JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 107–113

Electrochemical characteristics of the Mn(III)/Mn(II) and Co(III)/Co(II) systems at platinum in anhydrous acetic acid solutions

J. MALYSZKO, S. MICHALKIEWICZ, D. GORAL, M. SCENDO

Institute of Chemistry, Pedagogical University, 25-020 Kielce, Poland

Received 4 March 1997; revised 8 June 1997

The electrochemical oxidation of Mn(II) and Co(II) and reduction of Mn(III) and Co(III) at Pt in glacial acetic acid has been investigated by the rotating disc electrode technique. The diffusion coefficients of Mn(III), Mn(II), Co(III) and Co(II) ions, formal potentials and kinetic parameters of the Mn(III)/Mn(II) and Co(III)/Co(II) electrode reactions were evaluated. It was shown that the anodic oxidation of Mn(II) and Co(II) occurs at the surface blocked by a layer of adsorbed acetate ions. In addition, some experiments with an electrochemical quartz crystal microbalance (EQCM) were performed to explain the acetate adsorption on the surface of the polycrystalline platinum electrode.

Keywords: *Mn(III)/Mn(II), Co(III)/Co(II), platinum electrode, anhydrous acetic acid, electrochemical quartz crystal microbalance*

List of symbols

A	electrode area (cm^2)
D	diffusion coefficient (cm^2 s^{-1})
E	electrode potential (V)
$E^{\circ\prime}$	formal potential (V)
f	frequency (Hz)
I_D	disc current (A)
k_a	anodic rate constant (potential dependent)
k_c	cathodic rate constant (potential dependent)
k°	standard (formal) rate constant (cm s^{-1})

Greek symbols

α_a	anodic transfer coefficient (dimensionless)
α_c	cathodic transfer coefficient (dimensionless)
ω	circular frequency (rad s^{-1})

1. Introduction

Manganese(III) and cobalt(III) are powerful oxidizing agents, as indicated by their high standard redox potentials [1]. These species are often used in organic synthesis [2–5] and as oxidants for analytical purposes [6–10]. Another application is the destruction of organic wastes based on mediated electrochemical oxidation [11, 12]. Since the above mentioned species can be electrogenerated, the electrochemistry of the Mn(III)/Mn(II) and Co(III)/Co(II) redox couples has been investigated for several decades. Most electrochemical data reported concern aqueous solutions, whereas nonaqueous media are less frequently considered. However, the species are rather unstable in aqueous solutions. For instance, Co(III) reacts with water to evolve oxygen. The stability of Mn(III) and Co(III) can be enhanced when water is replaced by acetic acid.

The electrogeneration of Mn(III) ions in acetic acid and their chemical properties in this medium has been the subject of a number of studies [13–16]. This reagent was employed in some indirect organic syntheses such as formation of sorbic acid precursors [14] and addition of active methylene compounds to alkenes [16]. Likewise, the generation and practical use of Co(III) in this medium have been investigated. Some authors [17–19] have described the conditions for electrolytical preparation of Co(III) acetate. Pastor and coworkers [20–22] reported the anodic generation of Co(III) as a titrant for coulometric titration in acetic acid. They also described the use of Co(III) for the determination of some organic compounds (e.g. ascorbic acid, hydroquinone and its derivatives).

Despite the practical use of the Mn(III)/Mn(II) and Co(III)/Co(II) systems, their electrochemical characteristics in acetic acid have not been published so far. The aim of the present work was to give some detailed characteristics of the electrode reactions

$$\mathrm{Mn(II)} \rightleftharpoons \mathrm{Mn(III)} + \mathrm{e}^- \qquad (1)$$

and

$$\mathrm{Co(II)} \rightleftharpoons \mathrm{Co(III)} + \mathrm{e}^- \qquad (2)$$

on platinum in this medium. The main experimental technique was rotating disc electrode voltammetry (RDE). This paper is a continuation of our studies on the electrochemical properties of strong oxidants in acetic acid medium [23, 24].

Acetic acid is the most common acidic solvent used in practice. In contrast with water, it exhibits a low dielectric constant, $\varepsilon = 6.2$, and a very low basicity. These factors cause a slight dissociation of all electrolytes in this medium. Since free and triple ions contribute to the transport of electricity, a low electrical conductivity is expected [25]. According to Gordon [26], the 1 : 1 salts are associated to a high degree in acetic acid (about 90%). Therefore, we have used relatively concentrated potassium acetate, 1 M, as the background electrolyte. It should be stressed that the acetate ion is the strongest base that can exist in acetic acid medium.

2. Experimental details

Acetic acid puriss. p.a. ACS, indifferent against chromic acid and acetic anhydride p.a. (both Fluka) were used as obtained. Potassium acetate p.a. (P.O.Ch.) was purified by crystallization and then dried at 120 °C before use. Manganese(II) acetate tetrahydrate purum p.a., manganese(III) acetate dihydrate and cobalt(II) acetate tetrahydrate purum p.a. (all chemicals Fluka) were used without further purification. The content of Mn(III) in $Mn(CH_3COO)_3.2H_2O$ was determined iodometrically. Ferricinium picrate was prepared according to Kolthoff and Thomas [27].

All solutions were purged with argon for 30 min prior to electrochemical experiments. After deaeration, a blanket of argon was kept over the solution.

The working electrode was a home-made rotating ring-disc electrode (RRDE) of polycrystalline platinum ($r_1 = 0.250$ cm, $r_2 = 0.274$ cm, $r_3 = 0.374$ cm, $N_0 = 0.42$). The geometric area of the disc was 0.196 cm^2. The disc was used in some experiments as a stationary electrode. The electrode was mechanically polished with alumina powders of different grain sizes down to 0.05 μm, using water as lubricant, and was then repeatedly rinsed with water. Prior to experiments, the working electrode was kept at −0.5 V in the test solution. Such pretreatment of the electrode was repeated after each voltammetric measurement. Another Pt rotating disc electrode with a geometric area of 0.785 cm^2 was employed as the generating electrode in coulometric measurements.

All voltammetric experiments were carried out in a three-compartment glass cell. Electrode potentials were measured and reported against an external saturated calomel electrode with NaCl solution, SCE(NaCl), connected via a double-junction bridge. A platinum wire was used as the auxiliary electrode. Reference and auxiliary electrodes were individually isolated from the test solution by glass frits.

The electronic setup for voltammetric experiments consisted of a model EP 20A potentiostat (with *IR* compensation) and a model EG 20 function generator (ELPAN). Responses were recorded using a model 4103 X–Y recorder (Laboratorni Pristroje). In experiments with the rotating ring-disc electrode, the potential control was accomplished by means of a model 10/0.2 bipotentiostat (University of Lodz). A Radelkis OH-404A potentiostat/galvanostat with an OH-404B current integrator was used in the coulometric measurements. Electrode potentials were measured using a V-540 digital voltmeter (Meratronik).

The EQCM apparatus was constructed in the Institute of Physical Chemistry (Warsaw) to a published design [28]. Planar AT-cut quartz crystals (Omig, Warsaw) 1.4 cm in diameter were operated at the fundamental frequency of 5 MHz. Platinum film electrodes (0.323 cm^2 area) were evaporated on to the crystals (ITME, Warsaw). The roughness factor of the electrode surface was determined from measurement of the quantity of charge required to form a layer of adsorbed oxygen [29], and was found to be 1.49. The mass sensitivity, k_f, of the EQCM was determined experimentally from $\mathrm{d}f/\mathrm{d}Q$ for lead electrodeposition/dissolution [30] to be 5.65×10^7 Hz cm^2 g^{-1}. The changes in resonant frequency of the quartz oscillator due to mass change were measured on a Philips PM 6685 frequency counter and recorded on a model 4103 X–Y recorder. The frequency resolution of the measurement was approximately 0.1 Hz.

All electrochemical measurements were carried out at 25 ± 0.2 °C.

The viscosity of the solutions was determined at 25 ± 0.05 °C using a BH2 Höppler viscometer (Prüfgeräte-Werk Medingen).

3. Results and discussion

3.1. *Rotating disc electrode experiments*

The electrochemical investigations were carried out at Pt in glacial acetic acid using 1.0 M CH_3COOK as the background electrolyte. All the solutions contained 2 vol % acetic anhydride to remove the residual water. The oxidation and reduction reactions were investigated separately. RDE voltammetric curves were recorded over a range of rotation frequency from 8 to 30 Hz (50.3 to 188.5 rad s^{-1}) at a potential sweep rate of 5 mV s^{-1}. The current–potential curves, both anodic and cathodic were obtained by scanning the working electrode from the potential −500 mV in the anodic direction.

Figure 1 shows a series of RDE voltammograms (solid lines) for oxidation of Mn(II) as recorded at three different rotation frequencies. The lowest voltammogram (dashed curve) was obtained for the background electrolyte alone (namely, the residual current against potential) at the lowest rotation rate. The dotted curves were obtained upon subtracting the residual current from the corresponding current in the presence of Mn(II).

Analogous curves are depicted in Fig. 2 for the cathodic reduction of Mn(III) at a Pt RDE. As follows from Figs 1 and 2, the Mn(III)/Mn(II) system behaves irreversibly at Pt. There is a gap of about 0.3 V between the onset of Mn(III) reduction and Mn(II) oxidation.

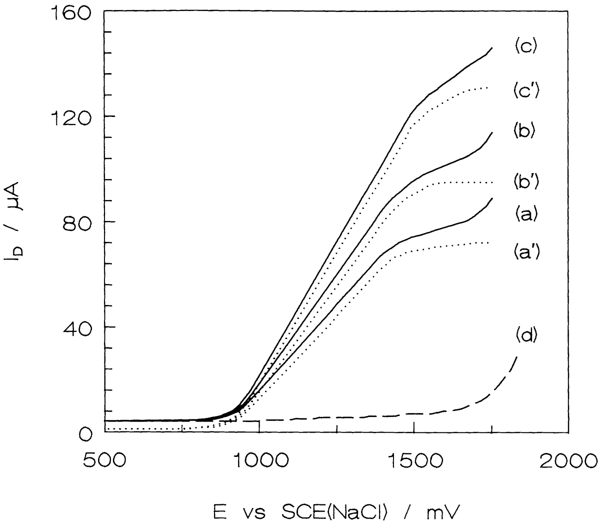

Fig. 1. Voltammetric curves for the anodic oxidation of 4.0×10^{-3} M Mn(II) on a Pt RDE in acetic acid solution containing 1.0 M CH_3COOK as the background electrolyte recorded at rotation frequencies: (a) 8, (b) 16 and (c) 30 Hz. The voltammogram (d) is the residual current obtained in the absence of Mn(II) at a rotation frequency of 8 Hz. The curves (a′), (b′) and (c′) were obtained upon subtracting the residual current from the corresponding anodic currents in the presence of Mn(II). Scan rate 5 mV s^{-1}.

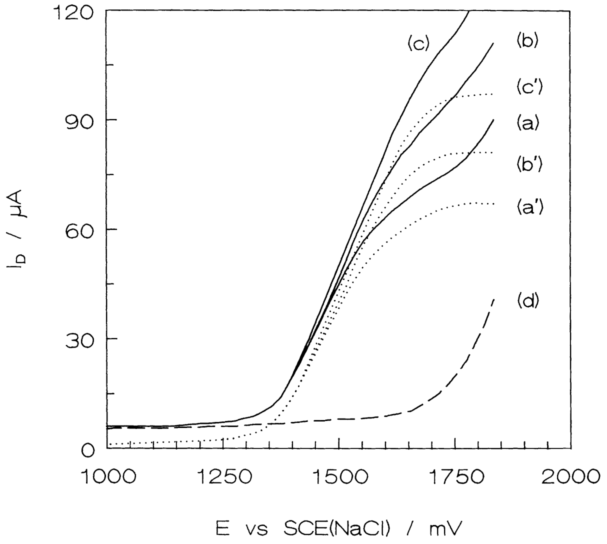

Fig. 3. Voltammetric curves for the anodic oxidation of 4.0×10^{-3} M Co(II) on a Pt RDE at rotation frequencies: (a) 8, (b) 16 and (c) 30 Hz. Curve (d) is the residual current. The curves (a′), (b′) and (c′) were obtained upon subtracting the residual current from the corresponding anodic currents in the presence of Mn(II). The other experimental conditions as in Fig. 1.

Further voltammetric experiments were performed with the Co(III)/Co(II) system. Figure 3 shows a family of voltammetric curves for the anodic oxidation of Co(II) at a Pt RDE. The curves recorded were then corrected for the contribution from the residual current similarly to those in Fig. 1.

Additional experiments were performed using the rotating ring-disc electrode technique (RRDE). In this set of experiments, cobalt(III) was generated at the disc electrode from a solution containing 4.0×10^{-3} M Co(II), and monitored at the ring. The ring current behaviour confirmed that the anodic reaction (2) occurs with a current efficiency of 100%. Co(III) solutions were then prepared by anodic oxidation of Co(II) under constant current from a solution containing 4.0×10^{-3} M Co(II). The increase in concentration of Co(III) was followed by coulometry. The final solution containing 1.46×10^{-3} M was used to record voltammetric curves for the cathodic reduction of Co(III) (not shown).

3.2. *Limiting currents*

The nature of the limiting currents was verified using the Levich equation. Figure 4 shows the limiting current against the square root of the circular rota-

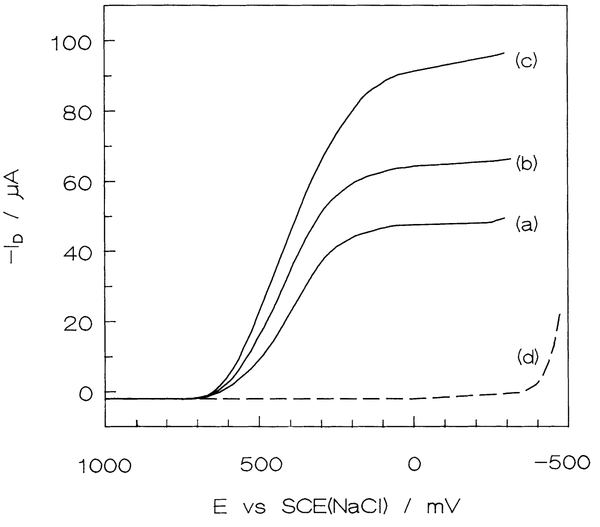

Fig. 2. Voltammetric curves for the cathodic reduction of 2.94×10^{-3} M Mn(III) on a Pt RDE at rotation frequencies: (a) 8, (b) 16 and (c) 30 Hz. Curve (d) is the residual current. The other experimental conditions as in Fig. 1.

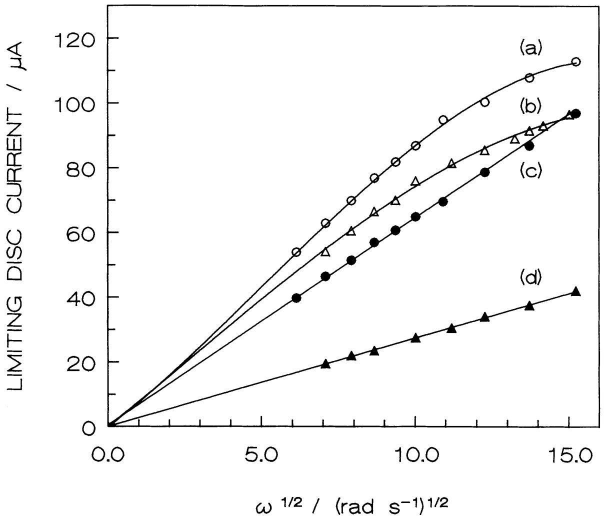

Fig. 4. Dependence of the limiting disc current for the anodic oxidation of (a) 4.0×10^{-3} M Mn(II), (b) 4.0×10^{-3} M Co(II) and cathodic reduction of (c) 2.94×10^{-3} M Mn(III), (d) 1.46×10^{-3} M Co(III) on the square root of the circular frequency.

tion frequency, $\omega^{1/2}$, for all the reactants studied. In the case of Mn(III) and Co(III) reduction, the plots are linear and pass through the origin, in agreement with the Levich equation for a diffusion-controlled limiting current. Otherwise, the dependencies of the limiting current on $\omega^{1/2}$ for the anodic oxidation of Mn(II) and Co(II) are linear only within a limited range of rotation frequency, at $\omega \rightarrow 0$. At higher rotation frequencies, deviation from linearity is seen.

From these data, the diffusion coefficients of Mn(III) and Co(III) ions were calculated via the Levich equation. The viscosity and density of 1.0 M CH_3COOK solution, needed for the calculations, were determined to be $3.81 \times 10^{-2}\,g\,cm^{-1}\,s^{-1}$ and $1.100\,g\,cm^{-3}$, respectively. The values of diffusion coefficients are given in Table 1. Based on the diffusion coefficients determined, we calculated the effective radii of these species using the Einstein–Stokes equation. Thus, values of 0.51 and 0.66 nm were obtained for Mn(III) and Co(III) ions, respectively.

3.3. *Adsorption of acetate ions*

The electrochemical oxidation of Mn(II) and Co(II) species seems to be linked to other processes occurring at the electrode. According to the theory developed by Scheller *et al.* [31, 32] and Delamar *et al.* [33, 34], such behaviour may result from the partial blocking of the electrode surface.

To confirm the above hypothesis, we recorded cyclic voltammetric curves using an RDE. In this experiment the scan was reversed in the cathodic direction at various potentials of the anodic wave of Co(II) oxidation (Fig. 5). The backward voltammograms obtained are markedly shifted in the positive direction with respect to the forward ones. The magnitude of this hysteresis increases progressively with increase in switch potential.

The above results indicate that Reactions 1 and 2 occur in the anodic direction on a partially blocked electrode surface. Similar results were obtained for the electrochemical oxidation of Tl(I) to Tl(III) in the same medium [23].

Adsorption of acetate ions from aqueous solutions is well known [35–42]. However, there were no data concerning the adsorption of acetate anions from acetic acid solutions.

Further experiments were carried out using voltammetric and EQCM techniques. The basic feature of this method is the linear relationship between the accumulation of mass Δm per cm^2 on the working electrode and the resulting change $-\Delta f$ in the resonance frequency, given by Sauerbrey [43]. This relationship may be described in the following form:

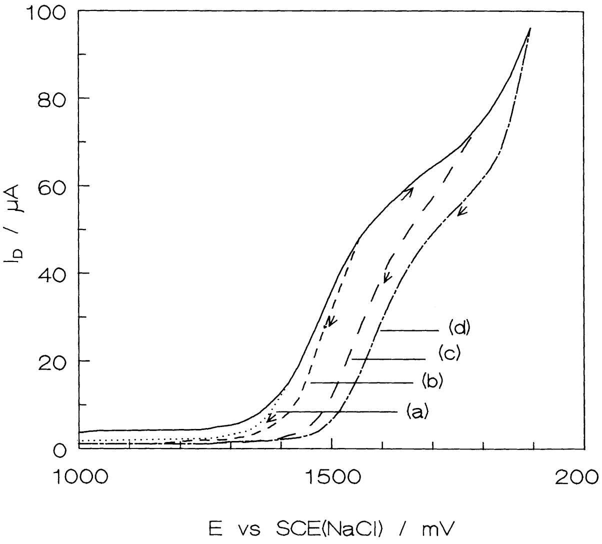

Fig. 5. Consecutive cyclic voltammetric curves obtained at a Pt RDE in solution containing 4.0×10^{-3} M Co(II) and 1.0 M CH_3COOK. All potential scans were initiated at 400 mV and reversed at (a) 1400, (b) 1560, (c) 1800 and (d) 1900 mV, respectively. Rotation frequency 8 Hz; potential scan rate $5\,mV\,s^{-1}$. Arrows indicate direction of potential scanning.

$$\Delta f = -k_f \Delta m / A \qquad (3)$$

where k_f is the mass sensitivity and A is the geometric surface area of the deposits.

In this series of experiments, the initial potential was scanned at $5\,mV\,s^{-1}$ from 0 to 1.7 V and back to 0 V. Figure 6 shows frequency-potential curves obtained for 0.2 M $NaClO_4$ electrolyte in the absence (curve a) and presence (curve b) of 0.02 M CH_3COONa. The $\Delta f/E$ curve recorded in the absence of acetate anions is essentially featureless. Only a small increase in mass is observed at potentials above 1.3 V. The present result points to the weakness of the adsorption of perchlorate anions on platinum and is not unexpected on electrostatic grounds.

The influence of CH_3COO^- ions on the frequency response is significant. The large decrease in frequency (about 5.6 Hz) between 0.75 and 1.75 V in the positive-going scan is attributed to the adsorption of acetate anions. During the reverse scan, the frequency remains constant in the potential range 1.75 to 1.0 V. A gradual frequency increase (i.e. mass decrease) occurs in the potential range up to 0.2 V. The frequency at 0 V after the potential scan returns to the initial value within experimental error. This mass loss can be ascribed to the reverse process (i.e. desorption of acetate ions). The results are in good agreement

Table 1. Formal electrode potentials and kinetic parameters of the Mn(III)/Mn(II) and Co(III)/Co(II) systems

Redox system	$E^{\circ\prime}$ *vs SCE(NaCl)* /mV	$E^{\circ\prime}$ *vs Fic*$^+$*/Foc* /mV	$10^6 D_{Me(III)}$ /$cm^2\,s^{-1}$	k° /$cm\,s^{-1}$	α_c	k°_{eff} /$cm\,s^{-1}$	α_a
Mn(III)/Mn(II)	746	390	1.12	2.3×10^{-5}	0.28	7.0×10^{-6}	0.31
Co(III)/Co(II)	926	570	0.87	3.0×10^{-6}	0.33	5.0×10^{-7}	0.34

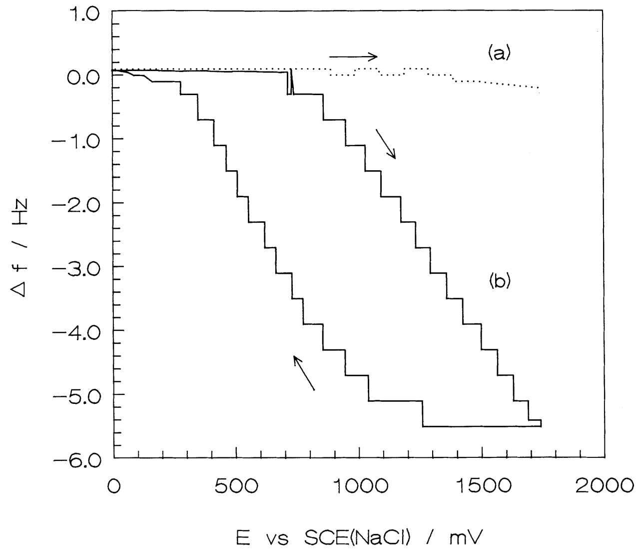

Fig. 6. Frequency-potential response curves for a single cyclic scans originating at 0 V in (a) 0.2 M $NaClO_4$ and (b) 0.2 M $NaClO_4$ + 0.02 M CH_3COONa. Scan rate 5 mV s^{-1}. Arrows indicate direction of potential scanning.

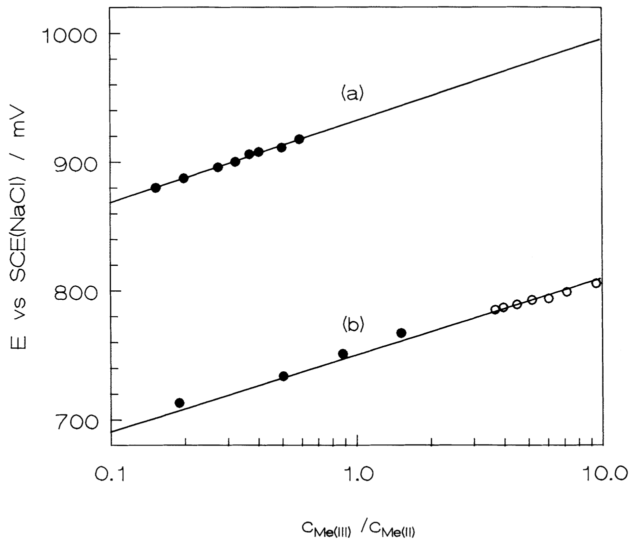

Fig. 7. Equilibrium potentials of the redox couples: (a) Co(III)/Co(II) and (b) Mn(III)/Mn(II) as a function of the concentration ratio $c_{Me(III)}/c_{Me(II)}$ where Me = Co, Mn. Data points (○) were obtained during the cathodic reduction of Mn(III).

with those obtained by cyclic voltammetry. The observed frequency change of 5.6 Hz corresponds to a net mass increase, Δm, of 31.8 ng, and a surface concentration of acetate anions equal to 1.12×10^{-9} mol cm^{-3}, assuming a roughness factor of 1.49. In the potential dependence of the mass changes, the ionic character of the $-COO^-$ group plays a dominant role. Thus, it is reasonable to assume that acetate ions are adsorbed vertically through the carbonyl group. Moreover, it seems that under the present experimental conditions no decomposition of acetates occurs.

From the above experiments, it is evident that strong adsorption of acetate anions on the Pt surface takes place in the same potential range in which Reactions 1 and 2 proceed in the anodic direction. In contrast, the cathodic reduction of Mn(III) and Co(III) ions occurs on the bare Pt surface if the electrode potential is scanned in the positive direction beginning from the onset of hydrogen evolution. The electrode surface can be cleaned by mild cathodization in the HER region.

3.4. *Formal potentials*

The formal potentials of the Co(III)/Co(II) and Mn(III)/Mn(II) redox pairs needed for the calculation of the standard (formal) rate constants were estimated by carrying out controlled-current macroelectrolysis. During the conversion of Me(II) into Me(III), where Me = Mn or Co, the increase in concentration of Me(III) was followed by coulometry. The electrolysis was repeatedly interrupted to permit the measurement of the equilibrium potential. In the case of the Mn(III)/Mn(II) system, the generation of Mn(II) from Mn(III) was also performed. Figure 7 shows these potentials as a function of the $c_{Me(III)}/c_{Me(II)}$ ratio, in semilogarithmic coordinates. The plots obtained are linear with a reciprocal slope of 60 and 63 mV $decade^{-1}$ for Mn(III)/Mn(II) and Co(III)/Co(II) system, respectively. These values are in reasonable agreement with theoretical predictions for a reversible one-electron reaction. The formal potentials were determined by extrapolation of these plots to $c_{Me(III)}/c_{Me(II)} = 1$.

The values of $E^{\circ\prime}$ were also expressed against the potential of the ferricinium ion/ferrocene (Fic^+/Foc) redox pair, which is recommended by Gritzner and Kuta [44] as a solvent independent system. The formal potentials of Fic^+/Foc electrode were evaluated from RDE voltammetric measurements performed under experimental conditions identical to those used in the study. All the $E^{\circ\prime}$ values obtained are listed in Table 1.

3.5. *Electrode reaction kinetics*

The kinetics of the electrode reactions Mn(III) + e^- → Mn(II) and Co(III) + e^- → Co(II) were investigated on bare Pt, within the potential limits of 0.25 to 0.6 V, by means of the RDE technique in a manner similar to that used in polarography for quasi-reversible waves. In order to evaluate the potential dependent rate constants, k_c, the voltammograms were analysed using relations derived earlier [45]. As shown in Fig. 8, the logarithms of the cathodic rate constants for the systems investigated are linear functions of the electrode potential. From the plots of k_c against E, the standard (formal) rate constants, k°, were found, and the cathodic transfer coefficients, α_c, were evaluated from the slopes. The kinetic parameters determined are given in Table 1.

The transfer coefficients for the reduction of Mn(III) and Co(III) were found to be 0.28 and 0.33, respectively. These data point to asymmetrical energy

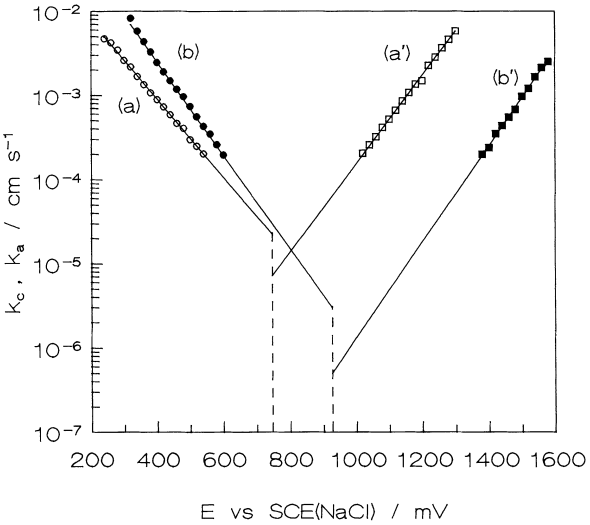

Fig. 8. Potential dependencies of the rate constant for the cathodic reduction of (a) Mn(III) and (b) Co(III), as well as for the anodic oxidation of (a′) Mn(II) and (b′) Co(II) at Pt. Vertical dashed lines correspond to the formal potentials of Mn(III)/Mn(II) and Co(III)/Co (II) couples.

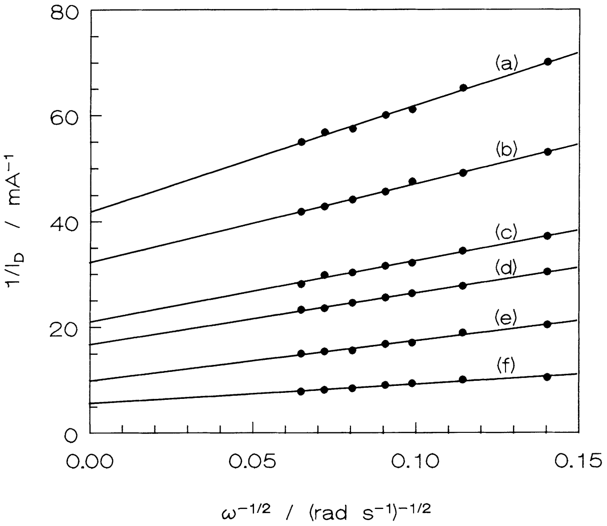

Fig. 9. Plots of the reciprocal disc current against the reciprocal square root of the circular frequency for the anodic oxidation of 4.0×10^{-3} M Mn(II). Composition of the solution as in Fig. 1. Electrode potential: (a) 1060, (b) 1080, (c) 1120, (d) 1160, (e) 1200 and (f) 1240 mV.

barriers of both electron transfer reactions. It should be noted that the same value of α_c was reported by Vetter and Manecke [46] for the Mn(III)/Mn(II) system in 7.5 M aqueous solution of H_2SO_4. An analogous comparison with the Co(III)/Co(II) system in aqueous noncomplexing solutions is impossible for lack of data. However, the kinetic parameters of this system are known for aqueous solutions containing several diamines as the ligands. In this case, Bartelt *et al.* [47–50] reported values of α_c varying between 0.24 and 0.40.

The potential dependent rate constants, k_a, for Reactions 1 and 2 in the anodic direction were evaluated using a modified method of Jahn and Vielstich [51, 52]. For this purpose, the disc current was measured point-by-point at a fixed potential and various rotation frequencies. The results were plotted as $1/I_D$ against $1/\omega^{1/2}$, to determine the activation currents by extrapolation to $\omega^{-1/2} \rightarrow 0$, that is, to infinite rotation frequency. The procedure is exemplified in Fig. 9.

The variation of k_a with the electrode potential is presented in Fig. 8. From these plots, values of the apparent standard rate constants, k°_{eff}, were evaluated by extrapolation to the formal potentials. From the slopes of these dependencies, the effective anodic transfer coefficients, α_a, were calculated.

As seen in Fig. 8, the values of the apparent standard rate constants, k°_{eff}, obtained from the kinetic data for anodic oxidation of Mn(II) and Co(II) are considerably lower than those evaluated from the Tafel curves for the cathodic reactions.

If both reactions were simple electron transfers, coefficients α_a and α_c would sum to one and the standard rate constants would be identical. In the case of the Co(III)/Co(II) and Mn(III)/Mn(II) systems, the sum of the two charge transfer coefficients is not equal to one because of the surface phenomena. The different rates for the anodic and cathodic reactions confirm that the anodic oxidation processes of Mn(II) and Co(II) are not simple electron transfer reactions. This, together with the decrease in standard rate constant indicates that the surface coverage of the electrode by chemisorbed acetate anions constitutes the main factor determining the kinetics of anodic oxidation of the ions studied. The interaction of the methyl group with the electrode surface in the considered potential range may be excluded. Hence, the acetate complexes of Mn(II) or Co(II) cations cannot approach the surface to enable the charge transfer which is achieved in the absence of the adsorbed layer.

The degree of coverage by adsorbed anions may be calculated by using the simple equation [53, 54]

$$k^\circ_{eff} = k^\circ(1 - \theta) \tag{4}$$

where θ denotes the degree of coverage of the electrode surface. The θ values thus obtained at the formal potentials are 0.70 and 0.83, respectively, for the Mn(III)/Mn(II) and Co(III)/Co(II) redox systems. From the position of the considered formal potentials, it is clear that the value of θ in the case of anodic oxidation of Co(II) is greater than that for the oxidation of Mn(II).

4. Conclusions

It has been shown that the cathodic reduction of Mn(III) and Co(III) ions occurs on a bare Pt surface. In contrast, the adsorption of acetate anions at the electrode has a strong inhibiting effect on the kinetics of the Mn(II) and Co(II) anodic oxidation. The degree of coverage of the electrode surface by acetate ions has been estimated to be 0.70 and 0.83 at the formal potentials of Mn(III)/Mn(II) and Co(III)/Co(II) systems, respectively.

Future studies will seek to obtain kinetic information for the mediated oxidation of some organic compounds by electrogenerated Mn(III) and Co(III) ions in glacial acetic acid.

References

[1] A. J. Bard, J. Jordan and R. Parsons (Eds), 'Standard Potentials in Aqueous Solutions', Marcel Dekker, New York and Basel (1985).

[2] R. A. Sheldon and J. K. Kochi, 'Metal Catalysed Oxidations of Organic Compounds', Academic Press, New York (1982).

[3] S. Torii 'Electroorganic Syntheses', Part I, VCH, Weinheim (1985).

[4] A. H. Haines 'Methods for the Oxidation of Organic Compounds', Academic Press, London (1988).

[5] P. Vaudano, E. Plattner and Ch. Comninellis, *Chimia* **49** (1995) 12.

[6] A. Berka, J. Vulterin and J. Zyka, 'New Redox Methods in Analytical Chemistry' (in Russian) Khimiya, Moscow (1968).

[7] J. Barek and A. Berka, *Chem. Listy* **69** (1975) 1056.

[8] A. Berka and J. Barek, *ibid.* **79** (1985) 242.

[9] T. J. Pastor, V. J. Vajgand and Z. Kicovic, *Microchim. Acta* **2** (1976) 525.

[10] T. J. Pastor, V. J. Vajgand and V. V. Antonijević, *ibid.* **2** (1978) 131.

[11] J. C. Farmer, F. T. Wang, P.R. Lewis and L. J. Summers, *J. Electrochem. Soc.* **139** (1992) 3025.

[12] J. C. Farmer, F. T. Wang, P. R. Lewis and L. J. Summers, *Trans. I. Chem. E.* **70B** (1992) 158.

[13] J. H. Wagenknecht, J. P. Coleman, R. C. Hallcher, D. E. McMackins, T. E. Rogers and W. G. Wagner, *J. Appl. Electrochem.* **13** (1983) 535.

[14] Sa van Ho *J. Appl. Electrochem.* **17** (1987) 398.

[15] J. P. Coleman, R. C. Hallcher, D. E. McMackins, T. E. Rogers and J. H. Wagenknecht, *Tetrahedron* **47** (1991) 809.

[16] J.-Y. Nedelec, I. Lachaise, K. Nohair, J. P. Paugam and M. Hakiki, *Bull. Soc. Chim. Fr.* **132** (1995) 843.

[17] J. Budesinky, J. Dolezal, B. Sramkova and J. Zyka, *Microchem. J.* **16** (1971) 121.

[18] U. Bakir Ogutveren, R. E. Plimley and I. Nieva, *J. Appl. Electrochem.* **22** (1992) 351.

[19] E. Sener, A. E. Karagozler and A. T. Pekel, *Anal. Chim. Acta* **335** (1996) 35.

[20] T. J. Pastor and I. Ciric, *Microchim. Acta* **2** (1985) 253.

[21] T. J. Pastor, V. V. Antonijevic and D. D. Manojlovic, *Anal. Chim. Acta* **258** (1992) 161.

[22] T. J. Pastor, V. V. Antonijević and J. Barek, *Microchim. Acta* **117** (1995) 153.

[23] J. Malyszko and S. Michalkiewicz, *Polish J. Chem.* **68** (1994) 153.

[24] J. Malyszko and S. Michalkiewicz, *in* The 2nd International Symposium 'Electrochemistry in Practice and Theory' (edited by H. Scholl) Lodz University Press, Lodz (1985), p. 12.

[25] O. Popovych and R. P. T Tomkins, 'Nonaqueous Solution Chemistry', J. Wiley & Sons, New York (1981), chapter 3.

[26] J. E. Gordon, 'The Organic Chemistry of Electrolyte Solutions', J. Wiley & Sons, New York (1975), chapter 3.2.

[27] I. M. Kolthoff and F. G. Thomas, *J. Phys. Chem.* **69** (1968) 3049.

[28] W. Koh, W. Kutner, M. T. Jones and K. M. Kadish, *Electroanalysis* **5** (1993) 209.

[29] R. Woods, *in* 'Electroanalytical Chemistry', Vol. 9 (edited by A. J. Bard) Marcel Dekker, New York (1976), p. 1.

[30] L. A. Larew, J. S. Gordon, Y.-L. Hsiao, D. C. Johnson and D. A. Buttry, *J. Electrochem. Soc.* **137** (1990) 3071.

[31] F. Scheller, R. Landsberg and H. Wolf, *Z. Phys. Chem.* **243** (1970) 345.

[32] *Idem*, *Electrochim. Acta* **155** (1970) 525.

[33] M. Delamar, Minh Chau Pham, P.-C. Lacaze and J.-E. Dubois, *J. Electroanal. Chem.* **108** (1980) 1.

[34] P.-C. Lacaze, Minh Chau Pham, M. Delamar and J.-E. Dubois, *J. Electroanal. Chem.* **108** (1980) 9.

[35] A. A. Yakovleva, S. N. Kaydalova, Ya. B. Skuratnik and V. I. Veselovskii, *Elektrokhimiya* **8** (1972) 1799.

[36] G. Horanyi, *J. Electroanal Chem.* **51** (1974) 163.

[37] A. A. Yakovleva, *Elektrokhimiya* **15** (1979) 1318.

[38] A. Wieckowski, J. Sobkowski, P. Zelenay and K. Franaszczuk, *Electrochim. Acta* **26** (1981) 1111.

[39] G. Horanyi and E. M. Rizmayer, *J. Electroanal. Chem.* **227** (1987) 223.

[40] L. M. Rice, E. K. Krauskopf and A. Wieckowski, *ibid.* **239** (1988) 413.

[41] D. P. Root and N. Priyantha, *Electrochim. Acta* **36** (1991) 2109.

[42] A. Rodes, E. Pastor and T. Iwasita, *J. Electroanal. Chem.* **376** (1994) 109.

[43] G. Sauerbrey, *Z. Phys.* **155** (1959) 206.

[44] G. Gritzner and J. Kuta, *Electrochim. Acta* **29** (1984) 869.

[45] J. Malyszko, *Chimia* **29** (1975) 166.

[46] K. J. Vetter, 'Elektrochmische Kinetik', Springer Verlag, Berlin (1961), chapter 4.

[47] H. Bartelt and H. Skilandat, *J. Electroanal. Chem.* **23** (1969) 407.

[48] *Idem*, *ibid.* **24** (1969) 207.

[49] H. Bartelt, *ibid.* **25** (1970) 79.

[50] *Idem*, *Electrochim. Acta* **16** (1971) 629.

[51] D. Jahn and W. Vielstich, *J. Electrochem. Soc.* **109** (1962) 849.

[52] J. Malyszko and D. Gierulska, *Monatsh. Chem.* **115** (1984) 1401.

[53] J. Lipkowski and Z. Galus, *J. Electroanal. Chem.* **61** (1975) 11.

[54] *Idem*, *ibid.* **98** (1979) 91.