BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1901—1908 (1969)

Polarographic Reduction of Cobalt(II) in Acetonitrile in the Presence of Acetate Ions

Eiki ITABASHI and Shigero IKEDA

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka

(Received October 28, 1968)

The effect of the nature and the concentration of the supporting electrolyte on the polarographic reduction of cobalt(II) acetate in acetonitrile has been investigated. An acetonitrile solution of cobalt(II) acetate yields a two-step and a three-step reduction wave in 0.05M $LiClO_4$ and in 0.05M $NaClO_4$ solution, respectively. The same solution gives ill-defined reduction waves in the presence of quaternary ammonium perchlorates, such as $(CH_3)_4NClO_4$, $(C_2H_5)_4NClO_4$, or $(n\text{-}C_4H_9)_4NClO_4$. The $Co(CH_3CN)_n^{2+}$, $Co(OAc)^+$, and $Co(OAc)_3^-$ species are present in a solution containing alkali metal perchlorate electrolyte. $Co(OAc)^+$ and $Co(OAc)_3^-$ are the predominant species in a quaternary ammonium perchlorate solution. The reduction potential becomes more negative with increase in the number of acetate ions coordinated to cobalt(II). The reduction potential of cobalt(II) acetate becomes less negative upon the addition of alkali metal perchlorate to the quaternary ammonium perchlorate supporting electrolyte. This effect is caused by the dissociation reaction of cobalt(II) acetate, in which an acetate ligand is transferred to the alkali metal ion.

The supporting electrolyte effects on the nonaqueous inorganic polarography have been reported by several investigators, especially Murray and Hiller,[1] who have done extensive work on the polarography of a number of metal acetylacetonates in acetonitrile and have found that the reduction potentials were shifted to less negative potentials by the addition of lithium perchlorate to the tetraethylammonium perchlorate supporting electrolyte. They concluded that this effect was due to the chemical reaction of the electrode reduction product, in which an acetylacetonate ligand was transferred to the lithium ion.

The present authors have previously reported on the supporting electrolyte effects on the polarographic reduction of nickel(II) in acetonitrile containing small amounts of glacial acetic acid.[2] The reduction potentials of nickel(II) acetate become less negative and the limiting current decreases with an increase in the radius of the cation of the supporting electrolyte. These effects have been explained by taking into consideration of the dissociation reaction of nickel(II) acetate. Nickel(II) acetate is dissociated into $Ni(CH_3CN)_n^{2+}$ or $Ni(OAc)^+$ by the addition of a supporting electrolyte.

Such a dissociation reaction upon the addition of a supporting electrolyte may also be expected in other acetato metal complexes.

The present paper is concerned with the supporting electrolyte effect on the polarographic behavior of cobalt(II) acetate in acetonitrile.

Experimental

Reagents. Acetonitrile and glacial acetic acid were purified by procedures which have been described previously.[2] Hexaaquocobalt(II) perchlorate, $Co(H_2O)_6(ClO_4)_2$, was prepared and recrystallized by the procedure given in the literature.[3] The analysis of $Co(H_2O)_6(ClO_4)_2$ gave the following results: Found: Co, 17.2±1.8; ClO_4, 52.6±1.3%. Calcd for $Co(H_2O)_6(ClO_4)_2$: Co, 16.11; ClO_4, 54.36%. A guaranteed reagent cobalt(II) acetate, $Co(CH_3COO)_2\cdot 4H_2O$, was recrystallized from an aqueous solution containing 5M acetic acid. The analysis of the salt gave the following results: Found: Co, 22.0±1.0; C, 19.21; H, 5.83%. Calcd for $Co(CH_3COO)_2\cdot 4H_2O$: Co, 23.66; C, 19.29; H, 5.67%.

A tetra-*n*-butylammonium acetate, $n\text{-}Bu_4NOAc$, was prepared by neutralizing an alcoholic solution of tetra-*n*-butylammonium hydroxide with acetic acid, after which the salt was recrystallized from benzene. The analysis of the salt gave the following results: Found: C, 71.48; H, 13.63; N, 4.48%. Calcd for $(n\text{-}C_4H_9)_4NCH_3COO$: C, 71.71; H, 13.03: N, 4.65%.

A dried tetramethylammonium perchlorate (Me_4NClO_4), tetraethylammonium perchlorate (Et_4NClO_4) and tetra-*n*-butylammonium perchlorate ($n\text{-}Bu_4NClO_4$) were prepared by the same procedure as has been described previously.[2] The water content of the polarographic solution containing supporting electrolyte and the depolarizer was determined by Karl Fisher titration to be *ca.* 20 mM.

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[1] R. W. Murray and L. K. Hiller, Jr., *Anal. Chem.*, **39**, 1221 (1967).

[2] S. Ikeda and E. Itabashi, This Bulletin, **41**, 1844 (1968).

[3] N. A. Matwiyoff and S. V. Hooker, *Inorg. Chem.*, **6**, 1127 (1967).

Procedures. The polarograms and current-time (*i-t*) curves of an individual drop at the constant potential were recorded with the circuit which has previously been described.[2]

The alternating current (*a. c.*) polarograms were recorded with a Yanagimoto PA-102 polarograph.

The dropping mercury electrode had an *m* value of 1.33_4 mg/sec and a drop time of 4.98 sec in a deaerated 0.1 M sodium perchlorate acetonitrile solution at −0.80 V *vs.* SCE and at a mercury height of 60 cm.

The potential of the DME was measured against a saturated calomel electrode (SCE).

The cell equipment was the same as has been reported on previously.[2] The dissolved oxygen in the solution was removed by bubbling pure nitrogen gas through the solution. Measurements were made at 25±0.1°C. In the following section, "current" (denoted *i* in the figures) means the maximum current observed just before the mercury drops.

Results

Cobalt(II) acetate $Co(OAc)_2 \cdot 4H_2O$ does not dissolve in an acetonitrile solvent alone, but it dissolves easily in the same solvent containing small amounts of glacial acetic acid.[*1] Typical polarograms for an acetonitrile solution of cobalt(II) acetate containing 0.4% glacial acetic acid and various supporting electrolytes are given in Fig. 1.

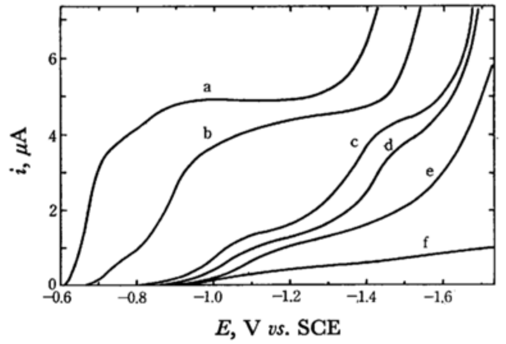

Fig. 1. Effect of supporting electrolyte on the polarograms of Co (II).

$[Co(OAc)_2 \cdot 4H_2O]$=0.5 mM, [HOAc]=0.4%

(a) 0.05M $LiClO_4$; (b) 0.05M $NaClO_4$;
(c) 0.05M Me_4NClO_4; (d) 0.05M Et_4NClO_4;
(e) 0.05M $n\text{-}Bu_4NClO_4$; (f) no electrolyte

The polarographic data on cobalt(II) acetate in various supporting electrolyte solutions are summarized in Table 1. An acetonitrile solution of cobalt(II) perchlorate in the same solvent containing 0.4% glacial acetic acid gives a reversible reduction wave, as is shown in Table 2. The polarographic behavior of cobalt(II) perchlorate in acetonitrile has been studied by several investigators. Their results are also listed in Table 2.

TABLE 1. SUMMARY OF POLAROGRAPHIC DATA OF $Co(OAc)_2 \cdot 4H_2O$ IN 0.05M PERCHLORATE SOLUTIONS CONTAINING 0.4% GLACIAL ACETIC ACID

Elecctrolyte	Co(II) mM	$E_{1/2}$ V *vs.* SCE	*x* value[a]	$E_{a.c.}$ V *vs.* SCE
$LiClO_4$	0.5	−0.66[c]	0.25	−0.75
		−0.80[d]	0.18	−0.88
$NaClO_4$	0.5	−0.72[c]	0.39	−0.76
		−0.88[d]	0.24	−0.97
		−1.15[e]	0.17	−1.26
Me_4NClO_4	0.2	−1.01[c]	0.45	−1.03
		−1.35[d]	0.67	—
Et_4NClO_4	0.2	−1.04[c]	0.44	−1.09
		−1.42[d]	0.71	—
$n\text{-}Bu_4NClO_4$	0.2	−1.08[c]	0.48	−1.15
	0.5	−1.10[c]	0.41	−1.15

a) The slope of the plot of log *i vs.* log *t* for the *i-t* curve at the potential region giving the limiting current.
b) The peak potential of a.c. polarogram, which is not corrected for the ohmic drop across the electrolysis cell.
c) 1st reduction step.
d) 2nd reduction step.
e) 3rd reduction step.

TABLE 2. SUMMARY OF POLAROGRAPHIC DATA OF COBALT(II) PERCHLORATE IN ACETONITRILE

Electrolyte	$E_{1/2}$ V *vs.* SCE	Reciprocal slope of log-plot mV	$E_{a.c.}$ V *vs.* SCE
0.05M $LiClO_4$[a]	-0.63_5	30	−0.75
0.05M $NaClO_4$[a]	-0.64_0	29	−0.76
0.05M Me_4NClO_4[a]	-0.62_0	31	−0.71
0.05M Et_4NClO_4[a]	-0.62_0	30	−0.72
0.05M $n\text{-}Bu_4NClO_4$[a]	-0.61_7	31	−0.70
0.1M $NaClO_4$[b]	−0.65	37	—
0.1M $n\text{-}Bu_4NClO_4$[c]	−0.67	41	—

a) This work. Acetonitrile solution contains 0.4% glacial acetic acid.
b) From Ref. 4
c) From Ref. 5
d) The peak potential of a.c. polarogram, which is not corrected for the ohmic drop across the electrolysis cell.

[*1] When cobalt(II) acetate was dissolved in acetonitrile containing small amounts of glacial acetic acid, cobalt(II) was present in the solution almost as $Co(OAc)_2(HOAc)_n(H_2O)_{4-n}$. The potentiometric titration of an acetonitrile solution of cobalt(II) acetate with anhydrous perchloric acid indicated that two moles of acetato ions are coordinated to cobalt(II), as in the previously-reported case of $Ni(OAc)_2 \cdot 4H_2O$.[2]

4) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 1852 (1957).

5) A. I. Popov and D. H. Geske, *ibid.*, **79**, 2047 (1957).

Alkali Metal Perchlorate Systems. In a 0.05M lithium perchlorate electrolyte solution, cobalt(II) acetate is reduced in two steps.

Cobalt(II) acetate in a 0.05M sodium perchlorate electrolyte solution gives three ill-defined steps.

A. c. polarograms of cobalt(II) acetate in the same solution show three peaks which correspond to the above-mentioned three steps of the d. c. polarograms. The limiting current of the first (at −0.82 V) and the second (at −1.16 V) steps, named from positive to negative potentials, are found to be partially kinetic-controlled, but that of the third step (at −1.30 V) is diffusion-controlled.

The total wave height of the three steps is proportional to the concentration of cobalt(II) acetate up to 2.5 mM. In both lithium and sodium perchlorate electrolyte solutions, the reduction current increases at potentials more negative than −1.35 V and −1.45 V *vs.* SCE, respectively, as is shown in Fig. 1.

The rising potential of the hydrogen ion reduction wave obtained in a 0.05M lithium perchlorate containing 0.4% glacial acetic acid is observed at −1.76 V *vs.* SCE. The reduction potential of hydrogen ion becomes less negative with an increase in the concentration of cobalt(II) acetate. As a result, the increase in the reduction current obtained at potentials more negative than −1.35 V *vs.* SCE may be caused by the catalytic reduction of the hydrogen ion.

Quaternary Ammonium Perchlorate Systems. Cobalt(II) acetate in tetramethyl- and tetraethyl-ammonium perchlorate electrolyte solutions gives a double step in a d.c. polarogram, but an a.c. polarogram shows a single peak, one which corresponds to the first step of a double wave.

The exponent of the *i-t* curve for the first step has a value of 0.45. On the other hand, that for the second step obtained at relatively low concentrations of cobalt(II) acetate has values of 0.67 and 0.71 in 0.05M tetramethyl- and tetraethylammonium perchlorate electrolyte solutions, respectively, as is shown in Table 1. The exponent value of the *i-t* curve of the second step is close to that of 0.67 to be expected for a pure kinetic-controlled electrode mechanism.⁶⁾

The *i-t* curve for the second step obtained at the concentrations of cobalt(II) acetate higher than 0.5 mM, shows an irregular shape (*cf.* Fig. 2).

When the concentrations of cobalt(II) acetate are greater than 1.0 mM, the second step shows a peak current. The residual current in a quaternary ammonium perchlorate electrolyte solution containing 0.4% glacial acetic acid begins to rise at about −1.7 V *vs.* SCE. These findings indicate that the second step in tetramethyl- and tetraethylammonium perchlorate electrolyte solutions does not correspond to the reduction of cobalt(II) acetate, but to the catalytic reduction of hydrogen ion.

The effect of the concentration of glacial acetic acid on the polarograms was investigated. No appreciable change in the reduction wave was observed up to 4% in volume. In the experiments described in the following section, the concentration of glacial acetic acid was maintained at 0.4% in volume unless otherwise stated.

Effect of Mixed Electrolytes. The step-by-step addition of lithium perchlorate to quaternary ammonium perchlorate electrolyte solutions containing cobalt(II) acetate causes the reduction potential to become less negative, a single wave to split into a double wave and the wave height of both waves to increase. Figure 3 shows polarograms of an acetonitrile solutions of cobalt(II) acetate containing various concentrations of lithium perchlorate and tetramethylammonium perchlorate at the ionic strength of 0.05.

Table 3 shows the exponent of *i-t* curve of the limiting current plateau for the double wave observed in the presence of various concentrations of lithium perchlorate. The exponent of the *i-t*

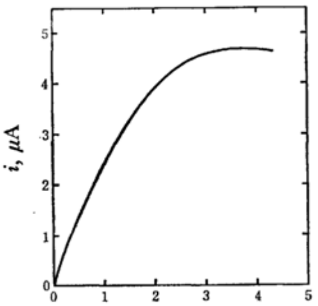

Fig. 2. Current-time curve of 0.5 mM cobalt(II) acetate measured at −1.50 V *vs.* SCE in 0.05M $LiClO_4$ electrolyte solution containing 0.4% glacial acetic acid.

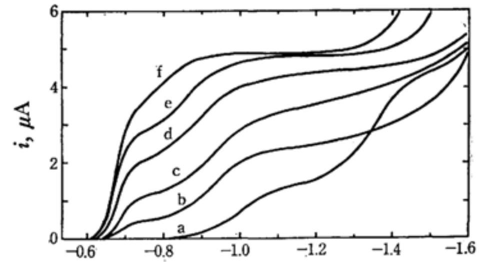

Fig. 3. Effect on concn. of $LiClO_4$ on the polarograms of Co(II) in Me_4NClO_4 solution (μ=0.05). $[Co(OACc)_2 \cdot 4H_2O]$=0.5 mM, [HOAc]=0.4% $[LiClO_4]$: (a) 0; (b) 0.5 mM; (c) 2 mM; (d) 10 mM; (e) 25 mM; (f) 50 mM

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6) P. Delahay, "New Instrumentation in Electrochemistry," Interscience Publishers, New York (1954), pp. 87—144.

TABLE 3. EFFECT OF $LiClO_4$ ON THE EXPONENT OF i-t CURVE FOR THE REDUCTION OF 0.5 mM $Co(OAc)_2 \cdot 4H_2O$ IN Me_4NClO_4 ELECTROLYTE SOLUTION CONTAINING 0.4% GLACIAL ACETIC ACID AT IONIC STRENGTH 0.05

Concn. of $LiClO_4$ mM	x at $i_l = kt^x$	
	1st wave	2nd wave
0	—	0.45
1.0	0.42	0.25
2.0	0.37	0.22
5.0	0.33	0.23
10.0	0.31	0.21
50	0.25	0.18

curve decreases with an increase in the concentration of lithium perchlorate up to about 10 mM.

There is no appreciable change in the wave height and in the exponent of the i-t curve upon the further addition of lithium perchlorate.

Effect of the Concentration of the Supporting Electrolyte. The d.c. and a.c. polarograms for an acetonitrile solution of cobalt(II) acetate in the presence of various concentrations of sodium perchlorate are shown in Figs. 4-a and -b, respectively.

Ill-defined reduction waves change to well-defined waves with increase in the concentration of sodium perchlorate. The a.c. polarogram obtained in 0.05M sodium perchlorate exhibits three peaks. The increase in the concentration of sodium perchlorate causes the height of the first peak to increase and that of the third one to decrease. The height of the peak is almost independent on the concentration of sodium perchlorate up to 0.5M, but the peak disappears upon further increases in the concentrations of the electrolyte. In the 1M sodium perchlorate electrolyte solution, a single peak is observed at the potential of −0.80 V *vs.* SCE.

When lithium perchlorate was employed as the supporting electrolyte, an a.c. polarogram with two peaks was observed at concentrations of lithium perchlorate lower than 0.2M.

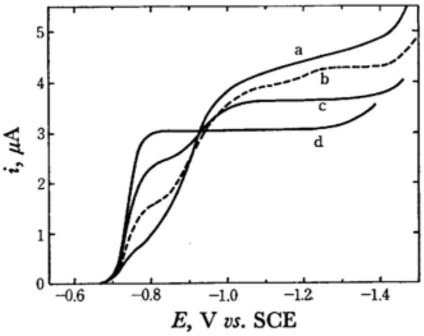

Fig. 4-a. Effect of concn. of $NaClO_4$ on the polarograms of Co(II).
$[Co(OAc)_2 \cdot 4H_2O] = 0.5$ mM, $[HOAc] = 0.4\%$
$[NaClO_4]$: (a) 0.05M; (b) 0.2M; (c) 0.5M; (d) 1.0M

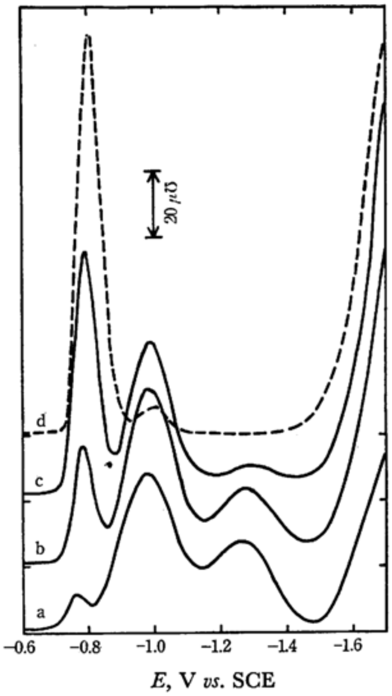

Fig. 4-b. Effect of concn. of $NaClO_4$ on the a. c. polarograms of Co(II).
$[Co(OAc)_2 \cdot 4H_2O] = 0.5$ mM, $[HOAc] = 0.4\%$
$[NaClO_4]$: (a) 0.05M; (b) 0.2M; (c) 0.5M; (d) 1.0M

With an increase in the concentration of lithium perchlorate, the height of the first peak increases and that of the second decreases.

A single peak corresponding to the first peak is observed when the concentration of lithium perchlorate is greater than 0.5M.

The d. c. and a. c. polarograms obtained in quaternary ammonium perchlorate electrolyte solutions, on the other hand, are not greatly influenced by the concentration of electrolytes. An increase in the concentration of the electrolyte causes the reduction potentials to become more negative and reduces the wave height, however.

Effect of Acetate Ions. Figure 5 shows polarograms of cobalt(II) perchlorate in a 0.05M tetra-*n*-butylammonium perchlorate solution containing 0.4% glacial acetic acid and various concentrations of tetra-*n*-butylammonium acetate.

An acetonitrile solution of cobalt(II) perchlorate, in the absence of tetra-*n*-butylammonium acetate, gives a reversible reduction wave with the half-wave potential of −0.62 V *vs.* SCE in 0.05M tetra-*n*-butylammonium perchlorate. The addition of tetra-*n*-butylammonium acetate causes the single wave to split into a double wave and the wave

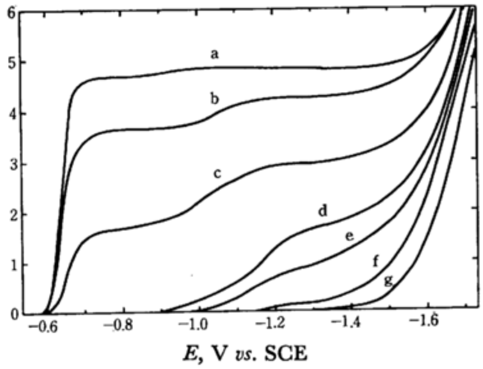

Fig. 5. Effect of concn. of n-Bu_4NOAc on the polarograms of Co(II).
$[Co(H_2O)_6(ClO_4)_2]=0.5$ mM, $[HOAc]=0.4\%$,
$[n\text{-}Bu_4NClO_4]=0.05$M
$[n\text{-}Bu_4NOAc]$: (a) 0; (b) 0.2 mM; (c) 0.6 mM;
(d) 1.0 mM; (e) 1.4 mM;
(f) 2.0 mM; (g) 3.0 mM

height of both steps to decrease.

When the concentration of tetra-n-butylammonium acetate is greater than 1 mM, the first step ceases to exist and an irreversible wave corresponding to the second step is observed. The irreversible wave also vanishes at concentrations of tetra-n-butylammonium acetate higher than about 2 mM.

In the presence of glacial acetic acid, the polarographic behavior of cobalt(II) at potentials more negative than −1.7 V *vs.* SCE is not clear because of the discharge of hydrogen ions produced by the dissociation of acetic acid.

The effect of acetate ion on the polarograms of cobalt(II) perchlorate in the absence of glacial acetic acid was also investigated. The results are reproduced in Fig. 6.

When the $[OAc^-]/[Co(II)]$ ratio is less than 2, three waves are observed. The first two waves are similar to those observed in the presence of glacial acetic acid. The reduction potential of the third step observed at potentials more negative than −2.2 V *vs.* SCE becomes more negative values and the wave height increases with an increase in the concentration of tetra-n-butylammonium acetate. When the $[OAc^-]/[Co(II)]$ ratio is greater than 2, but less than 3, cobalt(II) is precipitated.

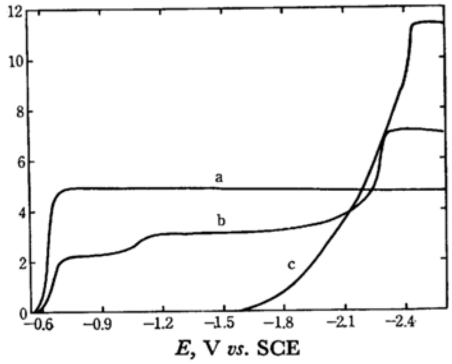

Fig. 6. Effect of concn. of n-Bu_4NOAc on the polarograms of Co(II) in the absence of glacial acetic acid.

$[Co(H_2O)_6(ClO_4)_2]=0.5$ mM,
$[n\text{-}Bu_4NClO_4]=0.05$M
$[n\text{-}Bu_4NOAc]$: (a), 0; (b), 0.5 mM; (c), 1.6 mM

Table 4. Effect of n-Bu_4NOAc on the exponent of i-t curve for the reduction of 0.5 mM cobalt(II) perchlorate in a 0.05 M n-Bu_4NClO_4 electrolyte solution in the absence (a) and the presence (b) of 0.4% glacial acetic acid

Concn. of n-Bu_4NOAc mM	x at $i_l=kt^x$		
	1st wave	2nd wave	3rd wave
0.20[a]	0.19	0.23	0.25
0.50[a]	0.18	0.23	0.24
0.75[a]	0.18	0.25	0.33
1.50[a]	—	—	0.65
2.0[a]	—	—	0.65
2.5[a]	—	—	0.67
3.0[a]	—	—	0.66
0[b]	0.19	—	
0.20[b]	0.19	0.23	
0.40[b]	0.18	0.23	
0.60[b]	0.18	0.25	
0.80[b]	0.19	0.32	
1.00[b]	—	0.40	
1.20[b]	—	0.44	
1.40[b]	—	0.56	

When the $[OAc^-]/[Co(II)]$ ratio is greater than 3, an ill-defined reduction wave is observed. The nature of the limiting current for the three steps is shown in Table 4.

The limiting current of the first step is diffusion-controlled. The exponent of the i-t curve for the second and third steps, on the other hand, increases with an increase in the concentration of tetra-n-butylammonium acetate. This indicates that the process has an appreciable contribution from a kinetic controlled electrode mechanism.[7]

Plots of the wave height against the $[OAc^-]/[Co(II)]$ ratio and the concentration of tetra-n-butylammonium acetate are given in Fig. 7.

The wave height of the first step decreases linearly with the increase of the concentrations of tetra-n-butylammonium acetate, becoming zero at the point where the $[OAc^-]/[Co(II)]$ ratio is equal to 2. The total wave height of the first two steps

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7) J. Kůta and I. Smolor, "Progress in Polarography," ed. by P. Zuman and I. M. Kolthoff, Vol. 1, Interscience Publishers, New York (1962), pp. 43—63.

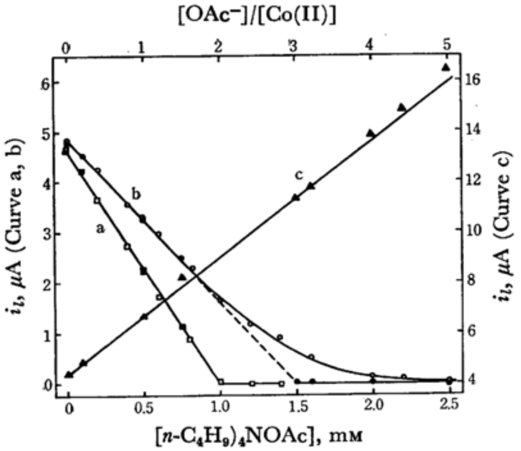

Fig. 7. Variation of limiting current with concn. of n-Bu_4NOAc in the absence (closed mark) and the presence (open mark) of 0.4% glacial acetic acid.

(a), 1st wave; (b), (a)+2nd wave; (c), (b)+3rd wave.

(curve b in Fig. 7) also decreases almost linearly with the concentration of tetra-*n*-butylammonium acetate to about 1 mM, but it deviates from the line at higher concentrations of tetra-*n*-butylammonium acetate containing 0.4% glacial acetic acid. In the absence of glacial acetic acid, the limiting current of the second step becomes zero at concentrations of tetra-*n*-butylammonium acetate higher than 1.5 mM. If curve b in Fig. 7 extrapolated to the point where the current is zero, the extrapolated point corresponds to [OAc⁻]/[Co(II)]= 3.0. The wave height at the potential where the third step is observed in the absence of glacial acetic acid (curve c in Fig. 7), on the other hand, is nearly proportional to the concentrations of tetra-*n*-butylammonium acetate to about 2 mM.

Discussion

The polarographic reduction of cobalt(II) perchlorate in acetonitrile containing acetate ions is dependent on the concentration of acetate ions. When the [OAc⁻]/[Co(II)] ratio is less than 2, the plots of the limiting current in relation to the acetate ion concentration indicate that the first step (wave I) involves the reduction of uncomplexed cobalt(II), while the second step (wave II) involves that of $Co(OAc)^+$. When the $Co(H_2O)_6(ClO_4)_2$ compound is dissolved in acetonitrile in the absence of acetate ions, cobalt(II) is present in the solution almost as $Co(CH_3CN)_6{}^{2+}$ ions.[8]

An acetonitrile solution of cobalt(II) perchlorate reacts with acetate ions to form $Co(OAc)_2$, which then dissociates into $Co(OAc)^+$ and $Co(OAc)_3{}^-$. $Co(OAc)_2$ is an electroinactive species; an acetonitrile solution of cobalt(II) acetate, in the absence of any supporting electrolyte, gives no apparent reduction wave, as Fig. 1 shows.

$$Co^{2+} + 2OAc^- \rightleftharpoons Co(OAc)_2 \tag{1}$$

$$2Co(OAc)_2 \rightleftharpoons Co(OAc)^+ + Co(OAc)_3{}^- \tag{2}$$

$$\text{Wave I: } Co^{2+} + 2e + Hg \rightleftharpoons Co(Hg) \tag{3}$$

$$\text{Wave II: } Co(OAc)^+ + 2e + Hg \longrightarrow Co(Hg) + OAc^- \tag{4}$$

where the coordinated acetonitrile molecules were omitted for the sake of simplicity.

The third step (wave III) observed in the absence of glacial acetic acid can be attributed to the reduction of $Co(OAc)_3{}^-$ produced by reaction (2):

$$\text{Wave III: } Co(OAc)_3{}^- + 2e + Hg \longrightarrow Co(Hg) + 3OAc^- \tag{5}$$

When the [OAc⁻]/[Co(II)] ratio is greater than 2, but less than 3, an acetonitrile solution of cobalt(II) in the presence of 0.4% glacial acetic acid gives a single irreversible wave corresponding to the wave II.

The over-all reaction can be represented by the equilibrium reaction (6) and the electrode reaction (4):

$$Co(OAc)^+ + 2OAc^- \rightleftharpoons Co(OAc)_3{}^- \tag{6}$$

The reduction wave of $Co(OAc)_3{}^-$ is not observed because of the discharge of hydrogen ions. The kinetic nature of the limiting current may be due to the equilibrium reaction (6).

When the [OAc⁻]/[Co(II)] ratio is greater than 3, an ill-defined reduction wave corresponding to the wave III is observed in the absence of glacial acetic acid. The limiting current of wave III receives an appreciable contribution from the kinetic-controlled electrode mechanism, judging from the results of the measurement of the *i-t* curve, shown in Table 4.

Although this kinetic mechanism is uncertain, wave III, under the proposed conditions, involves the reduction of $Co(OAc)_3{}^-$ but not of $Co(OAc)_4{}^{2-}$; wave III is also observed when the [OAc⁻]/[Co(II)] ratio is less than 2. The partial electrochemical reactions may be written as in the reactions (7) and (5):

$$Co(OAc)_3{}^- + OAc^- \rightleftharpoons Co(OAc)_4{}^{2-} \tag{7}$$

The $Co(OAc)_4{}^{2-}$ species may be unstable in the solution, if present at all.

Acetate ion yields a double anodic dissolution wave of mercury, as is shown in Fig. 8. The total limiting current is diffusion-controlled and is proportional to the concentration of acetate ions. In the presence of cobalt(II) perchlorate, the dissolution wave is not observed until the [OAc⁻]/[Co(II)] ratio exceeds 3, as is shown in Fig. 9. The curves a and b in Fig. 9 show the plots of the wave height

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[8] B. J. Hathaway, D. G. Holah and A. E. Underhill, *J. Chem. Soc.*, **1962**, 2444.

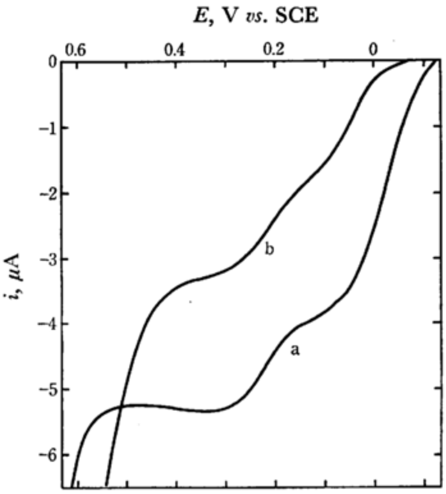

Fig. 8. Anodic dissolution waves of mercury for acetate ion in 0.05M n-Bu_4NClO_4 solution in the absence (a) and the presence (b) of 0.5 mM $Co(H_2O)_6(ClO_4)_2$.
[n-Bu_4NOAc]: (a), 1.0 mM; (b), 2.0 mM

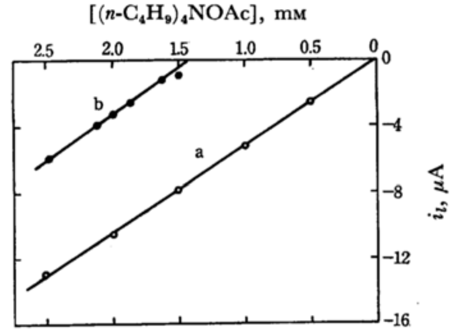

Fig. 9. Variation of total height of the anodic wave with concn. of n-Bu_4NOAc in the absence (a) and the presence (b) of 0.5 mM $Co(H_2O)_6(ClO_4)_2$.

against acetate ion concentrations in the absence and in the presence of cobalt(II), respectively. These results indicate that $Co(OAc)_4{}^{2-}$ is unstable and dissociates easily into $Co(OAc)_3{}^-$.

From the above arguments, the change in the reduction wave for an acetonitrile solution of cobalt(II) acetate in the presence of small amounts of glacial acetic acid can be said to be due to the variety of electroactive species of cobalt(II) in the solution.

The reduction wave for an acetonitrile solution of cobalt(II) acetate in the presence of quaternary ammonium perchlorate corresponds to the reduction of the $Co(OAc)^+$ which is produced by the dissociation reaction (2).

An acetonitrile solution of cobalt(II) acetate in the absence of any supporting electrolyte does not show any apparent reduction wave. This indicates that cobalt(II) acetate, in the absence of any supporting electrolyte, is only slightly dissociated in acetonitrile and that the dissociation reaction is accelerated by the presence of a supporting electrolyte; also, neutral cobalt(II) acetate $Co(OAc)_2$ is electroinactive at the DME.

The reduction waves of cobalt(II) acetate in alkali metal perchlorate supporting electrolyte solutions are dependent on the concentration of the electrolyte.

When the concentration of lithium perchlorate is less than 0.2M, a double wave corresponding to the reduction of $Co(CH_3CN)_n{}^{2+}$ and $Co(OAc)^+$ is observed, while a single wave corresponding to the reduction of $Co(CH_3CN)_n{}^{2+}$ is observed at concentrations of lithium perchlorate higher than 0.5M. The a.c. polarogram also suggests that two electroactive species are present in the solution containing 0.05M lithium perchlorate. The solution equilibria in a lithium perchlorate electrolyte solution can probably be represented by the following sequence:

$$2Co(OAc)_2 \rightleftharpoons Co(OAc)^+ + Co(OAc)_3{}^- \qquad (2)$$

$$Co(OAc)_3{}^- + 2Li^+ \rightleftharpoons Co(OAc)^+ + 2LiOAc \qquad (8)$$

$$Co(OAc)^+ + Li^+ \rightleftharpoons Co^{2+} + LiOAc \qquad (9)$$

The wave height of a double wave observed at relatively low concentrations of lithium perchlorate or that of a single wave at concentrations of electrolyte higher than 0.5M is proportional to the concentration of cobalt(II) acetate.

These findings indicate that $Co(OAc)_2$ and $Co(OAc)_3{}^-$ are only slightly present in lithium perchlorate electrolyte solutions. As a result, the predominant reaction participating in the electrode process of cobalt(II) acetate in lithium perchlorate electrolyte solutions may be presented by the reaction (9).

Three ill-defined steps are observed in a 0.05M sodium perchlorate electrolyte solution. The a.c. polarograms obtained in the same solution also show three peaks. These results show that three electroactive species of cobalt(II) are present in the solution. The solution equilibria of cobalt(II) acetate in a 0.05M sodium perchlorate electrolyte solution may be described by the following sequence:

$$2Co(OAc)_2 \rightleftharpoons Co(OAc)^+ + Co(OAc)_3{}^- \qquad (2)$$

$$Co(OAc)_3{}^- + 2Na^+ \rightleftharpoons Co(OAc)^+ + 2NaOAc \qquad (10)$$

$$Co(OAc)^+ + Na^+ \rightleftharpoons Co^{2+} + NaOAc \qquad (11)$$

Three steps are responsible for the reductions of $Co(CH_3CN)_n{}^{2+}$, $Co(OAc)^+$, and $Co(OAc)_3{}^-$, and the reduction potential becomes more negative with an increase in the number of coordinated acetate ions.

When the concentration of sodium perchlorate exceeds about 0.5M, the predominant species is $Co(CH_3CN)_n{}^{2+}$. When the concentration of sodium perchlorate is less than 0.2M, $Co(OAc)^+$ and $Co(OAc)_3{}^-$ are the predominant species.

The reduction potential of cobalt(II) acetate becomes less negative upon the addition of alkali metal perchlorate to the quaternary ammonium perchlorate supporting electrolyte solutions, and the wave height also increases, as is shown in Fig. 3. This effect may be attributed to the increases in the concentrations of $Co(CH_3CN)_n^{2+}$ and $Co(OAc)^+$, presented by reactions (8) and (9).

The authors wish to thank the Ministry of Education for the financial support granted for this research.