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ADSORPTION OF POLAR SOLUTES ON TO SOLIDS WITH MIXED POLAR, NON-POLAR SURFACES

Introductory Remarks

In recent years, there has been an increasing interest within the field of chemical engineering and powder technology in the fuller investigation of the surface properties of various powders. Apart from the development of a variety of other adsorption techniques which are being used in this field, calorimetric techniques are being employed more and more, since they facilitate the investigation of many interesting phenomena, such as immersion of solid substances and the adsorption of solid-liquid interface; since the latter is accompanied by heat evolution, the measurement of this heat evolution makes it possible to determine the stability of the adsorption layers, their structure and thickness, and in addition helps to resolve many other problems in the fields of thermodynamics and kinetics.

Microcalorimetry is becoming particularly significant in studying solids with small specific surfaces, since it enables accurate measuring of heat adsorption less than 10^{-3} cal. which in turn can lead to new discoveries about the powders surfaces. The applicability of calorimetry is thus large and it contributes considerably to a better understanding of the mechanisms of pigmentation, lubrication, photography, metallurgy etc.

In 1958, Prof. A. J. Groszek working in London¹⁾ developed a new apparatus called the Flow Microcalorimeter. It has been used for investigation of the phenomena of adsorption in a *dynamic system* as opposed to earlier microcalorimetric investigations which had dealt with a *static systems* and static microcalorimetry²⁾. So far, the Flow Microcalorimeter has been employed mainly in detecting the specific surface areas of adsorbents with a pure polar nature (such as TiO_2) and of some others with a predominantly non polar nature such as graphites; most often, the technique was directed at measuring the following parameters: integral energy of adsorption, free energy and entropy of adsorption, and the area occupied per solute molecule. Also there have been attempts for determining the orientation of the adsorbed molecules at the interface etc.

This work deals with the determination of the polar sites of two types of Carbon Black, a substance distinguished by its mixed polar and non-polar sites. It is connected with a more extensive research-project on the properties of the powders which has been carried out at the School of Powder Technology of the University of Bradford.*)

Description of the Apparatus

A schematical model of the Flow Microcalorimeter is given in Fig. 1. The instrument contains a metal block (1) the inside walls of which are cylindrical and where a Teflon calorimeter cell is located (2). The cell's upper

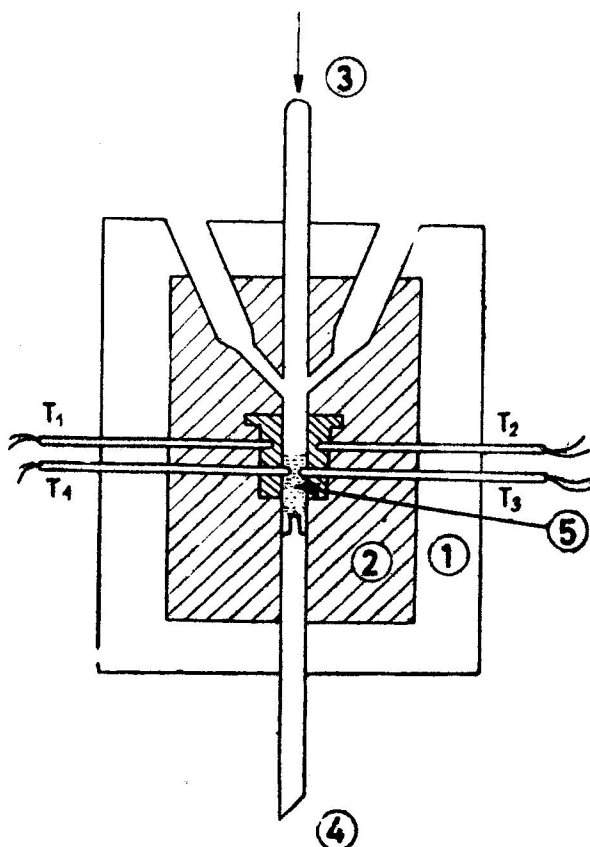


Fig. 1. Schematic diagram of the flow microcalorimeter

*) The work is based upon experiments conducted during my stay in Bradford University in 1972/73. These experiments were under the supervision of Dr. T. Allen for whose support and help I am most grateful,

side is connected to an inlet tube (3) and the lower side to an outlet tube (4). There is a 200 mesh stainless steel gauze fixed at the beginning of the outlet tube, where the powder is packed (5) and this forms what is called „a bed of adsorbents”.

The elements marked in Fig. 1 as T_1 , T_2 , T_3 , T_4 — represent thermistors, giving an indication of temperature changes. The first two are for reference and the next two for measurement. In the course of an experiment, the carrier liquid is allowed to flow down steadily through the bed of the powder, until a balance in the system is achieved. This implies an entire immersion of the powder and establishing of equal temperature within the system. This procedure lasts around 30 min. and the balance-stage is registered on the recording chart.

Then the carrier liquid is replaced by solution which causes adsorption of the solute into the powder, and in turn — a heat is generated. The temperature change which occurs is measured by the thermistors which are connected (through a Wheatstone bridge network) to a potentiometric recorder. As a result of the exothermic reaction of adsorption, a positive pulse is recorded on the instrument, while endothermic reaction-desorption, produces a negative pulse. The area under the peaks is proportional to the quantity of change in the heat. The constant flow of liquids allowed, is controlled by a small apparatus designed to pump up a given quantity of liquid in a given period of time.

The instrument is calibrated by known quantities of heat injected through a small coil (fixed to an inlet tube designed particularly for calibration) above which the powder under investigation is placed. The injection of known quantities of heat generates impulses proportional in magnitude.

Theory

The theoretical consideration for determining parameters relating to the adsorption occurring at solid-liquid interface, relies on the well-known Langmuir equation³⁾ for the adsorption of gas molecules onto solid surface:

$$\frac{P}{V} = \frac{1}{V_{mb}} + \frac{P}{V_m}$$

where V symbolises the volume of gas adsorbed at pressure P , V_m is the volume of gas adsorbed at monolayer coverage, and b is a constant. The characteristic Langmuir adsorption isotherms are obtained by a graphical presentation of the volume of gas adsorbed from a given quantity of adsorbent, and of the gas pressure as well.

Several studies so far have dealt with adsorption from solutions. Among the earlier and particularly significant were those by De Boer⁴⁾. This author demonstrated that the Langmuir's type of isotherms can be obtained when some long chain organic polar molecules are adsorbed on polar su-

faces. Thus, if the gas pressure is replaced by concentration of solute (C) and the volume by amount of solute adsorbed (X), the following relationship comes out:

$$\frac{C}{X} = \frac{1}{XmK} + \frac{C}{Xm}$$

To apply the Langmuir equation, the basic condition is that the energy should not be dependent on the presence of other adsorbed molecules. When experiments are carried out on a Flow Microcalorimeter-at the area of contact of solid and carrier liquid what is called a solid/liquid interface is formed. Then, adding up a solution, the solute molecules replace carrier liquid molecules on the interface. The heat generating from this replacement was found to be proportional to the concentration of the adsorbate in the solution. Therefore, and because under conditions of equilibrium the molecules of the adsorbate leave the surface at the same rate as they are being adsorbed, it made it possible for the Langmuir equation to be modified; Thus, a correlation is obtained between the heat generated at the monolayer coverage (q_m) and the heat generated (q) when the concentration of the solution is (c)

$$\frac{c}{q} = \frac{1}{K_1 q_m} + \frac{c}{q_m}; K_1 \text{ is a constant}$$

A plot of c/q versus c , from the above correlation, yields a straight line whose slope is $1/q_m$. If the tangents of the line's slope is measured up, the value of q_m is obtained. This enables the determination of specific surface area of a given solid (S_w), according to the equation: $S_w = Kq_m$.

The constant of proportionality (K) is dependent on enthalpy change per unit area in the process of replacement of the solvent from the adsorbent by solute molecules. This constant includes the cross-sectional area occupied by solute molecules on some particular adsorbents. Experimenting on the Flow Microcalorimeter and applying the above given equation, the surface area has been determined for many polar adsorbents^(5,6,7,8). In this way, the area had been measured of both polar and non-polar sites of graphites^(9,10).

Experimental

The experimental work was directed at an investigation of several types of carbons, with particular stress upon two of them: CARBON BLACK (ELF4) and CARBON BLACK(NHO67). Two techniques were applied in the course: mainly the technique using the Flow Microcalorimeter but also that of gas adsorption (B.E.T. method⁽¹¹⁾). It can be seen from the literature that specific surface area of carbons was investigated so far most frequently by B.E.T. method; here, as it is known, occurs the most complete adsorption of nitrogen molecules onto many adsorbents, at a temperature of condensation.

Also, of the two common and most important techniques of operation with Flow Microcalorimeter — the injection and the successive-saturation, the latter was used in these experiments. As it has been mentioned earlier, a solution, e.g. several solutions simultaneously and with increasing and exactly known concentrations, are added to the adsorbent which had been thoroughly moistened. The process of adsorption occurring in this stage lasts until the adsorbent is entirely saturated, with adsorbate. Therefore, the further adding of solutions of higher concentrations does not produce heat-effects. On the other hand, the gradual saturation of the adsorbent is reflected in drawing up pulses on the recorder's chart and these gradually decrease from the first to the last.

In measuring the area of the pulses, the technique of the weighing of carefully cut peak-areas was applied, since it is more accurate method than the planimetric.

One of the first problems which occurred in the course of examination of carbon black (ELF4) was the flow of the liquid through it. That is to say that the flow of liquid through the powder bed was not constant, but there were occasional interruptions. These were caused by the liquid collected in the cell of the instrument, which usually invalidates the experiment. It could have been noticed that such a different behaviour was because of accidental detention of an amount of liquid in the outlet tube, which before filling the cell by powder was filled by solution. It appeared that for operation with such a fine powder, there should be a detained column of liquid in the outlet tube ensuring the normal flow through the bed. In order to achieve this a glass-tube was placed inside the outlet tube, and thus the latter was made a capillary in which the detention of the liquid is a normal phenomenon. In such a way, the flow was ensured in the system, and its maximum was found to be 0,05 ml/min, which was used to carry out the experiment.

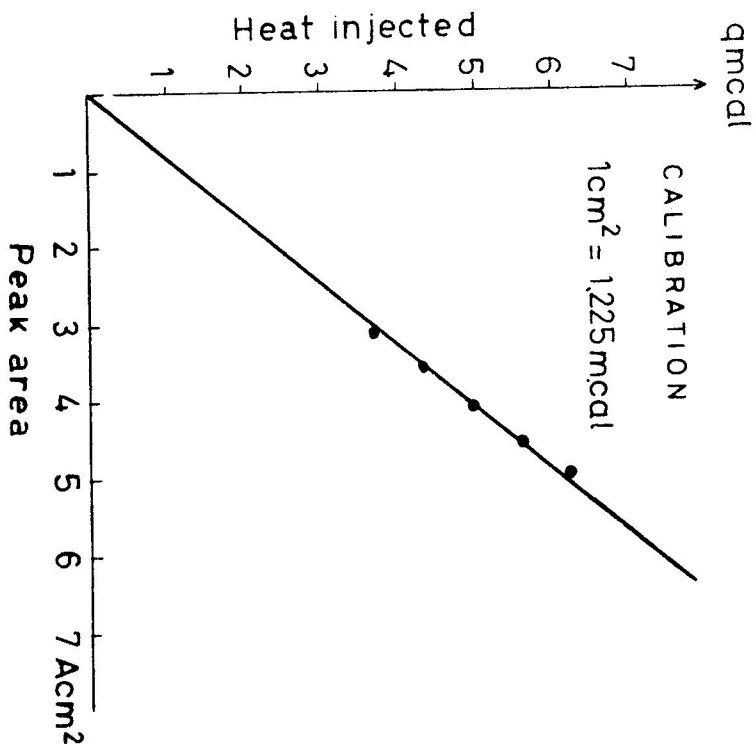
For all the experiments an amount of 50 mg of the powder has been used. This was because that amount, compared with other amounts which had been tested, proved to produce most favourable results, which is to say that it has filled the calorimeter cell most appropriate. The powder has been dried at 130°C. Experiments have been carried out with the adsorbent degassed earlier, but the results here did not differ from those of experiments using powder not degassed previously. This indicated that Carbon Black (ELF4) was not porous.

The non-polar substance n-heptane was used as a carrier liquid. It was purified and dried by allowing it through two columns of silica-gel. The solute was the first time the alcohol n-butanol, and the other time n-hexanol, both of which are polar substances. These were used for preparation of solutions in n-heptane at concentrations of 0,5; 1; 2; 3; 5; 5 and 10 g/l, which for the purpose of calculation were transferred into mol-fractions.

In order to calculate the results obtained by reaction of adsorption of alcohols onto the carbon, firstly calibration had to be made. For this purpose, the outlet tube with a heating coil was placed in the microcalorimeter cell, and the coil was used for allowing current of exactly known power, from outside. The results of this procedure are presented in the following Table—1 and Graph — 1:

TABLE — 1

Time — sec.	A cm ²	Q m. cal.
90	3.1477	3.726
105	3.5916	4.347
120	4.1162	6.968
135	4.6005	5.589
150	4.9838	6.210



Graph 1. Calibration graph for flow microcalorimeter

The time indicated in table — 1 is the time of injecting current into the system; A-represents areas drawn on the recorder; Q-symbolises the appropriate energy in milicalories, to be calculated. The ratio of A and Q on the Graph determines a straight line which serves to find out the energy, i.e. heat per unit area. This is in fact a calibration constant which in our case amounts to 1.225 m. cal/cm². The constant enables, each area drawn on the recorder in the course of adsorption, to be transferred into energy.

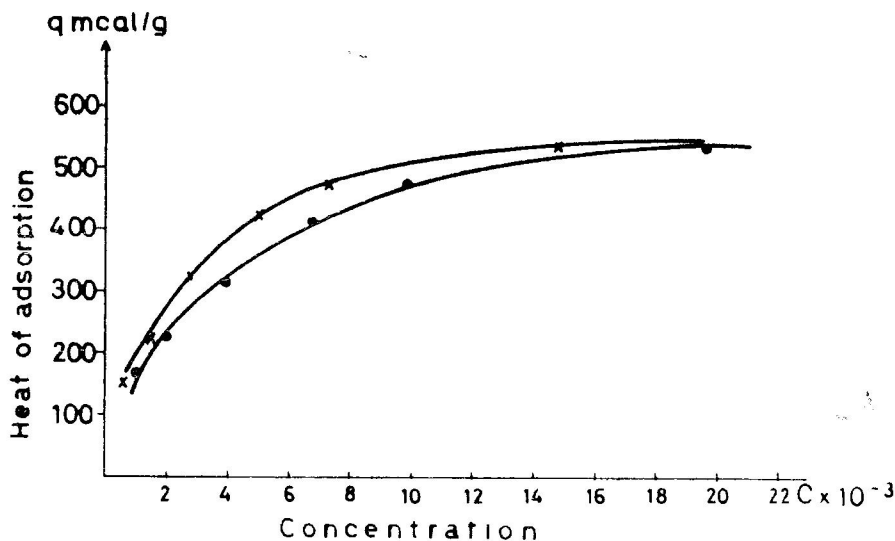
In the following two tables and in the graphs, data and results are presented of the applied successive adsorption when the powder Carbon Black (ELF4) was treated the first time with n-butanol (table—2) and the other time with n-hexanol (table — 3):

TABLE — 2

C mol. frac. 10^{-3}	Acm ²	qm. cal/g	c/q . 10^{-5}
0.9826	6.7188	164.610	0.5969
1.9792	9.3981	230.254	0.8595
3.9409	12.9224	316.598	1.2447
6.9071	16.7353	410.014	1.6846
9.8522	19.3528	417.144	2.0778
19.6598	21.8260	534.736	3.6765

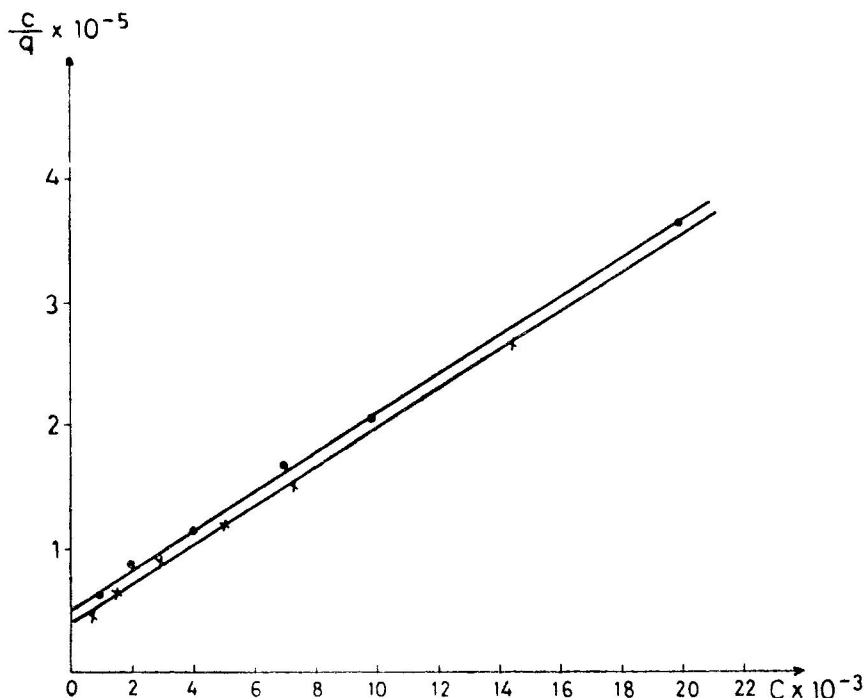
TABLE — 3

C moll fr. 10^{-3}	Acm ²	qm. cal/g	1/q . 10^{-5}
0.7189	6.3752	156.192	0.4602
1.4378	9.0617	222.012	0.6476
2.8756	12.9911	318.121	0.9034
6.0250	17.2839	423.455	1.1866
7.1890	19.3197	473332.	1.5188
14.3780	21.8237	534.681	2.6890



Graph. 2. Relationship between heat evolved and solute concentration; Adsorbent --- carbon black ELF 4; Soluts: (●) n-butanol in n-heptane, (x) n-hexanol in n-heptane;

As can be seen from graph — 2, typical Langmuir isotherms were obtained. On the graph — 3 it is possible to see the characteristic straight lines obtained by plotting (c/q) versus (c) . As it has been explained in the theoretical consideration, through the slope of these lines, the integral heat of adsorption evolved due to the formation of a monolayer coverage, can be determined. The monolayer coverage here is formed only on some particular places of the surface. It is also noticeable that the points deviate to a slight extent from the line, which can be expected since the Langmuir equation refers to ideal conditions. Such conditions are hardly obtainable in reality, because in a given moment the solute molecules affect slightly each other. Another possible reason for this is that the places which adsorb might not have been entirely equal in terms of energy.



Graph. 3. Langmuir plots.

The integral heat which was measured up was then used to determine the fraction of the surface area which had adsorbed, according to the equation $S_w = K \cdot q_m$. Here, the constants of proportionality for the adsorption of n-butanol from n-heptane (K_1) and of n-hexanol from n-heptane (K_2) were used, and they were, according to the earlier research of T. Allen and R. Pattel:

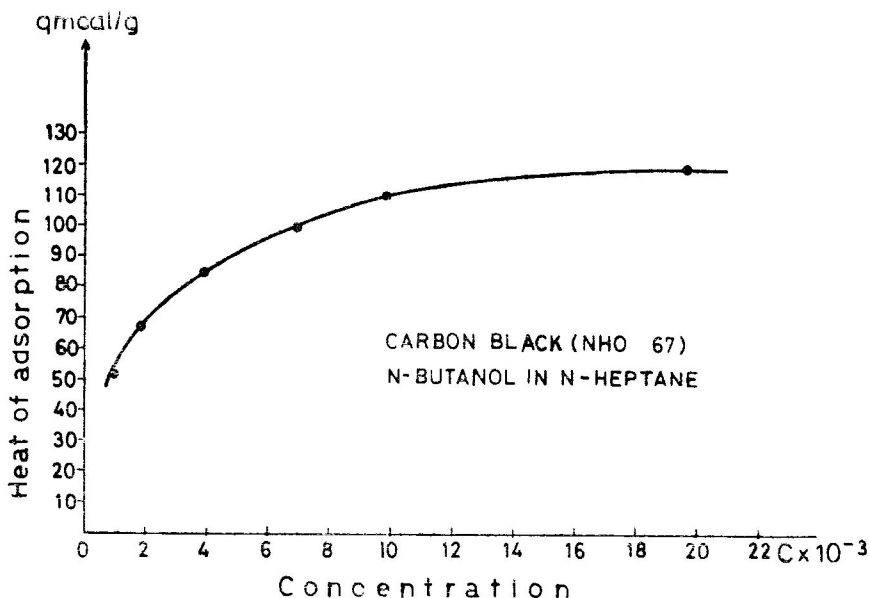
$$K_1 = 28.5 \text{ m}^2 \text{ cal.}^{-1}, \text{ and } K_2 = 25.6 \text{ m}^2 \text{ cal.}^{-1}$$

The integral heat of adsorption obtained from reaction with n-butanol (q_{m1}) is equal to 605.5 m cal/g. and the area which adsorbs (S_{w1}) is equal to 17.26 m²/g. As far as reaction with n-hexanol is concerned, it was found that q_{m2} was equal to 561.2 m cal/g and S_{w2} to 16.68 m²/g.

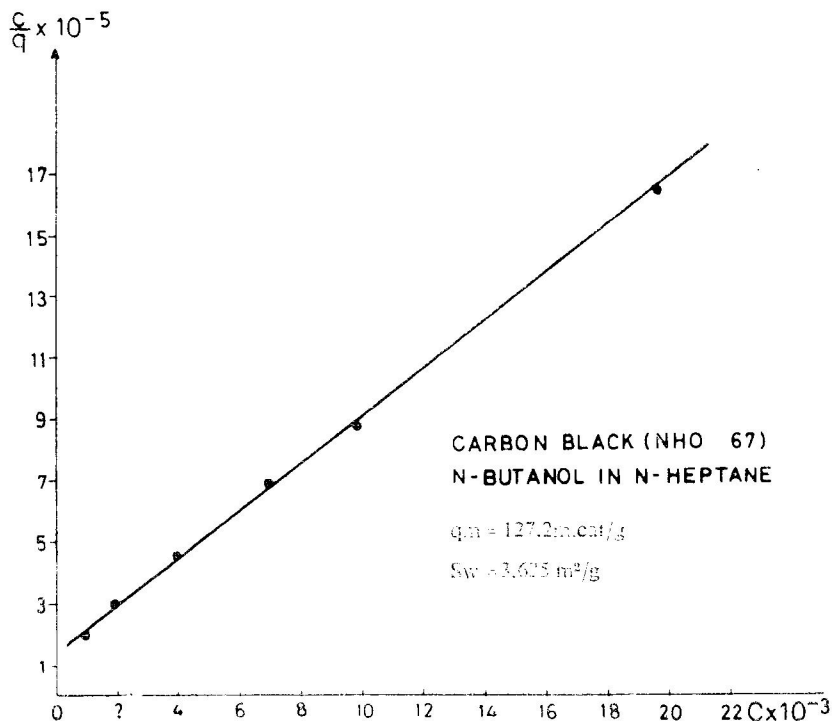
Using the B. E. T. method it was found that the specific surface area of Carbon Black (ELF4) amounted to 113 m²/g; That made it possible to find out the appropriate percentage of that part of the surface area which reacts with both adsorbats. This percentage for n-butanol from n-heptane is 15.07%±0.31%; The reproducibility has been examined by several simultaneous experiments and was found to be 2.06%. The percentage of the above mentioned part of the surface area which reacts with n-hexanol from n-heptane was found to be 14.76%, and that is almost equal to the earlier percentage.

A number of identical experiments have been carried out with Carbon Black (NHO67). An amount of 0.15 g was placed into the microcalorimeter cell and was then treated like the previous carbon. This type of carbon has a comparatively small specific surface area, which through the B. E. T. method was found to be 7.62 m²/g. It was determined from the reaction of solutions of n-butanol in n-heptane that the integral heat of adsorption was 127.2 m. cal/g. The fraction of the area (S_w) which was active was 3.625 m²/g, and this makes 47.57% of the total area.

Langmuir's isotherm obtained here is given in Graph --4, and in Graph -- 5 the plot c/q versus c is presented, which forms again a straight line. The experiments conducted by n-hexanol instead of n-butanol, indicated that both of them produce nearly the same percentages relating to the active surface area.



Graph 4. Relationship between heat evolved and solute concentration.



Graph. 5. Langmuir plot.

Conclusion

In order to understand the adsorption of polar adsorbates (alcohols) onto a part of the surface area of carbon blacks, i.e. onto polar sites of these adsorbents, it is necessary to indicate which sites are polar and which non-polar, and to give a brief account of the structure of carbon blacks. Generally, the term carbon blacks comprises a large number of finely divided carbon pigments obtained through pyrolyses of hydrocarbonic gases and oils⁽¹²⁾. Usually they contain various percentages of H, O, S, N, and have various sizes of specific surface areas, from 6 to 1.100 m²/g. The variety of the surface properties derives from the various treatments in obtaining a given type of powder, and of course, from the properties of the raw material used for producing individual carbons.

The temperature of processing is most important; generally, if the temperature is below 1000°C, carbons of large specific surface areas are obtained and at that temperature the rest of the elements present can hardly be liberated. On the other hand, at temperatures over 2000°C the carbons obtained are clean but have small surface areas⁽¹³⁾.

The structure of the carbon blacks' particles is examined most frequently by x-rays and by electroic microscope. It is established that such carbons have paracrystalline microstructure, i.e. that they appear in intermediate form consisting of both crystals and amorphous parts. As in graphites, here the hexagonal units of C-atoms build networks and layers. However, the layers here are not parallel but unevenly oriented towards each other (Fig. 2).

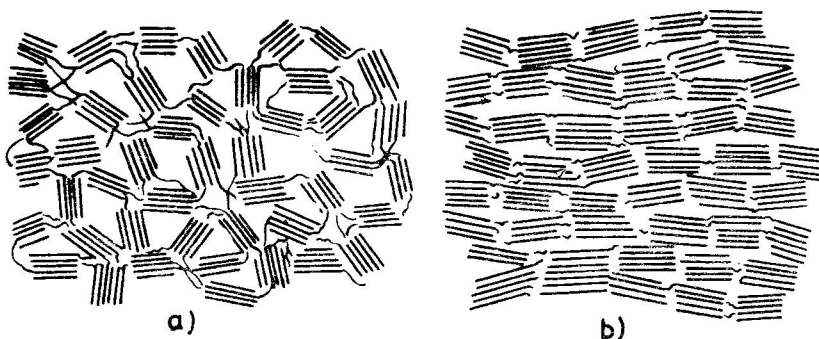


Fig. 2. Orientation of layers of a) Ungraphitized carbon, and b) Graphitized carbon.

Generally, the structure of carbon blacks is such that energetical dissimilarity can be expected. Thus, in terms of energy, the surface area the edges and corners of crystal units is much stronger than the surface area of the main planes^(15, 16). This is because the valencies of the C atoms on the edges are not saturated and they form what is called polar sites, while the main planes represent the non-polar sites of the carbon. The ratio between these two sites is not fixed. However, this is most significant because the determination of the size of the one site or the other in the total specific surface area, makes it possible to measure to what extent the paracrystal contains crystals⁽¹⁶⁾. Also, the knowledge of the ratio of the two types of energetical sites, is important for the examination of many surface properties (such as abrasion), which could be of significance for the use of the carbon.

Since, according to the general regularity confirmed in the literature, polar adsorbents tend to attract polar adsorbates of non-polar solutions, in our experiments we selected alcohols whose molecules show polarity, and n-heptane as non-polar solution. In carbon black (ELF4), the percentage found of polar sites was fairly low. It is possible that this percentage is an indicator of the actual presence of such sites in this particular carbon. However, it may be also assumed that a part of the polar points (places) have been previously saturated by connecting the existing oxygen, hydrogen or nitrogen presumably remaining in the powder if it was a case that this carbon had been obtained at not too high temperatures. The reported elements, according to the literature⁽¹⁶⁾ tend to be linked to energetically stronger points. The specific surface area of carbon black ELF4 is relatively large (113 m²/g) and it is believed that this carbon was obtained at not too high temperatures.

To establish which of these two possible explanations is more accurate, the percentage of the non-polar sites should be examined to see if this percentage together with that of the polar sites makes 100% of the total specific surface area.

The percentage of 47.57% of the carbon NHO67 is quite as expected. This type of carbon has such a small specific surface area that it is apparent that it has been obtained at high temperature at which the elements existing in the raw material were able to be liberated. Therefore the percentage obtained is probably the one of the polar sites which are here entirely free, i.e. do not have other connected elements.

No doubt, the above consideration could be developed further, using other methods of chemical analysis.

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Резиме

Целта на овој труд беше да се испитаат адсорбционите можности на неколку вида јаглени, при што се задржавме посебно на два вида: јаглен — црн (ELF4) и јаглен — црн (NHO67). Со користење на В.Е.Т. методата на гасна адсорпција најнапред беше наоѓана целокупната, односно специфичната површина на прашкастите материјали. Потоа со помош на проточниот микрокалориметар ја одредувавме интегралната топлина на адсорпција кога на јагленот како адсорбент

делувавме со раствори кои ги чинеа: неполарниот растворувач — хептан и површински активните, поларни субстанции — бутанол и хексанол.

Во текот на работата се јавија тешкотии во обезбедувањето на потребниот равномерен проток на растворот низ лежиштето од премногу ситниот прашок, но со мала измена на одводната цевка на апаратурата, се овозможи правилно квасење и реакција меѓу адсорбентот и адсорбатите од растворот.

Со определувањето на интегралните топлини на адсорбиција, ја пресметавме фракцијата од површината која била активна спрема адсорбатите. Така кај јагленот (ELF4) таа изнесува средно $16,97 \text{ m}^2/\text{g}$, и преставува 14,96% од вкупната површина која се добива кога прашокот би бил комплетно, монослојно покриен. Кај јагленот ННО67 најдената активна површина изнесува $3,62 \text{ m}^2/\text{g}$, кое претставува 47,57% од вкупната површина. Тоа што не дојде до потполна адсорбција туку само врз дел од површината, беше очекувано со оглед на енергетската невоедначеност на честичките на јаглените. Имено, кај нив рабовите и аглиите на кристалните единици се енергетски посилен од површините на активните рамнини. Првите ги чинат таканаречените поларни страни а вторите неполарните страни кај јаглените.

Со експериментите беше потврдена нашата претпоставка дека до адсорбција на поларни адсорбати од неполарни растворувачи би дошло токму на местата со поларен карактер. Така го определивме процентот на дадениот вид енергетски страни кај двата прашка, на основа на кои може да се заклучи до која мерка паракристалите на јагленот содржат кристали и воопшто — кој процент е значаен за многу површински својства поврзани со примената на јагленот.