78. S. Ya. Pshezhetskii and S. A. Kamenetskaya, Zhur. Fiz. Khim., 23, 136 (1949).
79. S. Ya. Pshezhetskii and I. N. Vlodavets, Zhur. Fiz. Khim., 25, 613 (1951).
80. A. I. Kurilenko, I. V. Kul'kova, I. A. Rybakova, and M. I. Temkin, Zhur. Fiz. Khim., 32, 1044 (1958).
81. Ya. M. Fogel', B. G. Nadykto, V. I. Shvachko, and V. F. Rybalko, Zhur. Fiz. Khim., 38, 2397 (1964) [Russ. J. Phys. Chem., 1294 (1964)].
82. A. A. Rakov, Candidate's Thesis, Karpov Physicochemical Institute, Moscow, 1947.
83. I. N. Pospelova, A. A. Rakov, and S. Ya. Pshezhetskii, Zhur. Fiz. Khim., 30, 1434 (1956).
84. R. Kh. Burshtein and A. N. Frumkin, Dokl. Akad. Nauk SSSR, 32, 327 (1941).
85. L. Ya. Margolis, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 225 (1959).

Institute of Electrochemistry,
USSR Academy of Sciences

Lomonosov Moscow State
University

U. D. C. 541.13-541.183.2

STUDY OF THE STRUCTURE OF THE ELECTRICAL DOUBLE LAYER ON PLATINUM BY THE RADIOACTIVE TRACER METHOD

N. A. Balashova and V. E. Kazarinov

When a metal is immersed in a solution of an electrolyte, a layer whose structure has a powerful influence on the course of electrochemical reactions (as first pointed out by Frumkin) appears at the phase boundary.

The primary process in the formation of this surface layer is adsorption of ions, atoms, and molecules, determined by the electrical and chemical forces which operate at the interface and by the properties of the adsorbed species. The complexity of these processes and their specificity with respect to particular systems necessitate a detailed study by methods of very high accuracy and sensitivity.

The structure of the surface layer is usually investigated by a variety of electrochemical methods. These give an insight, specifically, into the very important influence of the potential drop at the electrode–electrolyte interface upon the primary process. A large number of these studies, particularly at the liquid mercury electrode, have been reported.

However, electrochemical methods cannot give direct access to the qualitative and quantitative composition of the surface layer. For this, the methods of analytical chemistry are required. Euler was the first to study the adsorption of silver ions on silver by a chemical method[1]. Frumkin and Obrucheva first demonstrated the relationship between ion adsorption and the formation of an electrical double layer on platinum by chemical titration[2]. Kolthoff and Kameda[3] studied the adsorption of electrolytes by similar methods. The determination of amounts adsorbed by chemical methods is very difficult, and sometimes even impossible, because of the minute amounts involved and of the lack of suitable analytical techniques: therefore, chemical methods have not been widely applied to these problems.

The radioactive tracer method, in which the element under study is labelled with one of its radioactive isotopes in solution or in the solid phase, has proved very fruitful in this respect. Changes in the radioactivity of the experimental system give a fast, accurate, and very reliable indication of the transfer of species across the phase boundary. This method is the most sensitive of all the existing methods for observing the behaviour of the components of a metal–electrolyte system, and has achieved increasing importance in recent years. Its earliest applications to the study of metal ion adsorption, exchange, and discharge processes are due to Hevesy and Paneth[4-7] and to Spitsyn[8], who used naturally occurring radioactive isotopes, and more recently to Joliot-Curie[9], Haissinsky[10], and Erbacher[11-13], who also used artificial radioactive isotopes. In recent years, the rate of publication of papers on the adsorption of ions on metals, using radioactive tracers, has been increasing steeply. Among the most noteworthy are those by Hackerman[14], who studied the adsorption of SO_4^{2-} ions on iron, Heusler and Cartledge[15] and Iofa and Rozhdestvenskaya[16] on the adsorption of iodine on iron, Kolotyrkin and his coworkers on the adsorption of iodine on lead and silver[17,18], Schwabe and his coworkers on the adsorption of various ions on platinum[19-23], and others[24,26].

In all this work little attempt was made to measure the potentials of the adsorbents, and therefore the results cannot be used to characterise the relationship between the adsorption and the electrochemical behaviour of the metal–electrolyte system. A notable exception is the paper by Frumkin et al.[27], in which the adsorption of ions on platinum was studied by chemical titration, the change in the concentration of hydrogen ions in solution, due to the adsorption of cations and anions at different potentials, being determined. However, these changes characterise only the difference in extent of adsorption between anions and cations.

The present review discusses the results of the investigations of the double-layer structure and of the adsorption of ions on platinum, carried out in Frumkin's laboratory, using radioactive isotopes as indicators of the behaviour of the ions of interest. This work has relied on the simplest and most general radiochemical procedures, used in conjunction with electrochemical measurements — the typical approach of the Soviet workers in this field.

Concurrent measurements of adsorption and of the electrochemical parameters of the electrode provide information on the detailed structure of the surface layer, and on the direct relationship between the adsorption and the electrochemical behaviour of the layer. The radiochemical methods of identification and estimation of the amount adsorbed offer highly sensitive, simple, rapid, and specific measurements, and are therefore the most convenient. Frequently, they are the only direct method for investigating the dependence of the electrochemical behaviour of a metal upon the structure of the boundary between the metal and an electrolyte.

We shall show that this dependence is extremely important, and often determines the overall ionic adsorption at a metal surface resulting from electrostatic and also from other types of force operating at the solution boundary. In addition to the studies of adsorption as a function of potential, work has been done on the kinetics of the adsorption of ions, their dependence on the concentration of ions in solution, the degree of irreversibility of the adsorption (as measured by desorption under various conditions and by the exchange of adsorbed ions with the ions of the electrolyte), the influence of pretreatment of the metal on the adsorption, and the possibility of penetration of adsorbed ions into the bulk of the metal.

Different variants of the procedure have been developed and used to deal with particular problems; these consist in measuring the radioactivity of the solution, or alternatively in measuring the radioactivity of the electrode still wet with a layer of solution or rinsed under specified conditions.

Great care was taken into the experiments to observe the particular conditions needed to achieve correct results. These conditions include: standard preparation of the electrode surface, radiochemical and chemical purity of the tracers, and correct choice of the ratios of area of the adsorbing surface to volume of solution and of concentration of stable ions to concentration of radioactive ions in solution.

There are now available several new methods, in a number of variants, for measuring adsorption from the change in radioactivity of a metal specimen without removing the specimen from the solution where adsorption has taken place. Many of these are developments of the method of Joliot-Curie, put forward as long ago as 1930. Modern methods of measuring adsorption by using radioactive tracers have already been reviewed[28,29]. Most of the researches discussed in this paper have made use of a method, developed at the Institute of Electrochemistry of the Academy of Sciences of the USSR, in which adsorption is measured from the change in radioactivity of the electrode, withdrawn from the solution at predetermined intervals. A correction for the activity of the wetting layer is applied.

Studies of the surface layer at a metal–solution interface become more complicated if the metal is corrodible. The platinum electrode is particularly convenient in this respect because exchange between ions in solution and the metal is practically absent, and also because its electrochemical behaviour is known in fair detail and this facilitates comparison with the adsorption behaviour. The electrochemical behaviour of the platinum electrode has been studied by a variety of methods by Frumkin and some of his students — Shlygin, Ershler, Veselovskii — and also by a number of foreign workers — Breiter, Knorr, Wicke and Weblus, Wiebe and Winkler, and others. On the basis of the experimental results[27] obtained by his school, Frumkin has developed a theory of the platinum electrode.

The results show that the electrochemical behaviour of platinum changes in the region between the hydrogen and the oxygen electrode potential, and that this can be explained by the adsorption of hydrogen, of ions from the solution, and of oxygen. Experiments with labelled ions on a platinum electrode polarised to a known potential have made possible a quantitative study of the fine details of the ion adsorption process.

If the simplest picture of the structure of the electrical double layer on metals in the absence of specific adsorption is adopted, preferential adsorption of cations and of anions should occur in the region of negative and positive potentials respectively. The adsorption of both kinds of ion should vanish at the zero-charge potential. If the adsorption of ions is not determined exclusively by the surface charge, adsorption can occur at the zero-charge potential as well as on a charged surface. Ions showing strong specific adsorption shift the point of zero charge of the metal. These predictions of the theory have been repeatedly confirmed by experiments on mercury, but for solid metals there were practically no data of this type prior to the use of radioactive tracers.

According to their adsorption behaviour on mercury, ions can be classified into two groups: the surface-active and the surface-inactive.

We shall give an account of the results which have been reported on the adsorption of sulphate and phosphate anions, considered to be surface-inactive, and on the adsorption of chloride, bromide, and iodide anions, which are typical surface-active anions. Anion adsorption has been studied either separately from or jointly with the adsorption of the surface-inactive cations of sodium, caesium, calcium, and barium in acid and in alkaline solutions, and the surface-active cadmium cations in acid solutions.

Analysis of the results on the simultaneous adsorption of cations and anions leads to a complete picture of the structure of the electrical double layer and of the position of the point of zero charge of the metal. The idea was put forward by Frumkin and developed by his school.

Different anions are adsorbed to different extents at a given potential. Plots of anion and cation adsorption against potential for platinised platinum in acid and alkaline solutions of their salts are shown in Figs. 1–6. In some experiments the change in hydrogen ion concentration in solution corresponding to the difference between anion and cation adsorption was measured in parallel with the radiochemical measurements of the adsorption of anions and cations. In Figs. 2 and 3 this change is denoted by Γ_{H^+}, and referred to 1 cm^2 of true surface area. Increase in hydrogen ion concentration indicates preferential adsorption of cations ($-\Gamma_{H^+}$), whereas a decrease indicates preferential adsorption of anions ($+\Gamma_{H^+}$).

In Figs. 2 and 3, taken from Kazarinov[31], the curves for the anions, obtained from measurements of hydrogen ion concentration, are shown by broken lines (curves *2*). The intersection between these curves and the adsorption curves for Na$^+$ cations (curves *1*) provides an accurate value for the zero-charge potential of platinum. In the

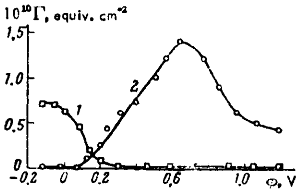

Fig. 1. Variation of the extent of adsorption of SO_4^{2-} anions (curve 2) and Cs$^+$ cations (curve 1) with potential of the platinum in 10^{-2} *N* Cs_2SO_4 + 10^{-2} *N* H_2SO_4; data of Kazarinov and Balashova[30].

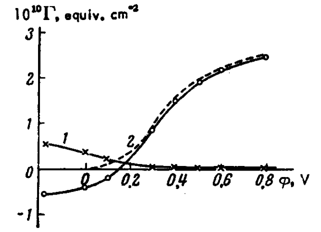

Fig. 2. Variation of the quantities Γ_{Na^+} (curve 1), Γ_{Cl^-} (curve 2), and Γ_{H^+} (curve 3) with potential; original solution 1×10^{-3} N NaCl + 1×10^{-3} N HCl.

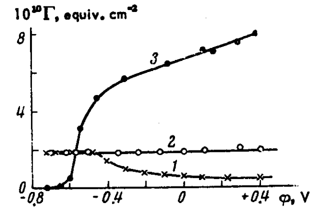

Fig. 6. Variation of the extent of adsorption of I^- anions and Cs^+ cations with potential in alkaline solution; curve 1 is for Cs^+ and curve 3 is for I^- in 10^{-2} N CsI + 10^{-2} N CsOH; curve 2 is for Cs^+ in 10^{-2} N CsOH; data of Kazarinov[32].

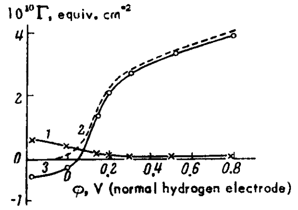

Fig. 3. Variation of the quantities Γ_{Na^+} (curve 1), Γ_{Br^-} (curve 2), and Γ_{H^+} (curve 3) with potential; original solution 1×10^{-3} N NaBr + 1×10^{-3} N H_2SO_4.

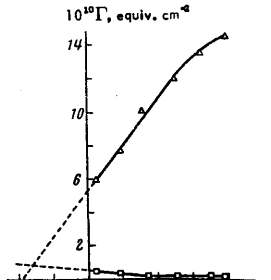

Fig. 4. Variation of the quantities Γ_{I^-}(Δ) and Γ_{Na^+}(□) with potential; original solution 5×10^{-3} N NaI + 5×10^{-3} N H_2SO_4.

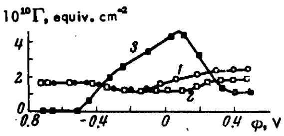

Fig. 5. Variation of the extent of adsorption of Br^- anions and Na^+ cations with platinum potential; solution 10^{-2} N NaBr + + 10^{-2} N NaOH (curve 2 for Na^+ and curve 3 for Br^-); curve 1 is for a 10^{-2} N NaOH solution; data of Kazarinov[32].

absence of specific adsorption of ions, the charge of the ionic double layer should be zero, but it is easy to see from the Table and from the figures that such is not the case, even in a solution of sulphuric acid and caesium sulphate. The extent of adsorption at the zero-charge potential in this solution amounts to 1.50×10^{-11} g-ion × × cm^{-2}, or 1/6 of the maximum extent of adsorption, corresponding to 0.01 of a monolayer. The tabulated data show that on changing from sulphate to halide anions, the extent of the superequivalent anion adsorption increases in the sequence $Cl^- < Br^- < I^-$ (since the cation remains the same). The same is true of changing from acid to alkaline solutions.

Figs. 1–6 show that the zero-charge potential in halide solutions is shifted towards more negative values as compared with its position in sulphate solutions. This shift is more marked, the higher the surface activity of the anion, i.e. it increases in the series $Cl^- < Br^- \ll I^-$. In an iodide solution and at potentials between -0.2 V and 0.06 V, in which the platinum surface carries a positive charge, Na^+ cations are adsorbed at the same time as iodide ions (Fig. 4). This means that iodide ions are adsorbed on the positively charged surface in greater numbers than required by the charge. The superequivalent adsorption of anions causes cation adsorption. Consequently, adsorption of iodide ions from acid solution reverses the charge of a platinum surface.

The zero-charge potentials obtained for acid solutions containing SO_4^{2-}, Cl^-, and Br^- anions are in satisfactory agreement with the results given by other methods[27,33],

TABLE*.

Solution	Zero-charge potential φ_0, V (n. hydrogen e-de)	Shift of φ_0, V	10^{11} × extent of adsorption at φ_0, g-ion cm^{-2}
10^{-2} N Cs_2SO_4 + 10^{-2} N H_2SO_4	0.17	—	1.5
10^{-3} N NaCl + 10^{-3} N HCl	0.10	−0.07	1.6
10^{-3} N NaBr + 10^{-3} H_2SO_4	0.04	−0.13	3.5
$5 \cdot 10^{-3}$ N NaI + $5 \cdot 10^{-3}$ N H_2SO_4	−0.50	−0.70	~10.0
10^{-2} N NaBr + 10^{-2} N NaOH	−0.38		15.5
10^{-2} N CsI + 10^{-2} N CsOH	−0.58		20.0
10^{-2} N $CdSO_4$ + 10^{-2} N H_2SO_4	~0.9	0.7	3.0
10^{-2} N $CdSO_4$ + 10^{-2} N $H_2SO_4^+$ + 10^{-2} N KBr	0.5	0.3	20.0
10^{-2} N $CdSO_4$ + 10^{-2} N $H_2SO_4^+$ + 10^{-2} N KI	0.01	−0.05	80.0

---

* All potentials are relative to the normal hydrogen electrode.

thus confirming the value of the radiochemical method in these systems. Comparative data for the other zero-charge potentials do not exist in the literature.

As Fig. 1 shows, the extent of cation adsorption in an acid solution of caesium sulphate is practically constant in the neighbourhood of the hydrogen potential. This is because the adsorption of cations depends on the number of hydrogen atoms adsorbed, which also contribute to the creation of a potential drop in this region.

In accordance with theory, the extent of anion adsorption increases and that of cation adsorption decreases as the platinum surface acquires a positive charge in acid solution, until a potential is reached where oxygen adsorption sets in (as shown by the charging curves). Oxygen and platinum form dipoles which are oriented with their negative ends towards the solution[27]. Before oxidation begins, the anions differ in extent of adsorption, in their influence on the position of the zero-charge potential, and in the degree of irreversibility of their adsorption. These differences are more marked, the greater the difference in surface activity of the anions. The SO_4^{2-} anions are the least surface-active on platinum, the surface activity increasing from sulphate to phosphate and further to the chloride, bromide, and iodide anions. These differences, associated with the nature of the anion, completely determine the behaviour of platinum towards oxygen. If the surface activity of the anion is much less than that of oxygen, oxygen is readily adsorbed on the platinum and displaces previously adsorbed anions into the solution. This effect has been observed under equilibrium conditions only with the sulphate anion. In this case, changing the potential from the hydrogen potential towards more positive values produces an adsorption curve with a maximum at the potential of incipient oxygen adsorption. At this maximum, the adsorption of sulphate anions amounts to $\sim 18\%$ of full coverage by sulphate. Therefore, even though $\sim 80\%$ of the surface remains free of SO_4^{2-} anions, the oxygen dislodges into the solution most of the adsorbed anions when it becomes adsorbed and forms dipoles with the platinum. The SO_4^{2-} anions which are more firmly held (not by electrostatic forces) may not be fully desorbed under these conditions, as shown by the curves of Fig. 1.

In every other solution which has been examined, the previously adsorbed anions are so firmly bound to the platinum that oxygen adsorption is hindered in proportion to the stability of the anion–metal bond, i.e. in proportion to the observed irreversibility of the adsorption. These barriers to oxygen adsorption take the form of an increase in the adsorption potential, as shown by the charging curves. The effect was first reported by Ershler[34] for Cl^-, and later by Obrucheva[35] for Cl^- and Br^-. Adsorption–potential curves for the anions $H_2PO_4^-$, Cl^-, Br^-, and I^- on a platinum surface not previously oxidised do not show a maximum.

The adsorption maximum observed (Fig. 5) for bromide anions in alkaline solution can be explained as follows. In the potential region from -0.2 V to the potential of the adsorption maximum the whole of the charge is expended effectively upon bromine adsorption, since the electrode capacity as calculated from the adsorption curves and the charging curves has the constant value 70 $\mu F\ cm^{-2}$. Hence, oxygen adsorption does not occur in this region. It can be seen from the charging curve that oxygen adsorption sets in at the potential of the maximum on the adsorption curve. The adsorbed oxygen displaces most of the bromine from the platinum surface. The residual trace of chemisorbed bromine is probably incorporated into the oxide film which forms on the platinum. Thus, the behaviour of the strongly surface-active bromide ions in alkaline solution is reminiscent of that of the weakly surface-active SO_4^{2-} anions in acid solution.

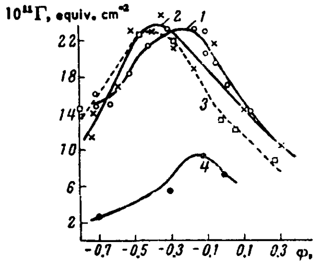

Fig. 7. Variation with potential of the extent of adsorption of cations from alkaline solution:
1) for Ca^{2+} from 10^{-3} N $Ca(OH)_2$; 2) for Ba^{2+} from 10^{-3} N $Ba(OH)_2$; 3) for Ba^{2+} from 10^{-3} N $Ba(OH)_2$ + 1 N NaOH; 4) for Ca^{2+} from 10^{-3} N $Ca(OH)_2$ + 1 N NaOH.

It is interesting to note that adsorption curves of the same general trend are observed during cation adsorption, in particular with calcium and barium on non-oxidised platinum in alkaline solutions (Fig. 7), although the maximum is entirely different in nature[36]. In the adsorption of these cations the increase of adsorption with potential up to a maximum may be due to oxygen adsorption. This is suggested, firstly, by the lack of a cation adsorption maximum on platinum which has not been carefully reduced. Secondly, it has been shown experimentally that complete desorption of calcium and barium cations requires decomposition of the oxide film (achieved by prolonged exposure to acid or, more rapidly, by cathodic polarisation of the electrode in an acid medium). Radiochemical measurements of the exchange between adsorbed Ca^{2+} and Ba^{2+} cations and the same cations in solution have shown that the strength of the bond between the adsorbed cations and the platinum depends on the adsorption potential. When adsorption takes place from alkaline solution at the hydrogen potential, exchange in a hydrogen atmosphere and in $Ca(OH)_2$ or $Ba(OH)_2$ solution proceeds to the extent of 26% in one minute, but after adsorption at the maximum potential or at still more positive potentials the exchange is strongly retarded. Thus, at an adsorption potential of 0.48 V exchange occurs to the extent of only $\sim 6\%$ in the same time. It is evident that over the whole of the potential region examined the cations are incorporated into the oxide film, but at potentials more positive than the maximum the binding of the cations to the adsorbed oxygen is weaker than at less positive potentials and some of the cations pass into the solution. This effect may be associated with the different degree of hydration of oxides formed at different potentials in alkaline solution.

The doubly charged cations Ca^{2+} and Ba^{2+}, when adsorbed from acid solution, are more weakly bound to the platinum over the whole range of potentials than cations similarly adsorbed from alkaline solutions. Thus, Ca^{2+} and Ba^{2+} undergo almost complete exchange with their ions in solution ($\sim$ 96–100% in one minute) when adsorbed from acid solution at the hydrogen potential, at which the platinum remains unoxidised. If the platinum is not given a preliminary reducing treatment the exchange proceeds only to the extent of 70–80%. At the potential which platinum attains in air, exchange of adsorbed cations is either undetectable or relatively small.

All these results show that cations are firmly bound to the oxide film on platinum after being adsorbed. As a result of this work, we are able to explain the mechanism of the influence of doubly charged cations on the reduction of oxygen on platinum in acid and in alkaline solutions. The phenomenon was observed in studies[37,38] of the electrochemical reduction of oxygen at a platinum electrode. It was found that small amounts (10^{-3} *N* in 1 *N* NaOH) of calcium, strontium, or barium salts decrease, in that order, the current efficiency of the formation of hydrogen peroxide by oxygen reduction. Balashova and Kulezneva[36] showed that under the conditions of the electrolysis experiments these cations are adsorbed and form adsorbed compounds with oxygen and platinum which are more stable than the compounds formed in the absence of the cations. The presence of a thousandfold excess of sodium cations decreases the extent of adsorption of Ca^{2+} (see curve *4* of Fig. 7), but has practically no effect on the adsorption of Ba^{2+} (curve *3* of Fig. 7), which accounts for the more marked effect of the latter cation.

In acid solutions the adsorption of the doubly charged cations Ca^{2+} and Ba^{2+} varies with potential in much the same way as the adsorption of singly charged cations (Fig. 8); at the potentials corresponding to incipient electrochemical reduction of oxygen the extent of adsorption of the cations Ca^{2+} and Ba^{2+} is small, and cannot have an appreciable effect on the process.

Müller and Sobol'[38] also concluded that the oxide film is stabilised by calcium, strontium, and barium cations. Those workers studied the effect of these cations on the polarisation curves obtained at a rotating disc platinum electrode combined with a ring electrode, and were able to demonstrate by their sensitive procedure the features of the separate stages in the reduction of oxygen in the presence of doubly charged cations.

Radiochemical and electrochemical measurements of the adsorption of anions on previously oxidised platinum have shown that the greater the adsorption of oxygen and the more stable its bonding to the platinum, the slower is the adsorption of anions, even when their surface activity is quite high. Thus, for example, bromide anions are adsorbed very slowly on platinum oxidised to a potential of 1.2 V, because they are required to dislodge previously adsorbed oxygen. However, if some of the adsorbed oxygen is removed by cathodic polarisation, rapid adsorption of the anion occurs and continues until the oxygen is completely removed[39]. Desorption of the anions begins at potentials such that hydrogen already imparts a negative charge to the surface. As a result, a maximum appears on the extent of adsorption–potential curves for the adsorption of a surface-active anion on previously oxidised platinum.

The retardation of anion adsorption by previously adsorbed oxygen is easily followed by radiochemical measurements of adsorption on platinum oxidised in air for different times. Experiments of this type have shown that the adsorption of the anions Br^-, $H_2PO_4^-$, etc., becomes slower, the longer the oxidation time of the platinum, i.e. the greater the adsorption of oxygen and the stronger its binding to the metal surface[39,40]. The difference in time of adsorption on oxidised platinum of different anions demonstrates the higher stability of the anion–platinum bond as compared with the oxygen–platinum bond. Slow anion adsorption on platinum is observed only in the presence of oxygen adsorbed on the platinum. As Schwabe and his coworkers have shown[20], on vacuum-deposited platinum the adsorption of surface-active anions goes to completion very rapidly (in less than one minute), whereas many hours are needed when the surface has been oxidised.

Some very interesting results have been obtained by the radiochemical method on the kinetics of simultaneous adsorption of iodide anions and caesium cations from alkaline solution on platinised platinum (Fig. 9). Curves *1* and *1'* describe the adsorption kinetics of the two kinds of ion on platinum previously oxidised in air for 30 min, curves *2* and *2'* refer to platinum oxidised for 16 h. During the initial period of the adsorption process cation adsorption is significantly higher than anion adsorption. The iodide anions are adsorbed slowly because they have to dislodge the previously adsorbed oxygen, whereas the cations can attach themselves directly to the oxide film. However, the extent of anion adsorption increases with time whilst that of cation adsorption decreases. The longer the preliminary oxidation of the platinum, the more is the falling off of the extent of cation adsorption delayed. The slope of the kinetic curves for the anions varies with time, denoting a change in the rate of adsorption, which is consistent with the displacement, initially, of the less firmly bound oxygen, and afterwards of the oxygen which

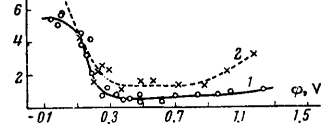

Fig. 8. Variation with potential of the extent of adsorption of the cations Ca^{2+} (curve 1) and Ba^{2+} (curve 2) from acid solutions [10^{-3} *N* $HClO_4$ + 10^{-3} *N* $Ca(ClO_4)_2$ and 10^{-3} *N* $HClO_4$ + + 10^{-3} *N* $Ba(ClO_4)_2$ respectively].

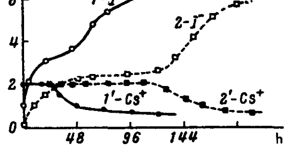

Fig. 9. Kinetics of the adsorption of I^- anions and Cs^+ cations on previously oxidised platinum.
1) and 1') 30 min oxidation; 2) and 2') 16 h oxidation.

is more firmly bound by virtue of the incorporation of cations. When the Pt–O–Cs bond is disrupted, the stable Pt–I bond can be formed.

We have recently obtained† some results on the adsorption of the surface-active Cd^{2+} cations on platinised platinum which demonstrate an appreciable similarity in behaviour (and in the effect on the structure of the surface layer at the platinum–solution boundary) between cation adsorption and anion adsorption in the presence of sufficiently high surface activity. A proof of the surface activity of cadmium cations was given by Frumkin and his coworkers in a series of investigations by different methods[41–45]. In our own work, we showed with the help of the radioactive isotope ^{115}Cd that the adsorption of doubly charged Cd^{2+} cations is very sensitive to the potential and is closely bound up with the adsorption of hydrogen and oxygen on platinum.

Fig. 10 shows the variation of the adsorption of Cd^{2+} with potential: a large maximum occurs near the reversible hydrogen potential. Its origin is not entirely clear, but the maximum is evidently related to the adsorption of hydrogen atoms.

The most interesting feature of the adsorption of Cd^{2+} cations is the positive shift by 700 mV of the point of zero charge as compared with its position in a solution of Na_2SO_4.

The extent of adsorption of Cd^{2+} is greatly in excess of that of Na^+ cations at all potentials. At the hydrogen potential the extent of adsorption of Cd^{2+} cations amounts to 3×10^{-10} g-ion per cm² of true surface area, i.e. about ten times higher than the extent of adsorption of Na^+ cations. This value is unusually high for ionic adsorption: it corresponds to a ratio of 1 cadmium ion to 6 platinum atoms, as compared with 1 singly charged ion to 36 platinum atoms in the case of Na^+ adsorption.

Charging curves obtained under the same conditions as the experiments on ion adsorption show that cadmium cations lower the extent of adsorption of hydrogen and oxygen on platinum whilst the charging curve is being explored. Cd^{2+} cations compete with these gases for adsorption on the platinum, just as in the adsorption of the surface-active anions Br^- and I^-. The high extent of adsorption of the Cd^{2+} cations, the great stability of their bonds with platinum, and the large shift of the zero-charge point of platinum all point to a chemisorptive type of adsorption for these cations. The Cd^{2+} ions form dipoles with the platinum atoms, with their positive ends pointing into the solution, which should give rise to a negative potential jump at the metal–solution interface. However, the Cd^{2+} ions which are adsorbed in amounts more than equivalent to the charge attract SO_4^{2-} anions at potentials more negative than the zero-charge potential in $CdSO_4$ solution, and as a result the potential jump is actually positive.

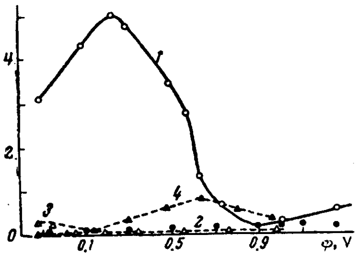

Fig. 10. Variation with potential of the extent of adsorption of cations and anions in acid solution; solutions:
1) and 2) 10^{-2} N $CdSO_4$ + 10^{-2} N H_2SO_4; 3) and 4) 10^{-2} N Na_2SO_4 + 10^{-2} N H_2SO_4.

When the electrolyte contains both surface-active Cd^{2+} cations and surface-active Br^- and I^- anions, the resulting effects on the structure of the surface layer are very complex. Cations and anions compete for adsorption on the platinum, and the net mutual effect is a sensitive function of the surface activities, of the rate of approach to adsorption equilibrium, and of the initial state of the surface.

As an example, the Table shows the zero-charge potentials of platinum under conditions of simultaneous adsorption of surface-active Cd^{2+} cations and Br^- and I^- anions. It is evident from these data that the anions Br^- and I^- have a more pronounced influence on the value of the zero-charge potential than the Cd^{2+} cations under the experimental conditions described above. As a result, the zero-charge potential shifts towards more negative values than cadmium sulphate solution in both cases, but especially so in the case of I^-. The effect of adsorbed cadmium cations is quite appreciable, however, since the zero-charge potential is more positive in cadmium bromide or cadmium iodide solutions than in sodium bromide or sodium iodide solutions.

Thus, all the results obtained for the adsorption of cations and anions on platinised platinum from acid or alkaline solutions point to the great complexity and specificity of the phenomena occurring at the platinum–electrolyte boundary. Detailed analysis of these data and comparison with the analogous data obtained for mercury indicates that the structure of the electrical double layer on platinum has a number of specific features. It follows that the concepts of the structure of the double layer on liquid mercury are not always applicable to solid metallic electrodes.

Allowance for the effect of cation and anion adsorption from the electrolyte and for the structure of the surface layer at the platinum–electrolyte boundary is essential in studies of the kinetics of electrode processes with platinum electrodes. This has recently been discussed by Frumkin[46].

1. H.V.Euler, Z.Elektrochem., 28, 446 (1922).
2. A.N.Frumkin and A.D.Obrutcheva, Z.anorg.Chem., 158, 84 (1926).
3. I.M.Kolthoff and T.Kameda, J.Amer.Chem.Soc., 51, 2888 (1929).
4. G.Hevesy, Z.Elektrochem., 16, 672 (1910).
5. G.Hevesy, Phil.Mag., 23, 628 (1912).
6. G.Hevesy and F.Paneth, Z.anorg.Chem., 82, 323 (1913).
7. G.Hevesy and M.Biltz, Z.phys.Chem., B3, 271 (1929).
8. V.Spitsyn, Zhur.Russ.Fiz.-Khim.Obshch., 49, 357 (1917).
9. F.Joliot, J.Chim.phys., 27, 119 (1930).
10. M.Haissinsky, "Chimie Nucleaire et ses Applications"

---

† With the assistance of G.Mansurov.

(Translated into Russian), Inostr. Lit., Moscow, 1961.

11. O. Erbacher, Z. phys. Chem., 164, 135 (1933).
12. O. Erbacher, Z. phys. Chem., A 156, 142 (1931).
13. O. Erbacher, Z. phys. Chem., 182, 256 (1938).
14. N. Hackerman and S. Stephans, J. Phys. Chem., 58, 904 (1954).
15. K. E. Heusler and G. H. Cartledge, J. Electrochem. Soc., 108, 732 (1961).
16. Z. A. Iofa and G. V. Rozhdestvenskaya, Dokl. Akad. Nauk SSSR, 41, 1159 (1953).
17. L. A. Medvedeva and Ya. M. Kolotyrkin, Zhur. Fiz. Khim., 31, 2668 (1957).
18. Ya. M. Kolotyrkin and L. A. Medvedeva, Dokl. Akad. Nauk SSSR, 140, 168 (1961); 143, 1384 (1962).
19. K. Schwabe, K. Wagner, and C. Weissmantel, Z. phys. Chem. (Leipzig), 206, 309 (1957).
20. K. Schwabe, Chem. Tech. (Berlin), 10, 469 (1958).
21. K. Schwabe, Chem. Tech. (Berlin), 13, No. 5 (1961).
22. K. Schwabe, Isotopen Tech., 1, 175 (1960–1961).
23. K. Schwabe and W. Schwenke, Electrochim. Acta, 9, 1003 (1964).
24. I. A. Kafalas and H. C. Gatos, Rev. Sci. Instr., 29, 47 (1958).
25. J. O'M. Bockris, Z. phys. Chem. (Leipzig), 214, 1 (1960).
26. E. Blombgren and J. O'M. Bockris, Nature, 186, 305 (1960).
27. A. Slygin, A. Frumkin, and W. Medwedowsky, Acta Physicochim. URSS, 4, 911 (1936); 3, 791 (1935).
28. N. A. Balashova and N. S. Merkulova, Symposium "Novye Metody Fiziko-Khimicheskogo Issledovaniya, Trudy Inst. Fiz. Khim. Akad. Nauk SSSR" (New Methods of Physicochemical Investigation, Transactions of the Institute of Physical Chemistry of the Academy of Sciences of the USSR), Izd. Akad. Nauk SSSR, Moscow, 1957, No. 6.
29. V. E. Kazarinov and N. A. Balashova, Pered. Nauch. Tekh. Opyt, Inst. Nauch. i Tekh. Inform., No. 17-63-883/7, 7, p. 18 (1963).
30. V. E. Kazarinov and N. A. Balashova, Dokl. Akad. Nauk SSSR, 157, 1174 (1964).
31. V. E. Kazarinov, Candidate's Thesis, Institute of Electrochemistry of the Academy of Sciences of the USSR, Moscow, 1962.
32. W. E. Kasarinov, Z. phys. Chem. (Leipzig), 226, 167 (1964).
33. N. A. Balashova and A. N. Frumkin, Dokl. Akad. Nauk SSSR, 20, 449 (1938).
34. B. Erschler, Acta Physicochim. URSS, 7, 327 (1937).
35. A. D. Obrucheva, Zhur. Fiz. Khim., 32, 2155 (1958).
36. N. A. Balashova and M. I. Kulezneva, Elektrokhimiya, 1, 155 (1965).
37. A. Kasawa, J. Electrochem. Soc., 110, 174 (1963); J. Electroanalyt. Chem., 8, 20 (1964).
38. L. Müller and V. V. Sobol', Elektrokhimiya, 1, 111 (1965).
39. V. E. Kazarinov and N. A. Balashova, Dokl. Akad. Nauk SSSR, 139, 640 (1961).
40. N. A. Balaschova, Wiss. Z. tech. Univ., Dresden, 12, 1177 (1963).
41. A. N. Frumkin and A. Titievskaya, Zhur. Fiz. Khim., 31, 485 (1957).
42. A. N. Frumkin and N. Polyanovskaya, Zhur. Fiz. Khim., 32, 157 (1958).
43. "Surface Phenomena in Chemistry and Biology", Pergamon Press, London, 1958, p. 189.
44. A. D. Obrucheva, Dokl. Akad. Nauk SSSR, 120, 1072 (1958).
45. A. D. Obrucheva, Dokl. Akad. Nauk SSSR, 142, 859 (1962).
46. A. N. Frumkin, Adv. Electrochem. Electrochem. Eng., 3, 287 (1963).

Institute of Electrochemistry,
Academy of Sciences of the
USSR

U. D. C. 541.6:541.15

ORGANIC SEMICONDUCTORS BASED ON POLYETHYLENE

N. A. Bakh, A. V. Vannikov, A. D. Grishina, and S. V. Nizhnii

CONTENTS

I. Introduction 736
II. Procedure 737
III. Electrical properties 737
IV. Electron spin resonance 739
V. Influence of impurities on the electrical properties 741
VI. Conduction mechanism 742
VII. Nature of the paramagnetism 744

I. INTRODUCTION

The earliest observations of properties characteristic of semiconductors in organic compounds were made with some polynuclear hydrocarbons and dyestuffs. Studies of the electrophysical properties of various compounds as a function of their structure led to the conclusion that semiconductor properties arise when a sufficiently well-developed system of conjugated double bonds is present in the molecules. This problem has been the object of many investigations, and has been discussed in a number of review articles [1-3]. It is now well established that organic polymers as well as low-molecular-weight compounds can exhibit semiconductor properties. This widens the scope of possible applications, since the synthesis of polymers with technologically desirable mechanical properties offers the advantages of controlled structure and controlled properties.

Polymeric semiconductors can be prepared either by synthesis from monomers which offer the necessary system of conjugated bonds, or by inducing polyconjugation into the complete polymers by one of several methods. In the former case the possibilities of generating polymers of different structures are almost limitless, but the resulting materials are mostly insoluble and infusible powders, and their molecular weight is not very high. It is possible also to convert a polymeric dielectric gradually into a polymeric semiconductor by radiation-induced structural changes followed by heat treatment. Many studies of the pyrolysis of polymers have been published. The electrophysical properties of the products have been most fully investigated for polyvinylbenzene [4] and polyacrylonitrile [5] for which heat treatment is clearly shown to be a very effective way of raising the conductivity.

Polyethylene is a suitable material for this purpose, because it has a stable polymeric structure and the effect of radiation on it has been studied in detail. It is well known that irradiation develops a structure in polyethylene,