

REFERENCES

1. Rifi M. R.: *Tetrahedron Letters* 1969, 1043.
2. Peacock R. E., Torupka E. J.: *J. Am. Chem. Soc.* 91, 4953 (1969).
3. Závada J., Krupička J., Sicher J.: *This Journal* 28, 1664 (1963).
4. Sease J. W., Chang P., Groth J.: *J. Am. Chem. Soc.* 86, 3164 (1964).
5. Gassman P. G.: *Gordon Research Conference* (1969).

**BEHAVIOUR OF URANYL ION UPON REDUCTION
FROM THE ETHYLENEDISULPHURDIACETIC ACID SOLUTION
AT THE DROPPING MERCURY ELECTRODE**

D.Ž.SUŽNJEVIĆ and M.V.ŠUŠIĆ

*Department of Physical Chemistry, University of Belgrade and
Institute for Chemistry, Technology and Metallurgy,
Belgrade, Yugoslavia*

Received June 29th, 1970

Chelate forming reactions between metal ions and S-containing organic ligands do not attract enough attention in the field of coordination chemistry. This probably is due to the low stability of some of the resulting compounds; also the data on polarographic behaviour of those reaction products are insufficient.

It was interesting, therefore, to investigate the stability, as well as the polarographic behaviour of the formed metal compounds from ethylenedisulphurdiacetic acid (H_2L) solution, because, on the other side, similar aminoacetic acids are well known as complex forming reagents.

Previous work of the author included investigations of some bivalent elements-chelates¹⁻³ as well as slightly soluble silver, mercury and copper salts with H_2L ⁴.

The aim of the present work was to study the polarographic behaviour of uranyl ion from H_2L as supporting electrolyte.

It was observed that the waves produced during UO_2^{2+} ion reduction at the D.M.E. from acidic perchlorate medium diminished on progressive addition of H_2L . The molar ratio $UO_2^{2+} : H_2L = 1 : 2$ having been reached the wave, asymmetrical to the half-wave potential, does not change on further addition of H_2L . The $E_{1/2}$ of this wave is somewhat more positive than that of the first wave obtained at the reduction of the uranyl ion from the perchlorate medium. It was noticed also that other two waves, ill-defined, exist at somewhat negative potentials. A similar picture was observed with the amperometric titration of UO_2^{2+} ion with H_2L in ascorbic acid solution.

It was assumed that the first wave was due either to phenomena caused by adsorption of the reduction form of the depolarizer or to the blocking of its slightly soluble form. However, the electrode reaction behaves in the same way in both cases.

EXPERIMENTAL AND RESULTS

The current-voltage curves were recorded on a polarograph Radiometer PO 4. The thermostated polarographic cell was used. Potentials of the D.M.E. were measured with reference to s.c.e. All experiments were carried out at $20 \pm 0.2^\circ\text{C}$. pH-values were measured with Beckman pH-meter (model G 8509). The instantaneous current on single drop (second drop mostly) was obtained into circuit with oscilloscope C 1A (produced in SSSR) and one $k \Omega$ resistor. Electrocapillary curves were obtained from average values of drop time measurements at different values of potential. Ionic strength was kept constant with NaClO_4 addition. pH was adjusted by addition of HClO_4 or NaOH . All chemicals used were chemical grade. H_2L was prepared in the Department of Inorganic Chemistry, Charles University, Prague.

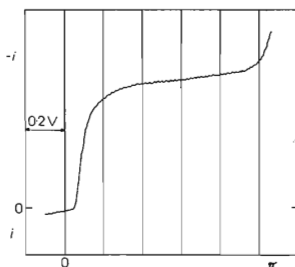


FIG. 1

Polarographic Wave of Uranyl Ion $1.77 \cdot 10^{-4}\text{M-UO}_2^{2+}$, $0.02\text{M-H}_2\text{Z}$, pH 2.6

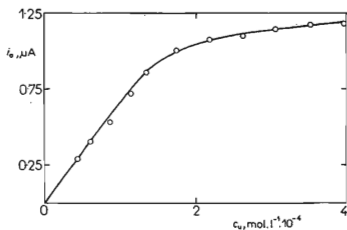


FIG. 2

Dependence of Limiting Current on UO_2^{2+} Concentration

Variation of the Wave Height with Depolarizer Concentration

For these experiments two series of solutions containing H_2Z in excess (0.02M) and different concentrations of UO_2^{2+} ion; first from $4 \cdot 10^{-5} - 4 \cdot 10^{-4}M$ and second from $4 \cdot 10^{-4} - 4 \cdot 10^{-3}M$, were prepared. All examined solutions were adjusted to the same pH value.

The results from first series of experiments show that at low uranyl ion concentration only one wave exists (Fig. 1), which varies linearly with concentration up to about $1.5 \cdot 10^{-4}M$ (Fig. 2) where the other two waves start to appear. Fig. 3 shows the existence of three waves and Fig. 4 their dependence on depolarizer concentration. As it is evident from Fig. 4, each wave shows limiting current saturation with increasing UO_2^{2+} ion concentration; also, the total height of the waves is not proportional to concentration.

The behaviour of the first wave was found to be as expected for an adsorption pre-wave. However, the other two waves have not "normal" characteristics as predicted from the theory⁵.

Variation of i_a with the Effective Mercury Height

At low depolarizer concentration, where single wave exists, the direct proportionality between wave-height and square root of effective mercury reservoir height $h_r^{1/2}$, was found.

At higher UO_2^{2+} -ion concentration, however, first wave became directly proportional to the mercury reservoir height. Because the other two waves are not well developed only the first one was analysed. However, the total wave height is not proportional to $h_r^{1/2}$.

This series of experiments gave clear evidence that the first wave is an adsorption pre-wave.

Effect of Uranyl Ion Concentration on the Electrocapillary Curve of Mercury

The electrocapillary curves of mercury obtained with several different depolarizer concentrations (at constant H_2L concentration and at pH 2.6) do not show remarkable changes in interfacial tension of mercury over all cathodic waves-potential range.

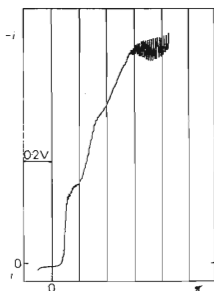


FIG. 3

Polarograms of Uranyl Ion in Solution Containing $1 \cdot 10^{-3}M$ UO_2^{2+} , 0.02M- H_2Z and at pH 2.6

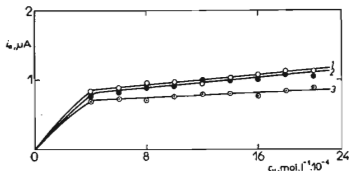


FIG. 4

Dependence of the Limiting Current of the First (e), Second (●) and Third (o) Polarographic Waves of Uranyl Ion on its Concentration

This fact, however, suggests that an insoluble product may be formed during U(VI) reduction from H_2L solution at the D.M.E. This product, as strong surface active species, accumulates at the electrode surface during the drop life and gives rise to phenomena similar to that for adsorption, without significant changes of capillary effects.

Analyses of the Current-Time Curves

Dependence of i on t was followed on a second drop in the whole range of the pre-wave potentials. At a lower concentration of depolarizer the curve was obtained, at the potential of limiting current having the shape of characteristic parabola with $t^{1/6}$ as in the Fig. 5a*. A log plot of i vs t is shown in Fig. 6a, it gives a slope about 0.19.

When higher UO_2^{2+} ion concentrations were applied, the $i-t$ curves showed, at potentials of limiting current, initial steep rise of current, passing a maximum and finally decreasing according to $t^{-1/3}$ function (Fig. 5b*). The plot of $\log i$ vs $\log t$ (Fig. 6b) gave two values of slope: ≈ 0.19 and ≈ 0.33 .

Reversibility of the Electrode Reaction and Determination of Number of Electron Consumption

Analysis of the plot $\log i/(i_d - i)$ vs E , for the pre-wave at low values of depolarizer concentration, where diffusion character of limiting current was noticed, gave a 57 mV slope. This value corresponds to the reversible one-electron electrode process.

Assuming that an insoluble product is formed upon reversible $U(VI) \rightarrow U(V)$ reduction from H_2L solution, and applying the known expression:

$$\partial E_{1/2} / \partial \log [A] = 0.059 n, \quad (1)$$

where $[A]$ is the concentration of the depolarizer, we obtain $n = 0.97$.

Calculation of the Number of Molecules Adsorbed per unit Area of Mercury Surface

From the general Brdička⁶ theoretical treatment of the adsorption waves, the number of adsorbed molecules reduced per second is i_a/nF . The rate of increase of mercury surface is $0.85 m^{2/3} t^{-1/3}$ (cm^2/s). The number of mol occupying surface is

$$z = i_a/nF 0.85 m^{2/3} t^{-1/3} \quad (2)$$

By substituting our following experimental values; $i_a = 8.8 \cdot 10^{-7}$ A, $m = 2.9 \cdot 10^{-3}$ gs^{-1} , $t = 3$ s per drop, the maximum number of adsorbed mol is $z = 2.14 \cdot 10^{-10}$ mol per cm^2 and the area occupied per molecule is about $1 \cdot 10^{14}$ molecule per cm^2 . This means that one molecule occupies, in the adsorbed state at the electrode surface, an area of about 80 \AA^2 .

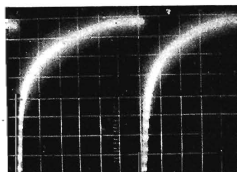
Evolution of Langmuir Factor and Free Energy of Adsorption

By increasing the depolarizer concentration the half-wave potential of the pre-wave shifts towards positive potentials. In order to relate the half-wave potential shift with Langmuir ad-

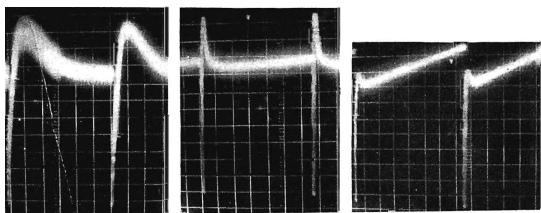
* See insert facing p. 936.

D.Ž.SUŽNJEVIĆ and M.V.ŠUŠIĆ

Behaviour of Uranyl Ion upon Reduction from the Ethylenedisulphurdiacetic Acid Solution



a



b

FIG. 5

Current-Time Curves

At the potential of the limiting current *a*: $1.77 \cdot 10^{-4} \text{M-UO}_2^{2+}$, $0.02 \text{M-H}_2\text{L}$, pH 2.6.
b: $1 \cdot 10^{-3} \text{M-UO}_2^{2+}$, $0.02 \text{M-H}_2\text{L}$, pH 2.6.

sorption coefficient ω , and free energy of adsorption ϕ (ref.⁶), we applied the following expression:

$$\omega = 2v_a \exp [2\Delta\pi F/RT], \quad (3)$$

where v_a is the corresponding dilution of the depolarizer in the solution, $\Delta\pi$ is the difference between potential which corresponds to the $i_a/2$ for the wave resulted from saturation of the electrode surface in adsorbed species, and the normal potential (identical with normal value of half-wave potential).

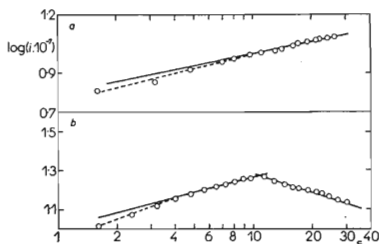


FIG. 6

Log i vs log t Curves

a : for low UO_2^{2+} concentrations, b : for higher UO_2^{2+} concentrations.

From our experimental values for $v_a = 5 \cdot 10^3 \text{ mol}^{-1} \text{ l}^{-1}$ and $\Delta\pi$ which were found to be 20 mV, the calculated value for ω is about 10^5 .

Assuming that the area occupied per molecule is about 80 \AA^2 , a rough value for the volume of one molecule of 8 \AA^3 is calculated. Using this value and considering the expression for molar adsorption energy:

$$\phi = 2\Delta\pi F + RT \ln (2v_a/V), \quad (4)$$

where V is the volume of one mol (in our cases $\approx 0.4 \text{ l}$) value of ϕ was found to be approximately 9 kcal.

REFERENCES

1. Sužnjević D., Doležal J., Kopanica M.: *J. Electroanal. Chem.* 20, 279 (1969).
2. Sužnjević D.: Unpublished results.
3. Sužnjević D., Rajković Lj.: Unpublished results.
4. Veselinović D., Rajković Lj., Sužnjević D.: *J. Electroanal. Chem.*, in press.
5. Heyrovský J., Kůta J.: *Principles of Polarography*. Academic Press, New York 1966.
6. Brdička T.: *This Journal* 12, 522 (1947).