INVESTIGATION OF CONDENSED HETEROAROMATIC SYSTEMS INCLUDING A THIOPHENE RING

XXII.* GAS-CHROMATOGRAPHIC BEHAVIOR OF POLYCONDENSED HETEROAROMATIC COMPOUNDS UNDER ISOTHERMAL CONDITIONS

V. P. Litvinov, V. A. Ferapontov,
D. D. Gverdtsiteli, and É. G. Ostapenko

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A method for the gas-chromatographic analysis of high-boiling polycondensed heteroaromatic compounds with a thiophene ring (CHC) containing up to five condensed rings was developed. The optimum analysis conditions were found, the retention times were determined, and the dependence of the elution characteristics on the column temperature and CHC structure was followed. Elution occurs in conformity with the number of rings in the CHC molecule, and compounds with the same number of rings (with allowance for substituents with a benzene ring) are arranged in sufficiently isolated groups. The phenomenon of inversion of the retention volumes of some CHC as the temperature rises was noted. A method for the indirect analysis of CHC by chromatography of the products of desulfurization of them was developed.

In connection with the synthesis and investigation of the dependence between the structure and physical and chemical properties of condensed heteroaromatic compounds with a thiophene ring (CHC), we attempted to develop gas-liquid-chromatography (GLC) methods for the analysis of CHC in order to determine the degree of purity of the compounds, establish structures (in conjunction with other physicochemical methods) [1], and study the products obtained when they are desulfurated. In addition, a method for the accurate and reliable expression of data on retention was worked out, and a search was carried out for dependences that link the retention values with the structures. This is necessary for the standardless identification of CHC in complex multicomponent mixtures and, in particular, in the high-molecular-weight portion of sulfurous oils, in which, as demonstrated by other methods, thiophene homologs with condensed cyclic systems are widely represented [2, 3]. The peculiarities of the physical and chemical properties of tri-, tetra-, and pentacyclic CHC (high boiling points, capacity of the sulfur atom not only for donor but also for acceptor interactions, etc.) and the fact that many of the compounds examined in this paper were synthesized for the first time caused considerable difficulties in the solution of the formulated problems. These difficulties were aggravated by the fact that at present the selection of inert and stable sorbents and stationary phases for high-temperature GLC is becoming more and more limited. Data on the separation of CHC only into groups of substances with the same number of condensed rings in the molecule (up to four rings) but not into individual components are presented in a small number of papers devoted to the GLC of some CHC [4] of individual petroleum fractions; this is due to both the difficulties indicated above and to the absence of standard compounds.

In the present paper we have investigated various condensed aromatic and heteroaromatic compounds (14 of them with thiophene rings) with from 2 to 5 condensed rings at 250, 275, and 325°C. A stainless-steel column (600 × 0.3 cm) with 2.22 wt.% Se-30 on Chromosorb W (80-100 mesh), washed with acid, proved to be the most suitable column for the analysis of the CHC. In order to decrease adsorption on the active centers that strongly tie up molecules of the substances to be separated, the entire chromatographic sys-

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*See [1] for communication XXI.

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tem was silanized by repeated introduction of 5-μliter samples of hexamethyldisilazan at a column and vaporizer temperature of 80-100° in a stream of helium. The following values were calculated for the characteristics of the investigated CHC: the retention time (τ), the retention time of the nonsorbed gas (τ_0), the corrected retention time (τ'), the retention volume (V), the dead volume (V_0), the corrected retention volume (V'), the corrected retention volume related to standard conditions (0° and 760 mm) (V_0') [5], the corrected relative retention volume (V'_{rel}), the efficiency of the chromatographic column (N) [6], the asymmetrical character of the peak (As) [7], the degree of separation of adjacent peaks (θ) [8], and the separation coefficient (α). An analysis of the data obtained (Table 1) makes it possible to draw a number of conclusions that are important for the identification of CHC.

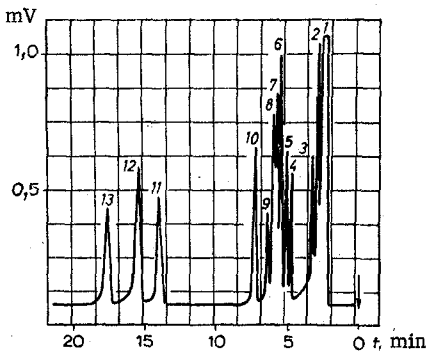

Fig. 1. Chromatogram of a mixture of CHC at 275° and a helium flow rate of 53 ml/min: 1) benzene, thiophene, and I; 2) IV; 3) VIII; 4) XI; 5) XIII; 6) XV; 7) XVI; 8) XVII; 9) XVIII; 10) XX; 11) XXI; 12) XXIII; 13) XXIV.

The compounds are eluted as a function of the number of condensed rings in the molecule. The sharp jumps in the V, V_0', and V'_{rel} values as the number of rings in the CHC molecules changes attests to this. An increase in the number of condensed benzene rings in the molecule of a "linear" heteroaromatic compound leads to a proportional change in the indicated values. It follows from Table 1 and Fig. 1, in which the chromatogram of a 14-component mixture of CHC is presented, that the peaks of these substances are arranged in distinctly separate groups as a function of the number of rings in the molecule of the condensed compound. These results differ from those previously obtained with a silicone column [4]. We note that although the loss of aromaticity of one of the condensed rings or the introduction of an alkyl substituent into the CHC molecule leads to a certain change in the retention values, it does not cause migration of the peak to the adjacent groups. At the same time, the introduction of benzene ring substituents (phenyl and benzyl) into the CHC changes the retention considerably and is equivalent to the addition of another condensed ring to the CHC molecule. Similar relationships are also observed in a number of polycyclic aromatic hydrocarbons.

The separation coefficients (α) in the series benzo[b]thiophene (II), dibenzothiophene (IV), benzo[b]-naphtho[2,3-d]thiophene (XIII), and anthra[2,3-b]benzo[d]thiophene (XXIII) are 5.44, 5.22, — at 250°; 4.39, 4.45, and 4.39 at 275°; and —, 3.37, 3.30 at 325°. As in the case of the series benzene, naphthalene, anthracene, satisfactory constancy of the coefficient values is observed at a given temperature for all of the members of the series. It is interesting to note that the ratio of the α coefficients at two different temperatures is the same for both series.

An appreciable decrease in the retention time and of all of the remaining elution characteristics is observed on passing from the linear anthra[2,3-d]benzo[d]thiophene structure (XXIII) to the angular anthra-[2,1-b]benzo[b]thiophene structure (XXI).

Despite the certain increase in molecular weight, the replacement of one benzene ring by a cyclohexane or cyclohexene ring in the benzo[b]naphtho[2,3-b]thiophene molecule (compare XI and XIII and XV and XVI) leads to a decrease in the elution time, which is observed at all temperatures.

The position of the methyl group in the benzo[b]naphtho[2,3-d]thiophene molecule (XIII) has comparatively little effect on the elution characteristics. However, a change in the order of elution is observed on passing from 250 to 275 and 325°: 4-methylbenzo[b]naphtho[2,3-b]thiophene (XVII) emerges after 7-methylbenzo[b]naphtho[2,3-g]thiophene (XVI).

The optimum conditions for the separation of most of the investigated CHC (with different numbers of rings) are achieved at 275° and a helium flow rate of 38 ml/min. However, not all of the substances are eluted with a sufficient degree of separation under these conditions. Separation coefficient α ranges from 1.05 to 1.01 for the following pairs of substances: VII and VIII, XII and XIII, XIII and XIV, XVI and XVII, XVIII and XIX, and XXIV and XXV. In general, separation improves when the temperature is lowered to 250°: XIII and XIV and XVIII and XIX are completely separated, and better separation is achieved for XII and XIII and XVI and XVII; in the latter two cases, the order of elution changes. Coefficient α remains practically constant only for VII and VIII; moreover, the order of elution also changes. Raising the temperature to 325° causes a decrease in α, but not for all of the pairs of substances. In individual cases, an

TABLE 1. Chromatographic Characteristics of the Investigated Compounds under Isothermal Conditions*

Comp.	Name	Column temp., °C	τ′, min	V'_0, ml	N, theoretical plates	As	V'_{rel}	α†	Calc. bp, °C‡
1	2	3	4	5	6	7	8	9	10
I	Naphthalene	250	0,221	1,9	48	1,0	0,028	1,06	—
		275	0,183	1,6	35	1,0	0,041	1,15	—
II	Benzo[b]thiophene	250	0,234	2,1	43	1,0	0,029	2,03	—
		275	0,210	1,8	28	1,0	0,047	1,45	—
III	Diphenylmethane	250	0,475	4,0	220	1,0	0,059	2,68	—
		275	0,304	2,6	74	1,0	0,069	3,03	—
IV	Dibenzothiophene	250	1,275	10,8	750	1,0	0,159	1,04	—
		275	0,921	7,9	560	1,0	0,208	0,98	—
		325	0,371	3,0	170	1,0	0,273	1,01	—
V	Anthracene	250	1,325	11,5	1380	1,0	0,165	1,54 (VIII)	—
		275	0,897	7,7	640	1,0	0,202	1,39	335
		325	0,375	3,0	190	1,0	0,276	1,08	—
VI	2-Phenylnaphthalene	250	2,130	18,1	1500	1,2	0,266	1,39 (IX)	—
		275	1,250	10,8	1130	1,0	0,282	1,09	351
		325	0,405	3,3	360	1,0	0,290	1,12	—
VII	Anthraquinone	250	2,110	18,0	1580	2,0	0,264	1,01 (VI)	—
		275	1,360	11,8	950	1,0	0,307	1,04	355
		325	0,454	3,7	340	1,0	0,334	1,12	—
VIII	Thianthrene	250	2,040	17,5	2000	1,0	0,255	1,03 (VII)	—
		275	1,420	12,3	820	1,0	0,320	1,30	358
		325	0,510	4,1	320	1,0	0,375	1,06	—
IX	4-Methyl-2-phenylnaphthalene	250	2,970	25,2	2760	2,0	0,371	1,27	—
		275	1,840	15,9	1740	1,2	0,415	1,30	370
		325	0,540	4,4	550	1,1	0,397	1,41	—
X	2,6-Dimethylthianthrene	250	3,770	32,0	3300	0,8	0,471	1,76 (XVIII)	—
		275	2,400	20,9	2360	1,0	0,541	1,48	383
		325	0,763	6,2	580	1,0	0,561	1,43 (XII)	—
XI	7,8,9,10-Tetrahydrobenzo[b]naphtho[2,3-d]thiophene	275	3,540	30,6	2760	1,15	0,800	1,12	400
		325	1,105	8,9	970	1,0	0,812	1,13 (XIII)	—
XII	1-Phenylanthracene	250	7,300	61,8	5500	2,3	0,912	1,08 (XV)	—
		275	3,960	34,3	4100	1,3	0,894	1,04	405
		325	1,090	8,8	950	1,2	0,801	1,01 (XI)	—
XIII	Benzo[b]naphtho[2,3-d]thiophene	250	6,650	56,6	4540	0,8	0,831	1,10 (XII)	—
		275	4,100	34,7	2780	2,0	0,925	1,08	408
		325	1,250	10,0	1240	1,1	0,919	1,02 (XV)	—
XIV	Tetracene	250	8,000	68,7	1540	2,3	1,000	1,06 (XVII)	—
		275	4,430	38,3	2830	2,3	1,000	1,05	410
		325	1,360	10,8	1220	1,6	1,000	1,04 (XVII)	—
XV	7-Methyl-9,10-dihydrobenzo[b]naphtho[2,3-d]thiophene	250	7900	67,7	6180	1,9	0,987	1,01 (XIV)	—
		275	4,650	40,3	2500	0,55	1,050	1,05	412
		325	1,285	10,4	—	1,0	0,944	1,05	—
XVI	7-Methylbenzo[b]naphtho[2,3-d]thiophene	250	9,150	77,7	5360	1,7	1,144	1,13 (XX)	—
		275	4,880	42,2	3920	1,1	1,101	1,02	414
		325	1,350	10,9	1470	1,2	0,993	1,01 (XIV)	—
XVII	4-Methylbenzo[b]naphtho[2,3-d]thiophene	250	8,500	72,1	5610	2,1	1,062	1,08 (XVI)	—
		275	4,970	43,1	2940	2,4	1,122	1,13	415
		325	1,420	11,5	—	1,0	1,044	1,09	—
XVIII	7-Oxo-7,8,9,10-tetrahydrobenzo[b]naphtho[2,3-d]thiophene	250	6,630	57,5	5410	1,8	0,829	1,00 (XIII)	—
		275	5,600	47,8	4540	1,0	1,264	1,04	420
		325	1,550	12,4	—	1,0	1,140	1,07	—
XIX	2-Phenylanthracene	250	11,200	96,6	4980	2,5	1,402	—	—
		275	5,830	50,5	5020	1,5	1,316	1,21	422
		325	1,662	13,3	1030	1,7	1,222	1,16	—
XX	7-Propylbenzo[b]naphtho[2,3-d]thiophene	250	10,380	89.4	4970	1,1	1,297	1,08 (XIX)	—
		275	7,030	60,0	4350	2,0	1,587	2,18	430
		325	1,920	15,4	1890	1,0	1,411	1,76	—
XXI	Anthra[2,1-b]benzo[d]thiophene	275	15,300	132,5	7080	1,1	3,533	1,14	461
		325	3,370	27,2	2280	2,4	2,478	1,08	—
XXII	7-Phenylbenzo[b]naphtho[2,3-d]thiophene	275	17,400	151,0	3860	3,1	3,927	1,03	465
		325	3,650	29,3	3060	1,0	2,684	1,13	—
XXIII	Anthra[2,3-d]benzo[b]thiophene	275	18,000	156,0	2350	4,0	4,063	1,23	466
		325	4,130	33,3	960	4,0	3,037	1,09	—
XXIV	7-Benzylbenzo[b]naphtho[2,3-d]thiophene	275	22,050	191,0	4860	2,3	4,977	1,01	474
		325	4,500	36,4	4250	1,0	3,309	1,10	—
XXV	Pentacene	275	22,200	193,0	6180	1,8	5,011	1,09	474
		325	4,940	39,2	1380	2,3	3,632	—	—

TABLE 1 (continued)

XXVI	7,12-*Dioxo*-7,12-dihydroanthra[2,3-d]-benzo[b]thiophene	275	24,200	210,0	7320	—	5,462	—	477
XXVII	n-$C_{23}H_{48}$	250	4,470	38,5	—	—	0,558	—	—
		275	2,280	19,5	—	—	0,514	—	—
		325	0,567	4,5	—	—	0,417	—	—
XXVIII	n-$C_{27}H_{46}$	250	12,400	106,9	—	—	1,550	—	—
		275	5,770	48.1	—	—	1,302	—	—
		325	1,204	9,6	—	—	0,985	—	—
XXIX	n-$C_{33}H_{68}$	250	55,600	478,0	—	—	6,950	—	—
		275	22,300	191,0	—	—	5,034	—	—
		325	3,480	27,7	—	—	2,560	—	—

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*With a 600 × 0.3 cm column with 2.22 wt.% SE-30 silicone on Chromosorb W (80-100 mesh). The helium flow rate (at 25°C) was as follows: 36 ml/min (250°), 38 ml/min (275°), and 37 ml/min (325°). The pressure at the inlet of the column was 5.7 atm (250°), 5.9 atm (275°), and 6.9 atm (325°). The pressure at the outlet was 1 atm. The recording ribbon rate was 1440 mm/h. The amount of SE-30 in the column was 0.236 g. The retention time (and volume) of benzene (from the instant of introduction of the sample) coincides with the retention time of the unsorbed gas (methane, ethane, etc.), τ', min: 2.21 (250°), 2.16 (275°), and 2.14 (325°).

†Coefficient α was calculated with respect to the compounds below it in the table or with respect to the compound indicated in parentheses, which emerges afterwards at a given temperature.

‡This was determined from the graph of the dependence of the logarithm of the corrected retention time on the boiling point of normal hydrocarbons.

increase in α is observed. Thus α increases from 1.01 (at 275°) to 1.10 for XXIV and XXV, from 1.04 to 1.12 for VII and VIII, from 1.03 to 1.13 for XXII and XXIII, and 1.04 to 1.15 for XII and XIII.

As a rule, an increase in the selectivity of separation is observed as the temperature rises for those pairs of substances the order of elution of which changes with temperature (for example, VII and VIII, XII and XIII, etc.). The change in the order of elution in the case of XVII and XVIII is particularly striking: they are completely separated at 275° and even at 325°, and XVII is eluted earlier than XVIII; at 250° the order of elution is reversed, also with complete separation of these compounds. The observed fact of the change in the order of elution as the temperature rises requires a thorough investigation. We note only that the change in order of elution is determined by the fact that the curves of the dependence of the logarithm of the presented corrected retention volume on the reciprocal of the absolute temperature intersect one another for each such pair of substances, and the angle of intersection determines the character of the inversion of the elution. This sort of inversion is probably a more or less common phenomenon in high-temperature gas chromatography, and it should be taken into account in practical work.

On the basis of the examination of the data obtained, one can conclude that the most suitable temperatures for separation of CHC with four and five rings are 275 and 325°, while 250 and 275° are the most suitable temperatures for the separation of compounds with three and four rings. The exit times for anthrabenzothiophenes (XXI, XXIII, and XXVI) are very great at 250°.

As seen from the data in Table 1, the efficiency of the action of the column (N), which is expressed by the number of theoretical plates, depends to a great degree on the column temperature, retention volume, and asymmetrical character of the peak (As) of the substance. As a rule, N decreases as the retention volume decreases. Thus the maximum efficiency of the column at 275° was observed with respect to quinone (XXVI) – 7320 theoretical plates – while the minimum efficiency was observed with respect to benzo[b]thiophene (II) – about 30 theoretical plates. One should bear in mind that somewhat depressed N values are obtained for the components that are eluted rapidly because a correction for the half width of the peak of the nonsorbed gas was not introduced into the peak half width.

While N generally characterizes the sharpness of the peak, As indicates the degree of deviation of its shape from the ideally symmetrical form because of overloading of the column (As < 1), absorption, or

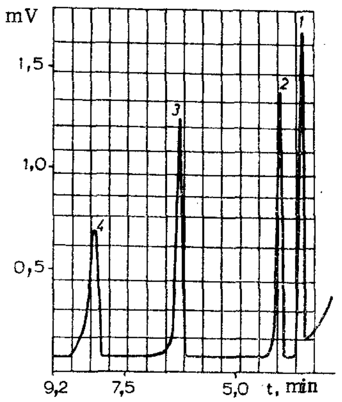

Fig. 2. Chromatogram of a mixture of products of desulfuration of some CHC at 275° and a helium flow rate of 38 ml/min: 1) VI; 2) IX; 3) XII; 4) XIX.

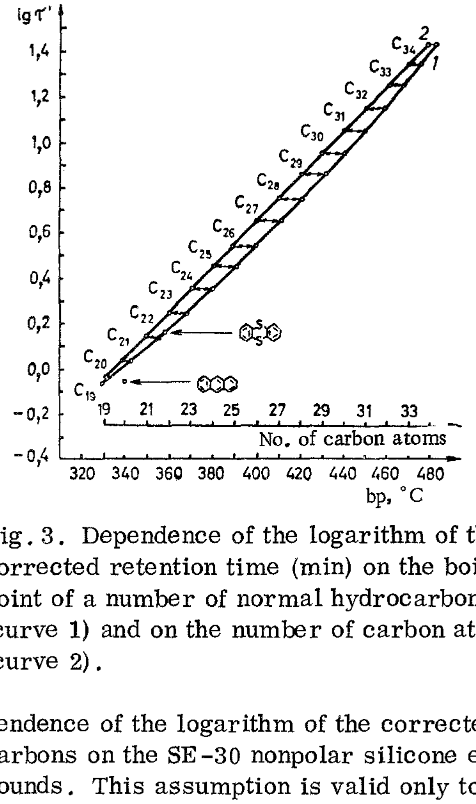

Fig. 3. Dependence of the logarithm of the corrected retention time (min) on the boiling point of a number of normal hydrocarbons (curve 1) and on the number of carbon atoms (curve 2).

other reasons (As > 1). For most of the investigated compounds, As differs only slightly from unity at different temperatures. However, As was three (XXII) and even four (XXIII) for some compounds. The peaks of these compounds had a diffuse tailing edge and were characterized by relatively low N values. The independence of As of the size of the introduced sample served as a criterion of reliability of the elution retention characteristics determined.

In order to identify a number of the CHC, their chromatograms were compared with the chromatograms of the corresponding desulfuration products. The chromatogram of the desulfuration products (Fig. 2) shows that the peaks of four hydrocarbons formed during their desulfuration – 2-phenylnaphthalene (VI), 5-methyl-2-phenylnaphthalene (IX), 1-phenylanthracene (XII), and 2-phenylanthracene (XIX) – correspond to the peaks of the four starting CHC – benzo[b]naphtho[3,3-d]thiophene (XIII), 7-methylbenzo[b]naphtho[2,3-d]thiophene (XVI), anthra[2,1-b]benzo[d]thiophene (XXI), and anthra[2,3-b]benzo[b]thiophene (XXIII). It was found that elimination of a sulfur atom from the CHC molecule leads to a sharp curtailment in the elution time by a factor of 2.5-3 at different temperatures. This method opens up the possibility for the indirect analysis of CHC at substantially lower temperatures by gas-chromatographic investigation of the desulfuration products.

We found it was possible to estimate the boiling points of most of the investigated compounds on the basis of the chromatographic data. Since the boiling points are unknown for any of the CHC or similar compounds, C_{19}-C_{34} normal hydrocarbons, which are present in paraffin with mp 65-75°, were selected as substances for comparison. The interpretation of the peaks on the chromatogram of paraffin was carried out with several standard normal hydrocarbons. Analysis of paraffin with a silicone column filled with SE-30 demonstrated that the dependence of log τ' on the number of carbon atoms in the normal hydrocarbon is conveyed by a line, while the dependence of log τ' on the boiling point is conveyed by a slightly curved line (Fig. 3). It was assumed that the dependence of the logarithm of the corrected retention time on the boiling point in the series of normal hydrocarbons on the SE-30 nonpolar silicone elastomer will also be retained on passing to other classes of compounds. This assumption is valid only to a certain degree. While thianthrene (VIII) with bp 360° [9] actually lies on the curve of the dependence of log τ' on T_b, one obtains a calculated boiling point that is 10° lower than that presented in the literature for anthracene (V) (bp 340° [10]). The boiling points found for some of the aromatic and heteroaromatic compounds from their corrected retention times and the curve of the dependence of log τ' on T_b are presented in Table 1. The values calculated in this manner are approximate, as demonstrated by the example with anthracene.

EXPERIMENTAL

The investigation was carried out with an LKhM-7A serial chromatograph (developed by the Scientific Design Bureau of the Institute of General Chemistry of the Academy of Sciences of the USSR), which we modified somewhat for high-temperature work: a special heater for the gas communications that link the thermostat of the columns with the catharometer thermostat and the flame ionization detector (FID) was introduced; the latter was let down into the inner wall of the upper cover of the thermostat of the column and was additionally heat insulated; the heating coil of the vaporizer was rewound to ensure uniform heating over its entire length. The vaporizer temperature in all cases exceeded the limiting temperature of the column by 50-60°. All of the communications and parts, commencing with the vaporizer and ending with the column and detector, were made of stainless steel. The indicated changes in the design of the apparatus eliminated the possibility of slow evaporation and condensation of the CHC vapors in the vaporizer, at the inlet and outlet from the column, and also at the inlet into the detectors; this increased the efficiency of separation at 250-325°. The samples (0.5-5 μl during operation with a catharometer and 0.05-0.1 μl during operation with an FID) were introduced with a microsyringe with a long steel needle (35-40 mm) through a 2-3 mm thick white vacuum rubber gasket. The sensitivities of the T-26 catharometer (at a bridge current of 120 mA) and of the FID with respect to ether and benzene at a helium flow rate of 36-38 ml/min and room temperature were 700 and 300,000 ml · mV/mg, respectively. The results were recorded with an ÉPP-09 (with a 2-mV scale), and the rate of traversal of the scale by the recorder pen was 1 sec. The rate of drawing of the diagram ribbon was set at 1440 mm/h and 360 mm/h for accurate determination of the elution time relative to low-volatility CHC and highly volatile CHC, respectively. The scale of attenuation of the detector signal varied from 1:1 to 1:4096, depending on the conditions.

The following stainless-steel columns were prepared and tested: 1) a 200 by 0.3 cm column packed with 10 wt.% SE-30 silicone elastomer on acid-washed Chromosorb W (80-100 mesh); 2) a 600 by 0.3 cm column packed with 2.22 wt.% SE-30 on Chromosorb W; 3) a 600 by 0.3 cm column packed with 0.5 wt.% SE-30 on chemically pure sodium chloride crystals (0.25-0.5 mm); 4) a 600 by 0.3 cm column packed with 1 wt.% SKTV-4 silicone on analytically pure sodium chloride crystals (0.25-0.5 mm); 5) a 15 by 0.3 cm column packed with 15 wt.% polyethylene glycol adipate on Chromosorb W. In addition, a copper capillary column (25 m by 0.25 mm), through which a 15% solution of Apiezon L in benzene was passed, was also tested. The testing was carried out at column operating temperatures from 170 to 325°. Prior to operation, the columns were conditioned in a helium stream at 20-30° above the operating temperature. In the case of columns with SKTV-4 and SE-30 on sodium chloride, an intensive and incessant loss of the liquid phase at 80° for SKTV-4 and at 130° for SE-30 below the maximum operating temperature of the phase was noted. A gradual shift and simultaneous pronounced fluctuation in the zero line were observed at temperatures above 160-170°; these effects increased as the temperature rose and were appreciable even during pronounced attenuation of the detector signal. In the case of operation with an FID, these phenomena became noticeable at lower temperatures than during operation with a catharometer. Moreover, the bottom of the cover, the electrodes, and the nozzle of the detector were coated with a deposit (apparently silicon dioxide), which could be removed only by mechanical means. Replacement of the NaCl sorbent by Chromosorb W completely eliminated these phenomena; SE-30 silicone on Chromosorb W is quite stable up to 330°. The results obtained are evidence that silicone elastomers SKTV-4 and SE-30 undergo intensive decomposition in the presence of NaCl. We note that a silicone grease has been used in studies devoted to the use of NaCl in GLC [11-14], and that no decomposition of the silicone liquids on the sodium chloride was noted in this case. This is possibly associated with the fact that detectors of low sensitivity were used. The problem of the stability of silicone on NaCl requires additional study, while the notion of the chemical inertness of NaCl as a liquid-phase support and sorbent in GLC should be verified thoroughly taking into account the data of a number of investigations of sodium chloride as an ionic catalyst of various cleavage reactions [15, 16].

The data on the inapplicability of copper columns, which were obtained in this study, are in conformity with the conclusions of a review devoted to the chromatographic analysis of compounds related to CHC [17].

The method used to prepare the CHC and their physical constants were presented in [1, 18, 19]. In addition, the following compounds were used: benzo[b]thiophene (II), synthesized by the method in [20], mp 31-32°; thianthrene (VIII), obtained by the method in [21], mp 157.5-158°; 2,6-dimethylthianthrene (X), obtained by the method in [22], mp 117-118.5°; commercial, chemically pure, previously sublimed naphthalene (I), anthracene (V), phenanthrene, anthraquinone (VII), tetracene (XIV), pentacene (XXV), and diphenylmethane (III).

LITERATURE CITED

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