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Original Scientific Paper

Square Wave Polarography of Uranium(VI). I. Aqueous Solutions of Acetylacetone

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Complex uranyl acetylacetonato species in aqueous solution are reduced with different sensitivity if square wave polarographic techniques are used. From the plot of uranyl S. W. peak height *vs.* the free ligand concentration, the consecutive stability constants were obtained as: $\log K_1 = 7.5$, $\log K_2 = 4.8$, and $\log \beta_2 = 12.3$.

A study was made of the specific influence of acetylacetone concentration on the S. W. peak height of different uranyl species present in the solution. Acetylacetone molecules seem to form an adsorption layer on the surface of the mercury drop, which is specifically penetrable. On the basis of this assumption the over-all stability constant of uranyl acetylacetonato complexes was determined as $\log \beta_2 = 12.5$. All measurements were made in 1.0 *M* $NaClO_4$ as supporting electrolyte.

INTRODUCTION

The electrochemical reduction of uranium(VI) to uranium(V) on the dropping mercury electrode in acidic or neutral media produces a polarographic wave with a half-wave potential of about —0.2 V *vs.* SCE[1-3]. The polarogram of uranyl ions shows an alternating current (A.C.) wave with the summit potential closely corresponding to the direct current (D.C.) half-wave potential[4]. Izatt *et al.* determined the stability constants of uranium(VI) acetylacetonato complexes[5] by means of potentiometric titration.

In the course of investigations on the polarographic behaviour of metal acetylacetonato complexes, some unusual phenomena were observed in square wave (S.W.) polarograms of uranium(VI) acetylacetonates. Specific sensitivity at the uranyl S.W. peak height was obtained for different species in solution: the free uranyl ion UO_2^{++}, the mono-acetylacetonato complex, UO_2Acac^+, and the bis-acetylacetonato complex, $UO_2Acac_2^0$. The specific influence of higher concentrations of acetylacetone on the S.W. peak height was observed, thus making possible the calculation of stability constants of the mentioned complexes.

EXPERIMENTAL

Polarographic measurements have been made using Barker's Merwyn-Harwell Square Wave Polarograph Mark III. The drop time of the DME was maintained at 5 sec. and the mercury pool anode was used for each determination. The polarographic cell was described earlier[6]. It was modified so that hydrogen for deaeration was delivered from the bottom of the cell, thus achieving a mixing action. The capillary was sealed into the thorn of the ground-glass joint, which had an exit for disposal of hydrogen through a water seal. *p*H was determined conveniently using a glass electrode.

All stock solutions were prepared by diluting analitically pure chemicals with quadruply distilled water, the last two distillations were carried out in an all-quartz still. The chemicals used were: uranyl nitrate, perchloric acid, and sodium hydroxide all »Merck« *p.a.*, acetylacetone (*für Chromatographie,* »Merck«) and sodium perchlorate (»Fluka« cryst. *puriss. p. a.*). The concentration of the stock solution of uranyl nitrate was determined by precipitation with ammonium hydroxide or, alternatively, with 8-oxiquinoline, and weighing as U_3O_8[7]. Stock solutions were diluted to the required concentrations.

Bidistilled mercury was used throughout.

The solutions were prepared by compounding the components in volumetric flasks in the following order: sodium perchlorate, acetylacetone, perchloric acid (or sodium hydroxide), uranyl nitrate, and then making up to 25 ml. The solutions were kept in a water bath at 25 ± 0.1 °C, the measurements being carried out 24 hours after their preparation at the same temperature. Before taking polarographic measurements, the deaeration of solutions was achieved by passing pure electrolytic hydrogen (about 10 minutes) through them.

RESULTS

Experiments have shown that the uranyl S.W. peak height is not influenced by sodium perchlorate concentrations in the range between 0.25 *M* and 1.0 *M*. In all measurements 1.0 *M* sodium perchlorate as supporting electrolyte was used.

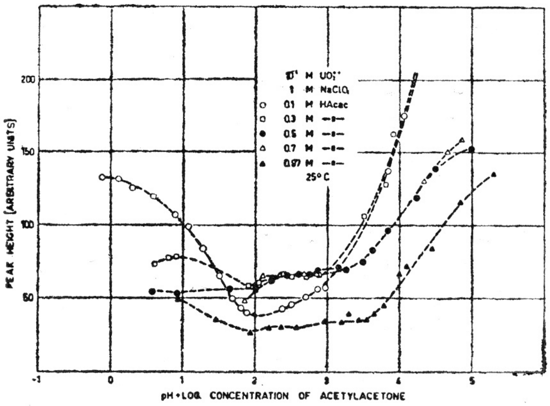

Fig. 1. Uranyl S.W. peak height (at 1/32 maximum sensitivity) against pH + log [HAcac] of the solutions: $10^{-4}M$ $UO_2(NO_3)_2$, 1 *M* $NaClO_4$, 0.1, 0.3, 0.5, 0.7 and 0.97 *M* acetylacetone, and *p*H varied by adding NaOH or $HClO_4$.

The curves in Fig. 1 illustrate the influence of acetylacetone concentrations (0.1, 0.3, 0.5, 0.7, and 0.97 *M*) on the uranyl S.W. peak height. In the first range of the free ligand concentration up to 1.7 of *p*H + log [HAcac] the increase in the acetylacetone concentration decreases the uranyl S.W. peak heights remarkably. The same effect is observed in the third range above 3.0 of *p*H + log [HAcac]. In the second range from 1.7 to 3.0 the S.W. peak height increases with the increase in the acetylacetone concentration (0.1, 0.3 and 0.5 *M*). If the concentration is further increased (0.5 and 0.7 *M*) the S.W.

peak height remains constant, and at still higher concentrations (0.7 and 0.97 *M*) the S.W. peak height decreases remarkably.

The influence of different acetylacetone concentrations on the S.W. peak height at constant consecutive levels of *p*H + log [HAcac] 0.4, 2.0, 2.8, 4.0 and 5.0 is shown in Fig. 2 (curves 1—5). In fact, this are five cross sections through the family of curves (Fig. 1). In Fig. 2 curves 1, 4 and 5 show the decrease of the uranyl S.W. peak heights in the first and the third range of the free ligand concentration. Curves 2 and 3 show this behaviour in the second range.

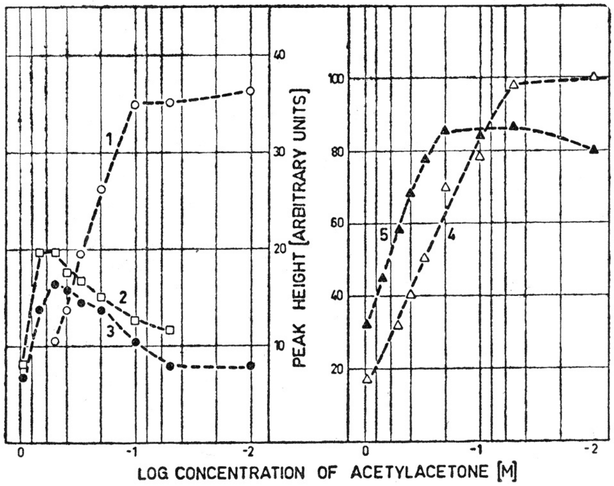

Fig. 2. Uranyl S.W. peak height (at 1/128 maximum sensitivity) against log. concentration of acetylacetone of the solutions: $10^{-4}M$ $UO_2(NO_3)_2$, 1 *M* $NaClO_4$, and *p*H varied by adding NaOH or $HClO_4$. Constant concentration of free acetylacetone ions, *i.e.* *p*H + log [HAcac]: curve (1) 0.4, curve (2) 2.8, curve (3) 2.0, curve (4) 4.0, and curve (5) 5.0.

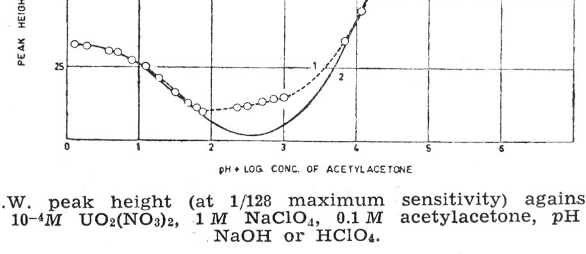

Fig. 3. Uranyl S.W. peak height (at 1/128 maximum sensitivity) against *p*H + log [HAcac] of the solutions: $10^{-4}M$ $UO_2(NO_3)_2$, 1 *M* $NaClO_4$, 0.1 *M* acetylacetone, *p*H varied by adding NaOH or $HClO_4$.

Fig. 3 shows the uranyl S.W. peak height in dependence on free ligand concentration at a constant 0.1 *M* acetylacetone. Curve 1 is obtained experimentally and curve 2 is the theoretical calculation on the basis of experimental results. Curve 2 presents summarized S.W. peak heights for the first and the third ionic species (UO_2^{++} and $UO_2Acac_2^0$), neglecting the second species (UO_2Acac^+). The experimentally obtained S.W. peak heights become constant at *p*H + log [HAcac] lower than 0.6 and above 6.0. This means that the composition of the solution is at constant concentration of the species present. Under such conditions all of the uranium present is found to be in the form of uranyl ion (UO_2^{++}) or uranyl-bis-acetylacetonato complex ($UO_2Acac_2^0$), respectively. On the basis of this assumption and guided by the shape of the experimental curve in the vicinity of the above described conditions, the distribution curves for the UO_2^{++} and the $UO_2Acac_2^0$ species were calculated. The specific sensitivity of the mentioned species on uranyl S.W. peak heights was taken into consideration. Curve 2 was obtained by summing the distribution curves of both species in the range where they overlap. Polarographic investigations in the whole *p*H range (from 0.5 to 7.5) show that only one uranyl S.W. peak is present. The experimentally obtained S.W. peak presents the total S.W. current of all the uranyl species present in solution.

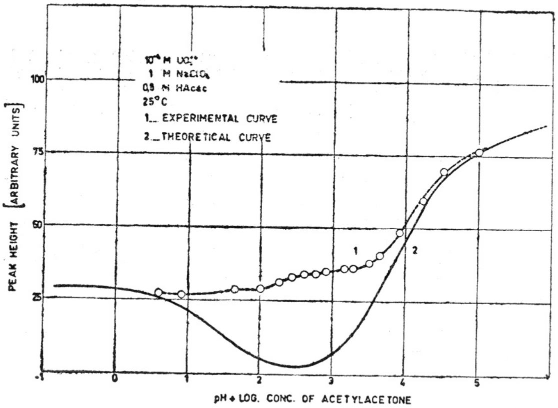

Fig. 4. Uranyl S.W. peak height (at 1/64 maximum sensitivity) against *p*H + log [HAcac] of the solutions: 10^{-4}*M* ($UO_2(NO_3)_2$, 1 *M* $NaClO_4$, 0.5 *M* acetylacetone, and *p*H varied by adding NaOH or $HClO_4$.

The same effect is obtained for 0.5 *M* acetylacetone (Fig. 4). It shows the increased difference between the experimental curve (curve 1) and the theoretically obtained curve (curve 2). It seems that with the increase of the acetylacetone concentration from 0.1 *M* to 0.5 *M* the specific S.W. peak height sensitivity for UO_2^{++} and $UO_2Acac_2^0$ decreases. The rise is remarkable for the UO_2Acac^+ species.

The differences between the theoretical (curves 2) and the experimental (curves 1) curve (Fig. 3 and 4), are shown in Fig. 5 as curves 1 and 2. In this way the curves 1 and 2 present the distribution curve with the specific sensitivity of the S.W. peak height for the second species (UO_2Acac^+) in dependence on the given free ligand concentration. In both concentrations of 0.1 *M* and 0.5 *M* acetylacetone, curves 1 and 2 have a maximum value at the same pH_{max} + log [HAcac] = 2.7. This data allowed the calculation of β_2.

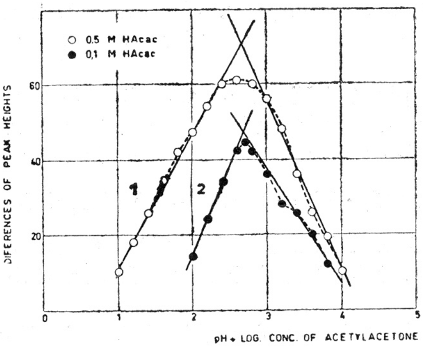

Fig. 5. Differences of uranyl S.W. peak heights between experimental (Curve 1) and theoretical curve (Curve 2) from Fig. 3 and Fig. 4 against *p*H + log [HAcac].

Evaluation of Stability Constants of Uranyl acetylacetonates

Consecutive stability constants K_1 and K_2 can be calculated from the *p*H + log [HAcac] point of 50% depression of the uranyl S.W. peak height on the basis of the following equations:

$$K_1 = \frac{[UO_2Acac^+]}{[UO_2^{++}]\,[Acac^-]} \qquad (1)$$

$$K_2 = \frac{[UO_2Acac_2^0]}{[UO_2Acac^+]\,[Acac^-]} \qquad (2)$$

$$\beta_2 = K_1K_2 = \frac{[UO_2Acac_2^0]}{[UO_2^{++}]\,[Acac^-]^2} \qquad (3)$$

$$K_a = \frac{[H^+]\,[Acac^-]}{[HAcac]} \qquad (4)$$

At the point of 50% depression ($pH_{50\%}$) of the peak height of the first uranyl species UO_2^{++}, the concentration of UO_2^{++} is equal to the concentration of UO_2Acac^+. Owing to this result and eqs. (1) and (4), the following expression could be obtained:

$$\log K_1 = pK_a - (pH_{50\%} + \log [HAcac]) \qquad (5)$$

The value of the dissociation constant (pK_a) of acetylacetone is $pK_a = 8.95$ according to G. Schwarzenbach and K. Lutz[8] ($pK_a = 8.94$), Wallish and Ruppersberg[9] ($pK_a = 9.0$), Eidinoff[10] ($pK_a = 8.93$), and Elstert[11] ($pK_a = 8.9$). The first consecutive stability constant $\log K_1 = 7.50$ was computed from pK_a, from the experimental value of $pH_{50\%}$ + log [HAcac] = 1.45 and by means of eq. (5).

At $pH_{50\%}$ of the third uranyl species, *i.e.* $UO_2Acac_2^0$, the concentration of the two consecutive species was equal, $[UO_2Acac_2^0] = [UO_2Acac^+]$. The experimentally obtained value was $pH_{50\%} + \log [HAcac] = 4.2$ (Fig. 4). Analogously to the former procedure, the second consecutive stability constant $\log K_2 = 4.8$ was evaluated from eqs. (2) and (4). The cumulative stability constant is obtained from the consecutive constants as: $\log \beta_2 = \log K_1 + \log K_2 = 12.3$.

At the maximum piont (pH_{max}) of the distribution curve of the second species, concentrations of UO_2^{++} and $UO_2Acac_2^0$ are equal. From pH_{max} and from eqs. (3) and (4) the following expression is derived:

$$\log \beta_2 = \log K_1 \cdot K_2 = 2pK_A - 2\,(pH_{max} + \log [HAcac]) \qquad (6)$$

Then the experimental maximum point (Fig. 6, curves 1 and 2) $pH_{max} + \log [HAcac] = 2.7$ is obtained and the cumulative stability constant $\log \beta_2 = 12.5$ evaluated.

The two described methods for the determination of the cumulative stability constant $\log \beta_2$ for the uranyl bis-acetylacetonato complex yield values which agree closely, the average value being $\log \overline{\beta_2} = 12.4 \pm 0.1$. The stability constants were obtained in a constant ionic medium of 1.0 *M* sodium perchlorate.

DISCUSSION

Preliminary D.C. polarographic investigations of the uranyl acetylacetonato complex ions disclosed irreversible waves, excluding thus the classical D.C. polarographic methods for the determination of stability constants. The sensitivity of the S.W. polarographic method depends on the degree of reversibility of the electrochemical reaction. If different ionic states result in different degrees of reversibility, the S.W. polarographic techniques could be applied for the determination of stability constants.

All the three mentioned uranyl ionic species present in the aqueous acetylacetone solution give a single cumulative, uranyl S.W. peak. Specific sensitivities for solutions of 0.1 *M* HAcac can be expressed approximately as the ratio 1 : 0.4 : 3 for UO_2^{++}, UO_2Acac^+, and $UO_2Acac_2^0$, respectively. Fig. 1 shows such behaviour representing the plot of uranyl S.W. peak height *vs.* the free ligand concentration, *i.e.* the continuous change in composition of the solution from the free uranyl ion to the uranyl-bis-acetylacetonato ion. It is possible to determine from this plot the distribution of uranyl species at different conditions of complexibility, and therefrom the stability constants.

With increased concentration of acetylacetone a specific effect on the uranyl S.W. peak height was observed. Acetylacetone adsorption on the mercury drop is enhanced for higher concentrations of acetylacetone (above 0.1 *M*) forming an adsorption layer which is hardly penetrable by the free uranyl and the uranyl bis-acetylacetonato species. If the uranyl mono-acetylacetonato ion is predominant in the solution, there is an increase in the sensitivity of the S.W. peak height due to the increased acetylacetone concentrations. It may be assumed that the concentration of uranyl mono-acetylacetonato ion is increased in the adsorption layer. Use of this effect was made in determination of the conditions at which the uranyl mono-acetylacetonato ion is present in the solution at the maximum concentration. The obtained value of the over-all stability constant, $\log \beta_2 = 12.5$, was found to be in agreement with $\log K_1 + \log K_2 = 12.3$.

Our method results in $\log \beta_2 = 12.4$ in a $1\,M\,NaClO_4$ solution. Using the solvent extraction method Rydberg[14] obtained for the same system, but at a ten times lower ionic strength ($0.1\,M\,NaClO_4$), a value of 13.1, while Izatt *et al.*[5] calculate for a zero-ionic strength, in case of potentiometric titration, a value of 14.1. In view of the difference in ionic strengths this is believed to be in good agreement between such different methods, so that our assumptions, though difficult to prove directly appear to be justified.

To confirm the concept of surface blocking of the mercury drop with acetylacetone, and in order to compare it with the action of another SAA, further investigations were performed[12]. In cases where such specific sensitivity of the S.W. polarographic method is sufficiently sensitive for the consecutive ionic species of metal complexes, use of this method could be made for the determination of stability constants.

The advantage of this method compared with the described methods[13] is in the possibility to determine the ionic states at very low metal concentrations.

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IZVOD

Pravokutno-valna polarografija urana(VI). I. Vodene otopine acetilacetona

Lj. Jeftić i M. Branica

Primijenjen je specifični utjecaj koncentracije acetilacetona na pravokutno-valnu polarografsku stepenicu uranila za određivanje konstanti stabiliteta kompleksa. Acetilaceton se pri višim koncentracijama ponaša kao površinski aktivna supstanca stvarajući adsorpcioni sloj na živinoj kapi. Čini se da je ovaj sloj specifično propustan za pojedine ionske vrste uranila (slobodni uranil UO_2^{++}, monoacetilacetonat UO_2Acac^+ i bis-acetilacetonat $UO_2Acac_2^0$). Inhibicija elektrodne reakcije poslužila je za izračunavanje konstanti stabiliteta. Iz 50% smanjenja pravokutnovalnog polarografskog vala za UO_2^{++} i $UO_2Acac_2^0$ dobijene su vrijednosti za K_1 i K_2, dok je β_2 neovisno određena iz specifično veće propusnosti UO_2Acac^+ kroz adsorbirani sloj acetilacetona na živinoj kapi.

Određene konsekutivne konstante stabiliteta za uranil-acetilacetonato komplekse u vodenim otopinama 1 *M* natrijeva perklorata, iznose:

$$\log K_1 = 7.5; \ \log K_2 = 4.8; \ \log \beta_2 = \log (K_1K_2) = 12.3 \ \text{ i } \ \log \beta_2 = 12.5$$

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