Polarographic Behavior of Tris(acetylactonato)ruthenium(III) in Aqueous and Acetonitrile Solutions

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In tetraethylammonium perchlorate–acetonitrile solution, $[Ru(acac)_3]$ was reversibly reduced at the dropping mercury electrode to $[Ru(acac)_3]^-$ with a conditional electrode reaction rate-contsant estimated to be *ca.* 0.2 cm s^{-1} or larger. The reduced form was stable in the solution under an inert gas atmosphere. In aqueous solutions, $[Ru(acac)_3]$ was reduced reversibly when the depolarizer concentration was less than 0.07 mol m^{-3} at 25 °C. At higher depolarizer concentrations, $[Ru(acac)_3]$ molecules were adsorbed onto the mercury surface, and the free molecules in solution were reduced through the adsorbed layer at a smaller rate; the adsorbed layer was removed at a certain negative potential, and the reversible reduction took place normally at the bare surface. The difference between reversible half-wave potentials observed in acetonitrile and aqueous solutions was discussed in terms of solvation energies of the oxidized and reduced forms.

Many electrochemical investigations have been carried out on various metal acetylacetonato-complexes.[1-5] In the course of studying some ruthenium complexes, tris(acetylacetonato)ruthenium(III), $[Ru(acac)_3]$, attracted our attention. It is known to act as a catalyst in organic reactions, for instance, hydrogenation of nitroarenes to amines.[6] Since tris(acetylacetonato)-metal complexes are usually poorly soluble in water, they have been studied in non-aqueous solvents such as acetonitrile and *N*,*N*-dimethylformamide. However, $[Ru(acac)_3]$ is exceptionally soluble in aqueous solution to as much as about 0.5 mmol dm^{-3} at 25 °C. In the present work its electrochemical behavior was examined in acetonitrile and aqueous solutions.

Experimental

Materials. The complex was prepared by the following procedure.[7] Ruthenium(III) chloride (1.9 g as Ru, dissolved in 150 cm^3 of 1 mol dm^{-3} HCl) was reduced with ethanol, and the mixture was evaporated nearly to dryness on a water bath. The blue residue was dissolved in 50 cm^3 of water, and the pH of the solution was adjusted to about 6 with 1 mol dm^{-3} KOH solution. The solution was refluxed with 15 cm^3 of acetylacetone and 50 cm^3 of ethanol for about 4 h. Then the solution was concentrated to about one-fifth the initial volume. Crystals of crude $[Ru(acac)_3]$ precipitated on cooling. The product, after being thoroughly washed with ethyl ether, was recrystallized from methanol and dried under vacuum at room temperature. The recrystallized, dark red crystals were readily soluble in acetonitrile, methanol, ethanol, and to a lesser extent in water. Found: C, 45.2; H, 5.2%. Calcd for $RuC_{15}H_{21}O_6$: C, 45.2; H, 5.3%. Further purification, when required, was carried out by sublimatography;[8] the crystals which condensed at 120 °C under a vacuum were collected.

Tetraethylammonium perchlorate (TEAP) was prepared from perchloric acid and tetraethylammonium iodide according to Given *et al.*[9] Acetonitrile was purified according to the procedure described by Forcier and Olver[10] and used within 10 days at the most. The water content of the solvent as determined by the Karl Fischer titration was less than 1 mmol dm^{-3}.

Other chemicals were of guaranteed reagent grade and used as received except for aluminium perchlorate, which was prepared by dissolving aluminium hydroxide in perchloric acid. Water was obtained by distilling deionized water in an all-glass apparatus and used throughout the experiments except for syntheses, in which deionized water was used.

Measurements. All the potentials were measured against an aqueous saturated calomel electrode (SCE), and all the measurements were carried out at (25.0±0.1) °C unless otherwise stated. For aqueous systems, an H-type salt bridge (saturated KCl solution) with filter-paper plugs was used for connecting the test solution with the SCE; for acetonitrile systems, the connection was made through an aqueous agar-plugged KCl bridge. As counter electrode, a spiral of platinum wire was used.

Deoxygenation of aqueous solutions was carried out with nitrogen which had been passed through an acidic vanadium(II) sulfate solution and water, successively; for acetonitrile systems, the purified nitrogen was passed through a calcium chloride column and then a wash bottle containing the solvent kept at 25 °C.

For acetonitrile systems, 0.05 mol dm^{-3} TEAP and 0.05 mol dm^{-3} $NaClO_4$ base solutions were used. Seven base solutions were used for aqueous systems: 0.2 mol dm^{-3} KCl, 0.033 mol dm^{-3} $Al(ClO_4)_3$, 0.066 mol dm^{-3} Na_2SO_4, 0.2 mol dm^{-3} $NaNO_3$, 0.2 mol dm^{-3} sodium *p*-toluenesulfonate, Sørensen buffer ($4.49 \leq pH \leq 6.81$), and Kolthoff buffer ($pH = 7.0$).

Dc and conventional ac polarograms were recorded with a potentiostat-type polarograph constructed in this laboratory. The instrument for phase selective ac (PSAC) polarography has been described elsewhere.[11] The root-mean-square amplitude of the superimposed ac signal was 3 mV for PSAC and 5 mV for conventional ac polarography. Two dropping mercury electrodes (DME) were used; their *m* values were as follows at 25 °C under a mercury head of 50 cm: No. 1, 1.78 mg s^{-1}; No. 2, 1.36 mg s^{-1}. Instantaneous currents at 3.50 s after beginning of drop growth were sampled by means of a dislodger-cutoff device previously described,[12,13] unless otherwise stated.

In PSAC measurements, correction was made for the uncompensated resistance, which was calculated from the PSAC polarograms of the base solution by assuming that the admittance was purely capacitive. The faradaic conductance (G_f) and susceptance (B_f) were obtained by subtracting the corresponding values for the base solution from the electrode conductance and susceptance in the presence of the depolar-

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izer.[11]

Controlled potential coulometry was carried out as described earlier[14] except that integration of the electrolytic current was carried out on a digital counter (Takedariken, Universal Counter TR-5104) by converting the current signal into pulses with a voltage-frequency converter (Aiko, VF500).[15] The electrolytic cell with a mercury pool working elecrode (surface area, about 7.1 cm^2) previously described[14] was used for both systems. When an acetonitrile test solution was placed in the working electrode compartment, the counter and reference electrode compartments were filled with aqueous potassium chloride solution. Contamination by a small amount of water leaking from the bridges was inevitable when electrolysis was prolonged, but no appreciable effect was noticed.

Cyclic voltammetry was carried out by means of the dc polarograph to which a programmable triangular signal generator[16] was connected. Voltammograms were displayed on an X-Y recorder (Riken Denshi, Model F-3D) for lower scan rates or on a cathode ray oscilloscope screen (National, Model VP-526) for higher scan rates. A Princeton Applied Research hanging mercury electrode assembly (Model 9323) was used, the radius of the mercury drops being about 0.44 mm.

A Hitachi 624 digital spectrophotometer was used for recording absorption spectra. Quartz cells of 1 cm and 0.5 cm were used for lower concentrations and a spacer cell of 1 mm, for higher concentrations.

Results and Discussion

Acetonitrile Systems. In 0.05 mol dm^{-3} TEAP solutions, a reduction step with half-wave potential ($E_{1/2}$) of -0.72_5 V was observed on the dc polarogram. The limiting current of the step was directly proportional to the depolarizer concentration and inversely proportional to the square root of the drop time of a mercury electrode dropping freely. As described below the step corresponds to the one-electron reduction to [Ru(acac)$_3$]$^-$. The log-plot resulted in a straight line with a reciprocal slope of -61 mV.

When the complex was partially reduced at the mercury pool electrode kept at a potential of the diffusion current plateau (-1.0 V), a single redox step appeared at the same half-wave potential. When the cathodic and anodic diffusion currents recorded intermittently in the course of the electrolytic reduction were plotted against the quantity of electricity, the magnitude of the former decreased and the latter increased linearly, and the plots indicated that the process was a one-electron reduction to [Ru^{II}(acac)$_3$]$^-$.

The reduced form was quantitatively reoxidized when it was electrolyzed at a potential of the anodic diffusion current plateau. It was readily oxidized also by atmospheric oxygen, but was not oxidized by perchlorate ions in the solution.

The polarographically reversible nature of the reduction is more clearly shown by the results of PSAC polarography (Table 1 and Fig. 1). Both the conductance and susceptance peak potentials coincided with $E_{1/2}$. The peak conductance and susceptance measured in the frequency range of 35—90 Hz agreed reasonably well with the theoretical value for a reversible or nernstian one-electron transfer. At higher frequencies cot ϕ, where ϕ is the phase angle of the faradaic admittance, tended to increase. The limited accuracy of the instrument, however, allowed us only to estimate that the lower limit of the conditional electrode reaction rate constant (at $E_{1/2}$) was about 0.2 cm s^{-1}.

Table 1. cot ϕ of 0.50 mmol dm^{-3} [Ru(acac)$_3$] in acetonitrile 0.05 mol dm^{-3} TEAP solution, 25 °C

f/Hz	35	70	90	190	270
cot ϕ	1.0_3	0.9_2	0.9_3	1.4_4	1.5_7

f, frequency; ϕ, phase angle of faradaic admittance; estimated error in cot ϕ is about 10%.

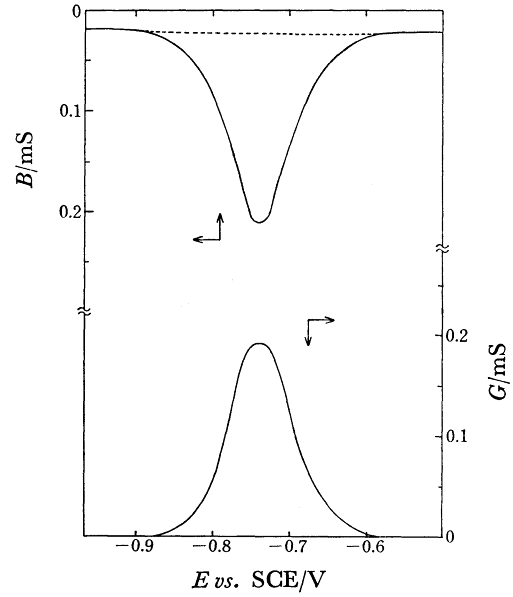

Fig. 1. PSAC polarograms of 0.50 mmol dm^{-3} [Ru(acac)$_3$] in acetonitrile 0.05 mol dm^{-3} TEAP solution. 35 Hz, 3 mV (r.m.s.); DME, No. 1; 25 °C; dashed line, base solution.

Aqueous Systems. Typical dc and ac polarograms are shown in Fig. 2. When the depolarizer concentration was less than 0.07 mmol dm^{-3}, a one-electron reduction dc step with $E_{1/2}=-0.51_6$ (curve A) and the corresponding ac wave, similar to those observed in acetonitrile solution, were observed. This step was reversible, as demonstrated by the PSAC polarographic data (Table 2).

At higher depolarizer concentrations, however, peculiar dc and ac polarograms were observed. The dc polarogram showed a small step prior to the main reduction step and a kink or a sudden increase in current magnitude at a potential of the shoulder of the main step. The ac polarogram was characterized by a marked depression of admittance starting from the potential of the small dc step and continuing to a round wave corresponding to the main dc step followed by a sharp peak at the potential where the sudden increase in dc current took place. When the temperature of the solution was varied (15—40 °C), the effect of its increase on the shape of the polarograms was similar to that of the decrease in the concentration: the potential of the small dc step shifted to negative, while that of the kink on the shoulder remained almost the same, and the ac polarogram changed correspondingly.

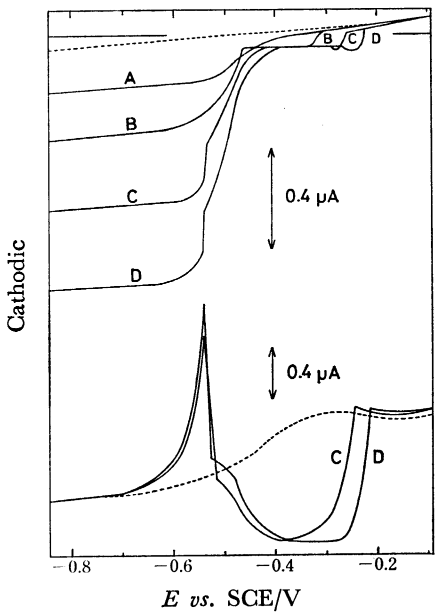

Fig. 2. Dc (upper) and conventional ac (lower) polarograms of [Ru(acac)$_3$] in aqueous 0.2 mol dm^{-3} KCl solution.
Depolarizer concentration/mmol dm^{-3}=0.05 (A), 0.1 (B), 0.2 (C), 0.3 (D). 35 Hz, 5 mV (r.m.s.); DME, no. 1; 25 °C; dashed lines, base solution. Ac polarograms for A and B are not shown for the sake of simplicity.

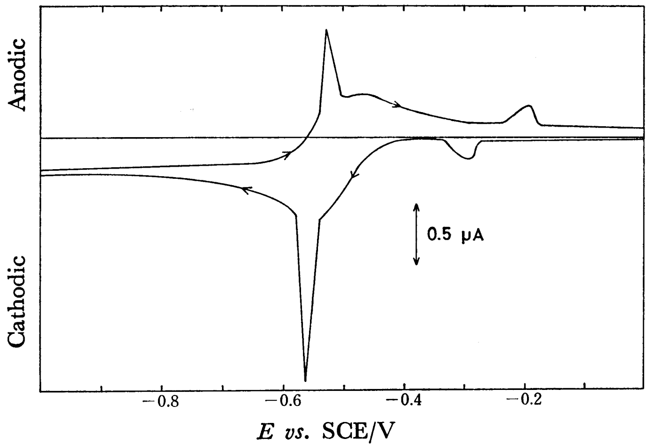

Fig. 3. Typical cyclic voltammogram of 0.20 mmol dm^{-3} [Ru(acac)$_3$] in aqueous 0.2 mol dm^{-3} NaNO$_3$ solution.
Scan rate, 168 mV s^{-1}; 25 °C.

Table 2. Faradaic peak conductance of 0.05 mmol dm^{-3} [Ru(acac)$_3$] in aqueous 0.2 mol dm^{-3} NaNO$_3$ solution, 25 °C

f/Hz	$G_{\mathrm{p,N}}/\mu\mathrm{S}$	$G_{\mathrm{p,obs}}/\mu\mathrm{S}$
23	24.15	24.7_2
58	38.36	39.5_9
90	47.78	50.3_7

f, frequency; $G_{\mathrm{p,N}}$, peak conductance calculated for nernstian one-electron transfer; $G_{\mathrm{p,obsd}}$, observed peak conductance.

The controlled potential coulometry of [Ru(acac)$_3$] at −0.7 V showed that the reduction was one-electron process and the reduced form was stable in the absence of oxygen. A partially reduced solution showed a single redox dc step at the same half-wave potential; the anodic step was accompanied by a small kink at the potential where the small step had appeared on the polarogram before the electrolysis. The reduced form was not oxidized by perchlorate ions, in contradistinction to the case of [Ru$^{\mathrm{II}}$(Hedta)(H$_2$O)]$^-$, which was reoxidized in aqueous perchlorate solutions.[14] The reduced form reacted with formate ions to produce electro-inactive entities, most probably some carbonyl species. The details of the reaction are under investigation; but the rate was much less than that of [Ru$^{\mathrm{II}}$(Hedta)(H$_2$O)]$^-$–formate reaction.[17] That [Ru$^{\mathrm{II}}$(acac)$_3$]$^-$ is less reactive than [Ru(Hedta)(H$_2$O)]$^-$ seems to be attributable to its symmetrical shape.

The dc and ac polarograms at higher depolarizer concentrations indicate the presence of adsorption; it was more clearly shown by the electrocapillary curves, in which a decrease in the interfacial tension was observed at the potentials between the small dc step and the kink. The possibility that the adsorption might be due to some impurities contained in the sample was excluded by the fact that the dc and ac polarograms of a purer sample obtained by sublimatography were identical with those of the simply recrystallized sample.

The concentration dependence of the dc polarogram clearly suggests that the adsorbed species is the oxidized form, not the reduced form (Fig. 2). This view is supported by the shape of the electrocapillary curve showing the adsorption of a neutral species and by the fact that the polarograms remained practically unchanged irrespective of the supporting electrolytes: KCl, NaNO$_3$, Na$_2$SO$_4$, Al(ClO$_4$)$_3$, and Sørensen and Kolthoff buffers of various pH (with the exception of sodium p-toluenesulfonate; see below).

Bis(acetylacetonato)cobalt(II)[18] and bis(acetylacetonato)nickel(II)[19] are known to dimerize in some nonaqueous solutions at higher concentrations. In the case of aqueous solutions of [Ru(acac)$_3$], however, no indication of such association was detected by the visible and ultraviolet spectra in the range of 190—650 nm even at 0.4 mmol dm^{-3} (about 80% of saturation), and the spectra agreed with those in acetonitrile solution.

These observations lead us to conclude that [Ru(acac)$_3$] is adsorbed onto the mercury surface in the potential region between the small step and the kink.

A typical cyclic voltammogram shown in Fig. 3 reflects the same situation: on each of the cathodic and anodic branches, two sharp adsorption-desorption peaks appeared, between which a round peak corresponding to the main dc step was seen. At higher scan rates the relative heights of the adsorption-desorption peaks to the round peak increased; at the same time, the potential separations between the anodic and cathodic peaks for each of the two pairs of the sharp peaks increased, suggesting that the adsorption-desorption process involved some kinetic character.

In the PSAC polarograms of 0.05 mmol dm^{-3} [Ru-

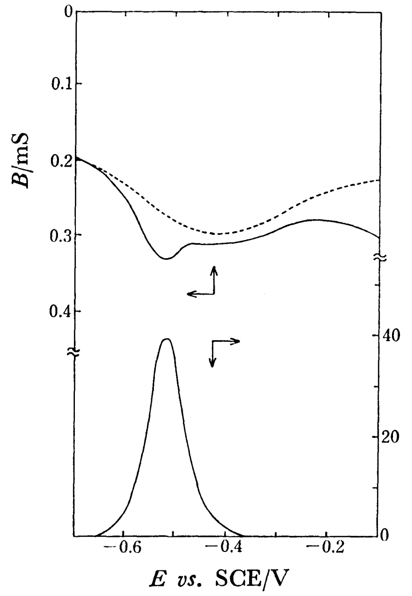

Fig. 4. PSAC polarograms of 0.05 mmol dm^{-3} [Ru(acac)$_3$] in aqueous 0.2 mol dm^{-3} NaNO$_3$ solution. 58 Hz, 3 mV (r.m.s.); DME, No. 2; 25 °C; dashed line, base solution.

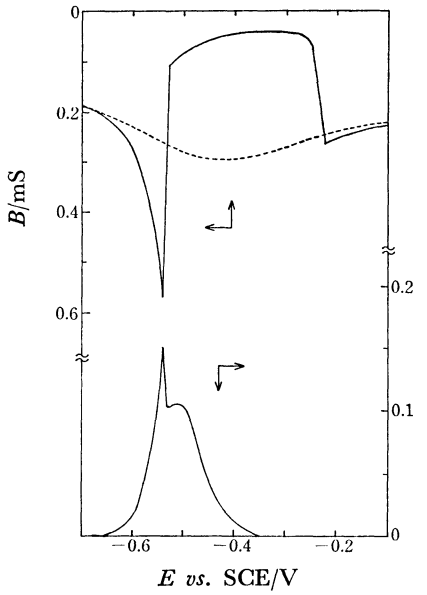

Fig. 5. PSAC polarograms of 0.3 mmol dm^{-3} [Ru(acac)$_3$] in aqueous 0.2 mol dm^{-3} KNO$_3$ solution. Conditions are the same as in Fig. 4.

(acac)$_3$] (Fig. 4) a shoulder at the positive side of the susceptance polarogram indicates that even at this concentration there was still some adsorption. However, the conductance component corresponded to a nernstian one-electron transfer as indicated by the value of the peak conductance (Table 2; the excessive values of the experimental peak conductance at higher frequencies may be due to the contribution of adsorption and/or instrumental errors).

The adsorption seems to affect the electron transfer. When the concentration was 0.30 mmol dm^{-3}, the susceptance polarogram showed a well-like depression corresponding to the adsorption, and the conductance polarogram showed a round peak followed by a sharp rise at its negative shoulder (Fig. 5). The potential of the latter coincided with the potential at which the sudden increase in current was observed on the dc polarogram. The height of the round peak was much less than the theoretical value for a nerstian one-electron transfer, but the values of the conductance at the potentials more negative than the sharp rise were roughly equal to those expected for a hypothetical nernstian wave with a peak potential of −0.52 V.

The susceptance polarogram showed a small peak at the positive edge of the depression (−0.23 V) when the frequency was 23 Hz, but no appreciable peak was observed at this potential on the conductance polarogram, so that the process was essentially capacitive. The susceptance peak became less clear with increasing frequency, probably owing to the kinetic character of the adsorption-desorption process as observed in the cyclic voltammetry.

The electrochemical behavior of [Ru(acac)$_3$] in the aqueous solutions is interpreted as follows. The complex is reduced at the mercury electrode to the corresponding Ru(II) species. This process is essentially reversible or nerstian as indicated by the results obtained at the lower concentrations. However, the Ru(III) complex molecules are adsorbed onto the electrode when the concentration is higher. The adsorbed molecules are stabilized and its reduction potential becomes more negative than that of the free molecules. The free molecules undergo reduction through the layer of adsorbed [Ru(acac)$_3$] at a lower rate. Beyond a certain potential (−0.54 V) the adsorbed layer of [Ru(acac)$_3$] no longer exists, and the reversible reduction takes place normally at the bare surface of the electrode. In view of the fact that this potential was practically independent of the depolarizer concentration and temperature, the adsorbed [Ru(acac)$_3$] molecules seem to be reduced at this potential to [Ru(acac)$_3$]$^-$, which is not adsorbable.

Interestingly, in 0.2 mol dm^{-3} aqueous sodium *p*-toluenesulfonate solution, a reversible one-electron dc step was observed even at higher depolarizer concentrations. The half-wave potential was the same as that of the reversible step observed at lower concentrations in the other aqueous base solutions. The positive branch of the electrocapillary curve of [Ru(acac)$_3$] in this solution lied below those obtained in the other supporting electrolyte solutions, whereas the negative branch was essentially the same. Probably, *p*-toluenesulfonate ions replaced the adsorbed [Ru(acac)$_3$] at least partially, and the adsorbed layer of the anions did not retard the electron transfer to any appreciable extent.

Half-wave Potentials. The observed reversible half-wave potentials of [Ru(acac)$_3$] in acetonitrile–TEAP system and in aqueous potassium chloride and other systems were -0.72_5 V and -0.51_6 V, respectively, both being measured against the aqueous SCE as described. The liquid-junction potential between the acetonitrile and the aqueous phases is unknown, but Coetzee and Campion$^{20)}$ have given a semiempirical value of 0.034 V (aqueous side positive) for the junction Et_4NClO_4 (0.1 mol dm^{-3} in acetonitrile)|KCl (saturated in water). Correcting the half-wave potential in acetonitrile for this value, we have a net difference of $E_{1/2}$(acetonitrile)$-E_{1/2}$(water)$=-0.17_5$ V, which may be related to the activities of $[Ru(acac)_3]$ and $[Ru(acac)_3]^-$ in both systems by the following equation:

$$\Delta E_{1/2} = -\frac{1}{nF}(\Delta\mu_{\mathrm{II}}^{\ominus} - \Delta\mu_{\mathrm{III}}^{\ominus}), \tag{1}$$

where $\Delta\mu_{\mathrm{III}}^{\ominus}$ and $\Delta\mu_{\mathrm{III}}^{\ominus}$ are the differences of the standard chemical potentials of $[Ru^{II}(acac)_3]^-$ and $[Ru^{III}(acac)_3]$, respectively, when each species is transferred from water to acetonitrile. The diffusion coefficients of the two species are assumed to be equal for each solvent, and the contribution of the activity coefficients are ignored.

We assume that $\Delta\mu_{\mathrm{II}}^{\ominus}$ is approximated by the Born equation[21]

$$\Delta\mu_{\mathrm{II}}^{\ominus} = -\frac{z^2 e^2 N}{8\pi\,\varepsilon_0\,a}\left\{\frac{1}{\varepsilon_{\mathrm{W}}} - \frac{1}{\varepsilon_{\mathrm{AN}}}\right\}, \tag{2}$$

and $\Delta\mu_{\mathrm{III}}^{\ominus}$ by

$$\Delta\mu_{\mathrm{III}}^{\ominus} = -RT\ln(c_{\mathrm{AN}}^{\mathrm{s}}/c_{\mathrm{W}}^{\mathrm{s}}), \tag{3}$$

where e is the elementary charge; N, Avogadro constant; z, the charge number of the ion ($=-1$); ε_0, the permittivity of vacuum; ε_{w} and $\varepsilon_{\mathrm{AN}}$, the relative permittivities of water and acetonitrile, respectively; $c_{\mathrm{w}}^{\mathrm{s}}$ and $c_{\mathrm{AN}}^{\mathrm{s}}$, the concentrations of the saturated solutions of $[Ru^{III}(acac)_3]$ in the respective solvent. Estimating the ionic radius a to be 0.5 nm, a not unreasonable value, we obtain $\Delta\mu_{\mathrm{II}}^{\ominus} \approx 1.9$ kJ mol^{-1} from Eq. 1. The solubility of $[Ru^{III}(acac)_3]$ in water was about 0.5 mmol dm^{-3}; no reliable estimate of its solubility in acetonitrile was made, but it seemed to be soluble up to about 0.2 mol dm^{-3}. These values lead to $\Delta\mu_{\mathrm{III}}^{\ominus} \approx -14.8$ kJ mol^{-1}. The value of $\Delta E_{1/2}$ thus estimated is about -0.17 V. This unexpectedly good agreement should not be given much confidence in view of the oversimplified model and very rough estimation involved. However, it does suggest that the half-wave potential observed in the acetonitrile–TEAP system represents the reversible half-wave potential of the $[Ru^{III}(acac)_3]/[Ru^{II}(acac)_3]^-$ couple in this solvent.

The reduction step in acetonitrile was shifted to positive potential when TEAP was replaced by sodium perchlorate. But the half-wave potential was independent of the depolarizer concentration at a given concentration of sodium ions. If the half-wave potential in the absence of sodium ions corresponds to the simple reduction as discussed above, this shift must be attributed to sodium ions. Such a shift of half-wave potential caused by alkali metal ions in solvents of lower dielectric constants have been explained by ion-pairing interaction or coordinative relaxation between the reduced form and the cation.[22,23] In the former case the half-wave potential is independent of the depolarizer concentration. Thus, the observed half-wave potential shifts were accounted for by ion-pair formation between $[Ru(acac)_3]^-$ and sodium ions. The details will be reported separately.

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