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Catalytic effects of the silver ion on the indirect electrochemical oxidation of toluene to benzaldehyde using Ce^{3+}/Ce^{4+} as mediator

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The catalytic effects of the silver ion on toluene oxidation by Ce^{4+} as well as the anodic generation of Ce^{4+} were investigated. The rates of toluene oxidation were first order with respect to both Ag^+ and Ce^{4+}. Argentic oxides formed on the surface of the platinum anode when Ag^+ was present in the anolyte, which increased the activity of the electrode. About 3×10^{-3} M of Ag^+ was needed to obtain maximum current efficiency

1. Introduction

The indirect electrochemical oxidation of organic compounds, such as the oxidation of toluene and its derivatives to the corresponding benzaldehydes, have been widely investigated recently [1–6]. Metal ionic couples such as Ce^{3+}/Ce^{4+}, Mn^{2+}/Mn^{3+}, Co^{2+}/Co^{3+} etc. were used as mediators or an oxygen carrier. The metal ions were oxidized from the lower oxidation state to the higher oxidation state and then reacted with the organic substrates. The chemical reactions of the substrates with the mediators may be carried out in-cell or ex-cell. In the latter case, the chemical reaction is carried out in a separate vessel and the mediator is recycled back to the electrolytic cell for regeneration.

The anodic generation of such oxidants with high current efficiency is one of the important factors for the indirect oxidation processes. Manganic sulphate can be generated with high current efficiency only if the H_2SO_4 concentration is greater than 50 wt% [2, 7, 8]. Otherwise, the formation of higher oxidation state compounds, such as MnO_2, should deactivate the anode surface and decrease the current efficiency. Co^{3+} is unstable in aqueous solution since it oxidizes H_2O with the evolution of oxygen [9–11]. Therefore, generating Co^{3+} with high current efficiency is difficult. The anodic oxidation of cerous sulphate to ceric sulphate in acid aqueous solutions is free from the formation of solid oxides of cerium on the electrode surface [9]. Because the solubility of cerous sulphate decreases sharply with the increase of the H_2SO_4 concentration, the current efficiency as well as the current density for generating ceric sulphate is decreased at high H_2SO_4 concentration. Dilute H_2SO_4 anolyte is better for anodic oxidation of cerous sulphate to ceric sulphate. However, the chemical reaction rates of ceric ion with organics are small in dilute H_2SO_4 solution [12, 13]. Several methods have been suggested for increasing the current efficiency of generating ceric ion in solutions of high H_2SO_4 concentration, such as increasing the solubility of cerous sulphate [14] and adding electrocatalyst in the electrolyte [11, 12]. Ag^+ has been used as an electrocatalyst in the anodic process. Boardman [11] has used silver ion as a catalyst for the anodic oxidation of Co^{2+} and Mn^{2+} and concluded that the silver ion is an effective catalyst. Comninellis and co-workers [12] have also reported that the current efficiency for generating ceric sulphate in a solution of 10 M H_2SO_4 increased if Ag_2SO_4 and $MnSO_4$ were present in the electrolyte solution.

Ag^+ has also been reported to be an effective catalyst in the oxidation of organic and inorganic compounds by ionic oxidants such as Ce^{4+} [15–18, 22], Co^{3+} [19] and $S_2O_8^{2-}$ [20, 21]. Goto [22] found that Ag^+ increased the rate of Cl^- oxidation by Ce^{4+}. Higginson [18] has studied the oxidation of mercurous ion to mercuric ion by Ce^{4+}. He also found that Ag^+ catalysed the reaction. Rennie [23] has used Ce^{4+} and Ag^+ as co-catalyst for the oxidation of aromatic compounds by $S_2O_8^{2-}$ [23]. Rao [17] has investigated the oxidation of dimethyl sulphoxide by ceric nitrate in the nitric acid medium. It was found that the reaction rates were fractional order with respect to Ag^+ and first order with respect to Ce^{4+}.

Catalytic effects of Ag^+ on both the anodic reaction and the subsequent chemical reaction of the redox mediator with the substrates are important in the indirect electrochemical oxidation processes. However, the catalytic effects of Ag^+ on the anodic reaction and the kinetics of the organic compound oxidation by Ce^{4+} using Ag^+ as a catalyst are not clear. In this work, the catalytic effects of the silver ion on toluene oxidation as well as the anodic generation of Ce^{4+} were investigated. The optimum conditions for the indirect oxidation of toluene to benzaldehyde using Ag^+ as a catalyst were discussed.

2. Experimental details

The electrolysis was carried out in an H-form divided

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cell. The anodic and cathodic compartments were separated by a No. 4 sintered glass disc 30 mm in diameter. Both anode and cathode were platinum plates. The anodic overpotential was measured against an SCE reference electrode. The d.c. current was supplied by a galvanostat (CHUNGYU CYE-D3022). The total amount of electricity passed during a run was measured by means of a coulometer (HOKUTO HF-201). A function generator (TAITIEN DFS-2) and a potentiostat (HOKUTO-3001) were used to supply the potential for the cyclic voltammograms. A YEW-3033 X–Y recorder was used to record the *I–E* curves. The experimental procedures are described in previous papers [24, 25].

The chemical reaction of toluene with Ce^{4+} was carried out in a glass reactor which was placed in a water bath agitated with ultrasonic waves (55 Hz, 270 W). The reactor, filled with 20 ml of aqueous sulphuric acid solution and 20 ml of toluene, was agitated and emulsified in advance for 10 min. Then 20 ml of ceric sulphate solution was poured into the reactor.

The concentration of Ce^{4+} was obtained by titration with standard ferrous ion solution. The organic products sampled from the glass reactor were analysed using a gas chromatograph (SHIMADZU GC-8A) with a flame ionization detector and a 3 m column packed with 3 wt % Apeizon-L and 1.5 wt % QF-1 on chromosorb W80/100.

3. Results and discussion

3.1. *Formation of argentic oxides on the anodic surface*

Fig. 1 shows the cyclic voltammograms of Ce^{3+} in the 1.5 M sulphuric acid solution. The current density on the backward scan (negative-going) was smaller than that on the forward scan in the absence of Ag^+ as shown in curve 1 of Fig. 1. This indicated that the formation of platinum oxide film on the anode surface might deactivate the anodic reaction. On the other hand, in the presence of Ag^+, the current density on the backward scan was higher than that on the forward scan. This showed that the addition of silver ion to the anolyte increased the activity of the anode.

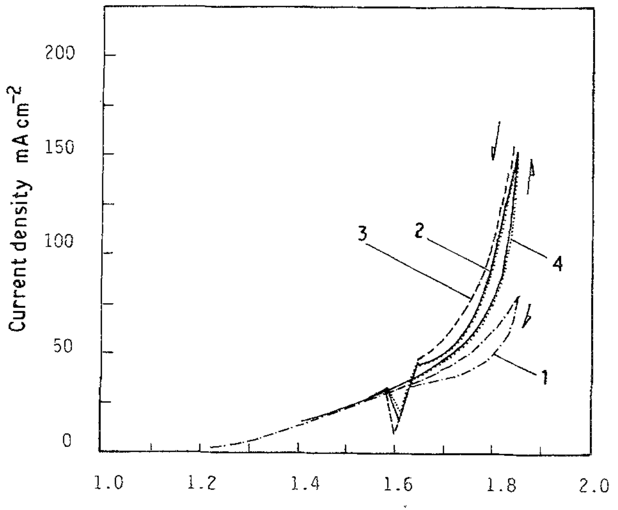

Fig. 1. Cyclic voltammograms for 0.1 M Ce^{3+} in 1.5 M H_2SO_4 at a platinum electrode. Scanning rate: curves 1, 2 & 3, 24 mV sec^{-1}; curve 4, 15 mV sec^{-1}. (1) Without Ag^+; (2) with 0.005 M Ag^+; (3) with 0.005 M Ag^+ and polarization to 1.90 V, (4) 0.005 M Ag^+.

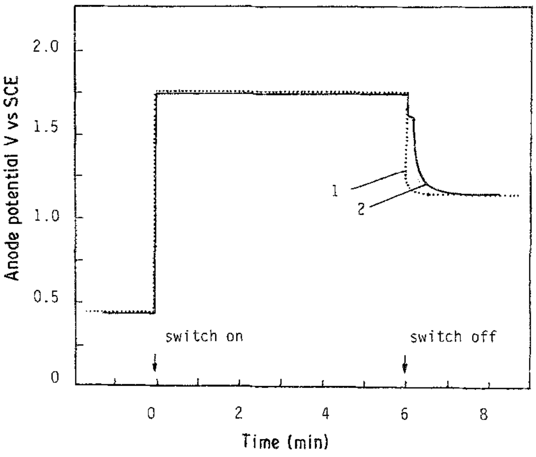

Fig. 2. Anode potential during passage of constant current and after its cessation (open-circuit voltage). Electrolyte: 1.5 M H_2SO_4, concentration of Ce^{3+}; 0.1 M, current density; 60 mA cm^{-2}. (1) Without Ag^+; (2) with 0.003 M Ag^+.

A reduction peak appeared at about 1.6 V (vs SCE) on the backward scan in the presence of Ag^+. The position and shape of the peaks did not change when the scanning rate was changed. This indicated that the peak was a reduction peak of oxidized species adsorbed on the surface of anode. The reduction peak might be due to the formation of an argentic oxide film since the position of the peak was approximately equal to the redox potential of AgO/Ag^+ [9]. Fig. 2 shows the anodic potential during the passage of constant current and after its cessation. The anodic potential shifted to 1.6 V (vs SCE) for a few seconds and then dropped to about 1.2 V (vs SCE) in the presence of Ag^+, whereas the anodic potential dropped immediately to about 1.2 V (vs SCE) in the absence of Ag^+ when the current was switched off. This further confirmed the formation of the argentic oxide film on the surface of the anode during the electrolysis. The rest potential of the anode was the potential of argentic oxide when the current was switched off and then dropped to the potential of Ce^{4+}, i.e. 1.2 V (vs SCE), as the argentic oxide film was consumed by the Ce^{3+} ion in the anolyte.

$$AgO + Ce^{3+} + 2H^+ \longrightarrow Ag^+ + Ce^{4+} + H_2O \tag{1}$$

The results shows that the catalytic effect of silver ion on the anodic oxidation of Ce^{3+} in dilute H_2SO_4 electrolyte was due to the formation of argentic oxide film on the anode surface. The oxide film, which may act as a heterogeneous redox mediator [31, 32], increases the anode activity. The constitution of argentic oxides is not known with certainty. Dugdale [26] has investigated the anodic formation of argentic oxides in sulphuric acid solution. The interpretation is complicated by the crystal growth of the higher oxide. Scatturin [27] has suggested that the argentic oxide is a silver(I)–silver(III) mixed oxide.

The argentic oxides were unstable. In very acid media these oxides can lead to the formation of Ag^{2+} [9, 33]. The catalytic effect of Ag^+ on the anodic reaction in concentrated H_2SO_4 (10 to 15 M) has been studied by Pletcher and Comninellis [7, 11, 12]. They suggested that the Ag^{2+}/Ag^+ ionic couple acts as a redox mediator.

3.2. *Effect of Ag^+ concentration on the current efficiency for generating Ce^{4+}*

The effect of Ag^+ concentration on the current efficiency for generating Ce^{4+} at various current densities is shown in Fig. 3. At either 50 or 90 mA cm^{-2} current density, the current efficiencies increased with concentration of Ag^+ in the range 0 to 3×10^{-3} M and then reached a limiting value. However, at either 25 or 150 mA cm^{-2}, the current efficiencies for generating ceric sulphate were not changed as Ag_2SO_4 was added to the electrolyte. At 25 mA cm^{-2}, the current efficiencies remained at about 91%. This is because the corresponding anodic potential was lower than the formation potential of argentic oxides, 1.6 V (vs SCE). At 150 mA cm^{-2}, the current efficiencies remained at about 26% and were independent of the concentration of Ag^+. This might be owing to mass transfer limitations. The currents going into Ce^{3+} oxidation and oxygen evolution were dominated by the competition reaction of the reacting species, i.e. H_2O and Ce^{3+}. The partial current leading to the generation of Ce^{4+} was limited by the mass transfer rate of Ce^{3+} near the anodic surface.

The results indicated that the optimum concentration of Ag^+ in the anolyte for promoting the current efficiency was independent of the current density. About 3×10^{-3} M of Ag^+ was necessary to establish the argentic oxide film on the anodic surface at either 50 or 90 mA cm^{-2}.

3.3. *Kinetics of toluene oxidation by Ce^{4+} using Ag^+ as catalyst*

Fig. 4 shows the effect of Ag^+ concentration on the initial reaction rate of toluene oxidation by Ce^{4+}. The plot of the reaction rate vs Ag^+ concentration was a straight line with a positive intercept of 4.0×10^{-4} M min^{-1} which was equal to the rate of the reaction of Ce^{4+} with toluene without Ag^+ as catalyst. This indicated that the oxidation of toluene by Ce^{4+} took place in both uncatalysed and catalysed paths in the presence of silver ion.

Fig. 5 shows a plot of Ce^{4+} conversion against time during the reaction of Ce^{4+} with toluene. The conversion of Ce^{4+} in the presence of silver, as shown in curve 2, was much higher than that without silver ions (curve 1). The behaviour of curve 2 fitted a first order reaction rate equation, i.e. $d[Ce^{4+}]/dt = k[Ce^{4+}]$. This indicated that Ce^{3+}, formed during the reaction, did not affect the rate of toluene oxidation. Fig. 6 shows the initial rate of toluene oxidation by Ce^{4+} at various Ce^{4+} concentrations. The results also showed that the reaction rate was first order with respect to Ce^{4+}.

The initial reaction rates at various sulphuric acid concentrations are shown in Fig. 7. Straight lines with zero slope were obtained. This indicated that the sulphuric acid concentration affects the rate of toluene oxidation insignificantly in the range 0.5 to 2.5 M H_2SO_4 in the presence of Ag^+. The reaction rate has been found to increase in high sulphuric acid concentration solution (8 M) in the absence of Ag^+ [12, 13].

Accordingly, the rate equation of the oxidation of toluene by Ce^{4+} using Ag^+ as catalyst may be expressed as follows

$$d[Ce^{4+}]/dt = (k1 + k2[Ag^+])[Ce^{4+}][\text{toluene}] \quad (2)$$

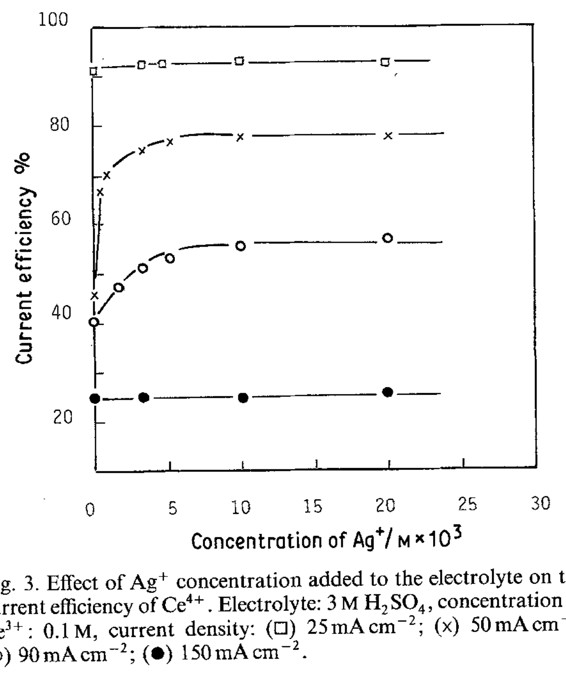

Fig. 3. Effect of Ag^+ concentration added to the electrolyte on the current efficiency of Ce^{4+}. Electrolyte: 3 M H_2SO_4, concentration of Ce^{3+}: 0.1 M, current density: (□) 25 mA cm^{-2}; (x) 50 mA cm^{-2}; (○) 90 mA cm^{-2}; (●) 150 mA cm^{-2}.

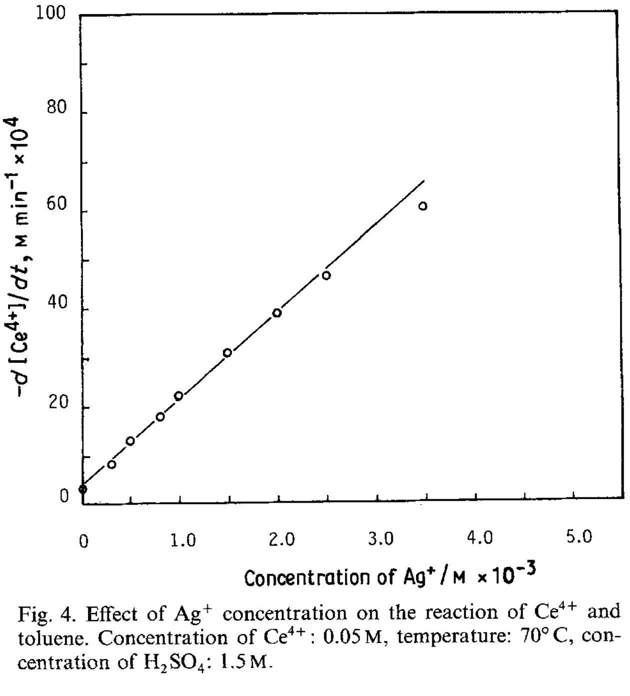

Fig. 4. Effect of Ag^+ concentration on the reaction of Ce^{4+} and toluene. Concentration of Ce^{4+}: 0.05 M, temperature: 70° C, concentration of H_2SO_4: 1.5 M.

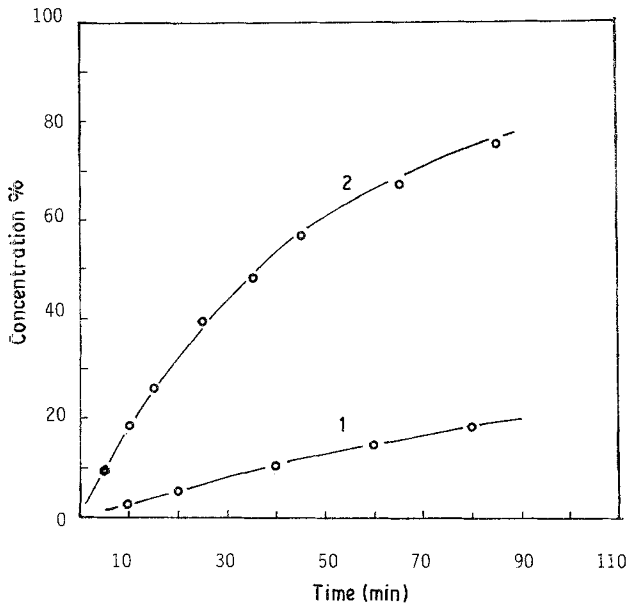

Fig. 5. Conversion of Ce^{4+} with time in the oxidation of toluene. Temperature: 70° C, concentration of H_2SO_4, 1.5 M; concentration of Ce^{4+}, 0.5 M; (1) without Ag^+; (2) with 3×10^{-3} M Ag^+.

In emulsion or violent agitation, the anolyte is saturated with toluene, and equation (2) may be rewritten as

$$d[Ce^{4+}]/dt = ([k' + k''[Ag^+])[Ce^{4+}] \qquad (3)$$

where $k' = k1 \times [\text{toluene}]_s$, $k'' = k2 \times [\text{toluene}]_s$, and $[\text{toluene}]_s$ is the saturation concentration of toluene in the solution.

Table 1 shows the pseudo rate constants at various temperature. The pseudo rate constants k' and k'' increased from 3.2×10^{-4} and 0.65 to 26×10^{-4} min^{-1} and 4.8 $M^{-1}min^{-1}$, respectively, as the temperature increased from 40 to 70° C. The values of k'' obtained at different Ag^+ concentrations were approximately equal.

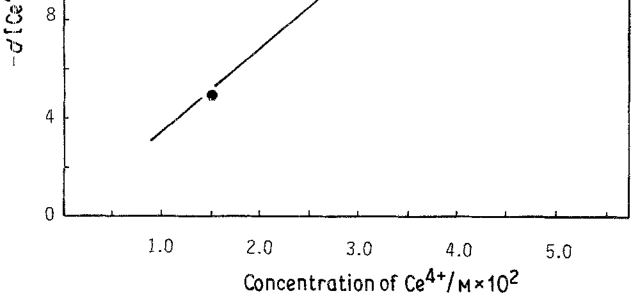

Fig. 6. Effect of Ce^{4+} concentration on the reaction of Ce^{4+} with toluene. Temperature: 70° C; concentration of H_2SO_4, 2 M; concentration of Ag^+, 0.008 M.

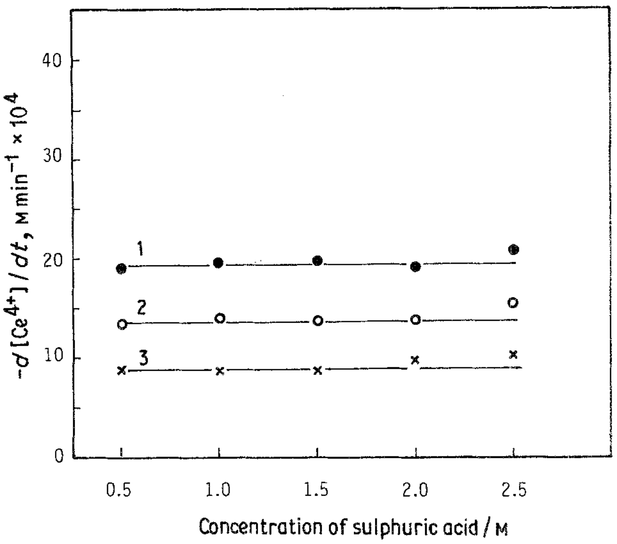

Fig. 7. Effect of H_2SO_4 concentration on the reaction of Ce^{4+} and toluene. Temperature: 70° C, concentration of Ce^{4+}: 0.05 M, concentration of Ag^+: (1) 0.008 M; (2) 0.005 M; (3) 0.003 M.

3.4. *Dependence of reactor design on Ag^+ concentration and temperature*

The results of gas chromatograph analysis revealed that the only detectable product was benzaldehyde in the reaction of toluene with Ce^{4+} either in the absence or presence of Ag^+. Other oxidation products, such as benzyl alcohol and benzoic acid, were not found. The yields of benzaldehyde basing on Ce^{4+} were 95 to 100%. Therefore, almost all the consumed toluene was converted to benzaldehyde. The material yield for the oxidation of toluene to benzaldehyde was 100% with or without Ag^+.

The indirect electrochemical oxidation process includes the oxidant generation and chemical oxidation steps. The reaction of the organic substrate with the oxidant is generally carried out in a separate reactor since the adsorption of organic compounds on the electrode surface increases the overpotential [25, 28] and leads to current loss [29, 30]. Several factors are important in designing the chemical reactor, such as toluene conversion and residence time. It is necessary to keep the benzaldehyde concentration below a critical value within the organic phase because the degree of toluene conversion affects the selectivity strongly [2]. Excess toluene has been used as organic solvent as well as reactant to avoid the formation of benzoic acid [4].

The residence time, *T*, depends on the conversion of

Table 1. Pseudo rate constants k′ and k″ of the oxidation of toluene by Ce^{4+} in the presence of Ag^+ in the solutions saturated with toluene

Concentration of Ag^+, M × 10^3	*Temperature* (° C)				*Comments*
	40	50	60	70	
0	3.2	4.8	11	26	(k'/min^{-1} × 10^{-4})
3	0.65	1.5	2.4	5.1	(k''/$M^{-1}min^{-1}$)
5	0.66	1.5	2.3	4.6	(k''/$M^{-1}min^{-1}$)
8	0.65	1.5	2.2	4.8	(k''/$M^{-1}min^{-1}$)

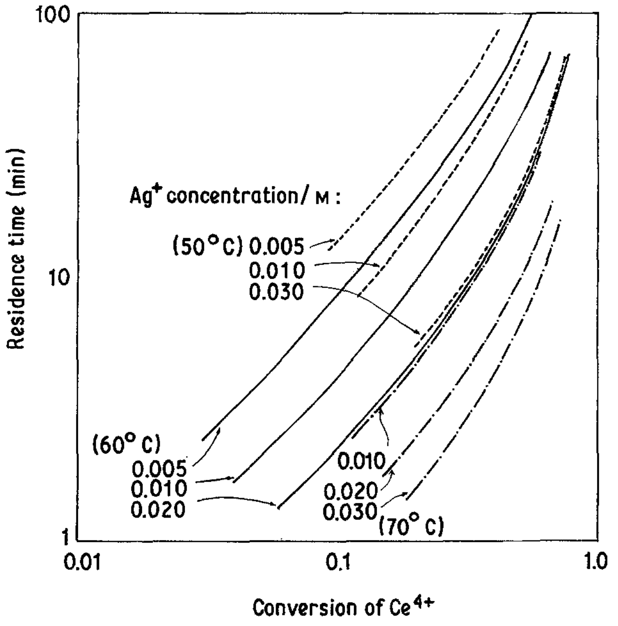

Fig. 8. Relationships of residence time and Ce^{4+} conversion at various temperatures and Ag^+ concentrations.

Ce^{4+}, concentration of Ag^+ and reaction temperature. For a continuous stirred tank reactor (CSTR), T is given by

$$T = V/v = X[Ce^{4+}]_0/r \quad (4)$$

$$= X[Ce^{4+}]_0/\{(k'\phi + k''[Ag^+])[Ce^{4+}]\} \quad (5)$$

$$= X[Ce^{4+}]_0/\{(k\phi + k''[Ag^+])[Ce^{4+}]_0(1 - X)\} \quad (6)$$

where V is the volume of the chemical reactor, v is the flow rate of the inlet and outlet streams, $[Ce^{4+}]_0$ is the concentration of Ce^{4+} in the inlet stream, r is the reaction rate and X is the conversion of Ce^{4+}.

The plots of the residence time of a CSTR chemical reactor vs conversion at various temperatures and Ag^+ concentrations are shown in Fig. 8. This provides information for designing the chemical reactor and the optimum operating conditions. The residence time decreases with increase in temperature and Ag^+ concentration. The values of residence time obtained at 50, 60 and 70°C with 30, 20 and 10 × 10^{-3}M Ag^+, respectively, are very close. The operation temperature can be decreased by increasing the Ag^+ concentration. In addition, higher space time yield, i.e. the rate of production per unit reactor volume, can be obtained by using Ag^+ as catalyst. The saturation concentrations of Ag^+ and Ce^{4+} in various concentrations of sulphuric acid solution are shown in Fig. 9. The results indicated that anolyte containing higher Ce^{4+} and Ag^+ concentrations can be applied by using dilute sulphuric acid solution as electrolyte. Anolyte containing a higher redox mediator concentration increases the current density as well as the current efficiency of the electrolyser.

4. Conclusions

Ag^+ added to the anolyte is an effective catalyst in the reaction of Ce^{4+} with toluene and the anodic generation of Ce^{4+}. The reaction rate of toluene oxidation by Ce^{4+} increases linearly with the concentration of both Ag^+ and Ce^{4+}. Using Ag^+ as catalyst, anolyte containing dilute sulphuric acid is preferred because the solubility of ceric sulphate in dilute sulphuric acid solution is higher. Ag^+ in the electrolyte, as well as promoting the oxidation of toluene by Ce^{4+}, leads to the formation of argentic oxides on the anodic surface and increases the current efficiency for generating Ce^{4+}.

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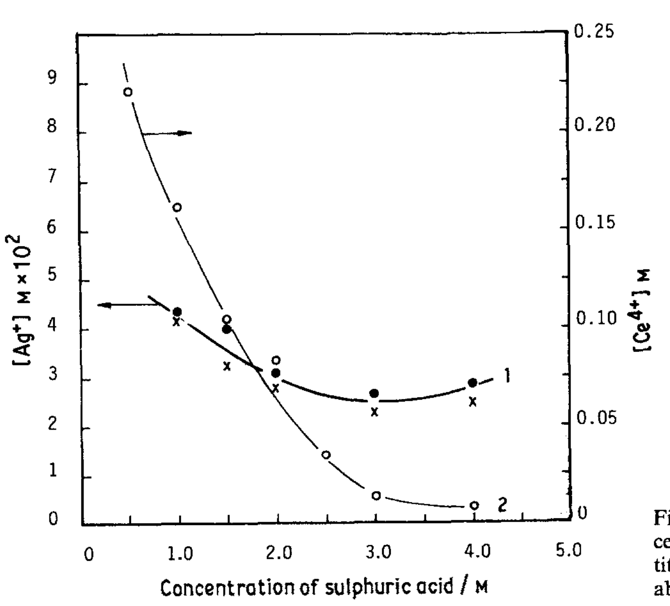

Fig. 9. Saturation concentrations of Ag^+ and Ce^{4+} in various concentrations of sulphuric acid solution. Temperature: 20°C, (x) by titration with aqueous KCNS solution, (●) by means of atomic absorption spectrometry, (○) by titration with ferrous ion solution.

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