RADIOCHEMICAL METHOD FOR STUDYING ADSORPTION ON SMOOTH METALS

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An earlier paper [1]* described a new method for studying adsorption from solutions on metals by means of radioactive isotopes. Its essential features are as follows: for the measurement of the radioactivity of the adsorbed species, an electrode in the form of a disc is lowered to the bottom of a cell, the foot of which consists of a membrane. The increase in the radioactivity due to the adsorption of the labeled substances is recorded by means of a radiation counter situated close to the membrane. At the present time this method has been used in a large number of investigations, in which adsorption has been studied on metals with a highly developed surface, for example, platinized [2], rhodized [3], and palladized [3] platinum. In [1] it is also pointed out that it is possible in principle to use this method to study adsorption on smooth metals.

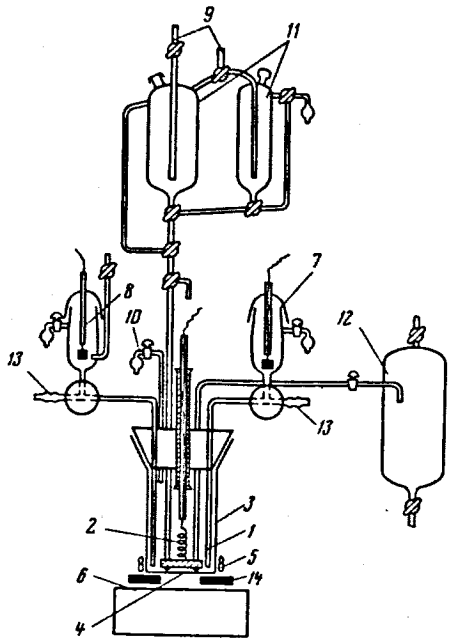


Fig. 1. Cell design: 1) working electrode; 2) spring made of fine platinum wire, to maintain contact in the electrical circuit with the electrode in the low position; 3) body of cell; 4) Terylene membrane; 5) device for attaching the membrane to the body of the cell; 6) radioactive radiation counter; 7) auxiliary electrode; 8) reference electrode; 9) gas input into cell; 10) gas outlet from cell; 11) vessels for the preliminary preparation of the solutions; 12) vessel for pouring off the solutions; 13) olives for washing the tubes connecting the main volume of the cell with the reference electrode and auxiliary electrode; 14) lead shield.

In order to carry out the measurements we constructed a cell with the design shown in Fig. 1. The body of the cell consisted of a glass (Pyrex) tube with internal diameter 19 mm. The electrode was prepared from platinum with a thickness of 3 mm (platinum concentration 99.990%) and had the form of a disc with diameter 17 mm. The lower end face of the body of the cell was polished, and the membrane was attached to it. The membrane was held stretched by means of a special device. Of the large number of synthetic films which we tested, terylene was found to be the most suitable. This material undergoes practically no swelling in aqueous solutions and adsorbs both inorganic and organic substances weakly (an exception among the large number of substances which we studied was the acetate ion). A membrane of this kind, with thickness $\sim 3\ \mu$, once stretched on the cell, sometimes serves for several weeks. The electrode was lowered to the foot of the cell by means of a cylindrical ground-glass joint. Breakdown of contact in the electrical circuit with the electrode in the low position was prevented (contact is necessary in order to keep the potential of the electrode constant) by means of a fine platinum spring joining the "foot" of the electrode to a platinum hook, sealed into the piston of the cylindrical ground-glass joint.

The end of the cell is fitted with tubes for the introduction and removal of the solutions and gases. The solutions were re-

* The same paper also gives a brief review of other methods for studying adsorption by means of isotopes.

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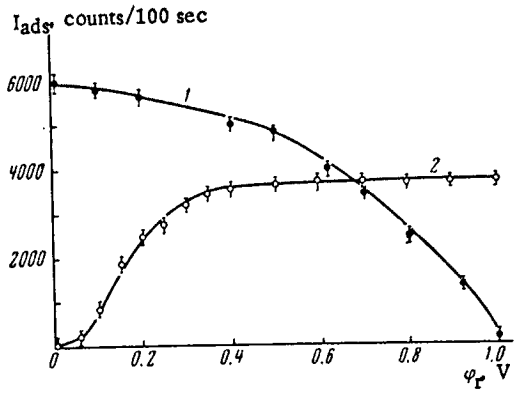


Fig. 2. Dependence of the radioactivity on the electrode potential for bromide anions (2) and thallium cations (1) adsorbed on a smooth platinum electrode from 10^{-1}N H_2SO_4 + 10^{-4} N NaBr and 10^{-1} N H_2SO_4 + 10^{-4} Tl_2SO_4 solutions, respectively.

moved by slightly reducing the pressure in the vessel by means of a syringe. The gases (argon, hydrogen) were passed successively by means of a system of taps through the vessel 11 and then through the main electrochemical cell. The design of the cell also makes it possible to pass the gases in parallel into different cells for the preliminary preparation of the solutions. The lid of the cell can be made of Teflon, carrying holes into which glass tubes are fitted. The glass-blowing is then reduced to a minimum.

The design of the cell described above is optimal, since it makes it possible to record the radioactivity of substances adsorbed on the electrode when the radioactivity of the "background" has been reduced to a minimum. The latter is achieved, on the one hand, by using a small volume of solution (1-2 ml) and on the other hand by using a large electrode thickness and by having a small distance between the electrode and the walls of the cell.

The results of the experiments on the study of the potential dependence of the adsorption of bromide anions and thallium cations on a smooth platinum electrode are given in Fig. 2. The "zero background," corresponding to the magnitude of the radioactivity measured for the low position of the electrode with practically no adsorption of radioactive* ions, amounted to 1500 and 900 counts/min for solutions of sodium bromide and thallium sulfate, respectively. These results are in good qualitative agreement with data on the determination of the dependence of the adsorption of these ions on potential by other methods [4].

In the experiments, we used electrodes, the surfaces of which, after factory treatment, were polished with chamois leather. Before the start of the experiments, the electrodes were activated by means of alternating anodic-cathodic polarization in 1 N H_2SO_4 with a current density of 1 mA/cm^2. Preliminary experiments (rapid charging curves) showed that the roughness coefficient of these electrodes did not exceed 3. The rate of change of potential in the experiments, the results of which are given in Fig. 2, was 20 mV · min^{-1}.

Thus, the present work has shown that the principle put forward in [1] can also be applied to the study of the adsorption of surface-active ions on smooth metals at low concentrations of the adsorbate (less than 10^{-3} M). In those cases where as a consequence of adsorption (or electrodeposition) there is a change in the concentration of the radioactive substances in the solution, an appropriate correction must be introduced into the "background," or the solution must be replaced by a fresh portion.

It should be borne in mind that the use of the method described encounters fundamental limitations when the potential of adsorption (or electrodeposition) can be maintained only by passing appreciable currents. Under these conditions, for the low position of the electrode, its surface shows appreciable departure from the equipotential state.

The version of the cell described in the present paper is also optimal when it is necessary to increase the sensitivity and accuracy of the measurement of adsorption on metals with a highly developed surface.

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* This was achieved by adding a large excess of a stable salt (NaBr, Tl_2SO_4) to the solution.

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