

Anodic oxidation of benzyl alcohol to benzaldehyde in the presence of both redox mediator and polymer-supported phase-transfer catalyst

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Using a polymer-supported phase-transfer catalyst (PTC) and a redox mediator, Cl^-/OCl^- , the anodic oxidation of benzyl alcohol was studied. The polymer support used in this study was synthesized by the method of suspension polymerization. The results revealed that on decreasing the crosslinking and increasing the content of chloromethylstyrene in the polymer support, the number of phase transfer active sites, tri-*n*-butylphosphine, in the polymer-supported PTC increased. The anodic oxidation of benzyl alcohol in the presence of the redox mediator, Cl^-/OCl^- , and polymer-supported PTC occurred in the reaction controlled region when the stirring rate exceeded 400 r.p.m. The results also revealed that the current efficiency for the anodic oxidation of benzyl alcohol was mainly affected by the characteristics and weight of the polymer-supported PTC, the pH, and the concentration of benzyl alcohol. However, the temperature affected the current efficiency only slightly.

1. Introduction

Phase-transfer catalysis in electrochemical systems has been discussed by several investigators [1-15] and some of this work is concerned with electrolysis in the presence of both a redox mediator and a phase-transfer catalyst (PTC) [1, 2, 11-15]. In our previous work [14, 15], with OCl^-/Cl^- as redox mediator, the role of mass transfer and parameters which affect the current efficiency [14] and the kinetics [15] of the anodic oxidation of benzyl alcohol in the presence of a homogeneous PTC were investigated.

However, in general, a homogeneous PTC is not easily separated and recovered from the solution in a phase-transfer catalysis system. Therefore, solid PTCs have attracted attention in recent years [16-37]. Solid phase-transfer catalysis has several advantages over homogeneous phase-transfer catalysis [33]: (a) the solid phase can easily be separated, recovered, and reused; (b) side reactions can be inhibited and the selectivity increased; (c) solid phase-transfer catalysis can be conveniently operated in a continuous reactor. Most solid PTCs are polymer-supported. Applications of polymer-supported phase transfer catalysis in displacement reactions have been widely discussed [17-22]. Some of this work [31-37] concerned oxidation reactions in the presence of polymer-supported PTC. Benzyl alcohol was oxidized by sodium hypo-

chlorite in the presence of polymer-supported PTC with *N,N*-dimethyl-*n*-butylamine as active group [31]. Commercial resins, such as Dowex-1 and AGMP-1, were used as the solid PTC for the oxidation of benzyl alcohol by sodium hypochlorite in three phase systems [33-37]; the reaction order with respect to benzyl alcohol was found to be one. A technique developed to use a solid PTC for indirect anodic oxidation of organic compounds would have several advantages. First, recovery of the catalyst and isolation of the product would be simplified. Second, there would be little or no pollution. Further, the active redox mediators could easily be regenerated and consumed *in situ*; hence the transportation of dangerous oxidants, such as hypochlorite or hypobromite, would be unnecessary.

The mechanism and kinetics of the oxidation of benzyl alcohol with tetrabutylammonium salt as PTC in the two-phase system were previously discussed [38]. We also demonstrated a high current efficiency for the anodic oxidation of benzyl alcohol in a two-phase system with a PTC [14, 15]. The work described in this study is the anodic oxidation of benzyl alcohol to benzaldehyde with a polymer-supported PTC and redox mediator, OCl^-/Cl^- . Hypochlorite ion was used as oxidant and was regenerated by the anodic oxidation of the produced chloride ion in the aqueous phase. The mechanism and the factors affecting the current efficiency were investigated.

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2. Experimental details

2.1. Preparation of polymer-supported phase transfer catalyst

A 1 dm³ cylindrical glass vessel was used as the polymerization reactor. To prepare various crosslinking resins, the suspension solution was formed by mixing the required compositions of the aqueous phase and organic phase solutions. The suspension solution was agitated with a motorized stirrer (Eyela DC-2RT) and the aqueous and organic vapours were condensed with a cryostat cooling system.

The polystyrene-co-chloromethylstyrene-dimethacrylate support was prepared by suspension polymerization according to the following procedure. The aqueous solution with a desired composition was charged into the reactor which was immersed in a water bath with the temperature controlled at 90°C. Oxygen in the aqueous solution was expelled by introducing nitrogen gas. After the desired temperature of the solution was reached, the organic solution with a desired composition was introduced into the reactor. The two immiscible phases were agitated by a motorized stirrer with a curved blade propeller. The stirring rate was kept at 800 r.p.m. in the preparation of 30% and 45% chloromethylstyrene polymer support and at 600 r.p.m. for the others. After 12 h, the polymerization was completed and the polymer support was obtained by filtration of solution. The polymer support was alternately rinsed with 1 M HCl aqueous solution and distilled water. Finally, the support was dried at 80°C for several hours.

For the immobilization of tri-*n*-butylamine onto the polymer support, 50 g dried polymer support and 100 g tri-*n*-butylamine were introduced into the reactor and stirred for 60 h at 90°C. The resin was then filtered and alternately rinsed with methanol and acetone for five cycles. After being dried under vacuum at 80°C, the immobilized tri-*n*-butylamine polymer-supported PTC was obtained.

For the immobilization of tri-*n*-butylphosphine, 50 g dried polymer support was swollen in 625 ml toluene at 90°C for 1 h. Tri-*n*-butylphosphine (50 g) was fed into this mixture and stirred at 90°C for 60 h. The procedures of filtration, rinsing, and drying were the same as above.

The content of chlorine in the polymer-supported PTC was determined by elementary analysis (Heraeus CHN-O-Rapid Analyzer).

2.2. Anodic oxidation of benzyl alcohol in the presence of both redox mediator and polymer-supported PTC

The experimental apparatus for the anodic oxidation of benzyl alcohol was as previously described [14]. For the anodic oxidation of benzyl alcohol, the emulsion was formed by mixing 70 ml organic solution containing a desired concentration of benzyl alcohol with 70 ml aqueous solution containing 1.0 M NaCl and a

desired weight of polymer-supported PTC. The pH was controlled by a pH controller (Tokyo Rikakikai, FC-1). The entire reactor was immersed in a water bath controlled at a desired temperature with a precision of $\pm 0.1^\circ\text{C}$. At the beginning of a run, the motorized stirrer was switched on and electrolysis was carried out at a constant current until a preset amount of charged had passed. During the run, the organic phase was sampled periodically and analysed by capillary GLC. (J. & W. Scientific, Inc., DB-1.)

3. Results and discussion

3.1. The characteristics of polymer-supported phase transfer catalyst

As shown in Table 1, two types of polymer-supported PTC, N1 and P1 to P5, were used. The active groups of N1 and P1 to P5 were tri-*n*-butylamine and tri-*n*-butylphosphine, respectively, which were immobilized on the polymer support. Table 1 shows that N1 had more active sites than P1 when a polymer support with 2% crosslinking was used in the immobilization. It may be that tri-*n*-butylamine substitutes chlorine more easily than tri-*n*-butylphosphine on the polymer support. Furthermore, the concentration of tri-*n*-butylamine was larger than that of tri-*n*-butylphosphine in the immobilization reaction. As illustrated in Table 1, less crosslinking of polymer support gave more active sites in the polymer-supported PTC. This reveals that less crosslinking of the polymer support favoured the immobilization of the active group, tri-*n*-butylphosphine, on the support.

On increasing the molar fraction of chloromethylstyrene monomer in the suspension polymerization, the content of chlorine atoms on the polymer supports increased. Therefore, the content of the active group (tri-*n*-butylphosphine) increased as shown for P3–P5 in Table 1. As shown for P4 in Table 1, the content of the active group was slightly affected by the catalyst particle size.

3.2. The mechanism of the anodic oxidation of benzyl alcohol in the presence of redox mediator, OCl^-/Cl^- , and polymer-supported PTC

The current efficiencies for the anodic oxidation of benzyl alcohol were 29.1% and 79.1% without and with polymer-supported PTC, respectively, as shown in Table 2. As illustrated in this Table, the current efficiency for the anodic oxidation of benzyl alcohol with unimmobilized polymer support was 42.0%, which was greater than without any PTC, 29.1%. These results revealed that the unimmobilized polymer support increased the contacting area between the organic and aqueous phases; then the hypochlorite ion produced on the anode was effectively transferred from the aqueous phase into the polymeric phase where it reacted with benzyl alcohol. We conclude that the oxidation of benzyl alcohol by hypochlorite ion occurred mainly in the polymeric phase.

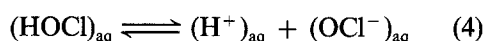
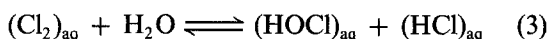
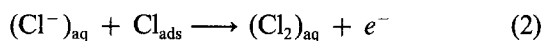
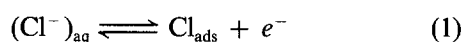
Table 1. Characteristics of the polymer-supported phase transfer catalyst

No.*	Degree of crosslink/%	Particle size/ mesh no.	Cl cont. before immobilisation/ meq g ⁻¹	Cl cont. after immobilisation/ meq g ⁻¹	Cont. of active group/ meq g ⁻¹
P1	2.0	50-100	1.16	1.07	0.09
N1	2.0	50-100	1.16	-	0.64 [†]
P2	0.5	50-100	1.53	0.94	0.59
P3	0.8	50-100	1.36	1.03	0.33
P4	0.8	50-100	2.04	1.34	0.70
P4	0.8	100-200	2.04	1.29	0.75
P4	0.8	200-400	2.04	1.25	0.79
P5	0.8	100-200	2.56	1.52	1.04

* P1 to P5 and N1 denote tri-*n*-butylphosphine and tri-*n*-butylamine active groups, respectively.

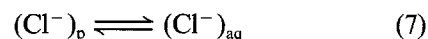
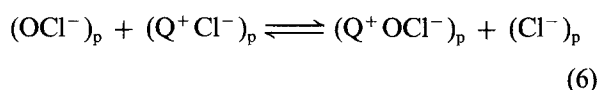
[†] The content of active group, tri-*n*-butylamine, is determined by analysis of the content of the element N in the PTC.

The mechanism of anodic oxidation of chloride ion to hypochlorite ion on graphite in a two-phase system has been previously discussed [14]. The chloride ion is oxidized to molecular chlorine on graphite in the aqueous phase and hypochlorite ion is formed by the hydrolysis of molecular chlorine in the bulk solution of the aqueous phase [39-41]:



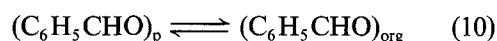
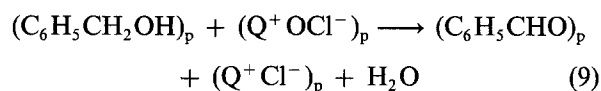
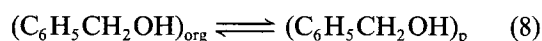
where 'aq' indicates the aqueous phase.

The hypochlorite ion is extracted from the aqueous phase into the polymer phase, in which a weakly solvated ion pair is formed.



where 'p' indicates the polymer phase, and Q⁺ indicates the PTC active site.

In general, benzyl alcohol can diffuse from the organic phase into the polymer phase and undergo rapid oxidation,



where 'org' indicates the organic phase. The mechanism of the anodic oxidation of benzyl alcohol in the presence of polymer-supported PTC is shown in Fig. 1.

3.3. Effect of type of electrolytic cell

Two types of divided cell and one type of undivided cell were used in this work. The separators of the divided cell were sintered glass and a cation-exchanged

Table 2. Current efficiency of the anodic oxidation of benzyl alcohol. (Temperature = 25°C, pH 7.0 ± 0.2, anode: graphite, current density = 10 mA cm⁻², stirring rate = 1100 r.p.m., organic solvent: CH₂Cl₂, V_{org} = 70 ml, V_{aq} = 70 ml, [NaCl]_{aq} = 1.0 M, weight of catalyst = 4.0 g, charge passed = 1.0 F mol⁻¹ of benzyl alcohol.)

No.	PTC/type	Particle size/ mesh no.	Type of cell	[C ₆ H ₅ CH ₂ OH]*/M	C.E./%
1	Dowex-1 1 × 4-Cl [†]	50-100	A	0.5	18.4
2	Dowex-1 1 × 4-Cl [†]	50-100	B	0.5	18.0
3	P3	50-100	A	0.5	30.8
4	P3	50-100	C	0.5	26.1
5	-	-	A	0.5	24.0
6	P4	50-100	A	0.5	33.3
7	P4	100-200	A	0.5	43.0
8	P4	200-400	A	0.5	59.9
9	P4	200-400	A	1.0	79.1 [‡]
10	unimmobilized	200-400	A	1.0	42.0 [‡]
11	-	-	A	1.0	29.1 [‡]

* Based on organic phase;

[†] 2.0 g of catalyst;

[‡] Charge passed = 0.5 F mol⁻¹ of benzyl alcohol.

A: undivided cell; B: cell divided by sintered glass; C: cell divided by Ionac MC-3470 cation exchange membrane.

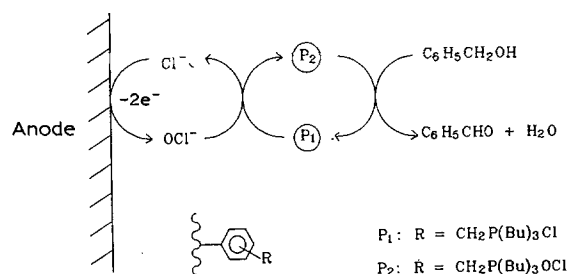


Fig. 1. Scheme of the anodic oxidation of benzyl alcohol in the presence of the polymer-supported phase transfer catalyst.

membrane (Ionac MC-3470), respectively. With a commercial ion-exchange resin, Dowex-1 $1 \times 4\text{-Cl}$, as PTC, benzyl alcohol was anodically oxidized in the undivided and divided (divided by the sintered glass) cells for which the current efficiencies were 18.4% and 18.0%, respectively, as shown in Table 2. The results also showed that the current efficiency for the anodic oxidation of benzyl alcohol with P3 polymer-supported PTC in the undivided and divided (divided by Ionac MC-3470 ion-exchange membrane) cells were not significantly different. These results indicated that the hypochlorite ion produced on the anode was effectively transferred from the aqueous phase into the polymer phase, and hypochlorite ion reduced on the cathode was insignificant.

3.4. Effect of particle size of polymer-supported PTC

With polymer-supported PTC of type P4, decreasing the catalyst particle size caused an increase in the current efficiency for the anodic oxidation of benzyl alcohol as shown in No. 6 to 8 of Table 2. In general, the surface area of the polymer-supported PTC increased when the particle size decreased for the same weight of catalyst. Therefore, the extraction efficiency of ClO^- and $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ from the aqueous and organic phases, respectively, into the polymer phase, as well as the current efficiency for the anodic oxidation of benzyl alcohol, increased as the particle size of the polymer-supported PTC decreased.

3.5. Effect of types of polymer-supported PTC

The crosslinking of P1, P2, and P3 polymer-supported PTCs were 2%, 0.5%, and 0.8%, respectively, as illustrated in Table 1. The results revealed that decreasing the catalyst crosslinking from 2% to 0.8% increased the current efficiency from 16.8% to 27.6% as shown in Table 3. This was due to the increase of the number of active sites on the catalyst when the catalyst crosslinking decreased as shown in Table 1. Further decrease in the catalyst crosslinking to 0.5% caused the catalyst resin to become too soft and the anodic surface was partly covered by the swollen resin. This caused a slight decrease in the current efficiency to 26.1%.

The current efficiency for the anodic oxidation of benzyl alcohol with Dowex-1 $1 \times 4\text{-Cl}$ and N1 catalysts was lower than with P1 to P5 catalysts. The active groups of Dowex-1 $1 \times 4\text{-Cl}$ and N1 catalysts

Table 3. Effect of the types of polymer-supported phase transfer catalyst on current efficiency. (Temperature = 25°C , $\text{pH} 7.0 \pm 0.2$, anode: graphite, current density = 10 mA cm^{-2} , stirring rate = 1100 r.p.m., weight of catalyst = 2.0 g, organic solvent: CH_2Cl_2 , $V_{\text{org}} = 70 \text{ ml}$, $V_{\text{aq}} = 70 \text{ ml}$, $[\text{NaCl}]_{\text{aq}} = 1.0 \text{ M}$, $[\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}} = 0.5 \text{ M}$, charge passed = 1.0 F mol^{-1} of benzyl alcohol, electrolysis cell: undivided cell.)

PTC/type	Catalyst particle size/mesh no.	Current efficiency/%
P1	50–100	16.8
Dowex-1 $1 \times 4\text{-Cl}$	50–100	18.4
N1	50–100	18.4
P2	50–100	26.1
P3	50–100	27.6
P4	50–100	33.3
P4	100–200	43.0
P5	100–200	36.7

are ammonium salts, $-\text{N}(\text{CH}_3)_3\text{Cl}$ and $-\text{N}(\text{C}_4\text{H}_9)_3\text{Cl}$, respectively. The active group of P1 to P5 catalysts is phosphine salt, $-\text{P}(\text{C}_4\text{H}_9)_3\text{Cl}$. Accordingly, the active group of phosphine salt was more effective than ammonium salt in extracting substances from both the aqueous and organic phases into the polymer phase. A similar result has been reported elsewhere [42].

Comparing P3 and P4 catalysts, the current efficiencies for the anodic oxidation of benzyl alcohol were 27.6% and 33.3%, respectively, as shown in Table 3. The results correlated well with the active group content of P3 and P4 catalysts which were 0.33 and 0.70 meq g^{-1} , respectively, as shown in Table 1. The results indicated that a greater active group content favoured the extraction of substances from both organic and aqueous phases into the polymer phase resulting in a higher current efficiency for the anodic oxidation of benzyl alcohol. Although the active group content of P5 catalyst (100–200 mesh) was greater than that of P4 catalyst (100–200 mesh), as shown in Table 1, the current efficiency for the anodic oxidation of benzyl alcohol with P5 catalyst was smaller than that of P4, as shown in Table 3. These results were due to the weak mechanical strength of P5 catalyst, and the fact that the surface area of the anode was partly covered with swollen catalyst. Therefore, the side reaction of the anodic oxidation of benzyl alcohol, oxygen evolution, increased when the P5 catalyst was used as PTC.

3.6. Effect of stirring rate

Using 200–400 mesh P4 polymer-supported PTC, increasing the stirring rate from 200 to 400 r.p.m. caused a sharp increase in the current efficiency from 10.5% to 59.9%, as shown in Fig. 2. Further increase of the stirring rate from 400 to 1100 r.p.m. caused the current efficiency for the anodic oxidation of benzyl alcohol to increase only slightly. The results revealed that mass transfer was the rate determining step when the stirring rate was less than 400 r.p.m. A similar result was obtained previously [14, 15, 38].

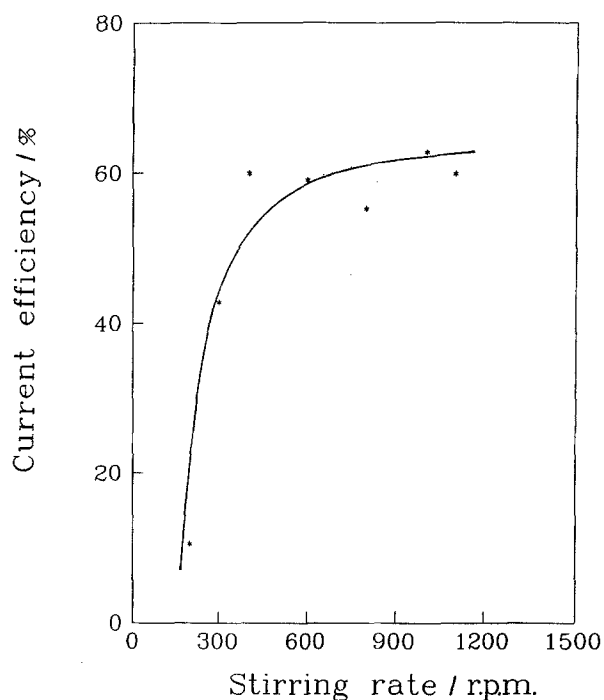
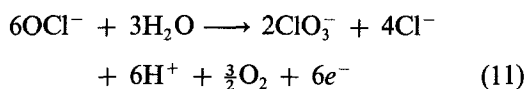


Fig. 2. Effect of stirring rate on current efficiency. Temperature = 25°C, $[\text{NaCl}]_{\text{aq}} = 1.0\text{ M}$, anode: graphite, current density = 10 mA cm^{-2} , organic solvent: CH_2Cl_2 , $\text{pH } 7.0 \pm 0.2$, $V_{\text{org}} = 70\text{ ml}$, $V_{\text{aq}} = 70\text{ ml}$, phase transfer catalyst: P4 200–400 mesh, weight of catalyst = 4.0 g, $[\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}} = 0.5\text{ M}$, charge passed = 1.0 F mol^{-1} of benzyl alcohol, electrolytic cell: undivided cell.

3.7. Effect of pH

As shown in Table 4, the best current efficiency was at pH 7.0. According to Equations 3 and 4, the hydrolysis of molecular chlorine was inhibited and the current efficiency for the anodic oxidation of benzyl alcohol decreased when the solution was kept at lower pH. At higher pH OH^- ions competed with hypochlorite ion to associate with the active group on the polymer-supported PTC. Furthermore, the side reaction [14, 40, 41]



was promoted under basic conditions. Hence the current efficiency decreased when the pH exceeded 7.0.

3.8. Effect of concentration of benzyl alcohol

With 200–400 mesh P4 polymer-supported PTC, the

Table 4. Effect of pH on the current efficiency. (Temperature = 25°C, $[\text{NaCl}]_{\text{aq}} = 1.0\text{ M}$, anode: graphite, current density = 10 mA cm^{-2} , organic solvent: CH_2Cl_2 , stirring rate = 1100 r.p.m., $V_{\text{org}} = 70\text{ ml}$, $V_{\text{aq}} = 70\text{ ml}$, phase transfer catalyst: P4 200–400 mesh, weight of catalyst = 4.0 g, $[\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}} = 0.5\text{ M}$, charge passed = 1.0 F mol^{-1} of benzyl alcohol, electrolytic cell: undivided cell.)

pH	Current efficiency/%
4.0 ± 0.1	49.1
7.0 ± 0.2	63.3
11.0 ± 0.1	41.1

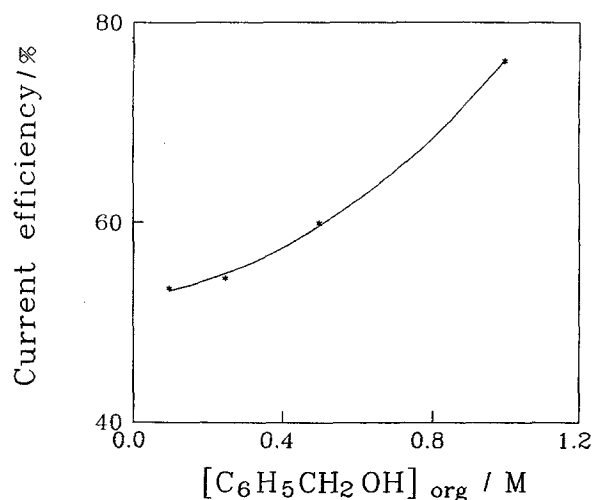


Fig. 3. Effect of concentration of benzyl alcohol in the organic phase on current efficiency. Temperature = 25°C, $[\text{NaCl}]_{\text{aq}} = 1.0\text{ M}$, anode: graphite, current density = 10 mA cm^{-2} , organic solvent: CH_2Cl_2 , $\text{pH } 7.0 \pm 0.2$, $V_{\text{org}} = 70\text{ ml}$, $V_{\text{aq}} = 70\text{ ml}$, phase transfer catalyst: P4 200–400 mesh, weight of catalyst = 4.0 g, stirring rate = 1100 r.p.m., charge passed = 1.0 F mol^{-1} of benzyl alcohol, electrolytic cell: undivided cell.

current efficiency increased with the concentration of benzyl alcohol as shown in Fig. 3. According to Equation 8, increasing the concentration of benzyl alcohol in the organic phase leads to an increase in the equilibrium concentration of benzyl alcohol in the polymer phase. Based on Equation 9, increasing the concentration of benzyl alcohol in the polymer phase caused an increase in the chemical reaction rate in the polymer phase. Accordingly, both the efficiency for the extraction of hypochlorite ion from the aqueous phase into the polymer phase and the current efficiency increased.

In addition, benzyl alcohol could also be directly oxidized on the anode [14]; hence the current efficiency for the direct anodic oxidation of benzyl alcohol also increased when its concentration increased.

3.9. Effect of temperature

As shown in Fig. 4, with 200–400 mesh of P4 polymer-supported PTC, the current efficiency increased with temperature. At increased temperature, both the reaction rate in the polymer phase, Equation 9, and the extraction efficiency of hypochlorite ion from the aqueous phase into the polymer phase increased.

3.10. Effect of weight of polymer-supported PTC

When the weight of the polymer-supported PTC increased, the number of phase transfer active sites increased. Accordingly, both the extraction efficiency of hypochlorite ion and benzyl alcohol from the aqueous and organic phases, respectively, into the polymer phase and the current efficiency increased. As shown in Fig. 5, with 0.5 F mol^{-1} charged the current efficiency increased from 27.9% to 63.3% when the weight of P4 polymer-supported PTC increased from 1.0 to 4.0 g.

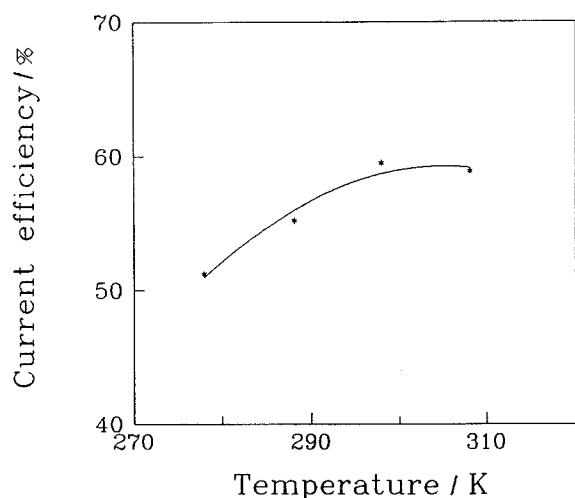


Fig. 4. Effect of temperature on current efficiency. Stirring rate = 1100 r.p.m., $[\text{NaCl}]_{\text{aq}} = 1.0 \text{ M}$, anode: graphite, current density = 10 mA cm^{-2} , organic solvent: CH_2Cl_2 , $\text{pH } 7.0 \pm 0.2$, $V_{\text{org}} = 70 \text{ ml}$, $V_{\text{aq}} = 70 \text{ ml}$, phase transfer catalyst: P4 200–400 mesh, weight of catalyst = 4.0 g, $[\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}} = 0.5 \text{ M}$, charge passed = 1.0 F mol^{-1} of benzyl alcohol, electrolytic cell: undivided cell.

3.11. Effect of current density

As illustrated in Fig. 6, the current efficiency decreased when the current density increased. This result was due to the anodic side reaction, oxygen evolution, increasing with current density.

As shown in Fig. 6, increasing the charge passed from 0.1 to 0.4 F mol^{-1} caused an increase in the current efficiency from 70% to 80% when the current density was 5 mA cm^{-2} . With increase of the charge passed to 5 F mol^{-1} , the current efficiency decreased slightly to 78.8%. In the initial period of electrolysis,

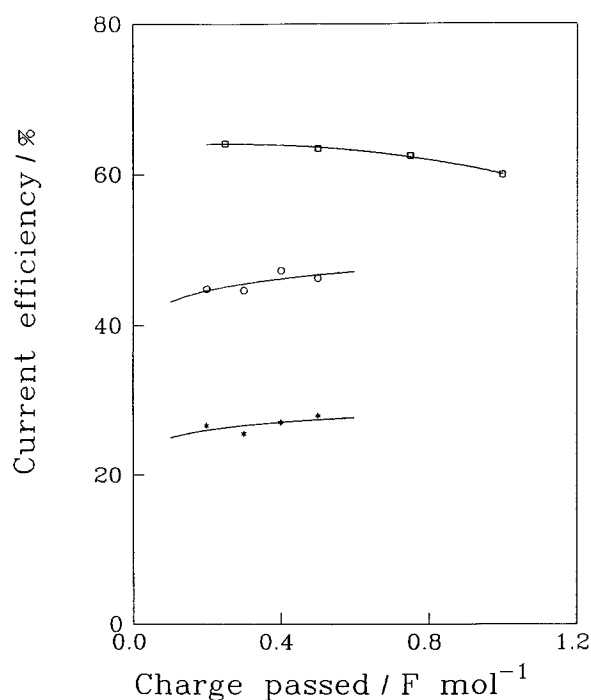


Fig. 5. Effect of charge passed on current efficiency. Temperature = 25°C , $[\text{NaCl}]_{\text{aq}} = 1.0 \text{ M}$, anode: graphite, current density = 10 mA cm^{-2} , organic solvent: CH_2Cl_2 , $\text{pH } 7.0 \pm 0.2$, $V_{\text{org}} = 70 \text{ ml}$, $V_{\text{aq}} = 70 \text{ ml}$, phase transfer catalyst: P4 200–400 mesh, $[\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}} = 0.5 \text{ M}$, stirring rate = 1100 r.p.m., electrolytic cell: undivided cell. Wt. of PTC: (*) 1.0, (O) 2.0 and (□) 4.0 g.

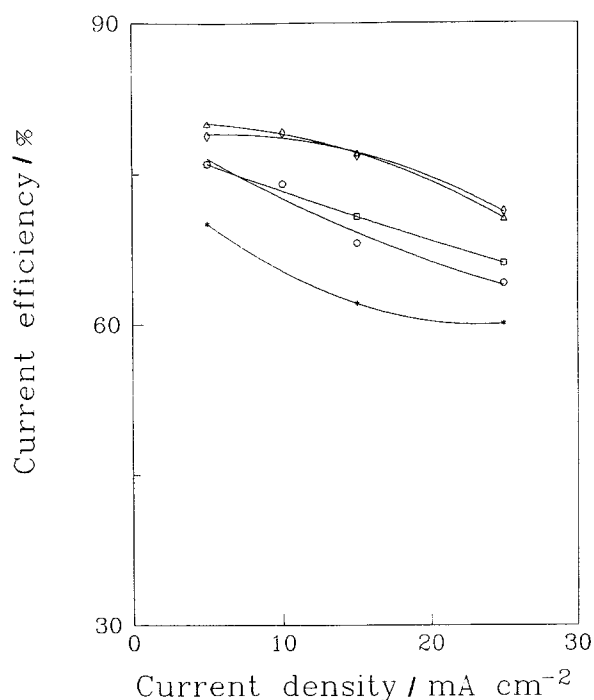


Fig. 6. Effect of current density on current efficiency. Temperature = 25°C , $[\text{NaCl}]_{\text{aq}} = 1.0 \text{ M}$, anode: graphite, stirring rate = 1100 r.p.m., organic solvent: CH_2Cl_2 , $\text{pH } 7.0 \pm 0.2$, $V_{\text{org}} = 70 \text{ ml}$, $V_{\text{aq}} = 70 \text{ ml}$, phase transfer catalyst: P4 200–400 mesh, weight of catalyst = 4.0 g, $[\text{C}_6\text{H}_5\text{CH}_2\text{OH}]_{\text{org}} = 0.5 \text{ M}$, electrolytic cell: undivided cell. Charge passed: (*) 0.1, (O) 0.2, (□) 0.3, (Δ) 0.4 and (\diamond) 0.5 F mol^{-1} .

the charge passed was mainly used in establishing an equilibrium concentration of hypochlorite ion in the aqueous phase [15]. Hence the current efficiency for the anodic oxidation of benzyl alcohol was smaller during the initial period. After this initial period, the equilibrium concentration of hypochlorite ion in the aqueous phase was established and the charge was then mostly used in the anodic oxidation of benzyl alcohol. When the charge increased further, the current efficiency decreased due to the decrease in the concentration of benzyl alcohol in the organic phase.

4. Conclusion

The number of active sites on the polymer-supported PTC prepared in this work increased when the cross-linking of the polymer support decreased.

The mechanism of the anodic oxidation of benzyl alcohol in the presence of polymer-supported PTC was evaluated. Hypochlorite ion was produced by the anodic oxidation of chloride ion in the aqueous phase. Benzyl alcohol and hypochlorite ion were extracted from the organic and aqueous phases, respectively, into the polymer phase in which the oxidation occurred. With the polymer-supported PTC prepared in this work, the current efficiency for the anodic oxidation of benzyl alcohol was greater than that using commercial ion exchange resins as polymer-supported PTC. The main factors affecting the current efficiency for the anodic oxidation of benzyl alcohol were the characteristics and the particle size of the catalyst, pH, the concentration of benzyl alcohol and the weight of catalyst. The current efficiency for the anodic oxi-

dation of benzyl alcohol was only slightly affected by temperature.

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