NOTES

A. C. Polarography of Uranium in Non-complexing and Complexing Media

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(Received June 20, 1962)

A. C. polarography of uranium has been studied at 50 c. p. s. by Breyer and Hacobian1) and the method has been applied for the estimation of uranium2). We have observed earlier3) that the a. c. peak height does not increase with the increase in the concentration of acid or oxalic acid though an increase in the d. c. current is observed. This paper reports a more detailed study of the a. c. polarography of uranium in non-complexing and complexing media.

Experimental

The apparatus and the method of measurement of the alternating current have been described earlier4). An H-cell with a saturated calomel electrode as the reference electrode was used but the current was measured across the mercury pool for low cell resistance (300 ohms)5).

All experiments were carried out at 30±0.5°C with deaerated solutions. Two capillaries [$m^{2/3} \cdot t^{1/6}$($mg^{2/3}\ sec^{-1/2}$)=1.75 (I) and 1.46 (II)] were used for the work. All solutions were made from reagent grade chemicals. Sodium perchlorate was used to maintain the ionic strength and the pH was adjusted with perchloric acid.

Results and Discussion

Non-Complexing Media.—Uranium gives two waves in weakly acid media and the disproportionation reactions are unimportant6). An a. c. polarogram of uranium in 0.1 M sodium chloride and 0.01 M hydrochloric acid showed two peaks corresponding to the two d. c. steps. The peak potentials corresponded to the half-wave potentials. Whereas the height of the second d. c. step was nearly double that of the first, the second a. c. peak was smaller than the first.

The peak currents were measured at different salt concentrations (Table I). The current for the first peak reached a constant value but that for the second increased with an increase in the concentration of sodium chloride. The height of the second peak was greater than that of the first at higher salt concentrations, though never double as in the d. c. polarography. The effect of frequency (Table II) showed that the current for the first peak increased upto 200 c. p. s. but that for the second increased only upto 100 c. p. s. Besides, the second peak height was smaller than the first at 500 c. p. s. The results are understandable as the second step is irreversible and the rates of the two electrode processes may be different.

The ratio of the peak current to uranium in 2 M hydrochloric acid (Table III) decreased

TABLE I. EFFECT OF SALT CONCENTRATION ON THE PEAK HEIGHTS OF URANIUM

Supporting electrolyte=NaCl+HCl 0.01 M
A. C. amplitude =45 mV. at 50 c. p. s.
Capillary I

Sodium chloride M	A. C. peak current μamp. Peak I	Peak II
0.1	14.1	9.3
0.2	15.0	20.9
0.5	15.1	21.5
1.0	15.1	22.9
1.6	15.6	24.3

TABLE II. EFFECT OF FREQUENCY ON THE PEAK HEIGHTS OF URANIUM

U=1 mM ; NaCl=1.6 M ; HCl 0.01 M
Capillary I
A. C. amplitude=45 mV.

Frequency cycl./sec.	A. C. peak current μamp. Peak I	Peak II
50	15.6	24.3
100	19.5	27.5
200	22.5	21.6
500	19.3	12.0

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2) B. Breyer and J. R. Beevers, *J. Electroanalyt. Chem.*, **1**, 345 (1959/60).

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4) K. S. G. Doss and A. Kalyanasundaram, *Proc. Ind. Acad. Sci.*, **33**, 298 (1951).

5) H. H. Bauer and P. J. Elving, *Anal. Chem.*, **30**, 334 (1958).

6) W. E. Harris and I. M. Kolthoff, *J. Am. Chem. Soc.*, **67**, 1484 (1945) ; **68**, 1175 (1946).

TABLE III. EFFECT OF URANIUM CONCENTRATION ON THE FIRST PEAK HEIGHT

Supporting electrolyte = 2.0 M HCl
A. C. amplitude = 14 mV. at 50 c. p. s.
Capillary II

Uranium c, mM	Peak current at -0.18 V. vs. S. C. E. i, μamp.	i/c μamp./mM
0.2	0.95	4.75
0.5	2.2	4.4
1.0	4.3	4.3
2.0	8.5	4.25

with increasing concentration of uranium contrary to that observed in conventional polarography. The increase in the d. c. current for the first step beyond that corresponding to one-electron diffusion controlled reaction is a function of the rate of disproportionation and as the rate in presence of acids in comparatively smaller than that in the presence of complexing agents, the height of the first peak has been studied in complexing media.

Complexing Media.—The polarography of uranium in thiocyanate⁷⁾, lactate⁸⁾ and oxalate⁹⁾ media has been reported. A shift in the half-wave potential to more negative values occurred in lactate and oxalate medium at pH 5 with no change in the limiting current. At this pH the peak potentials of the a. c. polarograms corresponded to the half-wave potentials and the peak currents were the same as that of the simple ion. The limiting current for the first step in these media increased with the concentration of the complexing agent in acidic solutions whereas the a. c. peak currents for low concentration of oxalate, lactate or thiocyanate were nearly the same as for the simple ion and decreased on further increase in the concentration. The peak potentials were the same viz., -0.18 V. vs. S. C. E. whereas the half-wave potentials in the case of oxalate (-0.13 V.) and thiocyanate (-0.11 V.) shifted to more positive potentials at high concentrations.

In explaining these results, the electrode reaction coupled with the chemical reaction will have to be considered. Uranium(V) produced at the electrode by the reduction of uranium(VI) with the half-wave potential at -0.18 V. vs. S. C. E. undergoes disproportionation to produce more of uranium(VI). This is again reduced at the electrode giving rise to an increase in the current. The half-wave potential is for the overall reaction. In a. c. polarography the peak potential of -0.18 V. corresponds to the electrode reaction. But the reversal of the electrode reaction takes place due to the superimposed a. c. and consequently no chemical reaction occurrs. Hence no increase in the a. c. peak current is observed and the peak potential remains same.

The decrease in the peak current at higher concentrations of the complexing agent might be due to the rate of the electrode recation. It was observed that the peak current reduced with the increasing concentration of the complexing agent (Fig. 1).

Thiocyanate was the only system for which a slope of 30 mV. for the log plot of the first wave was obtained whereas a slope of 60 mV. was obtained in the case of oxalate and lactate. Besides, a linear relationship between current and concentration of uranium and a temperature coefficient of less than 2% in the case of thiocyanate would appear to indicate that no kinetic considerations were involved in the reduction. The observations made herein indicated that this was also a case of disproportionation.

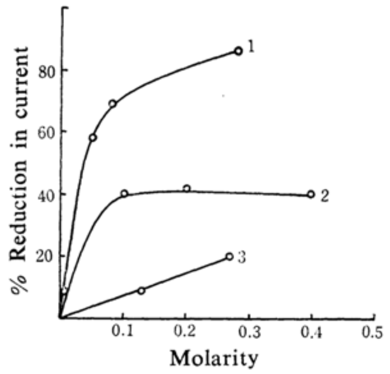

Fig. 1. % Reduction in current at different concentrations of complexing agent.
$U=1\cdot10^{-3}$ $\mu=1.0$ pH=1
1, $H_2C_2O_4$ 2, NH_4NCS 3, $CH_3CHOHCOOH$

The authors wish to thank Dr. V. T. Athavale, Head, Analytical Division, for his kind interest.

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