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GAS CHROMATOGRAPHIC SEPARATIONS OF ALKANES ON UREA INCLUSION COMPOUNDS WITH *n*-ALKANES AS STATIONARY PHASES

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SUMMARY

Urea adducts with *n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane and *n*-hexadecane have been studied as stationary phases in gas chromatography. With all the adducts examined, selective sorption of *n*-alkanes and of branched alkanes with a single methyl group in the side-chain was found. This sorption is caused by the presence of hexagonal channels with a diameter of 5 Å in the adduct inclusion structure. All factors that increase the dissociation, *i.e.* temperature or the content of the guest molecules, increase the adduct selectivity. On the other hand, all factors that suppress the dissociation, *i.e.* the chain length of the guest molecules and the vapour pressure of the guest molecules, decrease the selectivity. The sorption properties of the adducts were utilized for the separation of model alkane mixtures.

INTRODUCTION

Inclusion compounds are not formed by means of common chemical bonds, such as ionic, covalent or co-ordination covalent bonds, but their formation can be described as spatial merging of valence-saturated molecules¹. Their formation is based on complete inclusion of one component, called the guest, into the fixed structure of the other component, called the host. Both of these components are held together merely by Van der Waals forces and oriented dipole interactions.

The inclusion of one or more guest molecules is possible only when the dimensions of the cavities in the host crystals correspond to the dimensions of the guest molecules. This effect is the cause of the high selectivity of the inclusion process. In gas chromatography, of all these compounds only molecular sieves have been commonly used, as the host inclusion structure is constant for them even after the removal of the guest molecules. However, the structure of many other inclusion compounds is conditioned directly by the presence of the guest molecules and ceases after their removal. This paper is particularly concerned with this latter type of compounds, namely urea adducts with *n*-alkanes. We chose the urea adducts with *n*-alkanes mainly because of their ease of preparation and because of the readily available knowledge of their chemical and physical properties^{2,3}.

The urea adducts with *n*-alkanes could, under certain conditions, be an ad-

vantageous stationary phase. Their surface is filled with hexagonal channels with a diameter of about 5 Å, oriented parallel to the hexagonal structure axis. In these channels, selective sorption of molecules, sterically corresponding to their dimensions, may occur. However, in the absence of guest molecules, the hexagonal structure of the adducts is unstable and immediately recrystallizes to give the tetragonal structure of pure urea; on the other hand, the presence of guest molecules in the hexagonal channels prevents further sorption. However, if dissociation of the inclusion compound takes place, the guest molecules may leave the hexagonal channels and make them available for the sorption of other molecules. On the basis of this assumption, the individual urea inclusion compounds with *n*-alkanes were studied and the conditions for their analytical use optimized.

EXPERIMENTAL

Urea adducts with *n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane and *n*-hexadecane were selected for the study. The inclusion compounds, except for the urea adduct with *n*-octane, were prepared by shaking sieved urea powder of grain size 50–80 mesh with an excess of the appropriate *n*-alkane (60%, v/v) mixed with benzene (40%, v/v) for 24 h. For the preparation of the adduct with *n*-octane, pure *n*-octane was used, otherwise the procedure was identical. The urea adducts prepared were checked by the X-ray method and were packed into a glass U-tube of length 1.4 m and I.D. 4 mm.

The measurements were made with a Carlo Erba (Milan, Italy) Model D gas chromatograph with a flame ionization detector. Experiments in which the carrier gas was saturated with *n*-octane vapour were carried out using a Carlo Erba Model C gas chromatograph, equipped with a thermistor detector. The instrument was equipped with a vapour saturator connected to a multi-way stopcock placed immediately before the column inlet. Hydrogen and nitrogen were used as the carrier gases. The specific surface areas of the adducts were measured by the thermal desorption method, using an instrument developed in the Institute of Physical Chemistry of the Czechoslovak Academy of Sciences (*cf.* ref. 4).

RESULTS AND DISCUSSION

The following interactions were studied during the investigations of the possibility of using the urea adducts as stationary phases:

- (1) sorbate–pure dissolved urea (as a component of the stationary phase);
- (2) sorbate–fused urea (as the stationary phase);
- (3) sorbate–pure tetragonal urea;
- (4) sorbate–unstable hexagonal urea adduct;
- (5) sorbate–stable hexagonal urea adduct.

In the first two instances, the experimental conditions were chosen so as to correspond with those used for the formation of the inclusion compounds in the liquid phase. These experiments were analogous to those performed by Maczek and Phillips^{5,6}, who employed dissolved tri-*o*-thymotide and desoxycholic acid as components of the stationary phase. In our work, the selective urea effect was not, however, confirmed. Further, interactions of the sorbate with the solid phase were followed, the

solid phase being represented by pure tetragonal urea as the initial material for the adduct preparation, and recrystallized urea after distilling off the guest molecules, with which certain changes in the interaction with the gaseous phase may be expected. The same relative retentions of the sorbates were found on both of these stationary phases, but the specific retention volumes on the recrystallized urea were six times greater for all of the sorbates studied. This phenomenon can be explained by a considerable change in the specific surface area of urea during the inclusion process, which was confirmed by the results of specific surface area measurements. While the specific surface area of urea as the initial material for the adduct preparation can not be measured by the thermal desorption method, the specific surface areas of recrystallized urea and the adducts themselves attain values of 0.6–2.7 m²/g, depending on the number of clathration and declathration cycles of urea powder with *n*-octane.

The greatest attention was devoted to the study of the sorbate-urea adduct interaction. The manner in which the experiments were conducted and evaluated can be shown by using, as an example, the urea adduct with *n*-octane. In Fig. 1, the dependence of the weight of adduct in the column packing on time is shown, monitor-

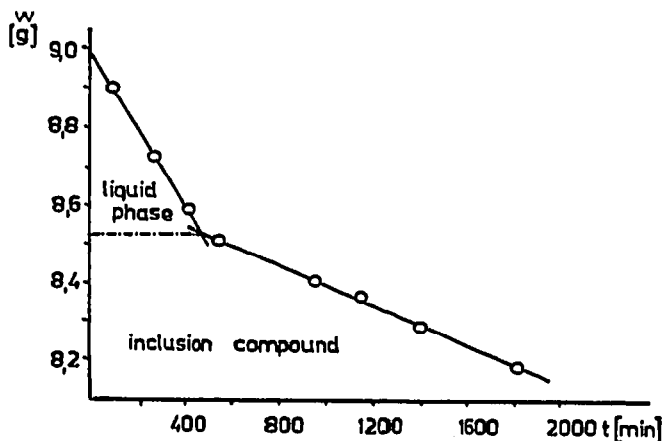


Fig. 1. Dependence of the column packing weight (w) on time (t). Stationary phase, urea adduct with *n*-octane; column temperature, 23°; flow-rate, 20.5 ml/min.

ed at a constant carrier gas flow-rate. At the beginning of the measurement, the column packing consists of particles of inclusion compound covered with a liquid film of *n*-octane. The steep straight line corresponds to the loss of the *n*-octane liquid phase and the other, less steep, line to the loss of the guest molecules. From Fig. 1, the stabilizing effect of the liquid phase on the inclusion compound is evident. Only after distilling off the liquid phase does the loss of the guest molecules in the inclusion compound take place.

An analogous dependence of the retention times is given in Fig. 2. In part I, the retention is caused by dissolution in the excess of liquid *n*-octane and by the selective effect of the inclusion structure. After distilling off the liquid film, in part II, the sorption on the adduct itself occurs. The retention of the active sorbates, *i.e.* those whose sorption is affected by the hexagonal channels in the inclusion structure (*n*-butane, 2-methylpentane and 3-methylpentane), depends on time and hence also on

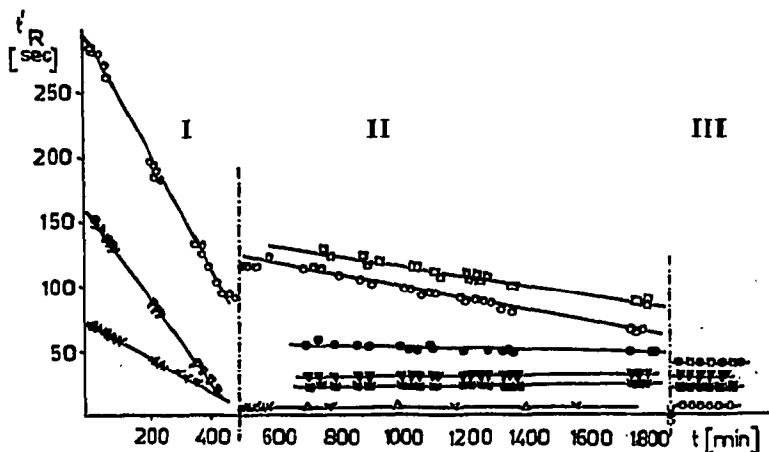


Fig. 2. Dependence of retention times (t_R) on time (t). Stationary phase, urea adduct with *n*-octane; column temperature, 23°; flow-rate, 20.5 ml/min. ×, Propane; △, isobutane; ○, *n*-butane; ■, 2,2-dimethylbutane; ▼, 2,3-dimethylbutane; ●, 3-methylpentane; □, 2-methylpentane.

the content of guest molecules. On the other hand, the retention of the inactive sorbates (2,2-dimethylbutane and 2,3-dimethylbutane) does not depend on the content of guest molecules and is not affected by the presence of the inclusion structure. At identical flow-rates, the retention times of these sorbates are the same both on the adduct and on urea after distilling off the guest molecules. However, the retention times of the active sorbates decrease linearly with the loss of the guest molecules, down to the values obtained on pure urea, which are shown in part III. The sorption of the active alkanes on the urea adduct can be divided into two contributions, on the basis of the above dependences. Firstly, sorption on the surface of the urea crystal occurs, and secondly, sorption into the hexagonal channels of the inclusion structure. The retention of the inactive sorbates is caused only by the sorption on the crystal surface, while the retention of active sorbates involves both of these contributions. In order to be able to determine the values of both contributions, it is necessary to find the specific elution volumes on the adduct and on urea after distilling off the guest molecules.

In Table I are given the retention data found on the urea adduct with *n*-octane, with the maximum content of the guest molecules (18.2%, w/w). The sorbates are arranged according to their order of elution; also given are the boiling points,

TABLE I

RETENTION DATA FOR THE UREA ADDUCTS WITH *n*-OCTANE

Column temperature 23°.

Sorbate	B.p. (°C)	V_{sa}^0	V_{su}	V_{sa}^0/V_{su}^0	% V_{sa}^0
2,2-Dimethylbutane	49.7	0.427	0.437	0.98	—
2,3-Dimethylbutane	58.0	0.541	0.548	0.99	—
3-Methylpentane	63.2	1.11	0.635	1.75	42
<i>n</i> -Butane	—0.5	2.42	0.092	26.3	96
2-Methylpentane	60.2	2.64	0.632	4.18	76

the specific elution volumes per square metre of the adduct (V_{sa}^0), the specific elution volumes on tetragonal urea after distilling off the guest molecules (V_{su}^0), the ratio of these two specific elution volumes, and the percentage of the specific elution volume ($\%V_{sa}^0$) that corresponds only to the effect of the hexagonal channels on the sorbate retention. The $\%V_{sa}^0$ values were calculated from the formula

$$\%V_{sa}^0 = \frac{(V_{sa}^0 - V_{su}^0) \cdot 100}{V_{sa}^0}$$

From the values given in Table I, inactive 2,3-dimethylbutane and active *n*-butane can be chosen as examples. 2,3-Dimethylbutane has approximately the same values of the specific retention volume on the adduct and on pure urea, as no retention in the adduct hexagonal channels occurs. On the other hand, *n*-butane is eluted only after 3-methylpentane, in spite of the large difference in the boiling points. Its specific retention volume on the adduct is 26 times larger than that on pure urea and the contribution of the hexagonal channels to the retention of *n*-butane is as much as 96%.

In the above manner, 27 alkanes with various structures were investigated on the urea inclusion compounds with *n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane and *n*-hexadecane. At the selected column operating temperatures, 23° and 26°, there is a loss of guest molecules with the adducts with *n*-octane and *n*-decane. The urea adducts with *n*-dodecane, *n*-tetradecane and *n*-hexadecane are stable at these column temperatures. A summary of the retention data on these adducts is given in Table II. The urea adduct with *n*-decane was added to the three stable adducts, because the loss of the guest molecules during the measurement is negligible with this adduct. The sorbates are arranged according to the number of carbon atoms in their molecules.

It follows from Table II that selective adsorption takes place even with stable adducts such as the urea adduct with *n*-hexadecane. Therefore, even a negligible extent of dissociation is sufficient for the manifestation of the selective properties of the adduct hexagonal structure.

The dissociation of the inclusion compounds is a necessary condition for selective sorption from the gaseous phase. Therefore, all factors that affect the dissociation were followed, *i.e.* the content of the guest molecules, their chain length, temperature, and the vapour pressure of the guest molecules.

The dependence on the guest molecule content has already been shown for the urea adduct with *n*-octane (see Fig. 2), and it follows from this dependence that the adduct selectivity decreases with the loss of guest molecules. The effect of the chain length of the guest molecules on the adduct dissociation follows from the data given in Table II. With an increase in the chain length, a decrease in the retention values occurs with all active sorbates.

The effect of temperature on the inclusion compound selectivity was followed on the urea adduct with *n*-dodecane. This adduct is stable in the temperature range 26–45°. The effect of temperature is best demonstrated by changes in the elution order of an active sorbate (*n*-hexane) at various temperatures:

26°: 2,5-dimethylhexane, *n*-hexane, 3-ethylhexane, 4-methylheptane, 3-methylheptane, 2-methylheptane;

30°: 2,5-dimethylhexane, 3-ethylhexane, *n*-hexane, 4-methylheptane, 3-methylheptane, 2-methylheptane;

TABLE II

RETENTION DATA FOR THE UREA ADDUCTS WITH *n*-DECANE, *n*-DODECANE, *n*-TETRADECANE AND *n*-HEXADECANE

Column temperature 26°.

Sorbate	<i>n</i> -C ₁₀		<i>n</i> -C ₁₂		<i>n</i> -C ₁₄		<i>n</i> -C ₁₆	
	V_{sa}^0	% V_{sa}^0	V_{sa}^0	% V_{sa}^0	V_{sa}^0	% V_{sa}^0	V_{sa}^0	% V_{sa}^0
	V_{su}^0		V_{su}^0		V_{su}^0		V_{su}^0	
<i>n</i> -Butane	3.85	74	1.71	42	1.10	9	1.02	
<i>n</i> -Pentane	10.00	90	2.62	62	1.42	30	1.08	7
2,2-Dimethylbutane	0.94		0.95		0.97		0.97	
2,3-Dimethylbutane	0.97		0.98		1.00		0.97	
3-Methylpentane	1.11	10	1.04		1.02		1.01	
2-Methylpentane	1.38	28	1.12	11	1.06	6	1.03	
<i>n</i> -Hexane	—	—	5.93	83	2.62	62	1.46	31
2,2,3-Trimethylbutane	0.98		0.98		1.00		0.96	
2,3-Dimethylpentane	1.05	5	1.03		1.05		1.02	
2,4-Dimethylpentane	1.08	7	1.05	5	1.02		1.03	
3-Methylhexane	1.34	25	1.14	12	1.05	5	1.02	
2-Methylhexane	2.67	63	1.46	31	1.13	11	1.06	6
<i>n</i> -Heptane	—	—	—	—	3.52	72	1.93	48
2,2,4-Trimethylpentane	1.01		1.03		0.99		1.02	
2,2,3-Trimethylpentane	1.00		1.04		1.01		1.01	
2,3,3-Trimethylpentane	0.98		1.00		1.01		0.98	
2,3,4-Trimethylpentane	0.99		1.01		1.00		0.99	
2,2-Dimethylhexane	1.13	12	1.07	7	1.02		1.02	
2,5-Dimethylhexane	1.11	10	1.09	9	1.01		1.00	
2,4-Dimethylhexane	1.09	8	1.04		1.02		1.01	
2,3-Dimethylhexane	1.08	7	1.07	6	1.03		1.01	
3,4-Dimethylhexane	1.04		1.02		1.01		1.01	
3,3-Dimethylhexane	1.04		1.04		1.02		1.01	
3-Ethylhexane	1.04		1.02		1.01		1.00	
4-Methylheptane	1.44	30	1.19	16	1.09	8	1.04	
3-Methylheptane	2.26	56	1.46	32	1.19	17	1.08	8
2-Methylheptane	—	—	2.24	55	1.53	35	1.16	14

35°: 2,5-dimethylhexane, 3-ethylhexane, 4-methylheptane, *n*-hexane, 3-methylheptane, 2-methylheptane;

40°: 2,5-dimethylhexane, 3-ethylhexane, 4-methylheptane, 3-methylheptane, *n*-hexane, 2-methylheptane.

The changes in the order of elution of the highly active sorbates confirm that the selectivity of the inclusion compound increases with increasing temperature.

The effect of vapour pressure on the inclusion compound selectivity can be shown, for example, by comparing the specific retention volumes (V_g^0) and the relative retentions (r) obtained on the urea adduct with *n*-octane (see Table III).

On increasing the *n*-octane vapour pressure from 15.7 to 19.7 Torr, an increase in the specific retention volume occurs at a constant guest molecule content, but the relative retention values decrease for active sorbates. These results prove that an increase in the *n*-octane vapour pressure leads to a decrease in the dissociation of the inclusion compound and consequently to a decrease in its selectivity.

TABLE III

SPECIFIC RETENTION VOLUMES (V_g^0) AND RELATIVE RETENTIONS (r) ON THE UREA ADDUCT WITH *n*-OCTANEA: temperature, 51°; *n*-octane vapour pressure, 15.7 Torr; guest molecule content, 14% (w/w).
B: temperature, 51°; *n*-octane vapour pressure, 19.7 Torr; guest molecule content, 14% (w/w).

Sorbate	A		B	
	V_g^0	r	V_g^0	r
<i>n</i> -Pentane	0.25	0.29	0.28	0.20
2,3,4-Trimethylpentane	0.56	0.66	0.92	0.65
2,2,5-Trimethylhexane	0.85	1.00	1.42	1.00
4-Methylheptane	0.89	1.05	1.40	0.99
3-Methylheptane	1.03	1.21	1.56	1.10
2-Methylheptane	2.40	2.82	2.85	2.01
<i>n</i> -Hexane	3.18	3.74	3.60	2.54
<i>n</i> -Heptane	4.03	4.75	4.68	3.30
<i>n</i> -Octane	5.16	6.07	—	—
<i>n</i> -Nonane	6.76	7.95	—	—

On the basis of these results, the original concept of the sorption character could be confirmed. By adduct dissociation, hexagonal cavities are uncovered, *i.e.* active centres for the sorbate molecules are formed. An increase in the degree of dissociation causes an increase in the number of selective interactions. Hence, all factors that increase the dissociation, *i.e.* increasing the guest molecule content and temperature, also increase the inclusion compound selectivity. On the other hand, all factors that suppress the dissociation, *i.e.* increasing the chain length and vapour pressure of the guest molecules, decrease the selectivity.

The gas chromatographic method also enabled a precise determination to be made of the sorbate structure effect. Studies in connection with the formation of inclusion compounds by interaction with the alkane liquid phase showed the possibility of the selective inclusion of *n*-alkanes from *n*-hexane upwards and of branched alkanes with a single methyl group in the side-chain, from 2-methyldecane upwards. Multiple repeating of equilibrium processes under the conditions in the chromatographic column permits the determination of the inclusion structure selectivity towards *n*-alkanes from *n*-butane upwards, and towards branched alkanes from 3-methylpentane upwards. Moreover, it also permits the exact differentiation of the degrees of selectivity for individual sorbates. This fact is shown by the retention data given in Table III.

Of alkanes with the same number of carbon atoms, *n*-alkane is the most affected by the inclusion structure. It is followed by alkanes with one methyl group in positions 2-, 3- and 4-, whose selectivity decreases in the above order. Contrary to expectations, a slight effect of the inclusion structure on some alkanes with two methyl groups (2,2-dimethylhexane and 2,5-dimethylhexane) was observed. Alkanes with three methyl groups in the side-chain are completely inactive.

From these results, the analytical use of the urea adducts with *n*-alkanes also follows. Principally, it is possible to separate readily active sorbates from inactive sorbates, and active sorbates with different selectivities towards the inclusion structure. On the other hand, inactive sorbates, whose boiling points do not differ much, cannot be separated.

Fig. 3 shows a chromatogram of a mixture of 2,3-dimethylbutane and *n*-pentane on the urea adduct with *n*-decane. This recording is a typical example of a separation of an active and an inactive sorbate, and simultaneously an example of the reversed elution order with respect to the boiling points of the two sorbates. The peak of an inactive sorbate is always sharp, while that of an active sorbate is markedly affected by the diffusion character of sorption. For analytical use, there is a certain drawback in the dependence of the retention times of the active sorbate on the guest molecule content with unstable adducts and the pronounced tailing of the peaks of these sorbates. Both of these drawbacks can be removed to a certain extent by saturating the carrier gas with the vapour of the appropriate *n*-alkane before the column inlet. By this means, the loss of the guest molecules is prevented and the peaks of active sorbates lose, to a certain extent, their tailing and are much more symmetrical.

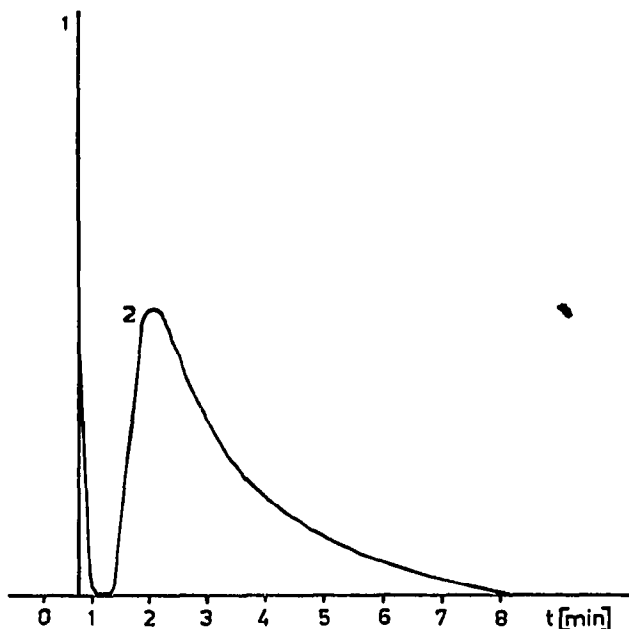


Fig. 3. Chromatogram of a mixture of 2,3-dimethylbutane (1) and *n*-pentane (2). Stationary phase, urea adduct with *n*-decane; column temperature, 26°.

Fig. 4 shows a chromatogram of a mixture of 4-methylheptane and 2-methylheptane. These isomers have identical boiling points and can be separated only in highly efficient capillary columns. Fig. 5 shows a chromatogram of a mixture of 2,2,3-trimethylbutane, 2,2,5-trimethylhexane and *n*-heptane. This chromatogram characterizes well both the separating efficiency of the urea surface (separation of the branched alkanes) and the selective effect of the inclusion structure (separation of *n*-heptane from both branched alkanes).

The urea inclusion compounds with *n*-alkanes are definitely not universal adsorbents. However, many specific problems could be solved with their aid. There is also a great advantage in the possibility of varying the selective properties of the

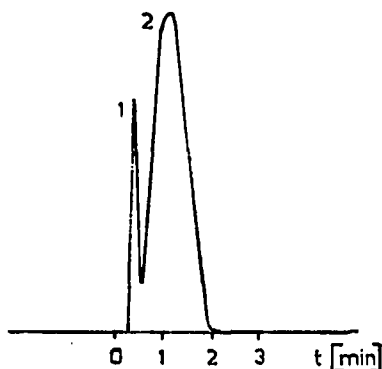


Fig. 4. Chromatogram of a mixture of 4-methylheptane (1) and 2-methylheptane (2). Stationary phase, urea adduct with *n*-octane; column temperature, 51°; *n*-octane vapour pressure, 15.7 Torr.

adduct according to the requirements of the separation, by a suitable choice of the degree of its dissociation.

In this paper we have considered the urea inclusion compounds with *n*-alkanes. However, urea also forms inclusion compounds with a number of other substances, e.g. fatty acids, esters, ketones, alcohols and organosilanes. Thiourea has similar properties, but, in contrast to urea, it forms inclusion compounds with branched alkanes. A number of other substances capable of forming inclusion compounds have been described in the literature.

It seems that a wide choice of host structures, differing in the dimensions of their lattices or channels and thus also in their selectivity towards various kinds of guest

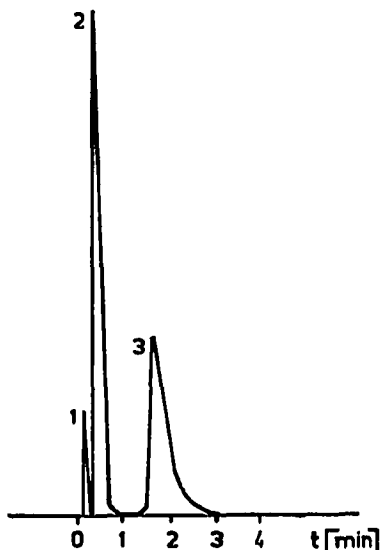


Fig. 5. Chromatogram of a mixture of 2,2,3-trimethylbutane (1), 2,2,5-trimethylhexane (2) and *n*-heptane (3). Stationary phase, urea adduct with *n*-octane; column temperature, 51°; *n*-octane vapour pressure, 15.7 Torr.

components, should find further application in gas chromatography, both from the point of view of the study of inclusion compounds and from that of their analytical utilization.

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