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Influence of aromatic reactants and products involved in the two stage electrochemical oxidation on the voltammetric behaviour of Ce(IV)/Ce(III) redox couple

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Abstract

The redox behaviour of the Ce(IV)/Ce(III) couple in 1.0 M nitric acid, 1.0 M sulfuric acid, 1.0 M perchloric acid and in different concentrations of methane sulfonic acid was investigated on a glassy carbon electrode using cyclic voltammetry. Quasi reversible redox behaviour with low ΔE_p value of 200 mV and below were observed in 1.0 M sulfuric acid and high concentrations of methane sulfonic acid. Anionic complexes apparently exist in this media. The reactants and products involved in the indirect oxidations are found to influence cerous/ceric redox behaviour in 2.0 M methane sulfonic acid in three distinct ways: (i) in the presence of cerous methane sulfonate organic compounds such as toluene, benzaldehyde and naphthaquinone do not exhibit substantial inhibitive effects; (ii) compounds such as *p*-xylene and *p*-tolualdehyde exhibit some inhibitive effect at higher concentrations; and (iii) compounds like naphthalene, *p*-ethoxy toluene and *p*-ethoxy benzaldehyde exhibit a fairly high level of inhibitive effect.

1. Introduction

The Ce(IV)/Ce(III) redox system has attracted attention in electroorganic synthesis for indirect oxidation of aromatic and alkyl aromatic compounds [1–5]. Since the oxidation potential of this system is quite high the choice of electrode, especially for electroanalytical investigations, has been difficult. A thin platinum ring electrode renewed at regular intervals by gas bubbles, known as a bubbling platinum electrode [6], has been used to obtain a distinct polarographic wave in sulfuric acid medium [7]. The kinetics of the Ce(IV)/Ce(III) redox reaction has been evaluated in perchloric acid, nitric acid and sulfuric acid media using stationary and rotating platinum disc electrodes [8–12] and platinised titanium [13]. A brief study in methane sulfonic acid [3] is also known. More distinct cathodic voltammetric responses for the reduction of Ce(IV) were noticed on pyrolytic graphite electrode [14]. Distinct voltammograms have also been obtained on vitreous carbon [15] and on boron-doped conductive diamond (BDD) [16].

Naphthalene is known to undergo direct electrochemical oxidation leading to formation of naphthaquinone [17]. The redox behaviour of naphthaquinone is well known [18–20]. Wendt et al. have studied the voltammetric behaviour of toluene and substituted toluenes in aqueous alcoholic and acetonitrile media [21]. In direct oxidations 35–75% selectivities of corresponding aldehydes have also been reported [22]. Direct anodic oxidation of *p*-methoxy toluene has been investigated in acetic acid [23] as well as acetonitrile media [24]. Despite such reports on direct oxidation, it appears [1–5] that indirect electrochemical oxidation for most of these compounds using Ce(IV)/Ce(III) redox systems leads to better yields and efficiencies.

There are only a few reports on the voltammetric behaviour of the Ce(IV)/Ce(III) redox couple on glassy carbon electrodes [15, 16] especially in methane sulfonic acid medium [3]. Hence, it was felt desirable to study the voltammetric behaviour of this redox system in methane sulfonic acid medium and to compare it with the behaviour in other acidic media on glassy carbon under otherwise identical conditions.

Some questions regarding indirect oxidation also deserve further consideration. Which of the methods namely direct or indirect oxidation method is suitable for the oxidation of toluenes and polynuclear aromatic hydrocarbons? In the indirect method what is the reason for adopting *ex situ* or two stage electrooxidation strategy? How does the presence of small quantities of organic reactants and products that are likely to be present during recycling of Ce(IV)/Ce(III) electrolyte solutions influence the voltammetric behaviour of this redox couple itself? Is there any catalytic or inhibitive effect of these organic compounds on the electrochemical oxidation of Ce(III) species? Can we attribute the current efficiency losses during recycling to these impurities as has been reported by Comninellis and coworkers in the case of indirect oxidation using Mn^{2+}/Mn^{3+} redox system? [25]. To address these objectives, a preliminary voltammetric investigation of cerous methane sulfonate in 2.0 M methane sulfonic acid in the absence and presence of typical organic reactants and products is presented in this work. Naphthalene and naphthaquinone were chosen as a representative of aromatic ring oxidation. *p*-Alkoxy toluene/*p*-alkoxy benzaldehyde is a typical system whose direct oxidation has been reported to be successful. Toluene/benzaldehyde couple and *p*-xylene/*p*-tolualdehyde couple have been chosen to assess the ease of oxidizability and solubility difference on the voltammetric responses.

2. Experimental details

An H-type cell with a glassy carbon working electrode, a platinum counter electrode and a saturated calomel electrode as the reference electrode was used for the voltammetric studies. Tokai GC A-type glassy carbon (5 mm dia.) was polished, cleaned and electrochemically activated using potential cycling according to the procedure described earlier [26]. All the experiments were carried out at 298 ± 1 K. For comparing the voltammetric behaviour in different acids, ceric ammonium nitrate was employed throughout. Since the acid concentration of 1.0 M is substantially higher than the concentration of nitrate ion added through ceric ammonium nitrate the effect of different acids could still be evaluated under reproducible experimental conditions. In the case of more detailed investigations in methane sulfonic acid, ceric methane sulfonate was used for comparative purposes.

Solutions of cerium methane sulfonate in methane sulfonic acid were prepared by neutralizing cerium carbonate in water by adding concentrated methane sulfonic acid. Desired concentrations of methane sulfonic acid were obtained by adding the required amount of methane sulfonic acid to this solution. All the other chemicals were of AR grade and were used as such. Triply distilled water was used throughout.

Since Ce(IV) species is taken as the starting material, the starting point for the voltammograms should normally be chosen in the positive potential region [14] and initial sweeps should be in the cathodic direction. However, on glassy carbon electrode it was found that setting the starting potential at zero volts and moving to the anodic potential region during potential cycling gave much more reproducible and well defined voltammograms. Hence, the voltammogram was started at zero volts throughout the experiments. All the other details relating to instruments and procedures have been described elsewhere [26].

3. Results and discussions

3.1. *Medium effects on Ce(IV)/Ce(III) redox behaviour*

Anodic oxidation of Ce(III) appears as a small wave along with background current in nitric acid medium at low concentrations (Figure 1). The anodic peak current (i_{pa}), as well as the cathodic peak current (i_{pc}), are found to increase linearly with concentration of Ce(IV) (Figure 2A) and square root of sweep rate ($v^{1/2}$) (Figure 2B). Peak current constants ($i_{pa}/cv^{1/2}$) as well as $i_{pc}/cv^{1/2}$ are found to be fairly constant. The anodic and cathodic peak current values are also quite similar. Figure 2A and B indicates that the Ce(IV)/Ce(III) redox couple undergoes a diffusion controlled quasi reversible charge transfer in all the four media. The E_{pa} and E_{pc} values are found to be around 1.5 V and 1.2 V, respectively, in nitric acid, perchloric acid and methane sulfonic acid (Table 1). It appears that in these three media the charge transfer rate constants for the Ce(IV)/Ce(III) redox couple are quite close to each other. For comparative purposes the voltammetric data of the Ce(IV)/Ce(III) redox couple in different acidic media at a constant sweep rate of 40 mV s^{-1} are summarized in Table 1.

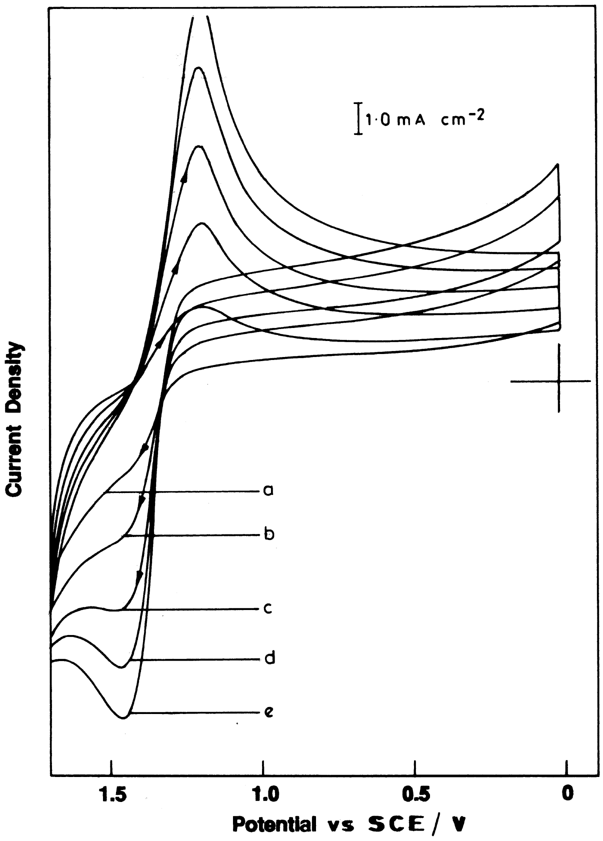


Fig. 1. Cyclic voltammograms showing effect of concentration of Ce^{4+} in 1.0 M nitric acid on GCE at 40 mV s^{-1}. ((a)–(e): 38, 74, 107, 138 and 167 mM CAN, respectively).

The equilibrium potential for the Ce(IV)/Ce(III) couple appears to be significantly lower in sulfuric acid medium when compared to other media. The E_{pa} and E_{pc} values are observed around 1.27 V and 1.05 V, respectively, in this medium (Figure 3). In earlier work lower values of redox potentials for Ce(IV)/Ce(III) in sulfuric acid were also reported [7, 14]. In this medium the sulfate complex for Ce(IV), as well as Ce(III), appear to be quite stable since this redox couple shows lower redox potentials:

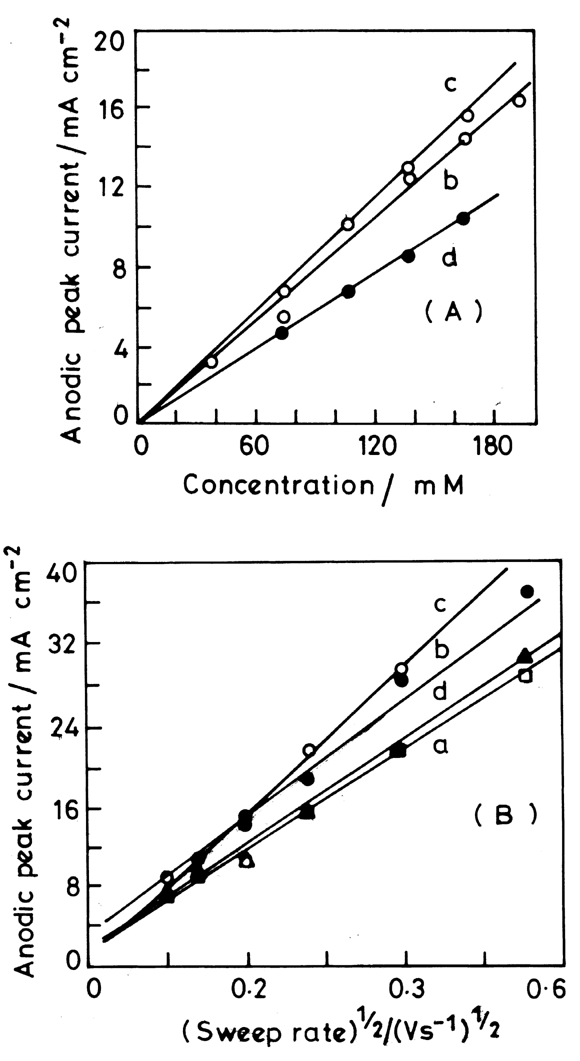
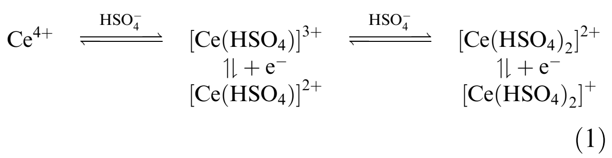


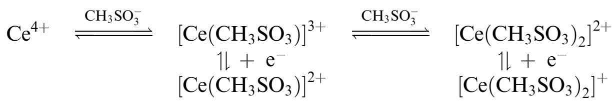
Fig. 2. (A) Plots of i_{pa} vs conc. of Ce^{3+} on GCE at 40 mV s^{-1} and (B) plots of i_{pa} vs $(v)^{1/2}$ of Ce^{3+} on GCE in different electrolytes. (a): 1.0 M HNO_3, (b) 1.0 M $HClO_4$, (c) 1.0 M H_2SO_4 and (d) 1.0 M MSA.



$$\begin{array}{ccccc} Ce^{4+} & \xrightleftharpoons{HSO_4^-} & [Ce(HSO_4)]^{3+} & \xrightleftharpoons{HSO_4^-} & [Ce(HSO_4)_2]^{2+} \\ & & \Updownarrow + e^- & & \Updownarrow + e^- \\ & & [Ce(HSO_4)]^{2+} & & [Ce(HSO_4)_2]^{+} \end{array} \quad (1)$$

The ΔE_p for Ce(IV)/Ce(III) is also found to be significantly lower (<0.22 V) in sulfuric acid as well as in methane sulfonic acids. It is interesting to note that in preparative electrolysis, 1.0 M sulfuric acid and 2.0 M methane sulfonic acid are indeed the preferred media of choice. In sulfuric acid media i_{pa} is generally found to be significantly higher than i_{pc} (Table 1 and Figure 3). It is possible that the anodic current in this medium always contains a small contribution due to weak adsorption of Ce(III) complex, along with the diffusion current component.

Another interesting observation is the second cathodic peak observed around 0.8 V in 2–6 M methane sulfonic acid (Figure 4) at slow sweep rates whenever the concentration of Ce(IV) and the concentration of methane sulfonic acid are higher. The Ce(IV)/Ce(III) redox couple can also exist as methane sulfonate complexes, as shown for sulfate complexes in Equation 1.



$$\begin{array}{ccccc} Ce^{4+} & \xrightleftharpoons{CH_3SO_3^-} & [Ce(CH_3SO_3)]^{3+} & \xrightleftharpoons{CH_3SO_3^-} & [Ce(CH_3SO_3)_2]^{2+} \\ & & \Updownarrow + e^- & & \Updownarrow + e^- \\ & & [Ce(CH_3SO_3)]^{2+} & & [Ce(CH_3SO_3)_2]^{+} \end{array} \quad (2)$$

The Ce(IV) species may thus exist in the monoligated as well as diligated methane sulfonates.

$$[Ce(CH_3SO_3)]^{3+} \xrightleftharpoons{CH_3SO_3^-} [Ce(CH_3SO_3)_2]^{2+} \quad (3)$$

The concentration of diligated species would increase with increasing concentration of Ce(IV), as well as methane sulfonate. Hence, the reduction peak observed at higher Ce(IV) and methane sulfonic acid concentrations in the lower potential region may be attributed to this diligated cerium species. The Ce(III) species is less soluble in methane sulfonic acid and in preparative work the cerous methane sulfonate is indeed obtained in the slurry form [2, 3]. This observation again suggests the existence of at least two different Ce(IV) species with different solubilities in solution. In general, with increasing concentration of methane sulfonic acid, the anodic peak current tends to decrease slightly (Table 1).

Table 1. Comparison of cyclic voltammetric data of Ce(IV) in different acid media
Sweep rate 40 mV s^{-1}.

Medium	Conc. of Ce^{4+} /mM	i_{pa} /mA cm^{-2}	i_{pc} /mA cm^{-2}	E_{pa} /V	E_{pc} /V	ΔE_p /V
1 M HNO_3	74	4.85	5.15	1.50	1.19	0.31
1 M HNO_3	167	10.50	12.40	1.46	1.20	0.26
1 M $HClO_4$	74	5.63	5.75	1.56	1.25	0.31
1 M $HClO_4$	167	14.60	16.13	1.53	1.24	0.29
1 M H_2SO_4	74	6.90	5.40	1.27	1.05	0.22
1 M H_2SO_4	167	15.7	13.0	1.28	1.06	0.22
1 M MSA	74	wave	4.05	–	1.20	–
1 M MSA	167	10.4	11.6	1.5	1.21	0.29
2 M MSA	33.3	3.90	3.55	1.51	1.37	0.14
4 M MSA	33.3	3.45	2.73	1.51	1.36	0.16
6 M MSA	33.3	2.40	1.57	1.52	1.28	0.24

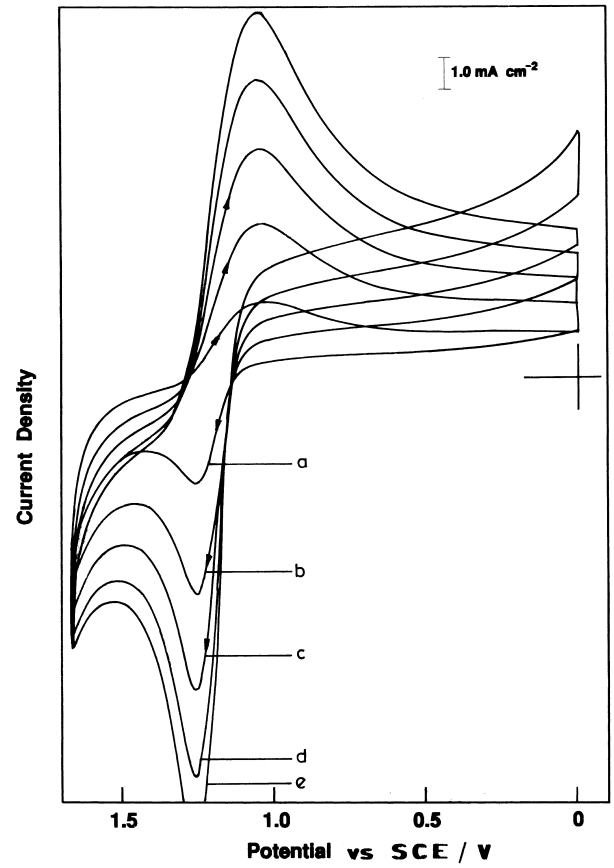


Fig. 3. Cyclic voltammograms showing the effect of concentration of Ce^{4+} in 1.0 M sulfuric acid on GCE at 40 mV s^{-1}. ((a)–(e): 38, 74, 107, 138 and 167 mM CAN, respectively).

This may be due to a decrease in the diffusion coefficient of the Ce(III) species due to increase in solution viscosity with concentration of methane sulfonic acid. In preparative electrolysis the decrease in current efficiency with increasing methane sulfonic acid concentration is also noticed.

3.2. *Influence of aromatic compounds on Ce(IV)/Ce(III) redox behaviour*

3.2.1. *Naphthalene/naphthaquinone system*

Naphthalene exhibits a distinct oxidation peak A_2 around 1.3 V and in the reverse sweep no cathodic peak (C_2), which corresponds to this anodic peak, is noticed (Figure 5A). But at much lower potentials a distinct cathodic peak C_1 due to the reduction of electrogenerated naphthaquinone is noticed. The naphthaquinone/naphthol redox peaks (A_1/C_1) are always noticed in the second and subsequent sweeps. The redox peak currents for A_1/C_1 do not change with sweep number; however the anodic peak current i_pA_2 decreases substantially with increasing sweep number. This is apparently due to the passive film formation of naphthalene and its oxidized intermediates on the electrode surface.

Figure 5B (curve (a)) shows the cyclic voltammetric response of 16 mM Ce(III) in 2.0 M methane sulfonic acid. Distinct oxidation and reduction peaks A_3 and C_3 are noticed at 1.55 V and 1.4 V, respectively. Typical multisweep cyclic voltammograms of 0.4 mM naphthalene in the presence of 16 mM Ce(III) are shown in Figure 5B ((b), (c) and (d)). The oxidation peak A_2 observed during the first sweep (Figure 5B curve (b)) decreases substantially in the second and subsequent sweeps (Figure 5B curve (c) and (d)). It appears that the surface concentration of naphthalene decreases substantially in the presence of the Ce(IV)/Ce(III) redox couple. Naphthaquinone does not significantly influence the redox peaks A_3 and C_3 noticed for the Ce(IV)/Ce(III) redox couple in this medium (Table 2). Both the redox couples (A_1C_1 and A_3C_3) also show a linear increase of peak current with square root of the sweep rate.

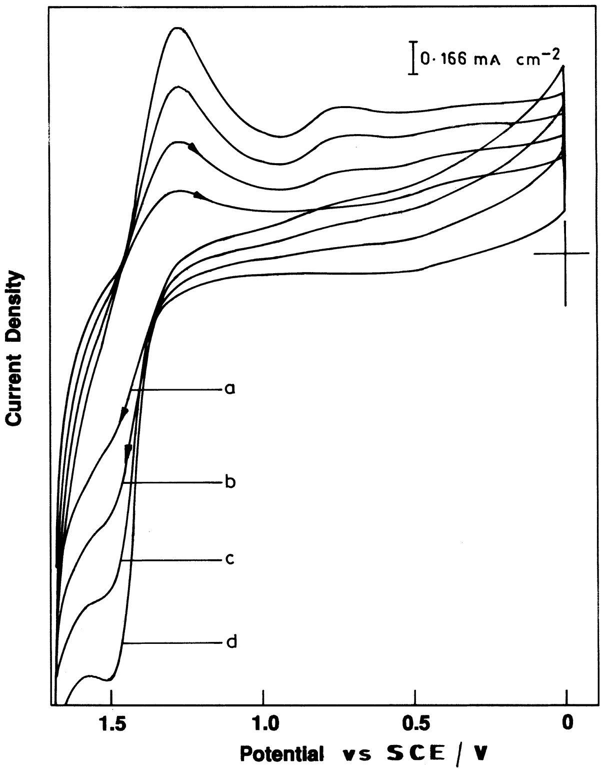


Fig. 4. Typical cyclic voltammograms showing the effect of concentration of Ce^{4+} in 6.0 M MSA on GCE at 40 mV s^{-1}. ((a)–(e): 7.7, 14.8, 21.4 and 27.6 mM CAN, respectively).

3.2.2. p-*Ethoxy toluene*/p-*ethoxy benzaldehyde system*

Two distinct anodic oxidation peaks are noticed around 1.25 V and 1.7 V for the oxidation of *p*-ethoxy toluene in 2.0 M methane sulfonic acid (Figure 6A). The first anodic peak currents increase linearly with concentration, the second anodic peak is very close to the background. Even in the presence of low concentrations of *p*-ethoxy toluene, the oxidation and reduction peaks due to the Ce(IV)/Ce(III) redox couple are found to decrease significantly. In multisweep cyclic voltammetric experiments the anodic peak currents were found to decrease substantially, as shown in Figure 6B.

p-Ethoxy benzaldehyde gives a distinct anodic oxidation peak around 1.7 V in this medium (Figure 7). This

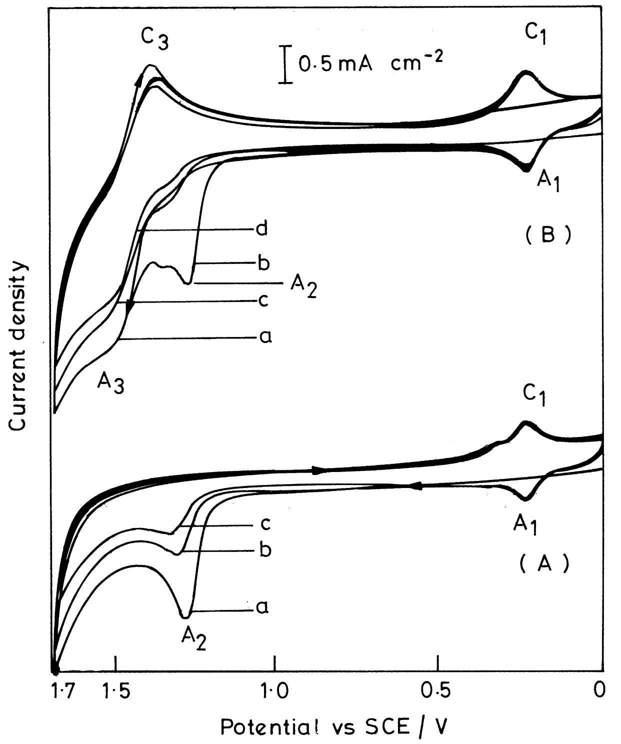


Fig. 5. Multisweep voltammograms of (A), naphthalene (NA) in 2.0 M MSA ((a)–(c): 1st, 2nd, 7th sweeps, respectively) and (B) Ce^{3+} in presence of naphthalene on GCE in 2.0 M MSA at 40 mV s^{-1}. (Conc. NA 0.4 mM, conc. Ce^{3+} 16 mM, (a): Ce^{3+} alone, (b)–(d): 1st, 2nd, 7th sweeps, respectively, in presence of naphthalene).

oxidation peak corresponds to the second anodic oxidation peak observed in the case of *p*-ethoxy toluene. This observation suggest that the second oxidation peak observed in the case of *p*-ethoxy toluene (Figure 6A) should be due to the oxidation of *p*-ethoxy benzaldehyde generated in the first oxidation potential region. The oxidation and reduction peak currents due to the Ce(III)/Ce(IV) redox couple are found to decrease with increasing *p*-ethoxy benzaldehyde concentration similarly to the case of *p*-ethoxy toluene (Table 2).

3.2.3. *Toluene/benzaldehyde system*

Toluene gives a single irreversible oxidation peak around 1.7 V in 2.0 M methane sulfonic acid on glassy carbon (Figure 8A). The peak current does not increase significantly with the toluene concentration (Figure 8A). In the presence of 16 mM Ce(III), the toluene oxidation peak is noticed, along with the oxidation and reduction peaks of the Ce(IV)/Ce(III) redox system. With increasing toluene concentration both the oxidation and reduction peaks decrease substantially (Figure 8B and Table 2). In this medium benzaldehyde gives no oxidation peak at all. Increasing the concentration of benzaldehyde decreases the anodic peak current due to Ce(III) oxidation to a small, but noticeable, extent (Table 2).

3.2.4. p-*Xylene*/p-*tolualdehyde system*

p-Xylene also gives an ill-defined oxidation peak around 1.5 V in 2.0 M methane sulfonic acid on glassy carbon. At higher concentrations of *p*-xylene the anodic peak becomes distinctly visible (Figure 9A). It is interesting to note that the oxidation of *p*-xylene and the oxidation of Ce(III) occur at the same potential region. Hence, in the presence of 16 mM Ce(III) the oxidation peak current due to Ce(III) oxidation increases slightly with increasing *p*-xylene concentration. At higher concentrations of

Table 2. Influence of aromatic compounds on Ce(IV)/Ce(III) redox peak currents
Sweep rate 40 mV s^{-1}.

Sl. no.	Aromatic compounds (conc. mM)	Ar compounds		Ce(IV)/Ce(III) redox peak currents in presence of aromatic compounds			
		E_{pa} /V	i_{pa} /mA cm^{-2}	1st sweep		7th sweep	
				i_{pa} /mA cm^{-2}	i_{pc} /mA cm^{-2}	i_{pa} /mA cm^{-2}	i_{pc} /mA cm^{-2}
1	Ce(IV)/Ce(III) (16)	1.55 1.40a	–	2.13	1.5	–	–
2	Naphthalene (0.4)	1.29 0.23-c1	1.66 0.3-c2	1.78	0.93	1.08	0.8
3	Naphtha quinone (0.33)	0.24 0.23-c1	0.6 0.6-c2	1.85	1.40	1.3	1.4
4	*p*-Ethoxy toluene (0.38)	1.25 1.69	0.78 1.73	b	0.66	b	0.65
5	*p*-Ethoxy benzaldehyde (0.45)	1.67	1.95	1.80	0.78	b	0.65
6	Toluene (0.43)	1.70	0.38	2.10	1.03	1.13	0.90
7	Benzaldehyde (0.53)	–	–	2.45	1.48	2.05	1.48
8	*p*-Xylene (0.42)	1.51	0.30	2.78	1.35	1.85	1.28
9	*p*-Tolualdehyde (0.44)	1.51	0.25	1.60	1.15	1.20	1.15

a 1.4 V corresponds to cathodic peak potential of Ce(IV) species.

b Anodic peak of Ce(III) merged with anodic peak of organic compound. However, anodic peak current of both Ce(III) and organic compounds is less in the 7th sweep compared to first sweep.

c1 and c2 refer to the cathodic peak potential and peak current of organic compound.

Ar Aromatic.

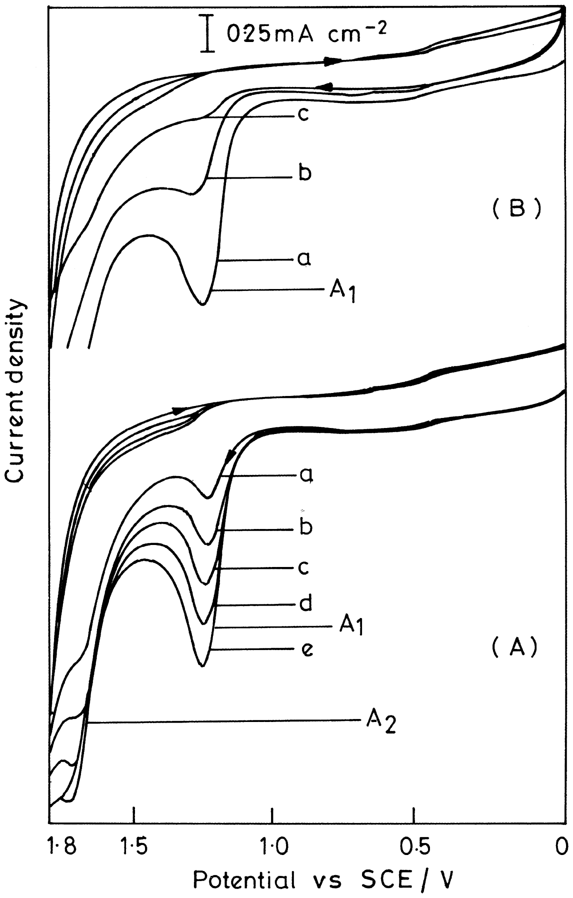


Fig. 6. (A) Cyclic voltammograms of *p*-ethoxytoluene on GCE in 2.0 M MSA at 40 mV s^{-1}. ((a)–(e): 0.38, 0.75, 1.125, 1.5 and 1.86 mM PET, respectively). (B) Multisweep voltammograms of 16 mM Ce^{3+} in presence of 1.86 mM PET on GCE in 2.0 M MSA at 40 mV s^{-1}. ((a)–(c): 1st, 2nd, and 7th sweeps, respectively).

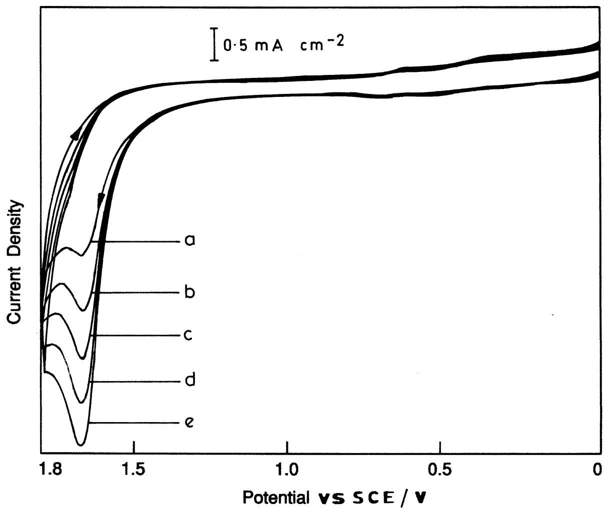


Fig. 7. Cyclic voltammograms of *p*-ethoxybenzaldehyde on GCE in 2.0 M MSA at 40 mV s^{-1}. ((a)–(e): 0.45, 0.896, 1.34, 1.78 and 2.2 mM PEB, respectively).

p-xylene, the anodic and cathodic peak currents, in fact, tend to decrease (compare curves (d) and (e) in Figure 9B).

p-Tolualdehyde also gives an oxidation peak in the same potential region. The anodic peak becomes distinctly visible only at higher concentrations. Addition of tolualdehyde to 16 mM Ce(III) in methane sulfonic acid has the same effect on the voltammetric response as that noted for *p*-xylene (Table 2).

The anodic peak potential values for different aromatic compounds obtained in the present work are also compared with the $E_{1/2}$ and E_p values reported in the literature (Table 3). The oxidation peak potentials in the literature obtained on platinum and graphite in earlier work are always found to be slightly higher than those obtained on glassy carbon electrode in the present work. It appears that the electrochemical oxidation of these compounds proceeds slightly faster at lower oxidation potentials on glassy carbon.

In the absence of Ce(III) the oxidative behaviour of the compounds chosen are indeed substantially different. Except for naphthalene, naphthaquinone and *p*-ethoxy toluene the oxidation peaks of all the other organic compounds occur close to the oxidation peaks of Ce(III) (Table 2). Hence, in the voltammetric responses of organic compounds in the presence of another compound the anodic oxidation peaks become less distinctly visible.

Different compounds were found to exhibit inhibitive effects to different extents. Naphthaquinone, toluene and benzaldehyde were found to exhibit a less inhibitive effect in the voltammetric experiments. Hence, the presence of small concentrations of these compounds during preparative electrolysis may have only limited influence on the conversion efficiency of the redox system.

p-Xylene and *p*-tolualdehyde exhibit significant inhibitive effects (as indicated by the decrease in anodic peak current) in the presence of about 2 mM of organic compound. Thus it appears that single stage electrochemical oxidation of *p*-xylene in the presence of Ce(IV)/Ce(III) redox couple is not viable. One should also ensure that these compounds are removed from the aqueous phase to the critical level of <1.0 mM before the Ce(III) electrolyte solution is subjected to regeneration.

A substantial inhibitive effect is noticed in the case of naphthalene, *p*-ethoxy toluene and *p*-ethoxy benzaldehyde. Despite the low oxidation potential of naphthalene and *p*-ethoxy toluene it appears that, at least in methane sulfonic acid, direct oxidation of these compounds would only lead to much higher inhibitive effects on the electrode surface. In the two stage synthesis much greater attention to cleaning the electrolyte solution before regeneration would be required for these compounds.

4. Conclusion

The Ce(IV)/Ce(III) redox couple undergoes a quasi-reversible diffusion controlled charge transfer on glassy carbon in nitric acid, perchloric acid, sulfuric acid and methane sulfonic acid. Comparison of ΔE_p values also suggests faster charge transfer kinetics in 1.0 M sulfuric

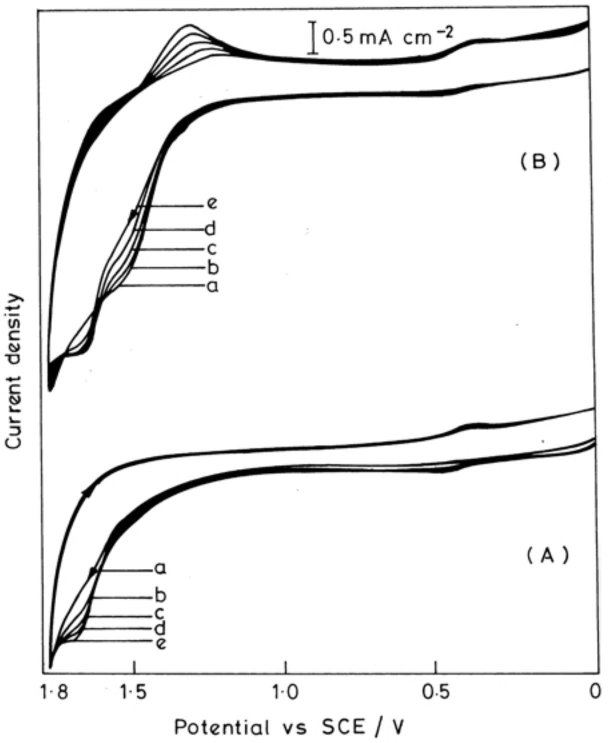


Fig. 8. Typical cyclic voltammograms of (A) toluene in 2.0 M MSA and (B)16 mM Ce^{3+} in presence of toluene on GCE in 2.0 M MSA at 40 mV s^{-1}. ((a)–(e): 0.43, 0.86, 1.29, 1.71 and 2.13 mM toluene, respectively).

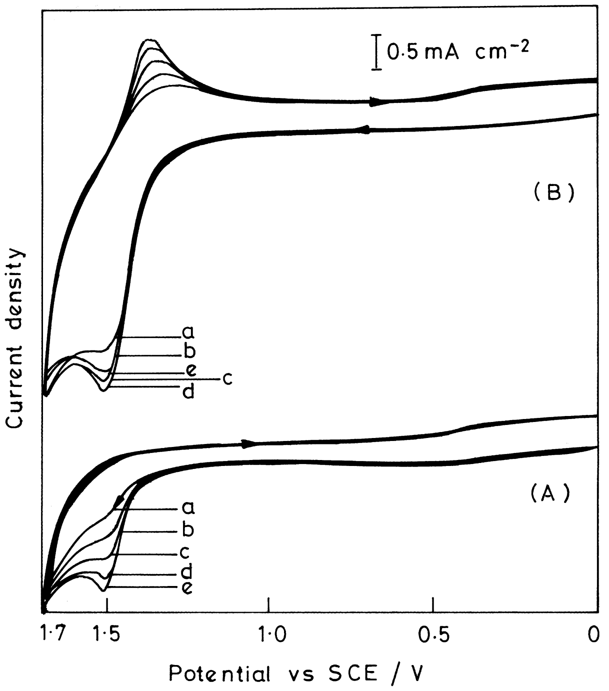


Fig. 9. Typical cyclic voltammograms of (A) *p*-xylene in 2.0 M MSA and (B) 16 mM Ce^{3+} in presence of *p*-xylene on GCE in 2.0 M MSA at 40 mV s^{-1}. ((a)–(e): 0.42, 0.84, 1.26, 1.67 and 2.08 mM *p*-xylene, respectively).

Table 3. Comparison of oxidation potential of aromatic compounds measured on GCE in 2.0 M MSA with reported values [18, 19, 21]

Sl. no.	Compounds	E_p(obs) /V vs SCE	$E_{1/2}$(rep) /V	Remarks
1	Naphthalene	1.30	1.310	Rotating Pt anode MeCN/0.5 M $NaClO_4$ vs (Ag 0.1 N Ag^+)
2	Naphthaquinone	0.235	0.470	Aqueous medium $E°$ vs NHE
3	*p*-Ethoxytoluene	1.25	1.366	Rotating disc electrode of graphite vs SHE in 0.005 M ethanol solutions
4	*p*-Ethoxy benzaldehyde	1.67	1.643	As above for no. 3
5	Toluene	1.70	1.750	As above for no. 3
6	Benzaldehyde	–	1.880	As above for no. 3
7	*p*-Xylene	1.51	1.650	Rotating disc electrode of graphite vs aqueous NHE in 0.005 M methanol solutions
8	*p*-Tolualdehyde	1.51	–	As above for no. 7

acid and 2.0 M methane sulfonic acid. A small adsorption effect is also noticed in 1.0 M sulfuric acid. The redox potential is close to the background oxidation potential in all the media other than sulfuric acid. However, with increasing cerium(IV) concentration the anodic peak becomes more distinct and appears at lower potentials. Hence, it is possible to achieve high conversion efficiencies during electrochemical oxidation of Ce(III) at high concentrations.

Among the compounds generally chosen for indirect electrochemical oxidation using the Ce(IV)/Ce(III) redox system, toluene, benzaldehyde and naphthaquinone exhibit less inhibitive effects, *p*-xylene and *p*-tolualdehyde exhibit inhibitive effect at higher concentrations, naphthalene, *p*-ethoxy toluene and *p*-ethoxy benzaldehyde exhibit a fairly high level of inhibitive effect in the presence of cerous methane sulfonate. It thus appears that, as a general strategy, these compounds are preferably oxidized through a two stage process using the Ce(IV)/Ce(III) redox couple in methane sulfonic acid medium. This justifies the general two stage approach adopted for these compounds.

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