Polarographic Studies on the Rare Earths. III. Yttrium.

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Polarographic studies on the reduction of the tripositive yttrium ion had been reported and discussed by Noddack and Brukl[1], Kolthoff and Lingane[2], and Purushottam and Raghava Rao[3], but the electrode reaction in the reduction process was not completely solved, because of the special properties of the aquo yttrium complex ion and of the anomalies of the reduction wave. Noddack and Brukl obtained a double wave for 0.01 M solution of yttrium sulfate, without any supporting electrolyte, having the half-wave potentials of -1.76 V. and -1.84 V. vs. S. C. E., respectively and concluded the reduction process to be $Y^{3+}\rightarrow Y^{2+}\rightarrow Y^0$. However, it is very doubtful. Kolthoff and Lingane suggested that it was more probable that the first wave resulted from the reduction of hydrogen ion produced by the hydrolysis of the aquo yttrium complex ion and the second wave corresponded to the three electron reduction to metal. Purushottam and Raghava Rao also obtained the double wave with yttrium chloride using lithium chloride as supporting electrolyte. From the reciprocal slope of the logarithmic plots of both waves, they concluded that the electrode reaction of the first wave was of one-electron change, and that of the second wave, of two-electron change, that is, $Y^{3+}\rightarrow Y^{2+}\rightarrow Y^0$ the same as before. However, all these results were incomplete because the effects of pH and concentration of yttrium ions on the diffusion current, the half-wave potential and further on the electrode reaction in reduction process were not discussed in detail. The present authors, for the purpose of solving the electrode reaction in the reduction process, studied the reduction wave of the aquo tripositive yttrium complex ion in an unbuffered solution under various conditions and obtained a different result from other reports. By the addition of a small amount of dilute acid to prevent the hydrolysis of the aquo yttrium complex ion, the hydrogen wave was completely separated from the reduction wave of the aquo yttrium complex ion, which was generally a single wave in a perchlorate solution and often a double wave in a halide solution. The electrode reaction of the single wave was irreversible and of a three-electron reduction. This wave was due to the reduction of the hydrogen ion which was produced from the dissociation of the aquo yttrium complex ion as the yttrium acid. In the case of the double wave, the first wave was irreversible or quasi-reversible and its electrode reaction was also of a three-electron reduction. The second wave was irreversible and anomalous. The two-stepped wave in the solution of the halide ions, added as supporting electrolyte, was considered to be attributed probably to the reduction of the aquo halo complex ion.

Experimental

All current-voltage curves were recorded by a Yanagimoto photographic polarograph PEL-Model 3. All cathode potentials were referred to a saturated calomel electrode. The capillary used had an m value of 0.706 mg./sec. and drop times of 3.25 sec. at -1.8 V. and 2.98 sec. at -1.9 V. vs. S. C. E., when measured in an air-free 0.1 M lithium perchlorate solution at 57.6 cm. of effective height of mercury. The measurement of pH was done with the Hitachi glass electrode pH meter Model EHM-1 for a micro amount scale. All experiments were carried out in a thermostat of 25.0±0.1°C.

An yttrium stock solution was prepared by dissolving pure yttrium perchlorate or sulfate. (As yttrium oxide, the purity was higher than 99.99%.). The concentration of the stock solution was 0.01 M. The lithium perchlorate and tetramethyl ammonium iodide which were used as the supporting electrolytes were guaranteed grade reagents and recrystallized before use. The concentration of these stock solutions were 1 and 0.2 M., respectively. The gelatine solution used as the maximum suppressor was prepared afresh in every experiment. Perchloric acid and sulfuric acid solutions of 0.01 N in concentration were prepared from the analytical pure reagents and used for the adjustment of pH.

To the sample solution of yttrium, appropriate quantities of the supporting electrolyte and gelatine were added to give the final concentrations, 0.1 M and 0.01% respectively. Then a micro amount of 0.01 N acid was added to prevent the hydrolysis of the aquo yttrium complex ion and to adjust the pH at the same time. The total volume of the solution was made up to 5 ml. with distilled water. The concentration of the yttrium ion was in the range from 0.5 to 2.0 millimol./l. and the pH of the solution

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[1] W. Noddack and A. Brukl, *Z. Angew. Chem.*, 50, 362 (1937).

[2] I. M. Kolthoff and J. J. Lingane, "Polarography". Vol. II. Interscience Publishers Inc., New York (1952), p. 436.

[3] A. Purushottam and Bh. S. V. Raghava Rao, *Anal. Chim. Acta*, 12, 589 (1955).

was varied from 4.00 to 2.60. Dissolved oxygen was removed by passing purified nitrogen gas through the solution at least for 20 min. The polarograms were recorded at 25.0±0.1°C.

The diffusion coefficient of the yttrium ion was calculated from Nernst's equation, using the value of equivalent conductance at infinite dilution[4].

D: 5.721×10^{-6} cm. sec^{-1} (for $Y(ClO_4)_3$)

D: 5.764×10^{-6} cm. sec^{-1} (for $Y_2(SO_4)_3$)

Results and Discussion

The reduction wave of aquo tripositive yttrium complex ion.—The reduction wave of the aquo yttrium complex ion (Fig. 1) at pH about 4.5 differed from the true reduction wave owing to the precedence of the hydrogen wave produced by the hydrolysis of the aquo yttrium complex ion. The typical reduction wave was obtained by adding a micro amount of acid to prevent the hydrolysis when the hydrogen wave was completely separated from the reduction wave of the aquo yttrium complex ion under a certain condition. The reduction wave was generally a single wave in a perchlorate medium and often a double wave in a halide (chloride or iodide) medium.

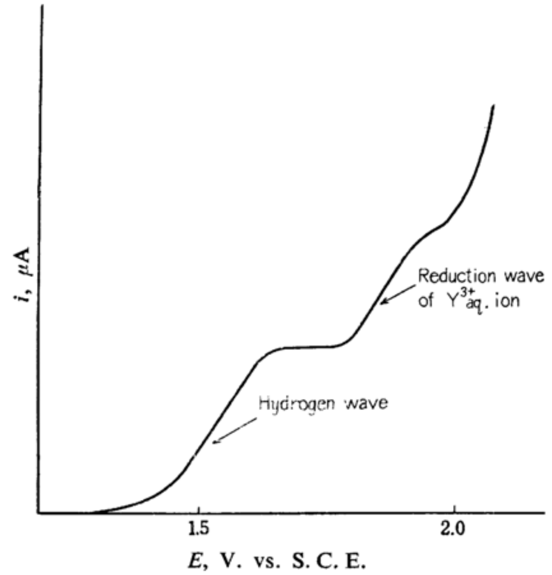

Fig. 1. Reduction wave of the aquo yttrium complex ion. (1) In perchlorate medium
Y^{3+} ion: 1.25 mM in 0.1 M $LiClO_4$ and 0.01% gelatine medium
pH: 2.95 S: 1/200 25.0°±0.1°C

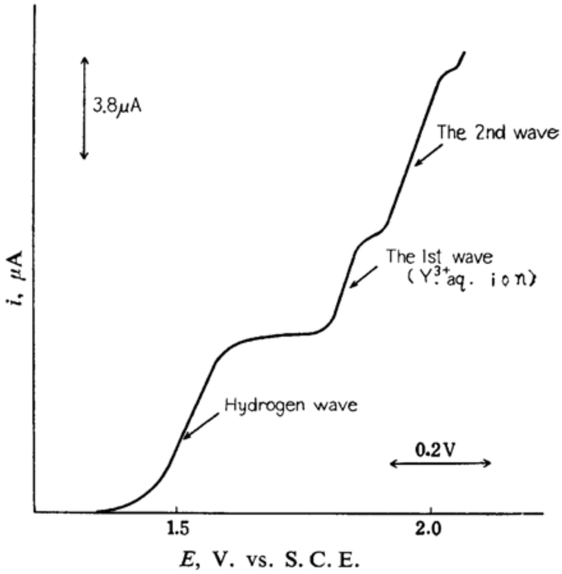

Fig. 1. Reduction wave of the aquo yttrium complex ion. (2) In iodide medium
Y^{3+} ion: 1.03 mM in 0.1 M $(CH_3)_4NI$ and 0.01% gelatine medium
pH: 3.09 S: 1/181 25.0°±0.1°C

From the results obtained by the variation in pH and the concentration of the yttrium ion, the following common characters of the reduction wave were derived: 1) At a pH higher than 3.4, only a single wave was obtained in both perchlorate and halide medium. 2) At a pH less than 2.7, only a single wave was observed, but as the height of the hydrogen wave became large, the wave was ambiguous. 3) At a pH between 2.7 and 3.4, in a perchlorate solution, only a single wave was obtained clearly and as the pH decreased, there was a tendency for a small maximum wave to appeare ofteh after the reduction wave. In a halide solution, when the two-stepped wave was obtained, the second wave decreased gradually as the pH decreased or the concentration of yttrium ions increased until it finally disappeared.

Dependence of the limiting current on the pressure upon the dropping mercury electrode and the influence of temperature on the limiting current and the half-wave potential.—A relationship between the limiting current and the height of mercury column is shown in Table I. As the limiting current is proportional to the square root of the height of mercury column, the limiting current was diffusion-controlled.

The temperature coefficient of the half-wave potential and that of the diffusion current in the range from 25° to 35°C were 0.7 mV./deg. and 1.86%/deg., respectively, which were nearly in agreement with the values that would be expected in the case of the diffusion-controlled process.

The plots of E vs. $\log\{i/(i_d-i)\}$.—The reduction waves of the aquo tripositive yttrium complex ion were analyzed by the logarithmic

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[4] F. H. Spedding and S. Jaffe, *J. Am. Chem. Soc.*, 76, 882 (1954); ibid., 76, 884 (1954).

TABLE I. DEPENDENCE OF LIMITING CURRENTS OF THE REDUCTION WAVE ON THE HEIGHTS OF MERCURY COLUMN

h cm.	h(corr.) cm.	i_l μA	$i_l/\sqrt{h}$
50	47.6	3.07	0.446
60	57.7	3.39	0.448
70	67.6	3.66	0.446

Y^{3+} ion: 0.992 mM in 0.1 M $(CH_3)_4NI$ and 0.01% gelatine medium. pH: 3.0.

h cm.	h(corr.) cm.	i_l μA	$i_l/\sqrt{h}$
50	47.5	2.96	0.431
60	57.5	3.32	0.448
70	67.6	3.61	0.439

Y^{3+} ion: 1.257 mM in 0.1 M $LiClO_4$ and 0.01% gelatine medium. pH: 2.9.

TABLE II. THE RECIPROCAL SLOPE OF E vs. $\log\{i/(i_d-i)\}$

pH	Reciprocal slope, V.	
3.50	0.059	
3.35	0.037	
3.00	0.027	
2.80	0.027	max.
2.65	0.022	〃

Y^{3+} ion: 0.611 mM in 0.1 M $LiClO_4$ and 0.01% gelatine medium.

pH	Reciprocal slope, V. 1st wave.	2nd wave.
3.70	0.043	
3.35	0.020	
3.05	0.019	anomalous
2.85	0.020	
2.60	0.020	

Y^{3+} ion: 1.00 mM in 0.1 M $(CH_3)_4NI$ and 0.01% gelatine medium.

TABLE III. THE EFFECTS OF pH ON HALF-WAVE POTENTIAL, DIFFUSION CURRENT AND DIFFUSION CURRENT CONSTANT

pH	Half-wave potential, $E_{1/2}$ V. vs. S. C. E.	Diffusion current, i_d μA	Diffusion current constant, I_d
3.75	−1.725	2.47	4.48
3.50	−1.727	2.43	4.36
3.35	−1.824	2.45	4.45
3.10	−1.870	2.45	4.45
3.00	−1.865	2.45	4.45
2.95	−1.865	2.47	4.50
2.80	−1.943	2.43	4.39
2.65	−1.945	2.47	4.53

(Y^{3+} ion: 0.611 mM in 0.1 M $LiClO_4$ and 0.01% gelatine medium.)

pH	Half-wave potential V. vs. S. C. E.		Diffusion current μA		Diffusion current constant, I_d
	$(E_1)_{1/2}$	$(E_2)_{1/2}$	i_{α_1}	i_{α_2}	
3.70	−1.737		3.42		3.40
3.55	−1.773		3.46		3.51
3.35	−1.801	−1.941	3.48	3.61	3.51
3.10	−1.826	−1.970	3.49	4.70	3.55
3.05	−1.834	−1.976	3.44	4.92	3.52
2.85	−1.852	−2.000	3.52	4.85	3.58
2.75	−1.864	−2.006	3.30	4.50	3.46
2.70	−1.878	−2.012	3.34	3.84	3.40

(Y^{3+} ion: 1.043 mM in 0.1 M $(CH_3)_4NI$ and 0.01% gelatine medium.)

plot. The results are shown in Table II. With decreasing pH, the value of the reciprocal slope of the reduction wave decreased. In a perchlorate solution, the electrode reaction was irreversible and at a pH less than 3.00, it indicated a tendency to approach to a three-electron reduction, provided that the reduction of the aquo yttrium complex ion is followed by amalgamation at electrode. This tendency was evidently observed in a halide midium. In a halide solution, at a pH less than 3.4, the electrode reaction of the first wave was irreversible, but it approached from irreversible to quasi-reversible and corresponded to three-electron change. The electrode reaction of the second wave was also irreversible and very anomalous.

The effects of pH on the reduction waves.—

The reduction waves were recorded at various pH from 4.00 to 2.60 under a certain condition. The results are shown in Table III.

Half-wave potentials of all reduction waves shifted to more negative potentials as pH decreased. It is considered that this was probably due to the increasing stability of hydroxo yttrium complex ion, which was formed by the hydrolysis of the aquo yttrium complex ion owing to the weak basicity of yttrium. This shift was always dependent only on the concentration of the free hydrogen ion. It was observed that at the same pH the half-wave potential was more negative in a perchlorate medium than in a halide medium under a given condition. The diffusion current of the reduction wave, i_d, was independent of pH from 3.4 to 2.6 and almost constant in a perchlorate medium. However it was observed that at a pH higher than 3.4, the diffusion current tended to decrease slightly. In the halide medium, at a pH higher than 3.6, there was the same tendency. The diffusion current of the second wave, in a halide medium, increased slightly with the decrease of the pH down to 3.1 and had a small maximum, but with the further decrease of the pH, i_d decreased gradually and anomalously. The diffusion current constant of the reduction wave, I_d, was constant at a pH from 3.4 to 2.6 in the perchlorate medium and that of the first wave in the halide medium, I_{d_1}, was also constant at a pH less than 3.6. The value of the diffusion current constant of the second wave, I_{d_2}, was irregular, and anomalous.

The effects of concentration of the yttrium ion on the reduction wave and the value of n, calculated from diffusion current constant.—The reduction waves were recorded in the range of concentration of yttrium ion 0.5 to 2.0 millimol./l. at a constant pH. The results are shown in Table IV.

The half-wave potential of the reduction wave shifted to more negative potentials slightly, with the increasing concentration at a constant pH. The diffusion current, i_d, was apparently proportional to the concentration of Y^{3+} ion in the perchlorate medium. The first diffusion current in the halide medium gave a similar result, but the second diffusion current was anomalous. The diffusion current constant of the reduction wave was constant, independent of the concentration of the yttrium ion and its average value was about 4.46 in 0.1 M $LiClO_4$ and about 3.51 in 0.1 M $(CH_3)_4NI$, while the theoretical value of the diffusion current constant is 4.34, which was calculated by assuming that the number of the electrons associated with the electrode reaction of the reduction wave, *n*, was three and the value of the diffusion coefficient of the yttrium ion *D*, 5.721×10^{-6} cm. sec^{-1} ($Y(ClO_4)_3$). It is considered that the average value observed in 0.1 M lithium perchlorate was almost equal to the theoretical one. The diffusion coefficient of the yttrium ion ($Y_2(SO_4)_3$) is 5.764×10^{-6} cm. sec^{-1} and the diffusion current constant was calculated to be 4.35. Although the average value of the diffusion current constant in the halide medium was smaller than the calculated one, it is also considered that the former was closer to the latter than the value which would be expected in the case of $n=2$. From these experimental values of the diffusion current constants, the number of the electrons involved in the electrode reaction, *n*, was calculated. The calculated value of *n* was 3.06 in the case of 0.1 M lithium perchlorate, where the perchlorate ion has no tendency to complex with cation. Therefore, the electrode reaction was of three-electron change. The calculated value of *n* for the first wave in the case of 0.1 M tetramethylammonium iodide, where iodide ion forms generally an aquo iodo

TABLE IV. THE EFFECTS OF CONCENTRATION OF YTTRIUM ION ON THE HALF-WAVE POTENTIAL, THE DIFFUSION CURRENT, AND THE DIFFUSION CURRENT CONSTANT

Y^{3+} ion mM	Half-wave potential, $E_{1/2}$ V. vs. S. C. E.	Diffusion current, i_d μA	Diffusion current constant, I_d
0.332	−1.815	1.39	4.54
0.428	−1.819	1.69	4.41
0.917	−1.881	3.70	4.49
1.529	−1.900	5.89	4.40

(pH=3.00, $Y(ClO_4)_3$, in 0.1 M $LiClO_4$ and 0.01% gelatine medium.)

Y^{3+} ion mM	Half-wave potential V. vs. S. C. E.		Diffusion current μA		Diffusion current constant
	$(E_1)_{1/2}$	$(E_2)_{1/2}$	i_{d_1}	i_{d_2}	
0.723	−1.850	−1.990	2.40	3.97	3.47
1.043	−1.852	−2.000	3.52	4.85	3.58
1.984	−1.857	−2.005	6.65	5.34	3.50

(pH=2.90, $Y_2(SO_5)_3$, in 0.1 M $(CH_3)_4NI$ and 0.01% gelatine medium.)

complex ion, was about 2.60, which seemed apparently smaller than three, owing to the probable formation of the aquo iodo complex ion. The value of the diffusion current constant of the second wave was irregular because of the anomaly of the reduction wave.

Polarographic depolarizing action of the hydrolyzable aquo yttrium complex ion.—The aquo tripositive yttrium complex ion, $Y(H_2O)_x^{3+}$ ion, behaves as a weak acid, "yttrium acid," in aqueous solution, owing to its weak basicity. Generally, the half-wave potential of the reduction wave which is due to the deposition of hydrogen from a weak acid, HA, has the following well known equation in excess of an indifferent electrolyte,

$$E_{1/2} = -3\boldsymbol{R}T/2\boldsymbol{F}\cdot\ln i_d/2 + k = -0.089 \log i_d/2 + k$$

where k is a constant. Accordingly, it follows that the half-wave potential of a weak acid should shift to more negative potentials with the increasing acid concentration and $dE_{1/2}/d\log(HA) = -0.089$ V. In fact, as shown in Table IV, the half-wave potential of the reduction wave shifted slightly to more negative potentials with the increasing concentration at a certain pH. The value of $dE_{1/2}/d\log(Y(H_2O)_x^{3+})$ for the reduction wave calculated by extrapolation and given as follows: $dE_{1/2}/d\log(Y(H_2O)_x^{3+})$ equals -0.090 V. in perchlorate medium and -0.088 V. in an iodide medium. These values are considered to be equal to the theoretical value of -0.089 V. This fact indicates that the reduction wave of the aquo yttrium complex ion was the same as the reduction wave of the hydrogen ion from the yttrium acid, that is, the reduction wave was not due to the reduction of the yttrium ion, (Y^{3+} ion), itself, but was attributed to the deposition of hydrogen from the yttrium acid. It is also in accordance with the results of irreversibility and of a three-electron change in electrode reaction. Of course, the hydrogen ion from "the yttrium acid" was at first combined and not free. Since the hydrogen ion was produced by hydrolysis of the aquo yttrium complex ion as the yttrium acid, the following equation would be given:

$$Y(H_2O)_x^{3+} + yH_2O$$
$$= Y(H_2O)_{x-y}(OH)_y^{(3-y)+} + yH_3O^+$$

where x is the coordination number of the tripositive yttrium ion (usually 6 in the case of a mononuclear yttrium ion), and y is the number of the hydrogen ion produced from the yttrium acid by hydrolysis at a certain pH. The yttrium acid $Y(H_2O)_x^{3+}$ has three hydrogen ions per one molecule to be released and reduced at electrode. Therefore the quantities of electricity to be exchanged by the hydrogen ions at dropping mercury electrode are just the same as those which tervalent yttrium ions require when reduced to metal. Actually, the reduction of the hydrogen ion from the aquo yttrium complex ion at dropping mercury electrode requires a large overpotential, but still the hydrogen ion seems to take an electron more easily than the aquo yttrium complex ion or the hydroxo yttrium complex ion does. Thus the electrode reaction was irreversible (or quasi-reversible in the halide medium) and three-electron change as described above. It is considered that the reduction proceeds for example as follows:

$$Y(H_2O)_x^{3+} + 3e^- \rightarrow 3/2H_2 + Y(H_2O)_3(OH)_3$$

The second wave in the halide medium, if it existed, was supposed also to be the hydrogen wave which is due to the reduction of the hydrogen ion from dissociation of water in the aquo halo complex. This wave was also irreversible. Consequently, it was concluded that the polarographic depolarising action of the aquo yttrium complex ion was indicated by the reduction of the hydrogen ion from the yttrium acid and not by the reduction of the yttrium ion itself to metal.

Conclusion

The logarithmic plot for the reduction wave of yttrium(III) indicated a straight line, independent of concentration of yttrium(III) at a pH less than 3.4. The value of its reciprocal slope approached the theoretical value for three-electron reduction with decreasing pH. The average value of the diffusion current constant was about 4.46 in 0.1 M lithium perchlorate and 3.60 in 0.1 M tetramethylammonium iodide from which the value of n was calculated to be 3, it being assumed that in the reduction of the aquo yttrium complex ion at dropping mercury electrode, amalgamation would follow. In short, the reduction wave was irreversible and three-electron reduction. However, it was found that the aquo yttrium complex ion behaved as a weak acid, "the yttrium acid", and that the reduction wave was due to the deposition of hydrogen from the hydrolyzable aquo yttrium complex ion as the weak acid. It is also supposed that the second reduction wave, if it appeared in the halide medium, was due to the deposition of hydrogen from dissociation of water in aquo halo yttrium complex formed during the first reduction step. This second reduction wave was irreversible and anomalous.

At pH 3.00, the half-wave potential of the reduction wave was -1.881 V. vs. S. C. E. for the concentration of Y^{3+} ion of 0.917 mM in 0.1 M lithium perchlorate and 0.01% gelatine medium.

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