EXAMINATION OF CARBON ADSORBENTS BY POTENTIOMETRIC TITRATION UNDER ISOELECTRIC CONDITIONS

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The adsorptive properties of carbon adsorbents have been studied by the method of potentiometric titration at constant total surface charge density Q which had been developed by A. N. Frumkin and O. A. Petrii and was experimentally verified for Pt group metals [1, 2]. This method represents a further improvement of the method of isoelectric potential shifts [3, 4], and allows one to examine in detail the effect of solution pH on electric double-layer structure at solid electrodes.

In the present work we examine the possibility of using the method of potentiometric titration under isoelectric conditions to obtain the dependence of the potential of zero total charge on solution pH in the case of carbon electrodes.

Earlier studies [5] of the isoelectric potential shifts of carbon electrodes had only been carried out in H_2SO_4 solution (pH 2) and in KOH solution (pH 12).

The experiments were done in 0.1 N K_2SO_4 on activated sugar charcoal with a surface area of $S=500$ m^2/g and on carbon black with $S=350$ m^2/g. The method of adsorbent preparation was reported in [6]. The surface area was determined by the BET method. Both adsorbents contained 0.2% Pt. The technique of potentiometric titration and the cell design were practically the same as those described in [1]. A weighed amount of activated carbon (0.06-0.07 g) or carbon black (0.1-0.12 g) was accommodated in a gold-plated platinum screen. The starting solution was 0.1 N K_2SO_4 acidified with H_2SO_4 (10^{-2} N) to pH 2.4. A glass electrode was introduced into the cell in order to control the pH variation during titration. A saturated calomel electrode was used as the reference electrode. The solution was agitated by passing argon. First the test electrode was cathodically polarized to a potential of $\varphi=-0.05$ V†, then anodically to a particular value of potential φ_r. At this potential the electrode was held until the current had dropped to zero. With a system of burets, a certain amount of 0.1 N $K_2SO_4+10^{-2}$ N KOH solution (pH 11.8) was added to the working part of the cell, and the pH change of the solution as well as the potential change of the working electrode were recorded. It must be noted that a long time is required to establish the equilibrium value of electrode potential; for electrodes of activated carbon, it takes up to 4-6 h when the pH is changed by one unit in the pH range from 2.4 to 4. This time becomes even longer as one goes to neutral and alkaline pH (up to 10-12 h).

At first we examined the reversibility of the potentiometric titration curves over the wide pH range from 2.4 to 11.8. To this end the pH of the starting solution was systematically brought to values of 3, 4, 5, etc., and then back titration was carried out with 0.1 N $K_2SO_4+10^{-2}$ N H_2SO_4 solution. It was found that reversibility exists in a narrow interval of pH values, which goes up to 4.5 in the case of activated carbon, and up to 6.5 in the case of carbon black. At higher pH values the potentiometric titration curves became irreversible, despite the fact that the electrode was held for a long time (up to 16-24 h) in each point during the back titration.

A similar effect had previously been noticed for Pt electordes [1]. Satisfactory reversibility in the neutral and weakly alkaline pH range could be achieved by adding 10^{-3} N H_3PO_4 as a buffer to the solution, just as done previously for Pt electrodes [1]. Since there is complete agreement between the charging curves measured in acidified 0.1 N K_2SO_4 solutions on carbon electrodes with and without the phosphoric acid addition, it seems that the introduction of 10^{-3} N H_3PO_4 has no effect on the adsorption process itself but only serves to level out the pH between different surface points during the titration. Reversible potentiometric titration curves could

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* Deceased.

† All potentials are reported relative to the reversible hydrogen electrode in the same solution (as φ_r).

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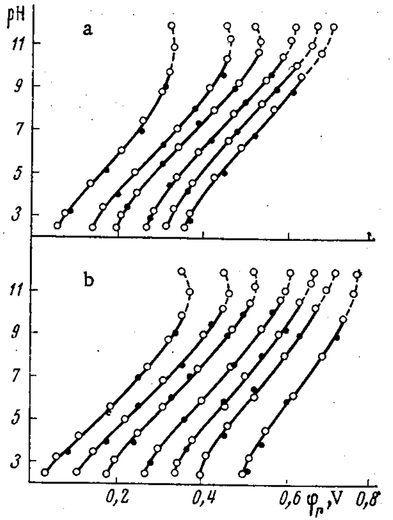

Fig. 1

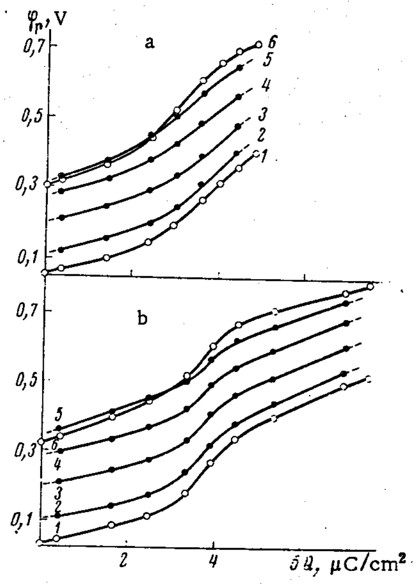

Fig. 2

Fig. 1. The potentials of carbon (a) and carbon black (b) electrodes as functions of pH at constant total surface charge density in 0.1 N K_2SO_4.

Fig. 2. Charging curves of carbon (a) and carbon black (b) electrodes in 0.1 N K_2SO_4 solutions with pH 2.4 (1), 4 (2), 6 (4), 10 (5), and 11.8 (6). [pH for (3) not given in Russian original – Consultants Bureau.]

thus be obtained in the pH range from 2.4 to 10; at higher pH reversibility could not be attained, which indicates that the adsorption process itself is slow.

While determining the potential range over which the pH–φ_r curves are reversible, we detected some difference in behavior between the carbon and carbon black electrodes. On carbon, reversibility is observed over the φ_r range from 0.06 to 0.36 V, while in the case of carbon black the φ_r range is considerably wider: from 0.04 to 0.5 V, i.e., it comprises, not only the hydrogen and "double-layer" regions of potential but also the starting section of the oxygen adsorption region on the electrode. This difference obviously is caused by the different structures of carbon and carbon black, more precisely the effect of the microporosity of the carbon samples on the adsorption processes at higher positive potentials. The potentiometric titration curves obtained under isoelectric conditions at different starting φ_r are reported in Fig. 1.

From the charging curve measured in 0.1 N $K_2SO_4 + 10^{-2}$ N H_2SO_4 solution (pH 2.4) and from the isoelectric potential shifts at different starting φ_r we calculated the charging curves of the first kind which correspond to the various pH values from 2.4 to 11.8 (Fig. 2). The curve for pH 10 thus calculated practically coincided with the charging curve measured directly in 0.1 N $K_2SO_4 + 10^{-2}$ N KOH solution with pH 11.8; this confirms that the measurements performed were correct.

The investigations made above enable us to find the potential φ_{pztc} ($\varphi_{Q=0}$) corresponding to zero total surface charge, as a function of solution pH. According to [7], the potential of zero total charge $\varphi_{Q=0}$ should be set up when an electrode previously completely degassed in vacuum is immersed into the solution. On car-

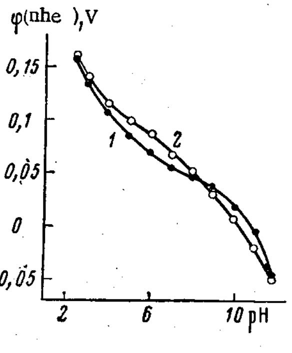

Fig. 3. The potential of zero total charge as a function of solution pH on carbon (1) and carbon black (2) electrodes.

bon in acidic solution, according to the data of [5], $\varphi_{Q=0}$ is +0.16 V (vs nhe). If this value is also taken as the potential of zero total charge for acidified 0.1 N K_2SO_4 solution, then one can calculate the curve which shows φ_{pztc} as a function of solution pH (Fig. 3). The average shift in φ_{pztc} over the pH range from 2.4 to 10 is about 20 mV for a pH change of one unit. From the data reported in [5], which were obtained in H_2SO_4 solution of pH 2 at $\varphi = 0.22$ V (nhe) and in KOH solution of pH 12 corresponding to a potential of -0.05 V, the potential change is 27 mV for a pH change of one unit.

The results obtained show that the method of potentiometric titration under isoelectric conditions which previously had been used for Pt and Rh electrodes can also be used for examining the effect of solution pH on electric double-layer structure of carbon electrodes.

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NEW TYPE OF INHIBITOR AGAINST THE THERMOOXIDATIVE DEGRATION OF POLYMERS

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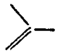
Various processes for the production of polyarylenealkylenes (PAA) of low molecular weight (10^2-10^3) are widely known [1]. The effect, observed by us for polyarylenealkylenes having only the arylenemethylene residue  — CH_2~ in common, of inhibiting the thermooxidative degradation of polymers is somewhat unexpected. Nevertheless, this effect was established by us for linear and crosslinked polymethacrylates [2], polystyrene, polyformaldehyde, and several other polymers.

In the literature there are, altogether, a few references in which the possibility is raised that radical of the type R—CH— can participate in the inhibition of free radical reactions [3-7]. Amongst hydrocarbons not containing phenolic or amine groups, nor atoms of phosphorus, nitrogen, oxygen and the like, only polyconjugated systems giving EPR signals have been examined as antioxidants or heat stabilizers [5-8]. The inhibiting action of 2-arylindanediones-1,3 containing the C—H link and a tertiary carbon atom has been demonstrated in the case of the liquid phase oxidation of ethylbenzene [3]. It has been suggested [4] that the hydrogen atoms of the methylene bridge in bisphenols can participate in chain scission during radical oxidation, along with the hydroxyphenols. The important role of the methylene groups of bisphenols in the inhibition of the oxidation of paraffins is pointed out in [6], while in [9] mention is made of the utilization of diphenylmethane and diphenanthrylmethane to inhibit undesirable processes in processing polyvinyl chloride.

The addition of PAA in quantities of 0.1-10 wt.% considerably reduces the loss in mass of polystyrene (Fig. 1) and polymethylmethacrylate (PMMA) under conditions of thermooxidative degradation at 200-220° C. In the latter case (Table 1) the stabilizing action was assessed in terms of the ratio between the loss in mass of unstabilized and stabilized samples of block PMMA ($\bar{M}_V = 9 \cdot 10^5$). If the reaction responsible for inhibiting the thermooxidative degradation of PMMA is that of the formation of a methene radical in the PAA on account of

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