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Electrochemical Behaviour of Uranium at a Mercury Electrode in Aqueous Solutions

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In aqueous solutions hexavalent uranium is reduced at a mercury electrode to the quadrivalent or tervalent state and in some cases even to the metal itself. The number of stages observed in the cathodic process and also the final valence form of uranium depend on the composition of the solution, in particular on the presence of complex-forming agents and the pH of the medium. As an analytical method, the polarography of uranium is at present finding only limited applications. The bibliography includes 131 references.

The first studies dealing with the electrolysis of aqueous solutions of uranium salts at a mercury cathode were published in 1880.[1-2] In these and in subsequent investigations[3-9] carried out in 1901—1919, it was shown that a uranium amalgam is not formed when aqueous solutions of uranium(VI) chlorides, sulphates, nitrates, acetates, and carbonates are electrolysed, since, depending on the initial pH, precipitates of tetravalent or hexavalent uranium are deposited at the mercury cathode owing to the increase of the alkalinity of the solution during electrolysis (in the absence of effective complex-forming agents from the solution, hexavalent uranium is precipitated at pH > 4.5 and tetravalent uranium at pH > 3.5).[10-13] Indeed, the reduction of hexavalent uranium at the cathode involved hydrogen ions in accordance with the mechanism[10,14]

$$UO_2^{2+} + 4H^+ + 2e \rightarrow U^{4+} + 2H_2O,$$

while in the anodic process fewer hydrogen ions are produced for the same consumption of electricity:

$$H_2O - 2e \rightarrow 2H^+ + \frac{1}{2}O_2.$$

On the other hand, in the presence of ions which are oxidised at the anode, for example chloride or acetate ions, the increase in the alkalinity of the solution is more pronounced. For this reason, it is now generally believed that in the electrolysis of its aqueous solutions uranium is not reduced to the metal at a mercury cathode[10-12,15-18]. (The potential of the U^{3+}/U_{met} system is -1.8 V relative to that of the hydrogen electrode[19].) Moreover, in analytical practice electrolysis at a mercury cathode is a known method for the elimination of metallic impurities from uranium[10,14,20-24].

In 1901 a report was published claiming the preparation of a uranium amalgam by the electrolysis of a hydrochloric acid solution of uranium(IV) at a mercury cathode[25]. The author quotes in support of his claim the finding that the residue after vacuum distillation of mercury is pyrophoric. However, according to the literature, pyrophoric properties are characteristic not only of metallic uranium but also of some of its oxides[7,26,27]. Later special investigations[28,29] failed to confirm this report[25].

According to another report[29], the electrolytic preparation of uranium amalgam from aqueous solutions is possible only when certain conditions are fulfilled, namely a high acidity of the electrolyte ($>2\,N\ H_2SO_4$), a high cathodic current density (more than 6 A cm^{-2}), and intense cooling of the solution. Under these conditions, about 1 ml of amalgam paste containing 0.5 g of metallic uranium (3.3 wt.%), the solid phase of which can be separated from the liquid on a glass sinter, is formed after 4 h.

According to communications by the same investigators[29,30], uranium(VI) can be reduced to the metal not only by electrolysis at a mercury cathode, but also by incorporation with zinc and tin amalgams; this contradicts a number of literature data, which indicate that zinc and its amalgam can reduce uranium(VI) only to the tervalent state and tin amalgam can reduce it only to the quadrivalent state[10,14,23,31-33].

In the electrolysis of solutions of hexavalent and tetravalent uranium at moderate current densities (less than 0.5 A cm^{-2}) at a mercury cathode, uranium may be reduced at most to the tervalent state[28].

It has been claimed[34] that uranium amalgam containing about 0.016 wt.% of the metal may be obtained by the incorporation of hexavalent uranium with sodium amalgam (0.13 wt.%) in acetate solutions at pH 4.

In the electrolysis of aqueous solutions of uranium(VI) at solid cathodes (Pt, Al, Ta, Nb, Cu, Pb, etc.), crystalline cathodic deposits are formed[2,9,35-45]: UO_2 or UF_4 (in the electrolysis of fluoride solutions), which is used for the preparation of samples of uranium in the determination of its isotopic composition by the α-spectrometric method. Partial or complete replacement of water by organic solvents improves somewhat the physical properties of these deposits (density, uniformity of distribution on the surface of the cathode) without, however altering their composition[2,9,10,46-49]. The report[48] that uranium may be reduced to the metal at a solid cathode in anhydrous alcoholic solution was not confirmed[27].

Thus in the electrolysis of aqueous and non-aqueous solutions, uranium is not reduced to the metal at solid cathodes. On the other hand, the possibility of reducing uranium to the metal at a mercury cathode is due to the fact that uranium forms intermetallic compounds with mercury[11] which shifts the potential of the U^{3+}/U_{met} system towards less negative values. The formation of uranium amalgam is also promoted by a high overvoltage for the discharge of hydrogen ion at the mercury electrode.

As shown above, the principal aim of the studies on the electrolysis of solutions of various uranium compounds was to find the limiting degree of its reduction and in particular to elucidate the possibility of an electrolytic preparation of uranium amalgam. On the other hand, the kinetics of the stepwise transition of uranium from the highest to the lowest valence states were not as a rule studied. In this connection, polarographic data are of definite interest for the investigation of the electrochemical behaviour of uranium at a mercury electrode.

The first studies on the polarography of hexavalent uranium were published in 1925 and 1928.[50-52] It was stated that in hydrochloric acid solutions at pH 1—2 multistage reduction of hexavalent uranium to the tervalent states takes place at a dropping mercury electrode (d.m.e.

Starting in 1945, the publication of a series of studies devoted to the systematic investigation of the polarographic behaviour of uranium began. One should note that most of these studies were carried out to extend the analytical applications of polarography[10,23] and relatively few[53-62] were concerned primarily with the electrochemical behaviour of uranium at a mercury electrode. In particular, it was shown that the reduction of hexavalent uranium at a dropping mercury electrode is a multistage process which depends significantly on the composition of the solution. In acid solutions of uranium(VI) free from complex-forming agents, for example in chloride or perchlorate solutions, two principal waves are observed[53-69] (Fig. 1). The first wave in the range of potentials between 0.12 and −0.28 V (s.c.e.)† is generally believed to correspond to the reversible reduction of sexivalent uranium to the pentavalent state. With increase of the acidity of the solution above 0.1 *N*, the half-wave potential for the first stage in the reduction of hexavalent uranium shifts towards negative values[53] and the height of the wave increases if the uranium(VI) concentration remains constant. This phenomenon is explained in the following way[53]. Pentavalent uranium, formed as a result of the electrode reaction disproportionates according to the following mechanisms depending on the acidity of the solution[53-69]:

$$2\,UO_2^+ + H^+ \rightarrow UO_2^{2+} + UOOH^+ \quad (\text{at pH} < 1),$$
$$2\,UO_2^+ + 2\,H^+ \rightarrow UO_2^{2+} + UO^{2+} + H_2O \quad (\text{at pH} > 1).$$

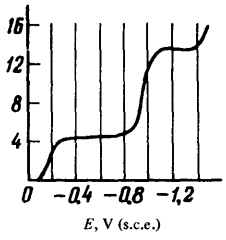


Figure 1. Polarogram for the reduction of uranium(VI) in 10^{-3} M UO_2Cl_2 + 0.03 M HCl + 0.1 M KCl solution containing 2×10^{-4}% of thymol[55].

With increased acidity of the solution, the rate of disproportionation of uranium(V) increases too, which in turn raises the rate of regeneration of uranium(VI) and hence the height of the first wave. This is confirmed by the decrease of the height of the first reduction wave for hexavalent uranium in the presence of tetravalent uranium, which reduces the rate of disproportionation of pentavalent uranium[53]. On the other hand, when precipitants and complex-forming agents for tetravalent uranium are added, the height of the wave increases as a result of the disproportionation of pentavalent uranium[60]. When the acidity of the solution is above 5 *N*, the wave becomes irreversible[60] owing to the elimination of oxygen atoms from the uranyl ion in the bulk of the solution[70]. One should note that the proportionality of the height of the first wave to the concentration of hexavalent uranium holds only in the acidity range 0.01−0.1 *N* and at higher acidities the height increases faster than the concentration of uranium(VI).[53-55] Thus the final product of the electrode reaction corresponding to the first main wave may be either tetravalent uranium or a mixture of tetravalent and pentavalent uranium (the literature data on this question are ambiguous).

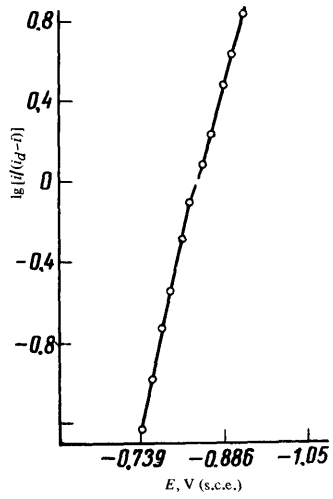


Figure 2. Analysis of the second wave for the reduction of uranium(VI) in 10^{-3} M $UO_2(ClO_4)_2$ + 0.1 M $HClO_4$ solution[59].

In aqueous chloride and perchlorate solutions of uranium(VI), the second main wave, observed in the potential range between −0.7 and −1.2 V (s.c.e.), is believed[53-67] to be due to the postulated limiting degree of reduction of uranium to the tervalent state. It is noteworthy that there is no generally accepted explanation of the nature of the second uranium(VI) wave, since it corresponds to the reduction of uranium to a valence state which has not been determined unambiguously. Thus, many investigators[53,61] believe that the wave corresponds to the reduction of pentavalent uranium to the tervalent state, while others[56,57] explain it by the reduction of a mixture of pentavalent and tetravalent uranium ions to the tervalent state. Some workers[59] think that in a hydrochloric acid solution (>0.1 *N*) the second main wave is associated with the reduction of only tetravalent uranium to the tervalent state owing to the high rate of disproportionation of pentavalent uranium. The plot of E against $\lg[i/(i_d - i)]$ corresponding to this wave has a break[53] or even a discontinuity[59], which indicates the complexity of the electrode process corresponding to the wave (Fig. 2). The height of the second wave is equal to that of the first when the acidity of the solution is about 0.1 *N*; on the other hand, with increase of the acidity above this value, the height of the second wave increases and in 6 *N* HCl is twice as high as that of the first wave, which, as stated above, also increases somewhat[60]. The increased heights of both uranium(VI) waves with increasing acidity of the solution can be accounted for by the fact that they correspond not only to the reduction of uranium but also to the catalytic

† Relative to the saturated calomel electrode.

discharge of hydrogen ions. One should note that kinetic data on the disproportionation of pentavalent uranium are necessary for an unambiguous explanation of the nature of both the second and first wave. However, the literature on this question does not meet this requirement (the most reliable method for the investigation of this reaction is at present the polarography of hexavalent uranium itself[71,72]).

At pH 2—3.5, in solutions free from complex-forming agents, the second uranium(VI) wave splits into two steps with half-wave potentials of −0.85 and −1.15 V (s.c.e.).[55,57,59,61]. There is no generally accepted explanation in the literature of the reasons for this phenomenon. For example, some workers[55,57] explain it in the following way. At a high pH, part of the hexavalent uranium or its reduction products form electrochemically indifferent deposits on the mercury cathode which rules out the possibility of quantitative reduction of uranium to the final (for aqueous solutions) tervalent state. On the other hand, starting from pH 2—3.5, the deposits dissolve. The low rate of this process is responsible for the marked kinetic arrest of the reduction of uranium in the deposits, which is in turn responsible for the appearance of the additional step on the second wave. However, the dissolution of uranium deposits in solutions at pH 2—3.5 rules out the possibility of their formation, so that the above explanation of the causes of the splitting of the second uranium wave fails. We believe that the reason for the separation of the second uranium(VI) wave into two steps is as follows. The pH range in which this phenomenon is observed coincides with the range where pentavalent uranium is most stable according to a number of reports[64-67]. According to some data[73], in this pH range the rate of disproportionation falls so much that the concentration of pentavalent uranium in solution can reach 10^{-3} M. Therefore, in the pH range 2—3.5, there is not sufficient time for the disproportionation reaction to convert pentavalent uranium fully into the hexavalent and tetravalent forms. The residual pentavalent uranium is reduced at potentials which are intermediate between those for the reduction of hexavalent and tetravalent uranium[74] and its reduction appears as a separate stage.

Additional data concerning the nature of the second uranium(VI) wave are provided by the results of certain studies on the polarography of tetravalent uranium. In particular the upper step on the second uranium(VI) wave has the same half-wave potential as the cathodic wave of tetravalent uranium[54,57,59]. This confirms the above hypothesis that in the pH range 2—3.5 hexavalent uranium is not reduced quantitatively to the tetravalent state because in the potential range of the second wave, corresponding to the reduction of uranium to the tervalent state, an additional wave, corresponding to the reduction of pentavalent uranium to the tetravalent state, appears.

As stated above, the limiting degree of reduction of hexavalent uranium in aqueous solutions at a mercury electrode is generally believed[50-56,59-69] to correspond to the tervalent state. However according to one report[57], in 0.1 N HCl a third wave with a half-wave potential of approximately −1.60 V (s.c.e.), corresponding in the author's view to the reduction of tervalent uranium to the metal, was observed together with the two principal uranium(VI) waves described above. This wave is largely masked by the hydrogen wave[57] and subsequently could not be reproduced even in special investigations[62].

Thus, in acid aqueous solutions free from complex-forming agents, uranium(VI) is reduced at a mercury electrode to the pentavalent state at potentials between −0.12 and −0.28 V (s.c.e.) and is then converted into the tetravalent form owing to the high rate of disproportionation. At potentials between −0.65 and −1.2 V (s.c.e.), tetravalent uranium is reduced to the tervalent state. Owing to a lower rate of disproportionation in solutions at pH 2—3.5, the reduction of pentavalent uranium takes place partly as a separate stage at potentials close to the reduction potential of uranium(IV).

Partial replacement of water by organic solvents does not have a significant influence on the electrochemical behaviour of uranium at a mercury electrode. In particular, as in aqueous solutions, uranium(VI) is reduced to the final tervalent state in two main stages[75-86].

The electrochemical behaviour of uranium at a mercury electrode in aqueous solutions containing complex-forming agents differs from that in chloride and perchlorate solutions. Thus, depending on the stability of the complexes, the primary effect is a widening of the pH range in which polarography of uranium is possible. In addition, there is a change in the very nature of its polarograms.

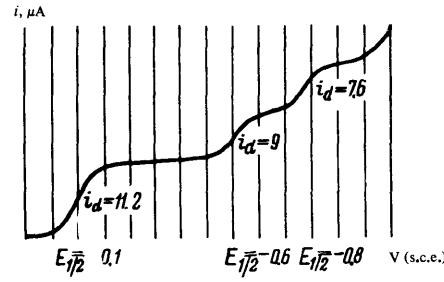


Figure 3. Polarogram for the reduction of uranium(VI) in 1.9×10^{-3} M UO_2SO_4 + 0.025 N H_2SO_4 + 0.1 N Na_2SO_4 solution[61].

In those cases where weak complex-forming agents are present in solution, for example sulphate ions {hexavalent uranium forms the sulphate complex[23] $[UO_2(SO_4)_2]^{2-}$ with $K_{inst} = 1.4 \times 10^{-3}$}, the maximum pH at which polarography of uranium is possible reaches 6—7; on the other hand, the principal characteristics of the behaviour of uranium at a mercury electrode remain the same[57,61,87-91]. In particular, in sulphate solutions, as in chloride and perchlorate solutions, two main waves are observed, the second of which corresponds to the reduction of uranium to the tervalent state[57,61,87-91] (Fig. 3). Compared with chloride and perchlorate solutions, the splitting of the second uranium(VI) waves into two steps in sulphate solutions is observed over a wider pH range (0—7) [89] (in chloride and perchlorate solutions the corresponding pH range is 2—3.5). With increase of acidity from 0.01 to 1.0 N (at a constant hexavalent uranium concentration), the height of the first wave increases and that of the lower step of the second wave falls, but their sum remains constant[88]. A number of investigators[61,88,89] believe that the reason for the splitting of the second wave into two steps in sulphate solutions is a lower rate of disproportionation of pentavalent uranium owing to its complex formation, i.e. the lower step of the second wave corresponds to the reduction of pentavalent uranium and the upper step to the reduction of tetravalent uranium to the final tervalent state.

In solutions of other weak complex forming agents, for example acetates, the following uranium(VI) complexes are known: $[UO_2Ac]^+$, $[UO_2Ac_2]$, and $[UO_2Ac_3]^-$ with $K_{inst} = 2.3 \times 10^{-3}$, 2.2×10^{-5}, and 5.7×10^{-7} respectively[23]; the electrochemical behaviour of uranium(VI) in such solutions does not differ significantly from its behaviour in sulphate solutions. Thus in uranium(VI) acetate solutions two main waves are observed as in solutions of its simple salts. Many investigators believe[54,55,92-96] that the first wave in their experimental pH range (2.5—6) corresponds to reversible one-electron reduction of uranium(VI) to the pentavalent state. On the other hand, the second wave corresponds to the irreversible reduction of pentavalent uranium to the tervalent state[92-96]. It should be noted that the somewhat higher stability of uranium acetate complexes compared with the sulphate complexes suppresses the disproportionation of pentavalent uranium to such an extent that the polarographic pattern is not complicated by the partial conversion of uranium into the tetravalent form in the first stage of the reduction of hexavalent uranium. As with solutions of simple uranium(VI) salts, the second wave splits into two steps at pH 3 [55,93] or at pH 5.[94,95] With increase in the concentration of acetate ions from 0.004 to 0.2 M (at a uranium concentration of 10^{-3} M), the half-wave potential for the second stage of the reduction of uranium(VI) shifts from −0.18 to −0.40 V (s.c.e.) without an appreciable change in the height of the wave[94]. Under the same conditions, the overall height of the second wave, observed at potentials of about 1 V (s.c.e.) falls to a value which is no longer susceptible to measurement[94]. Many investigators explain the splitting of the second uranium(VI) wave into two steps by the retardation of the disproportionation of pentavalent uranium in acetate solutions owing to its binding into acetate complexes[93,94]. It is difficult to agree with this explanation. Indeed, the independence of the height of the first wave of acetate ion concentration shows that the disproportionation of uranium(V) is slow in such solutions and therefore the second wave corresponds to the reduction of pentavalent uranium. We believe that the reason for the splitting of the second uranium(VI) wave into two steps is the considerable difference between the compositions and stabilities of uranium(V) and uranium(IV) acetate complexes {the complexes $[UO_2Ac]$ with $K_{inst} = 2.6 \times 10^{-2}$ and $[UOAc_2]$ with $K_{inst} = 2.4 \times 10^{-6}$ have been suggested for uranium(V) and uranium(IV) [93] respectively}. This means that at high acetate ion concentrations the reduction of uranium(V) to the tetravalent state takes place as a separate stage of the overall electrode process corresponding to the reduction of uranium(V) to the tervalent state. On the other hand, the decrease of the overall height of the second uranium(VI) wave with increase of the concentration of acetate ions can be accounted for by the formation of negatively charged uranium(V) acetate complexes, which are reduced at the negatively charged surface of the mercury electrode with a marked kinetic arrest.

Thus, in the presence of weak complex-forming agents the electrochemical behaviour of uranium(VI) at a mercury electrode does not differ significantly from its behaviour in solutions of its simple salts. On the other hand, in the presence of powerful complex-forming agents, the electrochemical behaviour of uranium differs sharply from that in its simple salt solutions or solutions containing weak complex-forming agents. It is then greatly influenced by the differences between the stabilities of complexes of uranium in different valence states. For example, in uranium(VI) carbonate solutions (pH > 10), owing to the low stability of the uranium(IV) carbonate complex (the composition of which has not established exactly[23,97]) and probably also the uranium(V) complex, only one wave is observed in the range of potentials between −0.9 and 1.20 V (s.c.e.); according to a number of investigators[55,97-106], this corresponds to the reduction of uranium(VI) to uranium(V), which is converted into the final (under these conditions) tetravalent state as a result of disproportionation.

In the pH range 8—10, yet another weak wave is observed in carbonate solutions[97,103-105]; the authors state that it arises because part of the tetravalent uranium is not involved in disproportionation owing to the formation of its hydroxide and is reduced to the tetravalent state (the lowest possible under these conditions) at more negative potentials, ranging from −1.2 to −1.4 V (s.c.e.). The absence of this wave in carbonate solutions at pH > 10 is explained by some workers[104,105] by the high rate of formation of a uranium dioxide deposit, which in turn accelerates the disproportionation of pentavalent uranium. In connection with the foregoing, studies on the electrolysis of uranium(VI) carbonate solutions at a mercury macrocathode are of definite interest. In particular, after the electrolysis of these solutions at pH 8—10, tetravalent uranium was detected, in addition to uranium(VI), both in solution and in the form of a uranium dioxide precipitate[104,105]. It has been reported[104] that under these conditions the solutions contain appreciable amounts of uranium(V), which is doubtful owing to the high rate of its disproportionation.

Uranium in different valence states forms complexes with ethylenediaminetetra-acetic acid (EDTA), the stabilities of which differ markedly. However, in contrast to carbonate solutions, in EDTA solutions uranium(IV) and not uranium(VI) complexes are the more stable[107-109]. Data on the polarography of uranium(VI) in EDTA solutions are not unambiguous. Thus, according to some results[95,110-113], obtained by the method of classical polarography, only one wave is observed for solutions containing EDTA. The half-wave potential for this process is independent of uranium(VI) and EDTA concentrations, but, when the pH is changed from 3 to 7, it shifts from −0.35 to −0.45 V (s.c.e.).[112,113] The height of this wave at pH 3—5 is proportional to the concentration of uranium(VI). However, with increase of pH at a constant uranium(VI) concentration, it diminishes and at pH > 7 merges with the wave of the supporting electrolyte[112]. The reason for this effect is a decrease of the concentration of uranium(VI) owing to its precipitation (in EDTA solutions at pH > 7.5, hexavalent uranium is precipitated quantitatively as the diuranate[107-109,112,113]).

According to other data[113] obtained by oscillographic polarography, two cathodic peaks corresponding to one-electron processes are observed in the same solutions at high rates of application of potential. The same investigators showed that, at relatively low rates of application of potential, the height of the first peak decreases with increasing pH, which they believe to be due to the limited rate of disproportionation of uranium(V). They state that in uranium(IV) solutions in the presence of EDTA cathodic peaks are not observed.

We believe that, despite a certain ambiguity of the polarographic data for uranium in EDTA solutions, they lead to the conclusion that, owing to the high stability of the uranium(IV) complex in such solutions, the rate of disproportionation of uranium(V) is also high and for this reason the final product of even the first stage in the

reduction of uranium(VI) is not only pentavalent but also tetravalent uranium.

The elucidation of the causes responsible for the absence of the wave corresponding to the reduction of uranium(IV) in solutions of hexavalent or tetravalent uranium containing EDTA is of definite interest. One of the possible causes may be a pronounced kinetic arrest of the reduction of uranium(IV) due to the formation of a negatively charged complex with EDTA. It has been found[112,113] that in this complex the ratio U^{IV} : EDTA = 1 : 1. This implies that uranium(IV) must enter into this complex in the ionic form UO^{2+}. Moreover, other investigators suggested[107-109] that, depending on the pH and the excess EDTA present, uranium(IV) enters into complexes in different ionic forms and that the molar ratio of EDTA and uranium in such complexes may exceed unity. The reasons for the absence of the uranium(IV) reduction wave may be also a high negative potential of the U^{IV}/U^{III} system due to the fact that the uranium(IV) complex of EDTA is much more stable than the corresponding uranium(III) complex. The lack of unambiguous data on the composition of uranium(IV) complexes of EDTA and also data on the stabilities of the possible uranium(III) complexes of EDTA precludes at the moment an unambiguous conclusion concerning this problem.

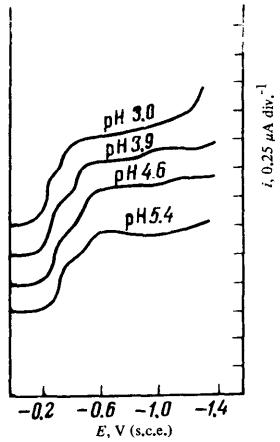


Figure 4. Polarogram for the reduction of uranium(VI) in 2×10^{-4} M $UO_2(NO_3)_2$ + 0.1 M H_3Cit + 0.1 M KCl solution containing 2.6×10^{-4}% of gelatine[117].

In solutions containing complex-forming agents which bind uranium in stable complexes in all its valence states, its electrochemical behaviour differs sharply from that in all the cases discussed above. For example, uranium(VI) forms the citrate complex[114] $[UO_2cit]^-$ with $K_{inst} = 2 \times 10^{-9}$, while according to other data[115,116] uranium(IV) forms compounds in which the citrate ion : uranium ratio varies from unity to two. The polarograms for the reduction of uranium(VI) in citrate solutions show two principal waves[63,117] (Fig. 4) as for the solutions of its simple salts. Thus at a pH of about 2, the corresponding half-wave potentials are −0.21 and −0.90 V (s.c.e.).[117] In the pH range 3—5, the first waves splits into two steps[117]. (Owing to the inhibition of the disproportionation of pentavalent uranium, in chloride and perchlorate solutions the second wave consists of two steps.) It is believed[117] that splitting of the first wave is due to inhibition of the disproportionation of uranium(V) caused by the formation of its complexes with citrate ions, as a result of which the reduction of pentavalent uranium to the tetravalent state takes place as an independent stage. With increase of the pH of the citrate solution from 3 to 5, the half-wave potentials for the two steps of the first wave shift towards negative values by approximately 30 and 20 mV respectively (until they completely merge); on the other hand, the sum of their heights remains constant[117]. Thus the first uranium(VI) wave in citrate solutions corresponds to its reduction to the tetravalent state.

With increase of the pH of the citrate solution from 3 to 5, the height of the second wave decreases until it merges completely with the wave of the supporting electrolyte[117]. The above investigators acknowledge that the nature of the second wave is ill-defined, since, according to their data for citrate solutions of uranium(IV), no waves are observed under these conditions[117]. We believe that this inconsistency is due to the appreciable difference between the composition of the uranium(IV) citrate complex prepared by mixing solutions of its simple salt and of the complex-forming agent and the composition of the uranium(IV) citrate complex obtained from the uranium(VI) complex as a result of a rapid electrode reaction, i.e. in the polarography of the uranium(VI) citrate complex the electrode process corresponding to the first wave results in the formation of an intermediate form of the uranium(IV) citrate complex which does not have sufficient time during the recording of the polarogram for conversion into the final electrochemically passive state.

Thus in citrate solutions uranium(VI) is reduced to the tervalent state in two stages. At pH 3—5, the first stage in the reduction of uranium(VI) to the tetravalent state also involves two stages.

Additional data on the electrochemical behaviour of uranium at a mercury electrode have been provided by oscillographic and cyclic polarographic studies and also by an investigation of the electrochemical oxidation of uranium in lower valence states at mercury and platinum electrodes. In particular, the results of these studies demonstrate that, depending on the composition of the solutions and their pH, two- and three-stage reduction of uranium(VI) to the tervalent state takes place at a dropping mercury electrode; the potentials of the cathodic peaks occur under these conditions in the ranges where the corresponding waves are observed on the classical polarograms for the reduction of uranium(VI).[113,118-125] However, whereas in the case of classical polarography the reduction of pentavalent uranium occurs as a separate stage only in solutions of specific composition, in oscillographic polarographic studies this stage in the reduction of uranium is observed when the rate of application of potential to the dropping mercury electrode is increased[118-125].

Together with the reduction of the higher valence forms of uranium, its lower valence forms are oxidised irreversibly at the dropping mercury electrode (the oscillographic polarograms show anodic peaks which are appreciably lower than the corresponding cathodic peaks and are displaced towards positive potentials relative to the latter)[121,125]. It is noteworthy that the relatively low heights of the anodic peaks compared with those of the cathodic peaks may be caused not only by the irreversibility of the anodic processes but also by diffusion of part of

the reduced uranium, obtained in the cathodic polarisation of the electrode, from the layer near the electrode into the bulk of the solution. Moreover, as shown above, the reduction of uranium at a mercury electrode should be accompanied by the catalytic discharge of hydrogen ions, which increases the heights of the cathodic peaks.

Polarographic data on the anodic oxidation of uranium(IV) are ambiguous. Thus it has been stated[59,125,126] that the oxidation of uranium(IV) takes place not only at a platinum electrode but also at a mercury electrode, while, according to another report[57], the oxidation of uranium(IV) is not observed even at platinum electrode potentials reaching +0.45 V (s.c.e.).

It is noteworthy that quantitative characteristics of the uranium reduction and oxidation processes at a mercury electrode have not yet been obtained from oscillographic polarographic data. The reason for this is the inadequacy of the theoretical interpretation of the experimental data. For example, in studies on the reduction of uranium(VI) [120] and the oxidation of lower valence forms of uranium[119,121], the processes were interpreted quantitatively (i.e. the diffusion coefficients, activation energies, and transfer coefficients were calculated) on the basis of the experimental data in terms of a theory developed for another case[127-129]. Indeed this theory is concerned with electrode processes involving substances diffusing from the solution to the surface of the electrode (and not conversely as in the oxidation of the lower valence forms of uranium obtained on the electrode during its brief cathodic polarisation in a hexavalent uranium solution[119,121]). Moreover, the theory does not provide for the possible disproportionation of the reduction products of the test substances.

A wave associated with the oxidation of uranium amalgam to uranium(IV) has been reported[130,131]. However, the results of this study and also their explanation are not sufficiently convincing, since the wave is observed in 1 N H_2SO_4 at potentials of −1.42 [130] or −1.52 [131] V (s.c.e.) (beyond the hydrogen wave), i.e. more negative than the potentials at which uranium(IV) is reduced reversibly to the tervalent state[53-55,59,61]. Moreover, according to another report[34], when uranium amalgam comes into contact with aqueous solutions it is oxidised to uranium(III), which is clearly detected.

As already stated, the height of the first wave for the reduction of uranium(VI) in chloride and perchlorate solutions, observed in the potential range from −0.1 to −0.25 V (s.c.e.), is proportional to its concentration in the range 10^{-5}—10^{-3} M when the acidity is between 0.01 and 0.1 N. In certain cases this can have analytical applications. However, the narrow range of acidities in which polarographic determination of uranium in solutions of its simple salts is possible involves a number of disadvantages. In the presence of even weak complex-forming agents, for example sulphate ions, the range of permissible acidities of the solution analysed extends to 0.01—2.5 N.[10,23] The use of more powerful complex-forming agents permits the determination of uranium in neutral and even alkaline solutions[23]. The complex dependence of the height of the second wave for the reduction of uranium(VI) on solution composition rules out its employment for analytical purposes. The available methods for the polarographic determination of uranium require the preliminary separation of a number of impurities which are reduced at potentials corresponding to the first wave of uranium(VI). Therefore these methods for the determination of uranium in most cases cannot compete with other available procedures, for example spectrophotometric techniques[23]. At the present time the polarographic method is mainly used for the remote monitoring of the concentration of uranium solutions in certain technological processes[10,23].

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