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The Polarographic Reduction of Praseodymium

BY ALF W. SWENSEN AND GEORGE GLOCKLER

Noddack and Brukl[1] reported that a polarographic study of 0.01 *M* aqueous solutions of the rare earth sulfates including scandium and yttrium, without supporting electrolyte, indicated that all of the elements studied underwent a two-step polarographic reduction, indicative of two reductions—one from the trivalent to the bivalent state and a subsequent one to the metallic state. Unfortunately polarograms were not given to substantiate their statements. The authors failed to report the half-wave potentials of these ions, the generally accepted procedure, but referred to "knickpunkte," the points of greatest inflection.

Holleck and Noddack[2] stated that aqueous solutions of the sulfates of scandium, yttrium, lanthanum and the rare earths were reduced to the bivalent state and that in this form they reacted with definite amounts of 0.01 *N* potassium permanganate. This evidence is, however, not conclusive. Klemm[3] questioned the possibility that all of the rare earth sulfates could exist in the bivalent state. Heyrovsky,[4] and Kolthoff and Lingane[5] voiced the same objections. Leach and Terrey[6] observed that the single wave, produced when an aqueous solution of scandium chloride in potassium chloride was electrolyzed, gradually developed into two waves as increasing amounts of *N*/6 hydrochloric acid were added. The first wave was due to the discharge of the hydronium ion and the second, the reduction of the scandium ion.

This study was undertaken to establish the half-wave potentials of the praseodymium ion with and without various supporting electrolytes, its diffusion current constant, the possibility of the existence of the bivalent state of praseodymium, and the effect of age on both the hydrolysis of a praseodymium solution and the polarographic reducibility of the praseodymium ion.

Experimental Procedure

Apparatus.—The polarograms were recorded with a Sargent Model XX Polarograph, which has been described in detail by Lingane.[7] A K-type potentiometer was used to check the applied potentials, which are referred to the saturated calomel electrode (S. C. E.). The electrolytic cell was of the H-cell design as described by Lingane and Laitinen.[8] The temperature in all cases was maintained at 25.0 ± 0.1°. The values of *m* and *t* in the Ilkovic equation were determined for twenty-five drops of mercury at the potential where the diffusion current was determined. The diffusion currents were corrected for the residual currents. Half-wave potentials were corrected for the *IR* drop in the cell. The Macbeth, and the Beckman, Model H, line operated; the Beckman, Model G, battery operated and the Type 200 Coleman Electrometer *p*H meters were used in the *p*H determinations.

Materials.—The anhydrous praseodymium sulfate was prepared from the oxide by adding an excess of concentrated sulfuric acid to the spectrographically pure oxide. This mixture was heated very carefully on a hot plate until all fumes of sulfur trioxide were evolved, then in a thermostatically controlled oven at a temperature of 450° for two hours. A light green amorphous powder was produced. Conductivity water was used for the preparation of all solutions. The supporting electrolytes were prepared from chemicals which meet A. C. S. standards. Dissolved oxygen was removed from all solutions by bubbling pure nitrogen through the electrolyte for twenty minutes.

Results

No Supporting Electrolyte. No Maximum Suppressor.—Several attempts were made to repeat the recorded results of Noddak and Brukl.[1] Solutions of praseodymium sulfate, varying in concentration from 1.7944 to twenty millimolar, were electrolyzed using for anode a mercury pool. The solutions varied in age from a few hours to twelve months. In no instance was there a double wave; Fig. 1. Table I indicates that the half-wave potential became more negative with increasing concentration and that the age of the solution had no effect on its polarographic reducibility.

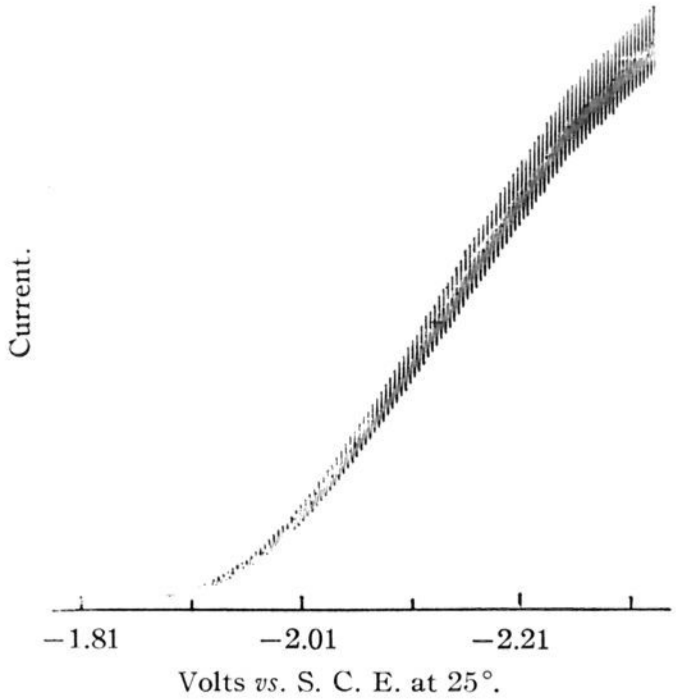

Fig. 1.—Polarogram of 20 millimolar praseodymium sulfate solution: age, one day; supporting electrolyte, none; maximum suppressor, none; sensitivity, 3–25–5 $E_{1/2}$, −2.11 volts *vs.* S. C. E., at 25°.

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

[2] Holleck and Noddack, *ibid.*, **50**, 819 (1937).

[3] Brukl and Noddack, *ibid.*, **49**, 533 (1936).

[4] Heyrovsky, "Fortschritte der Polarographie 1936–1938," Dritter Band of W. Böttger's "Physikalische Chemie," p. 443.

[5] Kolthoff and Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, pp. 304–306.

[6] Leach and Terrey, *Trans. Faraday Soc.*, **33**, 480 (1937).

[7] Lingane, *Ind. Eng. Chem., Anal. Ed.*, **18**, 734 (1946).

[8] Lingane and Laitinen, *ibid.*, **11**, 504 (1939).

TABLE I

THE HALF-WAVE POTENTIALS OF PRASEODYMIUM WITHOUT SUPPORTING ELECTROLYTE AND NO MAXIMUM SUPPRESSOR

Concentration of Pr^{+3} millimolar	Age of solution	$E^1/_2$ *vs.* S. C. E.
20.0	11 months	−2.06
20.0	1 day	−2.05
17.944	1 day	−2.01
10.0	3 hours	−2.04
8.972	3 hours	−1.98
1.7944	3 hours	−1.84

Lithium Chloride as Supporting Electrolyte.—Well defined waves were obtained, Fig. 2, when 0.1 *N* lithium chloride was used as a supporting electrolyte with 0.01% gelatin as a maximum suppressor, Table II.

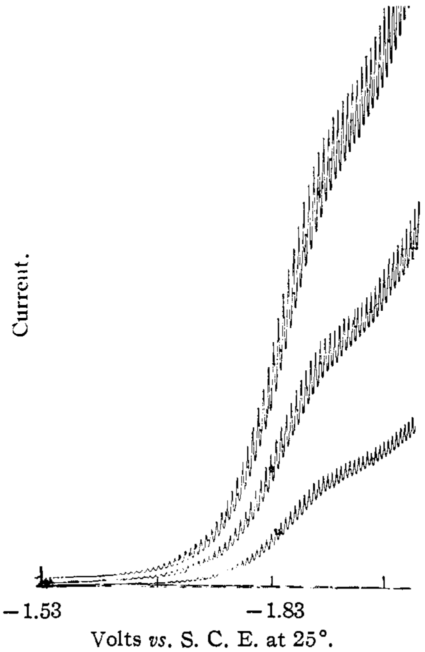

Fig. 2.—Polarograms of 4.8996 millimolar praseodymium sulfate solution: supporting electrolyte, 0.1 *M* lithium chloride; maximum suppressor, 0.01% gelatin; sensitivities, 3-25-5, 3-50-5 and 3-90-5 $E_{1/2}$, −1.83 volts *vs.* S. C. E., at 25°.

TABLE II

PRASEODYMIUM SULFATE IN 0.1 *N* LITHIUM CHLORIDE AND 0.01% GELATIN

Concentration of Pr^{+3}, millimolar	$E^1/_2$ *vs.* S. C. E.	i_d, microamp.	I_d
10.125	−1.83	64.68	3.58
8.972	−1.81	54.0	3.53
6.75	−1.82	45.45	3.68
5.063	−1.80	32.86	3.51
4.486	−1.78	28.46	3.57
2.53	−1.75	17.30	3.67

Tetramethylammonium Iodide as Supporting Electrolyte.—Well defined waves were obtained when polarograms were recorded using one-tenth normal solutions of tetramethylammonium iodide together with 0.01% gelatin as the maximum suppressor; Fig. 3. The data are tabulated in Table III.

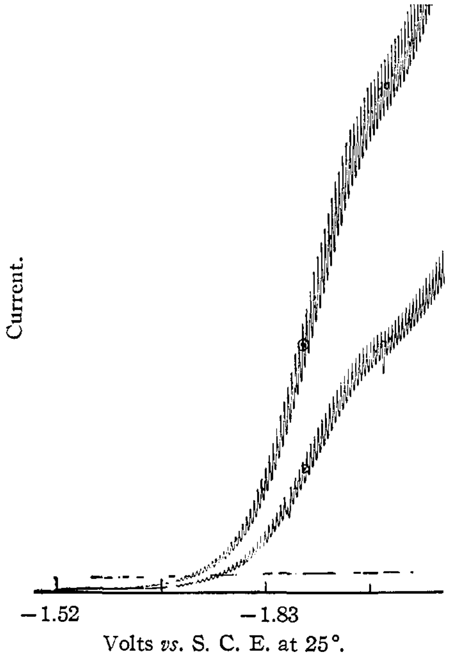

Fig. 3.—Polarograms of 19.5983 millimolar praseodymium sulfate solution: supporting electrolyte, 0.1 *M* $(CH_3)_4NI$; sensitivities, 3-25-5 and 3-50-5 $E_{1/2}$, −1.96 volts *vs.* S. C. E., at 25°.

TABLE III

PRASEODYMIUM SULFATE IN 0.1 *N* TETRAMETHYLAMMONIUM IODIDE AND 0.01% GELATIN

Concentration Pr^{+3}, millimolar	$E^1/_2$ *vs.* S. C. E.	i_d, microamp.	I_d
19.598	−1.96	131.4	3.63
9.799	−1.89	64.89	3.45
4.90	−1.83	31.91	3.49
2.45	−1.79	15.57	3.31

Addition of Sulfuric Acid.—When the *p*H of the solution was lowered by the addition of one-tenth normal sulfuric acid two well-defined waves were obtained. The first wave was due to the reduction of the hydronium ion and the second was due to the reduction of the praseodymium ion. In no instance were three waves found; Fig. 4. The data are tabulated in Table IV.

Age of Solution.—Polarograms were made of solutions that varied in age from three hours to twelve months to ascertain whether or not age had any effect on the polarographic reducibility of the praseodymium ion. Figure 1 represents a polarogram of a solution that was three hours old. A polarogram made twelve months later of the same solution was identical with the origi-

TABLE IV

PRASEODYMIUM SULFATE, 6.75 MILLIMOLAR, IN 0.1 N LITHIUM CHLORIDE AND 0.01% GELATIN AT VARIOUS pH VALUES

pH	$E^1/_2$ vs. S. C. E.	i_d, microamp.	I_d
5.88	−1.85	45.45	3.68
3.08	−1.86	47.55	3.91
2.75	−1.89	45.80	3.71
2.50	−1.90	45.50	3.80
2.40	−1.93	45.32	3.72

nal. It is manifest that age has no appreciable effect on the polarographic reducibility of the praseodymium ion.

Hydrolysis of Praseodymium Sulfate.—In order to determine whether or not there was a progressive hydrolysis of praseodymium solutions the pH was determined for various concentrations at different intervals of time. In this study several pH meters were used as checks against each other.

Bodländer[9] determined the hydrogen ion concentrations of $N/10$ and $N/32$ chloride solutions of scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium dysprosium, erbium and neoytterbium by means of the hydrogen electrode at 25°. The values for praesodymium are tabulated in Table V.

TABLE V

HYDROGEN ION CONCENTRATION DATA FOR AQUEOUS PRASEODYMIUM SALT SOLUTIONS

Solution	Concn., N	pH	Hydrolysis, %	Analyst
$PrCl_3$	0.1	5.37	0.00427	Bodländer[9]
$PrCl_3$	.1	3.10		Kleinheksel,[10] *et al.*
$Pr(NO_3)_3$	.01	4.23		Neish,[11] *et al.*
$PrCl_3$	.01	4.50		Kleinheksel,[10] *et al.*
$Pr_2(SO_4)_3$	.1	5.40	.00399	Swensen and
$Pr_2(SO_4)_3$	.01	5.69	.0204	Glockler
$PrCl_3$	.1	5.47	.00339	Swensen and
$PrCl_3$	.01	5.66	.0219	Glockler

Kleinheksel and Kremers[10] determined the pH values of 0.1 N and 0.01 N chloride solutions of yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, dysprosium, holmium and erbium at 25°, using a hydrogen electrode. Their reported values are considerably lower than those of Bodländer,[9] Neish and Burns[11] and those of the authors. They ascribe this difference to the fact that anhydrous salts were used in the preparation of the solutions. The authors used anhydrous salts in the preparation of their solutions, so this apparently cannot account for the difference. Denham[12] reported that the pH of several solutions varied with age. Using as electrodes the calomel electrode and the hydrogen electrode Denham found that the pH of $N/64$ cerium chloride varied from 3.95 to 4.91 over a period of nine days, Table VI.

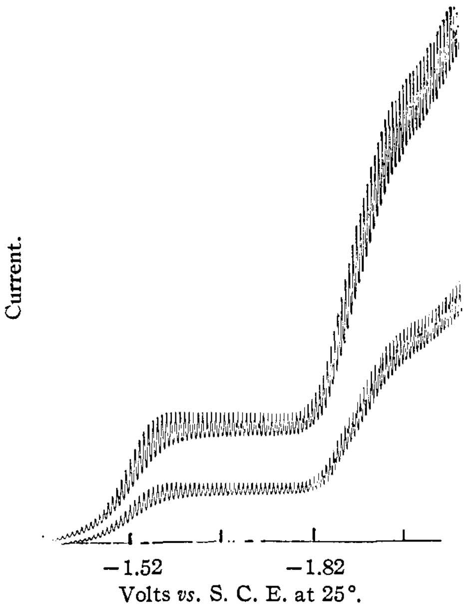

Fig. 4.—Polarograms of 6.75 millimolar praseodymium sulfate: supporting electrolyte, 0.1 N lithium chloride; maximum suppressor, 0.01% gelatin; sensitivities, 3–25–5 and 3–50–5 $E_{1/2}$, −1.89 volts vs. S. C. E., at 25°, pH, 2.75.

TABLE VI

DATA ON pH VALUES OBTAINED BY DENHAM ON $N/64$ SOLUTIONS OF CERIUM CHLORIDE, USING HYDROGEN AND CALOMEL ELECTRODES

Days	pH	Days	pH
0	4.75	5	4.04
1	4.91	6	3.95
2	4.10	7	4.20
4	4.34	8	4.59
		9	4.30

TABLE VII

DATA ON THE pH VALUES OF PRASEODYMIUM SOLUTIONS, USING GLASS AND SATURATED CALOMEL ELECTRODES

Days	pH $Pr_2(SO_4)_3$ 0.1 N	pH $PrCl_3$ 0.1 N	Days	pH $Pr_2(SO_4)_3$ 0.1 N	pH conductivity water[a]
0	5.63	5.47	0	5.47	5.75
39	5.61	5.86	1	5.52	5.78
40	5.62	5.65	2	5.56	5.73
41	5.63	5.69	3	5.59	5.79
42	5.61	5.72	4	5.61	5.81
44	5.40	5.68	5	5.52	5.76
45	5.56	5.50	6	5.48	5.82
46	5.46	5.60	7	5.49	5.72
50	5.51	5.61	10	5.51	5.80
52	5.62	5.62	12	5.61	5.69
54	5.61	5.63	13	5.61	5.76
55	5.55	5.61	14	5.63	5.88
540		5.40	15	5.65	5.79
578		5.63	16	5.42	5.79
589		5.65	17	5.51	5.81

[a] Acidity due to dissolved carbon dioxide.

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(9) Bodländer, Inaugural Dissertation, Berlin, 1915.

(10) Kleinheksel and Kremers, THIS JOURNAL, **50**, 959 (1928).

(11) Neish and Burns, *Can. Chem. Met.*, **5**, 69 (1921).

(12) Denham, *Z. anorg. Chem.*, **57**, 378 (1908).

In order to ascertain whether or not the hydrolysis of a praseodymium solution varied similarly with age, the pH values of solutions of various concentrations and various ages were determined. The results are tabulated in Table VII. They indicate that there is no appreciable consistent variation with time in the hydrolysis of a praseodymium solution.

Summary

1. The polarographic behavior, hydrogen ion concentration and hydrolytic properties of praseodymium solutions were studied.
2. In contrast with the observations of Noddack and Brukl and in agreement with Heyrovsky and Kolthoff and Lingane, only a single reduction step was observed in the polarographic reduction of the trivalent praseodymium ion.
3. The corrected half-wave potentials for the praseodymium ion were found to be: (a) with no suppressor or supporting electrolyte: -2.06 for 20 millimolar, -2.04 for 10 millimolar and -1.89 for 2 millimolar: (b) with supporting electrolyte and suppressor: -1.84 for 9 millimolar in 1 M lithium chloride, -1.94 for 20 millimolar in 0.1 M lithium chloride, -1.96 for 20 millimolar in 0.1 M $(CH_3)_4NI$, -1.95 for 20 millimolar and 0.1 N lithium chloride at pH of 5.88 and -1.96 for 20 millimolar and 0.1 M lithium chloride and at a pH of 3.08.
4. The half-wave potential varied with the concentration, becoming more electronegative with an increase in concentration.
5. The half-wave potential varied with the pH. The lower the pH value the more electronegative the half-wave value became.
6. The pH of a praseodymium salt solution was found to be independent of age.
7. The degree of hydrolysis of praseodymium salt solutions of various concentrations was determined.
8. It was found that when the praseodymium ion was reduced it underwent a three electron change directly to the metallic state.

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[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Ternary System: Hydrazine–Water–Sodium Hydroxide

BY R. A. PENNEMAN[1] AND L. F. AUDRIETH

The hydrazine–water system exhibits a maximum boiling point at 120.1° (760 mm.) corresponding to a composition containing 58.5 mole per cent. hydrazine and 41.5 mole per cent. water[2] (71.5% and 28.5% by weight, respectively). The removal of water by fractional distillation from very dilute hydrazine solutions, such as are obtained in the Raschig synthesis, is effective only until the maximum boiling composition is reached. In practice, however, concentration by this method is continued only until a product containing about 85% hydrazine hydrate (54.4% N_2H_4 by weight) is obtained. To concentrate hydrazine beyond this stage it is customary to distil from such dehydrating agents as barium oxide,[3] sodium hydroxide,[4] or potassium hydroxide.[5]

In the course of experimental work on the preparation of anhydrous hydrazine it was found that certain mixtures of 85% hydrazine hydrate and sodium hydroxide form two liquid phases when heated above approximately 60°. This observation suggested the possibility of concentrating hydrazine by removal of the hydrazine-rich phase. Since this phenomenon had not been reported previously, a quantitative investigation was made of the hydrazine–water–sodium hydroxide system as a function of temperature in the range 50–100°. In addition, hydrazine, water, and (a) potassium hydroxide and (b) potassium carbonate were studied quantitatively at 50°. A qualitative study using still other compounds was carried out in an unsuccessful attempt to find another ternary hydrazine system separating into two liquid phases in the temperature range from 25–100°.

To undertake investigation of the ternary system, hydrazine–water–sodium hydroxide, it was necessary to devise an analytical method for the determination of hydrazine and sodium hydroxide in the presence of each other. Certain precautions, described in the experimental portion of this paper, were necessary to prevent oxidation of hydrazine by atmospheric oxygen during sampling and analysis and to eliminate operational hazards since hydrazine vapor has been found to explode by sparking at 100°.[6]

Experimental

Apparatus.—The equilibrium studies were conducted in a nitrogen atmosphere (to prevent air oxidation) using a closed Pyrex cell (18 × 2.5 cm.) with vigorous internal stirring accomplished by means of a solenoid stirrer similar to one used by Booth and Martin.[7] Stanolind mineral

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[2] De Bruyn and Dito, *Akad. Amsterdam Versl.*, **11**, 155 (1902/1903); Gmelin-Kraut, "Handbuch der anorganischen Chemie," Vol. 23, Ed. VIII, Verlag Chemie, Berlin, 1936, p. 548.

[3] Hale and Shetterly, THIS JOURNAL, **33**, 1071 (1911); Giguere and Rundle, *ibid.*, **63**, 1135 (1941).

[4] Raschig, *Ber.*, **43**, 1927 (1910).

[5] Wenner and Beckman, THIS JOURNAL, **54**, 2787 (1932).

[6] Bamford, *Trans. Faraday Soc.*, **35**, 1239 (1939).

[7] Booth and Martin, *Ind. Eng. Chem., Anal. Ed.*, **17**, 528 (1945).