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THE SO-CALLED CARBON MOLECULAR SIEVES IN GAS CHROMATOGRAPHY

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SUMMARY

By using model adsorbates with a convenient critical molecular diameter, no molecular sieve effect was observed with any of the microporous activated charcoal adsorbents. From the heats of adsorption measured for the individual adsorbates, it follows that all of the activated charcoals studied can be classified among the Type I adsorbents of the Kiselev and Yashin classification. The surfaces of such adsorbents carry neither ions nor active functional groups.

INTRODUCTION

Adsorbents that are characterized by pores of uniform size possess the ability to sorb selectively molecules of certain critical diameters. This molecular sieve effect is characteristic of the adsorbents of the zeolite type, for which the uniform size of the pores is determined by the crystalline structures of the individual adsorbents.

The microporous structure was also established with the so-called Saran activated charcoal, prepared by thermal decomposition of the polyvinylidene chloride-polyvinyl chloride copolymer. By measuring the adsorption of 24 substances with different sizes of the molecules, Racey and Thomas¹ found that as the critical diameter of the molecule increases, the time required to attain equilibrium during sorption also increases. The pores in the Saran form irregular cracks that have diameters between 5 and 10 Å.

Results obtained by using Saran carbon in gas-solid chromatography were published by Kaiser², who found that on the adsorbent carbon molecular sieve B, which has an average pore diameter of 12.4 Å, desorption of hydrocarbons with more than six carbon atoms does not take place until a temperature has been reached at which thermal decomposition begins. This precludes the possibility of checking the molecular sieve effect by using model adsorbates with a suitable effective diameter of the molecule.

Jüntgen *et al.*³ prepared a sorbent on the basis of black coal that was given the name "Molekularsiebkoks", possessing the ability to separate oxygen from nitrogen. They attributed this property to the existence of micropores formed as a result of cracking of the walls of large cavities. The adsorption isotherms of oxygen and

nitrogen corresponded to isotherms of Type I in the Brunauer classification, which are characteristic of microporous adsorbents. The mean diameter of the pores was not given.

It is therefore clear that the molecular sieve effect has not been proved with any of these microporous charcoals at low degrees of coverage by the adsorbate. In the present work, the existence of this effect in microporous activated charcoals was investigated in samples that had such average pore diameters as would permit us to use, as model sorbates, relatively small molecules for which it was possible to expect desorption to occur at temperatures at which thermal decomposition does not set in.

The samples used in this study were microporous activated charcoals with effective pore diameters of 4, 5 and 6 Å from a foreign source, and three types of microporous activated charcoal from Czechoslovakia.

EXPERIMENTAL

The experiments were conducted on a Chrom II laboratory gas chromatograph with a flame ionization detector. The retention time of nitrogen was measured on a simple instrument of our own construction with a thermal conductivity detector.

The microporous activated charcoals CMS 4, 5 and 6 were of foreign origin, the numbers indicating the diameters of the micropores (4, 5 and 6 Å, respectively). Three Czechoslovak charcoals, designated 63, 66 and 67, differing in their method of preparation, were also investigated.

Before packing the glass columns (70 cm × 4 mm I.D.), the samples were crushed, and their screening and de-dusting yielded a fraction with grain diameters ranging from 0.2 to 0.4 mm. The adsorbents were dried in a stream of helium at 220° before use.

The dependence of the retention volumes upon temperatures was monitored in the range 160–195° for C₁–C₃ hydrocarbons and 35–55° for nitrogen. Elution of the mixtures was carried out at 195°.

From the course of the dependence of the retention volumes on the linear velocity of the carrier gas, we determined the optimal velocity, in the proximity of which the retention volumes were independent of the carrier gas velocity, and for the carrier gas helium it was found to be 35 ml/min for all columns.

The following adsorbates were used: methane, ethane, ethene, propene, 2,2-dimethyl-propane, propane and nitrogen. The impurity content of about 0.01% was determined chromatographically. The retention volumes were calculated from the retention times determined from the positions of the mean of individual chromatographic curves on the time axis.

The heats of adsorption were calculated from the dependence of the corrected retention volumes on temperature⁴.

RESULTS AND DISCUSSION

The existence of the molecular sieve effect with individual adsorbents was investigated by means of the model adsorbates. The critical diameters of the selected molecules are listed in Table I. In Table II the corrected retention volumes of the C₂ and C₃ hydrocarbons are listed.

TABLE I
CRITICAL DIAMETERS OF MODEL ADSORBATE MOLECULES

Adsorbate	Critical diameter of molecule (\AA) ^s
CH ₄	4.0
C ₂ H ₄	4.25
C ₂ H ₆	4.44
C ₃ H ₆	5.0
C ₃ H ₈	4.89
C(CH ₃) ₄	6.88
N ₂	3.48

TABLE II
CORRECTED RETENTION VOLUMES (V_{cor}) OF C₂ AND C₃ HYDROCARBONS ON THE ACTIVATED CHARCOALS

Temperature, 195°; helium flow-rate, 35 ml/min; sample size, 2 μ l.

Adsorbent	V_{cor} (ml/g)			
	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆
CMS 4	4.39	5.05	19.57	26.18
CMS 5	14.70	11.37	88.88	95.54
CMS 6	17.51	12.73	123.94	107.20
63	0.67	1.07	3.22	1.38
66	0.71	1.10	3.31	1.44
67	0.63	1.02	3.16	1.31

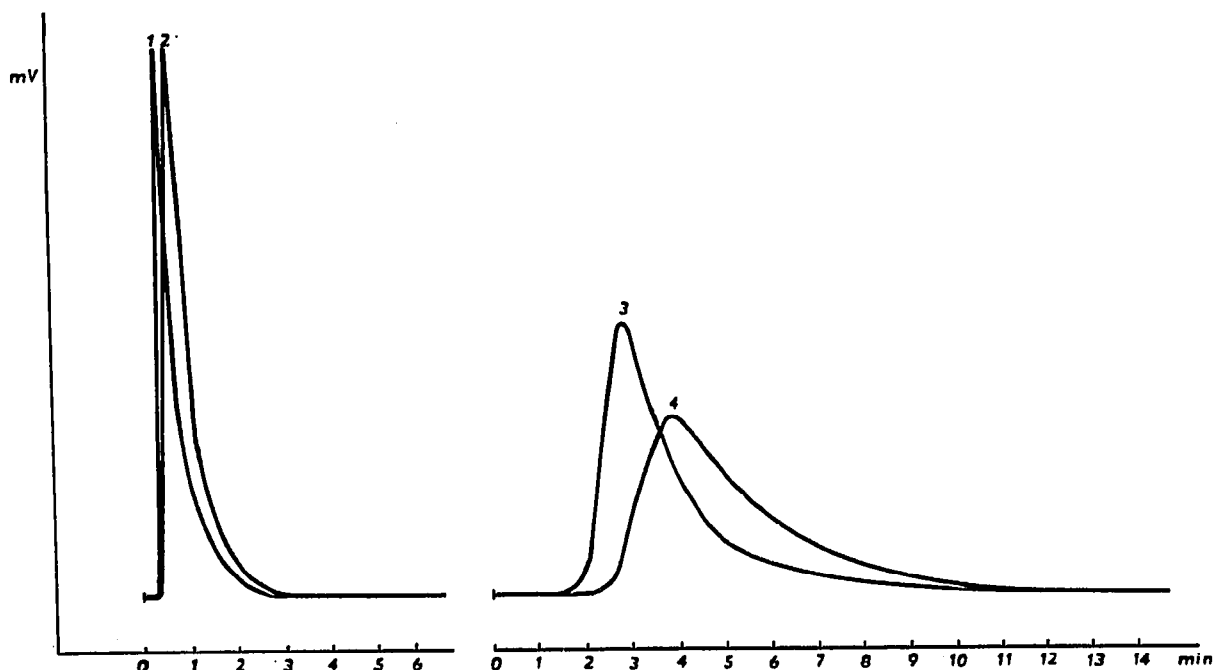


Fig. 1. Elution curves of C₂ and C₃ hydrocarbons on CMS 4. 1 = Ethane; 2 = ethene; 3 = propane; 4 = propene. Temperature: 195°. Helium flow rate: 50 ml/min. Adsorbent: carbon molecular sieve 4 \AA , particle size 0.2-0.4 mm. Column: 70 cm \times 4 mm I.D.

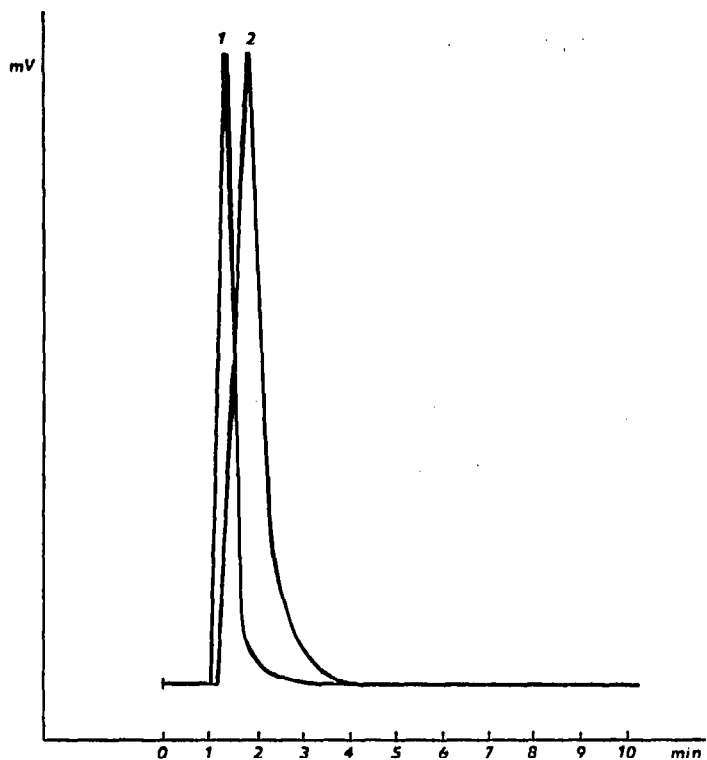


Fig. 2. Elution curves of C_2 hydrocarbons on CMS 5. 1 = Ethene; 2 = ethane. Conditions as in Fig. 1, using carbon molecular sieve 5 Å, particle size 0.2–0.4 mm.

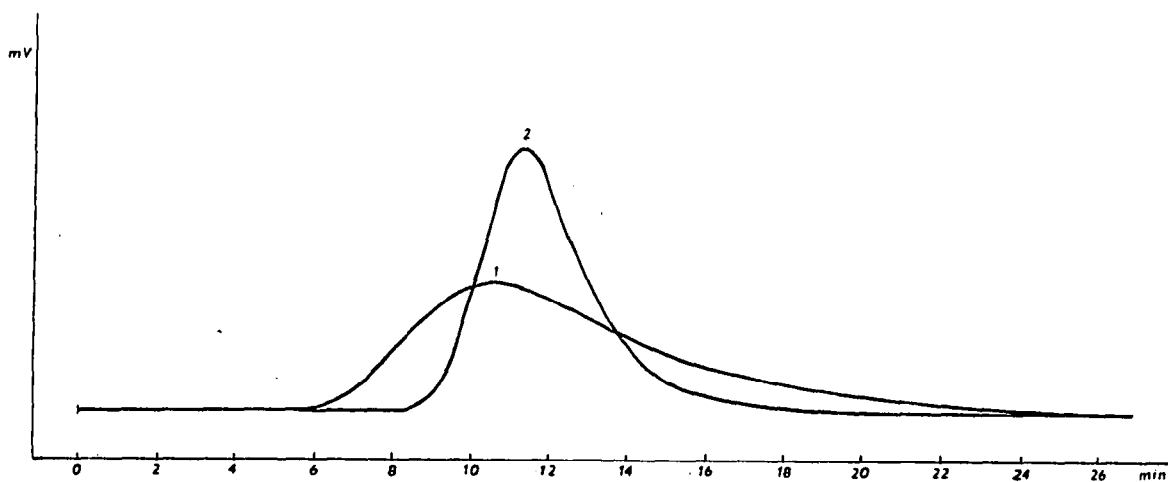


Fig. 3. Elution curves of C_3 hydrocarbons on CMS 5. 1 = Propane; 2 = propene. Conditions as in Fig. 1, using carbon molecular sieve 5 Å, particle size 0.2–0.4 mm.

Figs. 1-5 show the shapes of the chromatographic elution curves of the C_2 and C_3 hydrocarbons on CMS 4, 5 and 6 and 63. The elution curves of these adsorbates on adsorbents 66 and 67 are not given, as they do not differ significantly from the shapes on adsorbent 63.

It can be seen that on the CMS adsorbents, the retention volumes increase with increase in the effective pore diameter. However, there are also shifts between the

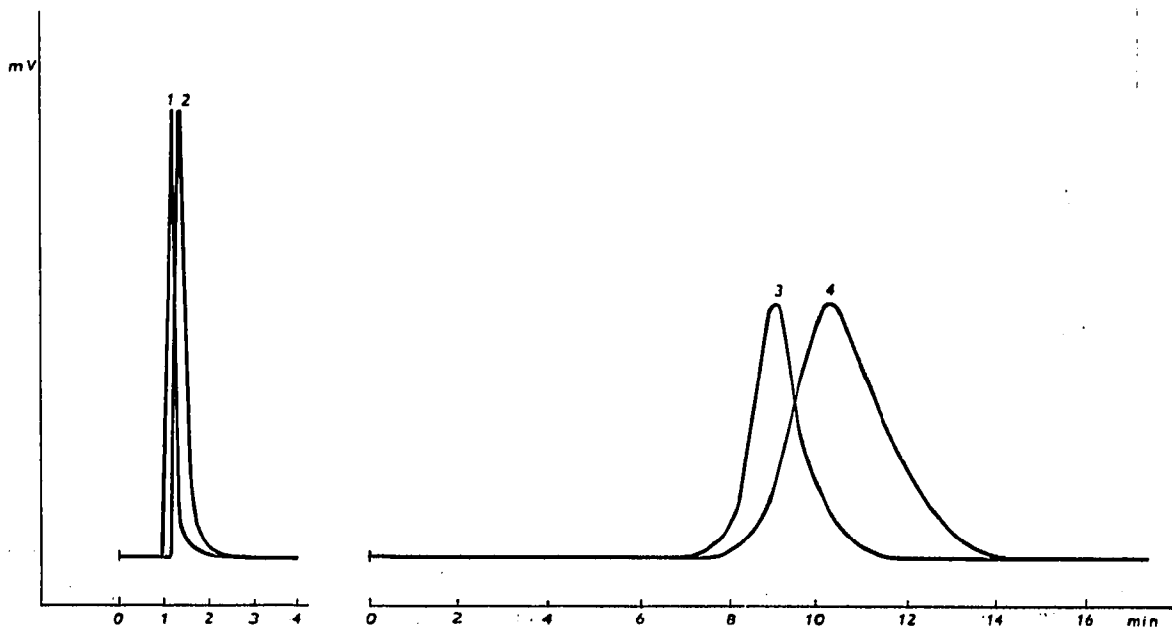


Fig. 4. Elution curves of C_2 and C_3 hydrocarbons on CMS 6. 1 = Ethene; 2 = ethane; 3 = propene; 4 = propane. Conditions as in Fig. 1, using carbon molecular sieve 6 Å, particle size 0.2-0.4 mm.

saturated and the unsaturated hydrocarbons, and changes in the shapes of the elution curves. The corrected retention volumes of the hydrocarbons on adsorbents 63, 66 and 67 were substantially lower and no changes in the sequences were found. The shifts in the sequences of retention volumes of saturated and unsaturated hydrocarbons on different adsorbents indicate that the application of Rohrschneider's constants for the characterization of the separation properties of these adsorbents is not satisfactory.

Heats of adsorption for the C_1 - C_3 hydrocarbons and nitrogen were calculated from the course of the dependence of $\log V_{cor}$ on the reciprocal of the absolute temperature, and are tabulated in Table III.

The course of the dependence of the heats of adsorption on the number of carbon atoms in a molecule for the C_1 - C_3 saturated and unsaturated hydrocarbons is illustrated in Figs. 6 and 7.

The values of the heats of adsorption of individual hydrocarbons are in good agreement with the values calculated by Habgood and Hanlan⁶ from the chromatographic retention data for microporous activated charcoals. From their results, it

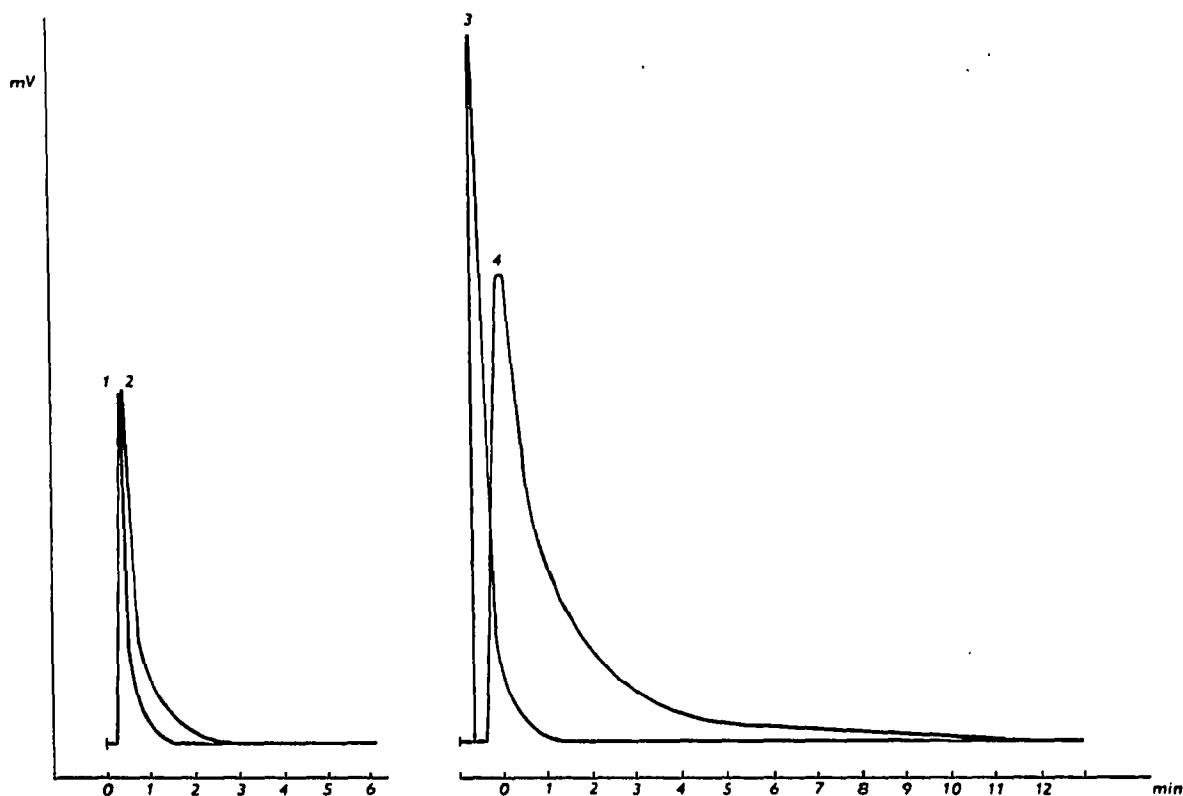


Fig. 5. Elution curves of C_2 and C_3 hydrocarbons on 63. 1 = Ethane; 2 = ethene; 3 = propane; 4 = propene. Conditions as in Fig. 1, using activated charcoal 63, particle size 0.2–0.4 mm.

follows that as a result of substantial increase of the pores owing to the activation of the adsorbent, the heats of adsorption for the initial coverage decrease.

The graphs of the dependence of the heats of adsorption on the number of carbon atoms in a hydrocarbon molecule are linear and parallel for the individual adsorbates investigated, for both saturated and unsaturated hydrocarbons. The linear

TABLE III

HEATS OF ADSORPTION OF C_1 – C_3 HYDROCARBONS AND NITROGEN ON CMS AND 63 ADSORBENTS

Adsorbent	Heat of adsorption (kcal/mole)					
	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	N_2
CMS 4	4.6	8.8	6.3	12.1	9.7	—
CMS 5	5.5	9.2	7.35	12.9	10.7	—
CMS 6	5.25	9.0	7.0	12.8	10.3	—
63	3.7	7.3	5.4	10.9	8.6	4.92
Barnebey– Cheney charcoal ⁶	5.3	8.0	7.7	11.9	10.6	—

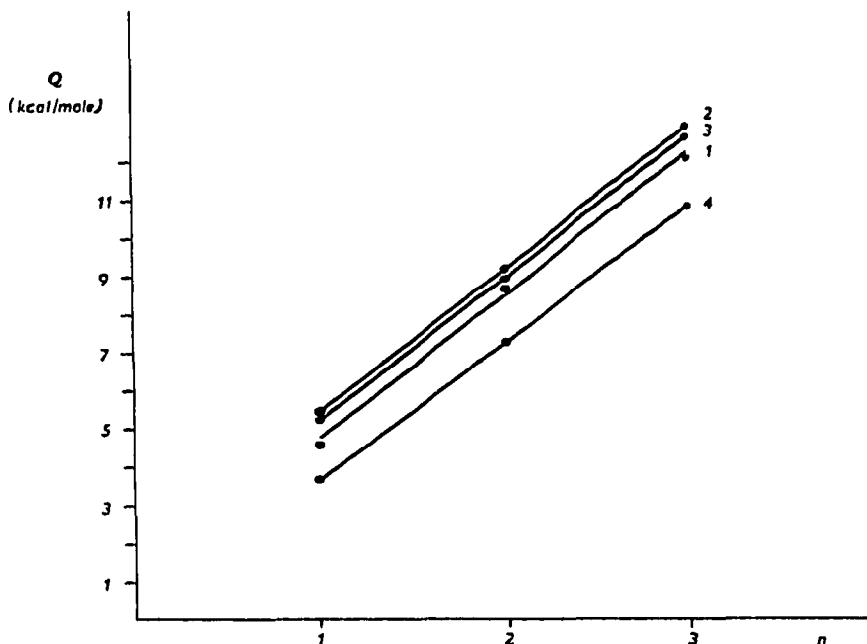


Fig. 6. Dependences of differential heats of adsorption, Q , obtained gas chromatographically, on the number of carbon atoms, n , in molecules for alkanes for adsorption on (1) CMS 4, (2) CMS 5, (3) CMS 6 and (4) 63.

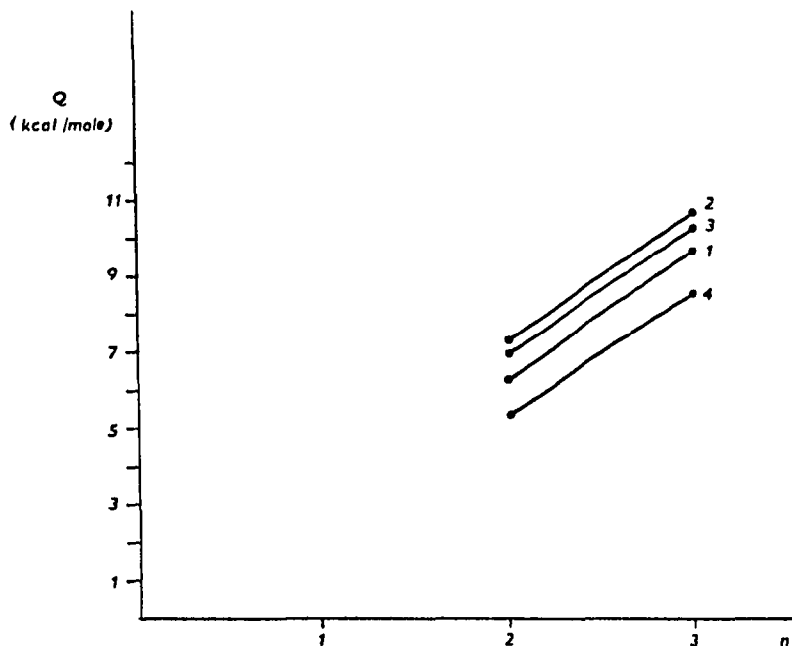


Fig. 7. Dependences of differential heats of adsorption, Q , obtained gas chromatographically, on the number of carbon atoms, n , in molecules for alkenes for adsorption on (1) CMS 4, (2) CMS 5, (3) CMS 6 and (4) 63.

increase in the heats of adsorption (the contribution of the CH_2 group being 3.6 kcal/mole) is characteristic of adsorbents of Type I of Kiselev and Yashin's classification⁷, and classes all the activated charcoals examined as non-specific adsorbents, the adsorption energy of which depends predominantly upon non-specific dispersion interactions. The heats of adsorption of unsaturated hydrocarbons are lower than those of the saturated hydrocarbons with equal numbers of carbon atoms in the molecule, which is in agreement with the lower values of the average polarizability of the molecules of unsaturated hydrocarbons. This result shows that there are no active centres on the surfaces of these adsorbents that are capable of specific interactions. The heat of adsorption of nitrogen of 4.9 kcal/mole is in good agreement with the calorimetric value of 4.7 kcal/mole for Saran charcoal⁸ at zero coverage.

The fact that all the microporous charcoals investigated demonstrated adsorption of all the hydrocarbons proves unambiguously that no molecular sieve effect was established under the GC conditions used. Assuming such an effect, the adsorption of propene with a critical molecular diameter of 5 Å on CMS 4 could not occur, because this effect would result in a substantially lower retention volume in comparison with the retention volume of ethene. Assuming that propene cannot enter the micropores, a substantial drop in the heat of adsorption would also have to occur, thereby disturbing the linearity of the course of dependences shown in Figs. 6 and 7.

The molecular sieve effect would also be bound to prevent sorption of 2,2-dimethylpropane, which has a critical molecular diameter of 6.88 Å, on all of the CMS charcoals. However, in fact, sorption of this hydrocarbon was so intense that desorption did not occur even at 300°.

The fact that no molecular sieve effect was established with the samples of microporous activated charcoals examined is closely related to their formation, when carbonization of polymers or other organic substances is not able to ensure complete uniformity of pore size, as is the case in the formation of the crystal lattice of zeolites. Conveniently chosen conditions of the reaction may, however, influence the microporous structure in such a manner that a certain substantial part of the micropores exhibit the smallest possible dispersion of the effective diameter. With charcoals that possess these properties, effects are then established that can be accounted for by diffusion phenomena related to the shape and diameter of the micropores.

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