Hydrodynamic methods (Ch. 9)

Theoretical treatment of convective systems
Rotating disk electrode (RDE)
Rotating ring & ring-disk electrodes (RRDE)

Introduction

Convective mass transport → hydrodynamic methods

(+)

Steady state is attained rather quickly

High mass transfer rate → smaller mass transfer contribution to e-transfer kinetics

(-)

Difficult to construct hydrodynamic electrodes

Difficult theoretical treatment

Theoretical treatment of convective systems

Convective system:

$x > \delta$ (diffusion layer): uniform bulk concentration

$0 \leq x \leq \delta$: no solution movement → mass transfer by diffusion

The convective-diffusion equation

Flux $\mathbf{J}_j = -D_j \nabla C_j - (z_j F/RT) D_j C_j \nabla \phi + C_j \mathbf{v}$

diffusion migration convection

Excess supporting electrolyte → neglect migration term (absent migration)

Velocity vector **v**, $\mathbf{v}(x, y, z) = \mathbf{i}v_x + \mathbf{j}v_y + \mathbf{k}v_z$

$$\nabla C_j = \mathbf{grad}C_j = \mathbf{i}\partial C_j/\partial x + \mathbf{j}\partial C_j/\partial y + \mathbf{k}\partial C_j/\partial z$$

$$\partial C_j/\partial t = -\nabla\cdot\mathbf{J_j} = \mathbf{div}\ \mathbf{J_j} = D_j\nabla^2 C_j - \mathbf{v}\cdot\nabla C_j$$

Two different types of fluid flow:

Laminar flow: smooth & steady flow, parabolic velocity

Turbulent flow: unsteady & chaotic

Reynolds number (Re): dimensionless term in hydrodynamic problems

$Re = v_{ch} l / \nu$

v_{ch}: characteristic velocity (cm/s), l: characteristic length (cm)

ν: kinematic viscosity, $\nu = \eta_s / d_s$ (cm^2/s, viscosity/density)

Reynolds number (Re): proportional to fluid velocity → high Re: high flow or high electrode rotating rate

Critical Re, $Re < Re_{cr}$: laminar, $Re > Re_{cr}$: turbulent

Rotating disk electrode (RDE)

Rotating rate: angular velocity → ω (s^{-1}) = $2\pi f$ f: frequency (revolutions/s)

The velocity profile at the RDE

Velocity profile, **v**

in cylindrical coordinates (y, r, ϕ)

$$\mathbf{v} = \mu_1 v_r + \mu_2 v_y + \mu_3 v_\phi$$

$$\nabla = \mu_1 \partial/\partial r + \mu_2 \partial/\partial y + (\mu_3/r)\partial/\partial\phi$$

$$\rightarrow \quad \nabla\cdot\mathbf{v} = (1/r^2)[\partial/\partial r(v_r r^2) + \partial/\partial y(v_y r^2) + \partial/\partial\phi v_\phi]$$

At disk surface ($y = 0$), $v_r = 0$, $v_y = 0$, $v_\phi = \omega r$

In the bulk solution ($y \rightarrow \infty$), $v_r = 0$, $v_y = -U_0$, $v_\phi = 0$ (U_0: limiting velocity)

Dimensionless variable, $\gamma = (\omega/\nu)^{1/2} y$

For small y ($\gamma << 1$),

$v_r = r\omega F(\gamma) = r\omega(a\gamma - \gamma^2/2 - (1/3)b\gamma^3 + \cdot\cdot)$ a = 0.51023, b = -0.6159

$v_\phi = r\omega G(\gamma) = r\omega(1 + b\gamma + (1/3)a\gamma^3 + \cdot\cdot)$

$v_y = (\omega\nu)^{1/2} H(\gamma) = (\omega\nu)^{1/2}(-a\gamma^2 + \gamma^3/3 - b\gamma^4/6 + \cdot\cdot)$

For the RDE,

Near the surface, $y \rightarrow 0$ (or $\gamma \rightarrow 0$)

$$\mathbf{v}_y = (\omega\nu)^{1/2}(-a\gamma^2) = -0.51\omega^{3/2}\nu^{-1/2}y^2$$

$$\mathbf{v}_r = r\omega(a\gamma) = 0.51\omega^{3/2}\nu^{-1/2}ry$$

For $y \rightarrow \infty$, limiting velocity (y direction)

$$U_0 = -0.88447(\omega\nu)^{1/2}$$

At $\gamma = y(\omega/\nu)^{1/2} = 3.6$, $\mathbf{v}_y \sim 0.8U_0$

$\rightarrow y_h = 3.6(\nu/\omega)^{1/2}$, hydrodynamic boundary layer thickness

$\rightarrow$ thickness of the layer of liquid dragged by the rotating disk

For water,

$y_h = 0.036$ cm for $\omega = 100\ s^{-1}$(= $2\pi f$, f ~ 1000 rpm)

3.6×10^{-3} cm for $\omega = 10^4\ s^{-1}$

Solution of the convective-diffusion equation

<u>For limiting current region</u> ($C_O(y = 0) \sim 0$) for steady-state limiting current
(cf. no convection at planar: i decays to zero, convection: i to steady-state)
$\rightarrow \partial C_O/\partial t = 0$

$$v_r(\partial C_O/\partial r) + (v_\phi/r)(\partial C_O/\partial \phi) + v_y(\partial C_O/\partial y) = D_O[\partial^2 C_O/\partial y^2 + \partial^2 C_O/\partial r_2 + (1/r)\partial C_O/\partial r + (1/r^2)(\partial^2 C_O/\partial \phi^2)]$$

At $y = 0$, $C_O = 0$, $C_O\ (y \rightarrow \infty) = C_O^*$

Cylindrical symmetry $\rightarrow \partial C_O/\partial \phi = (\partial^2 C_O/\partial \phi^2) = 0$ (C_O is not a ftn of ϕ)
$\mathbf{v}_y$ does not depend on r & at $y = 0$, $(\partial C_O/\partial r) = 0$
$0 \leq r \leq r_1$ (r_1: electrode radius), $(\partial C_O/\partial r) = 0$ for all y

$$v_y(\partial C_O/\partial y) = D_O \partial^2 C_O/\partial y^2$$

or

$$\partial^2 C_O/\partial y^2 = (-y^2/B)(\partial C_O/\partial y), \qquad B = D_O \omega^{-3/2} \nu^{1/2}/0.51$$

$$\rightarrow \quad \partial C_O/\partial y = (\partial C_O/\partial y)_{y=0} \int \exp(-y^3/3B)dy$$

Integrating from 0 to C_O^*,

$$C_O^* = (\partial C_O/\partial y)_{y=0}\ 0.8934(3D_O \omega^{-3/2} \nu^{1/2}/0.51)^{-1/3}$$

Current is the flux at the electrode surface

$$i = nFAD_O(\partial C_O/\partial y)_{y=0}$$

Limiting current

$$i_{l,c} = 0.62nFAD_O^{2/3}\omega^{1/2}\nu^{-1/6}C_O^* \qquad \text{Levich equation}$$

→ totally mass transfer limited condition at RDE, $i_{l,c}$: ftn of $\omega^{1/2}$ & C_O^*

Levich constant: $i_{l,c}/\omega^{1/2}C_O^*$

Current is the flux at the electrode surface

$$i_{l,c} = nFAm_OC_O^* = nFA(D_O/\delta_O)C_O^*$$

For RDE

$$m_O = D_O/\delta_O = 0.62D_O^{2/3}\omega^{1/2}\nu^{-1/6}$$

$$\delta_O = 1.61D_O^{1/3}\omega^{-1/2}\nu^{1/6}$$

Concentration profile

Concentration profile for the limiting-current condition

Integrating between 0 to $C_O(y)$

$$\int dC_O = C_O(y) = (\partial C_O/\partial y)_{y=0}\int \exp(-y^3/3B)dy$$

$$(\partial C_O/\partial y)_{y=0} = C_O^*/0.8934(3B)^{-1/3}$$

$$C_O(y) = (C_O^*/0.8934)\int \exp(-u^3)du$$

Where $u^3 = y^3/3B$, $Y = y/(3B)^{1/3}$

i-E curves at the RDE

For nonlimiting-current condition

$$C_O^* - C_O(y) = (\partial C_O/\partial y)_{y=0} \int \exp(-y^3/3B)dy$$

Current

$$i = 0.62nFAD_O^{2/3}\omega^{1/2}\nu^{-1/6}[C_O^* - C_O(y = 0)]$$

$$i = i_{l,c}[(C_O^* - C_O(y = 0))/C_O^*]$$

$$i = nFAD_O[C_O^* - C_O(y = 0)]/\delta_O = nFAm_O[C_O^* - C_O(y = 0)]$$

O + ne = R, reduced form

$$i = i_{l,a}[(C_R^* - C_R(y = 0))/C_R^*]$$

Where $$i_{l,a} = -0.62nFAD_R^{2/3}\omega^{1/2}\nu^{-1/6}C_R^*$$

For a nerstian reaction

$$E = E_{1/2} + (RT/nF)\ln(i_{l,c} - i)/(i - i_{l,a})$$

Wave shape for a reversible reaction: independent of ω

Deviation of i vs. $\omega^{1/2}$: kinetic limitation in e-transfer rxn

Totally irreversible one-step, one-electron rxn

$$i = FAk_f(E)C_O(y=0)$$

Where $k_f(E) = k^0\exp[-\alpha f(E - E^{0'})]$

$$i = FAk_f(E)C_O^*(1 - i/i_{l,c})$$

Define $$i_K = FAk_f(E)C_O^*$$

$$1/i = 1/i_K + 1/i_{l,c} = 1/i_K + 1/0.62nFAD_O^{2/3}\omega^{1/2}\nu^{-1/6}C_O^*$$ Koutecky-Levich equation

i_K: current in the absence of any mass-transfer effects → kinetic limitation under efficient mass transfer

$i/\omega^{1/2}C$: constant when i_K (or $k_f(E)$) is very large

Otherwise, curve shape for $1/i$ vs. $\omega^{1/2}$ plot

→ $i = i_K$ as $\omega^{1/2} \rightarrow \infty$

Plot of $1/i$ vs. $\omega^{-1/2}$: linear, intercept of i_K: $\rightarrow$ i_K at different E gives k^0 & α

e.g., reduction of O_2 to HO_2^-

Experimental application of RDE

Lower limit of ω : hydrodynamic boundary layer ($y_h \sim 3(\nu/\omega)^{1/2}$) ~ disk radius r_1

$\rightarrow r_1 > 3(\nu/\omega)^{1/2} \rightarrow \omega > 10\ \nu/r_1^2$

e.g., $r_1 = 0.1$ cm, $\nu = 0.01$ cm^2/s, $\omega > 10\ s^{-1}$ (f ~100 rpm)

Upper limit of ω: onset of turbulent flow, $Re_{cr} > 2 \times 10^5$

$\rightarrow \omega < 2 \times 10^5 \nu/r_1^2$, $\omega < 2 \times 10^5\ s^{-1}$

Maximum rotation rate (due to not perfect flat disk electrode): $\omega \sim 1000\ s^{-1}$ or 10,000 rpm

Experimental RDE: $10\ s^{-1} < \omega < 1000\ s^{-1}$, 100 rpm < f < 10,000 rpm

Rotating ring & ring-disk electrode (RRDE)

Rotating ring disk electrode: reversal technique

Disk: O + ne → R, ring: R → O + ne

Rotating ring electrode (disk is disconnected): mass transfer to a ring electrode is larger than to a disk at a same A and ω

(because flow of fresh solution occurs radially from the area inside the ring, as well as normally from the bulk solution)

Rotating ring electrode

Inner radius: r_2

Outer radius: r_3 [$A_r = \pi(r_3^2 - r_2^2)$]

Angular velocity ω

Steady-state convective-diffusion equation

$$v_r(\partial C_O/\partial r) + v_y(\partial C_O/\partial y) = D_O(\partial^2 C_O/\partial y^2)$$

Boundary condition for the limiting ring current

$C_O = C_O^*$ for $y \rightarrow \infty$

$C_O = 0$ at $y = 0$ for $r_3 > r \geq r_2$

$\partial C_O/\partial y = 0$ at $y = 0$ for $r < r_2$

Limiting ring current

$$i_{R,l,c} = 0.62nF\pi(r_3^3 - r_2^3)^{2/3} D_O^{2/3} \omega^{1/2} \nu^{-1/6} C_O^*$$

Or, in general

$$i_R = i_{R,l,c}\{[C_O^* - C_O(y = 0)]/C_O^*\}$$

RRE vs. RDE

$$i_R = i_D[(r_3^3 - r_2^3)^{2/3}/r_1^2]$$

or

$$i_R/i_D = \beta^{2/3} = (r_3^3/r_1^3 - r_2^3/r_1^3)^{2/3}$$

A ring electrode produces a large current than a disk electrode of the same area

(+) better sensitivity

(-) difficult to construct a RRE

Rotating Ring-Disk Electrode (RRDE)

Disk: no influence by ring (same as RDE)

RRDE: two potentials (E_D & E_R) & two currents (i_D & i_R)

→ separately adjust E_D and E_R with a *bipotentiostat*: (a)

However, ordinary potentiostat can be used: (b)

Different experiments at the RRDE

(a) Collection experiments

<u>The disk generated species is observed at the ring</u>

Disk: potential E_D → produce cathodic current i_D for O + ne → R

Ring: sufficient positive potential E_R for R → O + ne, the surface concentration of R becomes zero at the ring surface → i_R?

Steady-state convectve-diffusion equation

$$r(\partial C_R/\partial r) - y(\partial C_R/\partial y) = (D_R/B')(1/y)(\partial^2 C_R/\partial y^2)$$

$B' = 0.51\omega^{3/2}\nu^{-1/2}$

Boundary conditions

At the disk ($0 \leq r < r_1$), $D_R(\partial C_R/\partial y)_{y=0} = -D_O(\partial C_O/\partial y)_{y=0}$

$$(\partial C_R/\partial y)_{y=0} = - i_D/nFAD_R = - iD/nF\pi r_1{}^2 D_R$$

In the insulating gap ($r_1 \leq r < r_2$), no current flows, $(\partial C_R/\partial y)_{y=0} = 0$

At the ring ($r_2 \leq r < r_3$), under limiting conditions, $C_R(y=0) = 0$

R is initially absent: $C_R = 0$ as $y \rightarrow \infty$

Ring current

$$i_R = nFD_R 2\pi\int \; (\partial C_R/\partial y)_{y=0}\, rdr$$

Collection efficiency, N

$$N = -i_R/i_D$$

N: depends on r_1, r_2, r_3. independent of ω, $C_O{}^*$, D_O, D_R

$$N = 1 - F(\alpha/\beta) + \beta^{2/3}[1 - F(\alpha)] - (1 + \alpha + \beta)^{2/3}\{1 - F[(\alpha/\beta)(1 + \alpha + \beta)]\}$$

where $\alpha = (r_2/r_1)^3 - 1$, and $\beta = r_3^3/r_1^3 - r_2^3/r_1^3$

$$F(\Theta) = (\sqrt{3}/4\pi)\ln\{(1 + \Theta^{1/3})^3/(1 + \Theta)\} + 3/2\pi \arctan[(2\Theta^{1/3} - 1)/3^{1/2}] + 1/4$$

If $N = 0.555 \rightarrow$ 55.5% of the product generated at the disk is collected at the ring

N becomes larger as the gap distance $(r_2 - r_1)$ decreases and as ring size $(r_3 - r_2)$ increases.

Concentration profile of R

At the disk $(0 \leq r < r_1)$, $\partial C_R/\partial r = 0$

In the gap $(r_1 \leq r < r_2)$, $(\partial C_R/\partial y)_{y=0} = 0$

At the ring $(r_2 \leq r < r_3)$, $C_R(y=0) = 0$

$C_R = 0$ as $y \rightarrow \infty$

Collection experiment

1. i_D vs. E_D
2. i_R vs E_D with $E_R = E_1$ (const)

Shielding experiment

3. i_R vs. E_R, $i_D = 0$ ($E_D = E_1$)
4. i_R vs E_R
   with $i_D = i_{D,l,c}$ ($E_D = E_2$)

(b) Shielding experiment

The flow of bulk electroactive species to the ring is perturbed because of the disk rxn (when both ring and disk are in same potential for the reduction of O, some of O reaching to the ring decreases due to the shielding by the disk)

Limiting current at the ring with $i_D = 0$ (disk is open circuit) = RRE

$$i^0_{R,l} = \beta^{2/3} i_{D,l}$$

Disk current changes to finite i_D value → flux of O to the ring is decreased
(decreased amount = flux of R = Ni_D)

$$i_{R,l} = i^0_{R,l} - Ni_D$$

for $i_D = i_{D,l}$

$$i_{R,l} = i^0_{R,l}(1 - N\beta^{-2/3})$$

→ "shielding factor" < 1