

The fact that replacement of ether molecules by water molecules in the second solvate layer exerts little effect on the position of the bands of water in the first layer indicates that they have similar proton-accepting properties (Fig. 3).

The acidity of water coordinated with uranyl nitrate supports the analogy of the mechanism of ethereal extraction of uranyl nitrate hydrates to that of acids and acid-metal complexes⁹. The latter are extracted by basic organic solvents through formation of soluble oxonium compounds¹¹. In uranyl nitrate extraction the acid function is to some extent performed by the coordinated water.

The stratified structure of the uranium-coordination sphere presupposes two functions of the water of hydration in extraction and solution of uranyl nitrate in ethers. The water in the first solvate layer is essential for extraction of uranyl nitrate into the ethereal layer since it forms strong acid-base bonds with the solvent. The water of the second solvate layer, on the contrary, hinders solution by competing with solvent molecules for position within the second solvate layer.

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SUMMARY

1. Absorption spectra of solutions of uranyl nitrate dihydrate in diethyl ether, β, β' -dichlorodiethyl ether, dipropyl sulphide, acetonitrile and nitromethane and of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{D}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in diethyl ether were measured in the region of $\text{OH}(\text{OD})$ valency-vibration frequencies. The bands of water coordinated with uranyl nitrate are displaced towards longer wave-lengths and are more intense than those of free dissolved water; the displacement increases with increasing proton-accepting properties of the solvent.
2. Additional bands of free dissolved water and new bands, lying between those of free dissolved and bound water in uranyl nitrate dihydrate solution, make their appearance when water or H_2O is added to $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ solutions.
3. The results suggest that water in the coordination sphere of hexavalent uranium is polarised and that an acid-base type of bond is formed between the water of hydration and the solvent molecules. When further molecules of water become coordinately bound to uranyl nitrate dihydrate they are less firmly linked to uranium than the first two molecules.

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MECHANISM OF THE ELECTROCHEMICAL OXIDATION OF ALCOHOLS AND ALDEHYDES ON PLATINUM. III. THE SHAPE OF THE POLARISATION CURVES FOR THE OXIDATION OF ETHYL ALCOHOL

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In spite of a great deal of experimental work, the literature contains extremely contradictory data on the shape of the polarisation curves for the oxidation of ethyl alcohol on platinum. Thus, for example, several authors have obtained polarisation curves with two maxima in acid and one maximum in alkaline media¹, whereas others have obtained curves with one maximum in acid and two maxima in alkaline media². Curves have also been reported with one maximum in alkaline and one in acid solutions.

It is of interest to discover the reason for such discrepancies, and also to determine the conditions under which curves of different types are obtained. These problems are considered in the present paper.

EXPERIMENTAL

Figs. 1 and 2 give polarisation curves obtained on a large platinised platinum electrode without stirring, and also on a rotating platinised disc*. As can be seen, the curves have two maxima, one at 0.9 V, and the second** at 1.25 V, each accompanied by a considerable drop in current.

In the literature such reductions in current are generally associated with passivation of the electrode by oxygen³ or with the retarding effect of specifically adsorbed anions⁴.

These two postulates explain some experimental data, but in our view are not always adequate, especially when the polarisation curve is complex. Thus, for example, if the process occurs within the potential range preceding evolution of molecular oxygen (as in the case in our experiments), the presence of two maxima on the polarisation curve cannot be explained solely by the appearance of adsorbed oxygen, since at these potentials platinised platinum is not covered even with a monolayer of oxygen⁵.

We suggest that the two falls in current strength have different causes. The first drop, at 0.9 V, is caused by

* The large electrode had an apparent surface of 20 cm², and the rotating disc 0.2 cm².

** Potentials are always given with respect to the reversible hydrogen electrode in the same solution.

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the retarding effect of an intermediate product, acetaldehyde, formed in the electrochemical oxidation of ethyl alcohol; the second drop, at a potential of 1.3 V, is due to the appearance of adsorbed oxygen on the electrode. Many experimental facts confirm this hypothesis.

Thus, if in the electrochemical oxidation of ethyl alcohol the electrode potential is maintained constant (e.g. at 0.6 V, when no adsorbed oxygen is present), the current falls continuously with time, which can be due only to the accumulation on the electrode surface of an intermediate product which is unreactive at that potential. The low reactivity of acetaldehyde compared with alcohol is evident from the fact that the maximum current for the former is many times smaller than that for the latter, and the direct addition of acetaldehyde to a system containing alcohol leads to a retardation of the electrochemical oxidation. In this connection we carried out the following experiments.

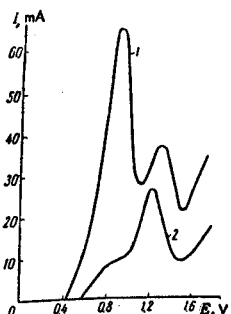


Fig. 1. Polarisation curves for oxidation in $N H_2SO_4$ in the absence of stirring:

1) CH_3CH_2OH ; 2) CH_3CHO .

To solutions of a given concentration of alcohol different quantities of acetaldehyde were added, and in each case the current was chosen to keep the electrode potential constant near its value at the first maximum. This relationship between the maximum current and the quantity of acetaldehyde in the system is illustrated in Fig. 3.

As can be seen from the diagram, the presence of only 5% of acetaldehyde leads to a sharp fall in the maximum current.

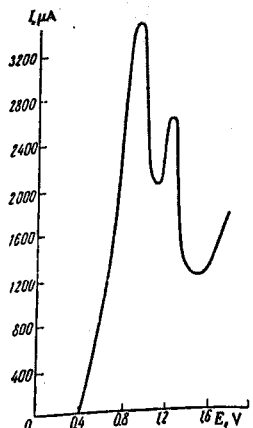


Fig. 2. Polarisation curves for the oxidation of M ethyl alcohol in $N H_2SO_4$ at a rotating platinumised disc.

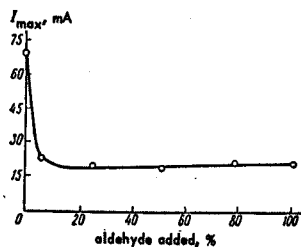


Fig. 3. Relationship between maximum current for the electrochemical oxidation of ethyl alcohol in $N H_2SO_4$ and the quantity of acetaldehyde in the system.

A similar effect was also observed in the oxidation of ethyl alcohol by molecular oxygen in the presence of platinum black. A weighed amount of platinum black was introduced into a special cell filled with $N H_2SO_4$. After saturation of the system with molecular oxygen, ethyl alcohol containing acetaldehyde was introduced, and the quantity of oxygen consumed was estimated with vigorous shaking (1000 shakes/min). The variation of the rate of oxidation of alcohol with the amount of acetaldehyde* is illustrated in Fig. 4. It is seen that in this case also 5% of aldehyde is sufficient to lead to a sharp drop in catalytic activity. It is also significant that the first maximum can be displaced along the potential axis in either the anodic or the cathodic direction. This depends to a considerable extent on the initial concentration of alcohol. As has already been pointed out⁶, a high initial alcohol concentration leads to a shift in the maximum in the anodic direction.

Fig. 7 shows a polarisation curve obtained with a rotating disc electrode when the alcohol concentration is low, 10^{-3} M. In this case the first maximum is at 0.6 V.

A convincing and graphic proof that the second drop in current (at a potential of 1.3 V) is caused by oxygen is provided by experiments on an electrode previously poisoned with mercury. If ethyl alcohol is oxidised at such an electrode, visible blackening of the surface, due to the oxidation of mercury, is observed at a potential of 1.3 V, which corresponds precisely with the start of the second drop in the current. Finally, if the current is switched off in the second descending section of the polarisation curve, the electrode potential remains at a value characteristic of oxidised platinum.

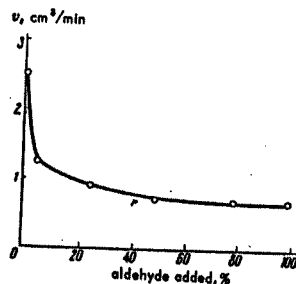


Fig. 4. Relationship between the rate of catalytic oxidation of ethyl alcohol in $N H_2SO_4$ and the quantity of acetaldehyde in the system.

* The results for each concentration of added acetaldehyde were obtained with a fresh weight of catalyst from the same sample.

Thus the two drops in current observed on the polarisation curve for the oxidation of ethyl alcohol are due to passivation of the electrode by adsorbed oxygen and to the retarding effect of an intermediate product.

In addition to curves with two maxima we have obtained also polarisation curves having only one maximum⁶. This can be interpreted as follows. Experiment shows that the shape of the polarisation curve for the oxidation of ethyl alcohol is determined by the intermediate product, acetaldehyde, whose rate of electrochemical oxidation depends on the state of the surface. If the electrochemical oxidation of acetaldehyde occurs on a given surface at a negligible rate, the polarisation curve for ethyl alcohol obtained on this electrode will have a single maximum, at a potential of 0.9 V (Fig. 5). If, however, the electrochemical oxidation of acetaldehyde occurs at an appreciable rate, but more slowly than the electrochemical oxidation of alcohol to acetaldehyde, the polarisation curve for ethyl alcohol will have two maxima, one at 0.9 V and the second at 1.3 V (Fig. 1).

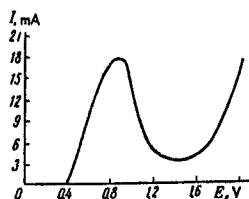


Fig. 5. Polarisation curves for the oxidation of ethyl alcohol in $N H_2SO_4$ at an inactive electrode in absence of stirring.

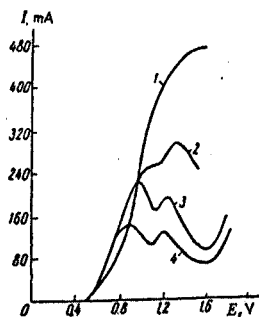


Fig. 6. Polarisation curves for the oxidation of ethyl alcohol in $N H_2SO_4$ at a previously activated electrode, in absence of stirring.

Finally, if the electrochemical oxidation of acetaldehyde occurs at a rate which is not less than the rate of electrochemical oxidation of alcohol, the maximum at 0.9 V is absent, and the polarisation curve obtained has only one maximum, at a potential of 1.3 V. This type of polarisation curve can be realised by preliminary activation of the electrode by intense anodic and cathodic treatment (Fig. 6).

If a number of polarisation curves are obtained, one after the other, two maxima gradually appear (Fig. 6), which points to the temporary character of the activation.

We can explain all these facts on the basis of an electron-radical mechanism for the electrochemical oxidation of ethyl alcohol and acetaldehyde. As has already been

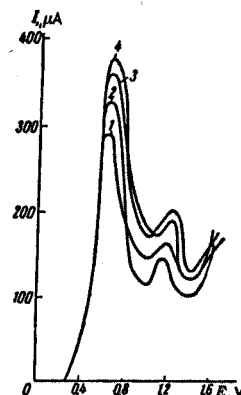


Fig. 7. Polarisation curves for the oxidation of ethyl alcohol in $N H_2SO_4$ at a platinised disc rotating at (1) 240, (2) 780, (3) 3200 and (4) 5000 rev/min.

noted, the electrochemical oxidation of acetaldehyde involves the participation of $OH\cdot$ radicals. Activation of the electrode lowers the overvoltage for the discharge of water molecules, as a result of which the formation of $OH\cdot$ radicals occurs at a greater rate and closer to the cathode potential. Increase in the rate of formation of $OH\cdot$ leads to an increase in the rate of electrochemical oxidation of acetaldehyde. In this case the electrochemical oxidation of ethyl alcohol is not retarded by the intermediate product, and the polarisation curve shows only one drop in current, due to adsorbed oxygen (at 1.3 V).

On a less active electrode the rate of formation of $OH\cdot$ radicals, and also the rate of electrochemical oxidation of acetaldehyde, are lower. In this case the retarding effect of the intermediate product begins to be evident, and the polarisation curve for the oxidation of alcohol can show two drops in current, one due to aldehyde (at 0.9 V) and the other due to oxygen (at 1.3 V). On an inactive electrode, on which the oxidation of acetaldehyde occurs at a very low rate, only one maximum is observed (at 0.9 V).

It must be noted that the falls in current caused by blocking of the surface with intermediate products are not always observed. Thus, for example, such reductions are not observed when polarograms are obtained at a dropping mercury electrode, since in this case the surface is continually renewed.

The most favourable conditions for the occurrence of falls in current caused by reaction products are: low reactivity of the intermediate compared with the initial substance, large, or at least adequate, capacity for being adsorbed, small volume of solution and presence of a large electrode, and low concentration of initial substance.

Experiments on the effect of stirring on the rate of electrochemical oxidation of ethyl alcohol were carried out with a rotating platinised disc electrode in $N H_2SO_4$ at low alcohol concentrations (10^{-3} M) and with the disc rotating at 100–5000 rev/min. As can be seen from Fig. 7, increase in the rate of rotation leads only to an insignificant increase in the maximum current.

Under certain conditions the maximum current (with rotation) may diminish, but this decrease is not associated with the effect of rotation. Thus if, without subjecting the electrode to a preliminary cleaning treatment, a series of polarisation curves are obtained one after the other in the

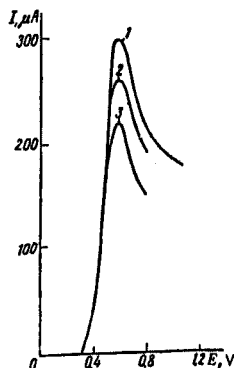


Fig. 8. Polarisation curves for the oxidation of 0.005 M ethyl alcohol in 0.5 N H_2SO_4 with successive increase in the rate of rotation:

1) 240; 2) 780; 3) 3200 rev/min.

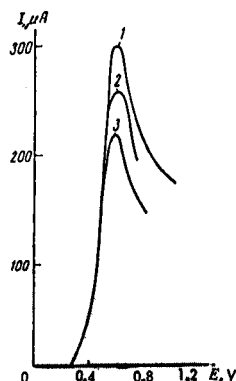


Fig. 9. Polarisation curves for the oxidation of 0.005 M ethyl alcohol in 0.5 N H_2SO_4 with successive decrease in the rate of rotation:

1) 3200; 2) 780; 3) 240 rev/min.

same solution, with the rate of rotation of the disc being steadily increased, a fall in the maximum current may be observed, and on this basis the (incorrect) conclusion could be drawn that rotation retards the process (Fig. 8). However, if experiments with a steadily decreasing rate of rotation are carried out under similar conditions, the maximum current falls too (Fig. 9). Consequently, the maximum current for the electrochemical oxidation of ethyl alcohol can diminish independently of the rate of rotation, apparently as a result of passivation of the electrode by the intermediate product.

Generalisation of these experimental results leads to the conclusion that three potential regions, at 0.5–1 V, 1–1.6 V, and above 1.6 V, can usually be distinguished in the electrochemical oxidation of ethyl alcohol at platinised platinum in acid solutions. Below 1 V only conversion of ethyl alcohol into acetaldehyde occurs. At 1–1.6 V a new stage starts, namely oxidation of acetaldehyde to acetic acid. Here the process is restricted by the rate of conversion of the aldehyde, and the transition to this region is usually accompanied by a fall in current.

Still another stage, the further conversion of acetic acid, starts at a potential of 1.6–1.7 V.

However, this generalisation is not rigorous, since the boundaries of these potential regions may be considerably displaced depending on the activity of the electrode.

SUMMARY

1. The shape of the polarisation curve for the oxidation of ethyl alcohol at platinised platinum in sulphuric acid is governed by the state of the electrode surface.
2. On active electrodes the polarisation curve shows only one drop in current, due to the appearance of adsorbed oxygen.
3. On inactive electrodes the polarisation curve for the oxidation of alcohol also has one drop in current, caused by the retarding effect of the intermediate product, acetaldehyde, and the products of its polymerisation.
4. With electrodes of medium activity the polarisation curve has two falls in current, caused by the intermediate product and adsorbed oxygen.

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ASSOCIATION OF IONS IN SOLUTION. IV. TRANSPORT NUMBERS AND THE PROBLEM OF ION TRIPLETS

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The hypothesis of the formation of ion triplets in solution was put forward by Fuoss and Kraus¹ to explain the appearance of minima in the conductance isotherms for univalent electrolytes in solvents of low dielectric constant. However, this is not the only explanation. The anomalous concentration dependence of the conductivity can be explained by a rapid decrease in the ionic activity coefficients, without bringing in ideas of ion triplets²⁻⁵.

No other experimental or theoretical evidence for the existence of ion triplets, apart from this theory of anomalous conductivity, is given in the literature.

A useful method for studying the composition and structure of charged ionic groupings would seem to be the measurement of transport numbers. The effectiveness of this method for the investigation of aqueous solutions is well known. Measurement of transport numbers in solutions of low dielectric constant is made difficult by the inapplicability of existing techniques to systems of high specific resistance. The present investigation was devoted to working out a technique and measuring transport numbers of the ions of several alkali-metal halide salts in butyl alcohol and its mixtures with hexane.