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POLAROGRAPHIC REDUCTION OF HEXAMINECOBALT (III) ION.
THE EFFECT OF COMPLEXING AGENTS

by

H. A. Laitinen and Pekka Kivalo

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POLAROGRAPHIC REDUCTION OF HEXAMINECOBALT (III) ION.
THE EFFECT OF COMPLEXING AGENTS

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ABSTRACT

The polarographic reduction of hexaminecobalt (III) ion to the divalent state has been studied in the presence of various concentrations of ammonia. Comparison of half-wave potentials with equilibrium potential measurements indicates that the first step in the reduction process is an electron transfer to form hexaminecobalt (II) ion. The irreversibility of the process may be attributed to a slow step, namely the transformation of the hexaminecobalt (II) ion from the initial d^2sp^3 hybridization structure to the stable sp^3d^2 structure. This mechanism is supported by the observation that the anodic current due to oxidation of hexaminecobalt (III) ion at the rotating platinum electrode is only of the order of 1 percent of the diffusion-controlled value, and must be limited by the rate of the reverse transformation.

In the presence of ethylenediamine, the reduction of hexaminecobalt (III) occurs at the reversible reduction potential of the trisethylenediaminecobalt (III) ion, although this species of ion is not present in solution. A mechanism for this process is suggested.

In concentrated chloride solution, the second step of the reduction was observed to be shifted 0.4 v. to a more positive potential, because of the formation of a chlorocomplex of cobalt (II) by rapid exchange of ligands by the hexaminecobalt (II) ion.

In concentrated hydroxide medium, a similar effect was observed, but with the shift of the second reduction step to a more negative potential.

Introduction

The polarography of hexamminecobalt (III) ion has been previously discussed by Brdicka,¹ Willis, Friend and Mellor² and in a

-
- (1) Brdicka, R., Coll. Czechoslov. Chem. Commun. 2, 112 (1933).
(2) Willis, J. P., Friend, J. A., and Mellor, D. P., J. Am. Chem. Soc., 67, 1680 (1945).
-

first paper on the subject from this laboratory.³

-
- (3) Laitinen, H. A., Bailar, J. C., Jr., Holtzclaw, H. F., and Quagliano, J. V., J. Am. Chem. Soc., 70, 2999 (1948).
-

The product of the first step of reduction has been regarded as being the aquated cobalt (II) ion.^{3,3} The present investigation was undertaken to determine the effect of various substances which form complexes with cobalt (II), in the hope of gaining further insight into the mechanism of electroreduction of the hexamminecobalt (III) ion.

Experimental

Materials.--Hexamminecobalt (III) chloride was prepared according to Bjerrum and Reynolds⁴ and was recrystallized twice from alcohol

-
- (4) Bjerrum, J., and McReynolds, J. P., "Inorganic Synthesis", McGraw-Hill Book Co., Inc., New York, N.Y., 1946, Vol. II, p. 216.
-

and hydrochloric acid. The salt was dried at 90°C . for 8 hours.

Apparatus.--Current-voltage curves were determined with a Leeds and Northrup Type E Electro-Chemograph, except for one series of experiments (Table 2) in which a Sargent Polarograph, Model XXI, using 0.5 v. span was employed. To avoid traces of agar an H-cell having a 20 mm. fine sintered glass plug separating the two compartments was used. The solution for analysis was placed in both compartments so that the liquid level was about 1 cm. higher in the cathode compartment than in the anode compartment. The reference electrode was a saturated calomel electrode connected to the anode compartment by means of a salt bridge containing saturated potassium chloride solution. The A.C. resistance of this type of cell was 680 ohms (minimal value at instant of drop fall), using 0.1 N potassium chloride solution with the dropping mercury electrode as one electrode and the saturated calomel electrode as the other electrode. Oxygen was removed from the solutions with oxygen-free nitrogen. The cell and the reference electrode were kept in a water thermostat having a temperature of $25 \pm 0.1^{\circ}\text{C}$. Two dropping mercury electrodes were used:

Electrode I, $m = 1.746 \text{ mg./sec.}$, $t = 4.68 \text{ sec.}$; Electrode II, $m = 1.538 \text{ mg./sec.}$, $t = 4.72 \text{ sec.}$ (open circuit) using a mercury column height of 60.0 cm.

For some experiments a rotating platinum electrode was used. The electrode was rotated with a small induction motor at about 500 r.p.m. The microelectrode, which was 1.5 mm. long and 0.2 mm. in diameter, protruded at an angle of 45 degrees from the

side of a piece of glass tubing. The distance between the tip of the electrode and rotation center was 5 mm. The rotating electrode was inserted in the H-cell, described above, through which nitrogen was bubbled continuously during the experiment. The cell was covered with a round rotating rubber disc, which was fastened to the electrode shaft through a hole in its center and which rotated barely above the edge of the cell.

Results and Discussion

The Effect of Ammonia Concentration

In 1941 Bjerrum⁵ showed by potentiometric titration that

-
- (5) Bjerrum, J., "Metal Ammine Formation in Aqueous Solution" P. Haase and Son, Copenhagen, Denmark (1941), p. 250.
-

the oxidation-reduction reaction of the hexamminecobalt (III, II) system is reversible. The titrations were made in media where the divalent hexamminecobalt complex is stable, i.e., in solutions containing ammonium salt and an excess of the complexing agent. In a 2 M ammonium nitrate solution the standard potential at 30°C. for this couple appeared to be -0.211 v.,⁶ vs. the saturated

-
- (6) V. M. Latimer has calculated the standard potential of the couple to be +0.1 v. vs. hydrogen electrode, which is about -0.14 v. vs. S.C.E. using the polarographic sign convention. "Oxidation Potentials" second Ed., Prentice Hall, Inc., New York, N.Y. (1952), p. 214.
-

calomel electrode (S.C.E.). Curve 1 in Figure 1 represents the oxidation-reduction potential for the system in question as a function of the activity of ammonia as obtained by Bjerrum. The standard potential for the system is represented by the straight line of -0.211 v. vs. S.C.E. and is obtained by the relationship

$$1) \quad E^{\circ} = E_{\text{redox}} + 0.0601 \log \alpha_s \quad (30^{\circ})$$

where α_s , the fraction of the total divalent cobalt being in the hexammine form, is a function of the activity of ammonia.

The polarographic reduction of hexaminecobalt (III) ion to the divalent form appears to proceed irreversibly in most media. Table 1 gives half-wave potentials and reciprocal slopes of the plots of E vs. $\log (i_d - i)/i$ obtained with non-complexing supporting electrolytes. Table 2 shows the results of a study of this reduction in the presence of various concentrations of ammonia. In order to be able to compare the results with Bjerrum's, the supporting electrolyte used was 2 M ammonium nitrate. The activity of ammonia was calculated on the basis of Bjerrum's experiments, which were run at 22-23°C. The temperature in the present experiment was 25°C., but the error due to the temperature difference is considered negligible. The α_s values were calculated for 25°C., and the corrected half-wave potentials were calculated by an equation similar to equation (1) but using the slope 0.0591 corresponding to 25°C. As can be seen, the half-wave potential becomes more negative with increasing ammonia concentration. The reciprocal slopes of the logarithmic plots seem to be

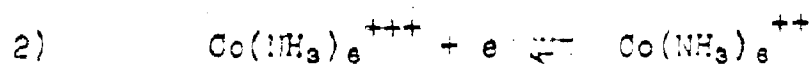
closer to the reversible values. Curves 2 and 3 in Figure 1 represent the plot of the half-wave potential and the corrected

Table I

<u>Cone. M</u>	<u>Supporting Electrolyte</u>	<u>E_{1/2}, v. versus S.C.E.</u>	<u>Reciprocal Slope of Log Plot</u>
1.0	NaNO ₃	-0.245	0.090
1.0	HNO ₃	-0.280	0.076
0.2	Ba(NO ₃) ₂	-0.246	0.086
0.1	NaClO ₄	-0.245	0.105
1.0	NaCl	-0.200	0.105
1.0	HCl	-0.216	0.116

half-wave potential, respectively, vs. the negative logarithm of the ammonia activity. A plausible explanation of the results of these experiments seems to be as follows:

The primary step in the reduction of hexamminecobalt (III) ion is the electrode transfer giving the divalent complex



Consider the expression

$$3) \quad E_{d.e.} = E^\circ = \frac{RT}{nF} \ln \frac{a^\circ \text{Co}(\text{NH}_3)_6^{++}}{a^\circ \text{Co}(\text{NH}_3)_6^{+++}}$$

where a° refers to activities at the surface of the dropping electrode and E° is the standard potential of reaction 2.

Assuming the activity coefficients and diffusion coefficients of the two forms to be equal, E^0 is identical with the corrected half-wave potential. Realizing that the concentration of the divalent hexamine complex at the half-wave potential is not equal to half of the bulk concentration of trivalent complex, but a fraction, α_2 , of the total divalent cobalt produced by the reduction, one can see from equation 3, that the half wave potential should become more negative with increasing hexaminecobalt (II) concentration. At low concentrations of ammonia, where only a small fraction of the total divalent cobalt is stable in the hexamine form, the kinetics of the decomposition of the hexaminecobalt (II) ion affects the potential. Curve 3 in Figure 1 shows this effect. Instead of being constant, the corrected half-wave potential becomes more negative with decreasing ammonia concentration thus indicating that the concentration of hexaminecobalt (II) ion is higher than predicted, i.e., the time has not been long enough to attain equilibrium between the different divalent cobalt amines.

From Figure 1 it can be seen that the polarographic reduction proceeds with an overpotential of about 0.1 v. Part of this may be due to the temperature difference (Bjerrum's potentials obtained at 30°C.) and the difference in the diffusion coefficients of the trivalent and the divalent forms of the complex, but the main part must be due to the slowness of the reaction. It was also found that, in accordance with Bjerrum's results, the half-wave potential became more positive with decreasing ammonium ion

concentration. For example, in 7.1 M ammonia the half-wave potentials in 2, 1 and 0.5 M ammonium nitrate were -0.291, -0.275, and -0.271 v. vs. S.C.E. respectively. The postulation that the reduction of hexamminecobalt (III) ion consists of the electron transfer to form the divalent hexammine cobalt ion, which in turn

Table 2

$[NH_3]$	$pa[NH_3]^*$	α_s^*	$E_{1/2}$ v. vs. S.C.E.	$0.059 \log \alpha_s$	$E_{1/2}$ Corr.	Reciprocal Slope of log. plot
0.71	+0.148	0.081	-0.2702	-0.0645	-0.3347	0.073
1.42	-0.185	0.212	-0.2754	-0.0397	-0.3151	0.072
2.13	-0.385	0.330	-0.2785	-0.0284	-0.3069	0.074
3.55	-0.655	0.503	-0.2812	-0.0175	-0.2987	0.073
5.69	-0.95	0.684	-0.2842	-0.0098	-0.2940	0.075
7.11	-1.11	0.760	-0.2912	-0.0071	-0.2982	0.075
9.25	-1.34	0.847	-0.2985	-0.0043	-0.3028	0.077
11.10	-1.53	0.90	-0.3040	-0.0027	-0.3067	0.078

* The activity of ammonia calculated on the basis of Bjerrum's data⁶ as well as the value of α_s which is the fraction of the total Co(II) being in hexamminecobalt (II) form.

decomposes more or less depending upon the medium, is supported by some recent radioactive tracer investigations on the rate of electron exchange between complex ions by Koshowsky, Holmes and McCallum⁷ as well as by Lewis, Coryell and Irvine.⁸ These authors

-
- (7) Hoshowsky, S. A., Holmes, O. G., and McCallum, K. J., Can. J. Research, 27B, 258-265 (1949).
(8) Lewis, W., Coryell, C. D., and Irvine, J. W., Jr., J. Chem. Soc. (Suppl. Issue, No. 2), S386-92 (1949).
-

reported a noticeable but slow rate of exchange of electron between hexamminecobalt (III) and hexamminecobalt (II), thus indicating a certain degree of reversibility. It is of interest to note that the trisethylenediamine cobalt (III, II) couple which has a much higher rate of electron exchange than the hexammine system, was shown by Bjerrum⁵ to be reversible. Nowever, both of the above mentioned systems have very slow rates of exchange compared to the rates of such reversible systems as Ce(IV, III) and MnO_4^- , MnO_4^{2-} . In this laboratory, M. W. Grieb (unpublished investigations) has studied the polarographic reduction of the trisethylenediamine couple and found that the half-wave potential is nearly identical with Bjerrum's redox potential for this system and that the reduction proceeds reversibly.

The electron exchange and thus the reversibility of both hexammine and trisethylenediamine system is, however, difficult to understand from the following point of view. Libby⁹ has postu-

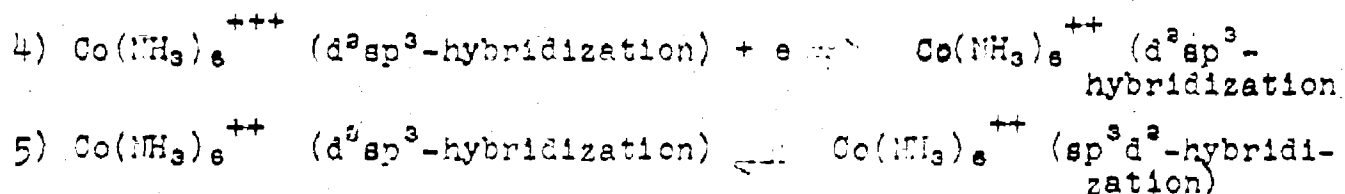
-
- (9) Libby, W. F., Preprints of Papers Symposium Electron Transfer and Isotopic Reactions, J. Phys. Chem., 56, 39 (Oct. 1952).
-

lated that electron exchange occurs only between symmetrical complexes. In the case of the cobalt complexes, the trivalent forms,

as is well known, have covalent bonds (d^2sp^3 -hybridization) and are distinctively inert (Taube's¹⁰ terminology) and the divalent

(10) Taube, H., Chem. Revs., 50, 69 (1952).

forma are labile, having ionic bonds (sp^3d^2 -hybridization). The electron configuration is too different to allow a reversible electron transfer. In order to satisfy Libby's symmetry principle, the following mechanism may be postulated for the hexamine cobalt couple:



Equation 4 would represent the reversible step and equation 5 the irreversible step involving an activation energy.

Alternating current polarography using a technique similar to that described by Müller, Garman, Droz and Petra¹¹ and by

(11) Müller, R. H., Garman, R. L., Droz, M. E., and Petra, J., Ind. Eng. Chem., Anal. Ed., 10, 339 (1938).

Breyer and Guttman¹² was employed in order to investigate the

(12) Breyer, B. and Guttman, F., Faraday Soc. Discussion, 1, 19 (1947).

reversibility of certain electrode reactions (unpublished investigations). In a solution containing 1 M sodium nitrate and 3 millimolar hexamminecobalt (III) and using a 60 cycle a.c. with a voltage amplitude of 50-100 mv. it was found that oxidation of the hexamminecobalt (II) complex formed during reduction actually takes place during the second half of the a.c. cycle, thus indicating a certain degree of reversibility.

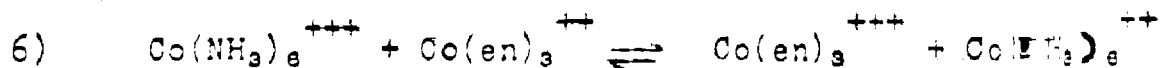
The oxidation of hexamminecobalt (II) ion was studied by using the rotating platinum electrode. Figure 2 shows current voltage curves obtained in 12.7 M ammonia and 1 M ammonium nitrate. The reduction of hexamminecobalt (III) ion gives a well defined diffusion current. $E_{1/2}$ is about -0.47 v. vs. S.C.E. However, by reversing the polarization from an increasing cathodic to decreasingly cathodic, the $E_{1/2}$ has changed to -0.36 v. vs. S.C.E. The hysteresis effect can be explained by the fact that with increasingly negative polarization the concentration of the hexamminecobalt (II) complex produced actually will stay higher than the equilibrium concentration and thus shifts the wave to more negative potential. When the polarization is decreasingly negative equilibrium conditions should be more closely approached. The oxidation experiments were conducted in the following manner: The supporting electrolyte containing the ammonia was first deaerated and then a few drops of a 2 M cobalt sulfate solution were added, preventing thus any air oxidation of the divalent ammine complex. In Figure 2, a few current voltage curves of the oxidation of divalent complex are presented. At this ammonia

activity about 90% of the total divalent cobalt present is in the hexammine form. The results are somewhat surprising. The half-wave potential seems to be roughly right (-0.260 v. - vs. S.C.E.) regardless whether the polarization is increasingly or decreasingly cathodic. The current is, however, only of the order of 1 percent of the expected value. The limiting current is not proportional to concentration but seems to become independent of it. This is shown in Figure 3. It might be mentioned that, as expected, the oxidation current decreases with decreasing ammonia concentration.

The results indicate that the oxidation proceeds very slowly and that probably the surface area of the electrode is one of the rate determining factors, approaching a zero-order of reaction with increasing concentration. A plausible mechanism for the slow rate would be represented by equation 5 and 4 reversed. Why the current is higher using decreasingly negative polarization than with the opposite polarization cannot be explained.

Reduction in Ethylenediamine

Lewis et al.⁸ in their studies on the rates of electron exchange, found a remarkably fast rate for the reaction

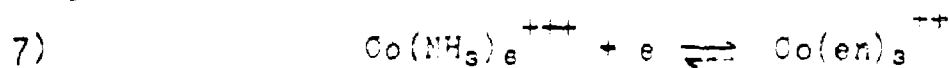


It was of interest to try the polarographic reduction of hexammine-cobalt (III) ion in the presence of ethylenediamine

It was first ascertained that the hexammine ion was stable in 0.1 M ethylenediamine. A millimolar solution of hexammine-

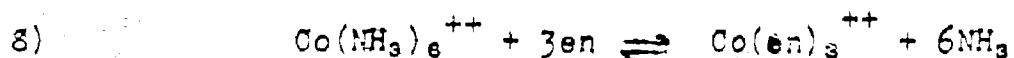
cobalt (III) chloride stood for 48 hours in 0.1 M ethylenediamine. The amine was then neutralized with acid and a polarogram recorded, showing that the original ion still was present. A different type of experiment led to the same conclusion: A 0.08 M ethylenediamine solution containing 0.012 M of the hexamminecobalt (III) chloride was allowed to stand for 48 hours. The hexamminecobalt (III) chloride was then precipitated using concentrated hydrochloric acid and alcohol. The dried product dissolved in water gave the same polarograms as the original material.

Figure 4 shows a family of polarograms obtain in a supporting electrolyte containing 0.1 M potassium nitrate and 0.1 M ethylenediamine. The reduction of the hexamminecobalt (III) ion proceeds apparently reversibly, the reciprocal slope of the logarithmic plot having a value of 0.064. The half-wave potential for this reduction was -0.465 v. vs. S.C.E. W. N. Grieb (unpublished investigations) has determined the half-wave potential for the reduction of trisethylenediaminecobalt (III) ion to be -0.451 v. vs. S.C.E. in this medium. Curve 2 in Figure 4 was obtained by having both hexamminecobalt (III) and trisethylenediaminecobalt (II) in solution and curve 3 represents the oxidation of the latter only. The procedure of forming the divalent complex in solution was the same as described above in connection with the oxidation of hexamminecobalt (II) complex. As can be seen, the couple



apparently represents a reversible system.

It is, however, clear that the hexamminecobalt (III) ion is reduced at the usual potential of about -0.250 v. vs. S.C.E. and the product, the divalent hexamine complex, being a labile complex¹⁰ which will rapidly come into equilibrium with the complexing agent in the solution:



Because of the excess of ethylenediamine and the relative stability of the complexes, the equilibrium is shifted to the right. As long as the potential is more positive than required for the reduction of trisethylenediaminecobalt (III), an oxidation of the divalent ethylenediamine complex occurs, thus resulting in a net current equal to zero. When the potential of the electrode is made increasingly negative, the oxidation will cease, with the half-wave potential equal to that of the trisethylenediamine system, and with the reversible slope, thus giving the impression that the system represented by Equation 7 is a reversible one.

Reduction in High Chloride Concentration

Brdicka¹³ found in 1930 that the reduction of the blue

(13) Brdicka, R., Coll. Czechoslov. Chem. Commun., 2, 489, 545 (1930).

chlorocomplex of divalent cobalt is more nearly reversible and occurs at 0.4 v. more positive potential than the reduction of the hexaaquo ion. The polarogram of hexamminecobalt (III) in 5 M

calcium chloride solution is shown in Figure 5, Curve 1. The first wave is drawn out, but $E_{1/2}$ is roughly normal at -0.260 v. vs. S.C.E. The second wave, the reduction of the divalent cobalt to metal, has a half-wave potential of -0.876 v. vs. S.C.E. and a logarithmic reciprocal slope of about 0.060 . Curve 2 represents the reduction of the divalent chloro complex of cobalt. $E_{1/2}$ is -0.822 v. vs. S.C.E. and the reciprocal slope of 0.042 . From the large shift of the second reduction wave of hexamminecobalt (III) it is obvious that a chlorocomplex of cobalt (II) must be formed by a rapid exchange of ligands by the hexamminecobalt (II) ion. Since the second wave of cobalt (III) is not identical in potential or shape with the cobalt (II) wave it is probable that the species involved in the two cases are not identical, i.e., that the exchange is not complete.

Reduction in High Hydroxide Concentration

Although it has been long known that cobalt (II) hydroxide will dissolve in concentrated alkali solution to form a blue solution,¹⁴ very little is known about the actual species formed.

(14) Gmelin, "Handbuch der Anorganischen Chemie", Verlag Chemie B.H.B.H., Berlin, 1932 (8th Ed.), Vol. 58, Teil A, p. 208.

Scholder¹⁵ reports preparing well crystallized compounds like

(15) Scholder, R., Z. angew. Chem. 46, 509 (1933).

$\text{Ba}_2[\text{Co}(\text{OH})_6]$ and $\text{Na}_2[\text{Co}(\text{OH})_4]$. More recently Gordon and Schreyer¹⁶

(16) Gordon, S., and Schreyer, J.M., J. Am. Chem. Soc., 74, 3169 (1952).

have studied spectrophotometrically the species of cobalt (II) in strongly alkaline solutions and report results indicating that a blue trihydroxocobalt (II) exists in solutions containing 3 to 12 M potassium hydroxide.

Some experiments were carried out in order to find out whether the blue complex of cobalt (II) is reducible at the dropping mercury electrode. The supporting electrolyte (10 M sodium hydroxide) deaerated and then a few drops of a 2 M cobaltous sulfate solution were added to it. A pink to blue precipitate was at first formed, but after 15 minutes stirring (nitrogen bubbling) a deep blue solution was obtained, containing about 2 millimolar of cobalt (II) as the hydro complex. Most of the precipitated cobaltous hydroxide remained undissolved. The reduction proceeded irreversibly, the half-wave potential being -1.54 v. vs. S.C.E.

The reduction of the hexaminecobalt (III) complex in 10 M sodium hydroxide was also studied. The first step comes at around -0.35 v. vs. S.C.E. and the second step has a half-wave potential of -1.54 v. vs. S.C.E. It seems obvious that the mechanism is similar to that described in the case of the chloro complex.

Whether the exchange here is complete or not cannot be said on the basis of this experiment.

Figure 1

- Curve 1: Oxidation-reduction potential for hexamminecobalt (III, II) couple acc. to J. Bjerrum obtained at 30°C. in 2 M ammonium nitrate.
- Curve 2: $E_{1/2}$ for the same couple at 25°C. in 2 M ammonium nitrate.
- Curve 3: $E_{1/2}$ corrected for α_s .

Figure 2

Polarograms obtained with the rotating platinum electrode in 1 M ammonium nitrate and 12.7 M ammonia.

Curve 0, residual current; Curves 1 and 1a, 1 millimolar hexamminecobalt (III); Curve 2, ca. 2 millimolar; Curves 3 and 3a, ca 3 millimolar; Curve 4, ca. 4 millimolar Co(II) total.

The arrow shows the direction of polarization.

The sensitivity setting, when recording the anodic currents, was ten times higher than when recording the cathodic currents.

Figure 3

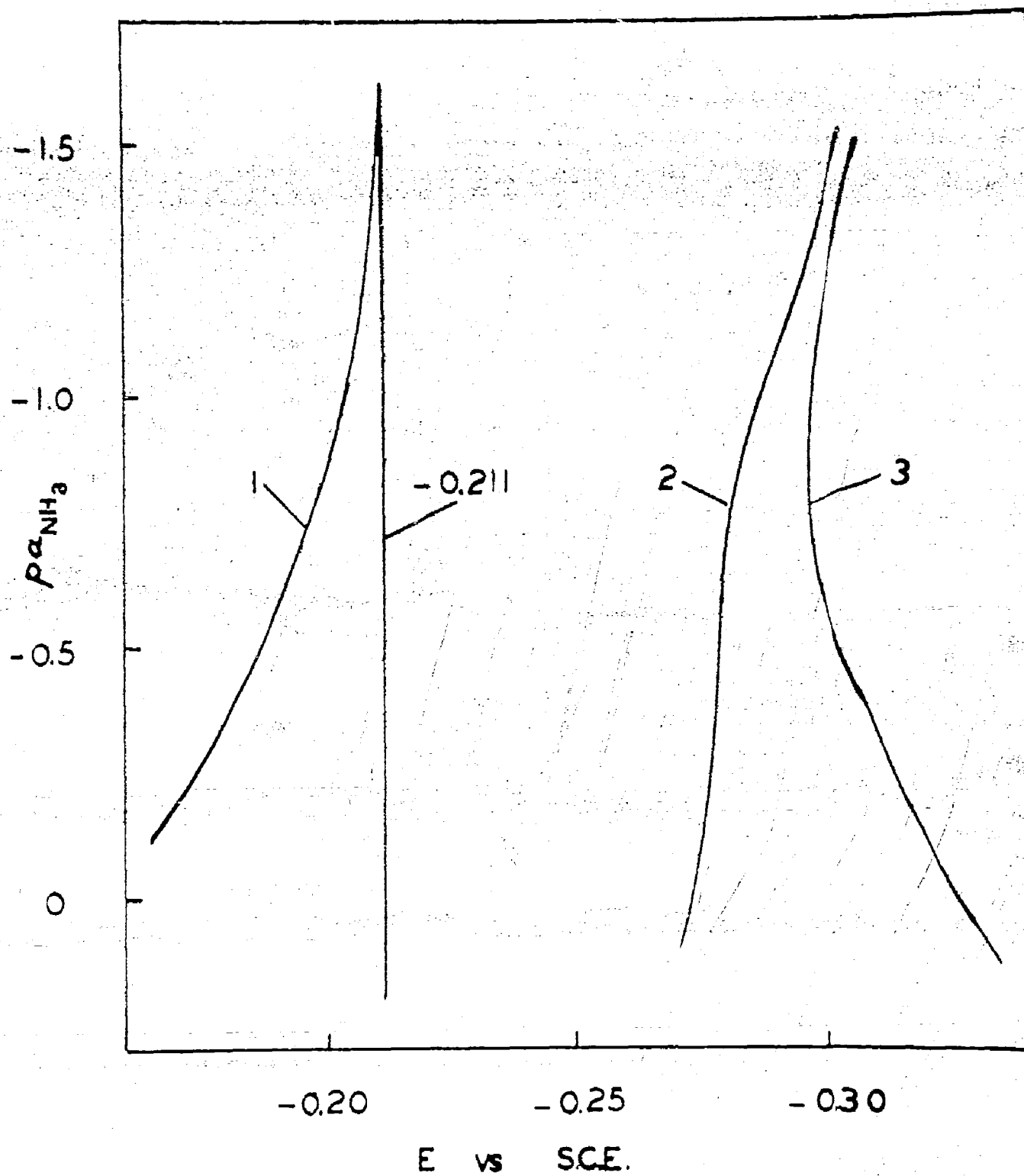
The diffusion current of the oxidation of hexamminecobalt (II) plotted against the concentration of the total divalent cobalt. Supporting electrolyte 12.7 M ammonia and 1 M ammonium nitrate. The polarization was increasingly negative.

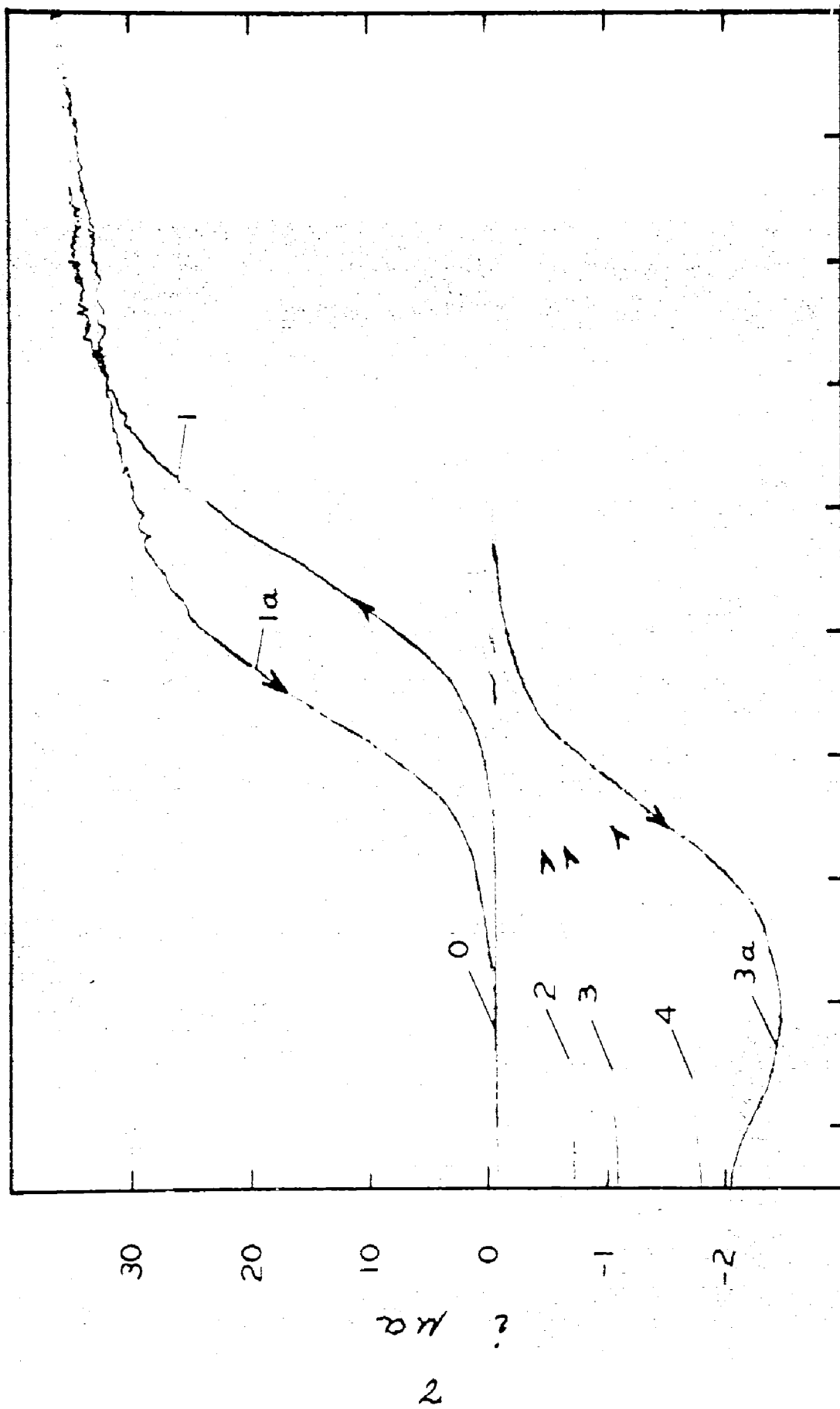
Figure 4

Polarograms obtained in 0.1 M potassium nitrate containing 0.1 M ethylenediamine, Electrode II, damping 1. Curve 1, 1 millimolar hexamminecobalt (III); Curve 2, ca. 0.55 millimolar hexamminecobalt (III) and ca. 0.44 millimolar trisethylenediaminecobalt (II); Curve 3, ca. 1 millimolar trisethylenediaminecobalt (II).

Figure 5

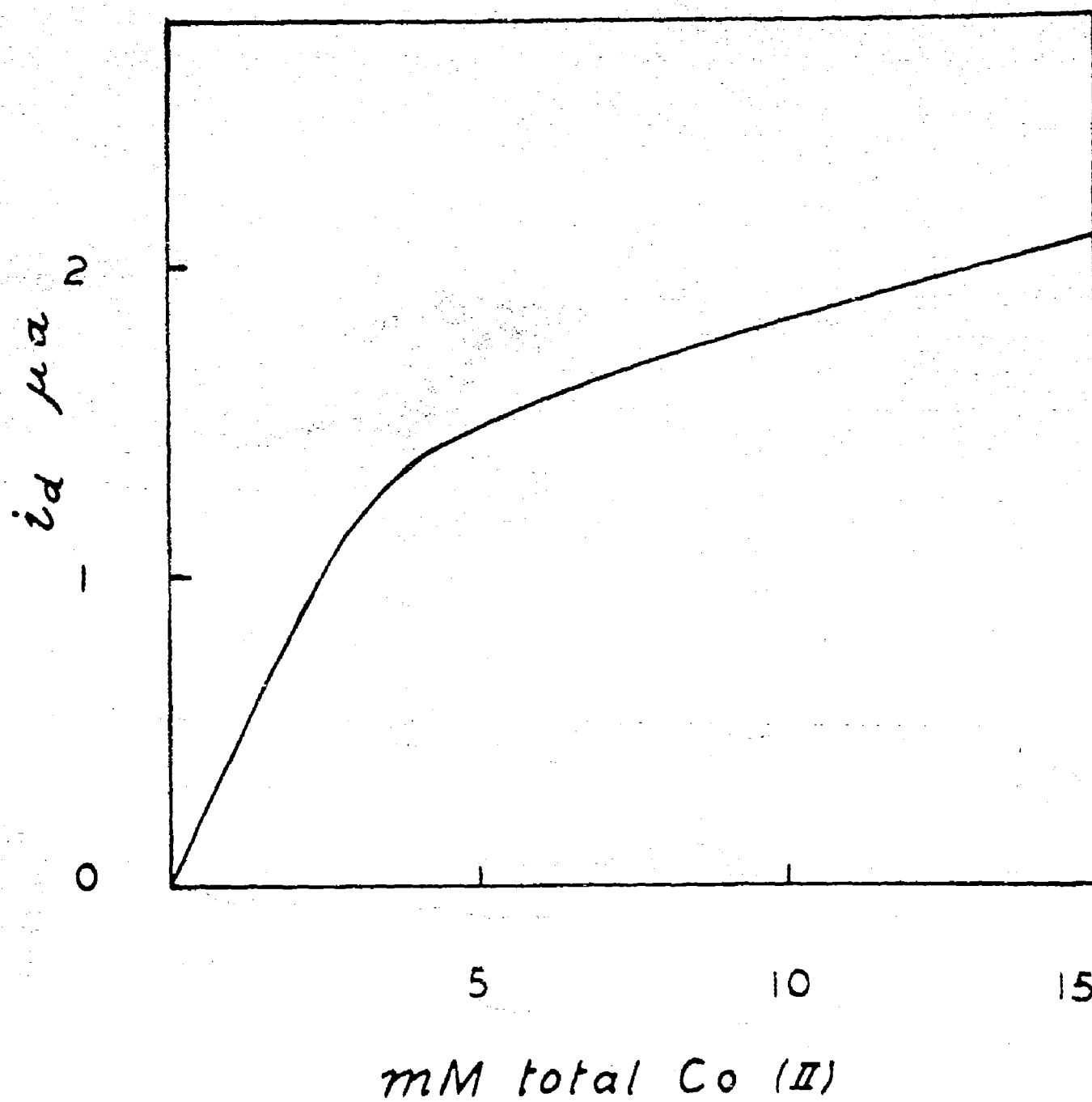
Polarograms obtained in 10 N calcium chloride, Electrode II, damping 1. Curve 1, 1 millimolar hexamminecobalt (III); Curve 2, 1 millimolar cobalt (II).

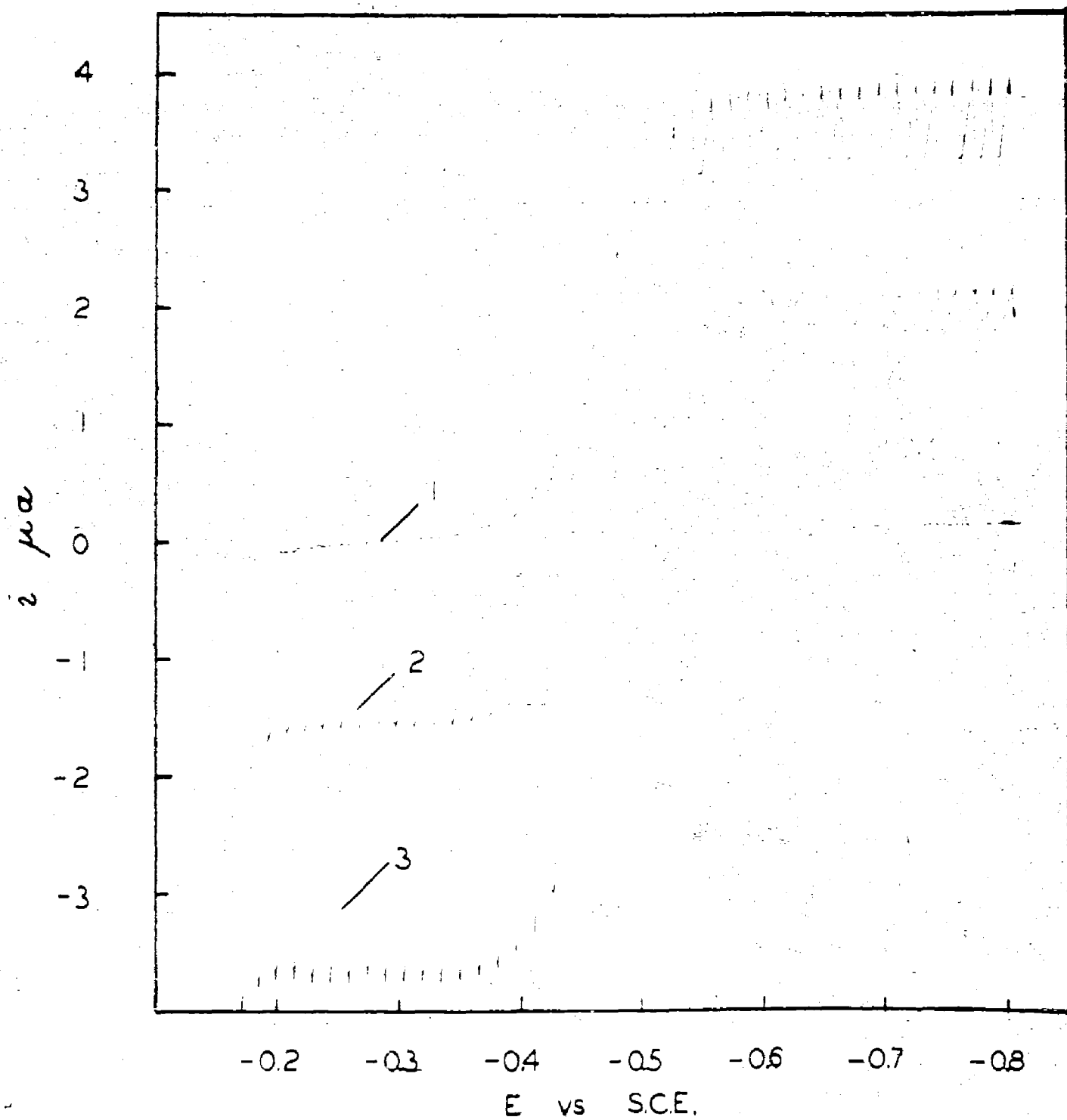


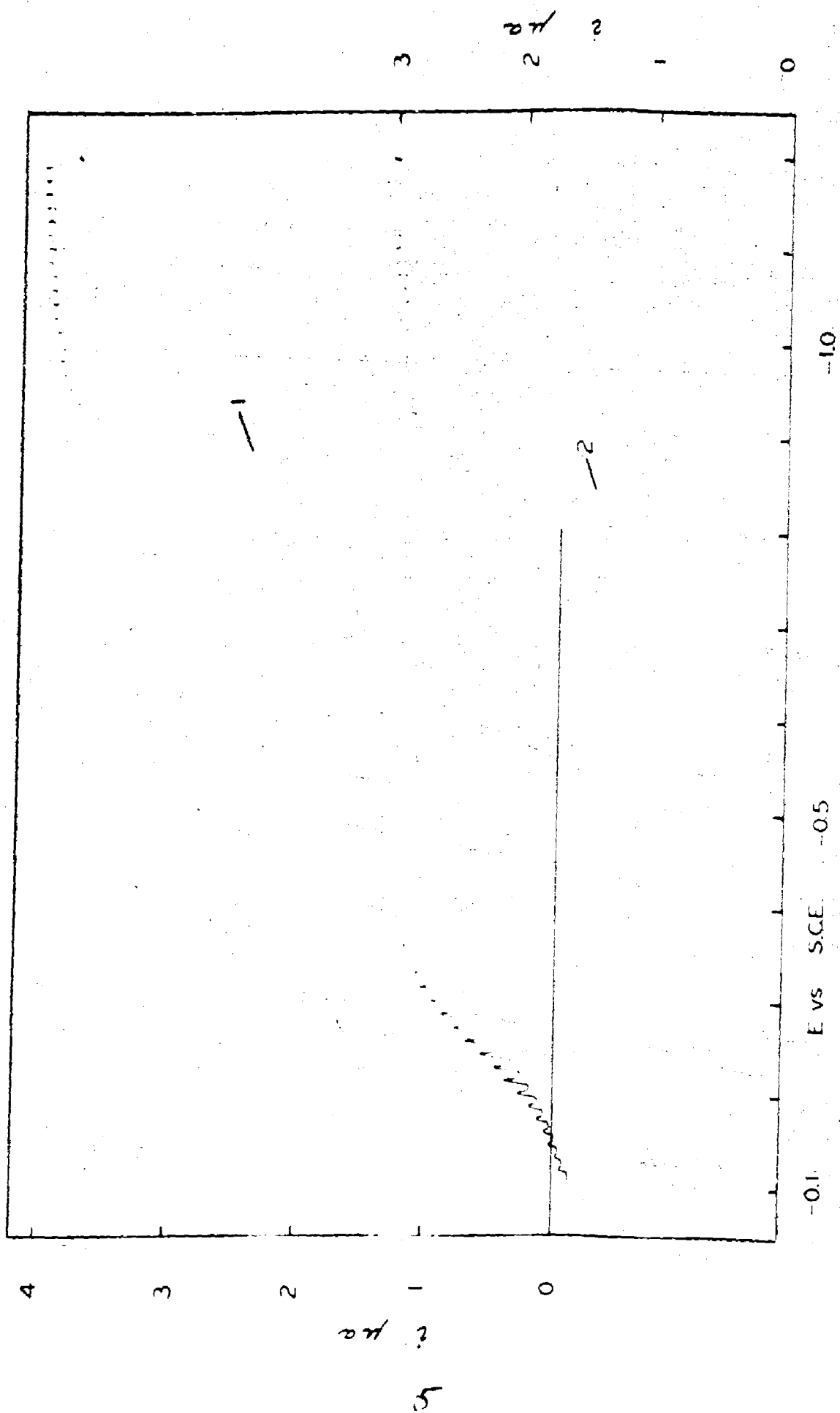


0 -0.1 -0.2 -0.3 -0.4 -0.5 -0.6 -0.7 -0.8

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