



Electrochemical behaviour of $\text{Mn}^{3+}/\text{Mn}^{2+}$, $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox mediators in methanesulfonic acid

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Abstract

The redox behaviour of $\text{Mn}^{3+}/\text{Mn}^{2+}$, $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ mediators commonly used in indirect oxidation of organic compounds were evaluated in methane sulfonic acid on a glassy carbon working electrode employing cyclic voltammetry. Manganic methanesulfonate exhibits higher instability in dilute methanesulfonic acid. The solid MnO_2 formed during disproportionation on the glassy carbon electrode further affects the reproducibility. Cobaltic methanesulfonate formation occurs only at oxygen evolution region rendering the overall oxidation process less efficient. Ceric methane sulfonate formation is highly efficient over a wide acid concentration range. Ceric methanesulfonate can also be employed over a wide temperature range to oxidize different aromatic compounds.

1. Introduction

In the indirect electrochemical oxidation of aromatic compounds, involving nuclear oxidation of naphthalene to naphthaquinone and side chain oxidation of alkyl group to aldehyde group, $\text{Mn}^{3+}/\text{Mn}^{2+}$, $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox mediators are commonly employed. Sulfuric acid, acetic acid, phosphoric acid, nitric acid and perchloric acid medium have been generally employed as electrolyte media for the electrogeneration of these oxidizing agents. Recently methanesulfonic acid (MSA) was found to possess some attractive features as electrolyte medium for the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox mediator in indirect electro organic synthesis [1–5]. A current potential curve showing a small diffused wave due to electrochemical oxidation of Ce^{3+} has been reported in methanesulfonic acid [3]. A more comprehensive voltammetric study along with the influence of organic additives on the voltammetric behaviour of $\text{Ce}^{4+}/\text{Ce}^{3+}$ in methane sulfonic acid has been reported from this laboratory recently [6].

However, $\text{Mn}^{3+}/\text{Mn}^{2+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ redox couples, which find applications in indirect electroorganic synthesis, have not been investigated in methanesulfonic acid. How does the voltammetric behaviour of these two redox systems compare with those of $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox system? What is the specific influence of methanesulfonic acid medium on the redox behaviour with special reference to their use as redox mediators? These questions are addressed in this study.

2. Experimental details

A single compartment cell with a glassy carbon working electrode, a platinum counter electrode and a saturated calomel reference electrode was used for the voltammetric studies. Tokai GC A-type glassy carbon (dia. 5 mm) was polished, cleaned and electrochemically activated using potential cycling according to the procedure described earlier [7]. All the chemicals were of AnalaR (AR) grade and were used as such. Triply distilled water was used throughout the experiments.

The stock solutions of manganous, cobaltous and cerous methanesulfonate were prepared by treating the respective carbonates (AR) and methanesulfonic acid in stoichiometric amounts to convert the carbonates to their methanesulfonate and finally adding water to get the desired concentration of the mediators and acid.

3. Results and discussion

3.1. Manganic/manganous redox couple in methanesulfonic acid

Typical cyclic voltammograms of 100 mM Mn^{2+} in 4.0 M methane sulfonic acid at different sweep rates are presented in Figure 1. At higher sweep rate ($\leq 40 \text{ mV s}^{-1}$), a broad anodic wave (a_f) is noticed around 1.4 V. This is followed by a cathodic peak (c_f) around 1.25 V in the reverse sweep. At slow sweep rates, a sharp oxidation

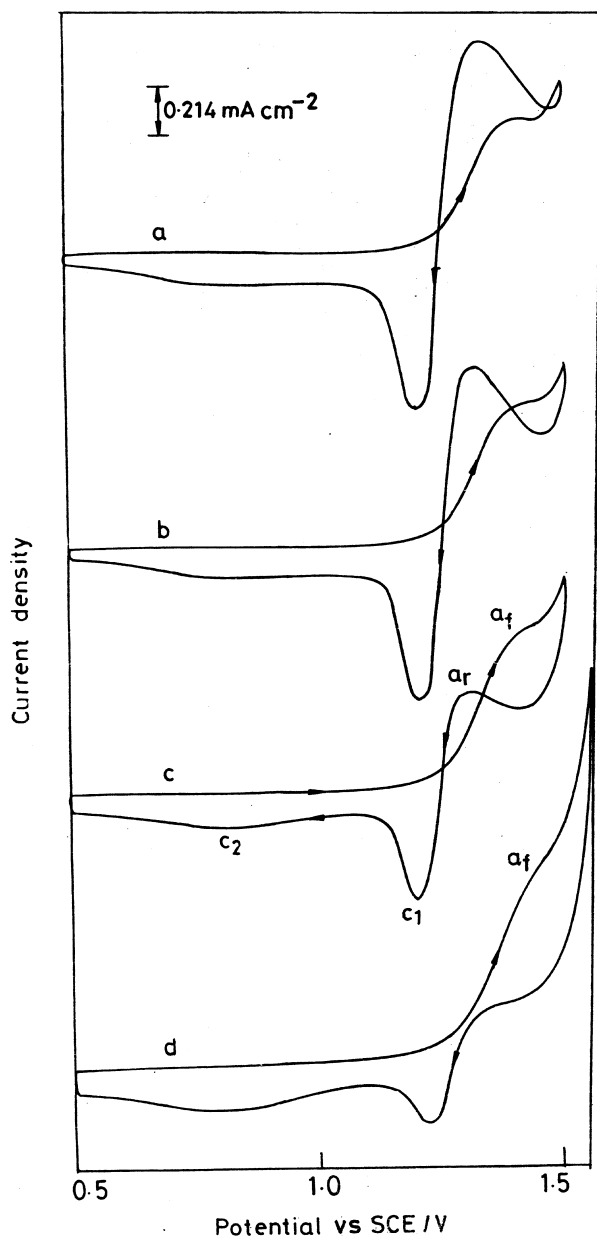


Fig. 1. Typical cyclic voltammogram of 100 mM Mn^{2+} in 4.0 M MSA on GCE at different sweep rates, v : (a) 5, (b) 10, (c) 20 and (d) 40 mV s^{-1} .

peak (a_r) around 1.3 V is noticed on the reverse sweep. The peak current value of this unusual anodic peak is found to increase significantly with decreasing sweep rate (Figure 1, curves (a) to (d)). No distinct cathodic peak is noticed in the potential region below 1.0 V upto 2.0 M MSA. However, a distinct new cathodic peak (c_2) is noticed around 0.9 V at 4.0 M MSA and above. At higher acid concentrations Mn^{3+} is stabilised to some extent and this species gives rise to the cathodic peak c_2 .

a_f is probably due to the oxidation of Mn^{2+} to Mn^{3+} . Based on the above and subsequent observations seen later it is proposed that, at the low acid concentrations of 2.0 M and 4.0 M methanesulfonic acid, Mn^{3+} generated on the anode surface immediately disproportionates leading to the formation of MnO_2 deposit on the

glassy carbon electrode surface. c_1 observed in the cathodic sweep is due to the reduction of this MnO_2 deposit on the electrode. At sufficiently slow sweep rate, significant MnO_2 nuclei are generated during the anodic polarization. Further growth of MnO_2 increases the anodic current even during the reverse sweep leading to the formation of the distinct anodic peak a_r .

Typical cyclic voltammograms showing the effect of concentration of Mn^{2+} in 8.0 M MSA at a slow sweep rate of 5 mV s^{-1} are presented in Figure 2. At higher concentrations of Mn^{2+} , some of MnO_2 formation is observed even in 8.0 M MSA especially at slow sweep rate. An increase in anodic current during the reverse sweep is noticed with increasing Mn^{2+} concentration (Figure 2, curves (a) to (c)). However, i_{par} is not greater than i_{paf} , as noticed in 2.0 M and 4.0 M MSA medium. These observations suggest that with increasing acid

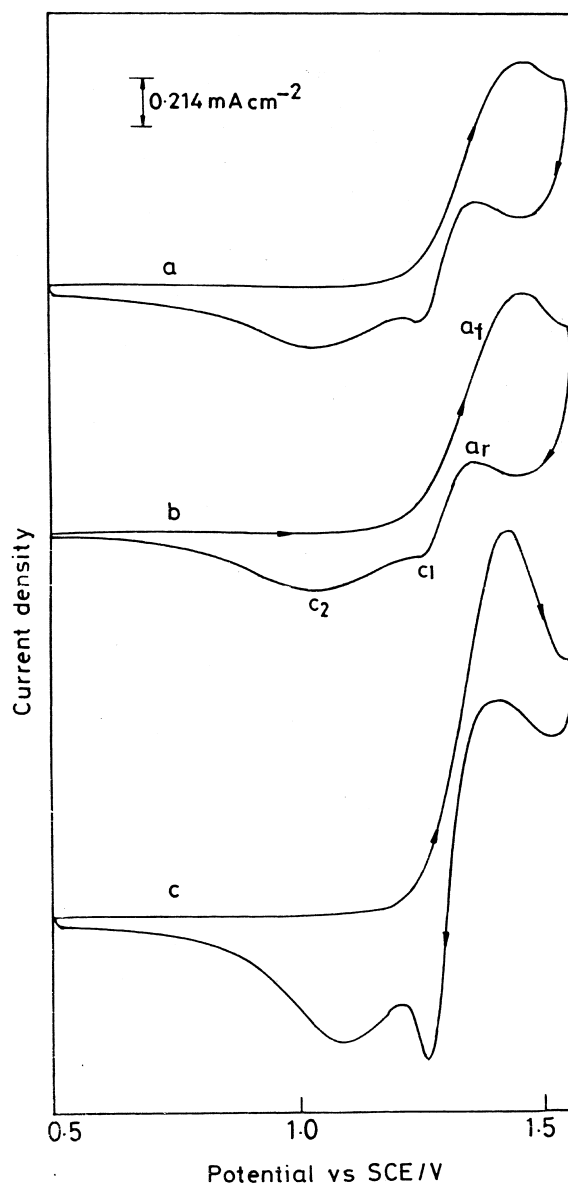


Fig. 2. Typical cyclic voltammograms showing the concentration effect of Mn^{2+} in 8.0 M MSA at 5 mV s^{-1} . Mn^{2+} concentration: (a) 80, (b) 100 and (c) 120 mM.

concentration there is considerable decrease in the formation of MnO_2 on electrode surface.

The anodic peak current values increase linearly with Mn^{2+} concentration. A close comparison of peak current values between i_{paf} and i_{pc2} in both Figures 1 and 2 indicates that, under identical experimental conditions, i_{paf} is substantially higher than i_{pc2} . This suggests that the anodic oxidation current always involves some competitive process such as MnO_2 formation, or oxygen evolution, or even chemical decomposition of electro-generated Mn^{3+} by reaction with water.

All these experimental results from cyclic voltammetric studies clearly indicate that Mn^{3+} disproportionation is also a predominant process in MSA. This process is similar to that observed in sulfuric acid [8, 9]. From the practical view point it appears that electrogeneration of Mn^{3+} in 8.0 M MSA at Mn^{2+} concentration below 100 mM would lead to maximum efficiency of electro-generation.

3.2. Cobaltic/cobaltous redox couple in methanesulfonic acid

Cyclic voltammetric measurements on the redox behaviour of $\text{Co}^{3+}/\text{Co}^{2+}$ in methanesulfonic acid led to some peculiar reproducibility problems. Preliminary voltammograms recorded using cobaltous methanesulfonate show a diffused oxidation peak around 1.7–1.8 V along with background oxidation. Even this could not be reproduced to a satisfactory level. The oxidation of the glassy carbon surface itself and the inhibiting effect of this oxide layer was presumed to be responsible for the irreproducibility problems. It was then decided to prepare cobaltic methanesulfonate electrochemically and evaluate its reduction behaviour, which required lower potential where glassy carbon oxidation can be completely avoided. Cobaltic methanesulfonate exhibited a distinct reduction peak around 0.5 V on glassy carbon at room temperature. Typical cyclic voltammograms recorded for 175 mM cobaltic methanesulfonate at room temperature at regular intervals of 15 min are shown in Figure 3A. A decrease in cathodic peak current with time clearly indicates fast kinetics for the reaction between cobaltic methanesulfonate with water or related side reactions. To further confirm the temperature effect, the bath temperature was reduced to 5 °C after recording curve (e) in Figure 3A. The cathodic peak current once again remained stable at 5 °C, as shown in Figure 3B. At 5 °C the cathodic peak current due to cobaltic methanesulfonate was found to increase linearly with concentration. The cathodic peak current was also found to increase linearly with square root of sweep rate. All these observations suggest that cobaltic methanesulfonate undergoes simple diffusion controlled reduction at 5 °C and the electrogenerated cobaltic methanesulfonate is also quite stable at this temperature.

The cyclic voltammograms obtained for cobaltic methanesulfonate in the presence of toluene recorded

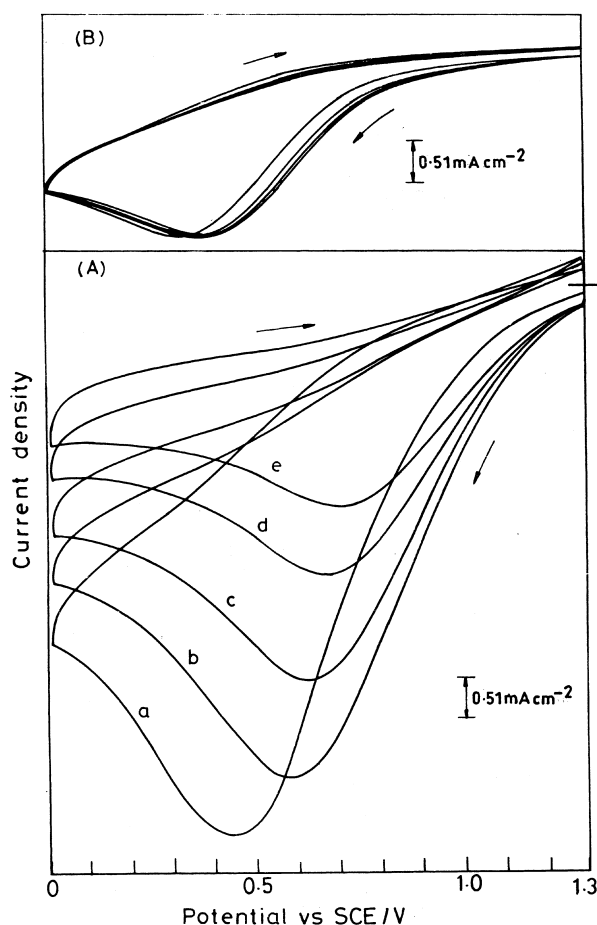


Fig. 3. Typical cyclic voltammograms of (A) 175 mM Co^{3+} in 4.0 M MSA at 40 mV s^{-1} and at $30 \text{ }^\circ\text{C}$; and (B) Co^{3+} solution after recording curve (e) in Figure 3A. Temp. $5 \text{ }^\circ\text{C}$. Both voltammograms (A and B) recorded at 15 min interval.

at regular time intervals of 30 min are shown in Figure 4. The cathodic peak current due to cobaltic species decreases with time indicating chemical oxidation of toluene at $5 \text{ }^\circ\text{C}$. Toluene is among the easier compounds which undergo oxidation with Co^{3+} . A fairly difficult compound, namely *O*-nitrotoluene, was also used for comparative evaluation. Since this compound was not soluble in methane sulfonic acid solution, 0.01% Cetyltrimethyl ammonium bromide (CTAB) was added to improve the solubility. The cyclic voltammograms of cobaltic methanesulfonate containing 42 mM *O*-nitrotoluene were recorded at regular time intervals. The consumption rate of cobaltic methanesulfonate as measured by the cathodic peak current at different time intervals for toluene and *O*-nitrotoluene are also compared in Figure 5. Even at prolonged times the cathodic peak current did not decrease substantially. This suggests that Co^{3+} does not exhibit a satisfactory oxidation rate for *O*-nitrotoluene at $5 \text{ }^\circ\text{C}$.

The present voltammetric investigation on cobaltic methanesulfonate in methane sulfonic acid suggests that the electrochemical generation of cobaltic species occurs at a potential close to oxygen evolution region. Hence, the overall current efficiency for electrogeneration under

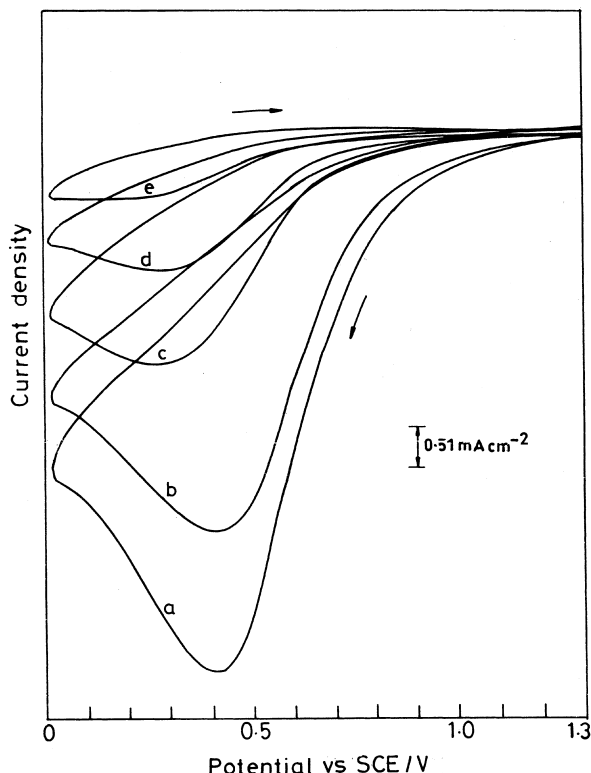


Fig. 4. Typical cyclic voltammograms of 175 mM Co^{3+} and 42 mM of toluene recorded at 40 mV s^{-1} . Temp. 5°C . Acid concentration 4.0 M MSA. Time: (a) 0, (b) 30, (c) 60, (d) 90 and (e) 120 min. after addition of toluene.

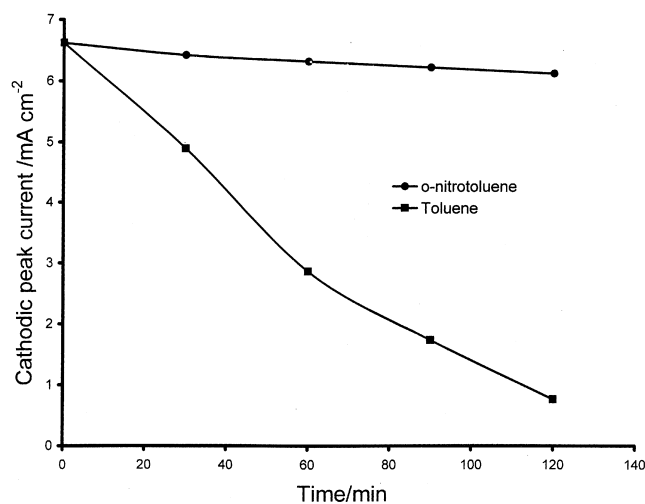


Fig. 5. Comparison of reaction rate on ONT and toluene with Co^{3+} at 5°C based on relative decrease in the peak currents due to Co^{3+} . Co^{3+} concentration: 175 mM, acid concentration: 4.0 M MSA. Conc. of toluene and ONT: 42 mM.

galvanostatic conditions is likely to be low. Cobaltic methane sulfonate can effectively oxidize facile compounds like toluene in 4.0 M MSA. The solubility of Co^{2+} as well as Co^{3+} species decreases with increasing MSA concentration. However, cobaltic methanesulfonate in 10.0 M MSA has been found to be an effective oxidizing agent for organic compounds in some prelim-

inary preparative scale experiments by the present authors. Nuclear oxidation of naphthalene and nitro-naphthalene was found to be more efficient with around 50% yield when compared to side chain oxidation of ONT (20% yield).

3.3. Ceric/cerous redox couple in methanesulfonic acid

The voltammetric behaviour of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox system in methanesulfonic acid was investigated in low, as well as high, acid concentrations. Typical cyclic voltammograms obtained for 34 mM cerous methanesulfonate in 4.0 M methane sulfonic acid at different sweep rates are shown in Figure 6. Unlike $\text{Mn}^{3+}/\text{Mn}^{2+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ redox systems, distinct oxidation peaks and reduction peaks are observed in the voltammograms. The peak current also increases with sweep rate and cerous concentrations.

Comparison of the voltammetric behaviour of cerous methanesulfonate in different acid concentrations of MSA revealed that the voltammograms are quite similar. The peak potential values and ΔE_p values are also quite comparable. The anodic peak current tends to decrease slightly with increasing methanesulfonic acid concentration. Increasing the MSA concentration increases the solution viscosity and decreases the diffusivity of the reactant.

Earlier studies have also indicated that the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple gives well defined responses in methanesulfonic acid in the concentration range from 1.0 to 8.0 M [6]. All these observations suggest much better electrochemical behaviour for the ceric/cerous redox

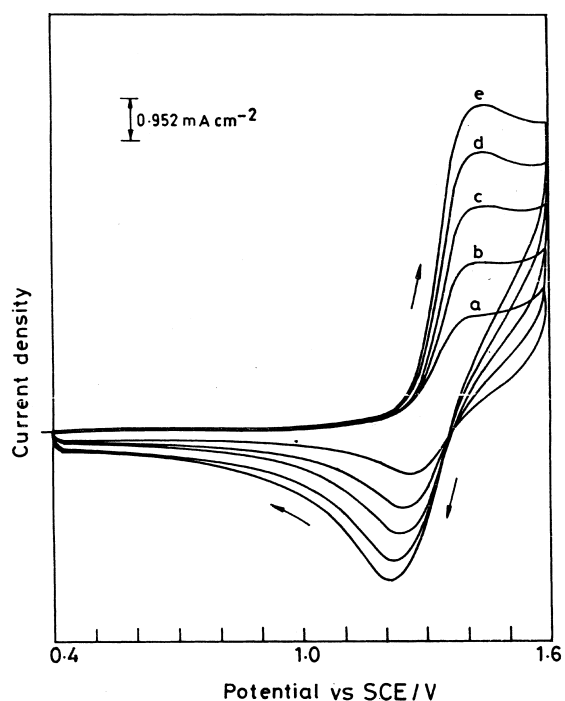


Fig. 6. Typical cyclic voltammograms of Ce^{3+} in 4.0 M MSA on GCE at different sweep rates, v : (a) 10, (b) 20, (c) 40, (d) 80, and (e) 160 mV s^{-1} . Ce^{3+} concentration: 34 mM.

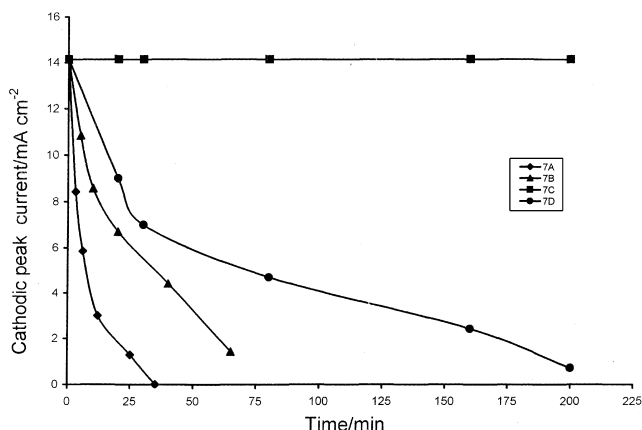


Fig. 7. Depletion of cathodic current of ceric ion on reaction with *p*-methoxy toluene (A,B) and *p*-tert-butyltoluene (C,D) at 15 °C (B), 30 °C (A,C) and 65 °C (D).

couple in methanesulfonic acid, when compared to $\text{Co}^{3+}/\text{Co}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$.

Some experiments were also carried out to find out the oxidizability of aromatic compounds. For these experiments electrogenerated ceric methanesulfonate stock solutions were employed. The reactants dissolved in dichloromethane/dichloroethane were used in the voltammetric studies to ensure miscibility of the reactant with redox mediator. The concentration of solvents in the overall electrolytic solution was maintained at a 1:4 ratio.

Typical cyclic voltammograms obtained at different time intervals for 250 mM ceric methanesulfonate containing 70 mM *p*-methoxy toluene (solvent DCM) at room temperature indicated that the ceric methanesulfonate concentration decreases substantially and the reaction is completed in about 35 min. For comparison, the same experiments were also repeated at a lower temperature of 15 °C. The ceric methanesulfonate concentration decreases much slowly with time and takes nearly 65 min for completion.

The variation of cathodic peak current with time for *p*-methoxy toluene at these two temperatures are also compared in Figure 7A and B. These results clearly suggest the possibility of using cyclic voltammetry for a quick assessment of oxidizability of organic compounds.

Further confirmation of this possibility was obtained by studying the oxidizability of *p*-tert-butyltoluene. For this compound even in a stronger medium of 4.0 M methanesulfonic acid, the peak current due to the reduction of ceric methanesulfonate in the presence of the organic reactant *p*-tert-butyltoluene dissolved in dichloroethane did not decrease with time at room temperature (Figure 7C). However, at a higher temperature of 65 °C the peak current decreases with time as shown in Figure 7D. The reaction goes to completion in 200 min. These results indicate that *p*-tert-butyltoluene

can be chemically oxidized at around 65 °C in 4.0 M methanesulfonic acid.

The voltammetric investigations thus indicate that, in methanesulfonic acid, the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox mediator can be used over a wide range of temperatures and concentrations. The voltammetric technique can also be used efficiently to evaluate the oxidisability of different compounds in ceric methanesulfonate solutions of widely different acid strengths and reaction temperatures.

4. Conclusion

The voltammetric investigations of the conventional redox mediators $\text{Mn}^{3+}/\text{Mn}^{2+}$, $\text{Co}^{3+}/\text{Co}^{2+}$, $\text{Ce}^{4+}/\text{Ce}^{3+}$ in methanesulfonic acid highlight out the potentials and limitations of the mediators in methanesulfonic acid. Manganic methanesulfonate undergoes substantial disproportionation and produces solid MnO_2 particles on the electrode surface in dilute methanesulfonic acid solutions. The interferences of this process is noticed to some extent even in 8.0 M MSA. The oxidation of Co^{2+} species occurs at substantially higher potentials in the oxygen evolution region. Hence, the current efficiency for the generation of cobaltic methanesulfonate is likely to be low. The cobaltic methanesulfonate also oxidises water at a significant rate at room temperature. But this redox mediator can be employed at the lower temperature of 5 °C. Ceric methanesulfonate can be generated with high current efficiency and the redox system behaves reversibly over wide acid concentrations and ceric/cerous concentration. This redox mediator can also be employed at different temperatures, depending on the ease of oxidizability of the aromatic compounds selected.

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