oleate and potassium laurate, and seven of the thirty-five were solubilized by Emulsol 607L and cetylpyridinium chloride. Tables III and IV of the present paper also include solubilization of 8 additional organic liquids by a non-ionic detergent, Triton X-100. Not shown in the tables are the results of solubilization of amyl valerate and of 1-chloronitropropane by decinormal Emulsol 607L at 25°, namely: 0.44 and 1.14 cc. total in 100 cc. solution, or 0.39 and 1.40 g. solubilized, or 0.25 and 1.14 mole ratio, respectively.

The order of solubilization by the six detergents of this and the previous study is maintained for most of the forty-three organic liquids tested, with comparatively minor exceptions or specificities. The non-ionic detergent Triton X-100 is the poorest solubilizer. Next comes potassium laurate. Then come, near together, sodium oleate and Emulsol 607L (one anionic and the other cationic). Much the best are the cationic dodecylamine hydrochloride and cetylpyridinium chloride.

It may have been over-emphasized in the previous publication[7] that high molecular weight of compounds undergoing solubilization hinders their solubilization. This is very true within any one homologous series, and it is emphasized when the volume or percentage solubilized is calculated in mole ratios. However, high molecular weight may be offset for such compounds as oleic acid by their belonging to an homologous series that is especially readily solubilized. Thus, although the mole ratio may be very small the actual volume or weight percentage solubilized may be quite comparable with that of such substances as *n*-decane.

Warren W. Woods and Dr. J. V. Robinson (Stanford Laboratories, unpublished) have found that castor oil is appreciably solubilized in lubricating oil by Aerosol OT, and similarly, sulfonated castor oil was solubilized in lubricating oil by Lead Aerosol OT.

Summary

1. Solubilization of organic liquids in solutions of the cationic detergents cetylpyridinium chloride and Emulsol 607L, and the non-ionizing Triton X-100 have been determined. The results, in general, follow the same order for different liquids as was previously described for three other detergents, dodecylamine hydrochloride, sodium oleate and potassium laurate. The non-ionic detergent Triton X-100 was the poorest solubilizer, and the best were the cationic cetylpyridinium chloride and dodecylamine hydrochloride.

2. Whereas all previous studies have shown that added salts greatly enhance solubility, and this is confirmed for the solubilization of benzene and octane by cetylpyridinium chloride, it is found that the solubilization of the polar compounds octyl alcohol and benzaldehyde is greatly depressed by the addition of sodium or potassium chloride. It is suggested that whereas with hydrocarbons and many other organic liquids solubilization occurs in the hydrocarbon portion of the micelles, with these polar compounds the solubilization occurs at the polar ends of the detergent molecules in the micelles.

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RECEIVED JUNE 30, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STATE UNIVERSITY OF IOWA]

The Polarographic Reduction of Gadolinium

BY SHERMAN W. RABIDEAU AND GEORGE GLOCKLER

On the basis of a dual wave obtained in the polarographic reduction of 0.01 *M* solutions of scandium, yttrium, and the rare earth sulfates without supporting electrolyte, Noddack and Brukl[1] concluded that the reduction proceeded first to the bivalent state and then to the metal. Leach and Terrey[2] observed a single wave in solutions of scandium chloride with 0.1 *N* potassium chloride as the supporting electrolyte. With additions of 1/6 *N* hydrochloric acid, the single wave gradually separated into two waves. The first wave was found to be due to the reduction of hydrogen ions while the second was attributed to the deposition of scandium.

Kolthoff and Lingane[3] expressed doubt that the double wave observed by Noddack and Brukl[1] corresponded in each case to the bivalent state, and suggested that it may have been caused by the discharge of hydrogen from the hydrolyzed solutions. This study was undertaken in an attempt to establish the half-wave potentials of gadolinium and to investigate polarographically the possibility of the existence of a bivalent state for this rare earth.

Experimental Procedure

The Sargent Model XX visible recording polarograph, the characteristics of which have been previously described by Lingane,[4] was used to record the current-voltage curves. The initial and span potentials were determined potentiometrically since the voltmeters supplied with the instrument are not of the requisite accuracy. All polarograms were recorded for uniformity with the damping control in position 5. An Erlenmeyer type flask served as the electrolysis vessel when the mercury pool anode was used. An H-cell of the design described by

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

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

[3] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

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

Lingane and Laitinen[5] was used in all other cases. The temperature was maintained at 25.0 ± 0.1°. Oxygen was removed from the solutions with nitrogen or hydrogen. With the exception of the waves recorded using the mercury pool anode, all diffusion currents have been corrected for the residual currents, and the half-wave potentials were corrected for the iR drop in the cell. Because of the lag of the recorder, and the difficulty of measuring the diffusion currents, the reported half-wave potentials are believed to be reliable within ±0.01 volt.

A spectrographic analysis of the rare earth confirmed the presence of traces of europium. Small amounts of terbium in the sample are suspected because of the disappearance of the brown color of the oxide in a reducing atmosphere. Because of the limited sample of rare earth it was necessary to recover the gadolinium for subsequent analyses. The gadolinium was precipitated as the oxalate in dilute hydrochloric acid solution, and ignited to the oxide. Before use in preparing a solution for polarographic analysis, the sample was carried through the oxalate-oxide conversion twice to remove salts of the supporting electrolyte and gelatin. The oxide was chosen as the weighing form, and precautions were taken to avoid the interference of carbon dioxide and moisture. The sulfate solutions were prepared from the dry oxide by adding an excess of sulfuric acid, evaporating to dryness, and finally heating to complete removal of fumes of sulfur trioxide. The desired molarities were obtained by dilution with conductivity water.

Experimental Results

The procedure of Noddack and Brukl[1] was followed in an attempt to repeat their work with regard to the polarographic reduction of gadolinium. A 0.01 M solution of gadolinium sulfate was electrolyzed using a mercury pool anode. A polarogram of the type illustrated in Fig. 1 was obtained. It is of interest to note that the step height of the wave is much less than would be predicted on the basis of results obtained with supporting electrolyte present. Though Noddack and Brukl[1] reported values of −1.810 and −1.955 volts *vs.* the N.C.E. for the *Knickpunkt* of the two waves, the results of Fig. 1 indicate that the second wave is not sufficiently well enough defined to establish the existence of a second reduction step.

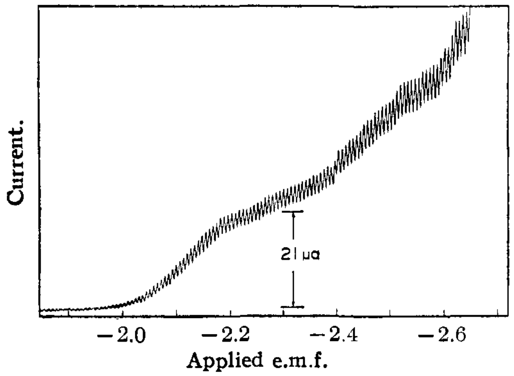

Fig. 1.—0.01 M gadolinium sulfate without supporting electrolyte: mercury pool anode.

The polarographic behavior of gadolinium sulfate was studied with a supporting electrolyte of 0.1 N lithium chloride plus 0.01% gelatin using the H-cell. A single well-defined wave was obtained with a linear relationship observed between the concentration and the diffusion current (Table I).

TABLE I

GADOLINIUM SULFATE IN 0.1 N LITHIUM CHLORIDE PLUS 0.01% GELATIN

Millimoles of Gd^{+3} per liter	$E^{1/2}$ *vs.* S. C. E. volts	$m^{2/3}t^{1/6}$	i_d microamp.	i_d/c	I_d
0.80	−1.74	1.693	5.1	6.4	3.8
1.60	−1.74	1.758	10.1	6.3	3.6
4.00	−1.77	1.716	26.2	6.6	3.8

To note the effect of additions of acid on the current-voltage curves, increasing quantities of 0.05 N hydrochloric acid were added to 14 ml. of 4.00 millimolar Gd^{+3}. As the solution became more acidic, the hydrogen wave increased proportionately with the half-wave at −1.5 volts *vs.* the S.C.E., but the wave height due to the reduction of gadolinium was not appreciably affected. The half-wave potential of gadolinium was shifted to more negative values with increasing acid concentration as shown in Table II.

TABLE II

EFFECT OF ACID ON THE HALF-WAVE POTENTIAL OF GADOLINIUM IN 0.1 N LITHIUM CHLORIDE PLUS 0.01% GELATIN

Ml. of 0.05 N HCl	$E^{1/2}$ *vs.* S. C. E., volts
0.00	−1.77
.10	−1.79
.20	−1.80
.40	−1.82
.60	−1.84
.80	−1.86
1.00	−1.86
1.50	−1.91
2.00	−1.93

Fig. 2 illustrates the effect of added acid with a supporting electrolyte of 0.1 N tetramethylammonium iodide plus 0.01% gelatin.

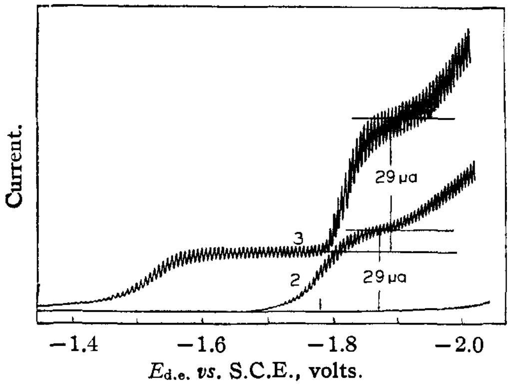

Fig. 2.—Gd^{+3} in 0.1 N tetramethylammonium iodide plus 0.01% gelatin: (1) residual current; (2) 4.0 millimolar; (3) 0.30 ml. of 0.05 N HCl added to 14 ml. of 4.0 millimolar.

The wave definition in a supporting electrolyte of 0.1 N potassium chloride was about the same

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(5) Lingane and Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

as that observed with lithium chloride. The results of the polarographic reduction of gadolinium sulfate in potassium chloride are given in Table III.

TABLE III

GADOLINIUM SULFATE IN 0.1 *N* POTASSIUM CHLORIDE PLUS 0.01% GELATIN

Millimoles Gd^{+3} per liter	$E_{1/2}$ S. C. E. volts	$m^{2/3}t^{1/6}$	i microamp.	i_d/c	I_d
0.80	−1.75	1.780	5.2	6.5	3.9
1.60	−1.75	1.788	10.3	6.4	3.6
4.00	−1.77	1.728	26.9	6.7	3.7

Discussion

The values of the quantity $m^{2/3}t^{1/6}$ were determined at the potential at which the diffusion current was measured. The average value of the diffusion current constant, I_d, for Gd^{+3} was found to be 3.7. Using equivalent conductance data given by Pascal,[6] and extrapolating to infinite dilution, a value of 125 ohm^{-1} cm.^{2} was obtained for gadolinium sulfate. If the value 80 is used for the sulfate ion, the equivalent ionic conductance of gadolinium is then 45 ohm^{-1} sq. cm. By substituting the value of the ionic conductance of gadolinium into the Nernst relation

$$D_i^0 = 2.67 \times 10^{-7} (\lambda^0/Z)$$

the diffusion coefficient is found to be 4.0×10^{-6} sq. cm. sec^{-1}. With the above quantities substituted into the Ilkovic equation, the number of electrons involved in the electrode reaction is found to be three. Thus the results indicate that the reduction of gadolinium at the dropping electrode takes place according to the reaction

$$Gd^{+3} + 3e \longrightarrow Gd^0$$

An analysis of the polarographic waves was made by noting the slope of the line produced in plotting values of log $i/i_d - i$ *vs.* $E_{d.e.}$ The irreversibility of the electrode reaction is indicated by the fact that the slope is not as steep as would be expected on the basis of a three electron reduction.

Summary

1. The results of Noddack and Brukl were not confirmed with regard to the polarographic reduction of gadolinium sulfate.
2. An increasing acid concentration shifts the half-wave potential of gadolinium to more negative potentials.
3. A value of 4.0×10^{-6} sq. cm. sec.$^{-1}$ was calculated for the diffusion coefficient of Gd^{+3} at 25°.
4. The results indicate that the reduction of gadolinium at the dropping mercury electrode involves three electrons.
5. The average value of the diffusion current constant for Gd^{+3} was found to be 3.7 at 25° in a supporting electrolyte of 0.1 *N* lithium chloride or 0.1 *N* potassium chloride.
6. The half-wave potential for 4.0 millimolar Gd^{+3} was found to be −1.77 volts *vs.* the S.C.E. with 0.1 *N* lithium chloride, and with 0.1 *N* potassium chloride as the supporting electrolytes.

IOWA CITY, IOWA RECEIVED JUNE 9, 1947

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(6) Pascal, "Traité de Chimie Minérale," Masson et Cie., Éditeurs, Paris, 1933.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STATE UNIVERSITY OF IOWA]

Reduction of Neodymium at the Dropping Mercury Electrode

BY C. R. ESTEE AND GEORGE GLOCKLER

The polarographic behavior of neodymium in the presence of supporting electrolyte has not previously been described. The present study was undertaken to allow the application of the Ilkovic equation[1] to obtain the *n*-value for the reduction of the trivalent neodymium ion, and to establish under proper polarographic conditions the half-wave potential for the reduction. No evidence of the previously reported[2] two-step reduction from water solutions was obtained.

Experimental

The polarograms were recorded with a Sargent Model XX Visible Recording Polarograph of the Heyrovsky type, the design and operating characteristics of which have recently been discussed by Lingane.[3] A conventional dropping mercury cathode assembly was used, the stand tube being provided with an adjustable mercury reservoir. The usual H-type electrolysis vessel[4] with a sintered glass plug and agar bridge was employed. Measurements were made with respect to a mercury anode. Solution temperatures were maintained at 25.0 ± 0.1° by means of a thermostat. The drop time was varied between two and five seconds. Hydrogen or nitrogen was bubbled through the solution to remove dissolved oxygen.

The neodymium salt was obtained as the nitrate and an examination of the absorption curve found with a Bell and Coleman spectrophotometer showed no detectable impurities. Neodymium oxide was prepared by ignition of the oxalate precipitated from a warm acid solution of the nitrate. The oxide was treated with an excess of sulfuric acid and heated for eight hours at 440° to give the octahydrate of neodymium sulfate. Solutions of supporting electrolytes prepared from analytical grade reagents showed no detectable impurities.

Diffusion coefficients of 6.03×10^{-6} sq. cm./sec. for the neodymium ion and 8.15×10^{-6} sq. cm./sec. for

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(1) Ilkovic, *J. chim. phys.*, **35**, 129 (1938).

(2) Noddack and Brukl, *Angew. Chem.*, **50**, 362 (1937).

(3) Lingane, *Ind. Eng. Chem., Anal. Ed.*, **18**, 734 (1946).

(4) Lingane and Laitinen, *ibid.*, **11**, 504 (1930).