[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polarographic Reduction of Hexamminecobalt(III) Ion. III. The Effect of Non-complexing Electrolytes

BY H. A. LAITINEN, A. J. FRANK AND P. KIVALO

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The diffusion current region of the first reduction wave of hexamminecobalt(III) ion in perchlorate, chloride and nitrate solutions shows anomalous dips at higher concentrations of reducible ion. The irregularities are due to formation of a film, probably of cobalt(II) hydroxide. The effects of gelatin, of various salts, and of *p*H on the film formation were studied. The *p*H range for film formation varies with the nature of the buffer. Reduction of hexamminecobalt(III) ion in the presence of aquated cobalt(II) ion showed that no addition to the second wave is caused by a small addition of cobalt(II). This is explained by precipitation of the latter by ammonia released during reduction of the hexamminecobalt(III) ion. At the second wave, this ion is reduced directly to the metal without the intermediate formation of the hexaaquocobalt(II) ion. Another type of film formation, caused by direct interaction of mercury, is found in the presence of bromide, thiocyanate or iodide ions. Although mercury is involved, the film consists of cobaltous hydroxide. A study of the effect of various electrolytes on the diffusion current shows that, after the effect of viscosity is taken into account, there remains a suppressing effect which increases with increasing anionic charge.

The results of a study of the reduction of the hexamminecobalt(III) ion in certain complexing media was previously reported.[1] The present investigation deals with reduction in non-complexing electrolytes. The experimental details were the same as previously described.

Results and Discussion

The Effect of Hexamminecobalt(III) Concentration.—In the polarographic reductions hitherto reported, the concentration of the complex ion has been millimolar or less. It was therefore of interest to determine if the characteristics of the reduction remained constant at concentrations approaching the upper limit of useful polarographic work. Figure 1 shows the current–voltage curves for the reduction of the complex at various concentrations in 0.1 *M* sodium perchlorate. It can be seen that at concentrations of 0.5 to 2 m*M*, fairly regular waves appeared for both the first and the second reduction steps, the half-wave potentials being, as usual, about −0.250 and −1.230 v. *vs.* S.C.E., respectively. As the concentration of the reducible ion was increased (curves 5 and 6) the current increased at the right potential, but did not reach the expected height and then, at increased potential, suddenly dropped to a minimum. The minimum appears to be independent of the concentration of the cobalt complex. When the potential was made more negative the current started to increase again. The current at the top of the second wave was proportional to concentration, and normal in magnitude.

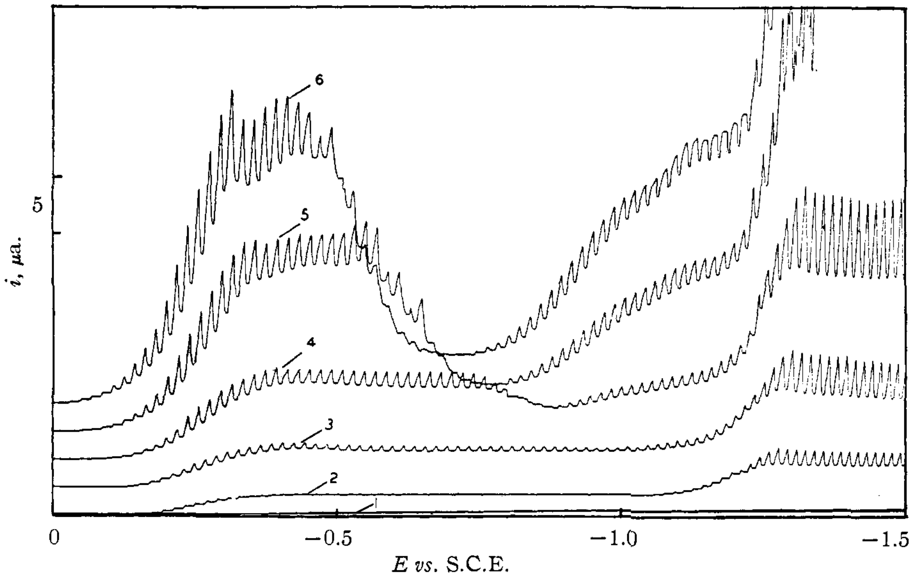

Fig. 1.—Polarograms obtained in 0.1 *M* sodium perchlorate, with various concentrations of hexamminecobalt(III) chloride: electrode I, damping 1.

Curve	1	2	3	4	5	6
Concn. m*M*	0	0.5	1	2	5	10

Similar curves were also obtained in 0.1 *M* sodium chloride and nitrate solutions. In the nitrate medium, the second reduction step starts about 200 mv. earlier than in the two other cases, and seems to consist of a "prewave," which precedes the actual second wave. Brdicka[2] has reported the same phenomenon in the reduction of cobaltous chloride in neutral solution. He explained the prewave as being due to the pentaaquomonohydroxocobalt(II) ion formed by hydrolysis, the ion being in slow equilibrium with the hexaaquocobaltous ion.

Gayer and Woontner[3] have recently shown that the hydrolysis of cobalt(II) actually exists. Figure 2 shows Brdicka's "prewave" obtained in the reduction of a mixture of 1 m*M* hexamminecobalt(III) and 4.78 m*M* cobalt(II) in 0.1 *M* sodium perchlorate containing 0.01% gelatin.

The sudden drop in the current, occurring at higher concentrations of the hexammine complex, is

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(1) H. A. Laitinen and Pekka Kivalo, THIS JOURNAL, **75**, 2198 (1953).

(2) R. Brdicka, *Collection Czechoslov. Chem. Communs.*, **5**, 113 (1933).

(3) K. H. Gayer and L. Woontner, THIS JOURNAL, **74**, 1436 (1952).

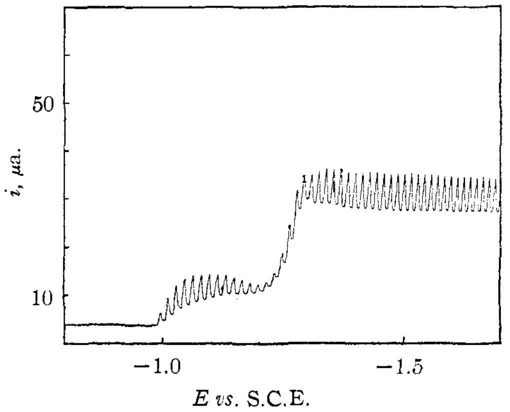

Fig. 2.—Polarogram obtained in 0.1 *M* sodium perchlorate containing 0.01% gelatin, 4.75 m*M* cobalt(II) and 1 m*M* hexamminecobalt(III): electrode I, damping 1.

no doubt caused by a film formation. Similar current limiting film formations have been reported, *e. g.*, by Kolthoff and Miller[4] and Kolthoff and Lingane.[5]

A plausible explanation for the occurrence of such a film may be postulated as follows: The first product of the reduction of hexamminecobalt(III) is the divalent hexammine complex.[1] The latter, however, being a labile complex rapidly exchanges its ligands to satisfy the equilibrium condition in the medium in question. If the supporting electrolyte is a non-complexing ion like nitrate or perchlorate, the result of the exchange will be the hexaaquocobaltous ion. Thus ammonia will be liberated, increasing the *p*H at the surface of the dropping mercury electrode. It is known that an addition of small amounts of ammonia to a cobalt(II) solution gives precipitates of corresponding basic salts.[6–9] In the present case, however, where the ammonia concentration is actually greater than the cobalt(II) concentration, it is likely that cobaltous hydroxide is precipitated.

That ammonia actually was liberated during the first step of the reduction, was shown by an experiment in which cadmium ions were present in the solution. It was thought that the reduction of cadmium would be affected due to the precipitation of a basic salt or the hydroxide of cadmium (cadmiumammine complexes are not likely to be formed at the low ammonia concentration). However, the experiment showed that the reduction wave of the cobalt(III) complex was itself almost suppressed up to the potential where cadmium was reduced. The small amount of cobalt(III) being reduced gave enough of ammonia to raise the *p*H to the point where a film, probably of a basic cadmium salt, was formed. When the potential became negative enough to reduce the cadmium, the reduction proceeded normally, the wave height was equal to the sum of the corresponding waves recorded separately.

As can be seen from Fig. 1, curve 4, the film formation starts at around −0.8 v. and disappears around −1.0 v. At higher concentrations the film formation starts earlier. This apparent dependence of the film formation on the potential probably is due to electrostatic effects on the colloidal precipitate formed at the electrode surface.

A microelectrolysis experiment was conducted in an attempt to make the film visible. The cell used was a special H-cell in which the cathode compartment held only 1 cm.[3] of solution. Utilizing a droplet of mercury as a cathode, a potential of −0.9 v. *vs.* S.C.E. was applied, the solution being a 5 m*M* hexamminecobalt(III) chloride in 0.1 *M* sodium nitrate. Oxygen was removed as usual with nitrogen by means of a fine glass capillary tubing inserted in the small cathode compartment. After a current of 60–100 microamperes had passed for an hour a greenish precipitate was observed on the mercury surface.

The Properties of the Current Limiting Film.—Some of the properties of the film were also studied. It was found that an addition of gelatin removed the film. The irregularities shown in Fig. 1, curve 5, disappeared after a minimum addition of 0.02% gelatin, which acts as a protective colloid preventing the formation of the adherent film. As previously reported from this Laboratory,[10] the addition of gelatin causes a large shift of the half-wave potential to more negative direction.

It was also found that by increasing the concentration of the supporting electrolyte the irregularities disappeared. The electrostatic adsorption of the colloidal precipitate is probably affected by the presence of high concentration of neutral salts. For instance, when the concentration of the complex was 5 m*M*, it was necessary to increase the concentration of sodium nitrate to 2 *M* in order to remove the irregularities.

On the other hand, it was expected that salts of higher charge type would coagulate the colloidal precipitate and make the film formation more pronounced. One-tenth molar barium nitrate solution used as supporting electrolyte, did, however, not show any film formation at all nor did 0.1 *M* sodium sulfate, or 0.1 *M* phosphate buffer (*p*H 6–10). The explanation might be a peptization effect of adsorbed ions and/or a complexing effect to form a soluble divalent cobalt compound. When a sufficient concentration of ammonia and ammonium salt was present to prevent the divalent cobaltammine from transforming to the aquated ion, no irregularities appeared. It was also found that an addition of ammonia only, actually increased the formation of the precipitate, which is explained by the fact that the divalent cobaltammines are stable only in the presence of ammonium salts.[11]

The Effect of *p*H.—The effect of variation of the hydrogen ion concentration was studied primarily to elucidate the film formation. The *p*H effect was, however, masked by side effects. The acidity was varied from 1 *M* hydrochloric acid to acetate buffer (total acetate concentration 0.1 *M*) *p*H 4.40

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[4] I. M. Kolthoff and C. S. Miller, *ibid.*, **63**, 1405 (1941).

[5] I. M. Kolthoff and J. J. Lingane, *ibid.*, **62**, 852 (1940).

[6] H. T. S. Britton, "Hydrogen Ions," D. Van Nostrand Co., Inc., New York, N. Y., 1929, p. 256, 278.

[7] J. Haberman, *Monatsh.*, **5**, 445 (1884).

[8] D. Strömholm, *Arkiv Kemi Min.*, **2**, 16 (1907).

[9] A. Bernardi, *Gazz. chim. ital.*, **57**, 232 (1927).

[10] H. A. Laitinen, J. C. Bailar, Jr., H. F. Holtzclaw and J. V. Quagliano, THIS JOURNAL, **70**, 2999 (1948).

[11] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 235.

to 6.65, phosphate buffer (total phosphate concentration 0.1 *M*) *p*H 5.80 to 9.80, borate buffer (total borate concentration 0.1 *M*) *p*H 7.85 to 9.80, and finally using sodium hydroxide up to a concentration of 2 *M*. As expected, in acid solution no film formation was observed, because of the fact that the ammonia formed during the reduction is immediately neutralized. In the case of the acetate buffer, the first sign of a precipitate occurred at *p*H 5.5 and the film formation became more pronounced with increasing *p*H. It is of interest to notice that when the *p*H was between 5.5 and about 6, the second reduction step started at around −0.9 v. *vs.* S.C.E., indicating a hydrolysis effect similar to that mentioned above. On both sides of this *p*H interval, the second step started at −1.15 v. As already mentioned, no film formation was observed when a phosphate buffer was used. Using boric acid buffer the *p*H had to be increased to 9 before any precipitation started.

In the experiments in which the supporting electrolyte contained sodium hydroxide, very interesting results were obtained. It was thought that because of the limited solubility of cobaltous hydroxide,[12] the reduction would be suppressed by a strong film formation. If the concentration of sodium hydroxide was between 0.005 and 0.03 *M* the first reduction wave was suppressed; the second wave again seemed to be of normal light. However, 0.1 *M* sodium hydroxide solution gave a very well defined diffusion current for 2 m*M* cobalt(III) complex, and the same was true for any concentration up to 2 *M* of the hydroxide. Even a 5 m*M* cobalt complex gave a smooth current–voltage curve with 0.1 *M* sodium hydroxide. It was observed that the half-wave potentials of the first wave stayed practically constant with increasing concentration of sodium hydroxide but the second wave shifted to more negative potentials (*ca.* 0.2 v.). However, no quantitative interpretations can be made because of the irreversibility of the reduction.

The disappearance of the film at higher alkali concentration can be due to two causes, either a peptization or a complex formation or both. It was shown in the first part of this investigation[1] that a hydroxo complex is formed as an intermediate in 10 *M* sodium hydroxide. This complex is said to exist also in 3 *M* alkali.[13] Gayer and Garrett[12] showed that the principal ionic reaction which determines the solubility of cobaltous hydroxide in dilute sodium hydroxide, is the formation of the acid anionic salt radical, or the trihydroxy complex

$$Co(OH)_2 + OH^- \rightleftarrows HCoO_2^- + H_2O \text{ or } Co(OH)_3^-$$

There is another possibility of forming a soluble product in the reduction of hexamminecobalt(III), namely, a formation of a mixed complex, for instance

$$Co(NH_3)_6^{+++} + e^- + OH^- \rightleftarrows Co(NH_3)_2OH^+ + 4NH_3$$

Such complexes do not appear to have been reported in the literature, but there seems to be no reason why they could not exist in solution as metastable intermediates.

Reduction of Hexamminecobalt(III) in the Presence of Co(II).—If the reduction of the hexamminecobalt(III) ion proceeds in a non-complexing medium with the hexaaquocobaltous ion as an intermediate, then the simultaneous presence of cobalt(II) in the solution should increase the height of the second wave. This was studied in an experiment in which a solution containing 0.1 *M* sodium perchlorate, 0.01% gelatin, 1 m*M* hexamminecobalt(III) and increasing concentrations of cobaltous nitrate was electrolyzed at the dropping mercury electrode and the height of the second wave recorded. It was found that the second wave did not increase until the concentration of cobalt(II) was about 1 m*M*. Because of the fact that the ammonia concentration at the surface of the drop is about 6 m*M* part of the divalent cobalt approaching the electrode will be precipitated. If the concentration of the divalent cobalt is below about 1 m*M*, all of it will be precipitated and will not be reduced at all. By increasing the concentration above this limit the current rises proportionally to it. By the precipitation of cobaltous hydroxide ammonium ions are formed, decreasing the *p*H enough so that the rest of cobalt(II) is soluble.

An important conclusion can be drawn from this experiment, namely, that the reduction to the metallic state occurs without the hexaaquo intermediate.

Reduction in the Presence of Halide and Thiocyanate.—The first reduction step of hexamminecobalt(III) is complicated with a film formation using halides and thiocyanate as supporting electrolytes. Figure 3 shows a family of curves representing the first reduction step in various halide and thiocyanate solutions. Chloride does not give a film formation, but the half-wave potential is more positive than that observed in a nitrate solution and the wave starts at zero applied potential with a small current. Bromide shows clearly a film formation and the fact that the reduction starts earlier than in the presence of chloride. Thiocyanate and iodide give a strong film formation. The iodide solution is only 0.1 *M* because of the limited

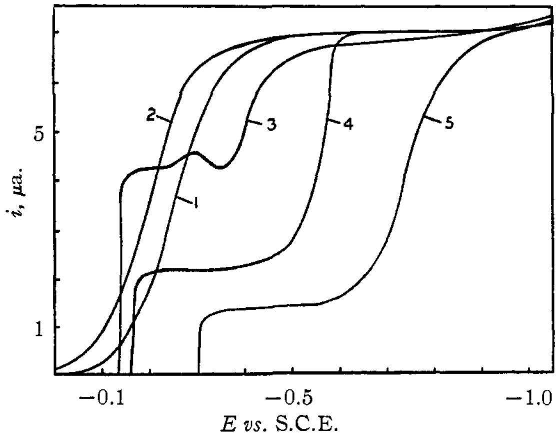

Fig. 3.—Polarograms of 2 m*M* hexamminecobalt(III) in various supporting electrolytes (first reduction step):

Curve	1	2	3	4	5
Supp.	1 *M*	1 *M*	1 *M*	1 *M*	0.1 *M*
Electrol.	$NaNO_3$	NaCl	NaBr	KSCN	NaI

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[12] K. H. Gayer and A. B. Garrett, THIS JOURNAL, **72**, 3921 (1950).

[13] S. Gordon and J. M. Schreyer, *ibid.*, **74**, 3169 (1952).

solubility of the hexamminecobalt(III) iodide. Figure 4 illustrates the fact that the reduction starts at early potentials, but is masked by the anodic dissolution of mercury.

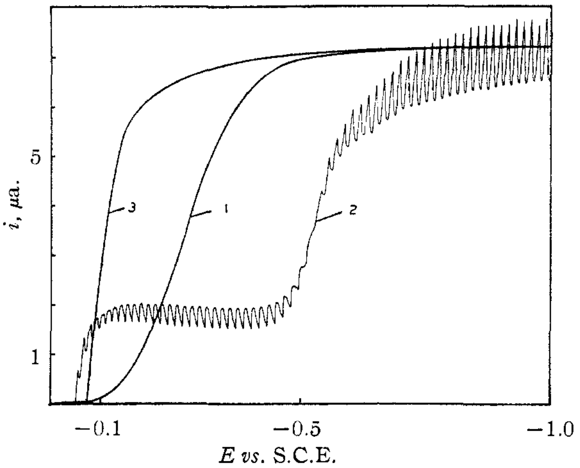

Fig. 4.—Polarograms of 2 m*M* hexamminecobalt(III) obtained in: curve 1, 1 *M* sodium nitrate; curve 2, 0.1 *M* potassium thiocyanate; curve 3, 0.1 *M* potassium thiocyanate containing 0.1 *M* ammonia and 0.1 *M* ammonium nitrate: electrode I.

The phenomenon has a simple explanation: the cobalt(III) complex oxidizes mercury in the presence of halides to form hexamminecobalt(II) and mercurous halide. The divalent cobalt complex decomposes by aquation and is precipitated as the hydroxide, which is the film forming substance. The mercurous ion is reduced electrochemically to give the current.

The height of the suppressed part of the first wave depends on the concentration of halide ion and seems to have a minimum around 0.1 *M* concentration in the case of thiocyanate. Calculations showed that the film cannot be pictured as a monolayer, but rather as a multilayer adsorption. It was also found that the film formation of 2 m*M* hexamminecobalt(III) did not have any effect on the electrocapillary curve of 0.1 *M* potassium thiocyanate, suggesting that the film is rather loosely adsorbed at the surface. However, the height of the suppressed part of the first wave was directly proportional to the height of mercury column, and the current–time behavior inverted (decreasing current with increasing time). Both of these observations are consistent with a surface-limited current.

That mercury is spontaneously oxidized by hexamminecobalt(III) in halide and thiocyanate solutions was confirmed by test-tube experiments. Deaerated solutions of halides containing the cobalt complex were shaken with mercury. It was found that the solutions turned green due to the formation of a precipitate and that ammonia was liberated. The relative time required to complete the reactions was shortest for iodide and increased for thiocyanate and bromide and for chloride actually was very long. The green precipitate was analyzed and consisted of cobaltous hydroxide. Curve 3 in Fig. 4 shows that an addition of ammonia buffer will remove the film, as expected, if it is cobaltous hydroxide. Apparently the rate of direct interaction between mercury and cobalt(III) complex is faster than the electroreduction of cobalt(III) at zero applied e.m.f. With increasing negative potential, the rate of the electrode reaction will increase. The correlation between the potential at which the film formation ceases and the solubility of the corresponding mercurous halide (Fig. 3) may be accounted for on the basis that adsorbed halide ion takes part in the direct reaction. The adsorption of halide ion will decrease with increasing potential again favoring the electroreduction reaction.

The second reduction step was found to occur at about the same potential in the presence of the halides as in nitrate solutions.

The Effect of Electrolytes on the Diffusion Current.—Laitinen, Bailar, Holtzclaw and Quagliano[10] observed that the diffusion current was suppressed in solutions containing sulfates, tartrates and citrates and also that the half-wave potential of the first wave varied with the supporting electrolyte. These effects were attributed to the formation of a "super complex," the hexamminecobalt(III) ion being the central ion of an aggregate held by electrostatic attraction.

Several investigators[14–17] have observed that the diffusion currents of various metal ions in certain supporting electrolytes are inversely proportional to the square root of the specific viscosity of the medium. Also it has been found[18] that the diffusion coefficient varies with ionic strength, thus affecting the diffusion current.

Since the diffusion rate of ion aggregates is masked by a viscosity effect, it was desirable to measure the diffusion current of hexamminecobalt(III) in various supporting electrolytes of different charge type and known viscosity.

In this investigation it was found that the diffusion current is inversely proportional to the square root of the viscosity and that the effect was independent of the nature of the electrolyte, provided the charge of the ion is kept constant. Figure 5 and the following table show the results of the experiments. Curve 1 is the plot of i_d *vs.* $\eta^{1/2}$ for univalent anions, curve 2 for divalent anions. The single point corresponding to a trivalent anion appears to lie on a third curve.

It can be concluded that after the effect of viscosity has been taken into account, there remains a suppressing effect, which increases with increasing charge of anion. This is consistent with the concept of an electrostatic clustering or "super complexing."

As mentioned above, the half-wave potential of the first reduction step is sensitive to variation of the supporting electrolyte. For instance, as seen in the table, the half-wave potential is shifted about 0.2 v. to the negative direction changing the supporting electrolyte from 1 *M* nitrate to 1 *M* sulfate. It was, however, found that this is not all due to the

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(14) I. M. Kolthoff and J. J. Lingane, "Polarography I," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, p. 97.

(15) B. Forss, *Acta Acad. Aboensis, Math. et Phys.*, **17**, No. 3, 1 (1951).

(16) A. Foffani and E. Vecchi, *Sbornik mezinarod. polarograf Sjezdu Praze 1st Congr.*, Pt. I, 64 (1951).

(17) A. Scholander, *ibid.*, 260 (1951).

(18) L. Meites, This Journal, **73**, 4257 (1951).

TABLE I

REDUCTION OF 1 mM $Co(NH_3)_6^{++}$ IN VARIOUS SUPPORTING ELECTROLYTES

Electrode I: Monovalent Anions

		Concn., M	$\eta^{1/2}$ [19]	i_d, μa.	$i_d \cdot \eta^{1/2}$	$E_{1/2}$, v. *vs.* S.C.E.
1	NaCl	1.0	1.047	3.59	3.75	−0.193
2	$CaCl_2$	1.0	1.073	3.31	3.55	− .220
3	Na benzoate	1.0	1.285	2.68	3.41	− .300
4	$NaClO_4$	1.0	1.023	3.56	3.65	− .240
5	NH_4NO_3	1.0	0.985	3.63	3.57	− .250
6	Na acetate	1.0	1.180	3.00	3.54	− .345
7	NaOH	0.5	1.051	3.53	3.71	− .355
8	$CoCl_2$	1.0	1.097	3.13	3.43	− .195
		Divalent anions				
9	Na tartr.	1.0	1.155	2.22	2.57	−0.380
10	Na_2SO_4	0.7	1.074	2.95	3.17	− .450
11	Na_2SO_4	1.0	1.110	2.64	2.94	− .465
12	$CoSO_4$	1.0	1.163	2.43	2.82	− .440
13	$(NH_4)_2SO_4$	1.0	1.055	2.96	3.12	− .465
14	K_2SO_4	0.7	1.036	3.09	3.20	− .465
15	H_2SO_4	1.0	1.043	3.19	3.33	− .385
16	Na_2SO_4	0.1	1.01	3.20	3.24	− .430
17	Na_2CO_3	0.5	1.135	2.82	3.20	− .455
18	$MgSO_4$	1.0	1.170	2.24	2.63	− .452
		Trivalent anions				
19	Na_3 citrate	1.0	1.175	1.75	2.06	−0.350

(19) N. W. Lange, "Handbook of Chemistry," 6th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1946, p. 1581.

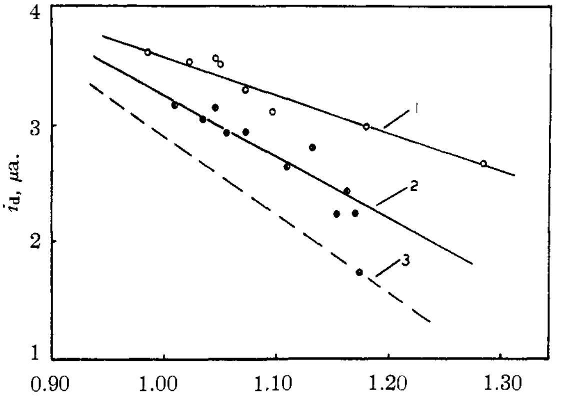

Fig. 5.—The diffusion current of a mM hexamminecobalt (III) plotted *versus* $\eta^{1/2}$ of various supporting electrolytes with electrode I.

super complexing but that the change of the ionic strength also affects the potential. Keeping the ionic strength practically constant (μ = 1) with potassium nitrate an addition of 0.1 M potassium sulfate shifted the potential only 25 mv. whereas the shift was 170 mv. if the supporting electrolyte consisted of only sulfate.

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URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Electrolytic Reduction of Perrhenate. I. Studies in Perchloric, Ethanesulfonic, Trifluoroacetic and Hydrochloric Acids

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Perrhenate solutions are reduced cathodically in trifluoroacetic or ethanesulfonic acids to insoluble oxide deposits. Perchloric acid is catalytically reduced at a cathode in the presence of perrhenate. In the presence of rhenium a mercury cathode is depolarized with consequent hydrogen evolution in both trifluoroacetic and hydrochloric acids. Conditions are given for the preparation of pure Re(IV) and Re(V) solutions in hydrochloric acid. Absorption spectra of these oxidation states in hydrochloric acid are given. Equilibria between the complex species present in hydrochloric acid solutions of Re(V) are rapidly established but only slowly in Re(IV) solutions. Re(V) can be quantitatively oxidized to perrhenate in hydrochloric acid while Re(IV) cannot.

Both polarographic and electrolytic studies of perrhenate reduction in different media have been reported.[1–4] The polarographic wave found in 2–4 M perchloric or hydrochloric acid has been interpreted as a reduction of perrhenate to Re(IV).[1,2] Rulfs and Elving, however, pointed out that the temperature coefficient of the diffusion current is not that of a diffusion controlled process and hence a value of three for the electron change would only be found at 25°. In addition, an attempt by these authors to electrolytically reduce Re(VII) in perchloric acid led to a continuous process which they attributed to the concurrent reduction of hydrogen ion.

According to Schmid[3] the electrolytic reduction of perrhenate in 6 M hydrochloric acid at a mercury cathode gives a yellow-green solution from which the Re(IV) salt, K_2ReCl_6, may be isolated. Further prolonged reduction gave an olive-green solution which he said was Re(III). Jakob and Jezowska[4] reported that the reduction in 6–10 M hydrochloric acid at either a Pd or platinized Pt electrode gives Re(V) solutions from which the salt, K_2ReOCl_5, can be isolated.

Although both the Re(IV) and Re(V) states have been obtained in hydrochloric acid by reduction wth reagents such as stannous chloride,[4–7] studies

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(1) J. J. Lingane, THIS JOURNAL, **64**, 1001 (1942).

(2) C. L. Rulfs and P. J. Elving, *ibid.*, **73**, 3284 (1951).

(3) H. Schmid, *Z. anorg. allgem. Chem.*, **212**, 187 (1933).

(4) N. F. Jakob and B. Jezowska, *ibid.*, **214**, 337 (1933).

(5) E. K. Maun and N. Davidson, THIS JOURNAL, **72**, 2254 (1950).

(6) H. Holemann, *Z. anorg. allgem. Chem.*, **217**, 105 (1934); **220**, 33 (1934); **235**, 1 (1937).

(7) S. Tribalat, *Compt. rend.*, **220**, 881 (1945); **222**, 1388 (1946); **223**, 34 (1946).