THE CHEMISORPTION OF OXYGEN AND THE ADSORPTION OF ELECTROLYTES ON ACTIVATED CARBON

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According to the electrochemical theory of the adsorption of electrolytes on carbon [1], carbon activated at 900° behaves in electrolyte solutions as a gas electrode. The adsorption of electrolytes is determined by the formation of an electrical double layer as a result of the ionization of electrochemically active oxygen or hydrogen chemisorbed on the carbon surface. The potential difference between the carbon and the solution depends on the chemical potential of the adsorbed gases and the pH of the solution. The ionization of oxygen may involve the attachment of two or four electrons depending on the chemisorption conditions [2]. The correctness of these ideas is confirmed by the existence of a linear relationship between the quantity of adsorbed ions and the potential of the carbon electrode [3].

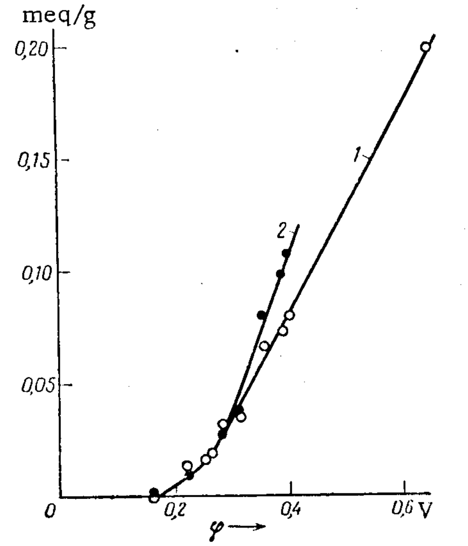
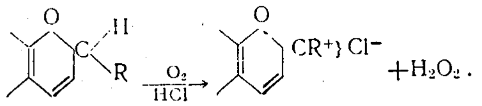


Fig. 1. Relationship between the adsorption of H_2SO_4 (1), the quantity of chemisorbed oxygen (2) and the potential of a carbon electrode in 0.01 N H_2SO_4. The point on curve 1 at $\varphi = 0.65$ was obtained with air admitted.

From the viewpoint of the chemical theory developed by Schilow, and coworkers [4], the adsorption of electrolytes on carbon is regarded as a process of salt formation resulting from the reaction between the surface oxides and the ions in the solution. The chemical theory was developed further by Garten and Weiss, who made an attempt to bring the conclusions reached on the basis of this theory closer to the results of electrochemical studies [5, 6].* Garten and Weiss consider that the adsorption of electrolytes involves the participation of the functional groups on the carbon surface; the structure of these groups changes on oxidation or reduction. The adsorption of acid is attributed to the presence of the chromene (benzopyran) structure which, on reaction with oxygen and acid, forms a carbonium ion and H_2O_2:



(1)

On the basis of this theory the authors derive an equation which can be represented in the form

$$E_h = E_{1/2} - \frac{2,3RT}{2F}\log\frac{1-\alpha}{\alpha}, \qquad (2)$$

where E_h is the potential of the redox system, α is the relative concentration of the oxidized form (the carbonium ion) which, in accordance with (1) is proportional to the adsorption of HCl, and $E_{1/2}$ is the value of E_h when $\alpha = 1/2$.

Garten and Weiss consider that proof of the correctness of their theory is provided by the fact that Eq. (2), which they derived, leads to results which agree with the data of Kuchinskii, Burshtein, and Frumkin on the relationship be-

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* Carbon which has been subjected to high temperature activation, and whose properties are examined in the present paper, is referred to by Garten and Weiss and by certain other non-Soviet authors as H-carbon.

tween the adsorption of acid on a carbon electrode and the potential [3]. Examination of the graph given by Garten and Weiss [5] shows that Eq. (2) does in fact describe approximately the experimental data if we assume the values $E_{1/2} = 0.42$ and $\alpha = A/0.303$, where A is the measured value of the adsorption in meq per g of carbon. At the same time, however, the coefficient of the logarithmic term in the right hand side of Eq. (2) must be given the value 0.24 instead of the theoretical value 0.029, so that the theory is not confirmed.

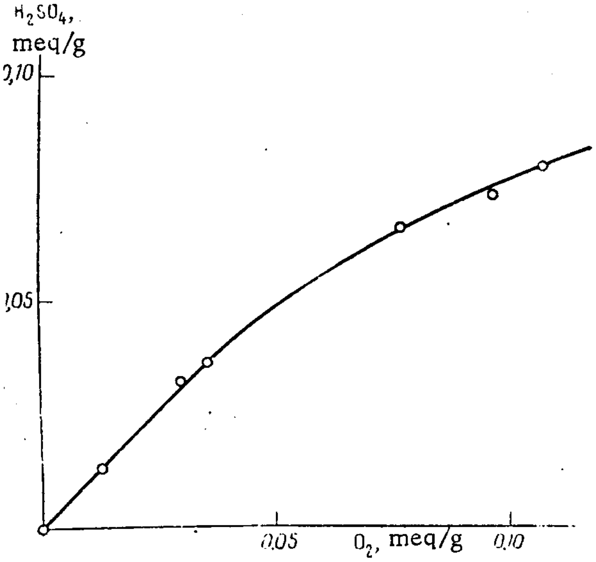

Fig. 2. Relationship between the adsorption of H_2SO_4 from 0.01 N H_2SO_4 and the quantity of chemisorbed oxygen.

In our earlier studies [2, 7, 9] it was shown that carbon which has been efficiently degassed at 950° does not adsorbe anions from dilute solutions of H_2SO_4 or HCl. In the study of the adsorption of acid on a carbon electrode whose potential is altered by cathodic polarization [3], it was found that the electrocapillary zero of the carbon lies in the potential range 0.05-0.15 V, relative to the normal hydrogen electrode.

It was of interest to determine directly the potential of degassed carbon and the change in potential accompanying the adsorption of different quantities of oxygen on carbon whose surface had been previously degassed by prolonged heating in vacuo at high temperature.

The procedure for degassing the electrolyte has been described earlier [8]. The relationship between the potential of the carbon electrode and the quantity of adsorbed oxygen and electrolyte was determined in an apparatus analogous to that described in the same paper. The lower part of the apparatus, in which the carbon was placed, was made from quartz. The electrodes, made of activated sugar carbon, were degassed at a temperature of 950° for 72-96 hours down to a pressure of $2.5 \cdot 10^{-6}$ mm, after which the apparatus was sealed off from the vacuum system. In the experiments on the adsorption of oxygen, the carbon was cooled to 20°, a measured quantity of gas was admitted and the apparatus was sealed off after adsorption equilibrium had been established. The ampoule containing the degassed solution of 0.01 N H_2SO_4 was then broken and, in order to determine accurately the concentration, which changes slightly when the solution is degassed, the electrical conductivity of this orginal solution was measured in a special cell sealed to the apparatus. The solution was then brought into contact with the carbon and the adsorption of acid on the carbon was determined from the change in the electrical conductivity. The potential of the carbon electrode was measured relative to an Hg-Hg_2SO_4 electrode. Curve 1 in Fig. 1 gives the relationship between the potential of the carbon electrode relative to a normal hydrogen electrode and the quantity of adsorbed acid.

The potential of a carbon electrode which had been thoroughly degassed in vacuo lay in the range 0.14-0.19 V, with an average value of 0.16 V relative to the normal hydrogen electrode. At this potential, no adsorption of SO_4^{2-} ions from the solution took place. When the oxygen was adsorbed, the potential of the carbon was displaced to more positive values, with increase in the quantity of adsorbed oxygen (curve 2 in Fig. 1). With increase in the positive value of the potential, there is an increase in the adsorption of H_2SO_4 and from 0.250 to 0.650 V, the relationship between the adsorption of acid and the potential is linear.

So long as the quantity of adsorbed oxygen is low, the quantity of adsorbed acid is equivalent to the quantity of oxygen adsorbed by the carbon (Fig. 2); in other words, the process of acid adsorption takes place by the mechanism

$$C_xO + 2H^+ + SO_4^{2-} \rightarrow C_x^{2+} \ldots SO_4^{2-} + H_2O. \tag{3}$$

The positive charges on the carbon and the negative charges of the anions form the two sides of the electrical double layer. This result is in complete accordance with the data obtained earlier [9]; under the conditions of our experiments, no hydrogen peroxide is formed. With increase in the quantity of absorbed oxygen, the relationship (3) breaks down, the adsorption of oxygen increasing more rapidly than the adsorption of acid (Fig. 1). In other words, not all of the absorbed oxygen exchanges with SO_4^{2-} anions according to Eq. (3) and a certain proportion of chemisorbed oxygen remains on the surface of the carbon in equilibrium with the solution, whereas at potentials $\varphi < 0.32$N the concentration of chemisorbed oxygen in equilibrium with the solution can be neglected.

These results agree in general with those obtained earlier, although the curve giving the relationship between the adsorption and the potential is displaced slightly (by 0.05-0.1 V) to more positive potentials compared with the curves given in [3], which were obtained for carbon subjected to cathodic polarization.

The fact that the degassed carbon does not adsorb the anions in the solution indicates that its surface does not carry a positive charge. On the other hand, the fact that the smallest displacement of its potential to more positive values leads to the adsorption of SO_4^{2-} ions indicates that the surface of the degassed carbon does not carry a negative charge, which might have been produced as a result of the chemisorption of OH^- ions from the water (see below). Thus the measured value of the potential of the degassed electrode must be regarded as the electrocapillary zero of the carbon surface for this method of preparation.* The diffusion of curve 1 in Fig. 1 from linearity close to this potential is possibly related to the highly diffuse character of the double layer at low surface charges.

We also studied the change in the potential of the degassed carbon electrode when the acid was replaced by alkali. After the carbon had been brought into contact with the acid, an ampoule containing alkali was broken in the apparatus, no air allowed to enter the apparatus, and the pH was brought to ~12 (Fig. 3). It was found that the potential in alkali (section b) is displaced by almost 0.2 V towards more negative values compared with the potential in acid (section a). When air is passed into the system, the electrode potential is gradually displaced in the positive direction to 0.18 V (section c) and when acid is added to the potential of the carbon in air reaches the value +0.65 V (section d).

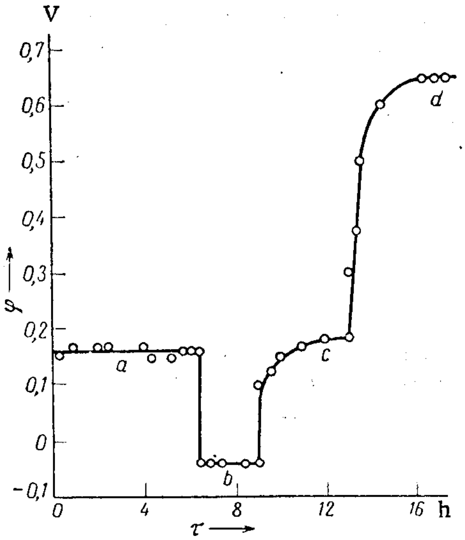

Fig. 3. The potential of a degassed carbon electrode: a) In 0.01 N H_2SO_4; b) after the solution has been made alkaline; c) after the passage of air; d) after acidification of the solution.

The displacement of the potential of the carbon to more negative values was accompanied by the adsorption of alkali (0.066 meq per g), which decreased to zero in contact with air. The adsorption of alkali on degassed carbon was discovered earlier by one of the present authors [10]. This adsorption was attributed to the ionization of hydrogen, which is present in the activated carbon and is not removed even on prolonged degassing at high temperatures. This explanation does not, however, agree with the results obtained here. Since the potential of degassed carbon in 0.01 N H_2SO_4 is close to the potential acquired by carbon in alkali in the presence of air, i.e., under conditions when chemisorption of oxygen undoubtedly takes place on the carbon surface, it must be assumed that on going from acid to alkaline solution, chemisorbed $>$O or $-$OH groups appear on the surface of the degassed carbon as a result of the discharge of OH^- ions. The negative charges which are produced on the surface in this process attract K^+ ions, i.e., the over-all effect is the adsorption of KOH, accompanied by a displacement of the potential to more negative values:

$$C_x + OH^- \rightleftarrows C_x^-(OH), \qquad (4)$$

where $C_x^-(OH)$ denotes the negatively charged carbon surface with chemisorbed OH (or O) groups. When oxygen is introduced into the system, the concentration of chemisorbed oxygen groups increases and Reaction (4) moves in the reverse direction, leading to a displacement of the potential to more positive values and desorption of the alkali.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
