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SELECTIVE ADSORPTION PROPERTIES OF THE SURFACES OF ATTAPULGITE AND SEPIOLITE

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SUMMARY

Representative samples of sepiolite and attapulgite, clay minerals of the hormite group characterized by a porous lattice, were tested as stationary phases in gas-solid chromatography.

The selectivity and efficiency of such adsorbents are largely dependent upon differences in surface geometry and homogeneity.

In gas analysis, the most interesting application of hormites appears to be the possibility of separating O₂, N₂, CO, CH₄, CO₂ and light hydrocarbons by using a single short column.

Configurational and steric isomers are easily resolved on hormites. The selectivity towards isomeric alkanes may be related to the different sizes of the open channels on the external surface of such minerals.

The resolution between *cis* and *trans* forms of disubstituted cycloalkanes is very high. For instance, there is a complete separation of all the dimethylcyclopentane isomers, and very high relative volatilities are shown by the *cis* and *trans* forms of dimethylcyclohexanes.

Efficiency values are such that the use of hormites in gas-solid chromatography has proved to be practical.

INTRODUCTION

The geometrical structure of an adsorbent is responsible for the separation of molecules according to their dimensions or steric configurations.

KISELEV AND YASHIN¹ classified as microporous homogeneous (type III) those adsorbents with a porous lattice and with holes all of the same size. Zeolites A and X are well known examples of this type.

The present paper deals with the gas chromatographic behaviour of hormites that may be considered as type III adsorbents. Well known members of this group of clay minerals² are sepiolite and attapulgite, the chemical compositions of which may differ according to the origin of the sediments. Sepiolite is completely magnesian, whereas attapulgite shows a considerable variation in the relative amounts of aluminium and magnesium that are present.

The projections (001) of unit cells according to BRADLEY AND NAGY^{3,4} are shown in Fig. 1. Both minerals consist of long silica chains parallel to the *c* axis, linked together through oxygen atoms at their longitudinal edges. Consequently, rectangular

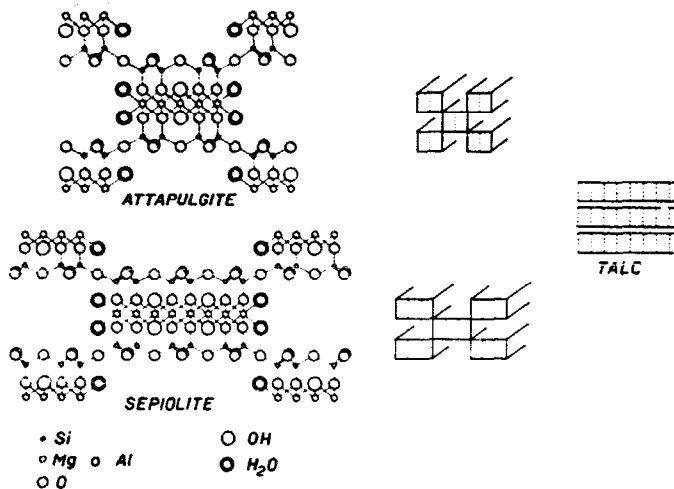


Fig. 1. Schematic representation of the structure (projection on 001) of attapulgite (after BRADLEY⁴) and sepiolite (after NAGY AND BRADLEY³).

for holes are formed, having a cross-section of 3.7 by 6 Å for attapulgite and 3.7 by 9 Å sepiolite⁵. Such holes, as in molecular sieves, are normally filled with zeolitic water that can be easily removed by heating at 150–200°; the structural water bound to aluminium and magnesium is lost only above 300°. No structural modification occurs up to this temperature, so that dehydrated sepiolite and attapulgite are stable in the temperature range of interest in gas chromatography.

Electron microscopy enables an accurate determination of the particle shape of these minerals to be made. Fig. 2 shows that Vallecas sepiolite occurs in elongate lath-shaped units. Size measurements from such electron micrographs agree with the results of FENOLL HACH-ALI' AND MARTIN VIVALDI⁶: the average dimensions of an individual lath (Fig. 3) are 8000 Å in length (1600 unit cells) and 200–250 Å by 26–40 Å in width (8–9 by 2–3 unit cells).

The electron micrograph in Fig. 4 shows that attapulgite also occurs both as individual laths and bundles of laths. A single lath appears to be nearly 1×10^4 Å in length and 50–100 Å in width.

X-ray diffraction results confirmed that the Vallecas sepiolite specimen is virtually pure, whereas the Attapulgas attapulgite contains some impurities (quartz and smectites).

Their adsorptive properties are related to the unusual surface structure, which is an ordered sequence of rectangular open channels whose size is the same as that of the inner holes. The surface areas, determined by the B.E.T. nitrogen adsorption method, are 220 m²/g for Vallecas sepiolite and 1.15 m²/g for Attapulgas attapulgite. The above investigation⁶ gave a calculated value of 252 m²/g for the external surface, whereas the theoretical value of the internal surface is 324 m²/g. Owing to the good agreement between the experimental B.E.T. value and that calculated for the external surface, it can be presumed that the internal holes are closed or at least unavailable even to small molecules. The electron micrograph examination of the Attapulgas



Fig. 2. Transmission electron micrograph of Vallecas sepiolite, Spain.

attapulgitic suggests a lower external surface area similar to the experimental value ($145 \text{ m}^2/\text{g}$).

The unusual surface configuration of these minerals indicates that a sieving effect similar to that with zeolites occurs, with weaker cation-dipole interactions

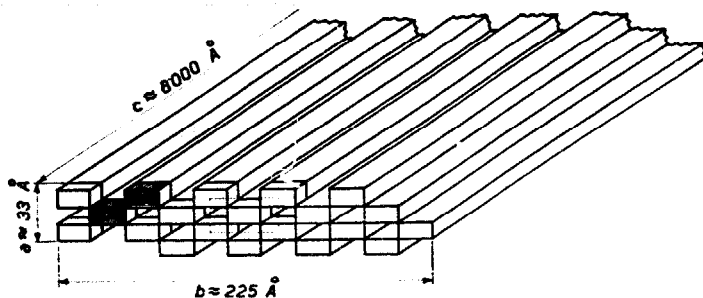


Fig. 3. Schematic representation of a single lath of Vallecas sepiolite.

owing to the lower cation-exchange capacity, which in this case is 3–15 mequiv. per 100 g and up to 300 mequiv. per 100 g in zeolites.

The separation described below shows the potential importance of sepiolite and attapulgite for use in gas–solid chromatography. The column packing was prepared from samples purified by decantation and made homo-ionic with sodium, the sieved fraction of 60–80 mesh being used. Columns were conditioned overnight at 200°. Owing to the great separating ability of hormites, short columns (0.8–1 m) were used.

EXPERIMENTAL AND DISCUSSION

Separation of inorganic gases

The open channels of hormites are not equally available to nitrogen, oxygen and carbon dioxide, even if Van der Waals' diameters of all these molecules are less than 3.7 Å, so that the results are governed by polarity rather than by molecular size.

Oxygen, nitrogen, carbon monoxide and methane are separated on sepiolite in that order at -78° ; carbon dioxide is eluted with a symmetrical peak at room temperature⁷. The separation on attapulgite is similar, but methane is eluted before carbon monoxide. The elution order on attapulgite is the same as that observed on molecular sieves 5Å containing up to 4% of water and on sepiolite it is the same as that reported for molecular sieves 5Å containing 9.5% of water⁸.

Figs. 5 and 6 show the chromatograms obtained in the separation of a mixture of such gases by a simple ballistic programme using an 80-cm column. The sharpest separation is produced on sepiolite. Such a separation could be of practical interest in analysis because of time savings and ease of operation, particularly with apparatus that operates at low temperatures. Molecular sieves, which are the most commonly used adsorbents used for the permanent gases, adsorb carbon dioxide irreversibly unless temperature programming up to 400° is used. Analyses of carbon dioxide–air mixtures are conventionally carried out with two columns joined in series, carbon dioxide being eluted on silica gel.

Separation of aliphatic hydrocarbons

The Van der Waals' cross-section of an aliphatic chain is larger than the openings in the hormites so that adsorption can occur only into open channels and on gutters.

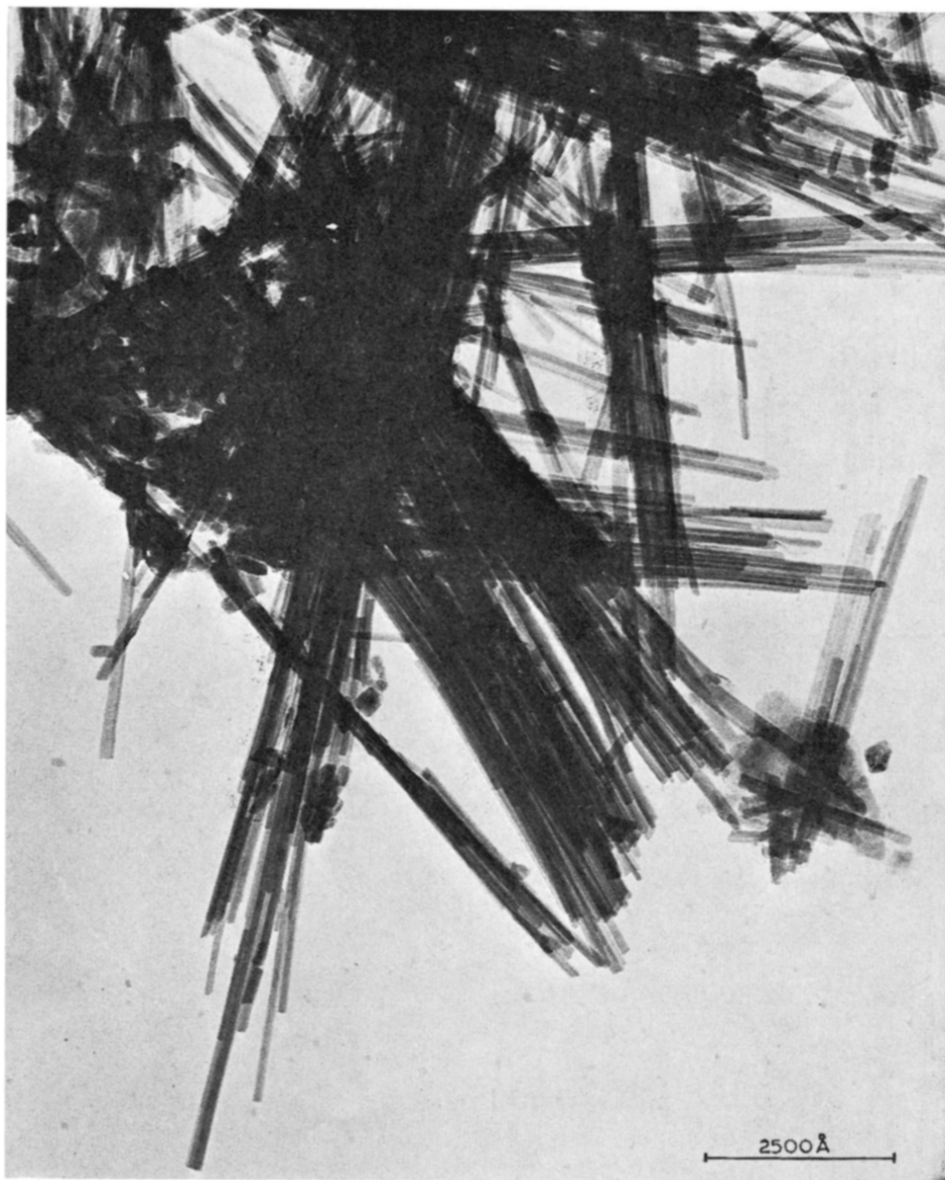


Fig. 4. Transmission electron micrograph of Attapulgus attapulgite, Georgia, U.S.A.

Table I summarizes retention values of some paraffins. In order to facilitate the comparison, in Fig. 7 are plotted the logarithms of the adjusted retention volumes at 155° versus the number of carbon atoms for 2,2-dimethylalkanes, 2-methylalkanes and *n*-alkanes that are eluted in that order.

On sepiolite, the separations are sharper than those obtained on attapulgite. Straight-chain alkanes are strongly retained on sepiolite and give very symmetrical peaks.

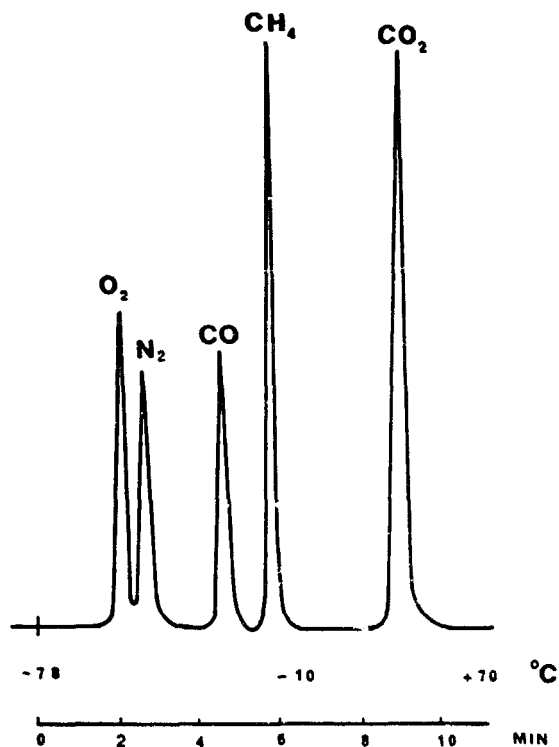


Fig. 5. Separation of oxygen, nitrogen, carbon monoxide, methane and carbon dioxide on Vallecas sepiolite. Column: 80×0.4 cm, 60-80 mesh; ballistic programme⁷.

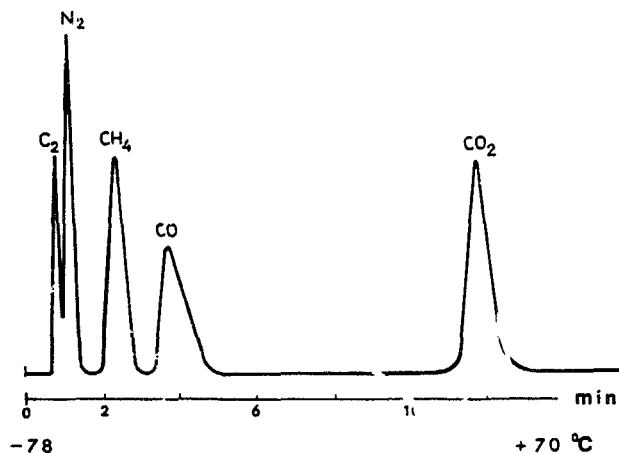


Fig. 6. Separation of oxygen, nitrogen, carbon monoxide, methane and carbon dioxide on Attapulgis attapulgit. Column: 80×0.4 cm, 60-80 mesh; ballistic programme.

The reduced selectivity of the Attapulgis attapulgit can be ascribed to the lower surface area and to the considerable amount of impurities present. The more satisfactory behaviour of sepiolite may be due to structural homogeneity, because

TABLE I

RETENTION VALUES OF VARIOUS ALKANES ON HORMITES

 Temperature 155°. I_r = retention index; V'_R = adjusted retention volume.

Hydrocarbon	Attapulgite		Sepiolite	
	V'_R	I_r	V'_R	I_r
2-Methylbutane	63.87	429	377.87	394
2,2-Dimethylpropane	41.33	390	37.73	217
2-Methylpentane	166	515	1,212.53	480
3-Methylpentane	157.73	511	629.87	432
2,3-Dimethylbutane	140.4	500	629.87	432
2,2-Dimethylbutane	100.93	470	94.48	283
2-Methylhexane	501.33	634	6,944	602
3-Methylhexane	490.4	612	2,754.7	540
3-Ethylpentane	316	574	881.9	457
2,3-Dimethylpentane	326.9	577	677.1	437
2,4-Dimethylpentane	300	569	510.1	416
2,2-Dimethylpentane	252.3	553	236	359
3,3-Dimethylpentane	236.3	547	220	354
2,4-Dimethylhexane			1,511.6	497
2,2-Dimethylhexane			629.9	432
2,2,4-Trimethylpentane	612.9	631	504	415
Propane	16		40.4	
<i>n</i> -Butane	48		409.33	
<i>n</i> -Pentane	124.4		1,574.7	
<i>n</i> -Hexane	408.3		6,456	
<i>n</i> -Heptane	1,271.5		25,194.6	

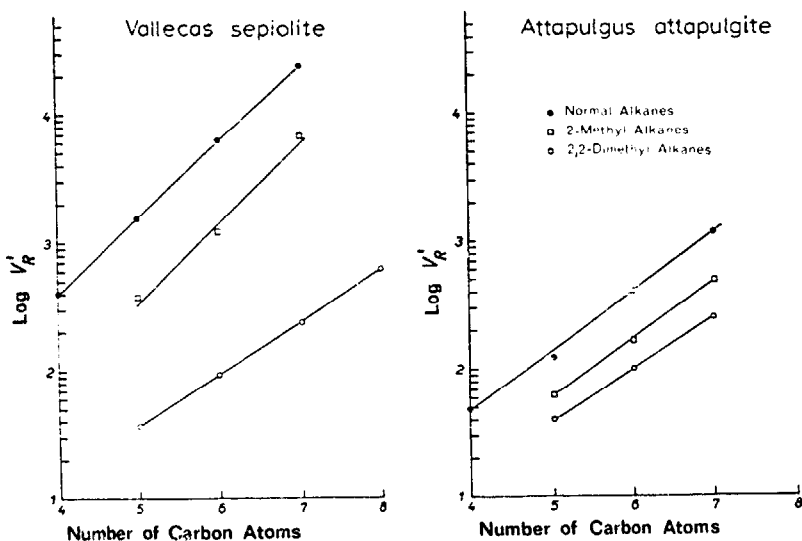


Fig. 7. Plots of log retention volume versus number of carbon atoms for normal alkanes (●), 2-methylalkanes (□) and 2,2-dimethylalkanes (○) on Vallecas sepiolite and Attapulgus attapulgite measured at 155°.

the tetrahedral positions are occupied only by magnesium atoms, while the attapulgite contains both magnesium and aluminium and the latter increases the acidity of the bound crystalline water.

BARRER *et al.*⁹ studied the sorption of normal and branched paraffins on attapulgite and sepiolite by a static technique. They found that the outgassing temperature is critical, so that above 88° for attapulgite and above 20° for sepiolite the selectivity between *n*-pentane and isopentane is reduced almost to zero. Their results do not agree with the present results mentioned above: selectivity in gas chromatography is not lost after outgassing at 200°; however, the comparison of the results from the two sets of experiments is not easy.

Corresponding straight-chain paraffins and olefins (*n*-pentane-pentene-1-*cis*-pentene-2-*trans*-pentene-2) are eluted almost together, regardless of the presence and position of the double bond and of the steric configuration.

Separation of alicyclic hydrocarbons

The results in Table II indicate that there is a complete separation of cycloal-

TABLE II

RETENTION VALUES OF VARIOUS CYCLOALKANES AND CYCLOALKENES ON HORMITES

Temperature = 155°. I_r = retention index; V'_R = adjusted retention volume.

Hydrocarbon	Attapulgite		Sepiolite		B.p. (°C)
	V'_R	I_r	V'_R	I_r	
Cyclopentane	60.5	424	534	420	49.26
Cyclohexane	127.7	492	644	434	80.74
Methylcyclopentane	137	498	989	466	71.81
Methylcyclohexane	337	579	1209.5	481	100.93
Cyclopentene	127	492	706.9	441	44.21
Cyclohexene	372.4	589	1231.2	482	82.98

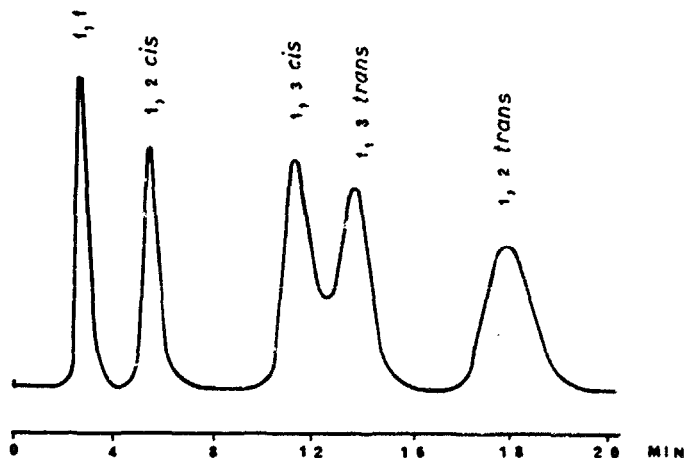


Fig. 8. Resolution of the dimethylcyclopentane isomers on Vallecas sepiolite. Columns: 100 X 0.4 cm, 60-80 mesh; temperature 170° (ref. 7).

kanes and the corresponding cycloalkenes, the latter being retained more strongly.

Even in the separation of cycloparaffins on sepiolite, steric effects prevail against the differences in boiling points. For instance, cyclopentane and cyclohexane are well separated, but their retention indices are similar; methylcyclopentane is eluted after cyclohexane, whose boiling point is higher (see Table II). With attapulgite, the influence of vapour pressure is more noticeable.

The unique properties of sepiolite are shown by the complete separation of all the dimethylcyclopentanes in Fig. 8: *trans* isomers are retained more strongly than *cis* isomers and the retention times are lower than those of normal paraffins.

Table III summarizes the relative volatilities of dimethylcyclopentanes and dimethylcyclohexanes. On attapulgite the values are close to unity, indicating that the influence of boiling points is enhanced, the elution order of configurational isomeric

TABLE III

RELATIVE VOLATILITIES OF CYCLOALKANES ON HORMITES

Hydrocarbon	Temperature (°C)	Relative volatility	
		Sepiolite	Attapulgite
Dimethylcyclopentanes			
1,2- <i>trans</i> /1,2- <i>cis</i>	176	4.7	0.91
1,3- <i>trans</i> /1,3- <i>cis</i>	176	1.2	0.97
Dimethylcyclohexanes			
1,2- <i>trans</i> /1,2- <i>cis</i>	195	3.9	1
1,3- <i>cis</i> /1,3- <i>trans</i>	195	3.9	1
1,4- <i>trans</i> /1,4- <i>cis</i>	195	8.7	1.62

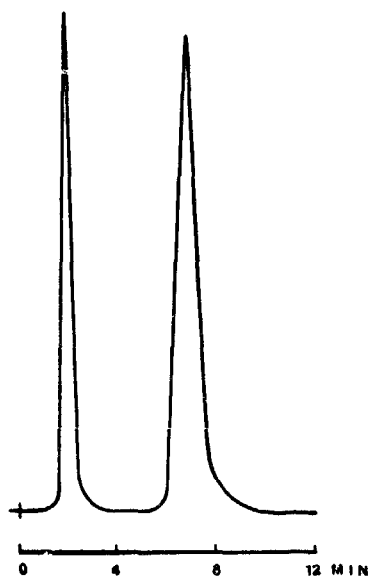


Fig. 9. Separation of *cis*- and *trans*-1,4-dimethylcyclohexanes on Vallecas sepiolite. Column: 80 × 0.4 cm, 60–80 mesh; temperature 195° (ref. 7). The *cis*-component is eluted first.

forms being reversed. The *cis* and *trans* isomers of the dimethylcyclohexanes are exceptionally well separated on sepiolite. Fig. 9 shows the separation of the 1,4-dimethylcyclohexanes on sepiolite.

Column efficiency

Vallecas sepiolite proved to be a good column packing for gas-solid chromatography, as the low values of HEPT (minimum 0.18 cm) indicate.

Fig. 10 shows plots of efficiency *versus* carrier gas velocity for *n*-pentane and isopentane. Identical results were obtained with a sample of sepiolite of different origin, from Mazaron, Spain. A lower efficiency was obtained with Attapulugus attapulugite, for which the minimum HETP value is 0.3 cm. With a specimen of Caceres attapulugite, very low retention values were obtained, so that its use in gas chromatography is impractical.

From these examples, it can be concluded that the morphology of the sample is greatly dependent on its origin. Likewise, a dependence of chromatographic behaviour on chemical composition has been reported for two different samples of polygorskite¹⁰.

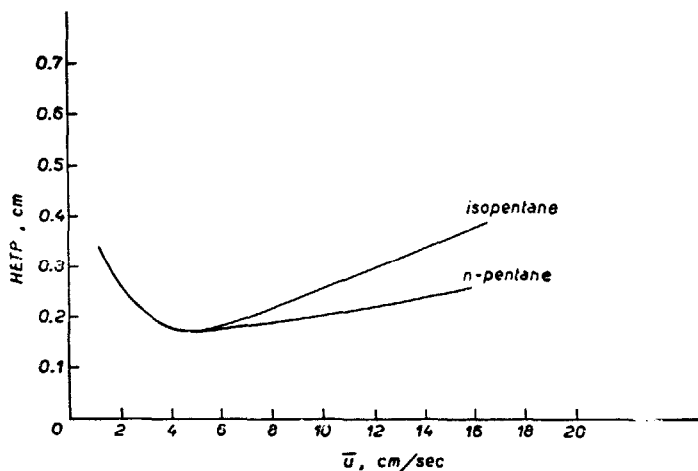


Fig. 10. Experimental plots of plate height (HETP) due to *n*-pentane and isopentane, against linear gas velocity (\bar{u}) in a column packed with Vallecas sepiolite at 155°.

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