

Simulation of an extractive electrochemical reaction operated under limiting current conditions in a parallel-plate reactor

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An extractive electrochemical reaction, which uses an extractive liquid (β) to separate the adherent product (S) on the electrode surface (e) in order to allow the continuation of the reaction (R) occurring electrochemically in a reacting phase (α), was investigated with the aim of studying the kinetics and reactor design. A kinetic model based on the competitive surface coverage (θ) by the reactant and the product, was developed to describe the performance in a parallel-plate reactor. The electrochemical reaction rate, defined as $KmA X_{\alpha/c}(1 - \theta)(C_{R/\alpha} - C_{R/c})$, is equal to the extraction rate, defined as $KdAX_{\beta/Se}\theta(C_{S/\beta}^{sat} - C_{S/\beta})$ under steady-state conditions where X is the dispersion function and A is the specific surface area. Simulation under limiting current conditions reveals that this system is dependent on the volume ratio of the two liquids, the dispersion effect and the reactor geometry and diffusion coefficients. Three dimensionless parameters $\phi_k (= K_m/K_d)$, $\phi_x (= X_{\alpha/c}/X_{\beta/Se})$ and $\phi_v (= V_\beta/V_\alpha)$ were used to describe this extractive electrochemical reaction.

Nomenclature

A	specific surface area (electrode area per unit reactor volume) ($\text{cm}^2 \text{cm}^{-3}$)	Z	axial distance (cm)
\bar{A}	surface area of electrode (cm^2)	α	continuous phase
C	concentration (mol dm^{-3})	β	dispersed phase
D	diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)	ϕ_k	mass transfer coefficient ratio ($= K_m/K_d$)
Q	volumetric flow rate ($\text{cm}^3 \text{min}^{-1}$)	ϕ_v	volume ratio ($= F_\beta/F_\alpha$)
F	Faraday's constant, 96487 C mol^{-1}	ϕ_x	ratio of probability factor ($= X_{\alpha/c}/X_{\beta/Se}$)
h	interelectrode gap (cm)	Φ	dimensionless group ($= \phi_k \phi_x$)
i	local limiting current density (mA cm^{-2})	σ	electrode surface area per unit length (cm)
I	total current (A)	θ	fraction of electrode surface area covered with product ($\text{cm}^2 \text{cm}^{-2}$)
K_m	mass transfer coefficient of continuous phase (cm s^{-1})	<i>Subscripts and superscripts</i>	
K_d	mass transfer coefficient of dispersed phase (cm s^{-1})	i	input
L	length of electrode (cm)	o	output
n	Faraday's per mol of substance electrolysed	r	reactor
U	fluid linear velocity (cm s^{-1})	R	reactant
V	volume (cm^3)	S	product
W	electrode width (cm)	α/e	α phase on clean electrode surface
X	ratio of the two liquids α and β remaining on the electrode surface	β/Se	β phase on electrode surface occupied by product (S)
		R/ α	reactant R in α phase
		S/ β	product S in β phase
		sat	saturated

1. Introduction

If a consecutive reaction of R to S to S' occurs in one liquid, α , and the desired product S is selectively soluble in another foreign liquid, β , the product distribution ratio $C_S/C_{S'}$ can be improved by introducing liquid β into the reactor to extract S as it forms. This operation is known as an extractive reaction which has become of interest in reaction engineering. If an electrochemical conversion is involved in the consecutive reaction, the operation is called an extractive electrochemical reaction [1].

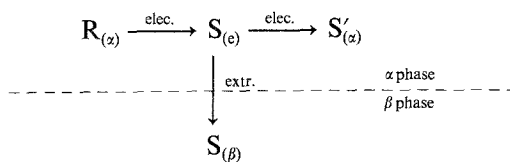
Several extractive electrochemical reactions have been reported such as the Purex process used in the nuclear industry to reduce Pu(IV) to Pu(III) [2]. The former complex is selectively soluble in an organic solvent while the latter complex is more soluble in an aqueous solution. Other examples include the two-step conversion of benzene to hydroquinone [3], the phase transfer catalysed cyanation of naphthalene [4] and the electrochemical oxidation of ferrocene–methylene chloride to ferricinium–water [1].

Though the selectivity of the reaction, even the reaction rate, can be favourably enhanced by applying a second liquid to the reacting liquid, few studies have analysed these extractive reactions because of their complex nature. For example, an extractive electrochemical reaction involves the simultaneous electrochemical reaction and solvent extraction. This system is heterogeneous and contains several phases. The reaction and the extraction occur mainly in the interfacial region such as the electrode surface and the immiscible liquid boundary.

This paper aims to establish an acceptable reaction mechanism and kinetic model to allow the analysis and design procedures of an extractive electrochemical reaction to be demonstrated. A simple simulation of an extractive electrochemical reaction was performed using a model reaction operated under limiting current conditions in a parallel-plate reactor.

2. Model reaction

A consecutive reaction of $R_{(\alpha)}$ to $S_{(e)}$ to $S'_{(\alpha)}$ is used here as an illustration.



The reactant R and the side product S' are soluble in the first liquid, α , which is also known as the continuous phase. The desired product S is formed on the electrode surface and inhibits the electrode reaction, or is further oxidized to side products if the operating conditions are changed. The desired product S can also be extracted by the second liquid, β , which is known as the dispersed phase. The chemical equilibrium can be favourably shifted by this extractive operation.

This model reaction represents the well-established behaviour of the anodic oxidation of sulphide anion to sulphur at a platinum electrode in basic solution [5]. The sulphur produced accumulates as a thin film on the anode and retards the reaction. Further oxidation leads to the formation of polysulphides, thiosulphates or even sulphate. The addition of an organic solvent such as benzene or toluene to the aqueous solution can assist extraction of the sulphur product [6].

Generally, batch reactors are used to study the chemistry and the equilibrium of an extractive electrochemical reaction. However, taking into account the mixing effect as well as the stable

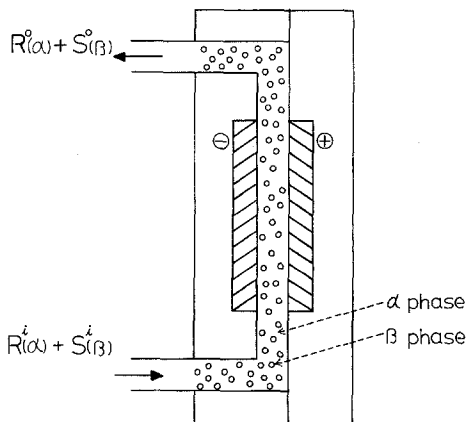


Fig. 1. Parallel-plate reactor used for the model reaction.

performance, a parallel-plate reactor is used in this report to analyse the kinetics (Fig. 1). A one-dimensional analysis is performed for the one-electrode reaction.

3. Parameters

In order to analyse the complex kinetics of the model extractive electrochemical reaction which contains two liquids and two solid phases, several assumptions have to be made. The electrode surface is divided into two regions: one is the clean surface ($1 - \theta$) which permits the electrochemical conversion of R to S, the other is the surface covered by product S (θ) which invites the second liquid β to attack. Due to their different wetting or contact affinities on the solid surfaces, the R-containing solution, α , and the S-containing liquid, β , should have different dispersed effects on the two parts of the electrode surface as illustrated in Fig. 2.

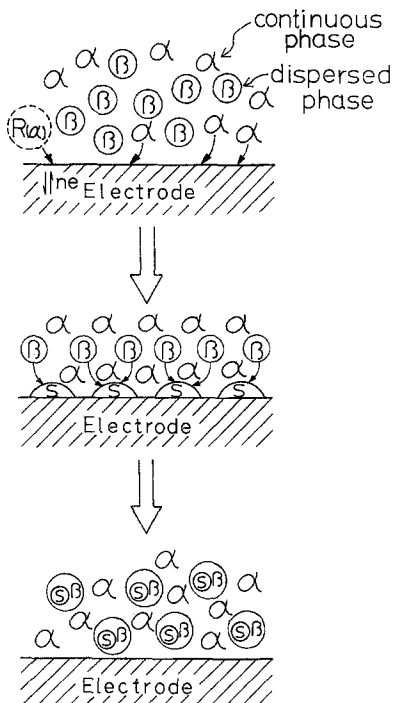


Fig. 2. Representation of the two liquids, α and β , on the electrode surface of the model reaction.

In other words the proportion of liquids α and β remaining on the solid surface should not be the same as their liquid volume ratio (V_α/V_β). This phenomenon affects not only the reaction rate of R on the electrode but also the extraction rate of S from the electrode. To describe this phenomenon, two parameters are introduced: $X_{\alpha/e}$, representing the probability of the R-containing solution, α , attacking the electrode surface in the presence of liquid β , and $X_{\beta/Se}$, representing the probability of the second liquid, β , on the S-covered electrode surface. As a result, the electrochemical reaction rate of S can be related to $X_{\alpha/e}(1 - \theta)$ and the extraction rate of S can be related to $X_{\beta/Se}\theta$.

Thirdly, based on the experimental results of a study by Alkire on the electrochemical oxidation of iodide in a two-phase system [7] and solvent extraction theory [8], the mass transfer coefficient K_m of R(α) and the extraction coefficient K_d of S(β) are defined as if only the α or β phase is present.

Therefore, three important dimensionless parameters, i.e. ϕ_k , ϕ_x and ϕ_v , are introduced here to describe this extractive electrochemical reaction:

$$\phi_k = K_m/K_d$$

$$\phi_x = \frac{X_{\alpha/e}}{X_{\beta/Se}}$$

$$\phi_v = V_\beta/V_\alpha = Q_\beta/Q_\alpha$$

Furthermore, the reaction rate of R is assumed to be proportional to the concentration change of ($C_{R/\alpha} - C_{R/e}$) and the extraction rate is affected by the concentration difference of ($C_{S/\beta}^{\text{sat}} - C_{S/\beta}$) [9].

4. Rate equations

Based on the proposed model, the electrochemical conversion rate of R in the continuous phase, α , can be expressed as

$$U_\alpha \frac{dC_{R/\alpha}}{dZ} = -K_m A X_{\alpha/e} (1 - \theta) (C_{R/\alpha} - C_{R/e}) \quad (1)$$

For operation under limiting current conditions the $C_{R/e}$ term can be eliminated to yield

$$U_\alpha \frac{dC_{R/\alpha}}{dZ} = -K_m A X_{\alpha/e} (1 - \theta) C_{R/\alpha} \quad (2)$$

Meanwhile, the extraction rate of S for the solid electrode surface to the dispersed β phase is given by

$$U_\beta \frac{dC_{S/\beta}}{dZ} = K_d A X_{\beta/Se} \theta (C_{S/\beta}^{\text{sat}} - C_{S/\beta}) \quad (3)$$

If the operation reaches steady state, the reaction rate of R and the extraction rate of S should be equal, to yield

$$U_\alpha V_\alpha \frac{dC_{R/\alpha}}{dZ} = -U_\beta V_\beta \frac{dC_{S/\beta}}{dZ} \quad (4)$$

where V_α and V_β are the volumes of α and β inside the parallel-plate reactor. Substitution of Equations 2 and 3 into Equation 4 gives

$$K_m A X_{\alpha/e} (1 - \theta) V_\alpha C_{R/\alpha} = K_d A X_{\beta/Se} \theta V_\beta (C_{S/\beta}^{\text{sat}} - C_{S/\beta}) \quad (5)$$

This equation forms the fundamental rate relation for the model extractive electrochemical reaction operated under limiting current conditions.

5. Mathematical solution

Numerical integration of Equation 4 with the assumption of $U_\alpha = U_\beta$, which is correct under well-mixed conditions, gives the product equation

$$C_{S/\beta} = \phi_v^{-1}(C_{R/\alpha}^i - C_{R/\alpha}) \quad (6)$$

This equation states that the conversion of the reaction is proportional to the volume ratio of the two immiscible liquids if the current efficiency is taken to be one for the extractive electrochemical reaction.

One parameter, Φ , representing the relative magnitude of the electrochemical reaction and the extraction is defined

$$\Phi = \phi_k \phi_x = (K_m/K_d)(X_{\alpha/e}/X_{\beta/Sc}) \quad (7)$$

Substitution of Φ into Equation 5 gives

$$\Phi(1 - \theta)V_\alpha C_{R/\alpha} = \theta V_\beta(C_{S/\beta}^{\text{sat}} - C_{S/\beta}) \quad (8)$$

which is further rearranged to give Equation 9 by the inclusion of Equation 6

$$\theta = \frac{\Phi C_{R/\alpha}}{[(\Phi + 1)C_{R/\alpha} + \phi_v C_{S/\beta}^{\text{sat}} - C_{R/\alpha}^i]} \quad (9)$$

This states that the surface coverage ratio, θ , is affected by Φ , $C_{R/\alpha}$, ϕ_v and other parameters. It has to be pointed out that Equation 9 gives $\theta = 1$ if V_β is equal to zero which means no extraction. The electrode surface is covered completely with product S and the reaction of R is either disrupted or is further reacted to the side product S'. This result reflects the phenomenon of the sulphide oxidation reaction to produce a thin film of sulphur on the electrode [5].

As a result a general rate equation to describe the model extractive electrochemical reaction is obtained by substitution of the function θ into Equation 2, yielding

$$\left(\frac{1}{C_{R/\alpha}} + \frac{\Phi}{C_{R/\alpha} + \phi_v C_{S/\beta}^{\text{sat}} - C_{R/\alpha}^i} \right) \frac{dC_{R/\alpha}}{dZ} = - \frac{K_m A X_{\alpha/e}}{U_\alpha} \quad (10)$$

which is further integrated from $Z = 0$ to $Z = Z$ to give a general solution

$$\Phi \ln \left(\frac{\phi_v C_{S/\beta}^{\text{sat}}}{C_{R/\alpha} + \phi_v C_{S/\beta}^{\text{sat}} - C_{R/\alpha}^i} \right) + \ln \left(\frac{C_{R/\alpha}^i}{C_{R/\alpha}} \right) = \left(\frac{K_m A X_{\alpha/e}}{U_\alpha} \right) Z \quad (11)$$

Assuming that the current efficiency is 100%, the local current density, i_z , is given by

$$i_z \left(\frac{\bar{A}}{nF} \right) = -U_\alpha V_\alpha \frac{dC_{R/\alpha}}{dZ} = K_m A X_{\alpha/e} (1 - \theta) V_\alpha C_{R/\alpha} \quad (12)$$

The total current is obtained by integration over the reactor length to give

$$I = \sigma \int_0^L i_z dZ = nFU_\alpha V\alpha\sigma(C_{R/\alpha}^i - C_{R/\alpha}^o) \quad (13)$$

6. Parameter estimation

The parameters used in the calculations are listed in Table 1. The measurable volume flow rates of Q_α and Q_β instead of V_α and V_β in the parallel-plate reactor are used.

The mass transfer coefficient, K_m , is dependent on the linear velocity, U_α , the diffusion coefficient

Table 1. Input parameters

Parameters	Range	Unit	Note
V_α	23.0 -247.0	cm ³	$V_\alpha = V_r Q_\alpha / Q_\alpha Q_\beta$
V_β	3.0 -227.0	cm ³	$V_\beta = V_r Q_\beta / Q_\alpha Q_\beta$
V_r	250.0	cm ³	$V_r = WLh$
X_α	0.8 -1.0		
X_β	0.0 -1.0		
K_m	0.63-1.7 × 10 ⁻⁵	cm s ⁻¹	1.85 × 10 ⁻⁴ U _R ^{1/3}
K_d	1.0 -2.7 × 10 ⁻⁵	cm s ⁻¹	
Q_α	6 -60	cm ³ min ⁻¹	
Q_β	0.6 -60	cm ³ min ⁻¹	
ϕ_k	0.63		
ϕ_v	0.1 -100.0		
ϕ_x	1.0 -20		
$C_{\alpha/R}^i$	0.1 -1.0	mol dm ⁻³	
$C_{S/\beta}^{\text{sat}}$	0.60	mol dm ⁻³	
U_R	0.04-0.8	cm s ⁻¹	
U_S	0.04-0.8	cm s ⁻¹	
A	2.0	cm ² cm ⁻³	
\bar{A}	500.0	cm ²	
Φ	0.063-12.6		
D_R	1 × 10 ⁻⁵	cm ² s ⁻¹	
D_S	2 × 10 ⁻⁵	cm ² s ⁻¹	
L	100.0	cm	
h	0.5	cm	
W	5.0	cm	

of the R species in the α phase, D_R , and the geometry of the reactor as given below [10]

$$K_m = 1.4675 D_R \left(\frac{U_\alpha}{h D_R L} \right)^{1/3} \quad (14)$$

For theoretical analysis, a typical diffusion coefficient of $D_R = 1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ is adopted [11] and the U_α is taken to be 0.1 cm s^{-1} . If h and L are 0.5 cm and 100 cm , respectively, the K_m value is found to be $8.6 \times 10^{-5} \text{ cm s}^{-1}$ or $1.85 \times 10^{-4} (U_\alpha)^{1/3}$.

The calculation of K_d is assumed to be the same as Equation 14 with the substitution of D_R and U_α by D_S and U_β . The diffusion coefficient, D_S , is taken to be $2.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which is true for most non-ionic species in the organic phase [11]. Consequently, the dimensionless constant ϕ_k ($= K_m / K_d$) is proportional to $(D_R / D_S)^{1/3}$ and equal to 0.63.

The probability factor, $X_{\alpha/e}$, is assumed to be close to one while another factor, $X_{\beta/Se}$, is related to the droplet size of the dispersed phase. Statistically, $X_{\beta/Se}$ is inversely proportional to the radius of the droplet. For perfect mixing $X_{\beta/Se}$ can be taken to be one and the dimensionless constant ϕ_x ($= X_{\alpha/e} / X_{\beta/Se}$) is also one. The linear velocities U_α and U_β should be the same for perfect mixing of the solution. Depending on the dispersion effect, the value of ϕ_x lies between one and infinity.

In addition, the saturated concentration, $C_{S/\beta}^{\text{sat}}$, varies according to the product species and also the extraction solvent and is assumed to be 0.60 M for the present case.

7. Results and discussion

The calculations of the design variables $C_{R/\alpha}$, $C_{S/\beta}$, i_z and I were performed numerically using an iterative procedure. The variables ϕ_k , ϕ_x , ϕ_v and Z were used with constant temperature and potential for the present limiting current operations. Due to the complex nature of the electro-

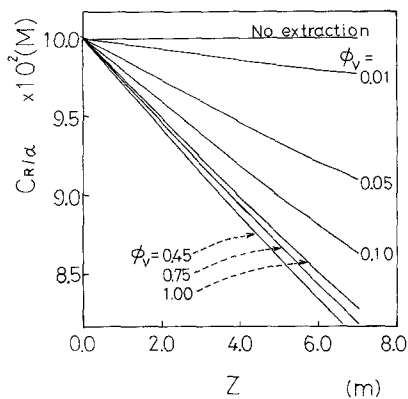


Fig. 3. The consumption of $C_{R/\alpha}$ along the reactor axis, Z , where $C_{R/\alpha}^i = 0.1 \text{ mol dm}^{-3}$, $Q_\alpha = 30 \text{ cm}^3 \text{ min}^{-1}$, $\phi_x = 1.0$.

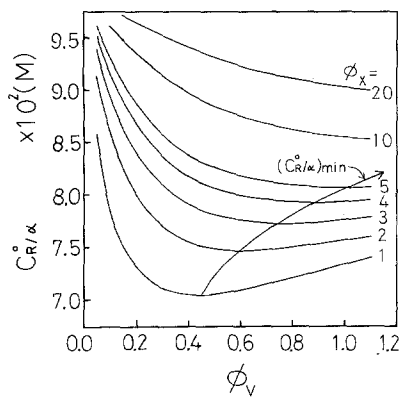


Fig. 4. The outlet concentration, $C_{R/\alpha}^o$, as a function of ϕ_v and ϕ_x where $C_{R/\alpha}^i = 0.1 \text{ mol dm}^{-3}$, $Q_\alpha = 30 \text{ cm}^3 \text{ min}^{-1}$, $Z = 1 \text{ m}$.

chemical reaction and the solvent extraction which are influenced respectively by the competitive terms $(1 - \theta)$ and θ , the calculation results show some interesting features which are qualitatively consistent with the reported experimental data [6, 7].

It is interesting from Fig. 3 that in addition to the normal gradual consumption of $C_{R/\alpha}$ along the perfect-mixed reactor axis for a fixed Q_α value, the rate of change of $C_{R/\alpha}$ is first augmented by the presence of Q_β (the increase of ϕ_v) due to the extraction process creating more clean surface. Nevertheless, as the extraction solvent reaches a certain proportion the accumulation of $C_{S/\beta}$ tends to retard the extraction rate because the $(C_{S/\beta}^{\text{sat}} - C_{S/\beta})$ term decreases. As a result, the extraction rate and also the reaction rate slow down, as also does the consumption of $C_{R/\alpha}$.

Fig. 4 shows a more explicit picture of the extraction solvent effect. For a fixed reaction length ($Z = 1 \text{ m}$) and a fixed inlet concentration, $C_{R/\alpha}^i$, the outlet concentration, $C_{R/\alpha}^o$, is influenced by the degree of dispersion (ϕ_x) and the volume ratio (ϕ_v). For a certain ϕ_v value the perfectly mixed system ($\phi_x = 1$) consumes more reactant than the less dispersed system which is characterized by a larger ϕ_x value. Meanwhile, the outlet concentration of product in the extraction solvent $C_{S/\beta}$ increases with the dispersion effect (ϕ_x) for a certain ϕ_v value. The $C_{S/\beta}$ value decreases gradually with increase of the proportion of the extraction solvent.

Fig. 4 also shows that an asymmetric hyperbolic function of ϕ_v can be used to describe the $C_{R/\alpha}^o$ curve for each ϕ_x value. A minimum, $(C_{R/\alpha}^o)_{\text{min}}$, can be obtained by numerical solution for each system. In other words, if ϕ_x is known for a reactor with a fixed geometry, the best ϕ_v can thus be found to produce the highest yield which is defined to be $1 - (C_{R/\alpha}^o/C_{R/\alpha}^i)$. For instance, the ϕ_v value for the perfectly mixed system ($\phi_x = 1$) is about 0.44 ($= Q_\beta/Q_\alpha$) for the fixed reactor. A smaller ϕ_v affords an inefficient extraction to create a larger θ and hence to retard the reaction rate. Meanwhile, a larger ϕ_v means a faster extraction rate to extract more product into the liquid β and, consequently, to affect the concentration difference term of $(C_{S/\beta}^{\text{sat}} - C_{S/\beta})$ to yield a slower extraction rate at the exit of the reactor and also to give a smaller conversion.

Since the local current density, i_z , reflects the local electrochemical reaction rate along the parallel-plate electrode, its value is also affected by the ϕ_k , ϕ_x and ϕ_v factors. As in most flow reactors the local current density also decreases along the reactor because of the continuous consumption of the reactant R. However, as shown in Fig. 5, i_z^o at the outlet of the reactor depends on ϕ_x and ϕ_v and has a maximum value for a fixed Q_α system.

Moreover, the total current, I , also changes with the ϕ_x and ϕ_v parameters. Fig. 6 gives the total current as a function of ϕ_x and $Q_\beta/(Q_\alpha + Q_\beta)$ (i.e. $\phi_v/(1 + \phi_v)$) as used by other workers [7]. A value for I_{max} was obtained by a numerical method.

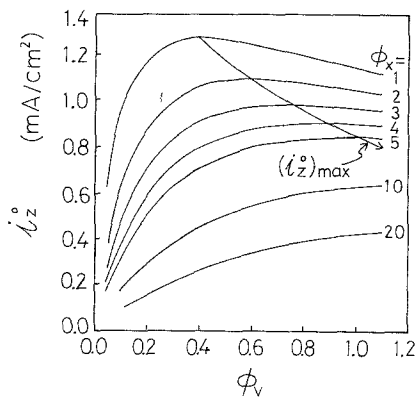


Fig. 5. The local current, i_z^0 , as a function of ϕ_v and ϕ_x , where $C_{R/z}^i = 0.1 \text{ mol dm}^{-3}$, $Q_a = 30 \text{ cm}^3 \text{ min}^{-1}$, $Z = 1 \text{ m}$.

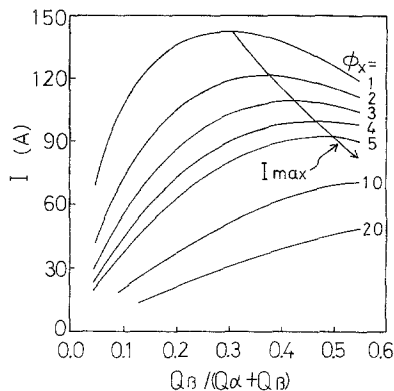


Fig. 6. The effect of $Q_\beta / (Q_\alpha + Q_\beta)$ on the total current, I , where $C_{R/z}^i = 0.1 \text{ mol dm}^{-3}$, $Q_a = 30 \text{ cm}^3 \text{ min}^{-1}$, $Z = 1 \text{ m}$.

Figs 3–6 provide a design base for a search for operating conditions under limiting current operations for the model extractive electrochemical reaction. Another parameter, ϕ_k , representing the properties of the solvent and reactant, was taken to be constant for the present case. However, the observed trend should be the same even with different ϕ_k values.

In addition to the operating parameters, ϕ_x and ϕ_v , one important variable, θ , should be discussed in order to understand the proposed mechanism (Fig. 2). Fig. 7 shows the calculated results for the surface coverage ratio, of product S as functions of Z and ϕ_v . Though θ by definition, is not constant along the reactor axis, it is interesting to observe that, for the present case, there exists a constant θ value of $\phi / (\phi + 1) = 0.386$ for $\phi_v = 0.167$ which just happens to be equal to the ratio of $C_{R/z}^i / C_{S/\beta}^{\text{sat}} (= 0.167)$. For a system with ϕ_v greater than 0.167, the calculated θ values increase along the reactor axis, while for smaller ϕ_v values the θ value decreases. This phenomenon is attributed to the compromise of reaction and extraction to each equilibrium. It must be recalled that the θ value equals one when the ϕ_v value equals zero which implies no further reaction.

8. Conclusions

Conversions which are higher than the equilibrium conversion can be obtained by the application of an extractive method. A theoretical model to study an extractive electrochemical reaction carried out in a parallel-plate flow reactor was developed. The model takes into account the transport properties influencing the reaction rates, i.e. the properties of the two immiscible liquids, the liquid

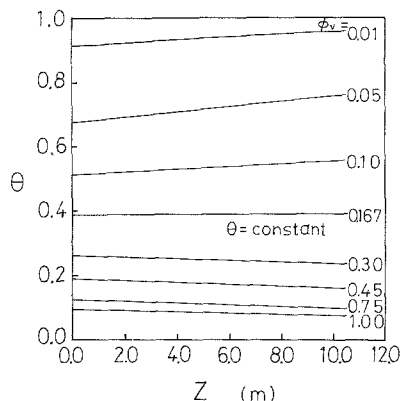


Fig. 7. The surface coverage ratio, θ , versus reactor axis, Z , where $C_{R/z}^i = 0.1 \text{ mol dm}^{-3}$, $Q_a = 30 \text{ cm}^3 \text{ min}^{-1}$, $\phi_x = 1.0$.

volume ratio, the dispersion state as well as the geometry of the reactor. It is shown that in order to obtain a simple description of the model system, three dimensionless parameters have to be introduced:

- (i) ϕ_k , proportional to the transport properties of reaction and extraction
- (ii) ϕ_x , proportional to the dispersion effect of the extraction solvent in the reaction liquid
- (iii) ϕ_v , proportional to the volume ratio of the two liquids.

In conclusion, this paper paves the way for the further study of other extractive electrochemical reactions including operation under non-limiting current conditions, operation in different reactors and other series or parallel reactions.

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