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Electrochemical Redox Processes of Uranium In Aqueous Solutions of Acetylacetone

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Electrochemical redox processes of uranium (VI) and uranium (V) in aqueous solutions of acetylacetone have been studied by means of various electrochemical techniques.

The presence of acetylacetone accelerates the rate of disproportionation of uranium (V), even under conditions such that uranium (VI) is not in the form of the acetylacetonato complex. The corresponding rate constants of disproportionation were determined.

The influence of the acetylacetonato ion concentration on the potential and on the rate of the uranium (VI) — uranium (V) electron transfer was investigated by means of cyclic voltammetry and square-wave polarography.

Both reduction and oxidation of uranium (V) were investigated by using the Kalousek commutator technique. A mechanism for those processes is proposed.

It was proved by electrocapillary measurements that besides the adsorption of acetylacetone, adsorption of several uranium acetylacetonato species plays an important role in the overall mechanism.

Taking into account the experimental results, the redox processes of uranium (VI) and uranium (V) in the presence of acetylacetone can be explained in terms of an ECE mechanism.

INTRODUCTION

Uranium ions form complexes with the acetylacetonate anion in aqueous solutions[1-3]. Acetylacetone is a weak acid (pK = 8.95) which, in a definite potential region and at concentrations higher than 10^{-2} M, is strongly adsorbed on the mercury electrode[4].

The electrochemical processes of uranium are markedly influenced both by the presence of acetylacetone in the bulk of the solution and by the adsorption of acetylacetone on the electrode surface.

The first one-electron reduction wave of uranium (VI) in aqueous solutions of acetylacetone has been already studied by using square-wave polarography[5,6], and the effect of the acetylacetone bulk concentration on the peak height of the uranium wave has been explained by the presence of different uranyl species.

In a further investigation[7] a second U (VI) wave, of kinetic character has been observed in the presence of acetylacetone at pH = 3.5. This wave was found to be strongly inhibited by the presence of surface active substances.

On the sole basis of the papers published so far[5–7], the mechanism of the electrochemical redox processes of uranium in aqueous solutions of acetylacetone cannot be fully assessed. Therefore, in order to elucidate the most probable mechanism, some electrochemical techniques not used in earlier papers[5–7], such as cyclic voltammetry, Kalousek commutator and electrocapillary measurements have been employed in the present study.

EXPERIMENTAL

D. c. polarographic measurements were carried out using either the Radiometer PO4 or the Radelkis OH-102 polarograph. The drop time was regulated with an electromagnetic detacher.

Square-wave polarographic measurements were carried out using a Merwyn-Harwell Mark III Square-wave polarograph (225 Hz).

Cyclic voltammetric curves were obtained using the hanging mercury drop electrode and were recorded with the Radelkis OH—102 or the Electrochemical system PAR-170.

The experiments with the Kalousek commutator technique (circuits I and II[8]) were performed using the Instrument ICEP (Instrument for Characterization of Electrochemical Processes[9]) connected to a Hewlett Packard 7035 B X—Y recorder. The current was recorded after a given time from the beginning of the potential half cycle (denoted on the figures as »percentage of delay«).

The electrocapillary measurements, performed at the J. Heyrovský Institute of Polarography, Prague, were done with a Lippmann capillary electrometer. In solutions containing uranium, the surface of the mercury was systematically renewed before changing the potential. In order to reach adsorption equilibrium the duration of the measurement was adjusted accordingly.

All potentials were measured and referred *vs.* the SCE.

All chemicals were reagent grade. Uranyl perchlorate was prepared from uranyl nitrate[10].

RESULTS AND DISCUSSION

1. Disproportionation of uranium (V)

In order to investigate the disproportionation reaction, the uranim (V) solutions were prepared by electrolyzing solutions of uranium (VI) at constant potential (—0.5 V). A known amount of acetylacetone was then added. The decay of the uranium (V) oxidation current was followed by d. c. polarography at 0.0 V (a similar method has already been used earlier in the study of uranium (V) disproportionation in solutions containing organic acids[11] and carbonate[12]). In the absence of acetylacetone the oxidation current of uranium (V) remained practically constant.

Linear dependence, with identical slope, of $1/[U(V)]$ *vs.* time was obtained for the examined concentration range of uranium (V) (from 10^{-4} to 5×10^{-4} M) and at a constant concentration of acetylacetone (0.2 M). The linear dependence of $1/[U(V)]$ on time in all the performed experiments shows that the reaction is second order with respect to uranium (V) ions.

Similar experiments were done at a constant initial concentration of uranium (V) and varying concentrations of acetylacetone.

These results, presented in Fig. 1, were obtained at a pH = 2.55, which is the most convenient for the chosen method. At lower pH's, the rate of disproportionation is significant even in the absence of acetylacetone, while at higher pH, hydroxo complexes can interfere.

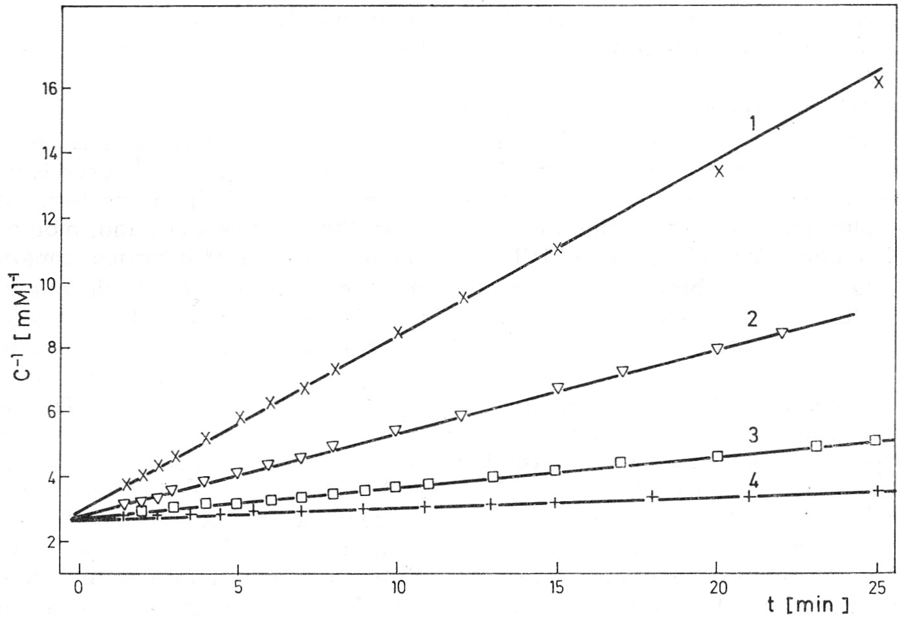


Fig. 1. Time dependence of $1/[U(V)]$. Solution composition: 4 10^{-1} *M* uranium (VI) in 1.0 *M* $NaClO_4$, pH = 2.55, acetylacetone concentration 0.3 (curve 1), 0.2 (2), 0.1 (3), and 0.04 *M* (4).

The apparent rate of the reaction (calculated from Fig. 1) increases considerably with the acetylacetone concentration (Table I).

TABLE I

Apparent rate constants of disproportionation of uranium (V) (initial concentration 4×10^{-4} *M, 1 M* $NaClO_4$*, pH = 2.55)*

Concentration of acetylacetone C mol l^{-1}	Apparent rate constant k_{app} mol^{-1} l min^{-1}	k_{app}/C mol^{-2} l^2 min^{-1}	k_{app}/C^2 mol^{-3} l^3 min^{-1}
0.04	0.36×10^2	0.90×10^3	22×10^3
0.10	0.97×10^2	0.97×10^3	9.7×10^3
0.20	2.60×10^2	1.30×10^3	6.5×10^3
0.30	5.50×10^2	1.85×10^3	6.2×10^3

However, neither k_{app}/C nor k_{app}/C^2 ratios remain constant. The former one should be independent of the acetylacetone concentration, if the reaction is first order with respect to acetylacetone. For a second order reaction, k_{app}/C^2 should remain constant. As it follows from the results presented in Table I, at low concentration of acetylacetone the k_{app}/C ratios are constant thus indicating that the order of the reaction with respect to acetylacetone is close to one. On the other hand, at higher concentrations of acetylacetone (0.2—0.3 M), the ratio k_{app}/C^2 remains practically constant, which means that the order of the reaction increases from 1 to 2, when the concentration of the acetylacetone increases.

In our opinion the nonconstancy of the rate constants of disproportionation in Table I may be due to the change of the rate constants because of the different degree of complexation of the uranium species. This influence is very complicated because the rate of disproportionation of U(V) in the form of a complex may be quite different (higher) than that of free U(V) and, moreover the complexation of U(VI) and U(IV) may favour the rate of disproportionation.

Our results obtained with the hanging mercury drop electrode allow to elucidate the pH effect on the reaction rate. This was performed by recording the cyclic voltammetric curves for 10^{-4} M uranium (VI) in 0.5 M acetylacetone and 1 M $NaClO_4$, at a scan rate of 0.8 V/min, the polarization being reversed at a potential 0.12 V more negative than the cathodic peak potential. The ratio of the anodic to the cathodic peak current was then measured taking the zero current line as anodic current base line (Fig. 2.). With this procedure the current ratio values obtained within the pH range 6.5—8 are typical of a one-electron direct electron transfer. The complicated dependence of the disproportionation reaction rate on the acidity of the solution indicates that pH is a cardinal factor. It follows from Fig. 2 that the disproportionation rate is low in two pH regions (high acidity and pH = 6.5—8). The slow reaction rate at high acidity is due to the low concentration of the ligand ($Acac^-$) while the decrease of the reaction rate in the pH range 6—8, where the concentration of $Acac^-$ ions is relatively high, is due to the low concentration of hydrogen ions. At

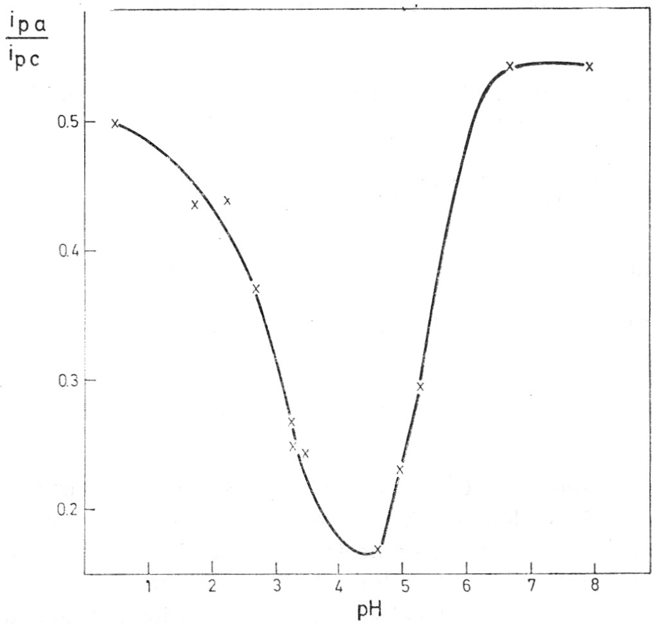


Fig. 2. The pH effect on the cyclic voltammetric anodic to cathodic peak current ratio. The zero current line was taken as base line for the anodic peak current. Solution composition: 10^{-4} *M* uranium (VI) in 1.0 M $NaClO_4$ and 0.5 *M* acetylacetone. Scan rate 0.8 V/min.

pH = 4.5, the combination of the two effects leads to a maximum rate of the disproportionation reaction.

2. *Electrode kinetics and mechanism of the reduction and oxidation of uranium (VI) and (V)*

According to the concentration of the acetylacetonato ion ($Acac^-$), the uranyl ion may exist in aqueous solution as the free ion (UO_2^{2+}), the mono-acetylacetonato (UO_2Acac^+) and the bisacetylacetonato (UO_2Acac_2) complex[1,2]. All three species are in mobile equilibrium and can be reduced to uranium (V)[13].

The influence of the acetylacetonato ion concentration on the potential of the uranium (VI) — uranium (V) electron transfer processes was investigated by the method of cyclic voltammetry. Since the kinetics of the electrode process varies to some extent in the investigated range of pH, neither the cathodic nor the anodic peak potentials (E_{pc} or E_{pa}), but half the sum of these potentials (E') has been plotted against the free ligand concentration. This value appears to be close to the formal potential and is less influenced by kinetic changes. The effect of the free ligand concentration on E' is shown in Fig. 3, curve 1; it is represented by an S-shaped curve. This dependence may be explained in terms of the formation of complexes between $Acac^-$ ions and UO_2^{2+} or UO_2^+ ions:

a) for log [$Acac^-$] < -7.5, the potential E' presents a constant value $(E')_I = -0.187$ V. The concentration of $Acac^-$ is too low to allow complex formation with UO_2^{2+} ions. Since the stability of the UO_2^+ - Acac complex can be expected to be even lower due to the smaller charge of the central ion,

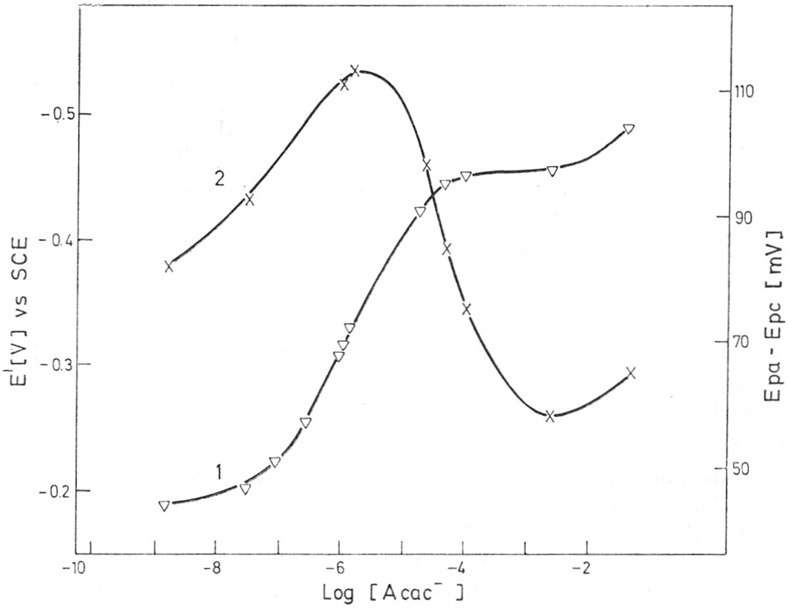


Fig. 3. The dependence of $E' = (E_{pa} + E_{pc})/2$ (curve 1) and $E_{pa} - E_{pc}$ (curve 2) on the free ligand concentration. E_{pa} and E_{pc} are respectively the anodic and cathodic cyclic voltammetric peak potentials. Solution composition: 10^{-4} *M* uranium (VI) in 1.0 *M* $NaClO_4$ and 0.5 *M* acetylacetone. Scan rate 0.8 V/min.

the dependence of E' on the free ligand concentration indicates that UO_2^{2+} is reduced to UO_2^+.

b) for log [Acac$^-$] $>$ — 4.5 the potential E' reaches a constant value $(E')_{II}$ = = — 0.455 V, a fact which indicates that the complex UO_2Acac_2 (which is predominant in the solution under these conditions[1,2,13]) undergoes a one-electron reduction to $UO_2Acac_2^-$, without change in the number of ligands.

c) for — 7.5 $<$ log [Acac$^-$] $<$ — 4.5 the value of E' changes gradually with the increase of free ligand concentration from $(E')_I$ to $(E')_{II}$. Under this conditions the process must be the reduction of UO_2Acac^+ and UO_2Acac_2 to UO_2^+ and UO_2Acac, respectively; *i. e.* the reduction is associated with the loss of one ligand.

The rate of the charge transfer between uranium (VI) and (V) was investigated by means of cyclic voltammetry and square-wave polarography. From voltammetric curves, the potential difference between the anodic and cathodic peaks (E_{pa} — E_{pc}) was calculated (Fig. 3, curve 2, with 0.5 M as total concentration of acetylacetone). From these values the standard rate constants were computed using Nicholson's treatment[14] (Table II). Calculations were carried out by assuming that the diffusion coefficients of uranium (VI) and (V) are equal and that the transfer coefficient was 0.5.

TABLE II

Standard rate constants of the U (VI)/U (V) system. Acetylacetone concentration = 0.5 M

log [Acac$^-$]	ψ*	k_s/cm s^{-1}
— 8.80	1.12	3.2×10^{-3}
— 7.50	0.72	2.1×10^{-3}
— 6.0	0.40	1.2×10^{-3}
— 5.95	0.38	1.1×10^{-3}
— 5.80	0.37	1.1×10^{-3}
— 4.65	0.58	1.7×10^{-3}
— 4.30	0.97	2.8×10^{-3}
— 3.97	1.66	4.8×10^{-3}
— 2.60	rev.	rev.
— 1.45	approx. 5	~ 1.5×10^{-2}

* Ref. 14

It has been found by cyclic voltammetry and square-wave polarography that the adsorption of Acac molecules inhibits the electrode reaction. This effect was studied in 1 M perchloric acid where the complexation of uranium (VI) and (V) is negligible, even at high (0.8 M) concentration of acetylacetone.

In the absence of complexing agent, the reduction of uranium (V) occurs at about —0.8 V. The mechanism of this reaction in acidic perchlorate media has been studied previously[15]. With gradual addition of acetylacetone a new wave appears at more positive potentials, while at the same time the reduction wave at —0.8 V decreases. This formation of the new wave is shown in detail in Fig. 4. Fig. 4a represents a cyclic curve recorded in the absence of acetylacetone. Two cathodic peaks are due to the reduction of uranium (VI) to uranium (V) (at the potential of —0.22 V) and uranium (V) to uranium (III) (at the potential

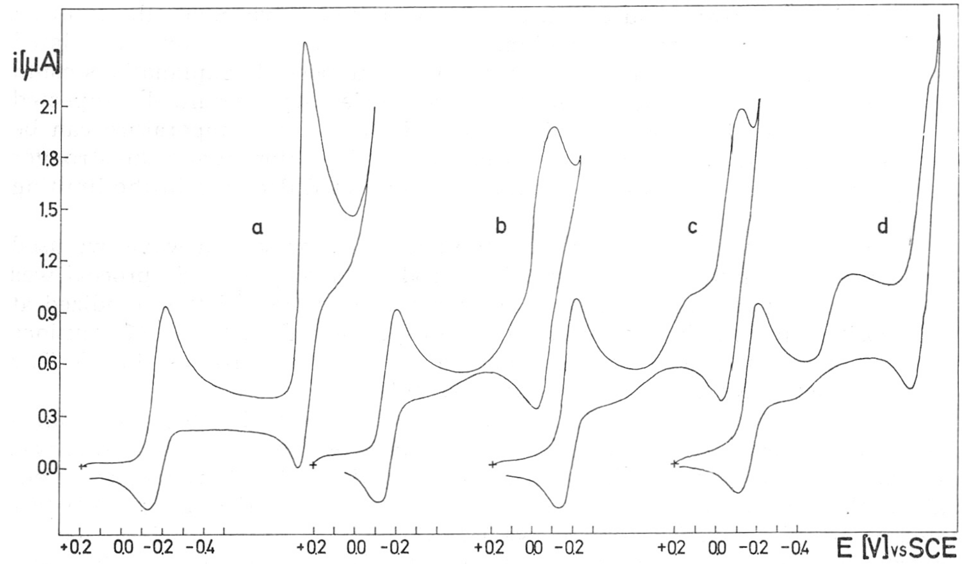


Fig. 4. Cyclic voltammetric curves of 10^{-3} *M* uranium (VI) in 10^{-2} *M* $HClO_4$ and 1 *M* $NaClO_4$. a) 0.0 *M*, b) 4 10^{-3} *M*, c) 10^{-2} *M* and d) 3 10^{-2} *M* acetylacetone. Scan rate 0.8 V/min.

of —0.93 V). The observed anodic peaks are due to the oxidation of uranium (III) to (IV) (at more negative potentials), and uranium (V) to (VI) (at potentials similar to the ones of the reduction of uranium (VI)). With acetylacetone present in the concentration of 4 × 10^{-3} M a new peak, at the foot of the second peak, appears (Fig. 4b). At the same time the second peak (now the third peak) shifts to more negative potentials.

In solutions of 10^{-2} M (Fig. 4c) and 3 × 10^{-2} M (Fig. 4d) in respect to acetylacetone, the new peak is much better defined and shifted further to more positive potentials. In such conditions the third reduction peak was poorly defined, since it shifts to more negative potentials with the increase of acetylacetone concentration and in the same time the reduction current of acetylacetone shifts to more positive potentials.

Results presented on Fig. 4 were given because they visualize so well the formation of the second wave, but quantitative interpretation was obtained by using clasical polarography. The relative height of the second polarographic wave of uranium (VI) is strongly influenced by the uranium concentration. By increasing the concentration of uranium from 10^{-4} M to 10^{-3} M in 0.2 M solution of acetylacetone at pH = 3.5, the relative height of the second wave increases from 45% to 85% in comparison with the height of the first wave (which is diffusion controled under these conditions). Similar results were obtained in 0.2 M $NaClO_4$ in the absence and in the presence of 0.02 M acetate buffer. Drop time of 0.5 s was selected as the most convenient for these measurements; at longer drop times adsorption effects become pronounced.

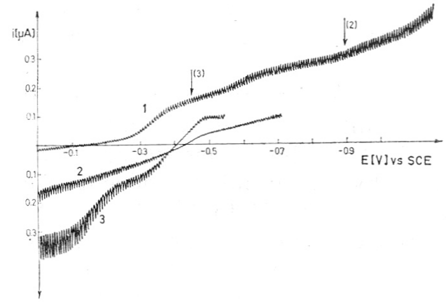
The half-wave potential of the second wave shifts toward more positive potentials with the increase of the uranium concentration. From the temperature dependence (0—40 °C) of the limiting current of 10^{-4} M uranium in 0.2 M acetylacetone at pH = 4.4 apparent activation energies were found to be 3.06

kcal* for the first wave and 2.42 kcal for the second wave. Since the limiting current of the second wave of uranium (VI) has a kinetic character, the related coefficient seems to be abnormally low[16]. One of the possible explanations could be ascribed to the adsorption of electroactive species. As a result, the expected increase of the limiting current of the second wave with temperature can be counterbalanced by the concomitant decrease in adsorption, while the stronger adsorption at lower temperatures reduces the expected decrease in the limiting current.

In order to elucidate more closely the nature of the second wave, we used the Kalousek commutator technique. The product of the electrode process was generated at a given potential for a short period of time and then oxidized at more positive potentials. Measurements were performed with 10^{-4} M solutions of uranium (VI) in 0.2 M acetylacetone in the pH range from 2 to 7.5. The results for some typical pH values are presented.

In Fig. 5 data are given for pH 3.7, curve 1 representing the d. c. polarogram, and curves 2 and 3, the »commutated« polarograms. The last two curves were obtained by changing the polarization potential from the reduction potentials at the limiting current of the first or second wave of uranium (VI) (denoted on the d. c. polarographic curve 1 as (3) and (2)) to potentials increasing linearly from 0.0 V toward more negative potentials. It can be concluded from the decrease of the anodic current of uranium (V), observed on curve 2, that the product of the second reduction wave of uranium (VI) is not oxidizable. This product is most probably uranium (IV) which, according to the literature[3], forms stronger complexes with acetylacetone than with uranium (VI) and (V) a fact which explains the electrochemical inertness of uranium (IV) in the considered potential range.

The nature of the second reduction wave of uranium was also investigated by stepping the polarization from a constant value (0.0 V) to potentials linearly increasing from 0.0 V toward negative values. The decrease of the anodic current observed in the potential region of the second wave (Fig. 6, curve 2) indicates that no reduction product may undergo reoxidation at 0.0 V.



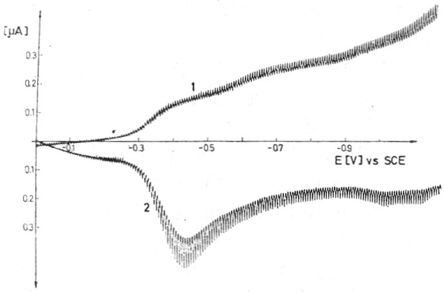


Fig. 5. Polarographic curves of 10^{-4} *M* uranium (VI) in 0.2 *M* $NaClO_4$ and 0.2 *M* acetylacetone, pH = 3.7. Drop time = 3s.
1. d. c. curve; 2. and 3. Kalousek commutator curves (scheme I, f = 64 Hz, timing = 10%). Auxiliary potential: (2) — 0.9V (curve 2) and (3) — 0.45 V (curve 3).

Fig. 6. Polarographic curves of 10^{-4} *M* uranium (VI) in 0.2 *M* $NaClO_4$ and 0.2 *M* acetylacetone, pH = 3.7. Drop time = 3s.
1. d. c. curve; 2. Kalousek commutator curve (scheme II, f = 64 Hz, auxiliary potential = 0 V, timing = 10%).

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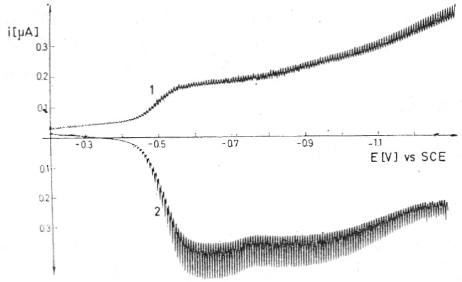
* 1 cal = 4.1840 J

With gradual increase of the free ligand concentration, *i. e.* with increasing pH of the solution above pH = 3, the second reduction wave of uranium (VI) shifts toward more negative potentials, and simultaneously decreases in height (*cf.* the data obtained for pH = 3.7 and 7.2, which are given in Figs. 6 and 7, respectively). The potential region at which the anodic current decreases (curve 2 in Fig. 7) is shifted toward potentials more negative than — 1.0 V. The reduction process of $UO_2Acac_2^-$ cannot be followed under those conditions.



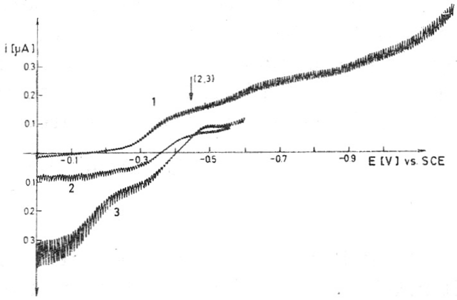
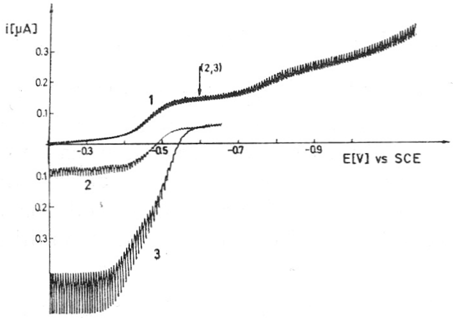


Fig. 7. Polarographic curves of 10^{-4} *M* uranium (VI) in 0.2 *M* $NaClO_4$ and 0.2 *M* acetylacetone, pH = 7.2. Drop time = 3s.
1. d. c. curve; 2. Kalousek commutator curve (scheme II, f = 64 Hz, auxiliary potential = 0 V, timing = 10%).

Fig. 8. Polarographic curves of 10^{-4} *M* uranium (VI) in 0.2 *M* $NaClO_4$ and 0.2 *M* acetylacetone, pH = 3.7. Drop time = 3s.
1. d. c. curve; 2 and 3. Kalousek commutator curves (scheme I, auxiliary potential = — 0.45 V, timing = 10%, (2) f = 4 Hz and (3) 64 Hz).

The characteristics of two anodic waves of uranium (V) at pH = 3.7, shown in Fig. 5, curve 3, have been studied by changing the frequency of the polarization potential. The data are presented in Fig. 8. The two waves observed at 64 Hz (curve 3) correspond to the oxidation wave of free uranium (V) (the more positive wave), and to the oxidation of the uranium (V) monoacetylacetonato complex (the more negative wave). At 4 Hz (curve 2) all of the uranium (V) is oxidized as the complex. The data obtained at pH = 5.5 are shown in Fig. 9. The two oxidation waves observed at 64 Hz (curve 3) can be ascribed to the



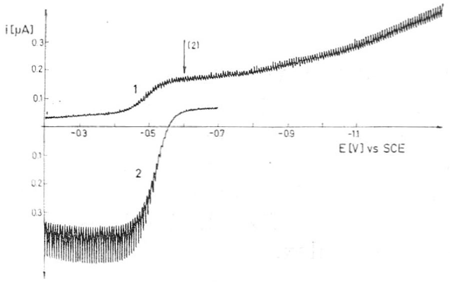


Fig. 9. Polarographic curves of 10^{-4} *M* uranium (VI) in 0.2 *M* $NaClO_4$ and 0.2 *M* acetylacetone, pH = 5.5. Drop time = 3s.
1. d. c. curve; 2. and 3. Kalousek commutator curves (scheme I, auxiliary potential = — 0.6 V, timing = 20%, (2) f = 4 Hz and (3) 64 Hz).

Fig. 10. Polarographic curves of 10^{-4} *M* uranium (VI) in 0.2 *M* $NaClO_4$ and 0.2 *M* acetylacetone, pH = 7.2. Drop time = 3s.
1. d. c. curve; 2. Kalousek commutator curve (scheme I, f = 64 Hz, auxiliary potential = — 0.6 V, timing = 40%).

oxidation of U (V) monoacetylacetonato complex (the more positive wave) and to the oxidation of U (V) bisacetylacetonato complex (the more negative wave). At a lower frequency (4 Hz) all of the uranium is oxidized under the form of uranium (V) bisacetylacetonato complex. At more higher pH values of the solution, only one oxidation wave remains, even at 64 Hz. It corresponds to the oxidation of the uranium (V) bisacetylacetonato complex, as can be seen for pH = 7.2 from Fig. 10.

In order to explain these experimental data, it is necessary to consider the characteristics of the first reduction wave of uranium (VI), as represented by the plot of potential E' vs free ligand concentration (Fig. 3, curve 2). At free ligand concentrations for which the reduction process involves the loss of one ligand, the following reactions are suggested:

$$UO_2Acac^+ + e^- \Longleftrightarrow UO_2^+ + Acac^-$$

$$UO_2Acac_2 + e^- \Longleftrightarrow UO_2Acac + Acac^-$$

If it is assumed that these reactions proceed under equilibrium conditions, it must be concluded that the apparent distribution of uranium (V) acetylacetonato complexes is shifted toward higher concentrations of the acetylacetonato ion, with respect to the bulk complexation equilibrium.

When the polarization potential is stepped at a frequency of 64 Hz from the limiting reduction plateau of uranium (VI) in 0.2 M acetylacetone to the oxidation potential of the product, the following reaction paths can be suggested for the oxidation process at pH = 3.7:

$$UO_2^+ - e^- \Longleftrightarrow UO_2^{2+} \qquad \text{(more positive wave)}$$

$$UO_2^+ + Acac^- \overset{k_1}{\rightleftarrows} UO_2Acac$$

$$UO_2Acac - e^- \Longleftrightarrow UO_2Acac^+ \qquad \text{(more negative wave)}$$

and at pH = 5.5:

$$UO_2Acac - e^- \Longleftrightarrow UO_2Acac^+ \qquad \text{(more positive wave)}$$

$$UO_2Acac + Acac^- \overset{k_2}{\rightleftarrows} UO_2Acac_2^-$$

$$UO_2Acac_2^- - e^- \Longleftrightarrow OU_2Acac_2 \qquad \text{(more negative wave)}$$

UO_2^+ and UO_2Acac are assumed to be the oxidizable species at pH 3.7, and UO_2Acac and $UO_2Acac_2^-$ at pH = 5.5. The oxidation of the higher complex takes place at more negative potentials and includes a preceding chemical step. Accordingly this reaction path becomes more predominent with lowering the commutating frequency of the polarization potential. It has been indeed observed that, for 4 Hz, all the uranium (V) is oxidized through the corresponding higher complex.

The commutated curves given in Figs. 5—10 were obtained by using different delay times in current measurements, in order to keep the maximum anodic current at about the same amplitude, for various pH values of the solution. The true increase of the anodic current at higher pH values could be explained by the increase of the rate constant (as shown in Table II) but it also indicates that some adsorption processes could be involved.

3. *Electrocapillary measurements*

It is evident from some of the above-mentioned results that, besides the acetylacetone, also some reactants and/or products are adsorbed. The adsorption phenomena were studied with a Lippmann capillary electrometer. The electrocapillary curves are given in Fig. 11.

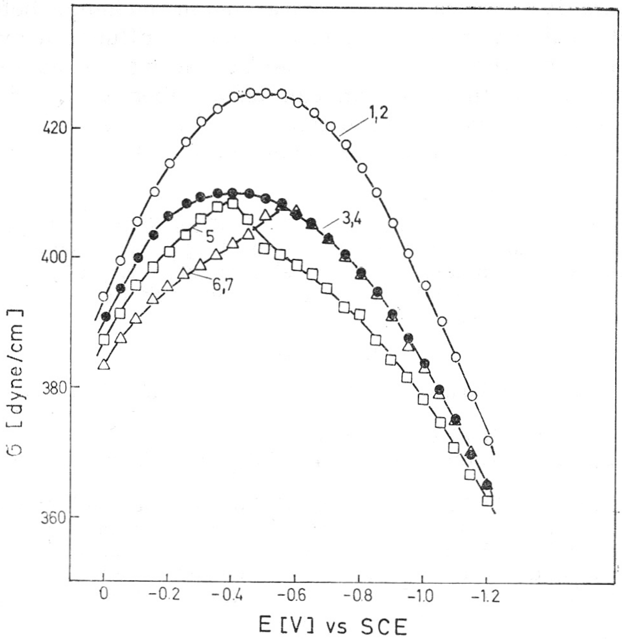


Fig. 11. Electrocapillary curves. Solution composition: 1. 0.2 *M* $HClO_4$; 2. 0.2 *M* $NaClO_4$; 3. 0.2 *M* $NaClO_4$ + 0.2 *M* acetylacetone, pH = 2.0; 4. — 7. 0.2 *M* $NaClO_4$ + 0.2 *M* acetylacetone + 5 10^{-3} M uranium (VI), pH = 2.0 (curve 4), 3.5 (5), 5.7 (6) and 6.5 (7).

In acidic solution (pH = 2.0), acetylacetone (0.2 M, curve 3) is strongly adsorbed. The addition of uranium (VI) to the solution does not produce further change in the surface tension (curve 4). However, adsorption of the reactant does occur when the pH is increased (curve 5 for pH = 3.5). This effect becomes more and more pronounced until a limiting pH is reached, beyond which no further change in adsorption is observed on the positive branch of the electrocapillary curve (as shown for pH = 5.7 and pH = 6.5 from curves 6 and 7). It is therefore very probable that the uranium (VI) bisacetylacetonato complex is the new adsorbed species on the mercury surface. The depression of the electrocapillary curve at potentials more negative than the electrocapillary maximum, as shown in curve 5, indicates that the product of the second reduction wave, uranium (IV), is also adsorbed on the mercury electrode. The pronounced adsorption (curve 5) which was observed in the whole potential range (from 0.0 V to — 1.2 V) under those conditions (pH = 3.5 and concentration of acetylacetone 0.2 M) indicates that uranium (V) monoacetylacetonato complex is also adsorbed.

CONCLUSION

Taking into account the presented results, the nature of the first and second reduction wave of uranium (VI) in aqueous solutions of acetylacetone can be explained by an ECE mechanism.

The uranium (V) monoacetylacetonato complex, formed either directly by reduction of uranium (VI) monoacetylacetonate or by chemical equilibration between uranium (V) species, undergoes a chemical change before reduction to uranium (IV). This chemical reaction is strongly influenced by the uranium concentration and by the presence of surface active substances[7]. The most probable mechanism of this reaction can be ascribed to the dimerization of the uranium (V) monoacetylacetonato complex which is strongly adsorbed, and therefore stabilized in the adsorbed layer of acetylacetone at the mercury surface.

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IZVOD

Elektrokemijski redoks procesi urana u vodenim otopinama acetilacetona

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Redoks procesi urana(VI) i urana (V) u vodenim otopinama acetilacetona ispitivani su elektrokemijskim tehnikama.

Nađeno je, da prisutnost acetilacetona ubrzava disproporcionaciju urana(V) i u uvjetima, gdje uran(VI) ne tvori acetilacetonato komplekse. Izračunate su odgovarajuće konstante brzine disproporcionacije.

Utjecaj koncentracije acetilacetona na potencijal i brzinu prelaza elektrona između urana(VI) i urana(V) ispitivan je metodom cikličke voltametrije i square-wave polarografije.

Tehnika Kalousekovog komutatora korištena je za ispitivanje redukcije i oksidacije urana(V), te je predložen mehanizam procesa.

Na osnovu elektrokapilarnih mjerenja dokazano je, da osim adsorpcije acetilacetona na ukupni mehanizam utječe adsorpcija nekih uran-acetilacetonato kompleksa.

Predložen je ECE mehanizam za redoks procese urana(VI) i urana(V) u prisutnosti acetilacetona.

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