

## Polarographic Behaviour of +6 Uranium in a Mixture of Salicylic and Sulphuric Acid

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The half-wave potential, the diffusion coefficient and the diffusion current constant of +6 uranium in the supporting electrolyte containing 1.60 g/l salicylic acid, 0.4% v/v sulphuric acid and 0.009% thymol (as maximum suppressor) have been determined. The electrocapillary curve of mercury in this electrolyte is also given.

An aqueous solution of salicylic acid (1.60 g/l) and sulphuric acid (0.4% v/v) containing 0.009% of thymol as maximum suppressor has proved a very suitable supporting electrolyte for +6 uranium.<sup>1</sup> In the present paper measurements and calculations are reported of the half-wave potential, the diffusion coefficient and the diffusion current constant of +6 uranium in this medium.

### EXPERIMENTAL

Reagents used in this study were the same as described previously.<sup>1</sup> In addition to the Cambridge polarograph, a »Polarograf Heyrowsky« Model V-301 (Československa Zbrojovka, Brno) was used. The recorder sensitivity of this apparatus was  $3.60 \times 10^{-9}$  A/mm.

A »Philoskop II« (Philips GM 4144) universal bridge with external current source (»NF-Schwebungsoszillator«, Philips GM 2307) and an electronic voltmeter Philips GM 6005 were employed for resistance measurements.

The potential difference on the bridge was calibrated with a standard Weston cell.

The rate of mercury flow from the capillary was measured by the method of Kolthoff and Lingane<sup>2</sup> using an experimental arrangement described by Filipović<sup>3</sup>. Measurements were carried out in the same electrolyte at 0 volts with respect to the saturated calomel electrode.

The temperature was kept at  $25 \pm 0.1^\circ\text{C}$  by means of a constant temperature water bath.

### RESULTS AND DISCUSSION

#### *The half-wave potential*

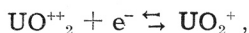
The half-wave potential of +6 uranium in the above mentioned electrolyte was calculated from the data given in Table 1 by applying the least-squares method.<sup>4</sup> The correction for the potential drop  $iR$  amounted to less than  $2 \times 10^{-4}$  volts and was neglected. The values of the diffusion current and the resistance  $R$  (for 3000 c./sec.) at the half wave potential were  $305.9 \times 10^{-9}$  A and 1300 ohms, respectively. Under these conditions a value of 0.2127 volts with standard error of  $\pm 0.0007$  volts was obtained for the half wave potential of +6 uranium.

TABLE 1

$E_{de}$ mV	175	180	190	200	210	220	225	230	240	250
$i$ mm	7.5	8.3	11.1	14.5	18.3	22.0	23.5	25.2	28.9	31.3
$i_d = 38.5$ mm										

The relationship between the potential ( $E_{de}$ ) and  $\log i/(i_d - i)$  was linear with a slope of  $0.0591 \pm 0.0006$  volts which is in perfect agreement with the theoretical value of 0.0591 volts for a reduction process at 25°C involving 1 F of electricity.

Therefore, it is reasonable to assume that under these experimental conditions the electrode reaction consists in a reversible cathodic reduction of uranyl ion according to the equation:



although the observed half-wave potential is slightly more negative than the standard potential ( $-0.180$  volts) of reduction of +6 uranium to +5 uranium as measured in other media<sup>5,6</sup>. This shift of the half-wave potential to the negative side is probably due to the complexing power of the salicylic acid and different acidity conditions.

#### The diffusion coefficient

The diffusion coefficient may be calculated either from the original<sup>7</sup> —

$$D = \left( \frac{i_d}{607 n C m^{2/3} t^{1/6}} \right)^2 \quad (1)$$

or the corrected Ilkovič equation<sup>8,9</sup>:

$$D' = \left[ \frac{m^{1/3}}{2 A t^{1/6}} \left( -1 + \sqrt{1 + \frac{4 A i_d}{607 n C m}} \right) \right]^2 \quad (2)$$

where  $i_d$  is the mean diffusion current in  $\mu\text{A}$ ;  $n$  the number of equivalents involved in the electrode reaction;  $D$  and  $D'$  the diffusion coefficients in  $\text{cm}^2 \text{sec}^{-1}$ ;  $C$  the concentration of the reacting substance in millimoles per liter;  $m$  the rate of flow of mercury from the capillary in  $\text{mg}\cdot\text{sec}^{-1}$ ;  $t$  the drop-time in secs; and  $A$  a constant having numerical value 39 (Lingane and Loveridge<sup>9</sup>) or 17 (Strehlow and von Stackelberg<sup>8</sup>).

In order to obtain a good estimate of the diffusion current constant and the diffusion coefficient 84 measurements of the diffusion current were performed for different uranium concentrations using two polarographs and two capillaries. Thus four independent estimates of the diffusion current were obtained for each concentration, each estimate being an arithmetic mean of two measurements. The uranium concentrations covered a range from 2 to 50  $\mu\text{g}/\text{ml}$ . The results of the measurements are given in Table 2. If the diffusion

currents are expressed in  $\mu\text{A}$ , only two series of results are obtained corresponding to the two capillaries used.

TABLE 2

		CAPILLARY							
		I				II			
		Polarograph				Polarograph			
		Cambridge		Heyrowsky		Cambridge		Heyrowsky	
No.	C	$h$	$\bar{h}$	$h$	$\bar{h}$	$h$	$\bar{h}$	$h$	$\bar{h}$
1	49.3	150.0	149.7	101.0	101.7	135.6	136.5	92.8	93.3
2		149.4		102.3		137.4		93.9	
3	39.4	117.0	116.7	84.4	83.7	108.6	108.9	72.8	73.7
4		116.4		83.0		109.2		73.5	
5	29.6	90.0	89.3	61.5	61.3	82.8	82.8	56.4	57.3
6		88.5		61.1		82.8		58.2	
7	19.7	58.8	59.4	42.9	42.8	53.4	53.4	38.2	38.3
8		60.0		42.6		53.4		38.4	
9	13.8	41.4	41.1	30.2	30.1	37.2	37.2	27.3	27.1
10		40.8		30.0		37.2		26.9	
11	13.8	41.2	40.6	31.2	30.8	36.6	36.3	27.4	27.0
12		40.0		30.4		36.0		26.6	
13	9.86	27.8	27.8	22.2	21.8	24.9	24.8	19.6	19.3
14		27.8		21.4		24.7		19.0	
15	7.89					19.2	19.1	16.0	15.9
16						19.0		15.8	
17	5.92	16.8	17.3	14.2	13.9	14.8	14.6	12.0	11.9
18		17.8		13.6		14.4		11.8	
19	3.94	12.0	11.8	8.4	8.3	8.8	8.9	8.2	8.1
20		11.6		8.2		8.0		8.0	
21	1.97	4.5	4.4	5.0	4.6	4.0	3.9	3.8	4.0
22		4.3		4.2		3.8		4.2	

C = uranium concentration in  $\mu\text{g/ml}$ ;  $h$  = wave height in mm.

The results of the linear regression analysis performed for these data are given in Table 3. The estimation of the diffusion current was done using the regression equations  $i_d = 7.83 C$  (for the capillary I) and  $i_d = 7.13 C$  (for the capillary II). Thus a fairly reliable estimate of the diffusion current for a

TABLE 3

Capillary	Variance about the regression $V$	Slope $b$	Standard error of the slope $s_b$
I	18.92	7.830	0.040
II	22.00	7.125	0.043

chosen uranium concentration was obtained. Other experimental data necessary for calculating the diffusion coefficient from the equation (1) and (2) are collected in Table 4. Table 5 contains the calculated values of the diffusion coefficient, if 39 is taken as the value of the constant  $A^9$ .

TABLE 4

Capillary	Mercury column height mm	Rate of flow of mercury $m$ mg sec <sup>-1</sup>	Standard error $s_m$ mg sec <sup>-1</sup>	Drop time at 200 mV $t$ sec	Standard error $s_t$ sec
I	540	1.421	0.003	3.084	0.005
II	440	1.153	0.010	4.102	0.003

TABLE 5

Capillary	Uranium concentration $C$ mM/l	Diffusion current $i_d$ $\mu$ A	Diffusion coefficient from eq. (1) $D \times 10^6$ cm <sup>2</sup> sec <sup>-1</sup>	Standard error of $D$ $s_D \times 10^6$ cm <sup>2</sup> sec <sup>-1</sup>	Diffusion coefficient from eq. (2) $D' \times 10^6$ cm <sup>2</sup> sec <sup>-1</sup>	Standard error of $D'$ $s_{D'} \times 10^6$ cm <sup>2</sup> sec <sup>-1</sup>
I	0.042004	0.0783	4.055	0.024	3.488	0.034
II	0.042004	0.0713	4.034	0.054	3.434	0.055
Mean values			4.045		3.461	

The following equations were used for estimating the standard error of  $D$  and  $D'$ :

$$s_D = D \sqrt{\varrho_i^2 + \frac{16}{9} \varrho_m^2 + \frac{4}{9} \varrho_t^2} \quad (3)$$

( $\varrho$  is the relative standard error; the subscripts  $i$ ,  $m$  and  $t$  refer to the measurements of the diffusion current, the rate of flow of mercury and the drop time, respectively), and:

$$s_{D'} = D' \sqrt{\left(\frac{B-1}{B-\sqrt{B}}\right)^2 \varrho_i^2 + \left(\frac{2}{3} - \frac{B-1}{B-\sqrt{B}}\right)^2 \varrho_m^2 + \frac{1}{9} \varrho_t^2} \quad (4)$$

with  $B = \frac{4 A i_d}{607 n C m} + 1$ . Both equations were derived by applying the well known rule for calculating the standard error of a computed result.<sup>11</sup>

#### The diffusion current constant

The same data (Table 5) were used in calculating the diffusion current constant<sup>12,13</sup> from the equation:

$$I = 607 n D^{1/2}$$

where for  $D$  either the value calculated from the original (1) or the corrected Ilkovič equation (2) can be substituted. Table 6 gives the calculated values of  $I$  and their standard errors.

TABLE 6

Capillary	Diffusion current constant calculated using $D$ $I$	Standard error $s_I$	Diffusion current constant calculated using $D'$ $I'$	Standard error $s_{I'}$
I	1.222	0.004	1.134	0.006
II	1.219	0.008	1.125	0.009
Mean values	1.221		1.130	

The standard error was estimated from the equation

$$s_I = \frac{607n}{2\sqrt{D}} s_D$$

#### *Electrocapillary curve of mercury in salicylic acid-sulphuric acid mixture*

Since the supporting electrolyte consisting of 1.6 g/l salicylic acid, 0.4% v/v sulphuric acid and 0.009% thymol is suitable for polarographic determination of various metal ions, the electrocapillary curve of mercury in this medium may be of some interest.

For a given capillary the drop time of mercury ( $t$ ) is proportional to the interfacial tension ( $\sigma$ ) ( $t = K \cdot \sigma$ ). Since in polarographic work it is important to know only the form of the electrocapillary curve and not the absolute values of the interfacial tensions, only the drop time ( $t$ ) of mercury was

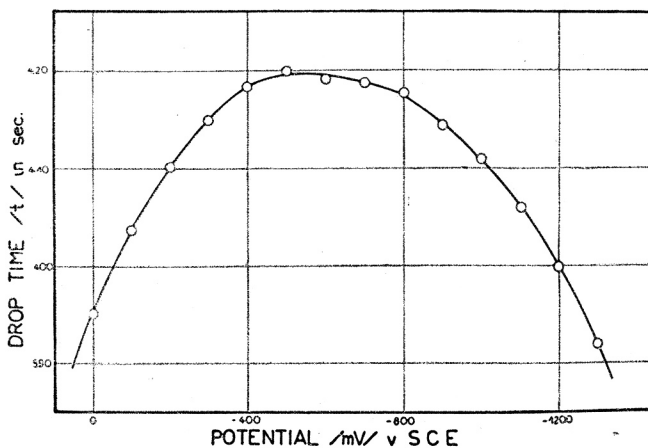


Fig. 1. Electrocapillary curve of mercury in 1.6 g/l salicylic acid — 0.4% v/v sulphuric acid. Ordinates: drop time ( $t$ ) in seconds; abscisae: applied potential relative to the saturated calomel electrode (in mV).

measured at different potentials. For each value of the applied potential the drop time for 50 drops was noted, and the drop time of a single drop calculated therefrom. A saturated calomel electrode was used as the reference electrode. The standard error of  $t$  did not exceed 0.005 seconds. Figure (1) shows the electrocapillary curve of mercury in this supporting electrolyte.

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## IZVOD

**Neke polarografske karakteristike +6 urana u sistemu salicilna kiselina-sumporna kiselina**

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U nastavku rada na određivanju urana polarografskom metodom<sup>1</sup> određene su ove polarografske karakteristike urana: poluvalni potencijal, koeficijent difuzije i konstanta difuzione struje. Kao osnovni elektrolit služila je smjesa salicilne i sumporne kiseline. Određena je i elektrokapilarna krivulja žive u tom elektrolitu.

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