# Polarographic Behaviour of Uranyl Ion in Maleic Acid and Maleate Buffer Solutions

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The polarographic behaviour of uranyl ion in maleic acid solution shows two reduction waves. The half wave potential of the first wave is shifted to more negative values in contrast to that of the second wave, which is shifted to less negative potentials on increase of the $pH$ of the solution. The first wave represents the reduction of the 1 : 1 uranyl-maleate complex, while the second wave represents the reduction of the 1 : 2 complex. The presence of 1 : 1 and 1 : 2 complexes is supported by spectrophotometric and conductometric methods. The stability constants were also determined and the reduction mechanism is discussed.

*(Keywords: Maleic acid; Maleate solution; Polarography; Uranyl ion)*

*Das polarographische Verhalten von Uranyl-Ionen in Maleinsäure- und Maleat-Puffer-Lösungen*

Die polarographische Kurve von Uranyl-Ionen in Maleinsäurelösung zeigt zwei Reduktionswellen. Das Halbwellenpotential der ersten Welle verschiebt sich bei ansteigendem $pH$ der Lösung zu negativeren Werten, im Gegensatz zur zweiten Welle, die eine positive Verschiebung zeigt. Die erste Welle repräsentiert die Reduktion des 1 : 1-Uranyl-Maleat-Komplexes, die zweite Welle hingegen die Reduktion des 1 : 2-Komplexes. Die Präsenz von 1 : 1- und 1 : 2-Komplexen wird auch durch spektrophotometrische und konduktometrische Messungen erhärtet. Die Stabilitätskonstanten wurden bestimmt, der Mechanismus der Reduktion wird diskutiert.

## Introduction

The properties of uranyl ion in maleic acid solution has been investigated by *Tsai-Teh*[1] using polarographic and conductometric methods; only one chelate $UO_2 Mal_2^{2-}$ was observed.

The aim of this work is to study the effect of the *pH* value on the reduction waves of uranyl ion in maleic acid, the mechanism of reduction at the electrode surface, and finally to determine the stability constants.
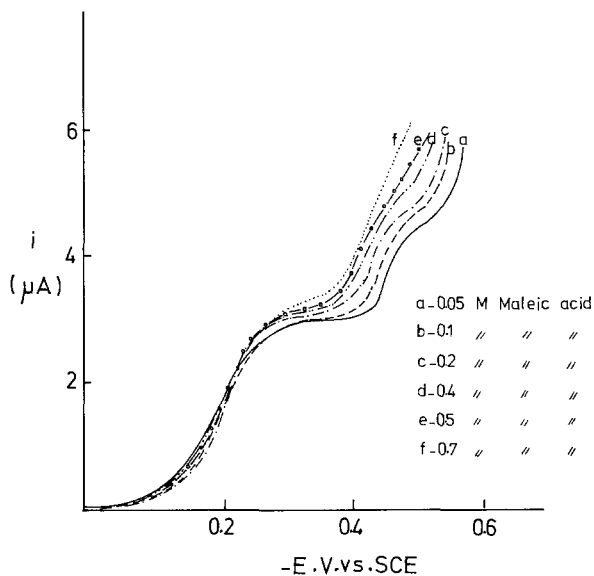


Fig. 1. Polarograms of $1 \text{ m}M$ $UO_2(ClO_4)_2$ at different molarities of maleic acid

## Experimental

Uranyl perchlorate was prepared from uranyl nitrate (G. R. Merck) as described in the previous paper[2]. The exact concentration of uranium was determined gravimetrically as $U_3O_8$. $1 M$ stock solution of maleic acid was prepared after twice recrystallization of a BDH sample of maleic acid. The potential curves were recorded by using an LP. 60 polarograph. The capillary characteristics were $m = 1.47 \text{ mg/s}$ and $t = 3.6 \text{ s/drop}$ in $0.1 M$ KCl at a height of a mercury column of 27 cm. The measurements were done using a Karl Zeiss USU-2-P-Jena spectrophotometer, a PYE conductivity bridge and a *pH* meter (type WGP PYE model 290).

## Results and Discussion

### *Effect of Maleic Acid*

The electroreduction of $1 \text{ m}M$ uranyl ion with $0.1 M$ perchloric acid as supporting electrolyte in presence of different concentrations of maleic acid is represented by the polarograms shown in Fig. 1. Two waves are
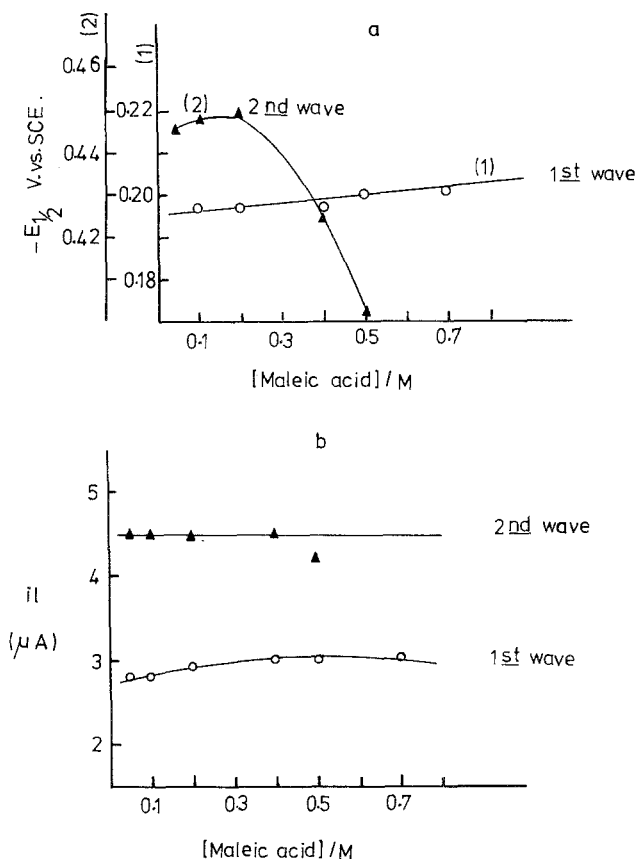
Fig. 2. *a* Effect of maleic acid concentration on the half wave potentials of uranyl waves. *b* Effect of maleic acid concentration on the limiting currents of 1 m*M* uranyl waves

obtained in absence of maleic acid which correspond to the reduction of the hexavalent uranium to the pentavalent one and the pentavalent to the trivalent one, respectively[3], with $E_{1/2}$'s $-0.17$ and $-0.83$ V vs. SCE. On adding maleic acid a new wave at a half wave potential of $-0.6$ volts appears which represents the reduction of maleic acid. Increasing the concentration of maleic acid reveals that the height of its wave increases till it is out of scale (i.e. at 0.04 *M* maleic acid). At 0.05 *M* maleic acid a new second wave is obtained with $E_{1/2}$ of $-0.455$ V vs. SCE.

Increasing the acid concentration, the second wave is destroyed and disappears above 0.5 *M* acid concentration. The half wave potential of the

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Table 1. *Effect of maleic acid on the reduction waves of* 1 m$M$ $UO_2(ClO_4)$

| Molarity of the acid | | $il$ | $-E_{1/2}$ | $0.059/\alpha n_a$ | $\alpha n_a$ | $S^a$ |
|---|---|---|---|---|---|---|
| 0.05 | 1st wave | 2.8 | 0.187 | 0.052 | 1.13 | 0.50 |
|      | 2nd wave | 4.5 | 0.455 | 0.035 | 1.70 | 0.24 |
| 0.10 | 1st wave | 2.8 | 0.197 | 0.062 | 0.95 | 0.45 |
|      | 2nd wave | 4.5 | 0.455 | 0.033 | 1.80 | 0.34 |
| 0.20 | 1st wave | 2.9 | 0.197 | 0.062 | 0.95 | 0.45 |
|      | 2nd wave | 4.5 | 0.460 | 0.033 | 1.80 | 0.40 |
| 0.40 | 1st wave | 3.0 | 0.200 | 0.064 | 0.92 | 0.44 |
|      | 2nd wave | 3.5 | 0.435 | 0.033 | 1.80 | 0.38 |
| 0.50 | 1st wave | 3.0 | 0.205 | 0.065 | 0.91 | 0.45 |
|      | 2nd wave | 4.2 | 0.412 | 0.033 | 1.80 | 0.37 |
| 0.70 | 1st wave | 3.0 | 0.210 | 0.068 | 0.87 | 0.50 |

[a] $S$ are slopes of the mercury height relation ($\log i/\log h$).

first wave is shifted to more negative values by increasing the concentration of maleic acid, whereas the second wave is shifted to less negative values as seen in Fig. 2 *a*. The limiting current of the first wave very slightly increases reaching a constant value upon adding further maleic acid. Furthermore, the second wave height is not affected by the increased maleic acid concentration (Fig. 2 *b*).

The relation between $\log i/i_d - i$ against $E$ in volts (analysis of the waves) are straight lines, from their slopes the values of $\alpha n_a$ are obtained ($\simeq$ 1 for the first wave and $\simeq$ 2 for the second wave), as shown in Table 1.

By plotting $\log i$ against $\log h$ (mercury height) straight lines are obtained. The slopes of the first wave are 0.5 indicating that the electrode process of this wave is mainly diffusion controlled. For the second wave, the slope values indicate that the process of reduction is mainly controlled by diffusion and partly by the rate of the chemical reaction (Table 1).

### Effect of pH

The reduction of 1 *mM* $UO_2$ $(ClO_4)_2$ in 0.1 *M* maleic acid containing 0.1 *M* $HClO_4$ as supporting electrolyte at the dropping mercury electrode was carried out in the *pH* range 1.3–6.13. The polarograms are recorded and shown in Fig. 3. The desired *pH* value is attained by the addition of the necessary quantity of sodium hydroxide to the electrolyte. All the solutions of different *pH*'s were kept at constant ionic strength by adding $NaClO_4$.
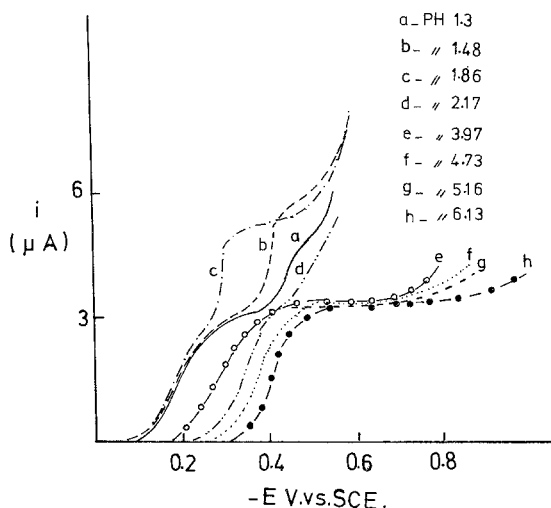
Fig. 3. Polarograms of 1 m$M$ UO$_2$(ClO$_4$)$_2$ at different hydrogen ion concentrations

Table 2. *Effect of pH on the reduction waves of* 1 mM UO$_2^{++}$ *in* 0.1 *M maleic acid*

| pH | | il | $-E_{1/2}$ | $0.059/\alpha n_a$ | $\alpha n_a$ | $S^a$ |
|---|---|---|---|---|---|---|
| 1.30 | 1st wave | 3.0 | 0.192 | 0.062 | 0.95 | 0.45 |
| | 2nd wave | 4.0 | 0.440 | 0.034 | 1.75 | 0.38 |
| 1.48 | 1st wave | 3.0 | 0.192 | 0.062 | 0.95 | 0.45 |
| | 2nd wave | 3.1 | 0.400 | 0.033 | 1.79 | 0.37 |
| 1.86 | 1st wave | 3.0 | 0.192 | 0.062 | 0.95 | 0.54 |
| | 2nd wave | 5.0 | 0.290 | 0.034 | 1.74 | 0.38 |
| 2.17 | 1st wave | 3.0 | 0.197 | 0.062 | 0.95 | 0.54 |
| 3.97 | 1st wave | 3.2 | 0.307 | 0.062 | 0.95 | 0.50 |
| 4.73 | 1st wave | 3.2 | 0.357 | 0.065 | 0.91 | 0.52 |
| 5.16 | 1st wave | 3.1 | 0.387 | 0.062 | 0.95 | 0.54 |
| 6.13 | 1st wave | 3.1 | 0.417 | 0.057 | 1.04 | 0.45 |

[a] $S$ are slopes of the relation $\log i/\log h$ (mercury height relation).

The electroreduction of one millimole uranyl ion at *pH* 1.3 took place by two reduction waves as shown in Fig. 3. Their half wave potentials are − 0.192 and − 0.43 V vs. SCE, their limiting currents values are 3.0 and 4.5 $\mu$A for the first and second waves, respectively. Increasing the *pH* of
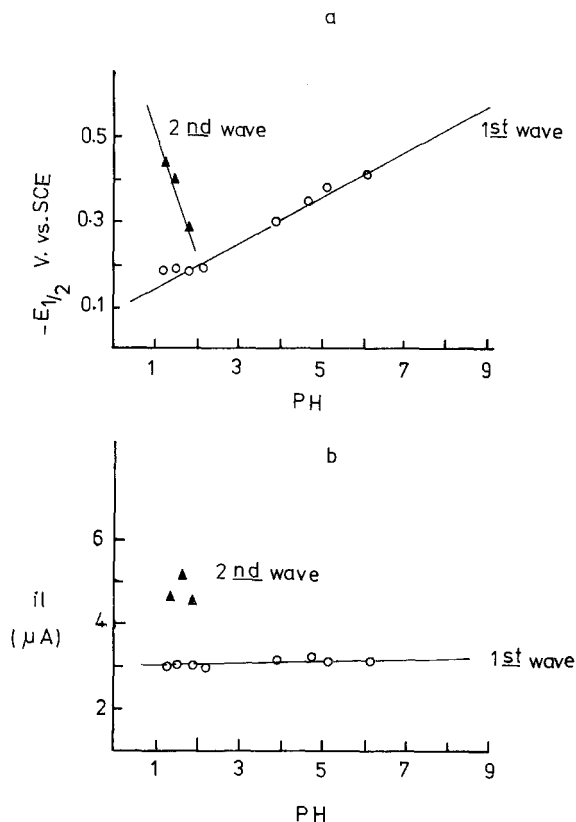
a



b

Fig. 4. *a* Effect of *pH* on the half wave potentials of the uranyl waves. *b pH* effect on the limiting current of $UO_2(ClO_4)_2$ waves

solutions is followed by a positive shift of the second reduction wave until it disappears at *pH* 2.17.

By analysing the first wave using the relation $\log i/i_d - i$ against *E* in volts, straight lines are obtained. From the slopes $\alpha n_a$ values were calculated and found to be approximately one and two for the first and second wave, respectively (Table 2).

From Fig. 4 *a* it is seen that the half wave potentials of the first wave are shifted to more negative values with increasing *pH* values. On the other hand $E_{1/2}$'s of the second wave were shifted to more positive values with increased *pH* values. The limiting currents of the first and second wave were almost not affected by changes of the *pH* as illustrated in Fig. 4 *b*. The *il* values of the second wave were merely double compared to that of the first reduction wave.

*Spectrophotometric and Conductometric Studies*

The stoichiometry of the uranyl-maleate complexes was determined by using UV spectrocopy. Using different molar ratios of uranyl ion and maleic acid at $\lambda = 290$ nm three straight lines were obtained. The break points of these curves are at 1 and 2 which correspond to 1:1 and 1:2 uranyl maleate complexes (Fig. 5 *a*).
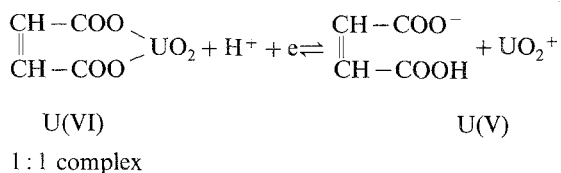
The stoichiometry of uranyl-maleate complexes was studied also using conductometric titration. 50 ml of uranyl ion solution of 2 *mM* concentration was placed in the titration cell which was immersed in an ultrathermostate at 25 °C, and titrated with $2 \cdot 10^{-2}$ *M* ligand solution added from a micro burette. Two break points were found (Fig. 5 *b*) at 5 and 10, corresponding to the formation of 1:1 and 1:2 complexes.

The stability constants were determined using *Job*'s method[4] and were found to be 4.05 and 6.15 for the 1:1 and 1:2 complexes, respectively. They were also supported by the method following *Irving* and *Rossotti*[5]: 4.0 and 6.8 for the two types of uranyl-maleate complexes.

*Reduction Mechanism*

The reduction mechanism was suggested from two facts: firstly $\alpha n_a$ values, which indicate that the reduction took place by one electron for the first wave and two electrons for the second wave; secondly, from spectroscopy and conductivity measurements it was proved that uranyl ion and maleic acid form two types of complexes (1:1 and 1:2 complexes). The reduction process of the two complexes of uranyl ion are affected by the hydrogen ion concentration as can be seen from the effect of *pH* on the reduction mechanism, indicating the participitation of hydrogen ions in the reduction processes.

It is thus seen that the reduction process of the first wave (one electron mechanism) corresponds to the reduction of the 1:1 (uranyl-maleate) complex. In this complex the heaxavalent uranium consumes one electron and one proton. This process of reduction took place at all acid concentrations and *pH* values, as follows:

$$\begin{array}{l} CH-COO \\ \| \quad\quad\quad > UO_2 + H^+ + e \rightleftharpoons \\ CH-COO \end{array} \quad \begin{array}{l} CH-COO^- \\ \| \quad\quad\quad\quad + UO_2{}^+ \\ CH-COOH \end{array}$$

U(VI) U(V)

1:1 complex

On the other hand, the reduction process of the second wave (two electrons mechanism) was achieved by the reduction of the 1:2 (uranyl-
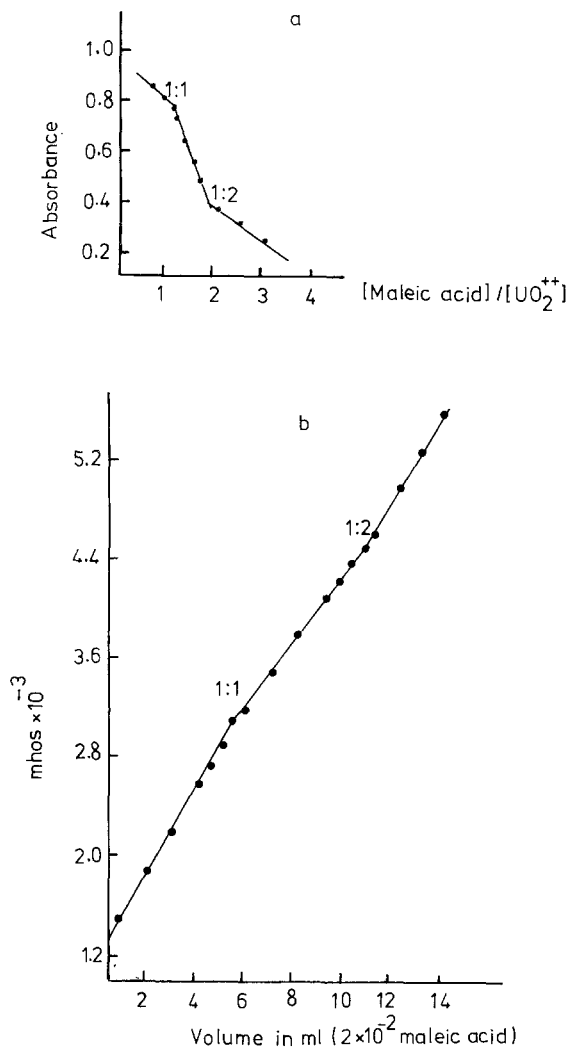
Fig. 5. Estimation of the stoichiometry of uranyl-maleate complexes: *a* Spectro-
photometry by using the molar ratio method. *b* Conductometric titration

maleate) complex. This second wave was found to involve two electrons
and two protons for the reduction of the heaxavalent uranyl ion to the
tetravalent one. It may thus be concluded that uranyl ion undergoes the
second reduction step only at low maleic acid concentrations ($< 0.5\,M$)
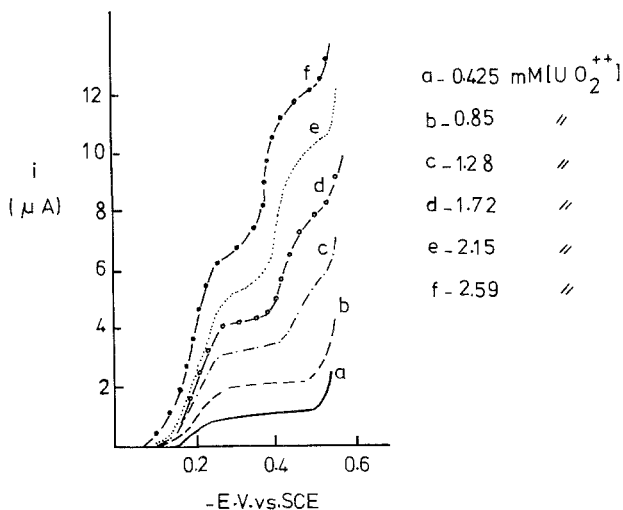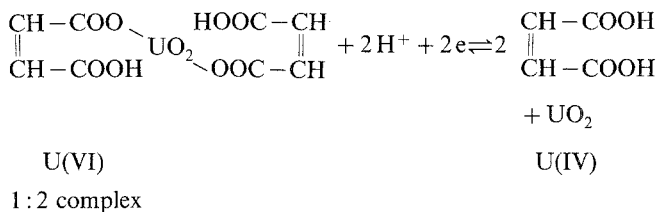and at lower *pH* values than 2.17.

a – 0.425 mM [U O$_2^{++}$]

b – 0.85     //

c – 1.28     //

d – 1.72     //

e – 2.15     //

f – 2.59     //

Fig. 6. Effect of the uranyl ion concentration on the waves of uranyl-maleate in presence of 0.1 $M$ maleic acid

$$\begin{array}{ccc} CH-COO & HOOC-CH & CH-COOH \\ \parallel \quad\quad UO_2 & \parallel \quad +2H^+ +2e \rightleftharpoons 2 & \parallel \\ CH-COOH \quad OOC-CH & & CH-COOH \end{array}$$

$$+ UO_2$$

U(VI)                                                                U(IV)

1 : 2 complex

Both mechanisms are reversible ones, which is indicated by the slopes of the analysis of the waves.

## Effect of Concentration of $UO_2^{2+}$

The polarographic behaviour of U(VI) at varying concentrations ranging from 0.43 to 2.6 m$M$ in 0.1 $M$ maleic acid and 0.1 $M$ HClO$_4$ as supporting electrolyte is represented in Fig. 6.

Each polarogram at a concentration lower than 1 m$M$ UO$_2^{++}$ consists of only one wave which correspondes to the first reduction wave of uranyl ion U(VI) → U(V).

The second wave starts to appear at 1 m$M$ U(VI). On increasing the uranium concentration, the second wave becomes well developed. The mean value of $i_d/c$ amounts to 2.45 $\pm$ 0.1 and 1.93 $\pm$ 0.3 $\mu$A/m$M$ for both the first and the second wave, respectively.

The validity of the *Ilkovic* equation is confirmed for both the first and the second waves. Therefore, any unknown concentration of uranyl ion can be determined.

## References

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