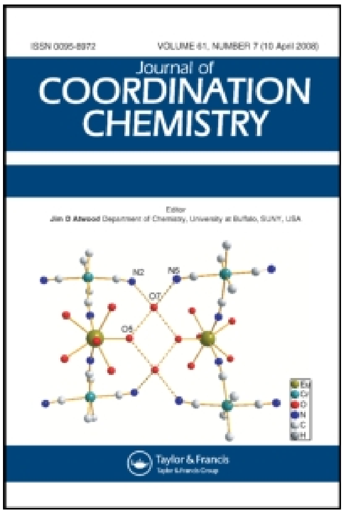

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Monika Moszner[a]; Michal Wilgocki[a]; Jozef J. Ziolkowski[a]
[a] Institute of Chemistry, University of Wroclaw, Wroclaw, Poland

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POLAROGRAPHIC STUDIES OF DIMERIC AND MONOMERIC RHODIUM(II) AND RHODIUM(III) COMPLEXES

MONIKA MOSZNER, MICHAL WILGOCKI and
JOZEF J. ZIOLKOWSKI*

Institute of Chemistry, University of Wroclaw, F. Joliot-Curie 14, 50–383 Wroclaw, Poland.

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The polarographic behaviour of $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$, [I], $[Rh_2(H_2O)_{10}]^{4+}$ ($Rh_2^{4+}{}_{(aq)}$), [II], $[Rh(H_2O)_6]^{3+}$, [III], in 3 M $HClO_4$ and $Rh_2(CH_3CO_2)_4(H_2O)_2$, [IV], and $[Rh_2(CH_3CO_2)_4(H_2O)_2]^+$, [V], in 3 M $HClO_4$ and 3 M $NaClO_4$ has been investigated at a Pt (planar) electrode. The cation [I], which is the reaction product of [II] with molecular oxygen, produced a single electron cyclic polarogram, while cations [II], $Rh_2^{4+}{}_{(aq)}$, and [III] do not show any wave. Formal potentials of the following couples were evaluated: $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}/[Rh_2(O_2^{2-})(OH)_2(H_2O)_n]^{2+}$, $E_f^\circ = 1.032 \pm 0.002$ V in 3 M $HClO_4$; $[Rh_2(CH_3CO_2)_4(H_2O)_2]^+/[Rh_2(CH_3CO_2)_4(H_2O)_2]$, $E_f^\circ = 1.208 \pm 0.002$ V in 3 M $HClO_4$, $E_f^\circ = 1.228 \pm 0.002$ V *vs* SHE in 3 M $NaClO_4$.

Keywords: Polarography, rhodium(II,III), superoxide, peroxide, formal potential

INTRODUCTION

Binuclear rhodium(II) complexes have proven to be unique and interesting systems for studying electronic structure and chemistry of orbitally complex small metal clusters. In recent years the electrochemical behaviour of binuclear rhodium(II) complexes has received considerable attention in the literature.[1] Among known dimeric Rh(II) complexes is the unusual $[Rh_2(H_2O)_{10}]^{4+}$ aquo-dimer. First reported in 1968 it has been little investigated.[2-8] In spite of the presence of a [Rh(II)–Rh(II)] core, the properties of $Rh_2^{4+}{}_{(aq)}$ are almost totally different to its analogues, where the [M–M] arrangement is surrounded by bidentate bridging ligands. The $[Rh_2^{4+}]$ core in tetracarboxylate complexes can be reversibly oxidized in a single electron transfer both by the chemical[9-11] and electrochemical methods,[12,13] to produce the $[Rh_2^{5+}]$ core. The $[Rh_2^{4+}]$ and $[Rh_2^{5+}]$ cores are stable enough to examine (in solids) electronic and molecular structures.[14,15] Substitution of oxygen ligands by stronger donors, *e.g.*, amide bridges, allowed the oxidation of the $[Rh_2^{4+}]$ core to $[Rh_2^{6+}]$ in a two electron electrode process.[1] The $Rh_2^{4+}{}_{(aq)}$ dimer, obtained in the innersphere electron transfer between $[Rh(H_2O)_5X]^{n+}$ ($X = H_2O, Cl^-, Br^-$) and $[Cr(H_2O)_6]^{2+}$ is known to exist only in strong acid solutions.[2,9] According to Legzdins *et al.*, the complex could also be obtained by protonation of the carboxylate bridges in $[Rh_2(RCO_2)_4]$ complexes in the presence of strong, non-coordinating acids.[3] Wilson and Taube have proved that this process proceeds only partially.[16] The presence of bridging ligands around the $[Rh_2^{4+}]$ core results in its resistance to H_2 and O_2 in normal conditions, while the

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* Author for correspondence.

dimer $Rh^{4+}_{2(aq)}$ is reduced to metallic rhodium in the presence of H_2, and in the presence of O_2 reacts depending on reaction conditions.[7,17] We have found that with slow diffusion of O_2 into a 3 M $HClO_4$ solution of $Rh^{4+}_{2(aq)}$, dimeric or polymeric $Rh(III)_{(aq)}$ cationic species with charge greater than +3 is formed. The paramagnetic superoxo complex [I] formulated as $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$ is produced when molecular oxygen is bubbled through acidic solutions of $[Rh^{4+}_{2(aq)}]$.[17] Contrary to $[Rh^{4+}_{2(aq)}]$, $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$ is stable in 1–3 M $HClO_4$ at room temperature.

In this paper the electrochemical properties of the complexes $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$, [I], $[Rh^{4+}_{2(aq)}]$, [II], $[Rh(H_2O)_6]^{3+}$, [III], $[Rh_2(CH_3CO_2)_4(H_2O)_2]$, [IV], and $[Rh_2(CH_3CO_2)_4(H_2O)_2]^+$, [V], in 3 M $HClO_4$ solution have been examined.

EXPERIMENTAL

All chemicals were of the highest purity commonly available. Water used as a solvent was redistilled from alkaline potassium permanganate in an all-glass still. Argon (99.995% pure) was freed of oxygen by passing the gas through two towers containing amalgamated zinc and a solution of Cr(II) in 0.5 M acid. $RhCl_3.3H_2O$ was purchased from Koch-Light Laboratory Ltd., $NaClO_4$ and $HClO_4$ from Merck. For the preparation of green solutions of the aquo dimer $[Rh^{4+}_{2(aq)}]$, the procedure described in Ref.4 was followed.

$[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$ was prepared according to the procedure described previously[17] by passing dioxygen through the green solution of cation [II] in 2–3 M $HClO_4$. After separation on a Dowex 50W-X2 column (H^+) the violet cationic species [I] was eluted with 3 M $HClO_4$. $[Rh_2(CH_3CO_2)_4(H_2O)_2]$ was prepared by a literature method[3] and $[Rh_2(CH_3CO_2)_4(H_2O)_2]^+$ as in Ref.9. $[Rh(H_2O)_6]^{3+}$ was prepared by the method of Ayres and Forrester[18] by the reaction of $RhCl_3.3H_2O$ with concentrated perchloric acid.

Polarographic studies were performed on a Laborarotni Pristroje Polarographic Analyzer (PA2 and PA3) and an XY recorder (types 4103 and 4105). The electrochemical cell was a closed jacketted vessel (with a thermostated water flow) which was provided with a planar platinum working electrode, Luggin capillary, salt bridge, reference (Hg/Hg_2Cl_2 satd. NaCl) electrode, Pt spiral auxiliary electrode, a side arm for introducing test solution, and a glass tube for gas inlet and outlet.[19]

The controlled potential coulometric measurements were carried out with a Radelkis OH 404A potentiostat associated with an OH 404C digital integrator unit. Bulk electrolyses were performed in the 50 cm^3 cell and in the micro-cell (0.5 cm^3 sample). The 50 cm^3 cell allowed both coulometric and polarographic studies in the same cell. In both cells the cathodic and anodic compartments were separated by a fine porosity frit. The working electrode was a platinum gauze, the auxiliary electrode was a platinum spiral and the reference electrode was SCE with a fine salt bridge. The anodic and cathodic compartments of both cells were provided with a glass tube for argon inlet and outlet and a side arm for transferring sample solution by argon pressure into a deoxygenated ESR capillary or a UV–VIS cell. Thus, the progress of the electrolysis was monitored coulometrically, polarographically or by ESR and electronic spectroscopy. The electrochemical cells were deoxygenated by passing a stream of argon (20 min) prior to introducing the test solution. The rhodium complex concentrations were between 10^{-3} and 10^{-4} M. All electrochemical measurements were performed at 20°C. ESR spectra of frozen solutions were recorded on a JEOL JS 3X spectrometer. Electronic spectra were recorded on a SPECORD M-40 spectrophotometer.

RESULTS AND DISCUSSION

The $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$ complex cation was found to produce well-shaped cyclic polarograms at the planar Pt electrode (Fig. 1) in 3 M $HClO_4$, while for the aquo dimer $Rh_2^{4+}{}_{(aq)}$ and $[Rh(H_2O)_6]^{3+}$ no electrode reactions were observed. For complex [I] a single reduction peak on the forward scan and a coupled reverse oxidation peak on the backward scan were detected for scan rates (2–500 mV/s) applied within the available potential range at the platinum electrode. The ratio of the cathodic to the anodic peak current, i_{pc}/i_{pa}, was close to unity (at all scan rates) and the values of $i_p/V^{1/2}$ were constant, indicating the absence of coupled chemical reactions and diffusion control of the electrode process. The analysis of peak separation and the half peak potentials led to the conclusion that the aquocomplex [I] is, polarographically, totally reversible ($E_{pc/2} - E_{pc} = 57 \pm 2$ mV, $E_{pa} - E_{pa/2} = 59 \pm 2$ mV) at low scan rates (2–5 mV). The scan rate increase is accompanied by slow increase of a contribution to the rate of the one-electron transfer in the overall electrode process rate (Fig. 1). Making the very plausible assumption that the difference between the diffusion coefficients of oxidized and reduced form of complex [I] is very small, the value of the formal potential was estimated for all scan rates studied (2–500 mV). In addition, the formal potential was also determined on the basis of computer analysis of the current-potential dependence and least-squares treatment of the data obtained (($\log i_c$, $\log i_a$) = f(E)) for several independently prepared solutions in question (see Appendix). Finally, the following value of the formal potential $E_f^\circ = 0.790 \pm 0.002$ V *vs* SCE was estimated numerically for the $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}/[Rh_2(O_2^{2-})(OH)_2(H_2O)_n]^{2+}$ couple in 3 M $HClO_4$.

The macro bulk electrolysis revealed that the violet dimer $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$, undergoes electroreduction only and that the reduced product is not stable over long electrolysis time scales. For that reason a micro scale electroreduction (at 0.4 V) for 0.5 cm^3 of sample was preformed. In this case even the longest electrolysis time was shorter than the recording time for the slowest polarographic course. Under electrolysis the consumption of charge was measured and electronic and ESR spectra were recorded. The starting superoxo $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$ dimer in 3 M $HClO_4$ shows bands at 420 nm ($\varepsilon = 140\ M^{-1}cm^{-1}$ per Rh) and 560 nm ($\varepsilon = 217\ M^{-1}cm^{-1}$ per Rh). Its ESR spectrum presents two peaks, of $g_\parallel = 2.0822$ and $g_\perp = 2.0199$ at −140°C. Representative ESR spectra, before electroreduction (curve 1) and after the consumption of 0.8 mol of electrons per mol of starting $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$ compound (curve 2), are shown in Fig. 2. The electroreduction is accompanied by a change of colour of the solution from violet to yellow. This corresponds to the decay of the absorption band at 560 nm and by absorption increase and formation of a shoulder at 400 nm. Simultaneously, in the ESR spectrum, stepwise intensity decrease of the abovementioned lines, combined with the presence of the superoxo bridge, is observed (Fig. 2). Thus, the polarographic, coulometric and spectroscopic data indicate that the cyclic polarographic waves, shown in Fig. 1, correspond to the redox process

$$[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+} \underset{-e}{\overset{+e}{\rightleftharpoons}} [Rh_2(O_2^{2-})(OH)_2(H_2O)_n]^{2+}.$$

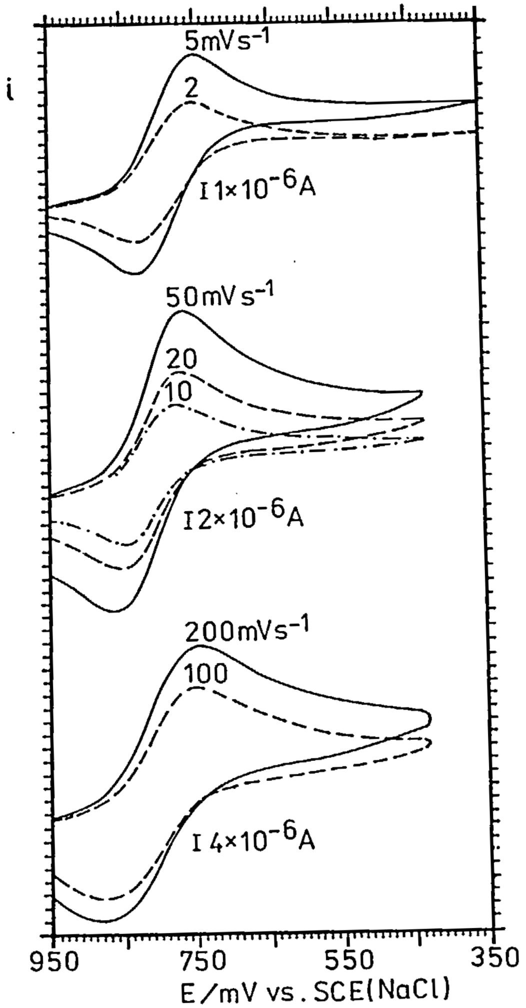

FIGURE 1 Cyclic polarograms of $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$ in 3 M $HClO_4$ *vs* SCE(NaCl).

Attempts to isolate $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$ as a solid have so far been unsuccessful. The proposed formula is based mainly upon ESR spectroscopy, magnetic moment ($\mu = 2.23$ M) and charge of species (2.9 ± 0.2) measurements[17], according to the Cady and Connick method.[20] Contrary to the superoxo complex, the peroxo form of complex [I] is stable in 3 M $HClO_4$ for only a few minutes. It was found that the decomposition of the peroxo complex is accompanied by the change of colour of the solution from yellow to grey-violet. The intensity of the resonance lines in the ESR ($g_\parallel = 2.0822$, $g_\perp = 2.0199$) increases, the visible spectrum corresponding to the superoxo complex is partially reproduced, and the cyclic polarographic curve obtained during or after macro scale bulk electrolysis declines. According to Gillard and Pedrosa de Jesus[21] and Springborg and Zender[22], Rh(III) superoxo complexes with amine ligands are stable in strong acid. The peroxo complexes undergo disproportionation with formation of the superoxo complexes.[23] The results obtained by us suggest that the electrolytically generated Rh(III) μ-peroxoaquo dimer undergoes disproportionation to a μ-superoxo and a μ-hydroxo complex like its amine analogues.

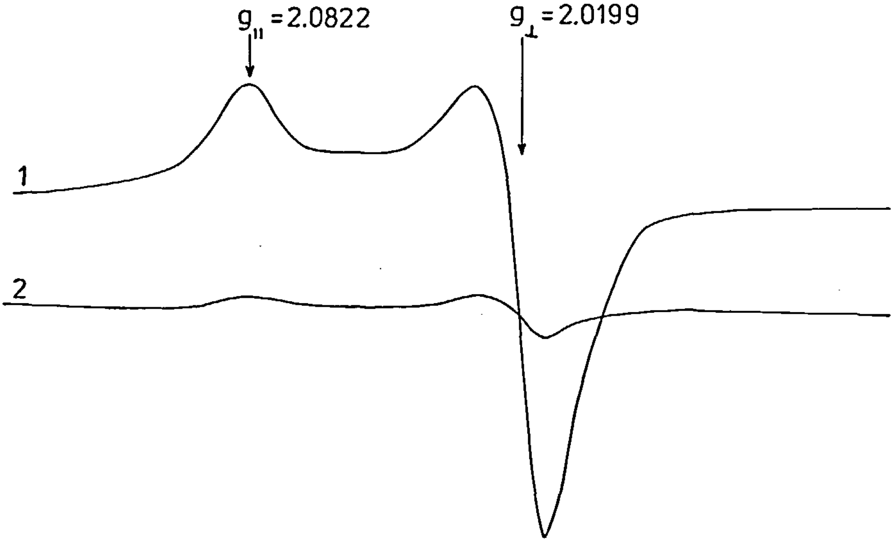

FIGURE 2 ESR spectra before electroreduction at 0.4 V (curve 1) and after the consumption of 0.8 mol of electrons per mol of $[Rh_2(O_2^-)(OH)_2(H_2O)F3n]^{3+}$ compound (curve 2).

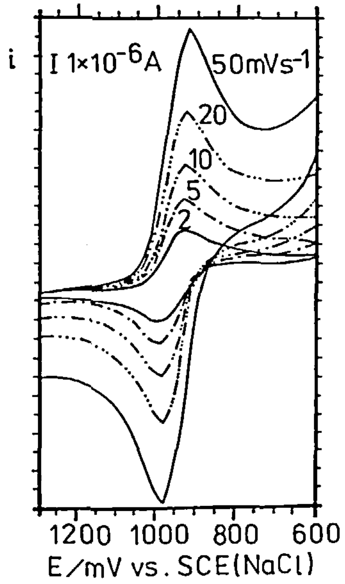

FIGURE 3 Cyclic polarograms of $[Rh_2(CH_3CO_2)_4(H_2O)_2]^+$ in 3 M $HClO_4$ *vs* SCE(NaCl).

The polarographic behaviour of $[Rh_2(CH_3CO_2)_4(H_2O)_2]$ and $[Rh_2(CH_3CO_2)_4(H_2O)_2]^+$ has also been studied in 3 M $HClO_4$ and 3 M $NaClO_4$. The cyclic polarogram of complex [V] for different scan rates is shown in Fig. 3. For both acetate complexes, one-cycle polarographic experiments produced a single reversible oxidation peak and a coupled reversible reduction peak in 3 M $HClO_4$ and 3 M $NaClO_4$. The value of i_{pc}/i_{pa} was close to unity, $i_p/V^{1/2}$ values were constant and $E_{pa}-E_{pc} = 62.5 \pm 5$ mV, indicating diffusion rate control of the overall electrode process and the absence of coupled chemical reactions. Finally, from reversible cyclic curves for acetate complexes the following value of the formal potential, $E_f^\circ = 0.966 \pm 0.002$ V and 0.986 ± 0.002 V *vs* SCE(NaCl), was estimated for the $[Rh_2(CH_3CO_2)_4(H_2O)_2]^+/[Rh_2(CH_3CO_2)_4(H_2O)_2]$ couple in 3 M $HClO_4$ and 3 M $NaClO_4$, respectively. Bulk electroreduction (at 0.8 V) of the pink dimer [V] produced the stable green dimer [IV], and the original dimer [V] could be obtained both upon macro and micro scale reoxidation at 1.1 V.

Comparison of the E_f° values obtained here with the formal potential values obtained by other authors[7,10,12,16] (Table I) revealed satisfactory agreement (considering differences in medium). In particular, the comparison of the results obtained in 3 M $HClO_4$ and 3 M $NaClO_4$ (Table 1) confirm the Taube and Wilson reports[16] that strong acids, even in high concentrations, do not destroy the carboxylate bridges. It is notable that both acetate dimers are oxygen resistant and, even after one hour oxygenation directly in the polarographic cell, no changes in cyclic polarograms have been observed.

TABLE I
Formal potentials of dimeric Rh(II) and Rh(III) complexes (V *vs* SHE)[a].

Complex	Medium	E_f°	Ref.
$[Rh_2(SO_4)_4]^{4-}$	0.2 M H_2SO_4	1.082[b]	7
$[Rh_2(O_2^-)(OH)(NH_3)_8]^{4+}$ $[Rh_2(O_2^{2-})(OH)(NH_3)_8]^{3+}$	1 M KNO_3	0.732[c]	23
$[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$	3 M $HClO_4$	1.032[d]	this work
$[Rh_2(CH_3CO_2)_4(H_2O)_2]^+$	0.1 M H_2SO_4	1.225[e1]	16
	1 M $HClO_4$	1.25[f]	10
	3 M $HClO_4$	1.206[e1]	this work
	3 M $NaClO_4$	1.229[e1]	this work
$[Rh_2(CH_3CO_2)_4(H_2O)_2]$	0.1 M KCl	1.264[e2]	12
	3 M $HClO_4$	1.209[e2]	this work
	3 M $NaClO_4$	1.227[e2]	this work

[a] No corrections for liquid junction potentials were made; [b] Recalculated from polarographic data given in Ref. 7; [c] Potentiometric data for $[Rh_2(O_2^-)(OH)(NH_3)_8]^{4+}/[Rh_2(O_2^{2-})(OH)(NH_3)_8]^{3+} = 0.25 - 0.4$, using a Pt electrode; [d,e1,e2] Polarographic data for: [d] $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$, [e1] [Rh(III)-Rh(II)], [e2] [Rh(II)-Rh(II)] starting complex; [f] Potentiometric titrations using a Pt electrode.

Summarizing the results we can conclude the following. The polarographically active $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$ superoxoaquo dimer of Rh(III) is formed as a product between dioxygen and deoxygenated solutions of the electroinactive $Rh_{2\,(aq)}^{4+}$ species. To our knowledge the $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$ complex is the first known rhodium superoxo dimer where the $[Rh(O_2^-)Rh]^{5+}$ electroactive group is surrounded by oxygen ligands.

The polarographic and spectroscopic properties of the $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$ complex are due to superoxo-bridge coordination, while in the case of $[Rh_2(CH_3CO_2)_4(H_2O)_2]^+$, due to $[Rh\text{-}Rh]^{5+}$ core. From the measurements for dirhodium tetraacetate complexes it follows that the formal potential determined in 3 M $HClO_4$ are 20 mV more negative than in 3 M $NaClO_4$.

It is noteworthy that the formal potential of the $[Rh_2(O_2)(OH)_2(H_2O)_n]^{3+/2+}$ couple (3 M $HClO_4$) is 0.3 V more positive than the formal potential of $[Rh_2(O_2)(OH)(NH_3)_8]^{4+/3+}$ couple (1 M KNO_3). This difference is due to the presence of the amine groups and, probably, partially due to the effect of protonation of the μ-peroxo ligand in the $[Rh_2(O_2^{2-})(OH)_2(H_2O)_n]^{2+}$ complex (as in some cobalt complexes)[24] on the E° value.[25] It is of interest that the E_f° value for the $[Rh_2(O_2)(OH)_2(H_2O)_n]^{3+/2+}$ couple is close to the E_f° values for (μ-superoxo/μ-peroxo) dicobalt amine systems in 0.45 M $NaClO_4$ (0.9–1.1 V *vs* SHE).[24]

Also worthy of note is the fact that standard deviations for the formal potential values of rhodium complexes estimated by static (potentiometry, Ref.23, p. 489) and dynamic (cyclic polarography, this work) methods are of the same order of magnitude (2 mV). This means that polarography could be successfully applied for estimation of E_f° value when one of the redox form is relatively unstable. Contrary to dicobalt complexes[24] however, the estimation of ligands effects (terminal and bridging) on E_f° value require further investigations of other (μ-superoxo/μ-peroxo) dirhodium(III) couples.

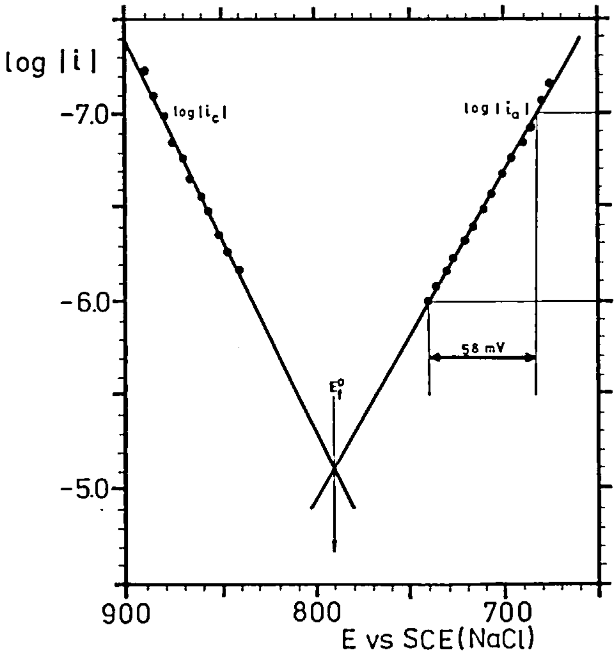

FIGURE 4 Estimation of an E_f° value for $[Rh_2(O_2^-)(OH)_2(H_2O)_n]^{3+}$ in 3 M $HClO_4$. Data are for cyclic polarogram at 2 mV s^{-1} scan rate. Details are given in the Appendix.

APPENDIX

The procedure used for numerical estimation of E_f° value as a supplement to the classical treatment is as follows.

At the foot of the cathodic part (*1*) and of the anodic part of the cyclic polarographic curve (*2*), the following equations are fulfilled (also for significant irreversibility of electrode process)[26],

$$\log|i_c| = A_c E + B_c \qquad (1)$$

$$\log|i_a| = A_a E + B_a \qquad (2)$$

where $A_c = -0.4343\,\alpha_c nF/RT$ and $A_a = 0.4343\,\alpha_a nF/RT$.
The $\log|i_c|$ and $\log|i_a| = f(E)$ data were treated separately by a least-squares procedure (as in Ref. 27) and the values of A_c, B_c, A_a, B_a and their standard deviations (σ) were estimated.
The formal potential value was obtained from (*3*)

$$E_f^\circ = (B_c - B_a)/(A_a - A_c) \qquad (3)$$

and the standard deviation for the E_f° value from (*4*)

$$\sigma_{E_f^\circ} = [(B_c^+ - B_a^+)/(A_a^+ - A_c^+)] - [(B_c^- - B_a^-)/(A_a^- - A_c^-)] \qquad (4)$$

where: $B_c^+ = B_c + \sigma_{Bc}, \ldots, A_c^- = A_c - \sigma_{Ac}$.
Typical results are illustrated in Fig. 4.
Using the calculated E_f° value, the cyclic current potential curve was simulated (assuming $D_{ox} = D_{red}$) and compared with the experimental cyclic polarogram (obtained for different switching potential and analysed at E_p, $E_{p3/4}$, $E_{p1/2}$ and $E_{p1/4}$) at a given scan rate.

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