Monatshefte für Chemie 119, 287—293 (1988)

Monatshefte für Chemie
Chemical Monthly

The Polarographic Electroreduction of Uranyl Ion in Arsenic Acid Solution

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(Received 27 November 1985. Revised 20 January 1987. Accepted 11 February 1987)

The electroreduction of uranyl ion in arsenic acid studied by d.c. polarography shows one reduction wave at all the used arsenic acid concentrations corresponding to one electron reduction mechanism. At low arsenic acid concentration (0.1–0.3 *M*) $UO_2(ClO_4)_2$ is reduced to HUO_2AsO_4. At higher acid concentration (0.6 *M*) the HUO_2AsO_4 molecules are reduced to UO_2^+ (pentavalent uranium). It is also reliable to study polarographic behaviour of uranyl ions in arsenic acid solutions up to *pH* 3.01. It is also possible to apply this method for the analytical determination of uranyl ion concentrations up to 2 m*M*.

(Keywords: Arsenic acid; Electroreduction; Polarography; Uranyl ion)

Die Polarographische Elektroreduktion von Uranyl-Ion in Arsensäurelösungen

Die Elektroreduktion von Uranyl-Ion in Arsensäurelösung zeigte bei allen untersuchten Arsensäurekonzentrationen eine polarographische Reduktionswelle, die einem Einelektronenreduktionsmechanismus entspricht. Bei niederen Arsensäurekonzentrationen (0.1—0.3 *M*) wird $UO_2(ClO_4)_2$ zu HUO_2AsO_4 reduziert. Bei höheren Säurekonzentrationen (0.6 *M*) werden die HUO_2AsO_4-Moleküle zu UO_2^+ (fünfwertiges Uran) reduziert. Das polarographische Verhalten der Uranyl-Ionen konnte bis zu einem *pH* von 3.01 untersucht werden. Es ist möglich, diese Methode zur analytischen Bestimmung von Uranyl-Ionen bis zu einer Konzentration von 2 m*M* einzusetzen.

Introduction

Herasymenko [1] found that the polarogram of uranyl salt solutions in 0.1 *N* KCl consists of three waves, with $E_{1/2}$ values approximately − 0.15, − 0.8 and − 1.0 V versus the saturated calomel electrode (V. vs. SCE). He

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concluded that these waves were due to the reduction of UO_2^{++} to + 5, + 4 and + 3 states, respectively. On the other hand, arsenic ions in the pentavalent state are not reduced at the dropping mercurey electrode in any supporting electrolyte, whereas in the trivalent state reduction waves under limited conditions [2–4] can be noticed.

Therefere, the aim of this work is to study the polarographic behaviour of uranyl ion in presence of the pentavalent arsenic ions (i.e. arsenic acid) and the application of the polarographical technique for the determination of uranium concentration in this medium.

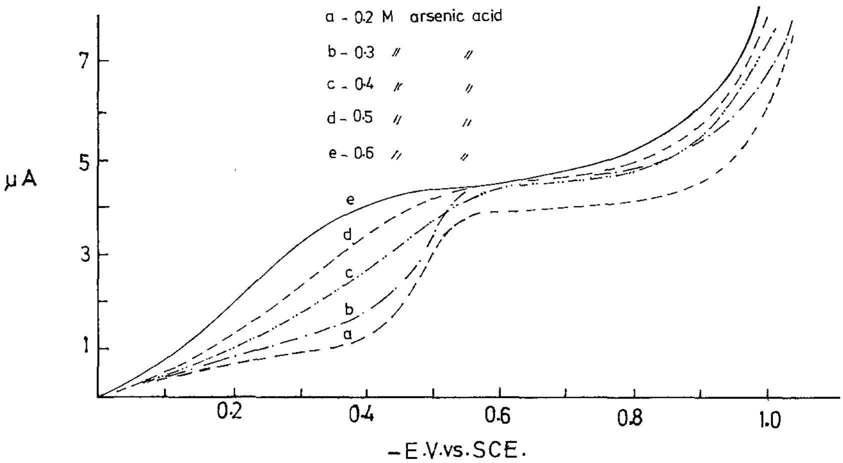

Fig. 1. Polarograms of 1 m*M* $UO_2(ClO_4)_2$ at different molarities of arsenic acid

Experimental

Uranyl perchlorate was prepared from uranyl nitrate (G. R. Merck) as in the previous papers [5, 6] and the exact concentration of uranyl is determined gravimetrically as U_3O_8. 1 *M* stock solution of arsenic acid was prepared from a BDH sample of arsenic acid. The potential curves were recorded by using a Metrohm E 506 polarograph. The capillary characteristics were $m = 1.47$ mg/s and $t = 3.6$ s/drop in 0.1 *M* KCl at a height of the mercury column of 30 cm.

Results and Discussion

Polarography of Hexavalent Uranium in Presence of Arsenic Acid

The electroreduction of 1 m*M* uranyl ion in 0.1 *M* perchloric acid as supporting electrolyte in presence of different concentrations of arsenic acid is represented by the polarograms shown in Fig. 1. Each polarogram consists of one wave. This was attributed to the reduction of U (VI) to

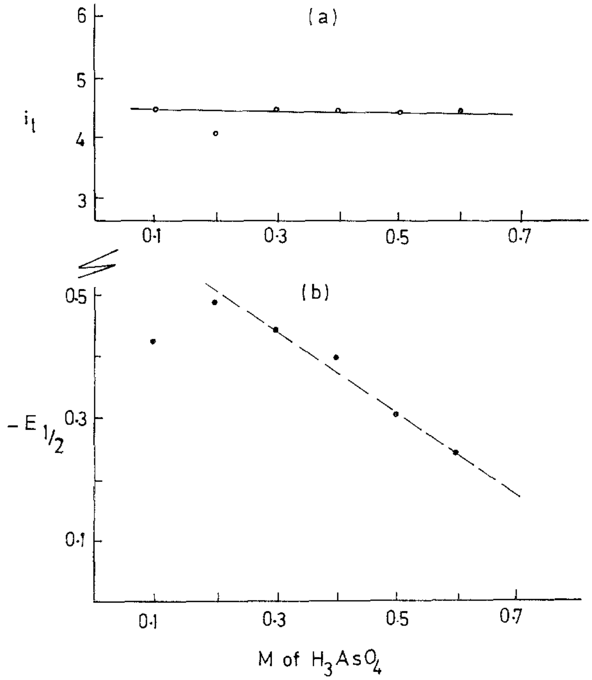

Fig. 2. *a* Effect of arsenic acid on the limiting currents of 1 m*M* U (VI) waves; *b* Effect of arsenic acid concentration on the half wave potentials of U (VI) waves

U (V). The limiting current obtained from Fig. 2a is about 4.5 μA, this value is independent of the acid concentration within the limits of the experimental errors.

The half wave potentials of the electroreduction of U (VI) at different arsenic acid concentrations are shown in Fig. 2 b. The half wave potential is shifted to less negative values on increasing the acid concentration expressed in molarities. The shift of the half wave potential to less negative values is due to the decrease in the complex character on adding more acid.

The relation between log $(i/i_d\text{-}i)$ against E in V (analysis of the waves) are straight lines, from their slopes the values of αn_a are obtained. It is found that these values of αn_a ranged from 0.2 to 0.393 indicating the irreversibility of the electroreduction process (Table 1).

By plotting log i (i is the limiting currents) versus log h (h is the mercury height), straight lines are obtained, their slopes lie between 0.35 and 0.55 (Table 1) indicating that the electrode process is mainly diffusion controlled electroreduction.

Table 1. *Effect of arsenic acid on the polarographic reduction of* 1 m*M* $UO_2(ClO_4)_2$

Molarities of acid	i_l	$-E_{1/2}$	S	αn_a	S'
0.1	4.5	0.426	6.7	0.395	0.55
0.2	4.0	0.49	6.6	0.389	0.6
0.3	4.52	0.445	6.4	0.378	0.55
0.4	4.50	0.40	4.8	0.283	0.4
0.5	4.50	0.31	4.4	0.259	0.45
0.6	4.50	0.250	3.4	0.201	0.35

S are slopes of $\log(i/i_{d-i})$ vs. E and S' are slopes $\log i$ vs. $\log h$ (mercury height relation)

It is observed in Figs. 1 and 2a that the limiting currents have a constant value, proving that the process of reduction consumes one electron at all the used arsenic acid concentrations. It is also seen from Fig. 2b that the half wave potentials are shifted to less negative values, indicating that the complexing ability of U (VI) and H_3AsO_4 decreases and the hydrogen participates in the reduction process.

Reduction Mechanism in the Presence of Arsenic Acid

Uranium forms the following compounds with arsenic [7], U_3As_4, $U_3(AsO_4)_2 \cdot 3H_2O$, $UH_2(AsO_4)_2 \cdot 2H_2O$, $UO_2HAsO_4 \cdot 4H_2O$ and $(UO_2)_2As_2O_7$.

Shilton and *Howe* [8] studied the structure of arsenate tetrahydrate $HUO_2 \cdot AsO_4 \cdot 4H_2O$ below temperatures of 274 and 301 °K. They also [9] studied the proton conductivity in polycrystalline uranyl arsenate tetrahydrate. They found that the last compound has a high conductivity of $0.6\,Ohm^{-1}\,cm^{-1}$ at 310 °K with activation energy of $31 \pm 2\,kJ\,mol^{-1}$.

The reduction process of uranyl ion takes place by a one-electron mechanism at all the used acid concentrations, because the reduction process produces a wave nearly equal to the first reduction wave of UO_2^{++} (one electron process) in perchloric acid as shown in Fig. 3. All the lower waves in Fig. 1 and Fig. 3 correspond to the reduction of U (VI) to U (V). On adding arsenic acid a less negative shift of $E_{1/2}$'s was followed, explaining the participation of the hydrogen ion in the reduction process at higher acid concentrations. Since the complex ion UO_2HAsO_4 is well known [7–9], the reduction of uranyl ion at low arsenic acid concentration took place as follows:

$$UO_2(ClO_4)_2 + H_3AsO_4 \rightarrow UO_2HAsO_4 + 2\,HClO_4 \qquad (1)$$

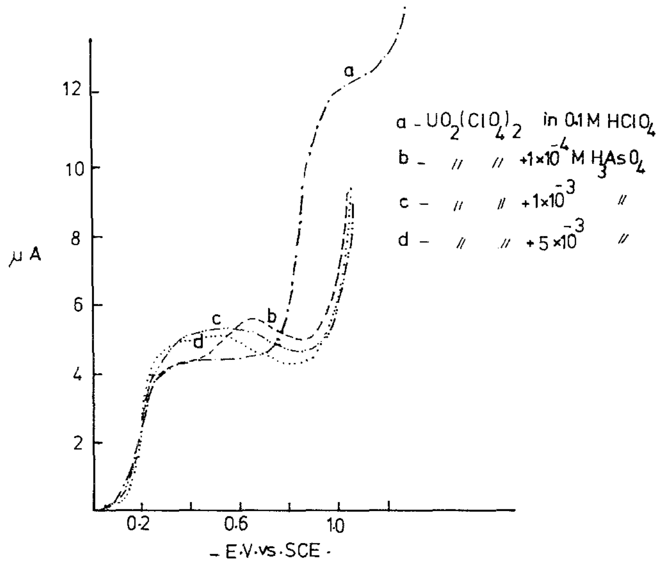

Fig. 3. Polarograms of 1 m*M* $UO_2(ClO_4)$ in presence of perchloric acid and low arsenic acid concentrations

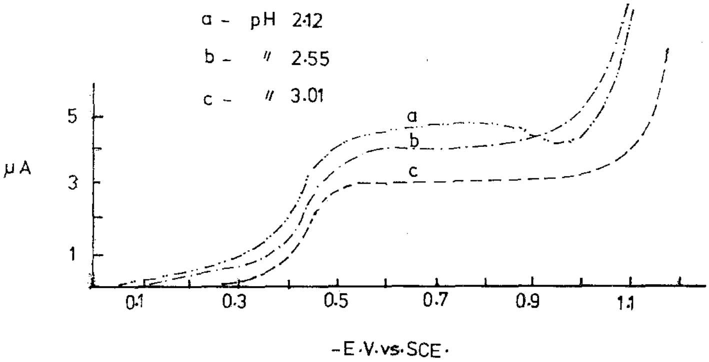

Fig. 4. Effect of different *pH*'s on the polarograms of uranyl ion in 0.1 *M* arsenic acid

However, at higher acid concentration the hydrogen ions participate in the reduction mechanism, shifting the process to less negative values. Therefore the suggested reduction mechanism at higher acid concentration is given by Eq. (2).

$$UO_2HAsO_4 + e + H^+ \rightarrow UO_2^+ + H_2AsO_4^- \qquad (2)$$

Table 2. *Effect of pH on the polarographic reduction of* 1 m*M* $UO_2(ClO_4)_2$ (*S*, *S'* see Table 1)

pH	$i_l(\mu A)$	$E_{1/2}$	*S*	αn_a	*S'*
2.12	4.6	0.425	20	1.18	0.4
2.55	4.2	0.44	10	0.59	0.5
3.01	3.0	0.45	10	0.59	0.52

The result of this reaction is the reduction of the hexavalent uranyl ion to the pentavalent one, consuming also one electron.

Effect of *pH*

Polarograms of 1 m*M* UO_2^{++} in 0.1 *M* arsenic acid (to which a small amount of sodium hydroxide was added to increase the *pH* value) are represented in Fig. 4. The *pH* was studied up to *pH* 3.01 because above 3.01 uranium hydroxide precipitates. The half wave potentials increase with increasing *pH*, whereas the limiting current decreases. The small shift in $E_{1/2}$ is due mainly to the shift of the reduction mechanism [Eqs. (1) and (2)] to a less easier one, due to the decrease of hydrogen ion concentration which participates in the reduction process. Increasing i_l values with decrease of *pH* are due to the increase of the dismutation of U (V) to U (VI) and U (IV). Thus an increase in U (VI) is observed during the reduction at the mercury electrode. The log *i* log *h* relation indicates that the process is diffusion controlled (slopes $\simeq$ 0.5 as in Table 2).

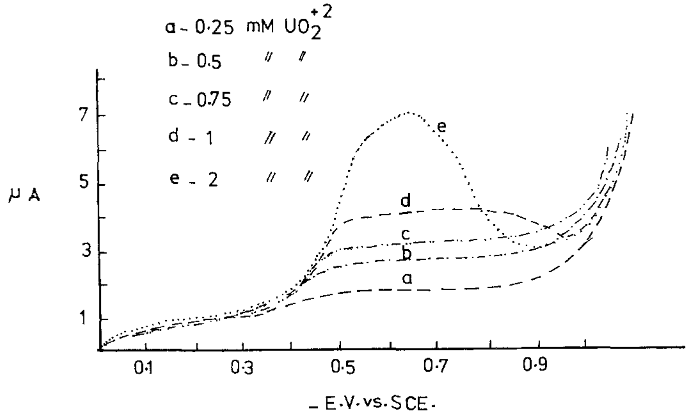

Fig. 5. Effect of different uranyl ion concentrations at 0.1 *M* arsenic acid

Effect of Concentration of UO_2^{++}

The effect of concentration of uranyl ions ranging from 0.25 m*M* to 2 m*M* in 0.1 *M* arsenic acid is shown in Fig. 5. Above 1 m*M* UO_2^{++} a maximum of the second kind appeared which makes it impossible to study above 1 m*M* UO_2^{++}. The limiting current shows a straight line relation after substracting their values from the limiting currents of the supporting electrolyte (Fig. 6). This straight line obeys the *Ilkovic* equation and can be used as an analytical method for the determination of uranyl ion in the presence of arsenic acid. With an increase of acid concentration the maximum disappeares, therefore it is possible to determine the concentration of uranyl ion up to 2 m*M* on using 0.6 *M* arsenic acid.

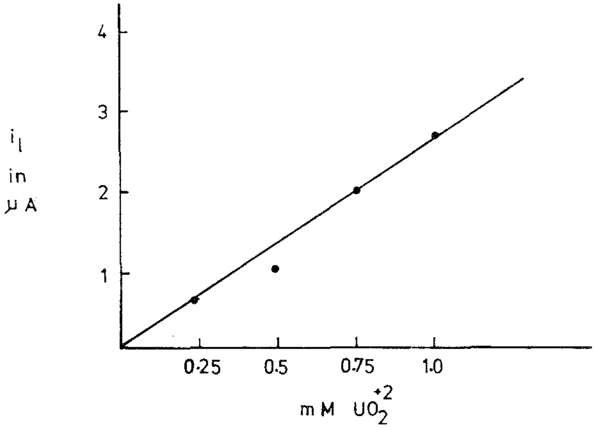

Fig. 6. Effect of different concentrations of UO_2^{++} on the limiting current of U (VI) wave at 0.1 *M* arsenic acid

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