248. *The Polarography of Niobium.*

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The polarographic behaviour of niobium in various complexing solutions has been studied with conventional polarographic equipment and with the square-wave polarograph. Previous work in sulphuric, hydrochloric, tartaric, and oxalic acid has been re-investigated. Polarographic steps for niobium have been found in a new series of complexing solutions, *e.g.*, malic, lactic, gluconic, and citric acid. The polarography of niobium in ethylenediaminetetra-acetic acid solutions has been studied in detail. Of these complexes, that of niobium citrate is the most stable to hydrolysis and is easily prepared. The step at $-0{\cdot}86$ v (*vs.* S.C.E.) from 2M-citric acid solutions of pH 1 can be used for the determination of from 0·1 to at least 250 μg. of niobium per ml. This step is free from interference by manganese, nickel, chromium, iron, or tungsten, but antimony, titanium, or molybdenum interferes.

Far less is known of the polarography of niobium than of many other transition metals. This is probably due to the difficulty of preparing stable solutions with this element. Niobium salts are readily hydrolysed in solution and this can be prevented only if care is taken that the solutions are strongly acid or, if the acidity is low, that an excess of a suitable complexing agent is present.

The first polarographic study of niobium was made by Zeltzer,[1] and of his conclusions the only one that has been substantiated is that a fairly well-defined step is obtained in M-nitric acid. The work of Stromberg and Reinus [2] and of Dhar [3] has shown, however, that this step is associated with catalytic phenomena and that its definition depends on the nitrate- and hydrogen-ion concentrations of the solution. The chemical difficulties mentioned above may also be responsible for Stromberg and Reinus's failing to detect steps for niobium in sulphuric, hydrochloric, tartaric, and oxalic acid solutions. Subsequently, Krylov, Kolebatova, and Samarina [4] have found a step in sulphuric acid solutions, Cozzi and Vivarelli [5, 6] have reported reductions in hydrochloric acid solutions, and Elson [7] has claimed that steps are produced in tartaric and oxalic acid solutions.

A survey of these base solutions, together with others which appeared to be more suitable for polarographic and analytical studies of niobium,[8] has been made both with conventional polarographic equipment and with the square-wave polarograph.

EXPERIMENTAL

Apparatus.—Conventional polarograms were recorded with an automatic pen-recording polarograph incorporating a Brown Electronik potentiometer constructed in this laboratory.[9] The equipment used for recording square-wave polarograms has already been described.[10]

Procedure.—*Hydrochloric acid.* Cozzi and Vivarelli [5] have shown that Nb^{5+} is reduced to Nb^{4+} in 11M-hydrochloric acid. The waves produced are fairly well defined, but the definition is improved by addition of ethylene glycol. Their investigations with a large mercury cathode [6] have shown that a number of reactions occur as a result of disproportionation of the reduced species.

We have found that suitable solutions for the polarographic investigation of these niobium chloride complexes may be prepared by dissolving freshly precipitated niobium hydroxide in concentrated hydrochloric acid. From these solutions a step with a half-wave potential of $-0{\cdot}54$ v against the mercury-pool anode was obtained. The plateau of this step is obscured by the hydrogen reduction wave but a well-defined and separated peak is observable on the square-wave polarogram (see Fig. 1). The shape of this peak indicates, however, that the reduction is not fully reversible. In agreement with the results of Cozzi and Vivarelli, we found that the polarographic step has increased definition when the solution contains 20% ethylene glycol.

It is apparent that at these high hydrogen-ion and chloride-ion concentrations, the competition between the chloride ion and the hydroxide ion is very much in favour of the formation of the niobium chloride complex. The strong affinity of the hydroxyl group for niobium is shown by the fact that only very poorly defined steps are found in 3M-hydrochloric acid solutions even when the chloride-ion concentration is raised to 20M by the addition of calcium chloride solutions. Kanzelmeyer and Freund's spectrophotometric studies [11] have shown a similar relation between the pH and the formation of the niobium chloride complex.

Sulphuric acid. Krylov, Kolebatova, and Samarina [4] have shown that solutions of niobium in 70% sulphuric acid yield steps corresponding to the reduction of niobium at the dropping-mercury electrode. The polarograms obtained by us under these conditions, like those reproduced by these authors, reveal poorly defined waves. The half-wave potential of this apparently irreversible reduction is about $-1{\cdot}07$ v *vs.* the standard calomel electrode (S.C.E.). No peak can be resolved with the square-wave polarograph.

We have found that the definition of this step, like that of the niobium chloride complex, deteriorates rapidly with decreasing acidity and no step can be detected in 40% sulphuric acid.

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[1] Zeltzer, *Coll. Czech. Chem. Comm.*, 1932, **4**, 319.

[2] Stromberg and Reinus, *Z. Phys. Khim. S.S.S.R.*, 1946, **20**, 693.

[3] Dhar, *Analyt. Chim. Acta*, 1954, **11**, 289.

[4] Krylov, Kolebatova, and Samarina, *Doklady Akad. Nauk S.S.S.R.*, 1954, **158**, 593.

[5] Cozzi and Vivarelli, *Ricerca sci.*, 1953, **23**, 2244.

[6] *Idem, Z. Elektrochem.*, 1954, **58**, 177.

[7] Elson, *J. Amer. Chem. Soc.*, 1953, **75**, 4193.

[8] Ferrett and Milner, *Nature*, 1955, **175**, 477.

[9] Whittem and Milner, Atomic Energy Research Establishment, Chemistry Memorandum 185 (1953).

[10] Ferrett and Milner, *Analyst*, 1955, **80**, 132.

[11] Kanzelmeyer and Freund, *Analyt. Chem.*, 1953, **25**, 1807.

Here, once again, reducible species only exist when the hydroxyl-ion concentation is very low. Spectrophotometric studies indicate that these concentrations of niobium (50 µg./ml.) in 40% sulphuric acid are still completely in solution. It appears that only the fully sulphated niobium complex can be reduced at the dropping-mercury electrode, and that when any of the sulphate groups is replaced by a hydroxyl group the complex is too stable to be reduced in the voltage range available for polarographic studies. It is clear that this step could find only a limited use in polarographic analysis, and this system was, therefore, not studied further.

Tartaric acid. Niobium forms complexes with tartaric acid and these can most readily be formed by extracting the melt formed by the bisulphate fusion of niobium pentoxide with an aqueous solution of tartaric acid. It has been shown [12] that solutions produced in this manner yield a niobium step with a half-wave potential at about −1·0 v *vs.* the mercury-pool anode. We have confirmed the existence of this step. It is best defined in 0·5M-solutions of tartaric acid at pH 1·5 (see Fig. 3). Even so, the step proved unsuitable for further study.

FIG. 1. *Square-wave polarogram for niobium in* 10M-HCl (Nb = 10 µg./ml.).

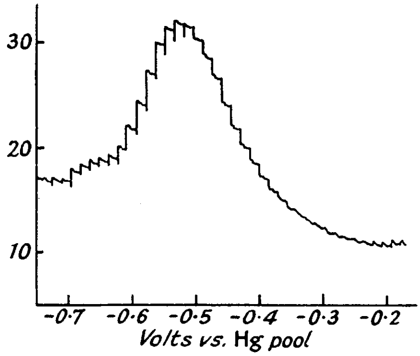
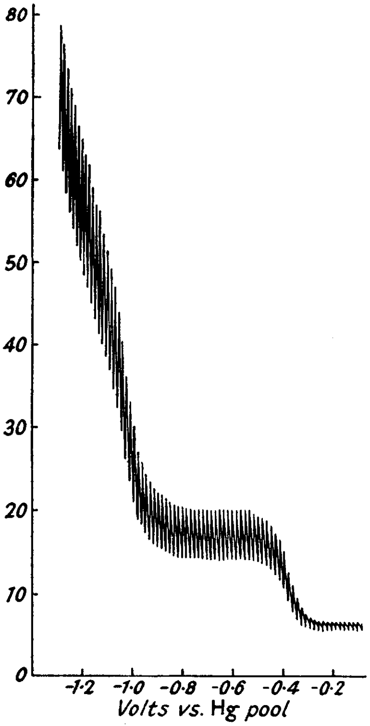


FIG. 2. *Polarogram for niobium* in 0·1M-EDTA, pH 3·1 (Nb = 150 µg./ml.).



Elson [7] has reported that niobium–tartrate complexes formed by the action of tartaric acid on precipitated niobium hydroxide produce steps with half-wave potentials in the range −1·96 to −2·00 v *vs.* S.C.E. According to our experience this method of preparing solutions proved unreliable for quantitative work, some of the niobium often remaining undissolved. We also failed to confirm the existence of steps for niobium in the potential region cited by this worker. It is noteworthy that Elson reported polarographic steps for tantalum from similar base solutions. Again, we were unable to find reduction steps for this element or to hold the tantalum satisfactorily in solution under the reported experimental conditions.

Oxalic acid. Elson has reported that niobium in oxalate solutions gives steps with half-wave potentials of −1·53 and −2·18 v *vs.* S.C.E., corresponding to the reduction to the Nb^{4+} and the Nb^{3+} state, respectively. The most convenient procedure for preparing oxalate solutions of niobium consists in fusing niobium pentoxide with potassium hydrogen sulphate and extracting

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[12] Mrs. B. Lamb, personal communication.

FIG. 3. *Square-wave polarogram for niobium in* 0·1M-EDTA, pH 3·4 (Nb = 15 μg./ml.).

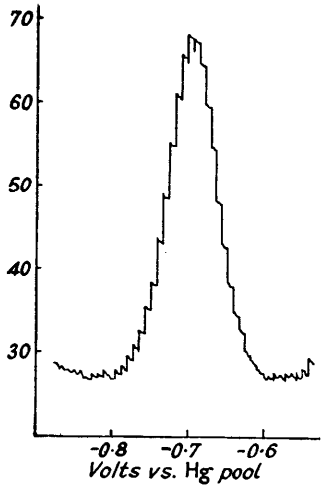


FIG. 5. *Polarogram for niobium in* 2M-*citric acid,* pH 3·7 (Nb = 250 μg./ml.).

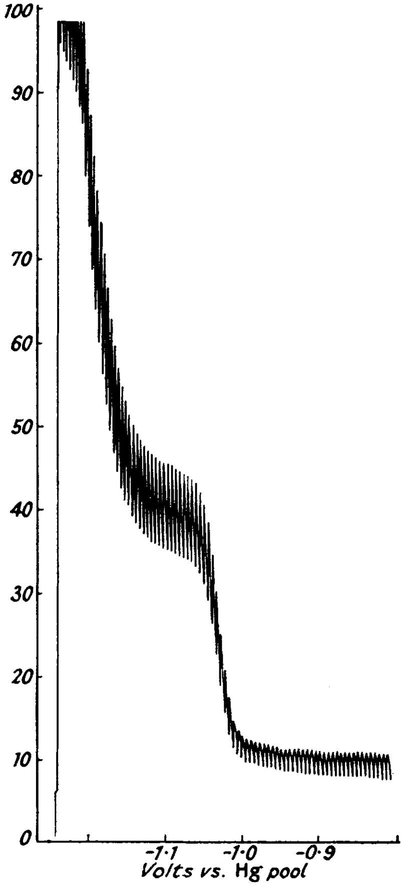


FIG. 4. *Square-wave polarogram for second niobium wave in* 0·2M-EDTA, pH 5·0 (Nb = 15 μg./ml.).

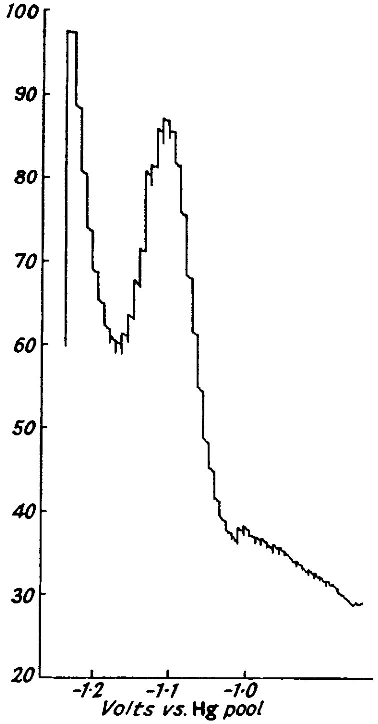
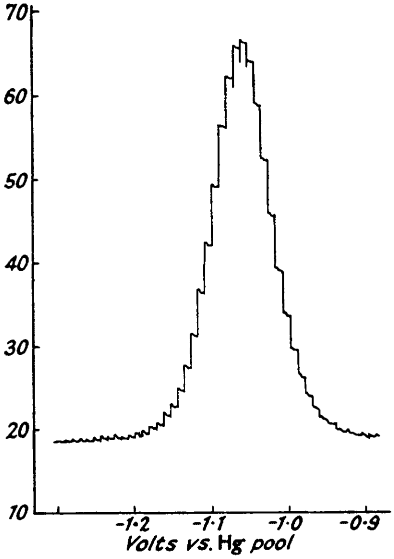


FIG. 6. *Square-wave polarogram for niobium in* 2M-*citric aicd,* pH 3·7 (Nb = 25 μg./ml.).



the melt with an aqueous solution of oxalic acid. With solutions so prepared, we failed to observe any steps for the reduction of niobium at the dropping mercury electrode.

Ethylenediaminetetra-acetic acid (EDTA). Experiments showed that a stable complex is formed by niobium with ethylenediaminetetra-acetic acid under certain pH conditions.[8] Satisfactory solutions can be prepared as follows : " Spec-pure " potassium niobate (40 mg.) is dissolved with warming in M-potassium hydroxide (15 ml.). Disodium ethylenediaminetetra-acetate (3·7 g.) is added, the whole is diluted to 90 ml. with water, the pH adjusted with 10% (v/v) sulphuric acid to the required value within the range 3—6, and the mixture made up to 100 ml. with water (this solution is 0·1M in EDTA). Solutions thus prepared give well-defined niobium steps : [8] at pH 3·05, for example (see Fig. 2), two steps are evident. The half-wave potential of the first is $-0·609$ and of the second $-1·05$ V *vs.* the S.C.E. The second step coalesces with the hydrogen wave and is difficult to measure with conventional equipment.

The pH range over which the first of these two steps is developed depends at the lower end upon the ethylenediaminetetra-acetic acid concentrations. At pH values below 3·0, the acid is precipitated from 0·1M-solutions. More dilute solutions, *e.g.*, 0·0001M at pH 1·0, give niobium steps, but these conditions become less suitable for study as the concentration of the acid approaches that of the niobium. At pH 6 and higher, the niobium complex begins to break down and niobium is precipitated from solution. Between these two limits the half-wave potential and reversibility of the first step at different pH values are given in Table 1.

TABLE 1. *Half-wave potential and reversibility data for niobium in solutions of ethylenediaminetetra-acetic acid.*

pH	[EDTA]	$E_{\frac{1}{2}}$	Slope *	pH	[EDTA]	$E_{\frac{1}{2}}$	Slope *
1·1	0·001	−0·427	0·065	3·40	0·1	−0·615	0·069
2·0	0·001	−0·419	0·060	3·40	0·02	−0·623	0·066
2·95	0·01	−0·572	0·064	3·60	0·1	−0·657	0·072
3·05	0·1	−0·609	0·059	4·05	0·1	−0·767	0·100
3·20	0·1	−0·613	0·062	4·75	0·1	−0·835	0·086

* This column represents the inverse slope of the applied voltage v against $\log_{10} i/(i_d - i)$ graph and is equal to $0·059/n$ for a reversible n-electron change.

The variation of the half-wave potential with pH is similar to that observed by Pecsok and Maverick [13] for the titanium–ethylenediaminetetra-acetic acid complex. It seems reasonable to suppose that the mechanism for the formation of these two complexes is very similar.

The slope for a reversible one-electron reduction should be 0·059 and it would appear, therefore, that the first step is due to the reduction $Nb^{5+} \longrightarrow Nb^{4+}$ and that this reduction is reversible at pH 3·2 and below. The polarograms obtained with the square-wave polarograph (see Fig. 3) also indicate that the reaction is a reversible one-electron change. For example, the peak-height obtained is similar to that obtained from a thallium solution of the same molarity, while the width of the peak at half its maximum height is the same for these two reductions. Barker and Faircloth [14] have shown that the half-width of the peak can be used as a measure of the number of electrons involved in a completely reversible reduction.

The conventional step could be used for the quantitative determination of niobium, since its height is proportional to the niobium concentration over the range 5—500 µg./ml. The greater sensitivity available with the square-wave polarograph has permitted the study of solutions containing 0·1—5 µg. of niobium per ml. Over this range also, the peak height is proportional to the niobium concentration.

The second step is best developed in solutions of higher pH, *e.g.*, pH 5·0 with an EDTA concentration of 0·2M. Although the step coalesces with the hydrogen wave when conventional polarograms are recorded, the peak can be clearly seen on the square-wave polarogram (see Fig. 4). In the region of pH 4 and 5 this second step has a small maximum which cannot easily be removed by the usual maximum suppressors (*e.g.*, gelatin, fuchsin).

It is not possible to analyse this second step, so as to determine the number of electrons involved in the reduction. The most likely process is $Nb^{4+} \longrightarrow Nb^{3+}$, so that an overall change of $Nb^{5+} \longrightarrow Nb^{3+}$ occurs over the complete potential range. This mechanism has been verified by a coulometric study of the reduction at a large stirred mercury cathode. The potential of

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[13] Pecsok and Maverick, *J. Amer. Chem. Soc.*, 1954, **76**, 358.

[14] Barker and Faircloth, personal communication.

this cathode was automatically controlled at $-1{\cdot}5$ v *vs.* S.C.E., and the current that flowed measured by an oxygen–hydrogen coulometer.[15] A solution 0·1M in ethylenediaminetetra-acetic acid at pH 4·0 was electrolysed with nitrogen passing through it until the background current fell to less than 1 mA. Then a small quantity of a solution of niobium in 0·1M-EDTA, containing 38·5 mg. of niobium was carefully added and the electrolysis was continued until the final current decreased to a value less than 1 mA. The total current measured in the coulometer was equivalent to 35 mg. of niobium, an overall two-electron reduction being assumed. After the reduction the solution was brownish-orange, a characteristic of tervalent niobium.

Although the reduction steps produced from these solutions are well defined, they are recommended for analytical use only when it is impossible to use a citrate base solution (see below). The main advantage of the citrate complex arises from its greater stability over the niobium–EDTA complex. Unfortunately, however, suitable citrate solutions can only be prepared from metallic niobium samples.

Citric acid. The niobium–citrate complex is most stable if prepared as follows : " Specpure " niobium metal (25 mg.), in a platinum crucible, is treated with water (1 ml.), concentrated nitric acid (5 ml.), and concentrated hydrofluoric acid (3 drops) and warmed, if necessary, to effect dissolution. Sulphuric acid (20% v/v, 5 ml.) is added and the solution heated until fumes of this acid appear. Water is added and the solution again heated until fumes appear, to ensure complete removal of fluoride. The solution is diluted slightly with water, treated with citric acid (42 g. in 50 ml. of water), adjusted to pH 1·0 with a 10% w/v potassium hydroxide solution, and diluted to 100 ml. with water.

The solutions prepared from the metal gave excellent polarograms (see Fig. 5). The height of the step was proportional to concentration over the range studied, *viz.*, 250—10 μg. of niobium per ml. Measurement of the slope of the polarographic step showed that the reduction was reversible and that, like the niobium–ethylenediaminetetra-acetic acid complex, it was due to the reduction of Nb^{5+} to Nb^{4+}. The square-wave polarogram is shown in Fig. 6. The height of the peak is proportional to the niobium concentration over the range 10—0·1 μg./ml. The solutions were stable for 24 hr. and longer, and the dissolution procedure was always reliable.

The niobium citrate reduction step can be obtained over a wide range of hydrogen-ion and citric acid concentrations. We have studied it from pH 6·0 to solutions 2M in sulphuric acid. Over the range pH 4·0—0·0, the half-wave potential shifts in a manner similar to that observed for the EDTA complex in Table 1. Thus at pH 4·0 the half-wave potential is $-1{\cdot}13$ v, and at pH 0 it is $-0{\cdot}75$ v *vs.* S.C.E. At pH 1·0, where most of our studies were made, it is $-0{\cdot}86$ v *vs.* S.C.E.

The reduction steps obtained from niobium citrate solutions when the citric acid concentration was in the range 0·1—0·4M were not well defined. They tended to coalesce with the hydrogen waves or to have sloping plateaux. Over the citric acid concentration 0·4—2M, the polarograms were well defined; the diffusion current decreases, however, with increasing viscosity of the solution. The conditions finally chosen were 2M-citric acid adjusted to pH 1.

The reduction step obtained in all the solutions studied behaved similarly to the first reduction step found in niobium–ethylenediaminetetra-acetic acid solutions. Measurements of the slope of the rising portion of the step showed that the reduction in citric acid base solutions also involved only one electron. No evidence for a second step was found in citric acid solutions, however.

This step is of analytical value and is well separated from the uranium wave in 2M-citric acid of pH 1·0. Manganese, nickel, tungsten, chromium, and iron also do not interfere, but antimony, titanium, and large quantities of molybdenum do.

Other α-hydroxy-acids. Niobium forms complexes with a number of other α-hydroxy-acids, *e.g.*, malic, lactic, gluconic, and tartronic acids. Solutions of the first three gave typical niobium polarograms and were prepared as described for citric acid. Further details of the results obtained are as follows :

Malic acid. The niobium malate complex is reduced to give a single step corresponding to a $Nb^{5+} \longrightarrow Nb^{4+}$ reduction. The malic acid available, however, contained an impurity which gave a reduction wave superimposed upon that of the niobium complex. It proved very difficult to purify this malic acid without laborious treatment, and further study was not carried out.

Lactic acid. Solutions of niobium lactate behaved similarly to those of malic acid, a large step being present, even in " AnalaR " samples of the acid. A triple precipitation of barium

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[15] Lingane, " Electro-Analytical Chemistry," Interscience Inc., New York, 1953, p. 349.

lactate, however, reduced this impurity considerably. The reduction in lactic acid solutions corresponds to $Nb^{5+} \longrightarrow Nb^{4+}$ and is proportional in height to the niobium concentration.

Gluconic acid. Niobium gluconate gives polarographic waves that are best defined in the pH range 4—6 in solutions 0·3M in gluconic acid. No interference from impurities in the gluconic acid is noticed here. The slope of the step in this case also corresponds to a $Nb^{5+} \longrightarrow Nb^{4+}$ reduction process.

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