A mass transfer model for the autocatalytic dissolution of a rotating copper disc in oxygen saturated ammonia solutions

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A mathematical model of mass transfer processes during autocatalytic dissolution of metallic copper in oxygen-containing ammonia solutions using the rotating disc technique is presented. The model is based on the equations of steady state convective diffusion with volumetric mass generation terms and boundary conditions of the third kind, in more generalized form, at the disc surface and of the first kind in the bulk solution. The boundary value problem was solved numerically using the finite difference method with variable mesh spacing. Comparison of calculated and experimental results indicates that the model quantitatively represents the measurements. The rate of the reaction 

\[ \text{Cu(II)} + \text{Cu} \rightarrow 2\text{Cu(I)} \]

determines the overall rate of the process.

Nomenclature

- \( A \): rotating disc surface area, (cm\(^2\))
- \( B \): dimensionless constant, \( B = k_3 c_i^0 \omega^{-1} \)
- \( c_i \): concentration of species \( i \), \( c_i = c_i(y) \) (mol cm\(^{-3}\))
- \( c_i^0 \): concentration of species \( i \) in the bulk of solution, \( c_i^0 = c_i^0(t) \) (mol cm\(^{-3}\))
- \( c_{i,0} \): concentration of species \( i \) at the disc surface, \( c_{i,0} = c_i(y = 0) \) (mol cm\(^{-3}\))
- \( C_i \): concentration ratio, \( C_i = c_i/c_i^0 \)
- \( C_i^0 \): concentration ratio (in the bulk of solution), \( C_i^0 = c_i^0/c_i^0 \)
- \( C_{i,0} \): concentration ratio (at the disc surface), \( C_{i,0} = c_{i,0}/c_i^0 \)
- \( D_i \): molecular diffusivity of species \( i \) (cm\(^2\) s\(^{-1}\))
- \( h \): space increment, \( h = \Delta \xi = (\omega/\mu)^{1/2} \Delta y \), dimensionless
- \( j_i \): mass flux of species \( i \) (mol cm\(^{-2}\) s\(^{-1}\))
- \( k_i \): first-order reaction rate constant (cm s\(^{-1}\) or cm\(^3\) mol\(^{-1}\) s\(^{-1}\))
- \( K_{i,j} \): diffusivity ratio, \( K_{i,j} = D_i/D_j \), dimensionless
- \( M \): number of space increments
- \( n_i \): total number of moles of Cu(II) entering the bulk of solution referred to the unit disc surface area (mol cm\(^{-2}\))
- \( r_i \): rate of production of species \( i \) by the chemical reaction (mol cm\(^{-3}\) s\(^{-1}\))
- \( \nu \): fluid velocity vector \( \mathbf{v} = (u, v, w) \) (cm s\(^{-1}\))
- \( \Delta t \): time increment (s)
- \( \Delta y \): space increment (cm)
- \( \mu \): stoichiometric coefficients
- \( \omega \): disc angular velocity (s\(^{-1}\))
- \( \xi \): dimensionless axial coordinate, \( \xi = (\omega/\mu)^{1/2} y \)
- \( \Delta \xi \): dimensionless space increment, \( \Delta \xi = (\omega/\mu)^{1/2} \Delta y \)

Greek letters

- \( \nabla \): nabla operator
- \( \nu \): kinematic viscosity of solution (cm\(^2\) s\(^{-1}\))
- \( \mu \): stoichiometric coefficients
- \( \omega \): disc angular velocity (s\(^{-1}\))
- \( \xi \): dimensionless axial coordinate, \( \xi = (\omega/\mu)^{1/2} y \)
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1. Introduction

An experimental study of spontaneous copper dissolution in oxygen-containing aqueous ammonia solutions carried out by Zembura and Maraszewska [1] shows that the sequence of reactions is as follows:

\[ \text{Cu} + 4\text{NH}_3 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Cu(NH}_3)_4^{2+} + 2\text{OH}^- \tag{1} \]

\[ \text{Cu + Cu(NH}_3)_4^{2+} \rightarrow 2\text{Cu(NH}_3)_2^{2+} \tag{2} \]

\[ 2\text{Cu(NH}_3)_2^{2+} + \frac{1}{2}\text{O}_2 + 4\text{NH}_3 + \text{H}_2\text{O} \rightarrow 2\text{Cu(NH}_3)_4^{2+} + 2\text{OH}^- \tag{3} \]

Reaction 1 proceeds in the diffusion-controlled regime [1] whereas Reaction 2, particularly at high concentrations of Cu(II) complexes, is very likely to occur in the mixed regime [2]. Because of the absence of Cu(I)
complexes in the solution, Reaction 3 can be assumed to be very fast in comparison with Reaction 2. Therefore, the rate of accumulation of Cu(II) complexes in the bulk solution is the sum of the rates of Reactions 1 and 2. The substrate of Reaction 2, Cu(II), is continuously reproduced in Reaction 3, making the dissolution process autocatalytic. The main purpose of this study is to formulate and solve the mathematical model for the mass transfer processes due to the reactions described above. Making use of the rotating disc technique, the mathematical model proposed by Levich [3, 4] can be utilized as the base for more rigorous analysis.

2. Mass transfer model

Generally, the diffusion and convection mass transfer processes can be described by a set of partial differential equations:

$$\frac{\partial c_i}{\partial t} + (\mathbf{v} \cdot \nabla)c_i = \nabla(D_i \cdot \nabla c_i) + r_i$$

(4)

where $c_i = c_i(x, t)$, $r_i = r_i(c_i, c_j, t)$, $D_i = D_i(c_i, c_j)$, and $\mathbf{v} = (u, v, w)$. Based on the analysis of experimental data [1] the Equations 4 can be significantly simplified by assuming that the concentration of all species, $i$, changes very slowly with time so that $\frac{\partial c_i}{\partial t} = 0$. This means that the process can be considered as quasi-steady state. To simplify the problem further we assume that the Reaction 3 is first order and irreversible for dissolved oxygen and Cu(I) complexes and that these species are at low concentration in comparison with ammonia and water. Additionally, the molecular diffusivity of all species, $i$, in the liquid, $D_i$, can be assumed independent of concentration and mass transfer processes can be considered as unidimensional. Under such assumptions, based on the Levich model [3], the equations of convective diffusion take the simplified form:

$$D_i \frac{d^2c_i}{dy^2} - v \frac{dc_i}{dy} + \mu_i k_i c_i = 0 \quad \text{(for } i = 1, 2, 3)$$

(5)

where $c_i = c_i(y)$ and $(D_i, k_i) = \text{constant}$.

The axial component of the fluid velocity can be calculated using the analytical solution obtained by Cochran [5]. Indices $i = 1, 2, 3$ refer to oxygen in Reaction 1, Cu(I) complexes in Reaction 2 and Cu(II) complexes in Reaction 3, respectively. Stoichiometric coefficients $\mu_i$ are: $\mu_1 = -1/2, \mu_2 = -1$ and $\mu_3 = 1$.

Assuming, further, that the Reactions 1 and 2 are also first order and irreversible for oxygen and Cu(II) complexes, the boundary conditions at the disc surface, for $y = 0$, are expressed:

$$D_i \frac{dc_i}{dy} \bigg|_0 = k_i c_i$$

(6)

$$D_2 \frac{dc_2}{dy} \bigg|_0 = -2k_2 c_3$$

(7)

In the bulk of solution the asymptotic boundary conditions, for $y \rightarrow \infty$, are expressed:

$$c_1 = c_1^0$$

(9)

$$c_2 = 0$$

(10)

$$c_3 = c_3^0$$

(11)

Introducing dimensionless variables, the boundary value problem (Equations 5-11) can be rewritten as mass transfer equations in the form:

$$\frac{d^2C_i}{d\xi^2} - S_i H(\xi) \frac{dC_i}{d\xi} + \mu_i B_i C_i C_j = 0,$$

(12)

where, according to the Cochran solution [5],

$$H(\xi) = -0.51 \xi^2 + 0.333 \xi^3 - 0.103 \xi^4 + \ldots$$

with boundary conditions for $\xi = 0$:

$$\frac{dC_1}{d\xi} = W_1 C_1$$

(13)

$$\frac{dC_2}{d\xi} = W_2 C_2$$

(14)

$$\frac{dC_3}{d\xi} = 2K_{1,2} \frac{dC_1}{d\xi} - W_2 C_2$$

(15)

and for $\xi \rightarrow \infty$:

$$C_1^0 = 1$$

(16)

$$C_2^0 = 0$$

(17)

$$C_3^0 = c_3^0/c_1^0$$

(18)

The flux of copper entering the solution from the disc surface, $\xi = 0$, is the sum of the fluxes of Cu(I) and Cu(II) complexes and, in the presence of very fast Reaction 3 can be expressed by:

$$j_{Cu} = j_{Cu(II)} = -\left(D_2 \frac{dc_2}{dy} \bigg|_0 + D_3 \frac{dc_3}{dy} \bigg|_0 \right)$$

(19)

or in a dimensionless form, for $\xi = 0$:

$$j_{Cu(II)} = \left(-\left(D_2 \frac{dc_2}{d\xi} \bigg|_0 + D_3 \frac{dc_3}{d\xi} \bigg|_0 \right) \left(\omega/\mu\right)^{1/2} C_1^0 \right)$$

(20)

The solution of the boundary value problem formulated above allows calculation of the values of $j_{Cu(II)}$. To verify the model these values are compared with the fluxes of Cu(II) calculated from experimental data using the mass balance equation for Cu(II) complexes in the bulk solution which takes the form:

$$\frac{V}{At} \frac{dc_3^0}{dt} = \frac{V}{At} \frac{dc_3^0}{dt}$$

(21)

The data from Zembura and Maraszewska's experimental study [1], given in the form of $n_{Cu(II)} = f(t)$, have been used in the calculations, with the initial condition $c_3^0(t = 0) = 0$. 