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MEDIATED ANODIC OXIDATION OF TOLUENE WITH THE Ce(IV)/Ce(III) SYSTEM IN SULPHURIC ACID MEDIUM

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ABSTRACT. The Ce(IV)/Ce(III) couple was used as a mediator to oxidize an emulsion of toluene in aqueous H_2SO_4 medium, on graphite electrode using a divided electrochemical cell. The only oxidation product that could be identified, was benzaldehyde. The influence of several parameters upon benzaldehyde formation was investigated. The best yield for benzaldehyde formation, under the conditions employed was about 36%. Cyclic voltammetry was used to study the Ce(IV)/Ce(III) couple. Diffusion coefficients, reaction orders with respect to Ce (IV) and Ce(III) as well as the rate constants for Ce(IV) reduction and Ce(III) oxidation were determined. Ce (IV) regeneration on graphite electrode in H_2SO_4 medium using a divided cell was investigated. Good yields over 80% were obtained working under best conditions we found.

Keywords: cerium, toluene, benzaldehyde, voltammetry, mediated electrosynthesis.

In recent years the anodic oxidation of aromatic hydrocarbons aroused considerable interest. Substituted toluenes were oxidized up to 80-90% in an organic medium[1-5], while the degree of transformation for toluene did not exceed 20%[1,6-8]. The main disadvantage of direct electrochemical oxidation of these organic compounds is its low selectivity. In aqueous medium where the oxidation potentials of toluene and substituted toluenes are higher than that of the solvent, mediated electrosynthesis gave better results than direct electrochemical oxidation. This procedure proved to be highly selective for the oxidation of toluene and substituted toluenes to the corresponding aldehydes. The Ce(IV)/Ce(III) couple has been the target of several studies of mediated electrochemical oxidation[9-13]. That is because of its high selectivity for partial oxidation of organic compounds

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accompanied by the possibility of electrochemical regeneration of Ce(IV) in various acidic media, with high current efficiencies[9,13-18]. The best results for mediated electrooxidation are mentioned for p-chlorotoluene in $HClO_4$, between 80 and 90%[10], and for p-methoxytoluene in HNO_3, about 63%, in the presence of phase transfer reagents[13].

Mediated electrooxidation of toluene by Ce(IV)/Ce(III), in aqueous H_2SO_4, was less studied[12], that is why we have chosen this to the subject of our present paper. We report here also the results of voltammetric investigations and Ce(IV) regeneration in aqueous H_2SO_4 medium, on graphite electrode.

EXPERIMENTAL

Voltammetric measurements were performed in an undivided glass cell, using either a stationary or a rotating disc graphite electrode (*rde*) (diameter 4 mm), a 3,6 cm^2 Pt foil counter electrode and *SCE* reference electrode separated from the working electrode by a Luggin capillary. The electrodes were connected to a potentiostat controlled by PC. Current - potential data were stored directly on the computer memory. Ce(IV) regeneration was conducted in a divided cell of H-type, where compartments were separated by a large glass frit. A 6,84 cm^2 graphite bar was introduced in the anode compartment of volume 50 cm^3 fitted with a magnetic stirrer bar. The cathode, a Pt strip, was always immersed in an aqueous H_2SO_4 solution. The instrumentation employed included a stabilized power supply, a voltmeter and a miliampermeter. During a run, current and cell potential readings were taken every 10 min. The Ce(IV) formed by electrolysis was monitored by titration. The samples taken at intervals were shaken with a measured volume of 0.01 mol/dm^3 KI solution, followed by the titration of the formed iodine with $Na_2S_2O_3$.

The mediated electrosynthesis was carried out in the same cell, with the same instrumentation as Ce(IV) regeneration. Experiments were performed under methane gas atmosphere, to avoid further oxidation of benzaldehyde. After neutralizing the samples with NaOH, the content of benzaldehyde was estimated volumetrically. The method we employed recommends the transformation of benzaldehyde into the corresponding oxime, followed by titration with NaOH[19]. The content of benzaldehyde determined with this titration technique was in satisfactory agreement with that obtained by gas-chromatograph (*gc*) analysis (Table 1)

Table 1

Comparison between benzaldehyde content of samples analyzed by *gc* and by titration.

	Benzaldehyde %			
Titration	25.5	29.6	27.5	31.6
Gc	24	27.3	29.1	30.4

All chemicals came from commercial sources and were used without further purification. Solutions were prepared in twice distilled water. All measurements, unless otherwise stated, were made at room temperature, 18±2^{0}C.

RESULTS AND DISCUSSIONS

Voltammetry

Cyclic voltammograms recorded on stationary graphite electrode (Fig. 1.) in aqueous H_2SO_4 exhibited a well formed anodic peak at 1,25V/*SCE* and a corresponding cathodic peak at 1,19V/*SCE*, while oxygen evolution becomes important at about 1,5V/*SCE*. Increasing the potential sweep rate, v, between 10^{-2} and $15*10^{-2}$V/s, when the [Ce(IV)/Ce(III)] ratio was unity, no shift of peak potential was observed neither for the anodic, nor for the cathodic peak. The separation of peak potentials, $\Delta\varepsilon$, varied between 60 and 70 mV, but peak current ratio was higher than one and slightly increased from 1,25 to 1,43, when v was varied between the limits mentioned above. That is why the Ce(IV)/Ce(III) system should be considered just quasireversible. Voltammetric investigations with the *rde* were also performed, but no influence of electrode rotation speed upon half-wave potentials could be observed.

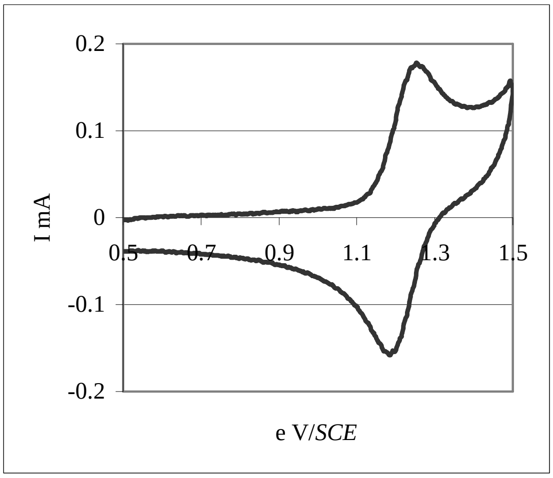

Figure 1. Cyclic voltammogram of the Ce(IV)/Ce(III) system in 0,5 mol/dm^3 H_2SO_4 on stationary graphite electrode

Linear plots I_v=f ($v^{1/2}$) for the stationary electrode and I_L=f ($\omega^{1/2}$) for the *rde* (Fig. 2.) served to determine the diffusion coefficients for Ce(IV) and Ce(III) in aqueous 0,5 mol/dm^3 H_2SO_4: at the stationary electrode D =(9,68±0,06)*10^{-5}cm^{2}s^{-1} for Ce(III) and D =(6,36±0,21)*10^{-5}cm$^2\cdot$s^{-1} for Ce(IV); at the rotating disc electrode D =(1,72±0,29)*10^{-6}cm$^2\cdot$s^{-1} for Ce(III) and D =(1,37±0,33)*10^{-6}cm$^2\cdot$s^{-1} for Ce(IV).

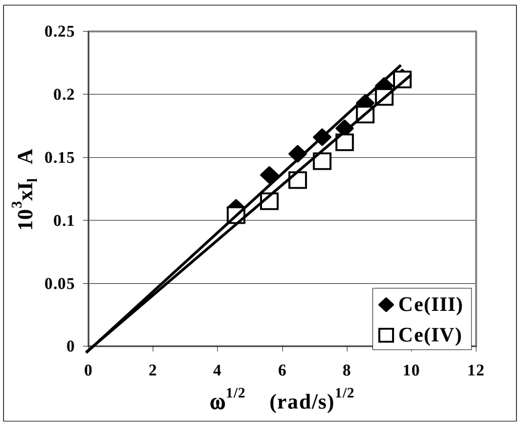

Figure 2. Levich linear plots for the Ce(IV)/Ce(III) couple at graphite electrode in 0.5 mol/dm^3 H_2SO_4

Peak currents and limiting currents, used for the determination of diffusion coefficients, don't occur at the same potential, that means the diffusion coefficients in our experiments were not determined at the same potential. This may be a possible explanation for the differences noticed between the values of diffusion coefficients obtained from stationary electrode and from rotating disc electrode data.

The oxidation and reduction reactions at the electrode are probably:

Anode: $CeSO_4^{+} + 2SO_4^{2-} \rightarrow Ce(SO_4)_3^{2-} + e^-$

Cathode: $Ce(SO_4)_3^{2-} + e^- \rightarrow CeSO_4^{+} + 2SO_4^{2-}$

because in H_2SO_4 medium Ce(IV), as well as Ce(III) may form many sulphatocomplexes[20-23] like: $CeSO_4^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_2^{3-}$ or $CeSO_4^{+}$, $Ce(SO_4)_2^{-}$, $Ce(SO_4)_3^{3-}$, respectively. The dominant species, in 0,5 mol/dm^3 H_2SO_4, or solutions of higher concentration, is the voluminous $Ce(SO_4)_3^{2-}$ sulphatocomplex. Ce(III) has a less pronounced tendency to form sulphatocomplexes than Ce(IV), this may account for the slight higher values of diffusion coefficients in the case of Ce(III).

Diffusion coefficients of cerium, we obtained from *rde* experiments, are smaller than those obtained, by the same method in $HClO_4$ or HNO_3 medium[16, 24], because sulphato- complexes of cerium are stronger than other anions.

Voltammograms of *rde* experiments were used to find reaction orders with respect to Ce(IV) and Ce(III) from I=f ($\omega^{1/2}$) plots at different potentials. The orders were determined according to a procedure recommended in literature[25] by means of equation[24]:

$$\mu = \frac{\log I_2/I_1}{\log[I_{L,1}/(I_{L,1}-I_1)] - \log[I_{L,2}/(I_{L,2}-I_2)]}$$

where: I_1 and I_2 are the currents recorded at the same potential for different square roots of angular velocity: $\omega_1^{1/2}$ and $\omega_2^{1/2}$

$I_{L,1}$ and $I_{L,2}$ are the limiting currents corresponding to $\omega_1^{1/2}$ and $\omega_2^{1/2}$
Rate constants, for the oxidation of Ce(III) and the reduction of Ce(IV) respectively were calculated from the intercepts of these plots.

Linear 1/I=f $(1/\omega^{1/2})$ plots for the relation

$$\frac{1}{I}=\frac{1}{z\cdot F\cdot A\cdot k\cdot C}+\frac{1{,}61\cdot \nu^{1/6}}{z\cdot F\cdot D^{2/3}\cdot A\cdot C}\cdot\frac{1}{\omega^{1/2}}$$

were obtained. The mean values obtained for the reaction orders were: $\bar{\mu}$ = 1.12±0.11 for Ce(IV) and $\bar{\mu}$ =0.5±0.025 for Ce(III), while the rate constants were: $10^3\cdot k_{red}$= 2,68±0.05 cm/s and $10^3\cdot k_{ox}$=1.6±0.05 cm/s
A possible explanation for the small reaction order with respect to Ce(III) is the adsorption of inactive Ce(III) sulphatocomplex, like $Ce(SO_4)_2^-$ or solvent molecules on the electrode.

Ce(IV) regeneration at graphite electrode in aqueous H_2SO_4 medium

In order to approach to conditions of mediated anodic oxidation the electrolysis was carried out when 10^{-2} mol/dm^3 Ce(IV) was also initially present.

By increasing the current density from 0,2 to 1,6 mA/cm^2 the degree of Ce(IV) formation increased till it reached a maximum value at about 1,2 mA/cm^2 (Fig .3)

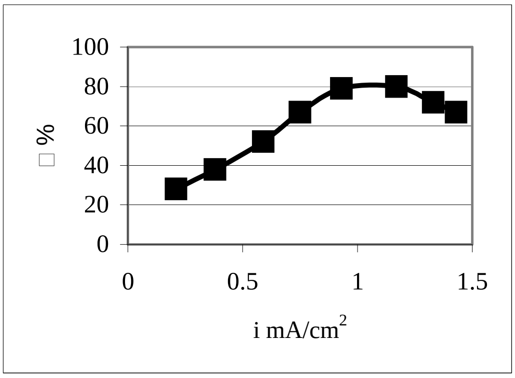

Figure 3. The influence of current density upon the conversion of Ce(III) to Ce(IV); $[H_2SO_4]$ = 1mol/dm^3; [Ce(IV)]/[Ce(III)] = 2, t = 20^{0}C

To achieve sustained electrolysis, experiments had to be performed at a cell potential, where both Ce(III) oxidation and oxygen evolution is possible. As expected, the conversion of Ce(III) to Ce(IV) decreased at higher current densities due to the increasing significance of the oxygen evolution reaction.

Sulphuric acid concentration exerted a positive effect on Ce(IV) regeneration till about 1 mol/dm^3 (Fig. 4.).

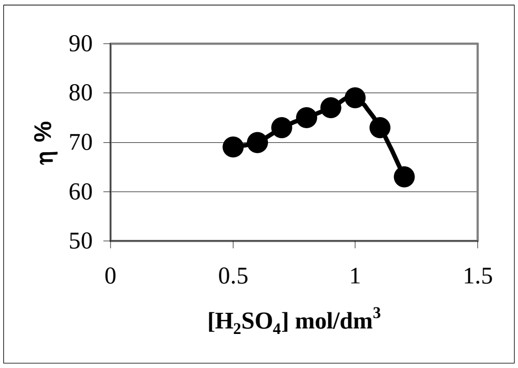

Figure 4. The influence of H_2SO_4 concentration upon the conversion of Ce(III) to Ce(IV); i = 0.97 mA/cm^2; [Ce(IV)]/[Ce(III)] = 2; t = 20^{0}C

As mentioned above, at higher concentrations of H_2SO_4, voluminous sulphatocomplexes of Ce(IV) and Ce(III) are dominant. The low mobility and the small diffusion coefficients of these species caused the decrease of Ce(IV) formation at concentrations over 1 mol/dm^3 H_2SO_4.

When [Ce(III)] was increased at constant Ce(IV) concentration, the best results were obtained for a [Ce(IV)/Ce(III)] equal to one (Fig. 5).

The presence of toluene exerted a negative influence on the regeneration process as it results from Table 2.

Table 2.

The influence of toluene concentration upon Ce(IV) regeneration process; [Ce(IV)/Ce(III)] = 10^{-2} mol/dm^3, i = 0,965mA/cm^2, [H_2SO_4]= 1 mol/dm^3, t = 20^{0}C

[Toluene] mol/dm^3	0,1	0,5	0,75
η% without toluene		79	
η%with toluene	61	60	58

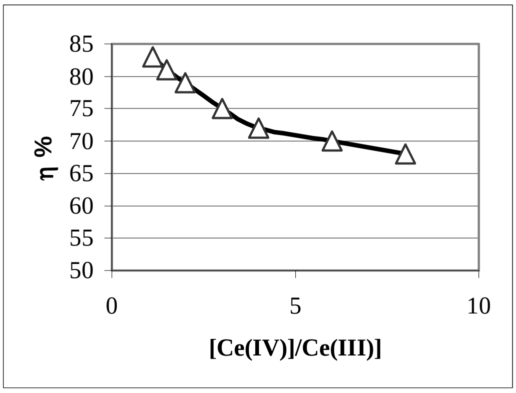

Figure 5. The influence of [Ce(IV)]/[Ce(III)] ratio upon the conversion of Ce(III) to Ce(IV); i = 0.97 mA/cm^2; [H_2SO_4]= 1mol/dm^3; t = 20^{0}C

Mediated electrosynthesis of benzaldehyde

Due to low solubility of toluene in the aqueous medium the experiments were carried out in a two-phase system, under vigorous stirring. In this case the oxidation of toluene by Ce(IV) occurs at the boundary between the two phases and homogeneously in the aqueous solution. The role of the second phase is to maintain a saturation of the aqueous solution by the toluene and also to extract the product.

As mentioned earlier in this paper the only product was benzaldehyde. The formation of benzyl alcohol and benzoic acid was not observed. The amount of formed benzaldehyde increased with the content of mixtures in toluene up to 0,023 mole toluene/50ml mixture. Further increase of the content in toluene had no significant influence upon benzaldehyde formation (Table 3.)

Table 3.

The influence of initial amount of toluene upon mediated electrosynthesis of benzaldehyde [Ce(IV)/Ce(III)] = 10^{-2} mol/dm^3; [H_2SO_4] = 1mol/dm^3; $V_{mixture}$ = 50ml; i = 0,965 mA/cm^2; t = 20^{0}C

Toluene	mmole	8	12	23	47	71
Benzaldehyde	mmole	2,3	3,3	6,1	6,1	6,2
η	%	28,75	27,50	26,53	12,97	8,73

This behaviour is probably due to low saturation of the aqueous phase with toluene and to the slow chemical reaction between Ce(IV) and toluene.

To improve the solubility of toluene in the aqueous phase n-propanol was added to the reaction mixture. An increase in the material yield of benzaldehyde was observed till the content of n-propanol reached 30% (Table 4.).

To increase the solubility of toluene we tested also nonionic surfactant like polyoxiethylenelauril ether, with the commercial designation Brij 35. The surfactant had positive influence upon the formation of benzaldehyde, but the results did not surpass that one obtained in the presence of n-propanol (Table 4.).

Better results were achieved at higher rates of the chemical reaction between Ce(IV) and toluene, obtained by increasing temperature. Best yields for the formation of benzaldehyde were observed at 60^{0}C in a mixture containing 0,023 moles of toluene in the presence of surfactant (Table 4.).

Table 4.

Influence of additions (n-propanol and surfactant) and temperature upon mediated electrosynthesis of benzaldehyde; [Ce(IV)/Ce(III)] = 10^{-2} mol/dm^3; [H_2SO_4] = 1 mol/dm^3; $V_{mixture}$ = 50 ml, i= 0,965 mA/cm^2, t = 20^{0}C; 0,023 moles of toluene; reaction time 10 h.

n-propanol	%	10	20	30	40
Benzaldehyde	mmole	6,4	6,7	7,1	7
10^3surfactant	mol/dm^3	0,5	0,7	1	2
Benzaldehyde	mmole	6,8	6,9	7	6,9
Temperature	K	293	313	323	333
Benzaldehyde	mmole	6,1	6,8	7,5	8,4

CONCLUSIONS

(i) The Ce(IV)/Ce(III) redox couple exhibits a quasi-reversible behaviour at a graphite electrode in H_2SO_4 medium.

(ii) The smaller values of the diffusion coefficients of Ce(IV) and Ce(III), compared to other acidic media, are due to the voluminous ceric and cerous sulphatocomplexes present in H_2SO_4 solutions.

(iii) The electrode kinetics of the Ce(IV)/Ce(III) couple is rapid in aqueous sulphuric acid medium. The reaction order less than unity found with respect to Ce(III) is probably caused by the adsorption of voluminous, inactive cerous sulphate complexes or solvent molecules at the electrode.

(iv) Ceric sulphate was successfully regenerated electrochemically working under optimum conditions we found: [Ce(IV)/Ce(III)] =1, $[H_2SO_4]$=1mol/dm^3, i= 1,2 mA/cm^2

(v) The mediated electrooxidation of toluene with the Ce(IV)/Ce(III) mediator yields no other products but benzaldehyde. Because of the slow chemical reaction between mediator and toluene, even best yields in benzaldehyde are not encouraging, although they are better than those mentioned for direct anodic oxidation of toluene in organic solvents[1].

SYMBOLS

ε	potential
ω	angular velocity
A	electrode area
I_v	peak current
I_L	limiting current
z	number of exchanged electrons
F	Faraday constant
k	rate constant of electron transfer
ν	kinematic viscosity
C	concentration
μ	reaction order
η	material yield

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