Adsorption of Electrolytes on Charcoal

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Introduction

In the present paper it is proposed to summarize in the light of new experimental data, some of the results obtained in investigations on the adsorption of electrolytes on charcoal carried out in our laboratory over a period of a number of years. The question of the electrokinetic behaviour of charcoal, however, will not be touched upon here; it will be dealt with in a separate communication.

In accordance with the conception which was evolved in the previous investigations carried out in our laboratory, the adsorption of electrolytes on charcoal is determined by the potential at the charcoal-solution interface and by the capacity of the double layer. In its turn, the magnitude of the potential difference depends, under ordinary conditions, upon the presence of electrochemically active, chemisorbed gases on the charcoal surface[1].

[1] Frumkin and Donde, Ber. Deutsch. Chem. Ges., **60**, 1816 (1927); Bruns and Frumkin, Z. physik. Chem., (A), **141**, 141 (1929); Burstein and Frumkin, Z. physik. Chem., (A), **141**, 158 (1929); Frumkin, Koll. Z., **51**, 123 (1930); Bruns and Frumkin, Z. physik. Chem., (A), **147**, 125 (1930); Burstein, Frumkin and Lavrovskaya, Z. physik. Chem., **150**, 421 (1930); Bruns and Piloyan, Z. physik. Chem., **155**, 77 (1931); Frumkin, Lewina and Zarubina, Z. physik. Chem., **155**, 41 (1931); Bruns and Pyzhov, Z. physik. Chem., **157**, 57 (1931); Bruns and Zarubina, J. Phys. Chem. (Russ.), **2**, 680 (1931); Frumkin, Burstein and Levin, Z. Physik. Chem., (A), **157**, 442 (1931); Bruns, Pos, Gorodetzkaya and Perelman, Sow. Phys., **2**, 497 (1932). Frumkin, Sow. Phys., **4**, 239, 287 (1933); Burstein, Levin and Petrov, Sow. Phys., **4**, 197 (1933). Lewina, Frumkin and Lunev, Acta Physicochimica URSS, **3**, 397 (1935); Burstein, Acta Physicochimica URSS, **6**, 371 (1937).

If oxygen, which has been adsorbed at low temperature is present on the charcoal surface, the charcoal becomes positively charged and attracts anions from the solution (positive oxygen-charcoal). The magnitude of the oxygen potential of charcoal may be increased by the action of ozone or by the introduction of platinum into the charcoal; it may be decreased by placing the charcoal with adsorbed oxygen in an atmosphere of hydrogen. At room temperature, however, only a partial decrease in the positive charge takes place in the absence of catalysts. Upon igniting the charcoal in an atmosphere of hydrogen[2], or, still better, after the action of hydrogen on the charcoal into which a small amount of platinum has been introduced, negative hydrogen-charcoal is obtained. In this case the hydrogen is electrochemically active. Such a charcoal becomes negatively charged in aqueous solutions, discharging hydrogen ions into the solution and attracting cations from the latter. A weaker negative charge may be imparted to platinized charcoal by the action of carbon oxide instead of hydrogen. The experiments of Lewina, Frumkin and Lunev[1] have proved that the mechanism of the action of platinum in platinized charcoal is of an electrochemical nature: in an atmosphere of hydrogen the platinum forms local cathodes, which impart their potential to the whole charcoal surface, although they cover only an insignificant part of it. The same effects may be obtained upon purely mechanical contact of charcoal with platinum. Still earlier it was shown that with the aid of mixtures of $H_2 + O_2$, or by employing charcoal with a very small platinum content, continuous transition from positive oxygen- to negative hydrogen-charcoal may be realized.

Upon outgassing the charcoal by prolonged ignition in vacuum, the charcoal surface becomes freed of adsorbed gases. Such charcoal, upon being brought into contact with dilute solutions of electrolytes, exhibits practically no adsorption effects. However, as shown

[2] We take this opportunity to correct the erroneous indication in the work of Bach and Zimin (Acta Physicochimica URSS, 7, 451, 1937) according to which the oxide film covering the charcoal is not reduced even upon igniting in an atmosphere of hydrogen. In this investigation the charge on the charcoal after ignition in hydrogen remained positive, evidently, owing to the fact that the apparatus was not sufficiently hermetic and thus did not exclude the possibility of traces of oxygen penetrating it after ignition.

by the most exact experiments carried out by Burstein[1], it is never possible to outgas charcoal completely: the surface retains very small traces of hydrogen continuously renewed at the expense of the hydrogen which is invariably present in activated charcoal. It may further be mentioned that, as has been proved experimentally in the case of oxygen-charcoal, and still more in the case of hydrogen-charcoal, the charging of the charcoal surface during the adsorption of electrolytes is actually accompanied by the consumption of the corresponding electrochemically active gases.

Since the adsorption of electrolytes is, from the point of view of the electrochemical theory, connected with the formation of a double layer, a linear relation should hold between the amount adsorbed and the potential of the carbon electrode. Such a relation, however, can only be considered as a first approximation, since it assumes that the capacity of the double layer remains constant. A change in the potential may be effected in two ways: by polarization of the electrode at constant composition of the solution, or by changing the pH of the solution in the presence of a definite electrochemically active gas. From the foregoing it follows that a linear relation between the amount adsorbed and the logarithm of the hydrogen ion concentration should hold in the latter case. This conclusion has been wholly confirmed in the case of the adsorption of cations on hydrogen-charcoal within the interval from pH = 1.5 to pH = 13.5[3]. In the case of positive oxygen-charcoal a linear relation has been found to hold within the pH interval from 2.5—3.0 to 8.8. At lower pH values the adsorption of acids is greater than that which should be expected on the basis of the linear relation.

In this simple electrochemical scheme embracing a large amount of experimental data, it is necessary to consider two additional factors. Firstly, in a number of cases, along with purely electrostatic adsorption of ions which accompanies the formation of the double layer, the specific adsorption of ions, particularly of anions, must also be taken into account. The latter accounts for a number of adsorption phenomena — those, for example, which are observed in not too dilute solutions of acids. Secondly, positive oxygen-

[3] Bruns, Burstein, Fedotov and Lifshitz, Acta Physicochimica URSS, 8, 47 (1938).

charcoal is obtained only during the adsorption of oxygen on the charcoal surface at low temperatures, for example, upon contact with the atmosphere at room temperature after activation in CO_2, as was found by Bartell and Miller[4].

If the interaction between oxygen and charcoal takes place at 300—400° C, the oxygen is bound in another form and in considerably larger amounts, as was first shown by Kruyt and de Kadt[5] and, independently, by Dubinin[5]. The charcoal obtained in this manner (negative oxygen-charcoal) becomes charged negatively upon being brought into contact with aqueous solutions sending hydrogen ions into them, and adsorbs cations, *i. e.*, behaves as if acid groups, for example carboxyl groups, had formed on its surface. However, a somewhat different interpretation of the adsorptive behaviour of negative oxygen-charcoal is also possible.

If it is taken into account that the bond between carbon and adsorbed oxygen has a dipole moment, the oxygen constituting the negative end of the dipole, the formation of an oxide film should shift the zero point of the adsorption of ions in the direction of more positive potentials, so that, at definite degrees of oxidation, transition from the adsorption of anions to the adsorption of cations may be observed. The potential difference charcoal-solution, caused by the adsorption of ions, changes its sign at a constant total potential as a result of the appearance of a considerable positive potential difference caused by the oxide film. Frumkin and Šlygin[6] were the first to propose such an interpretation to explain entirely analogous phenomena which they observed upon the appearance of an oxide film while studying adsorption on highly disperse platinum; the same interpretation was advanced by Verwey

[4] Bartell and Miller, J. Am. Chem. Soc., **44**, 1866 (1922); **45**, 1100 (1923); Miller, J. Am. Chem. Soc., **46**, 1150 (1924); **47**, 1270 (1925); J. Phys. Chem., **30**, 1031, 1062 (1926); **31**, 1197 (1927); Coll. Symp. Mon., **5**, 55 (1928).

[5] Kruyt u. de Kadt, Koll. Z., **47**, 44 (1929); de Kadt, Dissert., Utrecht (1929). Kruyt u. de Kadt, Koll. Beih., **32**, 250 (1931); Dubinin, Z. physik. Chem., (A), **150**, 145 (1931). Later work on the adsorptive properties of charcoals oxidized at 400° C: Bruns, Maximova and Pos, Koll. Z., **63**, 286 (1933); Kruyt and Truus Kruyt, Proc. Acad. Sci. Amsterdam, **38**, 570 (1935); Verlinden, Dissert., Utrecht (1935).

[6] Frumkin, Sow. Phys., **4**, 258 (1933); Šlygin, Frumkin and Medvedovsky, Acta Physicochimica URSS, **4**, 911 (1936).

and de Boer[7] to explain the behaviour of negative oxygen-charcoal. Similar phenomena are also observed, apparently, in the case of adsorption on silver[8]. In interpreting the behaviour of these charcoals it must be kept in mind that, in contradistinction to the surfaces of positive oxygen- and negative hydrogen-charcoal, the surface of Kruyt and de Kadt's charcoal is not electrically uniform: this follows from the possibility of the simultaneous adsorption of cations and anions on these charcoals[5]. Negative oxygen-charcoal is the stable form into which positive charcoal gradually changes even at room temperature, particularly in alkaline solutions[9]; at elevated temperatures, this process of transformation proceeds, of course, still more rapidly.

In order to obtain the most simple and reproducible results possible while studying the adsorptive behaviour of positive charcoal, it is necessary that the oxygen should be adsorbed at room temperature shortly before the charcoal is used as adsorbent. As is known, the technique of obtaining positive charcoal, based on high-temperature activation with carbon dioxide, with subsequent cooling in an atmosphere of this gas, was worked out for the first time by Bartell and Miller[4], and later was perfected somewhat in our laboratory. Unfortunately, in some investigations, for example in those of King and his co-workers[10], this method has hitherto been insufficiently utilized. During activation with oxygen — a method employed by King — a certain number of negative groups are bound to arise while cooling the charcoal, and the behaviour of the charcoals obtained in this manner is less reproducible than that of pure positive charcoals. This probably explains why Bennister and King could not find any parallelism between the electrokinetic and adsorptive behaviour of charcoal, whereas this has been well established in the investigations of other authors.

In contradistinction to the "electrochemical" point of view evolved in this paper, Shilov and his co-workers have developed

[7] Verwey u. de Boer, Rec. Trav. Chim. Pays-Bas, **55**, 675 (1936).

[8] Veselovsky, Acta Physicochimica URSS, **11**, 815 (1939).

[9] Bruns and Piloyan, *l. c.*; Miller, J. Phys. Chem., **36**, 2697 (1932); Bach and Zimin, *l. c.*

[10] King, J. Chem. Soc. (London), **1937**, 1489; Chambers and King, *l. c.*, **1938**, 688; Bennister and King, *l. c.*, **1938**, 991.

a "chemical" theory of the adsorption of electrolytes on charcoal[11]. This theory is based on the assumption of the formation of three surface oxides, *A*, *B* and *C*, corresponding to different valence schemes, of which the first two are basic, and the third acid in character.

The presence of oxide *A*, which does not dissociate at 1000° C, should explain the slight residual adsorption of acid which is observed, according to Shilov and Tshmutov, even in the case of outgassed charcoal. This result is in contradiction with the experimental data obtained in our laboratory, but, since it was analyzed in detail in one of our previous papers, we shall not revert to this question here. Oxide *C* corresponds to Kruyt and de Kadt's negative oxidized charcoal which has already been mentioned above; at the end of this paper we shall again touch upon the mechanism of adsorption on these charcoals in the light of new experimental data.

Let us now consider in somewhat greater detail the explanation of the adsorption phenomena on ordinary positive charcoal by the presence of an oxide *B*. In this connection it is highly important to draw an exact quantitative distinction between the conclusions of the "electrochemical" and "chemical" theories. In the latter, the process of adsorption of acid is treated as a process of surface salt formation involving hydroxyl groups of the hydrated oxide. If we consider the dependence of the adsorption of acid upon its concentration or the pH of the solution from this point of view, the conclusions will depend very markedly upon additional assumptions on the nature of the surface compounds.

It is evident that one is not permitted to ascribe the properties of individual immiscible phases to these compounds; for in this case, *e. g.*, on decreasing pH, the adsorption of acid would at a certain pH, pass *per saltum* from the zero value to the maximum. Developing the conceptions of the chemical theory, Lepin and Strachova[12] assume that the ordinary law of mass action applies

[11] Shilov and Tshmutov, Z. physik. Chem.. (A), **143**, 41 (1929); **148**, 233 (1930). Shilov, Shatunovskaya and Tshmutov, *l. c.*, **149**, 211 (1930); **150**, 31 (1930). Lepin, Sow. Phys., **4**, 282 (1933).

[12] Lepin and Strachova, Acta Physicochimica URSS, **10**, 175 (1939).

to the adsorbed groups. If we denote by a_s the adsorption of acid at a certain value of [H·], and by $(a_s)_{max}$ the maximum possible value of the acid adsorption at which the salt-formation process proceeds to completion, then, as a simple calculation shows, at an anion concentration [A] and upon the assumption that the law of mass action is applicable, the following relation holds:

$$\frac{a_s}{(a_s)_{max}} = \frac{[H^\cdot]\,[A]}{k_1 + [H^\cdot]\,[A]} = \frac{[A]}{k_2\,[OH'] + [A]}. \qquad (1)$$

If $[H^\cdot] = \frac{k_1}{[A]}$, then $a_s = 0.5\,(a_s)_{max}$; at a value of [H·] ten times smaller, $a_s = 0.09\,(a_s)_{max}$, while at a value of [H·] ten times larger, $a_s = 0.91\,(a_s)_{max}$. Thus, according to equation (1), upon decreasing the pH the increase in the adsorption of acid from very small values to maximum ones should take place in a comparatively narrow interval of two pH units — a fact which is in complete contradiction with all experimental data on the adsorption of acids on charcoal[13].

[13] If Lepin and Strachova nevertheless arrive at the conclusion that the law of mass action is applicable to the adsorption of acids on charcoal, this can only be ascribed to the special conditions of their experiments. They start from a neutral KCl solution, which becomes alkaline on adsorption of HCl by charcoal. In this case a_s is evidently proportional to the equilibrium concentration of OH′ which is formed in the solution, and since $\frac{a_s}{(a_s)_{max}} \ll 1$, equation (1) reduces to the relation:

$$(a_s)^2 = \text{const.}\ [Cl']. \qquad (2)$$

Such a relation between the amount of ions adsorbed and the total concentration of the solution may be obtained in the limited concentration interval in which the experiments were carried out, owing to the change in the degree of diffuseness of the double layer. In a series of experiments with hydrogen charcoal, Petrov, Burstein and Kisselewa (Acta Physicochimica URSS, **11**, 59 (1939) studied the relation between the adsorption of the cation and the concentration of the salt over a wider concentration interval. As can be seen from their data, only over a small section of the investigated region may the results be described by a relation of the type of equation (2), whereas on the whole they quite satisfactorily conform to the conclusions arrived at from the theory of the double layer — a fact which confirms the electrochemical mechanism of adsorption.

In the derivation of equation (1) it has been assumed that the surface C — OH groups react independently of one another. Better agreement may be obtained if it is assumed that the dissociation constant of the surface C — OH groups decreases with an increase in the number of dissociating groups as a result of the influence of neighbouring surface charges on the dissociation process. In this case the interval of pH values within which a change in adsorption may be observed becomes wider. Adsorption isotherms of such kind are obtained, for example, during the adsorption of alkalies by many natural silicates; in these cases, within a certain pH interval, a linear relation between the amount adsorbed and the logarithm of the hydrogen ion concentration is observed instead of the Langmuir isotherm expressed by equation (1). The transition from the Langmuir isotherm to a logarithmic relation is a necessary consequence of the decrease in the work of adsorption with increasing degree of covering of the surface. Thus, if one makes a few additional assumptions, the "chemical" theory may also lead, within a limited concentration interval, to the same relations between adsorption and pH as the electrochemical theory.

The problem of the dependence of adsorption upon the potential at constant pH may be analysed in a similar manner. In this case also the quantitative character of the results which are obtained by making use of the chemical theory depends very markedly upon the equation of state ascribed to the layer of hydroxyl groups on the surface; upon making certain assumptions (repulsive forces or non-uniformity of the surface), a linear relation between the amount adsorbed and the potential may be obtained on the basis of the chemical theory also. The difference between the conclusions of the chemical and electrochemical theories consists, however, in the fact that from the point of view of the chemical theory this linear relation between adsorption and potential may only be observed over a certain limited pH or potential interval — namely, until the adsorption attains a value close to the maximum. In the electrochemical theory there is no such limitation. However, there is another, still more essential difference between the two theories. From the point of view of the electrochemical theory, the region in which adsorption of anions takes place, *i. e.*, in which the surface is charged positively, should, upon varying the charge, pass continuously

through the zero point into the region of the adsorption of cations, which corresponds to a negatively charged surface; the regions of the adsorption of cations and anions must not overlap unless, of course, they possess specific adsorbability. Such a continuous transition was already observed, as has been pointed out above, in experiments on slightly platinized charcoals with mixtures of $H_2 + O_2$, and the latter conclusion was confirmed; the potential of the charcoal surface, however, could not be measured. On the other hand, from the point of view of the chemical theory, there is no connection whatsoever between the adsorption of anions on positive charcoal and the adsorption of cations on negative hydrogen-charcoal. The question as to the adsorption mechanism on negative hydrogen-charcoal has not in general been given sufficient consideration from the point of view of the "chemical" theory, except for a few references to the possibility of surface hydrides of carbon or platinum (in the case of platinized charcoal) taking part in this process [14].

To obtain a complete picture of the mechanism of the adsorption of electrolytes on charcoal, it is therefore highly essential to make a quantitative study of the transition from anion adsorption to cation adsorption with a change in the potential of charcoal. Such a transition cannot be accomplished experimentally, however, if we start with positive oxygen- or negative hydrogen-charcoal and vary the pH of the solution. Indeed, as experiments show, the zero point of the adsorption on positive charcoal lies in the region of high pH values at which the adsorption behaviour of positive charcoal is complicated by the irreversible processes of formation of negative oxygen groups. The zero point of hydrogen-charcoal, on the other hand, lies close to $pH = 0$, *i. e.* in the region in which the specific adsorption of anions already begins to show a marked effect. Therefore, in order to solve the problem under consideration it was necessary to

[14] Here we shall not dwell on any further improvements that might be introduced into the chemical theory by assuming the simultaneous existence of oxides and hydrides on the charcoal surface and the mutual influence of the corresponding adsorption processes. In this manner, of course, we could still further smooth out the differences between the two conceptions, but the picture obtained would be very remote from the usual conception of the „chemical" mechanism of the adsorption of electrolytes on charcoal.

choose another method of varying the potential of charcoal — namely, its polarization in a solution of definite composition. This method had already been used successfully to study the mechanism of adsorption on a platinum electrode[6]. In order to be able to apply this method to the case of a carbon electrode, it was necessary first of all to solve the problem of preparing electrodes from activated charcoal, which would be porous, durable and electrically conductive.

Experimental part

Preparation of carbon electrodes. Considerable difficulties are met with when one attempts to prepare electrodes from ash-free activated charcoal. An attempt to prepare such electrodes by pressing activated sugar-charcoal proved a failure[15].

In one of the investigations carried out in our laboratory there was described a method for obtaining ash-free charcoal from bakelite suggested by Prof. A. Monosson. This method proved very convenient for obtaining carbon electrodes. Condensation of phenol and formaldehyde purified by distillation yields tar. To transform the latter into solid bakelite HCl is used as a catalyst.

The tar was drawn into thin glass tubes ($d = 3$ mm.) whose inner walls were wetted with hydrochloric acid. The tubes with the tar were then heated at 120° C for a few hours. In this manner solid bakelite sticks were obtained which were then burnt at 500° C. By varying the ignition temperature and air access, carbons of various porosity could be obtained. After combustion, the charcoal was activated in a current of CO_2 at 900° C until 35—45% were burnt, and before each experiment was heated in an atmosphere of hydrogen. The carbons obtained in this manner possess a considerable mechanical strength and may be used as electrodes.

Procedure. The relation between the potential of the carbon electrode and the amount of electrolyte adsorbed on it was studied

[15] Carbon electrodes from sugar charcoal were prepared as follows: sugar sirup was added to powdered sugar charcoal as a cement, after which the charcoal was pressed and activated. In this manner electrodes were obtained which were either insufficiently durable, crumbling easily, or durable but poorly active.

in the apparatus shown diagrammatically in Fig. 1. The carbon electrode *a* was placed into vessel *A*. In vessel *B* there was an auxiliary platinum electrode. Measurement of the electrical conductivity of the solution was carried out in vessel *C*. A glass filter was sealed between vessels *A* and *C*. Vessel *A* was separated from vessel *B* by stopcock *K* which was wetted with the electrolyte. Saturation of the

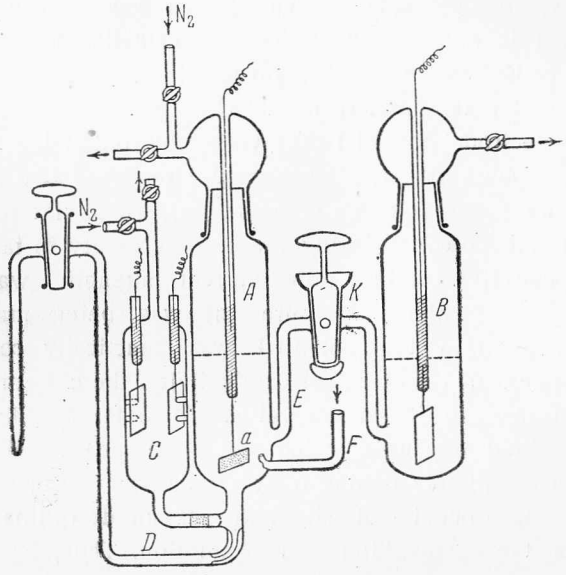

Fig. 1.

solution with the gases H_2, O_2, or N_2 was carried out through tube *F*. After filling the siphon *D*, which connected the liquid in *A* with the reference electrode, and the tube *E*, 7 cm.^{3} of the liquid undergoing investigation were poured into vessel *A*, and the electrical conductivity of the liquid was measured. The procedure in measuring the electrical conductivity was as follows: part of the solution from vessel *A* was transferred into vessel *C* under pressure of the gas and, after measuring the electrical conductivity, was returned to vessel *A*.

A small preliminarily weighed carbon electrode fastened to the end of a gold or platinum wire was dipped into this solution. The

material of the wire did not affect the results. The carbon electrodes used in the experiments weighed from 0.1 to 0.05 gm. In order to attain the oxygen potential and establish adsorption equilibrium, the carbon electrode in the case of adsorption from H_2SO_4 solutions, was left in the solution overnight in an atmosphere of oxygen; in the case of adsorption from KOH and Na_2SO_4 solutions, the carbon was left overnight in an atmosphere of N_2 in order to avoid formation of negative oxides, after which oxygen was passed through for 1—2 hrs. This was usually sufficient to establish the oxygen potential. The entire apparatus was placed in a thermostat which was maintained at a temperature of 25° C.

The electrode potential was varied by polarizing the electrode in an atmosphere of N_2 at a current strength $I = 5 \times 10^{-4}$ A, or by bubbling gases (oxygen or hydrogen). To obviate any noticeable change in the potential during the time necessary to take an electrical conductivity reading, the current strength was decreased to 2×10^{-4} A while a measurement was being made. At such a current strength the potential was practically constant. After a measurement of the electrical conductivity, the current strength was again increased to its former value. To obtain equilibrium values another method was used which will be described below.

Upon completely cutting off the polarizing current, the potential shifted in the opposite direction, the magnitude of this shift depending upon the composition of the solution. Thus, for example, the carbon was polarized cathodically to the value of the potential of a hydrogen electrode in the given solution. Then the current was switched off and in 40 hours the potential became more positive by 0.15 in 6 N H_2SO_4, by 0.23 in 1 N H_2SO_4 and by 0.4 in 1 N KOH.

The amount of electrolyte adsorbed on the charcoal at different potentials was determined from the electrical conductivity of the original solution and the electrical conductivities of the solution at corresponding values of the potential. It should be noted that in the experiments in which the potential was changed by polarization, the change in the electrical conductivity may partially depend on the transfer of ions. To allow for this factor, a blank experiment was carried out with a smooth platinum electrode, which was placed in vessel A instead of the carbon electrode. In the latter case

the change in the concentration of the solution was only brought about by the transfer of ions, since adsorption on a smooth platinum electrode is practically equal to zero. In calculating the amount of electrolyte adsorbed on the charcoal, we could, using these data, allow for the change in concentration in vessel A caused by the transfer of ions during the passage of the same amount of electricity.

The formation of carbon dioxide might also have affected the electrical conductivity of the solution. However, under the conditions in which our experiments were carried out, this effect had no influence on the results as shown by the adsorption curves, which are reversible both in acids and in alkalies. The presence of carbon dioxide should have led to irreversibility of the process, which would have shown up markedly in the experiments with alkaline solutions.

Whenever the experiment carried out in the apparatus shown in Fig. 1 was of long duration, the effect of electroosmosis became manifest. The walls of the closed stopcock formed a thin capillary, and electroosmosis along these walls led to a change in the volume of the solution in the adsorption vessel. To avoid this effect the stopcock K was left open during the polarization of the electrode and was only closed while taking a measurement of the electrical conductivity. The diameter of the stopcock canal was 0.25 mm. In order to find out whether any noticeable diffusion of liquid took place from one vessel into the other while the stopcock was open, which might have vitiated the results of the measured adsorption effect, the following blank experiment was carried out. Into vessel A there was poured a solution whose concentration was 50% less than that of the solution in vessel B, and the apparatus was left for a period of 20 hours with the stopcock open. It was found that the concentration of the solution in vessel A, measured before and after the experiment, did not change.

In order to carry out experiments without the necessity of taking into account the change in concentration caused by the transfer of ions, and also to do away with the electroosmosis effect, another apparatus was designed which is shown in Fig. 2. This apparatus differed from the one described above, in that vessel B was replaced by a tube L which was located in vessel A. A slightly

platinized auxiliary platinum electrode was present in this tube. The total volume of liquid in L during polarization amounted to about 0.03 cm.^{3}. Since O_2 was given off at the anode in tube L during cathodic polarization of the carbon, in order to expel it, H_2 was bubbled through the solution in L in a steady continuous stream which reacted with part of the O_2 on the platinum electrode and swept away the rest.

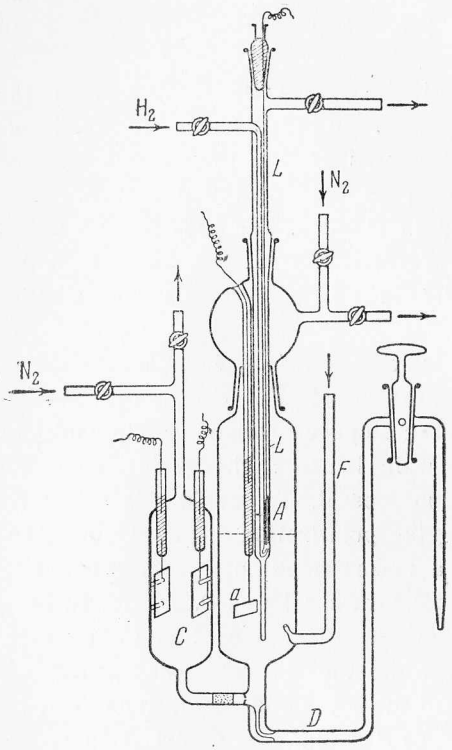

Fig. 2.

The experiments in this apparatus were carried out as follows: After attaining a desired potential, the polarization current was switched off and, to expel traces of oxygen, hydrogen was bubbled through the solution in L for some time. Then the liquid was forced from L into A under the gas pressure. By repeating this operation 3—4 times, the influence of the migration of ions upon the change in the concentration of the solution was eliminated. Whereas the apparatus shown in Fig. 2 is convenient for obtaining adsorption curves, it is less convenient for taking charging curves (see below) owing to the possible depolarizing action of the oxygen which forms in tube L.

The experiments in which the potential variation was effected by H_2 or O_2 were carried out with a platinized carbon electrode (0.2% Pt). The variation of the potential with time under the action of H_2 on oxygen-charcoal and O_2 on hydrogen-charcoal was observed together with the corresponding change in the electrical conductivity of the solution. In this case the variation of the electrical

conductivity of the solution is only connected with the changes in the amount of electrolyte adsorbed on the carbon surface. To avoid any appreciable shift in the potential while measuring the electrical conductivity, nitrogen was bubbled through the solution during the conductivity measurements.

All the values of the potential quoted below are referred to a normal hydrogen electrode. The amounts of electrolyte adsorbed are expressed in milliequivalents per gram of charcoal.

The course of the curves expressing the dependence of the adsorption upon the potential was always reproducible in the adsorption experiments both in acids and alkalies. On the other hand, the absolute amounts of electrolyte adsorbed on different carbon electrodes, even such as had been activated simultaneously, differed by 5—10%.

Experimental results

Adsorption from 0.01 N H_2SO_4. The data expressing the dependence of the amount of SO_4''-ions adsorbed by the activated carbon electrode on its potential are given in Table 1 and in Fig. 3,

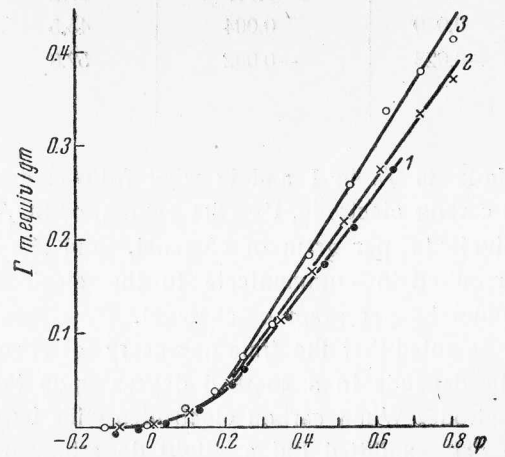

Fig. 3. Adsorption from 0.01 N H_2SO_4: *1* — variation of potential of non-platinized charcoal by the polarization method; *2* — the same relation for platinized charcoal; *3* — variation of potential of platinized charcoal produced by bubbling hydrogen.

urve *1*. In these experiments the polarization method was used to alter the potential of the carbon electrode, starting with the value of the potential which the carbon electrode acquires in the presence of oxygen. The cathodic polarization itself was carried out after the solution was saturated with nitrogen. The values of the potentials, referred to a normal hydrogen electrode, are plotted along the axis of abscissae, and the values of the amount of H_2SO_4 adsorbed, along the axis of ordinates.

Table 1

φ (in volts)	Γ (in milliequivalents per gram of charcoal)	A (in coulombs per gram of charcoal)
0.650	0.274	0
0.610	0.252	2.75
0.543	0.214	7.24
0.465	0.172	14.3
0.367	0.118	20.7
0.250	0.061	29.4
0.130	0.017	37.2
0.040	0.004	45.5
—0.028	—0.002	52.8

The symbols in Table 1 and in what follows denote: φ — the potential of the carbon electrode, Γ — the amount of SO_4''-ions adsorbed in milliequivalents per gram of charcoal, and A — the quantity of electricity required to communicate to the electrode the given potential in coulombs per gram of charcoal.

It should be noted that the time necessary for adsorption equilibrium to set in depends to a marked degree upon the porosity of the carbon electrode. When carbon electrodes with large pores were employed, the data exhibited but a slight departure from reversibility. On the other hand, when more compact electrodes were used, no reversibility of the adsorption curves was obtained upon successive cathodic and anodic polarization. For one of the compact

electrodes the data are shown in Fig. 4 in which curve *1* corresponds to cathodic polarization, and curve *2*, to anodic one. The irreversibility of the process in this case is caused by the fact that the experiment was carried out under non-equilibrium conditions.

To ensure completely reversible experimental conditions while altering the potential by the polarization method, the polarization current was switched off after the potential had been displaced to

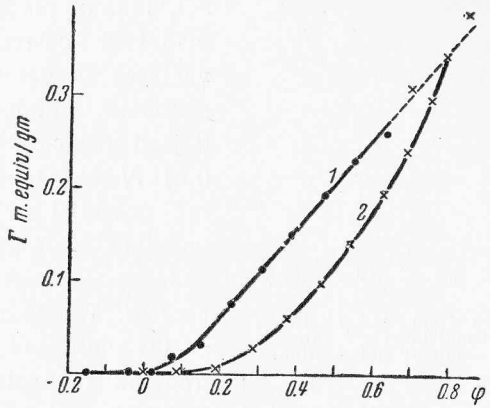

Fig. 4. Adsorption from 0.01 N H_2SO_4 under non-equilibrium condition: *1* — cathodic polarization; *2* — anodic polarization.

a definite value and, after waiting for an hour for adsorption equilibrium to set in, a measurement of the adsorption and potential was made. These experiments were carried out in the apparatus shown in Fig. 2. The results are given in Fig. 5.

The relation between the potential and the amount adsorbed was studied also on platinized charcoal electrodes; the results of these experiments are given in Fig. 3, curve 2, and can be compared with the curve for non-platinized charcoal.

These experiments were carried out in the apparatus shown in Fig. 1. The variation of the charcoal electrode potential in these experiments was effected by polarization. As can be seen from the experimental data, the character of the relation between the potential and the adsorption is exactly the same for both electrodes. The only difference between them is that the initial oxygen potential of the

platinized electrode (0.81) is higher than the initial potential of non-platinized electrode (0.65).

In 0.01 $N H_2SO_4$, from the oxygen potential to about +0.2, a linear relation exists between the adsorption and the potential. At more negative potentials, the adsorption of the electrolyte on charcoal depends considerably less upon the potential; at a potential close to that of the normal hydrogen electrode, adsorption of SO_4''-ions on platinized and non-platinized charcoal electrodes vanishes altogether. Similar results were obtained with a platinized charcoal electrode in a 0.01 N H_2SO_4 solution when the potential was varied by bubbling hydrogen. These results are represented in Fig. 3, curve *3*. The hydrogen potential of the platinized charcoal electrode in the solution we used was equal to — 0.125 V, whilst the reversible hydrogen potential of the platinized platinum electrode was — 0.132 V.

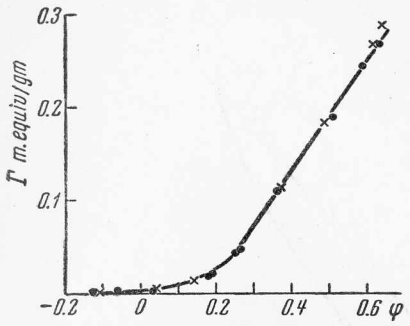

Fig. 5. Adsorption from 0.01 N H_2SO_4 under equilibrium conditions: ● — cathodic polarization; X — anodic polarization.

In order to obtain conditions closer to equilibrium in the experiments with platinized charcoal in which the potential was varied by bubbling gas, we proceeded as follows: after changing the potential to a definite value, N_2 was passed through the solution, after which we waited for 40 min. for adsorption equilibrium to set in. In this case the curves obtained upon transition from the hydrogen to the oxygen potential, and *vice versa*, only slightly differ from one another.

Besides the polarization experiments in which the transition from the original oxygen potential of the charcoal to the hydrogen potential, and *vice versa*, was studied, in a few experiments anodic polarization to more positive potentials ($\varphi = 1.05$) was carried out also. As can be seen from Fig. 6, the course of the adsorption curve remains linear even when the potential of the charcoal increases to these values. In Fig. 6 adsorption is expressed in coulombs per gram of charcoal.

While measuring the adsorption curves by the polarization method, the quantity of electricity, A, in coulombs per gram of charcoal, necessary to displace the potential of the electrode from a certain initial value to the given one, was also determined. We call the curves obtained in this manner charging curves (see the third column of Table 1). The position of the zero value of the charging curve on the axis of ordinates is of course arbitrary, since it only depends upon what value of the potential is taken as the initial one.

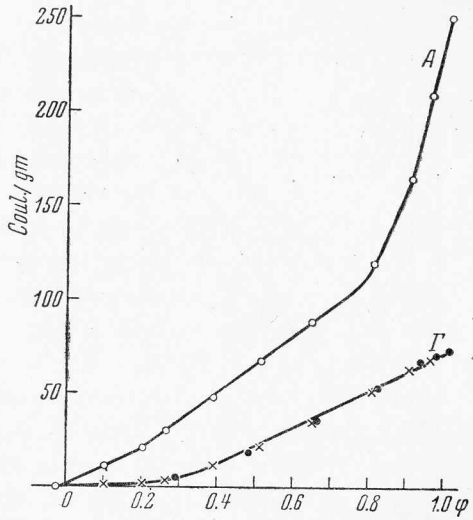

Fig. 6. Adsorption from 0.01 N H_2SO_4: Γ — adsorption curve; ● — anodic polarization, X — cathodic polarization; A — charging curve.

In Fig. 6, along with the adsorption curve, there is given the charging curve obtained on anodic polarization with 0.01 $N H_2SO_4$. As can be seen, it is approximately linear up to the potential 0.8 V.

At potentials more positive than the original oxygen potential, *viz.*, 0.8—0.9, a bend in the charging curve is observed, which corresponds to an increase in the capacity of the electrode. Upon switching off the current after anodic polarization up to 1.1, the potential and the adsorption return to the values corresponding to the oxygen potential.

Adsorption from a KOH solution. While studying the relation between the amount of KOH adsorbed from a 0.01 N solu-

tion and the potential of the carbon electrode (Table 2), it was established that when cathodic polarization was effected starting from the oxygen potential of the charcoal electrode in this solution, equal to 0.18 (at which, as is known, alkali is not adsorbed) up to — 0.1, the adsorption varied but slightly with the potential.

At more cathodic polarizations, the curve is observed to bend in the direction of a greater change in adsorption with potential.

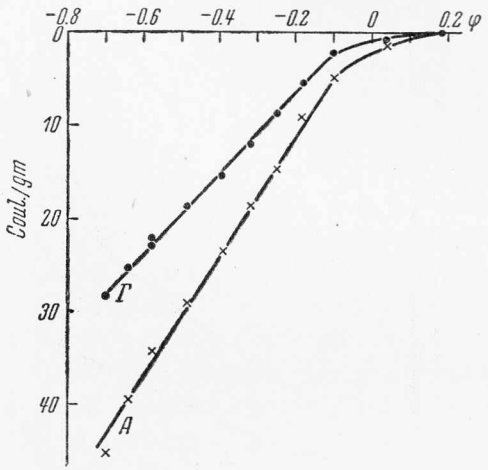

Fig. 7. Adsorption from 0.0108 *N* KOH: Γ — adsorption curve; *A* — charging curve.

A linear relation exists between the adsorption of the alkali and the potential in the region of potentials from — 0.1 to — 0.7, the value corresponding to the reversible hydrogen electrode in the given solution. These data are given in Fig. 7 (curve Γ) and in Table 2. In Fig. 7 adsorption is expressed in coulombs per gram of charcoal.

The course of the charging curve for the KOH solution (Fig. 7, curve *A*) is linear within the potential interval from — 0.1 to — 0.7; the curve bends towards the axis of abscissae at more positive potentials.

In order to be able to compare the results for the KOH solution with those for the H_2SO_4 solution, experiments were carried out

in which the electrodes used in either case were made from one and the same stick of charcoal. The data are represented by solid curves *1* and *2* in Fig. 8.

Adsorption from a 0.05 *N* Na_2SO_4 solution. The relation between the potential of the charcoal electrode and the amount of electrolyte adsorbed from a neutral 0.05 *N* Na_2SO_4 solution was studied in the same manner as in the case of acid and alkali, using the apparatus shown in Fig. 2. The oxygen potential of the carbon electrode in the given solution is equal to + 0.3 V.

In this experiment the carbon electrode was first subjected to cathodic polarization up to — 0.52, and then to anodic polarization up to + 0.52 V. Measurements of the electrical conductivity of the electrolyte were made for every change in potential. It is evident that, during hydrolytic adsorption, the electrical conductivity of the solution should increase regardless of whether an acid of alkali is being adsorbed on the charcoal. Minimum electrical conductivity corresponds to the zero point of adsorption.

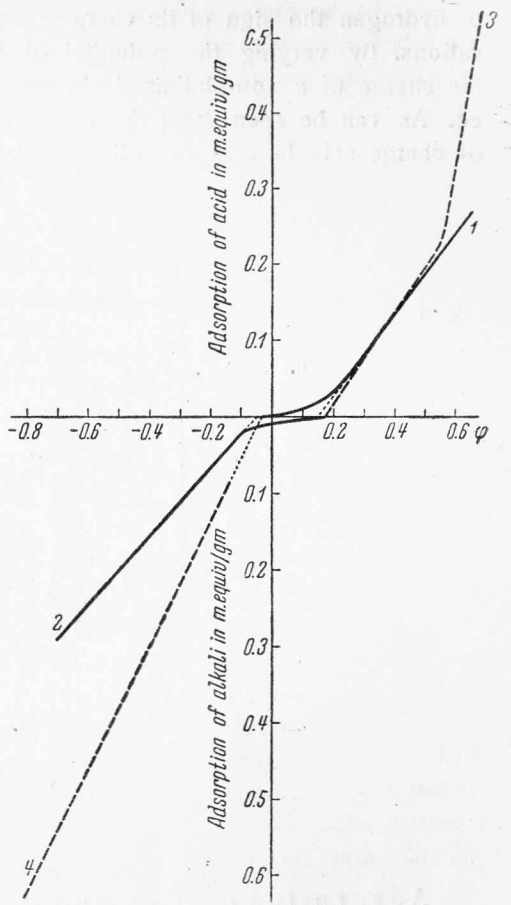

Fig. 8. Dependence of adsorption upon the potential: *1* — displacement of potential by polarization in 0.01 *N* H_2SO_4; *2* — the same in 0.01 *N* KOH; *3* — displacement of potential of oxygen-charcoal in 0.5 *N* Na_2SO_4 by changing the pH of the solution; *4* — displacement of potential of hydrogen charcoal in 0.5 *N* Na_2SO_4 by changing the pH of the solution. (The extrapolated parts of the curves are indicated with dots).

The experimental results are shown in Fig. 9. As is known from the work of our laboratory, platinized charcoal in a salt solution in an atmosphere of oxygen adsorbs anions, whilst in an atmosphere of hydrogen the sign of its charge changes and it begins to adsorb cations. By varying the potential of the charcoal by polarization, the charge of a non-platinized carbon electrode may also be reversed. As can be seen from the curve given in Fig. 9, the reversal of charge sets in at a potential $\varphi = 0.05$.

Table 2

Adsorption from 0.0108 *N* KOH

φ (in volts)	r (in milliequivalents per gram of charcoal)	*A* (in coulombs per gram of charcoal)
0.182	0	0
0.040	0.007	1.5
—0.099	0.022	4.8
—0.185	0.056	9.1
—0.248	0.090	14.6
—0.319	0,125	18.4
—0.392	0.158	23.5
—0.491	0.194	29.0
—0.582	0.226	34.1
—0.640	0.260	39.5
—0.700	0.293	45.2

Adsorption of H_2SO_4 and KOH on charcoal heated in an atmosphere of oxygen at 400° C. As has been pointed out in the introduction, at 400° C charcoal adsorbs a considerable amount of oxygen and acquires the property of adsorbing cations from the solution regardless of the nature of the gas atmosphere during the adsorption experiment.

Activated charcoal, prepared by the method described above, was heated for 12 hours at 400 °C, in a stream of purified air which passed over the charcoal at a rate of 100 cm.³ per minute. The relation between the potential and the adsorption was studied on an electrode prepared from such charcoal just as in the previous cases (Fig. 10). The experiments were carried out in the apparatus shown in Fig. 1. The initial oxygen potential of such a charcoal in 0.01 *N* H_2SO_4 is equal to +0.58, *i. e.*, by 0.07 lower than the value of the potential of charcoal activated at 950° C in carbon dioxide. The amount of acid adsorbed on this charcoal was equal to 0.008 milliequivalents per gram of charcoal. At a potential of 0.45 the adsorption fell to zero. In order to find out whether removal of oxides was taking place during cathodic polarization, oxygen was bubbled through the solution after polarization to —0.09. The carbon electrode acquired a potential of 0.57, and adsorption became equal to 0.029 milliequivalents per gram of charcoal. Apparently, a comparatively small part of the oxides was removed during cathodic polarization.

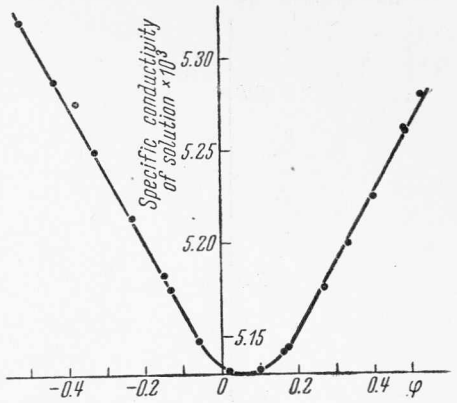

Fig. 9. Adsorption from 0.05 *N* Na_2SO_4.]

During the anodic polarization of the oxidized carbon electrode the adsorption of acid increases. In the potential interval from +0.73 to +1.14 adsorption varies linearly with the potential, whilst at potentials below 0.73 deviation from linearity is observed. The cathodic and anodic polarization experiments were carried out with different electrodes.

As has already been pointed out above, an oxidized carbon electrode in an alkaline solution adsorbs cations. In our case the adsorption of alkali from a 0.43 *N* solution of KOH amounts to 1.22 milliequivalents per gram of charcoal at an oxygen potential of the charcoal $\varphi = 0.11$. The relation between the potential of the carbon electrode and the adsorption is given in Fig. 11. As can be seen from this graph (curve *1*), during anodic polarization the adsorption of KOH falls linearly with the increase of potential from 0.11 to 0.45.

At more positive potentials (from 0.5 to 0.67), the adsorption is practically independent of the potential. Twenty hours after shutting off the polarizing current the potential returned to the value $\varphi = 0.17$, the adsorption simultaneously increasing to 1.40 milliequivalents per gram of charcoal. This increase in adsorption is apparently connected with the fact that at potentials greater than 0.5

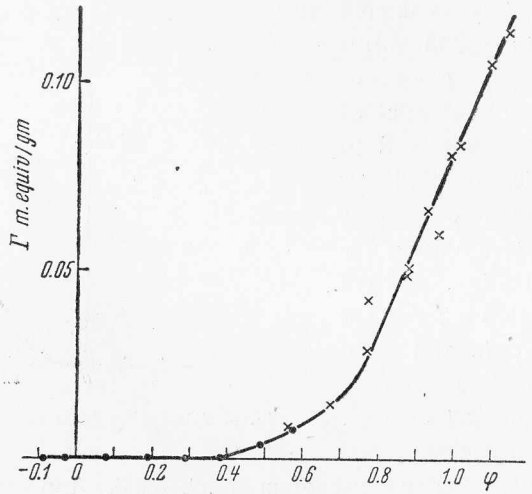

Fig. 10. Adsorption of acid on charcoal oxidized at 400° C from 0.01 *N* H_2SO_4: ● — cathodic polarization; X — anodic polarization.

additional oxidation of charcoal sets in, and the oxides are capable of adsorbing alkali. Then the carbon electrode was again polarized anodically up to a potential of 0.58, whereupon cathodic polarizing current was switched on immediately. As can be seen from Fig. 11 (curve *2*), the relation between the potential and the adsorption on the carbon electrode is linear over a range of potentials from +0.5 to −0.45.

After cathodic polarization was discontinued, the adsorption of alkali decreased from 1.95 to 1.78 milliequivalents within 20 hours. Then the electrode was again polarized cathodically to −0.8 (curve *3*) and, 20 hours after the current was switched off, the adsorption again fell from 2.0 to 1.77 milliequivalents per gram of charcoal, while the potential changed but insignificantly. The decrease in the

adsorption of alkali on the carbon electrode at potentials approaching that of a reversible hydrogen electrode in the given solution is apparently connected with the partial removal of acid oxides from the carbon electrode surface. Curve *4* represents the data obtained during anodic polarization of the carbon electrode from −0.8 to −0.1. In this case, just as in the case of cathodic polarization, a linear relation exists between the potential and the adsorption.

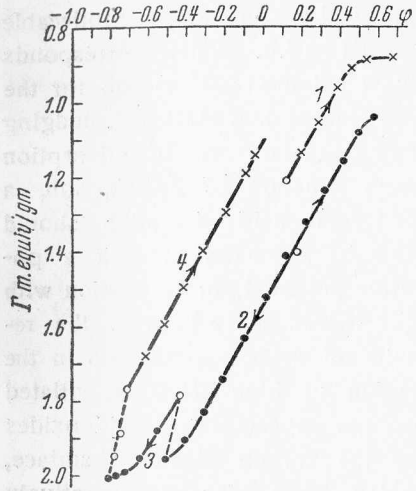

Fig. 11. Adsorption of alkali on charcoal oxidized at 400° C from 0.043 *N* KOH: X — anodic polarization; ● — cathodic polarization.

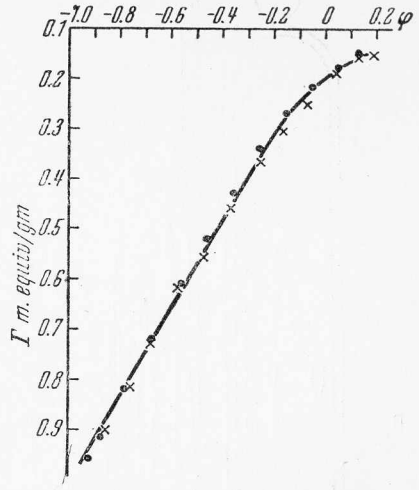

Fig. 12. Adsorption on charcoal oxidized at 400° C and heated in H_2 at 950° C from 0.043 *N* KOH: ● — cathodic polarization; X — anodic polarization.

Fig. 12 shows the relation between the potential and the adsorption, obtained after heating at 950° C in an atmosphere of hydrogen over a period of 10 hours the carbon electrode covered with oxides. As can be seen from these data, adsorption of alkali at the oxygen potential did take place to a small extent on this carbon electrode which bears witness to the fact that the acid oxides had not been completely removed from the surface of the electrode. Otherwise, the adsorption curve is of the same character as those obtained with ordinary activated charcoal.

The relation between adsorption and pH of the solution. It was of interest to compare the relation between the potential and the adsorption, obtained from experiments in which

the potential was varied by changing the pH of the solution, with the results obtained from experiments in which the potential was varied by the polarization method.

In an investigation carried out in our laboratory[2], in which a study was made of the relation between the pH of the solution and the adsorption of acid in an atmosphere of oxygen, it was found that the adsorption of anions is practically no longer noticeable at pH = 8.8, which corresponds to a potential of +0.33 for the oxygen-charcoal electrode. Judging by measurements of adsorption as a function of polarization, a noticeable acid adsorption should still be expected at such a positive potential. In connection with this it was assumed that the results of these experiments in the region of high pH were vitiated by the appearance of acid oxides on the carbon electrode surface, which takes place comparatively rapidly in alkaline solutions. In view of this it was decided to repeat these measurements in the present investigation. The apparatus in which these experiments were carried out is shown in Fig. 13. Into vessel *A* there were poured 10 cm.^{3} of a 0.5 *N* solution of Na_2SO_4 which was acidified with H_2SO_4 in such a manner that, after adsorption equilibrium had set in, the pH of the solution did not exceed 9. The measurement of the pH of the solution was carried out in vessel *B* as follows: the solution was forced by gas pressure from vessel *A* into vessel *B* which contained a platinum electrode. Hydrogen was passed through tube *C*. After measuring the pH, the solution was returned from *B* into *A* by releasing the gas pressure.

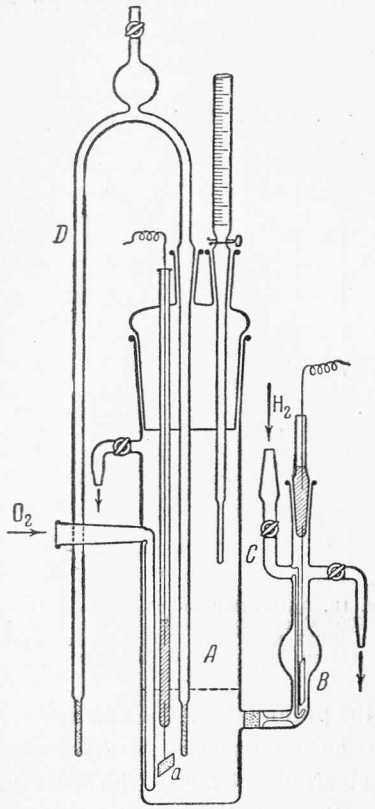

Fig. 13.

An electrode made of bakelite charcoal which weighed 0.02—0.03 gm., was immersed in the liquid in vessel *A*. The electrode was left in the apparatus overnight to ensure its being completely wetted by the solution. To avoid oxidation of the carbon, hydrogen was bubbled through the solution all the while. Then 0.5 gm. of powdered charcoal was added to the solution in vessel *A*, and oxygen was bubbled through until a constant value of the pH of the solution and the potential of the carbon electrode had set in. After equilibrium had been attained, the pH of the solution was 8.5, and the potential of the electrode +0.345. A change in the pH of the solution in vessel *A* was effected by adding a few drops of a solution of 0.19 *N* H_2SO_4 in 0.5 *N* Na_2SO_4 from a burette. The amount of electrolyte adsorbed on the electrode was determined by comparing the potentiometric titration curves of the solution with and without the charcoal. The potential of the carbon electrode was measured with the aid of an auxiliary calomel electrode, which was connected with the liquid in *A* by means of the siphon *D*. To avoid the formation of

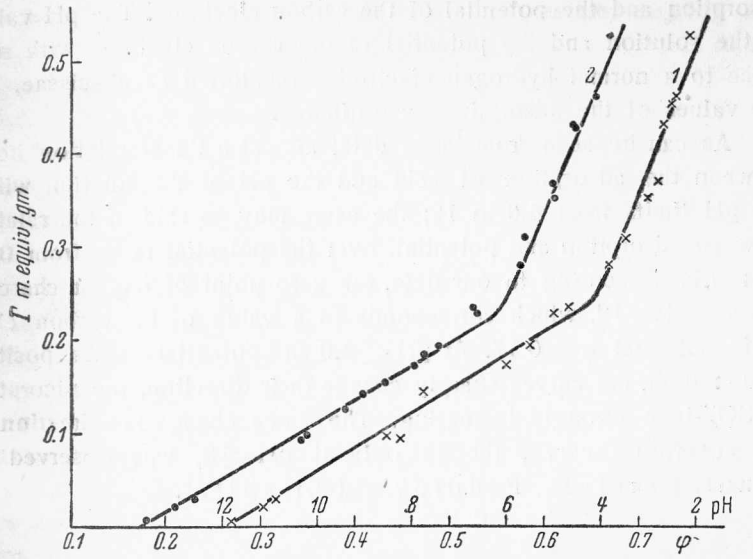

Fig. 14. Adsorption of acid on positive oxygen-charcoal as a function of (*1*) the pH of the solution; (*2*) the potential of the charcoal electrode.

acid oxides on the carbon in the pH region from 9 to 12 upon prolonged contact with the solution, inevitable when carrying out potentiometric titration by the method described, adsorption was determined for each pH value, from individual experiments with original solutions of various pH, by a volume titration of the solution before and after the adsorption experiment.

Curve *1* (Fig. 14) represents the dependence of the adsorption upon the pH of the solution, and curve *2*, the relation between the adsorption and the potential of the carbon electrode. The pH values of the solution and the potential of the carbon electrode with reference to a normal hydrogen electrode are plotted as abscissae, and the values of the adsorption as ordinates.

As can be seen from these data, almost a linear relation holds between the adsorption of acid and the pH of the solution within the pH limits from 4.0 to 12; the same may be said of the relation between adsorption and potential, over the potential range from 0.55 to + 0.17 According to our data, the zero point of oxygen-charcoal lies at pH = 12, which corresponds to a value of the carbon electrode potential $\varphi = 0.17$. At pH < 4.0 and potentials more positive than + 0.55, the curves sharply change their direction, the adsorption of SO_4''-ions strongly increasing. The same change in direction of the adsorption curve, though only at pH < 3, was observed by Bruns, Burstein, Fedotov and Lifshitz[2].

Discussion of results

The data quoted above attest in the first place to the fact that, both in the case of the adsorption of anions and in that of the adsorption of cations, a linear relation holds between the potential and the adsorption in complete agreement with the electrochemical theory. The decrease in the adsorption of anions during cathodic polarization of the carbon electrode in an acid solution is connected with the decrease in the positive charge of the carbon surface. The increase in the adsorption of cations during cathodic polarization of the carbon electrode in an alkaline solution is connected with the increase in the negative charge of the surface.

It is of particular interest that the smallest value of the cathodic polarization of oxygen-charcoal is sufficient to start the adsorption of cations from an alkaline solution.

If we assume the capacity of the double layer to be constant, and the position of the points of the zero charge to be the same for all patches of the carbon surface, the straight lines expressing the dependence of the adsorption of anions and cations upon the potential should, on crossing the axis of abscissae, form a continuous straight line. As can be seen from Fig. 8, in which curves representing the adsorption of acid and alkali (solid lines) are compared, this requirement is not completely fulfilled. At small values of the surface charge, a deviation from the linear course of the adsorption curves is observed both for the adsorption of anions and that of cations. Further, extrapolating the linear part of the curve representing the adsorption of acid to the point where it intersects the axis of abscissae, we find that this point lies at $\varphi = 0.15$ (the mean of a number of experiments), whereas upon extrapolation of the linear part of the curve representing the adsorption of alkali, we find that the intercept corresponds to $\varphi = -0.05$. It is approximately within this range of potentials, between 0.15 and − 0.05, that both adsorption of anions from an acid solution and adsorption of cations from an alkaline solution are observed. These small deviations from the conclusions drawn from the simplest scheme could be explained if we assumed, firstly, that the zero point of the charge at different points of the carbon electrode surface lies at different potentials and, secondly, that the capacity of the double layer decreases at small charges (transition to the diffuse layer). The first circumstance can explain the existence of a potential region in which there takes place the adsorption both of cations from alkaline solution and of anions from acid solution, whilst the second circumstance can explain the divergence of the values of φ obtained by extrapolation of the positive and negative branches to their points of intersection with the axis of abscissae.

However, at a concentration equal to 0.01 *N* the change in the degree of diffuseness of the double layer should be yet slightly pronounced. On the other hand, in the case of individual areas with different positions of their points of zero charge, simultaneous adsorption of cations and anions in the neighbourhood of the zero

point from one and the same solution should be expected. At the same time, as experiments on the adsorption behaviour of charcoal in KCl carried out by Frumkin, Lewina and Zarubina[1] showed, no such phenomenon is observed on transition from oxygen to hydrogen surface covering. Therefore, another explanation of the observed phenomena seems to be more plausible. This explanation follows from comparison of the curves showing the dependence of adsorption upon polarization with the curves showing the dependence of adsorption upon the potential, obtained by varying the pH of the solution. The latter are given in Fig. 8. The curve for oxygen-charcoal (*3*) was taken from our experiments, whilst that corresponding to hydrogen-charcoal (*4*), was plotted according to the data of Bruns, Burstein, Fedotov and Lifshitz.

Inasmuch as these measurements were carried out with different charcoals, the absolute values are not comparable with those obtained in the polarization experiments; however, the course of the curves obtained in both cases may be compared. The zero points obtained in the experiments with oxygen- and hydrogen-charcoals in solutions of different pH lie at $\varphi = 0.17$ and $\varphi = -0.03$, respectively. These values almost coincide with those obtained by extrapolating the curves obtained in the polarization experiments. Hence we may draw the following conclusion. There is a distinct difference in the positions of the zero points of oxygen- and hydrogen-charcoals, the zero point of oxygen-charcoal corresponding to a more positive potential, as should be expected from the character of the dipole bond between carbon and oxygen and in agreement with the experiments on charcoal oxidized at 400° C (see below). In the case of curves obtained in acid and alkali during cathodic polarization of charcoal which initially possessed an oxygen charge, gradual substitution of hydrogen for adsorbed oxygen takes place, with a corresponding transition from the zero point of oxygen-charcoal to that of hydrogen-charcoal. In order to be able to furnish an exhaustive explanation of the adsorption curves obtained experimentally, it is moreover necessary to assume that the decisive rôle in influencing the position of the zero point is played by those oxygen atoms which are deposited on the charcoal surface or removed from it within the interval, namely, from −0.05 to 0.15. This latter hypothesis requires further confirmation. It would also be necessary to elucidate

the influence of the porosity of charcoal on the degree of diffuseness of the double layer. When the adsorption curve is obtained in a neutral Na_2SO_4 solution, the zero point lies almost in the middle of the interval separating the value of the oxygen potential from that of the hydrogen potential in the same solution. In accordance with this the value of the potential at the point of zero change obtained in a Na_2SO_4 solution, namely, 0.05, lies between the values characterizing the oxygen- and hydrogen-charcoals.

As has already been pointed out above, the curve showing the dependence of the anion adsorption upon the pH of the solution for oxygen-charcoal begins to bend upwards sharply upon lowering the value of the pH below 4. Such an increase in the adsorption of the anion with increasing positive charge of the surface is often observed and may be explained by deformation of the anion and a corresponding increase in the double layer capacity. In the given case, since simultaneously with an increase in potential there occurs an increase in acidity, the appearance of molecular adsorption of the acid may also be conjectured. This bend, however, is absent on the adsorption curves obtained from polarization measurements. It is possible that this distinction is connected with the fact that the concentration of the anions is different in the two cases (0.01 *N* in the polarization experiments and 0.5 *N* in the experiments in which the pH is altered). To clear up this question it is necessary to carry out additional polarization experiments in solutions of various concentrations.

Since the capacity of the double layer formed by the cations is but slightly dependent upon the nature of the solid phase, the true charcoal surface may be determined from the slope of the adsorption curves for the adsorption of alkali, assuming that the value found for the capacity of a negatively charged mercury surface, *viz.*, 18 μF per cm.^{2}, holds in this case also.

Thus, for a change in potential of 0.3 V, the change in the adsorption of K^+-ions per gram of charcoal from a 0.01 *N* KOH solution corresponded to a change in the charge by 23 coulombs for one gram of charcoal. Hence, the following value is obtained for the surface area:

$$\frac{23 \times 10^6}{0.3 \times 18} = 4.3 \times 10^6 = 430 \text{ m.}^2.$$

For charcoal prepared in a different manner (Fig. 7), a similar calculation gives a value of 240 m.^{2} for the surface. Making use of these values for the size of the surface, we may find the value for the capacity of the double layer formed by the SO_4''-ions from the adsorption curves of the acid. In this manner a value of 21.5 μF per cm.^{2} is obtained from the polarization experiments with 0.01 N H_2SO_4. In the region where the curve expressing the dependence of the adsorption upon the potential bends upwards (experiments in which the pH is changed), a much higher value, about 90 μF per cm.^{2}, is obtained. Calculated by the method pointed out above from the curve expressing the dependence of the alkali adsorption upon the potential, the size of the surface of oxidized charcoal was found to be 495 m.^{2}, and, after destroying the oxide film by heating in H_2, 470 m.^{2}. Hence we may draw the conclusion that the capacity of the double layer for oxidized charcoal has a normal value. By extrapolating the various curves obtained with oxidized charcoal (Fig. 11) to the zero value of the alkali adsorption, we obtain the values of the potential corresponding to zero adsorption. These values lie within the limits $\varphi = 1.1 - 1.4$ V, depending upon the degree of oxidation which changes somewhat at strong cathodic and anodic polarizations. In other words, in accordance with the conceptions of Verwey and de Boer[7] and with the results obtained for a platinum electrode by Frumkin and Šlygin, in this case the presence of an oxide film causes an increase in the contact potenial at the carbon-solution boundary by an amount exceeding one volt.

The zero point determined from the curve expressing the dependence of the adsorption of acid upon the potential on oxidized charcoal lies at 0.67 V. Consequently, it is also shifted towards positive values, but to a considerably smaller degree than the zero point obtained from the adsorption curve for alkali[16].

[16] It is interesting to note that the zero point obtained by extrapolation of the curves representing the adsorption of acid by ordinary positive charcoal after anodic polarization to potential values higher than the oxygen potential, lies not at 0.15, as in the other experiments, but at 0.28 (Fig. 6), *i. e.*, is also somewhat shifted to more positive values. Evidently, under these conditions the amount of firmly bound oxygen on the surface also increases.

Thus, in the case of oxidized charcoal, there exists a considerable range of potentials in which both anion and cation adsorption may take place. This conclusion is in agreement with the data obtained in our laboratory previously, as well as with those of Kruyt's school[5], which show simultaneous adsorption of cations and anions by oxidized charcoal from solutions of neutral salts and indicate an appreciable difference in the electrical potential at different points of the oxidized charcoal surface. This is upheld by the following fact. The slope of the curve showing the dependence of acid adsorption upon the potential on oxidized charcoal (Fig. 10) is anomalously small (approximately four times smaller than that of the alkali adsorption curve). Actually, during adsorption measurements in solutions of acids we only take into account the change in the number of ions in the surface layer of the charcoal, which are bound to positive charges of the surface. However, along with positively charged patches, which attract SO_4''-ions, in the potential interval in which acid adsorption was studied, as follows from the determination of the zero point for the alkali adsorption, negatively charged patches which attract H^+-ions must also be present on the surface of this charcoal. During anodic polarization, the change in the phase-boundary potential is only partly brought about by an increase in the adsorption of anions; it is partly brought about by a decrease in the number of cations in the double layer, and this leads to a decrease in the slope of the adsorption curve for acid.

If all the adsorbed oxygen and hydrogen atoms took part in the formation of the double layer, the charging and adsorption curves would be parallel to one another. Actually, as can be seen from Figs. 6 and 7, the charging curves, which are linear over a considerable potential interval just as the adsorption curves, have a larger slope. The ratio of the slopes of the linear parts of the charging and adsorption curves amounts to 1.3—1.4. The difference between the two curves signifies that, simultaneously with the removal or deposition of ions which take part in the formation of the double layer, there also occurs a removal or deposition of gas atoms not taking part in its formation. From the linear course of the charging curves it follows that, over a considerable potential interval, the number of these gas atoms is a linear function of the potential, as was

also observed by Šlygin and Frumkin[17] in the case of platinum. In contrast to platinum, however, the degree of covering of the surface by these gases is very small (of the order of 2%)[18], and the regions of oxygen and hydrogen adsorption are not separated from one another. No signs of the formation of surface chemical compounds of a definite composition can be found on the charging curves, which is in agreement with the data of Frumkin, Burstein and Levin on the relation between the oxygen pressure and the amount of gas adsorbed by the charcoal. In order to explain the linear relation between the amount adsorbed and the potential, *i. e.*, the logarithm of the activity of the adsorbed gas, it is necessary to assume a considerable decrease in binding energy with an increase in the number of adsorbed gas atoms.

This conclusion is in agreement with the results of Blench and Garner[19], Keyes and Marshall[20] and others, who measured the heat of adsorption of oxygen on charcoal at room temperature. It was shown by these authors that, upon increase of the degree of covering of the charcoal surface with oxygen, the heat of adsorption falls from 70 to 4—5 kg. cals. In the case of charcoal, where the degree of covering of the surface is small, the latter may only be explained by the inequality of adsorption energies on different adsorption centers.

On transition to potentials more positive than the natural oxygen potential of the charcoal, the charging curve bends upward, *i. e.*, the amount of the oxygen used up increases markedly. This state, however, is far from a state of equilibrium, since after the current is switched off, the potential resumes its initial value. Unfortunately, the kinetics and the mechanism of the processes which tend to keep the value of the oxygen potential of charcoal constant, have not as yet been studied at all, and we cannot explain, for example, why, upon changing the pH of a solution by unity, the potential of the latter is displaced not by 0.058, but, on the average, only by

[17] Šlygin and Frumkin, Acta Physicochimica URSS, **3**, 812 (1935).
[18] There may also be electrochemically inactive atoms of adsorbed gases, particularly oxygen, present on the charcoal surface, which will not show any influence upon the course of the charging curves.
[19] Blench and Garner, J. Chem. Soc., **125**, 1288 (1924).
[20] Keyes and Marshall, J. Am. Chem. Soc., **49**, 157 (1927).

0.050. It is interesting that, on transition to the region of the hydrogen overvoltage (in alkaline solutions), no change whatsoever in the course of the charging curves is observed.

The deviation from the linear course which is observed over the initial section of the charging curve (see, for exmaple, Fig. 7, curve *2*), is connected, evidently, with a state of incomplete equilibrium through which we pass when polarizing with current. If we preliminarily polarize cathodically the charcoal in the same alkaline solution to which the charging curve of Fig. 7 refers, and then return it to its initial oxygen potential, the charging curve maintains its linear course even in the interval of potentials between $\varphi = -0.1$ and $\varphi = 0.2$.

Apparently a certain preliminary displacement of the potential from its initial value is necessary in order that the processes of removal and deposition of adsorbed atoms should proceed at a sufficient rate.

If we compare the character of the adsorption-potential curves which were obtained for charcoal and platinized platinum, the first thing that strikes us is the considerably more simple shape of these curves, and their closer approach to linearity in the case of charcoal. Since violation of the linear course of the curve in the case of platinum is in the main determined by the influence of adsorbed atoms on the mechanism by which the interfacial potential originates[21], this difference must be explained by the considerably smaller surface concentration of adsorbed atoms on charcoal in comparison with platinum, and also by the circumstance that the change in their surface concentration takes place, in contrast to platinum, quite regularly over a very wide potential interval. However, as has been pointed out above, the influence of adsorbed atoms on the structure of the double layer may be detected, in the case of charcoal also, and is manifested by the difference in the position of the zero points in solutions of acid and alkali. In the case of oxidized charcoals, on the other hand, where the surface concentration of oxygen is considerably larger, the presence of adsorbed atoms leads to a sharp change in the adsorption properties of the charcoal.

[21] Frumkin and Šlygin, Acta Physicochimica URSS, **5**, 819 (1936).

Summary

A study has been made of the relation between the amount of electrolyte adsorbed and the potential of an activated charcoal electrode in solutions of H_2SO_4, KOH and Na_2SO_4. This relation is linear over a wide interval of potentials, but begins to deviate from linearity in the neighbourhood of the zero-point charge of the charcoal. The data obtained by this method are compared with the results of adsorption measurements carried out with hydrogen- and oxygen-charcoal electrodes in solutions of different pH. It was shown that the position of the zero-point charge of the charcoal electrode, depending upon the conditions under which the determination is being carried out, varies within the limits from $\varphi = -0.05$ to $\varphi = 0.15$, and that these differences may be explained by the influence of adsorbed oxygen atoms upon the mechanism of the origination of the interfacial potential. It was shown that a linear relation exists between the quantity of electricity necessary to displace the potential of the charcoal electrode by a definite amount and the value of this displacement. There was studied the relation between the potential and the amount adsorbed for a charcoal electrode oxidized at a temperature of 400 ° C, and it was shown that the phenomena observed may in this case also be explained with the aid of the electrochemical theory if we take into account the dipole character of the bond between carbon and oxygen, as well as the non-uniformity of the surface of such charcoal electrodes.

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