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Kinetics of the anodic oxidation of benzyl alcohol in dichloromethane in the presence of redox mediator and phase transfer catalyst

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The kinetics of the anodic oxidation of benzyl alcohol in the two-phase system involving both, the redox mediator, OCl^-/Cl^-, and a phase transfer catalyst were investigated. The reaction order of the anodic oxidation of chloride ion in the aqueous phase was unity. The charge-transfer parameters, α, k_2^0 and the exchange current density, i_0, of the anodic oxidation of chloride ion in the aqueous phase were obtained. The theoretical model calculations correlated well with experimental data. The fractions of anodic surface covered by the aqueous phase were evaluated to be 0.89, 0.61, and 0.23 when the organic-to-aqueous volume ratios were 0.5, 1.0, and 2.0, respectively.

Nomenclature

A	area of the anode (cm^2)
F	Faraday constant (C)
f	the fraction of the anodic surface covered by the aqueous phase in the two-phase system
I	total current (A)
i	current density (A cm^{-2})
K_1	equilibrium adsorption constant of choloride ion on the anodic surface
k_2	reaction rate constant of the anodic oxidation of Cl^- (dm min^{-1})
k_2^0	reaction rate constant of the anodic oxidation of Cl^- at $\eta = 0$ (cm s^{-1})
K_3	equilibrium constant of the hydrolysis of Cl_2 (M^2)
K_4	dissociative constant of HOCl (M)
K_5, K_7	associative constants of $(Q^+OCl^-)_{aq}$ and $(Q^+Cl^-)_{aq}$ (M^{-1})
K_6, K_8	distribution ratio of ion pairs between organic and aqueous
k_9	reaction rate constant of the oxidation of benzyl alcohol (M^{-1} min^{-1})
m	reaction order of quaternary ammonium hypochlorite ion pair in the organic phase
n	reaction order of benzyl alcohol in the organic phase
N_0	initial total moles of phase transfer catalyst (mol)
N_{cl}	total moles of chloride ion (mol)
Q^+	quaternary ammonium cation
r	reaction rate of benzyl alcohol (M min^{-1})
R_v	organic-to-aqueous volume ratio
t	time (min)
V	volume of solution (lm^3)

Subscripts

aq	aqueous phase
org	organic phase
0	initial state

Greek symbols

α	charge-transfer coefficient
η	overpotential
θ_{cl}	fraction of the anodic surface covered by the adsorbed chloride ion

1. Introduction

Use of inorganic cations and anions as catalysts [1–3], oxidants [4–8], and reducing agents [8], have been widely discussed in the literature. In recent years, the anodic oxidation of organic molecules involving redox mediators has attracted consideration attention [9]. For example, the redox mediator, Ce^{4+}/Ce^{3+}, has been used in electroorganic synthesis involving a two-phase system [10–13]. Usually, the solubility of inorganic species in the organic solvents or solutions is very small. Therefore, reactions of the inorganic species with organic substances in two immiscible phases are often inhibited. Recently, the phase transfer catalyst has been widely used to improve the solubility of the inorganic and organic species in the immiscible solutions [14–15]. However, the mechanism and kinetics of the two-phase system in the presence of a phase transfer catalyst are seldom reported [16–22]. In our previous work, the extraction of hypochlorite ion from the aqueous phase into dichloromethane and the kinetics of the oxidation of benzyl alcohol in

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the presence of a phase transfer catalyst has been discussed [17].

Applications of phase transfer catalysis in electrochemical processes such as, the anodic cyanation of naphthalene and dimethoxybenzenes [23–24], aromatic nuclear acetoxylation [25–28], the anodic chlorination of naphthalene [29–30] have been proposed by several investigators). Unfortunately, few of these papers were concerned with the electrolysis systems in the presence of both phase transfer catalyst and redox mediator [12–13, 31–34]. In the presence of a phase transfer catalysis, the anodic oxidations of benzyl alcohol and some other alcohols in the presence of the redox mediator, OBr^-/Br^-, were preliminarily tested [31–32]. However, the electrode kinetics, chemical kinetics, extraction coefficients and the parameters which affect the current efficiency have not been sufficiently investigated. The hypochlorite ion has been found to be a mild and effective oxidizing agent for organic synthesis [4–7]. Using OCl^-/Cl^- as mediator, the role of mass transfer and the parameters which affect the current efficiency of the anodic oxidation of benzyl alcohol in the presence of a phase transfer catalyst has been reported by Do and Chou [34]. It is of interest to gain understanding of the kinetics of oxidation on the anodic surface and the kinetics of oxidation in the organic phase in the presence of both a phase transfer catalyst and a redox mediator, OCl^-/Cl^-.

With a phase transfer catalyst, a systematic study on the kinetics of the anodic oxidation of benzyl alcohol in the presence of a redox mediator, OCl^-/Cl^-, was carried out in this work. A kinetic model of the anodic oxidation of benzyl alcohol in the presence of the mediator, OCl^-/Cl^- and a phase transfer catalyst has been achieved.

2. Experimental

2.1. *Anodic oxidation of chloride ion in the aqueous phase*

The experiments were carried out in an undivided cell with graphite (NPL, Central Carbon Ltd.) as working electrode, a platinum wire as counter electrode and a saturated calomel electrode as reference electrode. The graphite electrode was polished with a fine emery paper, washed with distilled water, and polished again with polishing alumina (0.05 μm particles), and then washed thoroughly with distilled water.

The current-potential relationships were obtained by the steady state method. After 1 min at every applied potential, the steady state current was recorded. Anodic pre-electrolyses was carried out in solution by a potentiodynamic scanning over a range of potentials from 0.5 to 1.5 V (with respect to SCE).

2.2. *The anodic oxidation of benzyl alcohol in the two-phase system*

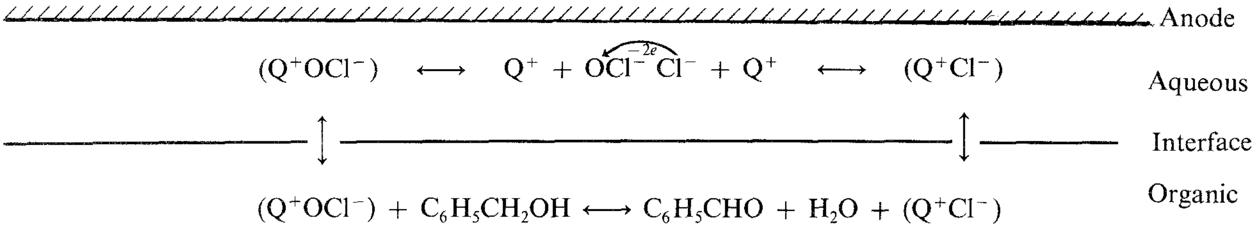
The anodic oxidation of benzyl alcohol in the two-phase system was carried out in an undivided cell which was a cylindrical glass reactor 80 mm in height and 55 mm in diameter. A graphite plate was used as working electrode, a platinum wire as counter electrode and a saturated calomel electrode with a Luggin capillary as reference electrode. A motorized flat-bladed stirrer (No. 1 propeller, EYELA) was used to agitate the two immiscible phases. The organic vapor was condensed using a cryostat cooling system. The whole reactor system was immersed in a water bath, and the temperature was controlled within ±0.1° C.

All the chemicals used were reagent grade. The aqueous solution was prepared by dissolution of a desired amount of sodium chloride in the buffer solution in which the pH was maintained at 9.0 ± 0.2. The organic phase was prepared by dissolving the desired amounts of tetrabutylammonium chloride (phase transfer catalyst) and benzyl alcohol in dichloromethane.

At the beginning of a run, the desired volumes of both the aqueous and organic solutions were fed into the cell, which was kept at a preset temperature. The desired stirring rate and voltage were applied to the reaction system. The reaction time was recorded immediately after the voltage was applied. Samples were taken periodically by using a hyperdermic syringe. The reactant and products were analysed using a DB-1 capillary GLC (GC 3300, Varian).

3. Theoretical analysis

The reaction mechanism of the anodic oxidation of benzyl alcohol in the presence of a phase transfer catalyst and mediator can be descried by Scheme I.



Scheme I

The tetrabutylammonium cation Q^+ shuttles between the aqueous and organic phases, i.e. Q^+ cation migrates with the oxidant OCl^- from the aqueous phase into the organic phase where a weakly solvated ion pair is formed and undergoes fast reduction by reaction with the benzyl alcohol. Then Q^+ returns to the aqueous phase with the anion Cl^- which is oxidized to OCl^- on the anode.

The mechanism of the anodic oxidation of chloride ion to form chlorine on the electrode surface is [35]:

$$Cl^- \underset{}{\overset{k_1}{\rightleftharpoons}} Cl_{ads} + e \tag{1}$$

$$Cl^- + Cl_{ads} \xrightarrow{k_2} Cl_2 + e \tag{2}$$

Hypochlorite ions are formed by hydrolysis of the chlorine molecule in the bulk of the aqueous phase:

$$Cl_2 + H_2O \underset{k_{-3}}{\overset{k_l}{\rightleftharpoons}} HOCl + H^+ + Cl^- \tag{3}$$

$$HOCl \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} H^+ + OCl^- \tag{4}$$

In general, the dissociation of ion pairs in the organic phase is insignificant [36], thus the interfacial mass transfer and the equilibria involving cation Q^+ and anions OCl^- and Cl^- can be expressed as

$$(Q^+)_{aq} + (OCl^-)_{aq} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} (Q^+OCl^-)_{aq} \tag{5}$$

$$(Q^+OCl^-)_{aq} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} (Q^+OCl^-)_{org} \tag{6}$$

$$(Q^+)_{aq} + (Cl^-)_{aq} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} (Q^+Cl^-)_{aq} \tag{7}$$

$$(Q^+Cl^-)_{aq} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} (Q^+Cl^-)_{org} \tag{8}$$

where the suffices aq and org indicate the aqueous and organic phases, respectively.

In the organic phase, the ion pair reacts with benzyl alcohol according to the following equation

$$\begin{aligned} C_6H_5CH_2OH + (Q^+OCl^-)_{org} &\xrightarrow{k_9} C_6H_5CHO \\ &+ (Q^+Cl^-)_{org} + H_2O \end{aligned} \tag{9}$$

3.1. *Extraction of the anion from the aqueous phase into the organic phase*

According to Equations 5–8, the ion pair concentration of Q^+OCl^- and Q^+Cl^- in the aqueous and organic phases can be expressed as follows

$$[Q^+OCl^-]_{aq} = K_5[Q^+]_{aq}[OCl^-]_{aq} \tag{10}$$

$$[Q^+OCl^-]_{org} = K_5K_6[Q^+]_{aq}[OCl^-]_{aq} \tag{11}$$

$$[Q^+Cl^-]_{aq} = K_7[Q^+]_{aq}[Cl^-]_{aq} \tag{12}$$

$$[Q^+Cl^-]_{org} = K_7K_8[Q^+]_{aq}[Cl^-]_{aq} \tag{13}$$

where $K_5 = k_5/k_{-5}$, $K_6 = k_6/k_{-6}$, $K_7 = k_7/k_{-7}$, and $K_8 = k_8/k_{-8}$.

Based on the material balance, the total initial moles of the phase transfer catalyst are the summation of the moles of the cation ion Q^+ and the ion pairs expressed in Equations 10–13. The result is

$$\begin{aligned} &V_{aq}([Q^+]_{aq} + [Q^+Cl^-]_{aq} + [Q^+OCl^-]_{aq}) \\ &\quad + V_{org}([Q^+Cl^-]_{org} + [Q^+OCl^-]_{org}) = N_0 \end{aligned} \tag{14}$$

where N_0 is the total moles of the phase transfer catalyst and V_{aq} and V_{org} are the volumes of the aqueous and organic phases, respectively.

Substituting Equations 10–13 into Equation 9,

$$\begin{aligned} [Q^+]_{aq} = &\{(1 + R_v)[Q]_0\}/\{1 + K_7(1 + K_8R_v)[Cl^-]_{aq} \\ &+ K_5(1 + K_6R_v)[OCl^-]_{aq}\} \end{aligned} \tag{15}$$

where $[Q]_0 = N_0/V_t$, $R_v = V_{org}/V_{aq}$, $V_t = V_{aq} + V_{org}$.

Substituting Equation 15 into Equation 11, the concentration of the Q^+OCl^- ion pair is obtained,

$$\begin{aligned} [Q^+OCl^-]_{org} = &\{K_5K_6(1 + R_v)[Q]_0[OCl^-]_{aq}\}/ \\ &\{1 + K_7(1 + K_8R_v)[Cl^-]_{aq} \\ &+ K_5(1 + K_6R_v)[OCl^-]_{aq}\} \end{aligned} \tag{16}$$

Equation 16 indicates that the concentration of the ion pair Q^+OCl^- in the organic phase depends on the initial concentration of the phase transfer catalyst, the concentrations of chloride ion and hypochlorite ion in the aqueous phase and the organic-to-aqueous volume ratio, R_v.

3.2. *Kinetics of the anodic oxidation of benzyl alcohol*

The current of anodic oxidation of chloride ion in the absence of the organic phase is

$$I = 2FAk_2^0 \exp(\alpha F\eta/RT)[Cl^-]\theta_{cl} \tag{17}$$

where A is the surface area of the anode, k_2^0 is the rate constant at $\eta = 0$, α is a charge-transfer coefficient, η is the overpotential of the anode , and θ_{cl} is the fraction of the anode surface covered by the adsorbed chloride ion.

Chloride ions are consumed by the anodic oxidation and generated by the oxidation of benzyl alcohol in the organic phase. The mass balance of chloride ion is

$$\begin{aligned} dN_{cl}/dt = &\; d\{V_{aq}[Cl^-]_{aq} + V_{org}[Q^+Cl^-]_{org}\}/dt \\ = &\; (-I'/2F) + V_{aq}\{k_3[Cl_2] \\ &- k_{-3}[HOCl][H^+][Cl^-]_{aq} \\ &- k_5[Q^+]_{aq}[Cl^-]_{aq} + k_{-5}[Q^+Cl^-]_{aq}\} \\ &+ V_{org}\{k_9[C_6H_5CH_2OH]^m_{org}[Q^+OCl^-]^n_{org}\} \end{aligned} \tag{18}$$

where N_{cl} is the total moles of chloride ion and

$$I' = fI = 2fFAk_2^0 \exp(\alpha F\eta/RT)[Cl^-]_{aq}\theta_{cl} \tag{19}$$

where f is the fraction of the anodic surface covered by the aqueous phase in the two-phase emulsion system.

In general, Reactions 3 and 5 are fast compared with the other reactions. Therefore they can be assumed to be always in equilibrium and hence the following relations exist

$$k_3[Cl_2] - k_{-3}[HOCl][H^+][Cl^-]_{aq} = 0 \tag{20}$$

$$k_5[Q^+]_{aq}[Cl^-]_{aq} - k_{-5}[Q^+Cl^-]_{aq} = 0 \tag{21}$$

Besides, based on our previous work [21], the concentration of Q^+Cl^- in the organic phase is much less than the concentration of chloride ion in the aqueous phase. Therefore Equation 18 can be reduced to

$$\mathrm{d}[Cl^-]_{aq}/\mathrm{d}t = -I'/2FV_{aq} + k_9[C_6H_5CH_2OH]^m_{org}[Q^+OCl^-]^n_{org}R_v \qquad (22)$$

The reaction orders of both benzyl alcohol and Q^+OCl^- in the organic phase are equal to one [17] and substituting Equation 17 into Equation 22, the material balance of chloride ion is

$$\mathrm{d}[Cl^-]_{aq}/\mathrm{d}t = -fAk_2^0 \exp(\alpha F\eta/RT)[Cl^-]_{aq}\theta_{cl}/V_{aq} + k_9R_v[C_6H_5CH_2OH]_{org}[Q^+OCl]_{org} \qquad (23)$$

and the mass balance of benzyl alcohol is expressed by

$$\mathrm{d}[C_6H_5CH_2OH]_{org}/\mathrm{d}t = -k_9[C_6H_5CH_2OH]_{org}[Q^+OCl^-]_{org} \qquad (24)$$

Substituting the concentration of Q^+OCl^- in the organic phase, i.e. Equation 16 into Equations 23 and 24, the material balance of the species of chloride ion and benzyl alcohol become,

$$\begin{aligned}\mathrm{d}[Cl^-]_{aq}/\mathrm{d}t = {} & -fAk_2^0 \exp(\alpha F\eta/RT)[Cl^-]_{aq}\theta_{cl}/V_{aq} \\ & + K_5K_6k_9R_v(1 + R_v)[Q]_0 \\ & \times [C_6H_5CH_2OH]_{org}[OCl^-]_{aq}/ \\ & \{1 + K_7(1 + K_8R_v)[Cl^-]_{aq} \\ & + K_5(1 + K_6R_v)[OCl^-]_{aq}\}\end{aligned} \qquad (25)$$

$$\begin{aligned}& \mathrm{d}[C_6H_5CH_2OH]_{org}/\mathrm{d}t \\ & = -K_5K_6k_9(1 + R_v)[Q]_0[C_6H_5CH_2OH]_{org}[OCl^-]_{aq}/ \\ & \{1 + K_7(1 + K_8R_v)[Cl^-]_{aq} \\ & + K_5(1 + K_6R_v)[OCl^-]_{aq}\}\end{aligned} \qquad (26)$$

The initial moles of chloride ion in the aqueous phase can be expressed as

$$\begin{aligned}[Cl^-]^0_{aq}V_{aq} = {} & ([Cl^-]_{aq} + [OCl^-]_{aq} \\ & + [HOCl] + [Cl_2] + [Q^+Cl^-]_{aq} \\ & + [Q^+OCl^-]_{aq})V_{aq} + ([Q^+Cl^-]_{org} \\ & + [Q^+OCl^-]_{org})V_{org}\end{aligned} \qquad (27)$$

where $[Cl^-]^0_{aq}$ is the initial concentration of chloride ion in the aqueous phase.

Our previous work [17] showed that the concentrations of both Q^+Cl^- and Q^+OCl^- in both the aqueous and organic phases were much less than the concentration of chloride in the aqueous phase. The terms $[Q^+Cl^-]_{aq}$, $[Q^+Cl^-]_{org}$, $[Q^+OCl^-]_{aq}$ and $[Q^+OCl^-]_{org}$ in the right hand side of Equation 27 can, therefore, be neglected. If Equations 3 and 4 are in equilibrium, then the concentration of chlorine is

$$[Cl_2] = [H^+]^2[Cl^-]_{aq}[OCl^-]_{aq}/K_3K_4 \qquad (28)$$

where $K_3 = k_3/k_{-3}$ and $K_4 = k_4/k_{-4}$. At 25° C, the equilibrium constants K_3 and K_4 are 4.48×10^{-4} M^2 [37] and 3.2×10^{-8} M [38], respectively. At pH = 9 and on substitution of K_3 and K_4 into Equation 28, the concentration of chlorine is

$$[Cl_2] = 7 \times 10^{-8}[Cl^-]_{aq}[OCl^-]_{aq} \qquad (29)$$

With $[Cl^-]_{aq} < 1$ M, the concentration of chlorine molecule is much less than chloride and hypochlorite concentrations in the aqueous phase. The term $[Cl_2]$ in the right hand side of Equation 27 can be neglected. Hence, Equation 27 becomes

$$[Cl^-]^0_{aq} = [Cl^-]_{aq} + [OCl^-]_{aq} + [HOCl] \qquad (30)$$

Based on Equation 4, the concentration of HOCl can be expressed as

$$[HOCl] = [H^+][OCl^-]_{aq}/K_4 \qquad (31)$$

Combining Equations 30 and 31, the concentration of hypochlorite ion in the aqueous phase is

$$[OCl^-]_{aq} = K_4([Cl^-]^0_{aq} - [Cl^-]_{aq})/(K_4 + [H^+]) \qquad (32)$$

Substituting Equation 32 into Equations 25 and 26, the material balance equations of chloride ion in the aqueous phase and benzyl alcohol in the organic phase are obtained, respectively,

$$\begin{aligned}\mathrm{d}[Cl^-]_{aq}/\mathrm{d}t = {} & -fAk_2^0 \exp(\alpha F\eta/RT)[Cl^-]_{aq}\theta_{cl}/V_{aq} \\ & + K_4K_5K_6k_9R_v(1 + R_V)[Q]_0 \\ & \times [C_6H_5CH_2OH]_{org}([Cl^-]^0_{aq} \\ & - [Cl^-]_{aq})/\{(K_4 + [H^+]) \\ & \times (1 + K_7(1 + K_8R_v)[Cl^-]_{aq}) \\ & + K_4K_5(1 + K_6R_v)([Cl^-]^0_{aq} \\ & - [Cl^-]_{aq})\}\end{aligned} \qquad (33)$$

$$\begin{aligned}& \mathrm{d}[C_6H_5CH_2OH]_{org}/\mathrm{d}t = -K_4K_5K_6k_9(1 + R_v)[Q]_0 \\ & \times [C_6H_5CH_2OH]_{org}([Cl^-]^0_{aq} - [Cl^-]_{aq})/\{(K_4 + [H^+]) \\ & \times (1 + K_7(1 + K_8R_v)[Cl^-]_{aq}) + K_4K_5 \\ & \times (1 + K_6R_v)([Cl^-]^0_{aq} - [Cl^-]_{aq})\}\end{aligned} \qquad (34)$$

The concentrations of benzyl alcohol in the organic phase and chloride ion in the aqueous phase against time can be evaluated by solving Equations 33 and 34 simultaneously with the initial concentrations of benzyl alcohol in the organic phase and of chloride ion in the aqueous phase.

4. Results and discussion

4.1. *Anodic oxidation of Cl^- ion*

4.1.1. Effect of the concentration of chloride ion. The anodic oxidation of chloride ion depends on the concentration of NaCl as shown in Fig. 1. At 700 rpm, the polarization curves are not affected by the stirring rate, and show no mass transfer effect on the oxidation. As shown in Fig. 1, increasing the concentration of

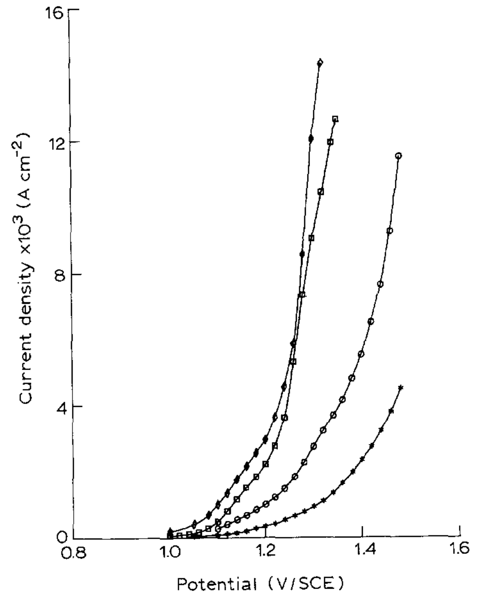


Fig. 1. Effect of the concentration of chloride ion on the *I-E* relationship. Anode: graphite: counter electrode: Pt; reference electrode: SCE; $[NaClO_4]$ = 1.0 M; temperature = 25°C; stirring rate = 800 rpm. Key: [NaCl] (*) 0.125, (○) 0.500, (□) 1.000, and (◇) 2.000 M.

chloride ion from 0.125 to 2.00 M the current density increases from 3.30×10^{-4} to 2.95×10^{-3} A cm^{-2} at 1.20 V (SCE).

The plot of the logarithmic current density against the logarithmic concentration of chloride ion yields a straight line with a slope of 0.98, which is the electrochemical reaction order of chloride ion. Accordingly, the θ_{cl} in Equation 17 is approximately constant,

$$I = 2FAk_2^0 \exp(\alpha F\eta/RT)[Cl^-]_{aq} \qquad (35)$$

Similar results have been reported by other investigators and θ_{cl} is proved to be about unity [35].

4.1.2. Charge-transfer kinetic parameters. By rearrangement of Equation 35, the current density is

$$i = i_0 \exp(\alpha F\eta/RT) \qquad (36)$$

where $i_0 = 2Fk_2^0[Cl^-]_{aq}$ and is constant when the concentration of chloride ion and the temperature are constant.

It is found that the Tafel curves change with temperature and a linear section for each Tafel curve is also found. The slopes of the linear sections of the curves change from 150 to 167 mV when the temperature increases from 278 to 318 K as shown in Table 1. The changes of the charge-transfer coefficients, α's, are insignificant when the temperature changes. The average charge-transfer coefficient is 0.372. The exchange current density, i_0, increases from 3.28×10^{-4} to 1.107×10^{-3} A cm^{-2} when the temperature increases from 278 to 318 K. Increasing the temperature from 278 to 318 K, the charge-transfer rate constant, k_2^0, increases from 1.70×10^{-6} to 5.74×10^{-6} cm s^{-1}.

Table 1. Effect of the temperature on the charge-transfer parameters

Temperature (K)	*Slope (mV)*	α	$i_0 \times 10^4$ ($A\,cm^{-2}$)	$k_2^0 \times 10^6$ ($cm\,s^{-1}$)
278	165	0.334	3.28	1.70
288	154	0.371	4.68	2.43
298	150	0.394	6.18	3.20
308	160	0.382	7.96	4.12
318	167	0.377	11.07	5.74

anode; graphite anodic area: 0.37 dm^2; counter electrode: Pt; reference electrode: SCE; electrolyte: 1.0 M $NaClO_4$ + 1.0 NaCl aqueous solution; stirring rate: 800 rpm.

4.2. *The anodic oxidation of benzyl alcohol in the presence of the phase transfer catalyst and the redox mediator, OCl^-/Cl^-*

As shown in Scheme I, hypochlorite ion/chloride ions play a role of mediator shuttling between the interface of the two-phase system. The chloride ion is oxidized on the anode and forms hypochlorite ion in the bulk solution of aqueous phase. This oxidant, OCl^-, is transferred into the organic phase from the aqueous phase with the cation of phase transfer catalyst, Bu_4N^+, by the formation of the ion pair, $Bu_4N^+OCl^-$. The dissociation constant of the tetrabutylammonium hypochlorite ion pair in the organic phase is very small [36]. Therefore, hypochlorite mainly exists in the organic phase in the form of the tetrabutylammonium hypochlorite ion pair, which reacts with the reactant, benzyl alcohol, regenerating chloride ions. The chloride anion is oxidized on the anode in the aqueous phase.

Mass transfer of the ion pairs across the interface plays an important role [17, 34]. Increasing the stirring rate, the mass transfer rate increases. The rate determining step shifts from mass transfer to electrooxidation on the anode or oxidation in the organic phase at higher agitation rates. It is found that the reaction rate of the system is located in a reaction control region and not affected by the mass transfer rate as the stirring rate exceeds 400 rpm [17, 34]. The concentrations of the reaction species, Cl^-, OCl^-, HOCl, and benzyl alcohol, can be expressed by Equations 30 to 34 when the stirring rate is larger than 400 rpm. The kinetic parameters of electrooxidation rate constant, k_2, equilibrium constants, K_3, K_4, extraction constants, K_5 to K_8, and the reaction rate constant, k_9, are illustrated in Table 2. Substituting the parameters into Equations 33 and 34, the concentrations of chloride ion and benzyl alcohol can be evaluated by solving Equations 33 and 34 simultaneously. The IMSL Subroutine DGEAR was used to solve the two ordinary differential equations [39].

4.2.1. Effect of the organic-to-aqueous volume ratio on the rate of anodic oxidation of benzyl alcohol. As shown in Fig. 2, the moles of benzyl alcohol decrease as the reaction time increases. Increasing the reaction time from 0 to 100 min, the moles of benzyl alcohol decrease from 14.16, 13.44 and 13.04 to 9.12, 1.68 and 1.20 mmol at R_v = 2.0, 1.0 and 0.5 respectively. The consumption of benzyl alcohol sharply decreases

Table 2. Parameters of the theoretical calculations

Parameter	*Value*	*Unit*	*Temp. (K)*	*Ref.*
k_2	$1.46 \times 10^{-5} \exp(0.372\, F\eta/RT)$	dm min^{-1}	288	This work
	$1.92 \times 10^{-5} \exp(0.372\, F\eta/RT)$	dm min^{-1}	298	This work
K_3	3.16×10^{-4}	M^2	288	[37]
	4.48×10^{-4}	M^2	298	[37]
K_4	3.20×10^{-8}	M	298	[38]
K_5	0.05	M^{-1}	293	[17]
K_6	17.39		293	[17]
K_7	4.00×10^{-3}	M^{-1}	293	[17]
K_8	87.70		293	[17]
k_9	42.01	M^{-1} min^{-1}	293	[17]

when the organic-to-aqueous volume ratio, R_v, increases from 0.5 to 2.0 as illustrated in Fig. 3. For example, at 80 min, the consumption of benzyl alcohol sharply decreases from 11.48 to 4.08 mmol when the organic-to-aqueous volume ratio increases from 0.5 to 2.0. Dividing the consumption of benzyl alcohol by the reaction time, the average reaction rate of anodic oxidation of benzyl is obtained as shown in Table 3. After 80 min from the beginning of the run, increasing R_v from 0.5 to 2.0, the average reaction rate of benzyl alcohol decreases from 0.144 to 0.036 mmol min^{-1}. In spite of the concentration of phase transfer catalyst in the run $R_v = 0.5$ being less than that for $R_v = 1.0$ and 2.0, the average reaction rate of benzyl alcohol for the run $R_v = 0.5$ is much larger than that of $R_v = 2.0$. The results reveal that the lower organic-to-aqueous volume ratio favours the anodic oxidation of benzyl alcohol. This is due to the fact that, as the organic-to-aqueous volume ratio increases, the fraction of the anodic surface occupied by the aqueous phase decreases. Therefore, increase in the organic-to-aqueous volume ratio decreases the current for the anodic oxidation of chloride ion in the aqueous phase and the rate of oxidation of benzyl alcohol in the organic phase at the same overpotential.

4.2.2. The fraction of anodic surface covered by the aqueous phase. At the given values of R_v and f, the theoretical concentrations of benzyl alcohol were obtained by solving Equation 33 and 34 simultaneously. Comparing the theoretical calculations and experimental data, the fraction of anode covered by the aqueous phase, f, was evaluated. Accordingly, the fraction of anode covered by the aqueous phase was obtained to be 0.89, 0.61 and 0.23 at $R_v = 0.5$, 1.0 and 2.0, respectively.

As shown in the experimental data of Fig. 4, increasing the reaction time from 0 to 90 minutes, the concentration of benzyl alcohol decreases from 0.326 to 0.033 M at $R_v = 0.5$. The theoretical calculations correlate well with the experimental data when the

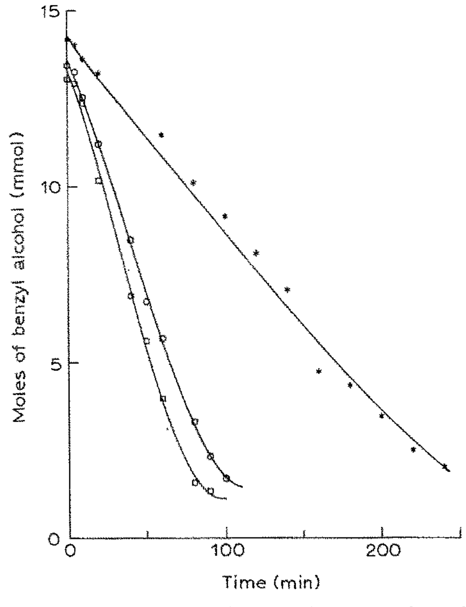


Fig. 2. Plot of the moles of benzyl alcohol against time with organic-to-aqueous volume ratio as parameter. $[Cl^-]^0_{aq} = 1.0$ M; buffer solution: 50 ml 0.1 M H_3BO_3 + 21.3 ml 0.1 N NaOH + 28.7 ml H_2O; organic solvent: CH_2Cl_2; pH = 9.0; stirring rate = 600 rpm; anodic potential = 1.35 V (SCE); $[Bu_4NCl] = 0.025$ M ($R_v = 2.0$ and 1.0) or 0.017 M ($R_v = 0.5$); $[C_6H_5CH_2OH]_{org} = 0.326$ M ($R_v = 0.5$), 0.192 M ($R_v = 1.0$) or 0.177 M ($R_v = 2.0$). Key: R_v = (*) 2.0, (○) 1.0 and (□) 0.5.

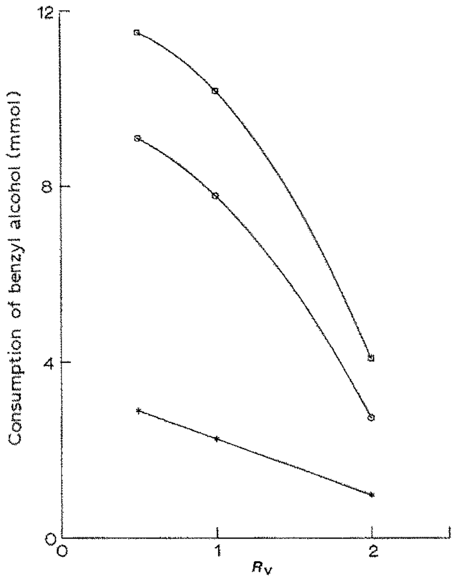


Fig. 3. Effect of organic-to-aqueous volume ratio on the consumption of benzyl alcohol. $[Cl^-]^0_{aq} = 1.0$ M; buffer solution: 50 ml 0.1 M H_3BO_3 + 21.3 ml 0.1 N NaOH + 28.7 ml H_2O; organic solvent: CH_2Cl_2; pH = 9.0; stirring rate = 600 rpm; anodic potential = 1.35 (SCE); $[Bu_4NCl] = 0.025$ M ($R_v = 1.0$ and 2.0) or 0.017 M ($R_v = 0.5$); $[C_6H_5CH_2OH]_{org} = 0.326$ M ($R_v = 0.5$), 0.192 M ($R_v = 1.0$) or 0.177 M ($R_v = 2.0$). Key: time (*) 20, (○) 60 and (□) 80 min.

Table 3. Effect of the organic-to-aqueous volume ratio on the average oxidation rate of benzyl alcohol

Run time (*min*)	$R_v = 0.5$ (*mmol* min^{-1})	$R_v = 1.0$ (*mmol* min^{-1})	$R_v = 2.0$ (*mmol* min^{-1})
20	0.204	0.136	0.048
60	0.169	0.130	0.037
80	0.144	0.114	0.036

$[Cl^-]^0_{aq} = 1.0$ M; buffer solution: 50 ml 0.1 M H_3BO_3 + 21.3 ml 0.1 N NaOH + 28.7 ml H_2O; organic solvent: CH_2Cl_2; pH = 9.0; anodic potential = 1.35 V (SCE) $[Bu_4NCl] = 0.025$ M ($R_v = 1.0$ and 2.0), 0.017 M ($R_v = 0.5$); $[C_6H_5CH_2OH]_{org} = 0.326$ M ($R_v = 0.5$), 0.192 M ($R_v = 1.0$), 0.177 M ($R_v = 2.0$); $V_{aq} = 80$ ml ($R_v = 0.5$), 70 ml ($R_v = 1.0$), 40 ml ($R_v = 2.0$); stirring rate = 600 rpm.

fraction of anode covered by the aqueous phase is equal to 0.89. Similarly, the theoretical calculations correlate well with the experimental data when the organic-to-aqueous volume ratios are equal to 1.0 and 2.0 as shown in Fig. 4.

The results indicate that by increasing the organic-to-aqueous volume ratio, the fraction of anode covered by the aqueous phase decreases and the total anodic current of the oxidation of chloride ion decrease. This is due to the fact that increasing the value of R_v, the volume fraction of organic phase in the solution increases and the fraction of anode covered by the aqueous phase decreases. Therefore, as the value of R_v is increased the current for the anodic oxidation of chloride ion in the aqueous phase decreases at the same overpotential and the rate of the anodic oxidation of benzyl alcohol also decreases.

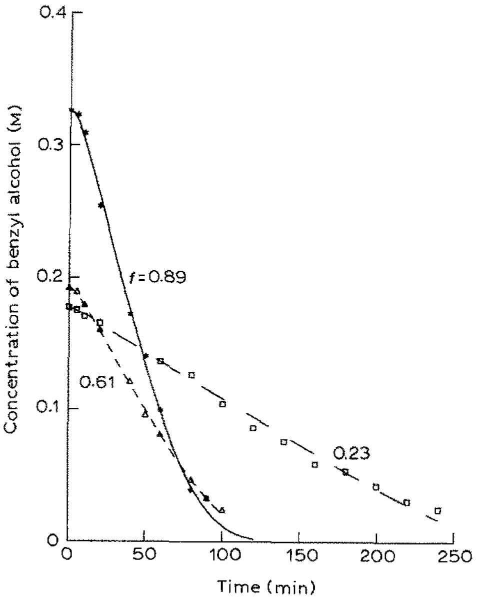


Fig. 4. Plot of the concentration of benzyl alcohol against time. $[Cl^-]^0_{aq} = 1.0$; buffer solution: 50 ml 0.1 M H_3BO_3 + 21.3 ml 0.1 N NaOH + 28.7 ml H_2O; organic solvent: CH_2Cl_2; pH = 9.0; stirring rate = 600 rpm; potential = 1.35 V (SCE); $[Bu_4NCl] = 0.025$ M ($R_v = 1.0$ and 2.0) or 0.017 M ($R_v = 0.5$). $[C_6H_5CH_2OH]_{org} = 0.326$ M ($R_v = 0.5$), 0.192 M ($R_v = 1.0$) or 0.177 M ($R_v = 2.0$). Key: $R_v = 0.5$ (*) (——), Rv = 1.0 (△) (- - -) and $R_v = 2.0$ (□) (— —) representing experiment (points) and theory (lines).

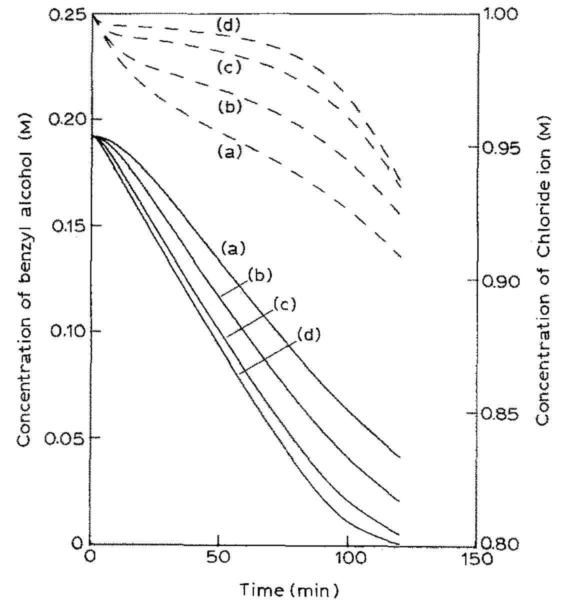


Fig. 5. Plot of the concentration of benzyl alcohol and chloride ion against time with the concentration of phase transfer catalyst as parameter. $R_v = 1.0$; $[Cl^-]^0_{aq} = 1.0$ M; organic solvent: CH_2Cl_2; pH = 9.0; stirring rate = 600 rpm; $f = 0.61$; anodic potential = 1.35 V (SCE); $[Bu_4NCl] = 0.025$ M; $[C_6H_5CH_2OH]_{org} = 0.192$ M; (- - -): the concentration of chloride ion in the aqueous phase; (——): the concentration of benzyl alcohol in the organic phase. Key: [PTC] = (a) 0.005, (b) 0.012, (c) 0.025 and (d) 0.050 M.

4.2.3. Effect of the concentration of phase transfer catalyst. 100 min from the beginning of the run and with an increase in the concentration of phase transfer catalyst from 0.005 to 0.050 M, the concentration of benzyl alcohol decreases from 0.063 to 0.011 M as shown in the solid curves of Fig. 5. This shows that with increase of the concentration of the phase transfer catalyst, the oxidation rate of benzyl alcohol in the organic phase increases. Based on Equation 16, at the same concentration of hypochlorite ion in the aqueous phase, increasing the concentration of phase transfer catalyst, Bu_4NCl, the concentration of the tetrabutylammonium hypochlorite ion pair in the organic phase increases and the rate of oxidation of benzyl alcohol in the organic phase increases.

As shown in the dashed curves of Fig. 5, 50 min from the beginning of the run, the concentration of chloride ion in the aqueous phase increases from 0.955 to 0.992 M when the concentration of phase transfer catalyst increases from 0.005 to 0.050 M. The results reveal that the concentration of chloride ion in the aqueous phase increases when the concentration of phase transfer catalyst increases. This is due to the fact that increasing the concentration of phase transfer catalyst, increases the oxidation rate of benzyl alcohol which reinforces the rate of anodic oxidation of the chloride ion to hypochlorite ion in the aqueous phase. Based on Equation 19, increasing the rate of anodic oxidation of chloride ion, the concentration of chloride ion increases.

As shown in the dashed curve (d) in Fig. 5, the concentration of chloride ion in the aqueous phase sharply decreases with time of electrolysis in the initial step. The decreasing rate of the concentration of chloride ion in the aqueous phase slows down after

5 min. As the electrolysis time is greater than 100 min, the decreasing rate of the concentration of chloride ion in the aqueous phase sharply increases again. Based on Equation 33, the decreasing rate of the concentration of chloride ion, $d[Cl^-]_{aq}/dt$, is accelerated by the anodic oxidation of chloride ion in the aqueous phase. This corresponds to the first term in the right hand side of Equation 33. Similarly, it is inhibited by the formation of chloride ions from the oxidation of benzyl alcohol in the organic phase that corresponds to the second term in the right hand side of Equation 33. In the initial stage, the concentration of hypochlorite ion in the aqueous phase is insignificant and the anodic oxidation of chloride ion is much more important than the formation of chloride ion in the organic phase. Accordingly, the concentration of chloride ion decreases sharply with electrolysis time in the initial stage. On the other hand, the importance of formation of chloride ion in the organic phase gradually increases and the decreasing rate of the concentration of chloride ion slows down after the initial stage of the run. After 100 min from the beginning of the run, the concentration of benzyl alcohol in the organic phase is less than 0.011 M as illustrated in the solid curve d of Fig. 5. Therefore, the rate of formation of chloride ion from the oxidation of benzyl alcohol in the organic phase is insignificant and the decreasing rate of the concentration of chloride ion in the aqueous phase is promoted again.

5. Conclusions

Both theoretical analysis and experiment results show that the electrochemical reaction order of chloride ion on the graphite anode is unity. The charge-transfer parameters, α, k_2^0, and exchange current density, i_0, of chloride ion oxidized on the graphite anode are obtained in the temperature range from 5 to 45° C. The model calculation of the anodic oxidation of benzyl alcohol by the theoretical analysis correlates well with the experimental results. Comparing the theoretical model calculations and the experimental data, the fraction of anode surface covered by the aqueous phase are obtained as 0.89, 0.61, and 0.23 when the organic-to-aqueous volume ratios equal to 0.5, 1.0, and 2.0, respectively.

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