packing had been prepared properly.

The maximum in the curve $\ln k = f(1/T)$ appears at a temperature somewhat lower than the final melting temperature of the ternary eutectic as measured thermooptically. This maximum therefore does not correspond to the temperature of melting of the last crystal, as is the case when the temperature is measured optically, but to the temperature at which the major part of the mixture melts. The fact that the energy state of the liquid crystal on the support is different from that of the

TABLE II
COMPARISON OF MEASURED AND CALCULATED RETENTION INDICES ON MIXED PHASES

I_{exp} = measured retention index; ΔI = difference between measured and calculated indices.

Phase	Benzene		1-Butanol		2-Pentanone		1-Nitropropane		Pyridine		Difference between the retention indices for <i>p</i> - and <i>m</i> -xylene	
	I_{exp}	ΔI	I_{exp}	ΔI	I_{exp}	ΔI	I_{exp}	ΔI	I_{exp}	ΔI	Exp.	Calc.
A ₃ + A ₅	853	1	899	7	900	4	1043	-1	1080	-10	18.6	21.1
A ₄ + A ₅	852	1	890	8	899	6	1036	0	1090	5	19.3	18.8
A ₅ + B ₂	837	0	882	4	885	2	1018	-3	1057	-6	21.0	20.3
A ₅ + B ₄	835		894		894		1017		1040		18.9	
A ₅ + C ₃	837	1	875	1	880	-1	1010	0	1036	8	18.4	19.8
A ₃ + A ₄	889	-1	930	-1	933	1	1086	-3	1133	-1	18.6	18.5
A ₃ + B ₁	829	1	853	3	862	5	981	0	1033	2	21.2	21.5
A ₃ + B ₂	868	-5	911	-9	907	-5	1050	-7	1075	0	20.9	19.0
A ₃ + B ₃	853	2	872	3	882	1	1010	-6	1057	0	18.8	19.0
A ₃ + B ₄	873		911		907		1049		1085		18.3	
A ₃ + C ₁	876	0	927	1	926	-2	1080	-5	1105	-9	19.0	19.6
A ₃ + C ₂	858	1	895	3	903	3	1040	3	1075	6	17.1	15.7
A ₃ + C ₃	854	7	890	2	892	0	1035	3	1064	1	18.7	20.0
A ₅ + A ₃ + C ₃	843	-2	881	-2	885	4	1024	4	1045	-5	19.7	19.9
A ₁ + C ₁	818	-1	867	-1	874	4	999	6	1022	-2	17.8	17.9
A ₁ + C ₃	815	-6	854	-6	861	4	980	-2	1017	-1	17.7	18.5
C ₁ + C ₃	830	-12	862	-12	869	1	991	-10	1038	0	17.0	18.4
A ₁ + C ₁ + C ₃	821	-4	853	-5	866	3	989	0	1022	0	16.2	18.3
A ₂ + C ₁	814	-1	858	2	868	-2	982	1	1028	1	15.9	15.7
A ₂ + A ₄	837	-5	864	7	880	4	1003	0	1080	2	14.7	15.2
A ₄ + C ₁	871	9	905	10	927	5	1064	4	1143	-8	16.2	15.7
A ₂ + A ₄ + C ₁	835	1	863	14	881	7	1008	2	1061	10	15.8	15.4
A ₁ + B ₂	816	0	856	1	862	-1	979	-1	1020	-3	19.6	19.0
A ₁ + B ₂ + C ₁	826	-5	866	4	878	-11	994	-5	1029	4	18.3	18.6
A ₁ + B ₂ + C ₃	824	-2	850	2	859	2	979	-2	1021	-3	17.7	18.8

crystal on a microscope slide also contributes to the shifting of the melting point. The effect of the support on the melting point of the mixed stationary phase is even more obvious when the content of the stationary phase on the support is small¹⁹.

To determine how the properties of the individual components affect the properties of the mixtures we compared the experimentally measured characteristics of the mixed stationary phases with the corresponding values calculated under the assumption that the individual contribution are additive.

The retention indices on the mixed phases were calculated from a formula derived as in ref. 20 for binary system

$$I = \sum_{i=1}^n g_i I_i, \quad g_i = \frac{\varphi_i b_i}{\sum_{i=1}^n \varphi_i b_i}$$

where φ_i is the volume fraction of component i in the mixture, I_i the retention index of the test substance on the single phase i and b_i is the natural logarithm of the relative retention time of successive n -alkanes on single phase i . The volume fractions, φ , were calculated under the assumption that the molar volumes of the components in the mixture are the same as the molar volumes of the (separate) individual components.

In Table II the experimentally determined values of the retention indices are listed for the benzene, butanol, pentanone, nitropropane and pyridine at 393°K on mixed phases, together with the differences between those values and the values calculated from the retention indices of the test substances on the individual component phases. We conclude that the retention indices can be predicted with high accuracy. Knowing the polarities of the single liquid-crystalline phases, we can determine the polarities of the mixed phases. Somewhat greater differences are observed for the mixed phases $A_4 + C_1$, $A_2 + A_4 + C_1$, $A_3 + B_2$ and $A_4 + A_5$. This can be explained by the less accurate measurements of the retention indices of the test substances on the single components (*e.g.*, in the cases of phases A_4 and B_2 the indices were found by extrapolation) or the departure of the mesomorphous solution from ideality.

Table II also shows the measured and calculated differences in retention indices for *p*- and *m*-xylenes. The value of this difference can be predicted to a good approximation from the respective values on the individual components. However, in most cases the measured values are lower than the calculated ones.

The retention indices of diethylbenzenes can be calculated in a similar way to those of xylenes. Their values at 393°K are summarized in Table III together with data characterizing the temperature dependence of the indices and the differences between the calculated and measured values.

Knowing the temperature dependences of the retention indices of diethylbenzenes and of the relative retention times of alkanes on the individual components of the mixed phases, we can calculate the retention indices of diethylbenzenes on the mixed phase at any temperature. Table IV shows the close agreement between the measured and calculated retention indices of diethylbenzenes at the melting temperatures of some mixtures of stationary phases.

It was expected that the selectivity of liquid-crystalline stationary phases for compounds of different molecular shapes could be predicted at any temperature. For that purpose it is convenient to characterize the selectivity in terms of the relative

TABLE III
RETENTION INDICES OF DIETHYLBENZENE ISOMERS, I_{exp} , ON THE TESTED PHASES AT 393°K. THE COEFFICIENT, $\partial I_{\text{exp}}/\partial T$, CHARACTERIZING THE TEMPERATURE DEPENDENCE OF THE RETENTION INDEX AND THE DIFFERENCE BETWEEN THE MEASURED AND CALCULATED INDICES $I_{\text{exp}} - I_{\text{calc}}$

Phase	<i>m</i> -Diethylbenzene			<i>o</i> -Diethylbenzene			<i>p</i> -Diethylbenzene		
	I_{exp}	$\frac{\partial I_{\text{exp}}}{\partial T} \cdot 10$	$I_{\text{exp}} - I_{\text{calc}}$	I_{exp}	$\frac{\partial I_{\text{exp}}}{\partial T} \cdot 10$	$I_{\text{exp}} - I_{\text{calc}}$	I_{exp}	$\frac{\partial I_{\text{exp}}}{\partial T} \cdot 10$	$I_{\text{exp}} - I_{\text{calc}}$
A ₃ + A ₅	1192.2	8.80	2.3	1217.0	9.58	2.7	1238.2	9.55	-0.7
A ₄ + A ₅	1192.9	8.42	-3.5	1219.2	9.11	-4.8	1237.6	9.10	-1.9
A ₅ + B ₂	1173.7	9.19	-3.2	1196.6	10.00	-4.0	1221.3	9.67	-2.7
A ₅ + B ₄	1170.8	9.45		1193.6	10.30		1217.5	9.92	
A ₅ + C ₃	1173.5	9.22	0.6	1196.7	10.20	-0.2	1218.8	9.89	2.0
A ₃ + A ₄	1222.4	8.47	1.1	1251.0	9.24	1.0	1267.3	9.66	-1.0
A ₃ + B ₁	1167.2	7.80	0.0	1187.0	8.60	0.4	1213.2	8.30	-4.0
A ₃ + B ₂	1194.6	8.93	9.5	1218.0	9.94	9.9	1243.0	9.72	8.1
A ₃ + B ₃	1186.1	8.18	4.0	1208.8	9.07	4.8	1228.2	8.73	1.9
A ₃ + B ₄	1203.5	9.15		1229.0	10.00		1250.0	9.98	
A ₃ + C ₁	1207.2	1.01	0.8	1230.4	1.13	-0.5	1256.4	1.08	-0.5
A ₃ + C ₂	1193.9	8.30	-4.2	1216.5	9.50	-5.0	1235.6	8.60	-3.8
A ₃ + C ₃	1193.1	8.16	1.8	1217.1	9.08	-2.2	1237.0	8.81	-5.3
A ₅ + A ₃ + C ₁	1181.1	8.32	0.8	1205.0	9.05	1.6	1226.0	8.96	-1.4
A ₁ + C ₁	1159.8	8.27	0.4	1178.6	9.29	0.5	1206.0	8.23	-0.3
A ₁ + C ₃	1159.1	7.87	-2.0	1179.7	8.73	-1.3	1202.3	8.19	-4.0
C ₁ + C ₃	1174.8	8.11	1.4	1196.8	8.99	2.8	1217.5	8.58	-0.9
A ₁ + C ₁ + C ₃	1163.9	7.81	0.8	1184.8	8.60	2.1	1207.9	8.08	-0.8
A ₂ + C ₁	1161.9	7.81	1.7	1181.5	8.71	3.0	1204.9	7.58	2.3
A ₂ + A ₄	1185.3	7.01	6.3	1210.2	7.62	8.8	1225.6	7.36	5.9
A ₄ + C ₁	1202.5	9.80	-8.1	1229.5	10.60	-7.3	1244.9	11.70	-9.9
A ₂ + A ₄ + C ₁	1178.0	7.60	-1.7	1201.0	8.16	-0.6	1219.1	7.79	-1.0
A ₁ + B ₂	1156.6	8.74	6.9	1176.6	9.53	8.7	1203.4	8.81	6.8
B ₂ + C ₁	1162.3	10.00	9.0	1181.0	10.76	9.9	1213.0	9.84	10.0
A ₁ + B ₂ + C ₁	1164.0	8.63	9.0	1184.4	9.35	10.7	1211.2	8.77	10.0
B ₂ + C ₃	1163.9	7.89	3.0	1186.2	8.59	5.4	1207.4	8.34	1.6
A ₁ + B ₂ + C ₃	1162.1	8.07	5.8	1183.5	8.93	8.0	1205.9	8.51	3.7

TABLE IV

COMPARISON OF THE CALCULATED AND MEASURED RETENTION INDICES OF DIETHYLBENZENES AT THE PHASE MELTING POINTS

Phase	Retention index of diethylbenzenes					
	<i>meta</i>		<i>ortho</i>		<i>para</i>	
	<i>Exptl.</i>	<i>Calc.</i>	<i>Exptl.</i>	<i>Calc.</i>	<i>Exptl.</i>	<i>Calc.</i>
A ₁ + B ₂	1148.7	1142.1	1068.0	1059.4	1095.5	1188.9
B ₂ + C ₁	1183.3	1175.9	1203.5	1195.8	1233.7	1224.2
A ₁ + C ₁	1153.4	1152.1	1171.4	1170.4	1199.6	1199.7
A ₁ + B ₂ + C ₁	1151.9	1143.3	1171.3	1160.1	1198.9	1190.6
A ₁ + C ₃	1145.6	1146.9	1164.9	1165.2	1188.4	1191.8
C ₁ + C ₃	1181.9	1181.0	1204.7	1202.6	1224.9	1226.2
A ₁ + C ₁ + C ₃	1149.0	1147.0	1168.4	1164.8	1192.5	1192.5
B ₂ + C ₃	1171.8	1169.8	1194.7	1190.5	1215.7	1215.1
A ₁ + B ₂ + C ₃	1144.4	1134.1	1163.9	1150.8	1187.2	1180.1

retention times of xylene or diethylbenzene isomers. To check whether it is possible to predict the selectivity from the equation derived by Waksmundski and Suprynowicz²¹, we calculated the coefficients determining the dependence of the relative retention times on temperature; use was made of the values calculated earlier for the single phases¹⁶. The results are summarized in Table V, where the experimentally determined coefficients are also given. The experimental values are smaller than the calculated ones, but this has little effect on the values of the relative retention times since the enthalpic and entropic factors increase simultaneously. Table V also lists the natural logarithms of the relative retention times of *p*- and *m*-diethylbenzenes as calculated from the experimental relationship, and found theoretically from the melting temperature of the mixture. The calculated relative retention times are equal to or greater than those determined experimentally. The deviations from this trend, observed in several cases, can be attributed to measurement errors.

The measured selectivity of mixed phases is usually somewhat lower than expected from the sum of the contributions of each component at the given temperature. However, in view of the fact that mixed phases have lower melting points than their components and that selectivity increases with decreasing temperature, we can conclude that the mixed phases have greater selectivities than the single phases. Thus, if we compare the selectivities of mixed phases with those of their components at the same temperature, the mixed phases usually reveal a lower selectivity. However, if we compare the selectivities at the melting points the opposite order is often found. This is particularly evident in the cases of mixed phases whose melting points are much lower than those of their components. For instance, the melting point of the mixed phase A₁ + B₂ + C₁ is 379°K, the melting points of the components being 393, 431 and 441°K, respectively. Where one of the components of the mixed phase is present in large proportion, as is the case of binary phases with compound A₅, the increase in selectivity related to the lowering of the melting point is small, since the decrease in that temperature is also small (Table I).

The selectivity of a mixture at the melting point may be lower than that of the

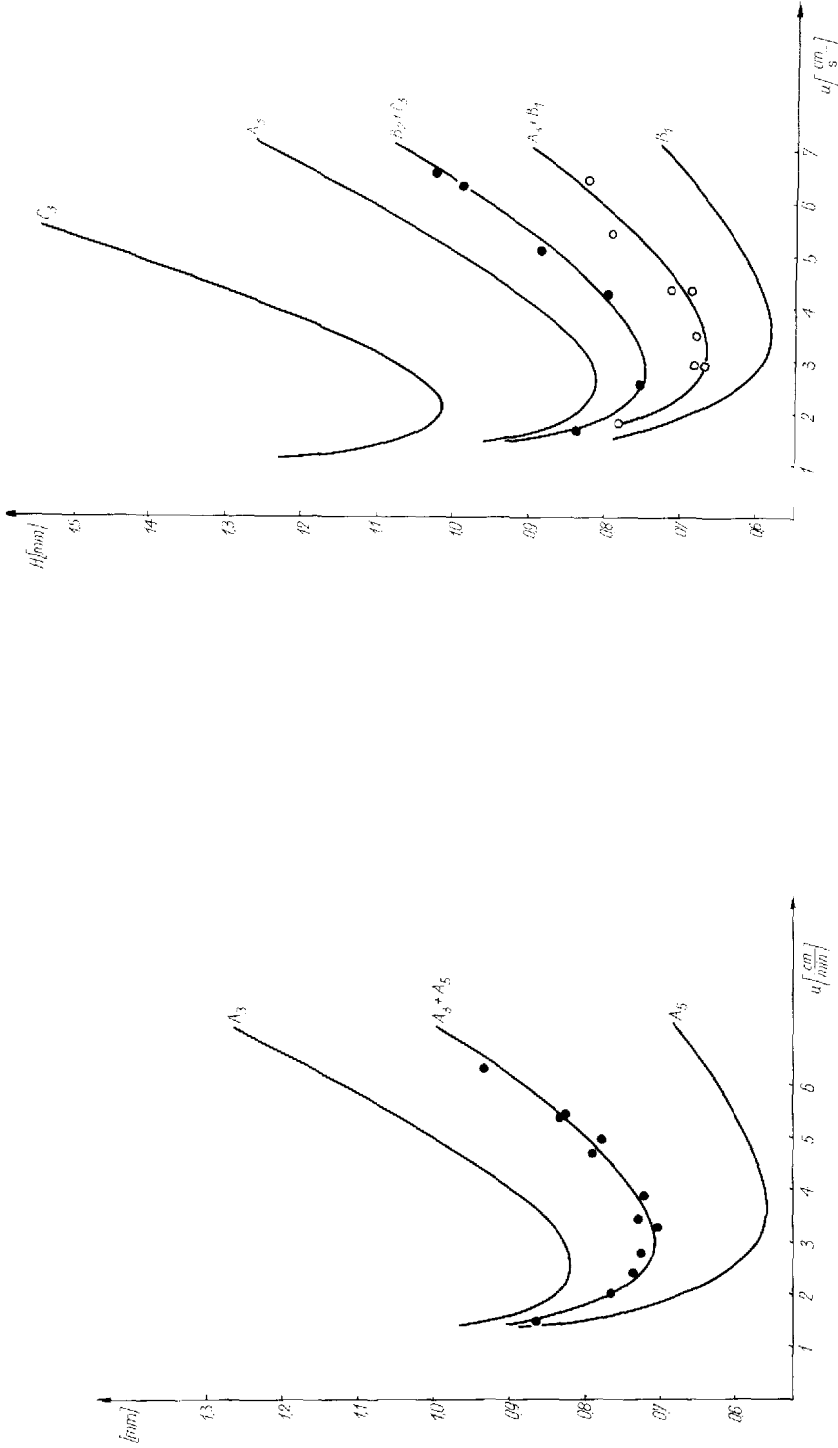


Fig. 2. Dependence of the real plate height on the carrier gas flow-rate for the $A_3 + A_5$ binary phase. The same plots for the single phases are also shown.

Fig. 3. Dependence of the real plate height on the carrier-gas flow-rate for the binary $B_2 + C_3$ and $A_3 + B_1$ phases. The same plots for the single phases are also shown.

TABLE V

COEFFICIENTS OF THE EQUATION DETERMINING THE TEMPERATURE DEPENDENCE OF THE LOGARITHM OF THE RELATIVE RETENTION TIME OF *m*- AND *p*-DIETHYLBENZENES AND THE LOGARITHMS OF THE RELATIVE RETENTION TIMES OF THOSE ISOMERS AT THE MIXED PHASE MELTING POINT

Phase	Experimental values		Calculated values		$\ln r_{p,m}$	
	$\frac{-\Delta H_p + \Delta H_m}{R} \cdot 10^3$	$\frac{\Delta S_p - \Delta S_m}{R}$	$\frac{-\Delta H_p + \Delta H_m}{R} \cdot 10^3$	$\frac{\Delta S_p - \Delta S_m}{R}$	Exptl.	Calc.
A ₅ + A ₃	0.179	-0.184	0.206	-0.233	0.304	0.328
A ₅ + A ₄	0.171	-0.173	0.200	-0.239	0.294	0.307
A ₅ + B ₂	0.212	-0.256	0.233	-0.303	0.317	0.327
A ₅ + B ₄	0.213	-0.265	0.211	-0.255	0.311	0.315
A ₅ + C ₃	0.187	-0.206	0.208	-0.251	0.311	0.324
A ₃ + A ₄	0.134	-0.081	0.173	-0.173	0.260	0.267
A ₃ + B ₁	0.187	-0.204	0.230	-0.297	0.294	0.317
A ₃ + B ₂	0.173	-0.157	0.239	-0.314	0.291	0.308
A ₃ + B ₃	0.159	-0.156	0.175	-0.188	0.253	0.261
A ₃ + B ₄	0.180	-0.189	0.168	-0.153	0.259	0.265
A ₃ + C ₁	0.204	-0.236	0.186	-0.193	0.287	0.282
A ₃ + C ₂	0.213	-0.293	0.210	-0.288	0.271	0.270
A ₃ + C ₃	0.157	-0.145	0.185	-0.196	0.263	0.282
A ₅ + A ₃ + C ₁	0.167	-0.156	0.209	-0.245	0.314	0.344
A ₁ + C ₁	0.236	-0.319	0.248	-0.347	0.293	0.296
A ₁ + C ₃	0.195	-0.234	0.212	-0.268	0.285	0.295
C ₁ + C ₃	0.178	-0.202	0.212	-0.274	0.242	0.253
A ₁ + C ₁ + C ₃	0.196	-0.234	0.222	-0.291	0.290	0.302
A ₂ + C ₁	0.240	-0.350	0.253	-0.376	0.264	0.271
A ₂ + A ₄	0.166	-0.182	0.209	-0.282	0.254	0.268
A ₄ + C ₁	0.218	-0.300	0.206	-0.272	0.246	0.244
A ₂ + A ₄ + C ₁	0.184	-0.225	0.219	-0.309	0.263	0.272
A ₁ + B ₂	0.233	-0.312	0.259	-0.370	0.294	0.304
B ₂ + C ₁	0.269	-0.386	0.311	-0.494	0.264	0.258
A ₁ + B ₂ + C ₁	0.226	-0.298	0.262	-0.379	0.300	0.313
B ₂ + C ₃	0.187	-0.219	0.223	-0.297	0.244	0.257
A ₁ + B ₂ + C ₃	0.189	-0.220	0.270	-0.399	0.289	0.328

TABLE VI

MASS TRANSFER RESISTANCE OF MIXED PHASES

C is the coefficient in the Van Deemter equation.

Phase	$C \times 10^{-2}$ (sec)					
	A ₃ + A ₅	A ₃ + B ₁	B ₂ + C ₃	A ₁ + B ₂ + C ₁	A ₁ + B ₂ + C ₃	A ₁ + C ₁ + C ₃
$C \times 10^{-2}$ (sec)	1.21	1.07	1.34	1.20	1.12	0.95

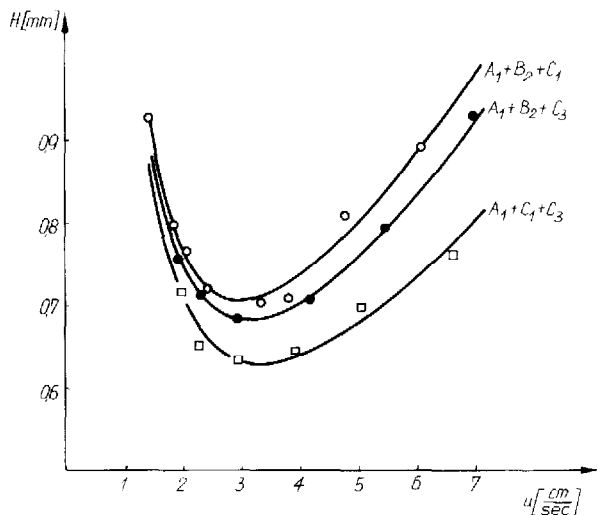


Fig. 4. Dependence of the real plate height on the carrier gas flow-rate for the ternary $A_1 + B_2 + C_1$, $A_1 + B_2 + C_3$ and $A_1 + C_1 + C_3$ phases.

component with highest selectivity at its melting point, despite the significant lowering of the melting point of the mixture with respect to its components when the second component has a very low selectivity. The mixture $A_3 + A_4$ can serve as an example. On this mixture the relative retention time of diethylbenzene *para* and *meta* isomers is 0.260, while on the A_3 and A_4 phases it is 0.265 and 0.210, respectively. Highly selective, mixed liquid-crystalline stationary phases are obtained from highly selective individual liquid crystals.

Most difficult to predict is the efficiency of columns with mixed stationary phases. The mass transfer resistance, which is the decisive factor for the column efficiency, is not an additive quantity. This is seen when we compare the corresponding values for the ternary phases and for their components (Table VI). Figs. 2–4 show plots of the real plate heights *versus* carrier gas flow-rate. For comparison purposes, Figs. 2 and 3 also show the respective curves for the individual components.

The experimental results indicate that the main component has a decisive effect on the efficiencies of columns with mixed phases and that the efficiencies are usually larger than expected from the additivity principle.

The possibility of predicting the properties of mixed phases shows that, contrary to the comments made in ref. 11, the mixed phases of eutectic composition show no anomalies in their properties with respect to mixtures of other compositions. This refers especially to polarity and selectivity. Probably the same could be said about the column efficiency, as evidenced by the results of Tsvetkov²² who studied the viscosity of a binary nematic system, which was an eutectic over a wide range of concentrations; he found that the mixture of eutectic composition had no anomalous properties compared with mixtures of other compositions. The considerable departure from additivity observed in ref. 11 was due to the fact that the mixed phases were compared with the individual components, the single phases being in the solid state on the support and the mixed ones already in the liquid state. In the former

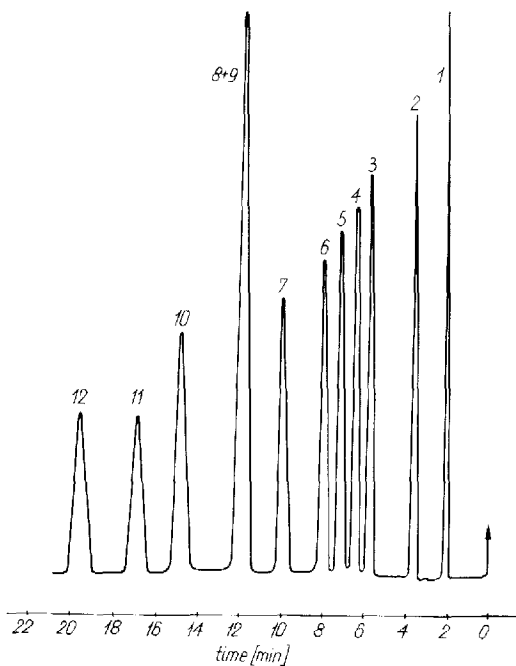


Fig. 5. Chromatogram of a mixture containing benzene (1), toluene (2), ethylbenzene (3), *m*-xylene (4), *p*-xylene (5), *o*-xylene (6), *m*-ethyltoluene (7), *p*-ethyltoluene (8), *o*-ethyltoluene (9), *m*-diethylbenzene (10), *o*-diethylbenzene (11) and *p*-diethylbenzene (12). The separation was carried out on a glass column (310 cm \times 3 mm I.D.) containing 15% of phase A₁ + B₂ + C₃ on Chromosorb W NAW. The temperature of the injector was 493°K and that of the column 377°K. Argon was the carrier gas at a flow-rate of 20 cm³/min.

case adsorption was the main process whereas in the latter dissolution predominated.

Certain similarities exist between the mixed and single supercooled liquid-crystalline stationary phases. Supercooled phases can be used at temperatures lower than the melting point, the selectivity increasing with decreasing temperature. However, the viscosity of the supercooled phase increases simultaneously and as a result of the increased mass transfer resistance we observed lowered efficiencies for columns containing such a phase. The supercooled state of some liquid-crystalline phases is very stable, of others it is unstable and some phases do not supercool at all. It is advantageous therefore to use mixed phases rather than supercooled single phases. If necessary the mixed phase can also be supercooled, to temperatures lower than those of its components.

The predicted separating properties of the mixed phases were confirmed by carrying out the separation of a mixture. A typical chromatogram is given in Fig. 5. The separation conditions were optimal for the xylene isomers which were separated in 6 min. This compares well with the use of capillary columns and liquid-crystalline stationary phases^{2,3,24}. The *p*- and *o*-ethyltoluenes were not separated on the highly selective, mixed liquid-crystalline stationary phases, due to the high selectivity of the phases towards the *meta* and *para* isomers. The relative retention of the *para* isomer increased so much that it was eluted from the column together with the

ortho isomer. A complete separation of ethyltoluene isomers would be possible if the liquid-crystalline stationary phase had a lower selectivity^{2,5}.

Better separations were obtained on the mixed phases than on the single phases.

CONCLUSIONS

The properties of mixed liquid-crystalline stationary phases of eutectic compositions can be fairly precisely predicted if the properties of the individual phases are known. Difficulties are encountered, however, in predicting the column efficiency. Better separations are obtained on mixed phases than on single phases, but the higher selectivity of the former is related to the lower melting temperature.

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