

## SOME SORPTION PROPERTIES OF A NEW TYPE OF ACTIVE CARBON

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### SUMMARY

The sorption properties of a new type of active carbon, prepared by decomposition of polytetrafluoroethylene by lithium amalgam, were tested under chromatographic conditions with various types of adsorbates. It was found that aliphatic hydrocarbons penetrate into the carbon skeleton. The high heats of adsorption for these molecules are the result of very close contact between the adsorbent and adsorbate.

Polar substances exhibit a physical adsorption that can be partially suppressed by the reaction product (LiF crystals) present in the carbon skeleton. This adsorbent was classified as a type I adsorbent according to Kiselev's classification.

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### INTRODUCTION

Active carbon was one of the first adsorbents employed in gas adsorption chromatography. In addition to materials formed by the thermal decomposition of natural substances, chiefly cellulose, others have appeared, prepared under similar conditions from, for example, polyvinylidene chloride—the saran active charcoals<sup>3</sup>. While with active carbons of the first type the porosity is chiefly determined by meso- and macropores, mainly due to additional treatment, saran active charcoals have an extensively developed microporous structure. On this basis, some workers explained certain sorption properties of saran active charcoals by the molecular sieve effect<sup>2-4</sup>. Walker<sup>5</sup> tested the sorption properties using gas-solid chromatography technique. Carbosieve, produced by Supelco (Bellefonte, Pa., U.S.A.) for chromatographic purposes<sup>6</sup>, is also based on a saran charcoal. The specific surface area of saran charcoals is about  $1072 \text{ m}^2 \cdot \text{g}^{-1}$ , the mean radius of the micropores being 1.24 nm (ref. 5).

Kiselev and Yashin<sup>7</sup> studied the sorption properties of graphitized thermal carbon black and the use of its separation properties. They showed that dispersion forces are almost exclusively operative in the adsorption of any adsorbate. It has been stated that thermal carbon blacks are the most homogeneous adsorbents known<sup>8</sup>.

In this work, the sorption properties of a new type of active carbon (JADO), prepared by electrochemical reduction of polytetrafluoroethylene (PTFE) by lithium amalgam at a low temperature<sup>9</sup>, were studied by gas chromatography. The work was

intended to clarify the nature of the interactions of the adsorbent with various types of adsorbate.

## EXPERIMENTAL

The preparation of active carbon powder by the electrochemical reduction of PTFE by alkali metal amalgams was described in detail earlier<sup>9,10</sup>. As the gas chromatographic column packing, JADO 1017 was prepared with a particle size of 0.3 mm. The non-porous PTFE particles, irregular hexahedrons in shape, were degreased and dried *in vacuo* at 150°. The resulting PTFE crumbs were then contacted with lithium amalgam in a glass apparatus at 25°, *in vacuo* and with stirring. After 60 min, the PTFE particles were covered with a 3- $\mu\text{m}$  black layer of reaction products, a solid mixture of carbon and lithium fluoride. The treated PTFE crumbs were then separated from the partially depleted lithium amalgam and washed several times with boiling water that had been acidified with hydrochloric acid in order to extract the lithium fluoride from the carbon skeleton. The washed PTFE crumbs covered with a layer of the JADO carbon were dried first in air and then *in vacuo* at 150°. For comparison, a sample was also prepared containing 90% of the reaction product, lithium fluoride (JADO 1051). The fully extracted sample (without lithium fluoride) was designated JADO 1053.

The experiments were carried out on a CHROM 4 laboratory chromatograph using a thermal conductivity detector.

The retention volumes were measured for each substance over a temperature range of 80° in 7° steps. The temperature intervals were selected according to the nature of the individual adsorbates. The flow-rate of the helium carrier gas was 30–40  $\text{cm}^3 \cdot \text{min}^{-1}$ . With symmetrical elution curves, the retention volumes were calculated from the average peak maximum times measured with an accuracy of  $\pm 0.2$  sec, obtained as the mean of the retention times measured in quadruplicate at each temperature. The elution curves for polar substances were not symmetrical at lower temperatures and therefore the retention volumes for these substances were determined not from the maxima but from the first statistical moment of the elution curve. All experiments were carried out on the same column (0.58 m  $\times$  3 mm I.D.).

The heats of adsorption were computed from the dependence of the corrected retention volumes ( $V_{\text{corr}}$ ) on the reciprocal temperature<sup>11</sup> using a simple program.

The following adsorbates were used: methane, ethane, propane, ethene, propene, water, methanol, ethanol and benzene.

## RESULTS AND DISCUSSION

For the purpose of testing the sorption properties of JADO carbon, the heats of adsorption ( $\Delta H$ ) were calculated from the chromatographic data for the JADO 1053 sample (without lithium fluoride) and even for JADO 1051 (90% lithium fluoride). In addition to the adsorbates exhibiting only non-specific interactions (saturated hydrocarbons), adsorbates capable of specific interactions due to  $\pi$ -electron bonds (ethene, propene) and hydroxyl group (water, alcohols) were used. The calculated  $\Delta H$  values are given in Tables I and II respectively and data for other types of adsorbates are given for comparison.

TABLE I  
HEATS OF ADSORPTION FOR HYDROCARBONS ( $\text{kJ} \cdot \text{mole}^{-1}$ )

Adsorbate	Adsorbent			
	JADO 1053	JADO 1051	Graphitized thermal carbon black <sup>12</sup>	NaX zeolite <sup>13</sup>
CH <sub>4</sub>	24.3 ± 0.5	23.3 ± 0.6	11.3	18.8
C <sub>2</sub> H <sub>6</sub>	34.6 ± 1.0	33.2 ± 0.8	18.0	25.9
C <sub>3</sub> H <sub>8</sub>	45.0 ± 0.8	45.7 ± 0.8	24.7	33.0
C <sub>2</sub> H <sub>4</sub>	33.1 ± 1.1	32.0 ± 1.5	16.7	38.5
C <sub>3</sub> H <sub>6</sub>	44.9 ± 0.7	45.6 ± 0.8	23.4	50.2

TABLE II  
HEATS OF ADSORPTION FOR WATER, METHANOL, ETHANOL AND BENZENE ( $\text{kJ} \cdot \text{mole}^{-1}$ )

Adsorbate	Adsorbent				
	JADO 1053	JADO 1051	Graphitized thermal carbon black <sup>14</sup>	Activated charcoal <sup>15</sup>	Heat of condensation
H <sub>2</sub> O	51.5 ± 2.2	47.3 ± 4.3	—	46.9	41.4
CH <sub>3</sub> OH	60.3 ± 2.1	47.7 ± 3.7	42.7	54.8	35.1
C <sub>2</sub> H <sub>5</sub> OH	65.8 ± 1.9	56.1 ± 4.5	50.6	62.8	38.9
C <sub>6</sub> H <sub>6</sub>	53.1 ± 2.3	49.9 ± 3.1	45.2	61.5	30.8

#### Interaction with hydrocarbons

The following conclusions can be drawn from the values in Table I.

(i) The heats of adsorption for saturated hydrocarbons are about 1 kJ higher than those for the corresponding unsaturated hydrocarbons. The absence of active sites capable of specific interaction with  $\pi$ -electron bonds (see  $\Delta H$  on NaX zeolite) confirms the energetic homogeneity of this adsorbent. The  $\Delta H$  values for both types of hydrocarbons on JADO carbon increase linearly with increasing number of carbon atoms in a molecule, the increment per CH<sub>2</sub> group being about 10 kJ.

(ii) The differences in  $\Delta H$  values for extracted and unextracted JADO carbon do not exceed the range of experimental errors. The presence of lithium fluoride in the carbon skeleton does not lead to any steric hindrance for the hydrocarbon molecules, limiting contact with the adsorbent. Neither the shapes of the elution curves (see Fig. 1) nor the values of the retention volumes (see Fig. 2) exhibit any changes of a diffusional character.

(iii)  $\Delta H$  values on JADO carbon for the hydrocarbons considered are about double those on the even surface of graphitized carbon black, and are close to the values for microporous saran charcoal with a pore diameter commensurate with the effective molecular diameter of the adsorbate<sup>16</sup>.

#### Interaction with water, methanol and ethanol

The results in Table II can be summarized as follows.

(i) The  $\Delta H$  values are systematically higher in comparison with the values for another type of charcoal (differences for water  $4.6 \pm 2.2 \text{ kJ} \cdot \text{mole}^{-1}$ , for methanol

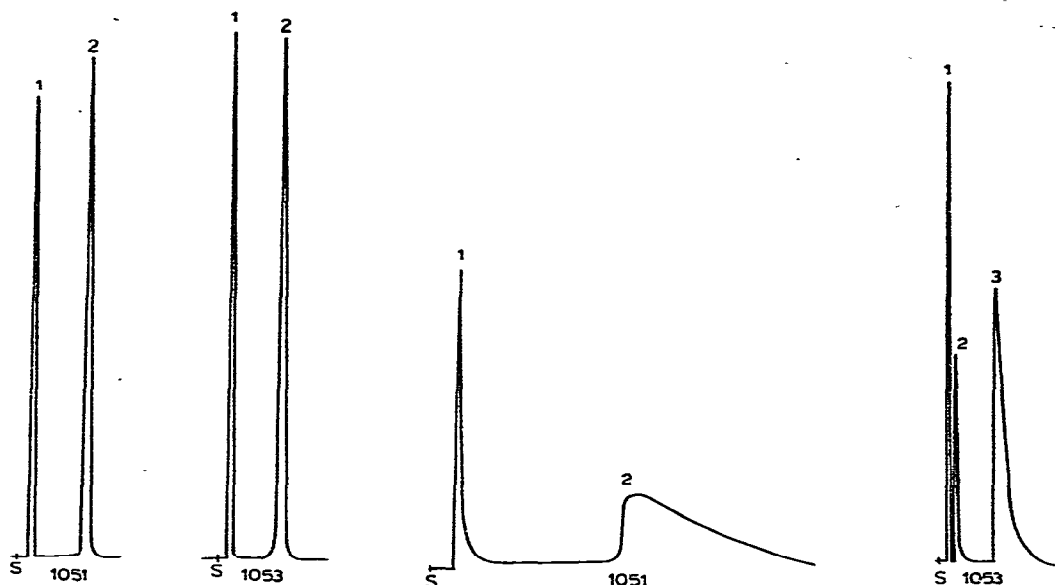


Fig. 1. Elution curves for ethane and propane on JADO 1053 (LiF extracted) and on JADO 1051 (LiF unextracted). Column, 0.58 m long, I.D. 3 mm; helium flow-rate,  $40 \text{ cm}^3 \cdot \text{min}^{-1}$ ; sample size,  $12 \mu\text{l}$ ; temperature,  $97^\circ$ . Retention volumes on JADO 1051: 1, ethane  $13.1 \text{ cm}^3$ ; 2, propane  $83.0 \text{ cm}^3$ . Retention volumes on JADO 1053: 1, ethane  $12.2 \text{ cm}^3$ ; 2, propane  $78.4 \text{ cm}^3$ .

Fig. 2. Elution curves for water and alcohols on JADO 1053 (LiF extracted) and on JADO 1051 (LiF unextracted). Column, 0.58 m long, I.D. 3 mm; helium flow-rate,  $40 \text{ cm}^3 \cdot \text{min}^{-1}$ ; sample size,  $0.17 \mu\text{l}$  on JADO 1053 and  $0.5 \mu\text{l}$  on JADO 1051; temperature,  $191^\circ$ . Retention volumes on JADO 1051: 1, water  $25.3 \text{ cm}^3$ ; 2, ethanol  $175.1 \text{ cm}^3$ . Retention volumes on JADO 1053: 1, water  $8.6 \text{ cm}^3$ ; 2, methanol  $17.8 \text{ cm}^3$ ; 3, ethanol  $46.1 \text{ cm}^3$ .

$5.5 \pm 2.1 \text{ kJ} \cdot \text{mole}^{-1}$  and for ethanol  $3.0 \pm 1.9 \text{ kJ} \cdot \text{mole}^{-1}$ ). These differences are not so important from the point of view of specific interactions.

(ii) The influence of lithium fluoride present in the JADO 1051 sample, causing a decrease in the  $\Delta H$  values instead of increasing them owing to the presence of ionic crystals, was unexpected. The extent to which this influence is suppressed by the fine dispersion of lithium fluoride crystals [by small-angle scattering of X-rays, the determined average length of the edge of the lithium fluoride cubic crystal is  $3.29 \text{ nm}$  (ref. 17)] and by the decrease in the effective area of the surface cannot be stated on the basis of the above experiments. The shapes of elution curves for polar compounds (see Fig. 3), in a similar manner to the values of the retention volumes (see Fig. 2), indicate the remarkable influence of lithium fluoride crystals on the rate of diffusion into the cavities of the carbon skeleton. The presence of lithium fluoride in the cavities leads to pronounced steric hindrance for these adsorbates. The heats of adsorption on such modified JADO carbon (JADO 1051) approach the values measured on the even surface of graphitized carbon black.

#### *Relationship between the structure and sorption properties of JADO carbon*

As follows from our previous work<sup>9</sup>, JADO carbon exhibits a highly developed porous structure. The specific surface area determined by the BET method is  $2600 \text{ m}^2$ .

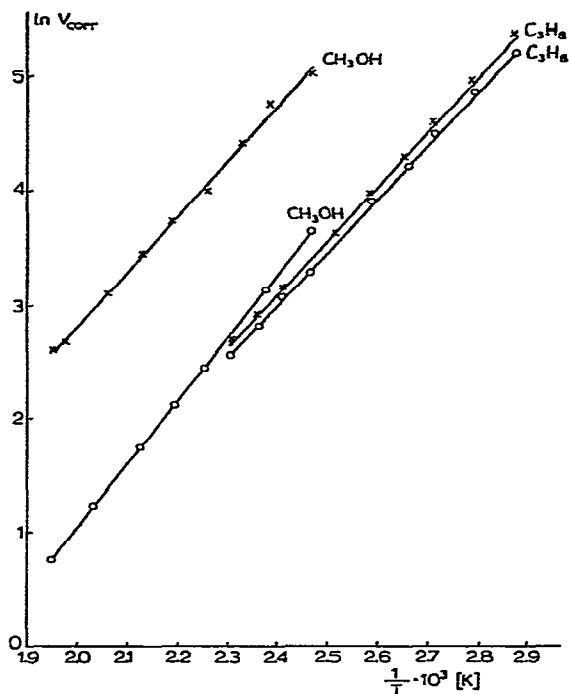


Fig. 3. Dependence of  $\ln V_{\text{corr}}$  on reciprocal temperature for propane and methanol on JADO 1051 ( $\times$ ) and JADO 1053 carbon ( $\circ$ ).

$\text{g}^{-1}$ , which represents a sorption capacity of 1.25 g of argon per gram of JADO carbon. These values agree with our knowledge of the structure acquired from electron microscopic and small-angle X-ray scattering data<sup>17</sup>. It was found that the structure of the JADO carbon is amorphous.

The high specific surface area and the unique cavity diameters are given by the structure, which can be illustrated schematically as shown in Fig. 4. Carbon fibres join the nodules of  $1.1 \pm 0.35$  nm in diameter. A "bead" carbon structure is created, the local orientation of the carbon chains being pre-terminated by the primary structure of PTFE. The distance between the centres of neighbouring nodules in the chain is  $1.9 \pm 0.3$  nm and the diameter of the cavities in the carbon skeleton is  $2.3 \pm 0.3$  nm. The lithium fluoride crystals are situated in these cavities and their formation during the electrochemical reaction is manifested by a 20% expansion in the primary PTFE volume. The cavities differ from the pores in a rigid matrix, their diameter being of the same order as the wall thickness of the carbon skeleton. The value of the calculated cavity diameter was also given indirectly by the adsorption measurements<sup>9</sup>.

We conclude that there are two mechanisms of interaction on JADO carbon, depending on the nature of the adsorbate. Aliphatic hydrocarbons penetrate the carbon skeleton, this interaction being similar to the solvation observed, for example, in interaction of benzene with Porapak<sup>18</sup>. The presence of lithium fluoride crystals in the cavities does not affect this interaction. High  $\Delta H$  values for hydrocarbons are caused by the very close contact between the adsorbent and adsorbate, similar to that which takes place during the adsorption in micropores.

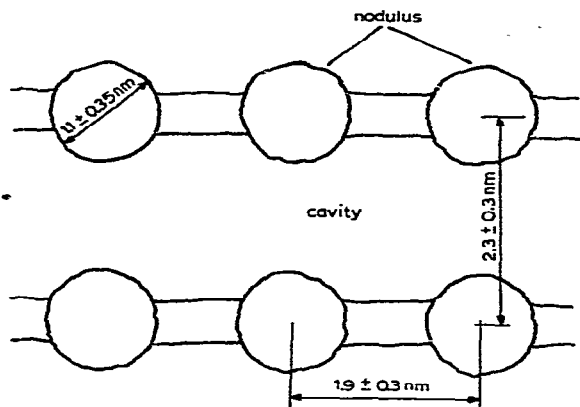


Fig. 4. Scheme of structural elements of JADO carbon.

Alcohols and water are adsorbed in the cavities of the carbon skeleton; the  $\Delta H$  values for these adsorbates indicate that only physical adsorption without a pronounced contribution of specific interactions occurs. For these adsorbates, the accessibility of the cavities is reduced by the presence of lithium fluoride crystals. A similar effect was also observed for benzene.

## CONCLUSIONS

(i) The JADO carbon does not have a significantly heterogeneous surface. It can be classified as a type I adsorbent according to Kiselev's classification.

(ii) The molecules of aliphatic hydrocarbons penetrate the carbon skeleton, the nature of the interaction being similar to solvation.

(iii) The molecules of polar compounds are adsorbed in the cavities of the carbon skeleton.

(iv) The presence of lithium fluoride crystals in cavities does not cause any increase in the specificity of the interaction for any of the adsorbates tested. It acts only to produce steric hindrance for the molecules that diffuse into the cavities.

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