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

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The anodic oxidation of benzyl alcohol has been studied in the two-phase system containing both the redox mediator, ClO^-/Cl^-, and a phase transfer catalyst (PTC). The reaction mechanism and the factors which affect the current efficiency of benzaldehyde production were explored. The experimental results reveal that the rate determining step shifts from the shuttling rate of the redox ions to the anodic oxidation of Cl^- when the agitation rate changes from 400 to 500 rpm in the presence of 0.05 M Bu_4NHSO_4. The results also show that benzyl alcohol is mainly oxidized in the organic phase by the shuttling of the ClO^-/Cl^- mediator. The current efficiency is mainly governed by the pH value and the nature of the organic solvent as well as the types and the concentration of PTC. The current efficiency is slightly affected by both the current density and temperature.

1. Introduction

The shuttling or interface mass transfer of redox mediators plays an important role in electroorganic synthesis involving two phases [1, 2]. Chou *et al.* [1, 2] used Ce^{4+}/Ce^{3+} as redox mediator to carry out the anodic oxidation of toluene in a two-phase reaction system and found that the interphase mass transfer was one of the key steps. The oxidation reactions mainly occurred in the aqueous phase by the transfer of toluene from the organic phase to the aqueous phase and the transfer of Ce^{4+}/Ce^{3+} between the aqueous and organic phases was difficult. In general, the reaction rate of an electroorganic synthesis involving two phases and redox mediators can be significantly improved by increasing the mass transfer of the redox mediator between the organic and aqueous phases.

Recently, phase transfer catalysis has been widely applied to organic synthesis involving organic and aqueous phases [3]. The applications of phase transfer catalysis in electrochemical processes have been discussed by several investigators [4–12]. However, few of these reports are concerned with electrolysis systems in the presence of both phase transfer catalyst (PTC) and redox mediator [13–17]. There are several advantages for electrolysis processes using both PTC and redox mediator: (a) In general, high conductivity and low power consumption compared with the direct electrolysis of the reactant in the organic phase; (b) Low or zero pollution, since the active redox mediators can be regenerated easily and consumed *in situ*; (c) Transportation of dangerous oxidants such as hypochlorite or hypobromite is unnecessary.

A two-phase process involving the anodic oxidation of bromide ion to hypobromite which might be transferred into the organic phase, amyl acetate, and reacted there with benzyl alcohol or some other alcohols, were first tested [13]. However, the kinetics as well as the parameters which affect the current efficiency are not clear. The rate of oxidation of benzyl alcohol by ClO^-/Cl^- redox mediator may be different from that of BrO^-/Br^-. It is of interest to understand the reaction mechanism as well as the rate determining step by using ClO^-/Cl^- as redox mediator for the anodic oxidation of benzyl alcohol in a two-phase system.

The anodic oxidation of benzyl alcohol to form benzaldehyde in the presence of both PTC and ClO^-/Cl^- redox mediator was systematically studied in this work. The hypochlorite ion was used as an oxidant and could be regenerated by the anodic oxidation of the chloride ion. Both ClO^- and Cl^- ions shuttle between the organic and aqueous phases in the presence of a PTC. Factors affecting the current efficiency, the behaviour of the anode in contact with the aqueous and/or organic phases and the mass and charge transfer across the aqueous–organic phase boundary were also explored.

2. Experimental

A cylindrical glass reactor 8.0 cm in height and 5.5 cm in diameter contained a graphite plate as anode, a platinum plate as cathode and a saturated calomel electrode with a luggin capillary as the reference electrode. The emulsion electrolyte was formed by mixing equal volume of aqueous and organic solutions. The electrolyte was agitated by a motorized

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stirrer (EYELA DC-2RT). The d.c. power was supplied by a potentiostat/galvanostat (HOKUTO HA-501) and the amount of electricity passed was measured by a coulometer (HOKUTO HF-201). The organic vapour was condensed by a cryostat cooling system.

The electrolysis procedure was described as follows: the emulsion was formed by mixing 70 ml of 0.5 M benzyl alcohol in organic solution with 70 ml aqueous solution which contained 1.0 M NaCl and the desired amount of PTC. If the tetrabutylammonium hydrogen sulphate was used as PTC then the aqueous solution was neutralized by 2.0 M NaOH solution and adjusted to a desired pH value. The pH value was controlled by preparing a 0.0249 M phosphate buffer solution for the runs of pH 6.9 or by pH controller (TOKYO RIKAKIKAI, FC-1) for other runs of any desired pH value. The whole reactor was immersed in a water bath which was controlled at a desired temperature with a precision within ±0.1° C. At the beginning of a run, the stirrer was switched on and the electrolysis was carried out at a constant current until a preset amount of electricity had been passed. During the run, the organic phase was sampled periodically and analysed by capillary glc with a programmed temperature from 120° C to 160° C at a programming rate 10° C min^{-1}. The concentration of ClO^- in the aqueous phase was analysed by iodometric titration.

3. Results and discussion

3.1. *The* I–E *relationship and reaction mechanism*

Figure 1 shows the *I–E* relationship in aqueous, organic and emulsive phases. Using graphite as anode, the oxidation voltages of chloride ion and water were 1.05 and 1.50 V (against SCE), respectively, as shown in curves 1 and 2 of Fig. 1. The results show that the anodic oxidation of chloride ion to the chloride molecule is faster than that of oxygen evolution. The chlorine is formed at the anode by electrooxidation of Cl^- and is hydrolysed in the aqueous phase [18–20].

$$2Cl^- \rightleftharpoons Cl_2 + 2e \quad (1)$$

$$Cl_2 + H_2O \rightleftharpoons HClO + HCl \quad (2)$$

$$HClO \rightleftharpoons ClO^- + H^+ \quad (3)$$

At the same applied potential the polarization curves both with and without benzyl alcohol in the methylene chloride solution (curves 3 and 4, Fig. 1) indicate a lower current density compared with that in the aqueous media (curves 1 and 2, Fig. 1). On the other hand, the anodic current density in the CH_2Cl_2 solution with benzyl alcohol (curve 4, Fig. 1) is higher than that without benzyl alcohol (curve 3, Fig. 1). The results also show that the benzyl alcohol can be directly oxidized at the anode when the anodic voltage exceeds 2.00 V (against SCE). Accordingly, the benzaldehyde is formed in two ways. One is the anodic oxidation of benzyl alcohol at the anode, the another is indirect oxidation of benzyl alcohol by hypochlorite ion which is formed as shown in Equations 1–3.

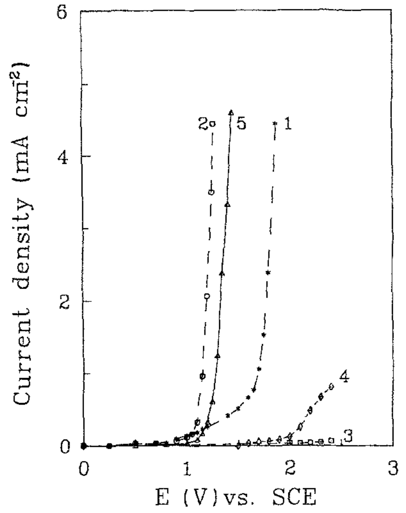

Fig. 1. The *I–E* relationship: temperature 25° C; anode, graphite; agitation rate, 600 rpm; 1, 0.1 M Bu_4NHSO_4 aqueous solution (neutralized by 2.0 M NaOH to pH 6.9); 2, 0.1 M Bu_4NHSO_4 and 1.0 M NaCl aqueous solution (neutralized by 2.0 M NaOH to pH 6.9); 3, 0.1 M Bu_4NHSO_4 methylene chloride solution (the Bu_4NHSO_4 is completely soluble in CH_2Cl_2); 4, 0.1 M Bu_4NHSO_4 and 0.5 M $C_6H_5CH_2OH$ methylene chloride solution; 5, 70 ml of 0.1 M Bu_4NHSO_4 and 1.0 M NaCl aqueous solution plus 70 ml of 0.1 M Bu_4NHSO_4 and 0.5 M $C_6H_5CH_2OH$ (neutralized by 2.0 M NaOH to pH 6.9).

In the H_2O/CH_2Cl_2 emulsion electrolyte with benzyl alcohol, the anodic current density is the summation of the anodic oxidations in both the aqueous and organic phases which contact the anodic surface. At the same applied potential, the current density in the emulsion electrolyte (curve 5, Fig. 1) was much higher than that in the organic electrolyte (curve 4, Fig. 1). This suggests that the anode is mostly covered by the aqueous phase in the emulsion electrolyte. It also reveals that the anodic current is mainly contributed by the anodic oxidation of the chloride ion to form hypochlorite ion in the aqueous phase. The hypochlorite ion is transferred across the phase boundary by the PTC,

$$R_4N^+ + ClO^- \rightleftharpoons R_4N^+ClO^-_{aq} \quad (4)$$

$$R_4N^+ClO^-_{aq} \rightleftharpoons R_4N^+ClO^-_{org} \quad (5)$$

where R is alkyl group.

Using an emulsion solution in the presence of 1.9 M Cl^- and in the absence of PTC, the current efficiency of benzaldehyde production was 24% as shown in Table 1. The low current efficiency indicates that only a small amount of benzyl alcohol is transferred into the aqueous phase where the benzyl alcohol is oxidized by the hypochlorite ion and forms benzaldehyde. On the other hand, the current efficiency significantly increases to 80% in the presence of both 0.05 M Bu_4NHSO_4 and 1.0 M NaCl as shown in Table 1. The result reveals that the oxidation of benzyl alcohol by the hypochlorite ion mainly occurred in the organic phase,

$$R_4N^+ClO^-_{org} + C_6H_5CH_2OH \longrightarrow R_4N^+Cl^-_{org} + C_6H_5CHO + H_2O \quad (6)$$

Then, the $R_4N^+Cl^-_{org}$ transfers from the organic phase to the aqueous phase

$$R_4N^+Cl^-_{org} \rightleftharpoons R_4N^+Cl^-_{aq} \quad (7)$$

$$R_4N^+Cl^-_{aq} \rightleftharpoons R_4N^+ + Cl^- \quad (8)$$

Using an emulsion electrolyte containing 0.025 M Bu_4NHSO_4 and in the absence of chloride ion, the current efficiency is 34% as shown in Table 1. This shows that most of the charge passed electrolyses the water molecule and only a small percentage of the applied current directly oxidises the benzyl alcohol to form benzaldehyde. On the other hand, the current efficiency sharply increases to 74% when the emulsion solution contains both PTC and chloride ion as shown in Table 1. The results show that the oxidation of benzyl alcohol by the redox mediator, Cl^-/ClO^-, which shuttles between the aqueous and organic phases of the emulsion system is more important that the benzyl alcohol which directly reacts at the anode in the organic phase. The results further confirm the proposed reaction mechanism, i.e. Equations 1–8.

3.2. *Effect of agitation*

The kinetics of the redox ion shuttling between the aqueous and organic phases may play an important role in this reaction system. In general, agitation can change both the mass transfer coefficient and the mass transfer interfacial area in a two-phase system. Therefore, the parameter of agitation to generate the emulsion was experimentally tested. The results reveal that the reaction system is significantly affected by the shuttling rate of the chloride and hypochlorite ions between the two phases when the agitation rate is less than 400 rpm as shown in Fig. 2. This indicates that the redox ions transfer rate across the phase boundary with PTC depends on the mass transfer coefficient of redox ions and the interfacial area between the two phases. On increasing the agitation rate from 400 to 500 rpm or more the reaction rate does not increase. This shows that the reaction system is not affected by the shuttling rate of the redox mediator across the phase boundary and reaction control occurs. The agitation rate was maintained at 600 rpm for the following runs to evaluate the other factors which affected the current efficiency.

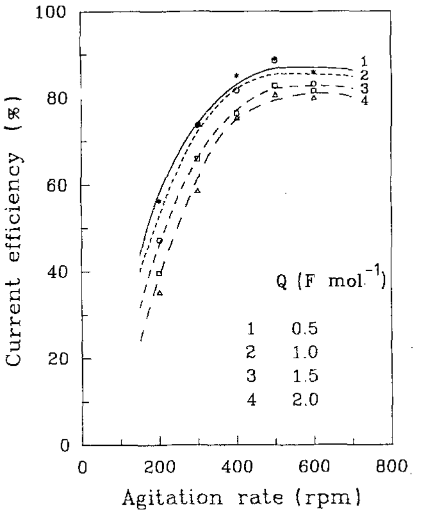

Fig. 2. Effect of agitation on the current efficiency: temperature, 25° C; $[C_6H_5CH_2OH]$ in organic phase, 0.5 M; current density, 20 mA cm^{-2}; volume of aqueous phase, 70 ml; volume of organic phase, 70 ml CH_2Cl_2 solution; [NaCl] in aqueous phase, 1.0 M; pH, 6.9; $[Bu_4NHSO_4]$, 0.05 M.

3.3. *Effect of the types of PTC*

One type of tetraethylammonium salt and three types of tetrabutylammonium salts were used as PTC in this system. As shown in Table 1, when the tetraethylammonium chloride was used as PTC the current efficiency was much less than with the tetrabutylammonium salts. The result reveals that the alkyl group of the PTC significantly affects the current efficiency. It has generally been found that tetraethylammonium salts do not have sufficient oleophilicity to function well as an anion transfer catalyst [21]. If the ClO^- ion cannot be sufficiently transferred into the CH_2Cl_2 phase by Et_4N^+, then the current efficiency of using Et_4N^{4+} as PTC will be much less than that of using Bu_4N^+.

Table 1. Current efficiency of benzaldehde production [$C_6H_5CH_2OH$] in the organic phase: 0.5 M; temperature: 25° C; agitation rate: 600 rpm; current density: 20 mA cm^{-2}; volume of organic phase: 70 ml; volume of aqueous phase: 70 ml; electricity passed: 2 F mol^{-1} of benzyl alcohol

Run	*PTC*$^{\&}$	C^*_{PTC} *(M)*	$C^{@}_{NaCl}$ *(M)*	*pH*$^{\#}$ *value*	*Current efficiency (%)*
1	–	0	1.0	6.9	24
2	Bu_4NHSO_4	0.025	0	6.9	34
3	Bu_4NHSO_4	0.025	1.0	6.9	73
4	Bu_4NHSO_4	0.050	1.0	1.8	58
5	Bu_4NHSO_4	0.050	1.0	6.9	80
6	Bu_4NHSO_4	0.050	1.0	12.5	34
7	Bu_4NCl	0.050	1.0	6.9	78
8	By_4NClO_4	0.050	1.0	6.9	53
9	Et_4NCl	0.050	1.0	6.9	27

$^{\&}$, phase transfer catalyst; *, based on the total volume (140 ml); $^{@}$, based on the aqueous phase only; $^{\#}$, the runs of pH 6.9 were controlled by 0.0249 M phosphate buffer solution; other runs were controlled by pH controller.

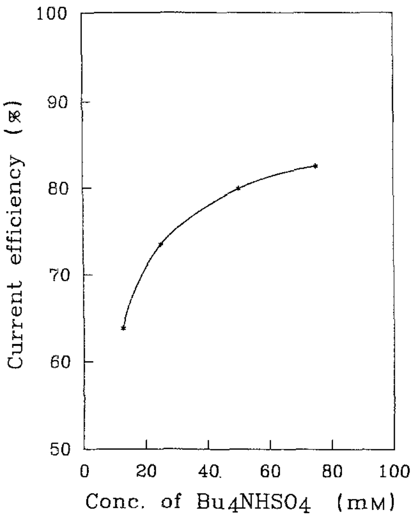

Fig. 3. Effect of the concentration of Bu_4NHSO_4 on the current efficiency: temperature, 25° C; $[C_6H_5CH_2OH]$ in organic phase, 0.5 M; [NaCl] in aqueous phase, 1.0 M; pH, 6.9; current density, 20 mA cm^{-2}; volume of aqueous phase, 70 ml; volume of organic phase, 70 ml CH_2Cl_2 solution; agitation rate, 600 rpm.

The current efficiency was also affected by the anion of PTC. Using Bu_4NClO_4, Bu_4NCl and Bu_4NHSO_4 as PTC, the current efficiencies were 53, 78 and 80%, respectively. The results reveal that the quaternary ammonium cations prefer to associate strongly with the large 'soft' anions, such as perchlorate, rather than with highly hydrated anions, such as Cl^- or HSO_4^-. If ClO_4^- is present in the system, the ClO_4^- will associate with the quaternary cations and prevent the R_4N^+ ion associating with ClO^-. These results were further confirmed by the literature [21].

3.4. *Effect of the concentration of PTC*

The concentration of PTC was one of the main parameters in the two-phase emulsion system. As shown in Fig. 3, increasing the concentration of Bu_4NHSO_4 from 0.0125 to 0.0750 M increased the current efficiency from 64 to 83%. The results indicate that the ClO^- ion is more efficiently transferred from the aqueous phase into the organic phase when the concentration of PTC increases. Further increasing the concentration of Bu_4NHSO_4 to 0.05 M, the increase of current efficiency slowed down and reached a constant as shown in Fig. 3. This means that the current efficiency may be determined by the anodic oxidation of the chloride ion to hypochlorite ion when the concentration of Bu_4NHSO_4 is more than 0.05 M.

3.5. *Effect of pH*

As shown in Table 1, the current efficiency was significantly affected by the pH values. A maximum current efficiency, 80%, was obtained at pH 6.9. The results show that the stability of ClO^- in aqueous solution depends on pH. According to Equations 2 and 3, hydrolysis of Cl_2 is inhibited by the H^+ ion at low pH and produces less ClO^- ions. This results in the current efficiency in the acid medium being less than that in the neutral medium. On the other hand, the anodic oxidation of hypochlorite ion would be significant at high pH as shown in Equation 9 [19, 20].

Table 2. The effect of organic solvent on current efficiency $[C_6H_5CH_2OH]$ in the organic phase: 0.5 M; temperature: 25° C; agitation rate: 600 rpm; current density: 20 mA cm^{-2}; volume of organic phase: 70 ml; volume of aqueous phase: 70 ml; $[Bu_4NHSO_4]$: 0.05 M; [NaCl] in the aqueous phase: 1.0 M; pH 6.9; electricity passed: 2 F mol^{-1} of benzyl alcohol

Organic solvent	*Current efficiency (%)*
CH_2Cl_2	80
CH_2ClCH_2Cl	75
$CHCl_3$	86
$CH_3COOC_2H_5$	64

$$6ClO^- + 3H_2O \longrightarrow 2ClO_3^- + 4Cl^- + 6H^+ + \tfrac{3}{2}O_2 + 6e \qquad (9)$$

This reaction causes a decrease in the current efficiency at high pH.

3.6. *Effect of solvent*

When ethyl acetate and chlorinated hydrocarbons were used as solvent, the current efficiencies lay between 64 and 86%, respectively, as shown in Table 2. With ethyl acetate as solvent, the current efficiency was less than for chlorinated hydrocarbons. The results indicate that the chlorinated hydrocarbons have a higher extraction capacity for $Bu_4N^+ClO^-$ from the aqueous phase than has ethyl acetate. Dehmlow *et al.* reported a similar phenomenon [22]. The current efficiencies changes slightly when different chlorinated hydrocarbonds were used as solvents.

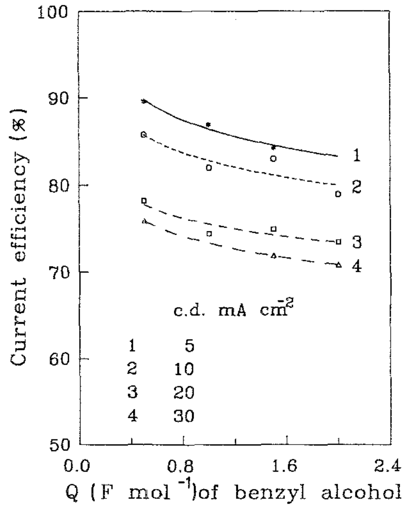

Fig. 4. Effect of current density on the current efficiency: temperature, 25° C; $[C_6H_5CH_2OH]$ in organic phase, 0.5 M; [NaCl] in aqueous phase, 1.0 M; $[Bu_4NHSO_4]$, 0.05 M; pH, 6.9; volume of aqueous phase, 70 ml; volume of organic phase, 70 ml CH_2Cl_2 solution; agitation rate, 600 rpm.

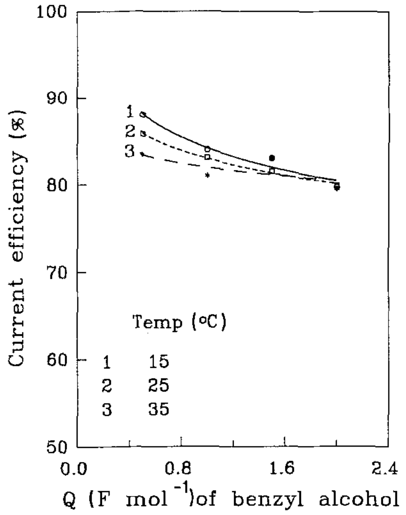

Fig. 5. Effect of temperature on the current efficiency: [$C_6H_5CH_2OH$] in organic phase, 0.5 M; pH, 6.9; [Bu_4NHSO_4], 0.05 M; [NaCl] in aqueous phase, 1.0 M; current density, 20 mA cm^{-2}; agitation rate, 600 rpm; volume of aqueous phase, 70 ml; volume of organic phase, 70 ml CH_2Cl_2 solution.

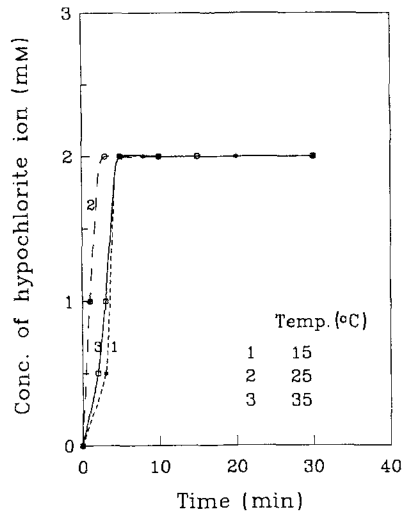

Fig. 6. Effect of temperature on the rate of generation of the ClO^-: [$C_6H_5CH_2OH$] in organic phase, 0.5 M; pH, 6.9; [Bu_4NHSO_4], 0.05 M; [NaCl] in aqueous phase, 1.0 M; current density, 20 mA cm^{-2}; agitation rate, 600 rpm; volume of aqueous phase, 70 ml; volume of organic phase, 70 ml CH_2Cl_2 solution.

3.7. *Effect of current density*

The results show that the current efficiency increases when the current density decreases. Decreasing the current density from 30 to 5 mA cm^{-2} at 25° C, 0.05 M Bu_4NHSO_4, pH 6.9 and CH_2Cl_2 as organic solvent, the current efficiency increases from 72–84% as shown in Fig. 4. This may be due to the increase of oxygen evolution when the current density increases. For any current density applied, the current efficiency decreased when the amount of electricity passed increased. For example, the current efficiency decreased from 90 to 84% when the amount of electricity passed increased from 0.5 to 2.0 F per mole of benzyl alcohol at a current density of 5 mA cm^{-2} as shown in Fig. 4. The results also reveal that at lower concentration of benzyl alcohol the side reactions increased when the amount of electricity passed increased.

3.8. *Effect of temperature*

As shown in Fig. 5, the current efficiency is slightly affected by change of temperature. In order to evaluate the temperature effect, the generation of ClO^- in the aqueous phase at different temperatures was studied. During the electrolysis the concentration of hypochlorite ion in the aqueous phase increased sharply and reached a constant value 0.002 M as shown in Fig. 6.

Based on the mechanism of Equations 1–8, the main steps of the reaction mechanism are the anodic oxidation of Cl^-, the redox ions shuttling between the aqueous and organic phases and the homogeneous reaction in the organic phase. As reported in the previous section, when the agitation rate is maintained at 600 rpm in the presence of 0.05 M Bu_4NHSO_4, the reaction system is not controlled by the rate of shuttling of Cl^- and ClO^- ions across the phase boundary. Also, the result shows a very low and constant concentration of ClO^- in the aqueous phase, and indicates that the homogeneous reaction in the organic phase is faster than the rate of electrolysis. This confirms that the rate determining step is the anodic oxidation of Cl^- and not the homogeneous reaction in the organic phase. Therefore, the current efficiency of benzaldehyde production is significantly affected by the current efficiency of hypochlorite ion production in the aqueous phase. The results also reveal that the effect of temperature on the electrolysis of Cl^- to form ClO^- may be insignificant.

In the absence of the organic phase, on changing the temperature from 10 to 50° C, the current efficiency of ClO^- changed slightly from 81 to 80% when 500 coulombs of charge was passed as shown in Fig. 7. This is similar to the temperature effect on the current efficiency of benzaldehyde production in the emulsion electrolyte. These results further confirm that the effect of temperature on current efficiency for benzal-

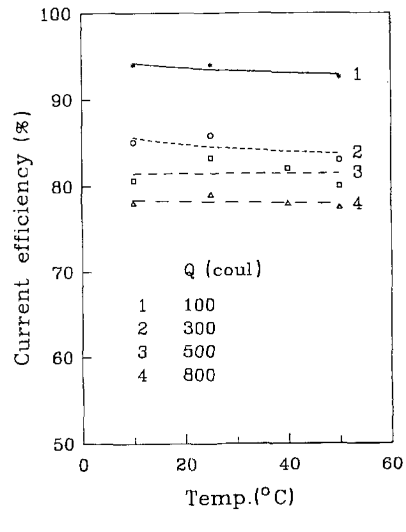

Fig. 7. Effect of temperature on the current efficiency of ClO^- in the aqueous solution: [NaCl], 1.0 M; agitation rate, 600 rpm; pH, 6.9; current density, 20 mA cm^{-2}.

dehyde production is insignificant and the rate determining step of benzaldehyde formation at 600 rpm is Equation 1 of the proposed reaction mechanism.

4. Conclusions

In this emulsion electrolysis, oxidation of benzyl alcohol to benzaldehyde at the anode is insignificant. The benzyl alcohol is mainly oxidized by the electrogenerated redox mediator, ClO^-/Cl^-, which shuttles between the organic and aqueous phases. It is found that both PTC and the redox mediator play important roles. Using 0.05 M Bu_4NHSO_4 as a PTC, the rate determining step is the shuttling of the mediator across the phase boundary or the anodic oxidation of the chloride ion to hypochlorite ion when the agitation rate is less than 400 or more than 500 rpm, respectively.

The main factors which affect the current efficiency of the anodic oxidation of benzyl alcohol in the presence of the PTC and the redox mediator are the pH, the types of organic solvent and the types and concentration of PTC. On the other hand, the current efficiency is insignificantly affected by the current density and temperature.

Acknowledgement

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