Mass Transfer and Product-Selectivity in Electroreduction of *p*-Methylbenzaldehyde

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Synopsis. Mass transfer coefficients estimated from the formation ratio of the hydrodimeric to hydromonomeric products in electroreduction of *p*-methylbenzaldehyde in parallel plate electrode–flow cell and rotating cylinder electrode–beaker cell systems were shown in good agreement (less than 8% difference) with those obtained by ordinary current–potential and concentration–time methods.

Electroreduction of carbonyl compounds yields the corresponding hydrodimers and hydromonomers. In 1960's, Udupa and co-workers[1)] found that the formation ratio of the hydrodimers to hydromonomers at a rotating electrode was larger than that at a stationary electrode. This means that mass transfer plays an important role in controlling product-selectivity in electroorganic synthesis, and it is interesting to describe such behavior by a mathematical model. In previous work,[2)] we developed a mathematical reaction model for the electroreductionof *p*-methylbenzaldehyde to the hydrodimer [1,2-bis(*p*-methylphenyl)-1,2-ethanediol] and the hydromonomer (*p*-methylbenzyl alcohol) at a rotating cylinder cathode in an acidic solution, and showed that the product-selectivity (formation ratio of the former to the latter product) is predictable if substrate concentration, current density and mass-transfer coefficient are known. Using the mass transfer coefficients obtained from polarization curves, the values of product-selectivity were estimated and found to be in good agreement with the experimental ones.

Inversely, it is also expected that mass transfer coefficient can be obtained from product-selectivity as described below.

Although a rotating electrode system is conveniently used for a small scale operation and one can control precisely mass transfer to and from electrode surface in this system, a flow cell system is much more practical in view of industrization.[1)] In this work, a modification of the above mathematical method devloped for a rotating electrode–beaker cell system was made to be applied to a parallel plate electrode-flow cell one.

Experimental

A parallel plate flow cell (Micro Flow cell, ElectroCell AB, Sweden) was equipped with a Pb plate cathode (3.2×3.2 cm) and a so-called USA anode with a similar dimension. The catholyte of 0.25 mol dm^{-3} H_2SO_4/50% v/v ethanol containing *p*-methylbenzaldehyde (0.08 mol dm^{-3}) was separated from the anolyte by a cationic membrane (Ionac MC-3470, Sybron Chemicals Inc., USA). The electrolytes were circulated with tubing pumps (Masterflex RA-71, Cole-Pamer, USA). Pre-electrolysis without *p*-methylbenzaldehyde was carried out for ca. 15 min before the preparative electrolysis. All the electrolyses were operated at 25±2 °C.

An electrolytic cell equipped with a rotating cylinder Pb cathode is described in the previous paper.[2)] The products were routinely analyzed with HPLC.

Results and Discussion

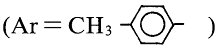
A Rotating Cylinder Electrode–Beaker Cell System. The reaction mechanism for electroreduction of *p*-methylbenzaldehyde in an acidic solution is proposed as follows:[2)]

$$\mathrm{ArCHO} \overset{H^+}{\rightleftharpoons} \mathrm{Ar\overset{+}{C}H(OH)} \qquad \text{(I)}$$

$$\mathrm{Ar\overset{+}{C}H(OH)} \xrightarrow{e} \mathrm{Ar\dot{C}H(OH)} \qquad \text{(II)}$$

$$\mathrm{Ar\dot{C}H(OH)} \longrightarrow \frac{1}{2}\,\mathrm{Ar\underset{OH}{C}H{-}\underset{OH}{C}HAr} \qquad \text{(III)}$$

$$\mathrm{Ar\dot{C}H(OH)} \xrightarrow{e\,+\,H^+} \mathrm{ArCH_2OH} \qquad \text{(IV)}$$


(Ar = CH_3- -)

The limiting current density (i_L) for the primary electron-transfer reaction (Eq. II), which yields the radical intermediate, is defined by

$$i_L = k_m F C, \qquad (1)$$

where k_m and C are mass transfer coefficient and bulk concentration of substrate, respectively, and F is the Faraday constant.

Under galvanostatic operation, the product-selectivity for a batch electrolysis at a rotating cylinder electrode is written according to whether current density (i) at the beginning of electrolysis is larger than i_L or not.[2)]

$i_L \geqslant i$ at t=0: Let t_0 be the time required to decrease i_L to i, then one has

$$C_0 = i/k_m F, \qquad (2)$$

$$t_0 = VF(C_i - C_0)/iA, \qquad (3)$$

where C_i and C_0 are the concentrations of substrate at t=0 and t=t_0, respectively, A is electrode area, and V is the volume of electrolyte.

The product-selectivity (ζ), defined as the formation ratio of hydrodimer (HD) to hydromonomer (HM), is then written as

$$\zeta = \frac{[\mathrm{HD}]}{[\mathrm{HM}]} = \frac{iA(2t_0 - t)/2VF + \{1 - \exp[-k_m A(t - t_0)/V]\}C_0}{iA(t - t_0)/VF - \{1 - \exp[-k_m A(t - t_0)/V]\}C_0} \qquad (4)$$

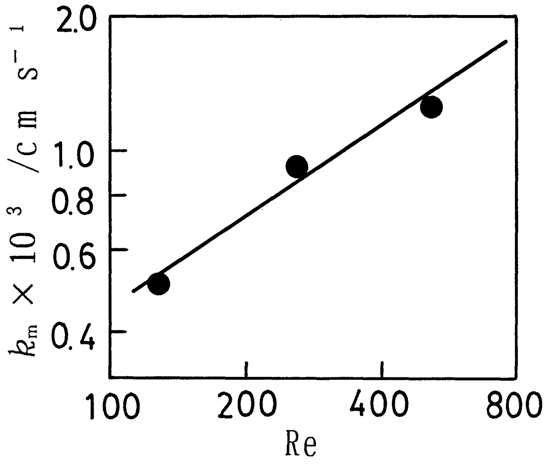


Fig. 1. Mass-Transfer coefficients (k_m) obtained by mathematical analysis of product-selectivity in a rotating cylinder electrode–beaker cell system. $Re = du_r/\nu$. Straight line: calculated from polarization curves. Plot: Experimentally obtained.

where [HD] and [HM] are the concentrations of HD and HM, respectively.[2]

$i_L < i$ at $t=0$: Substituting t_0 and C_0 with 0 and C_i, respectively, ζ can be calculated by Eq. 4.

If C_i, i and ζ are known, we can obtain k_m from Eq. 4 by Newton's method. Figure 1 shows the k_m values calculated at a rotating cylinder electrode using the data in the previous paper.[2] The sraight line in Fig. 1 is derived from polarization curves (Eq. 1), and it is noticeable that the k_m's obtained by both methods agree with each other. The relationship between k_m and Reynolds number (Re) can be expressed by Eq. 5.

$$k_m = 2.2 \times 10^{-5}\, Re^{0.66} \ (\text{cm s}^{-1}), \tag{5}$$

where $Re = du_r/\nu$, u_r is the peripheral velocity, $\nu = 0.0253$ cm^2 s^{-1} is the kinematic viscosity,[4] and $d = 0.50$ cm is the cylinder diameter. The slope in Fig. 1 is 0.66, and the characteristic value for a rotating cylinder electrode is between 0.61 and 0.70 for $100 < Re < 160000$.[5-7] It must be emphasized here that the mathematical analysis of mass transfer in a rotating cylinder electrode system has not been reported for electroorganic reaction so far as we know.

A Parallel Plate Electrode–Flow Cell System. $i_L \geq i$ at $t=0$: The concentration in the catholyte reservoir (C, i.e. the concentration at the entrance of the cell) decreases with t in the following way:

$$C = C_i - iAt/VF \qquad \text{when } t \leq t_0, \tag{6}$$

$$C = C_0 \exp\left[-p(t-t_0)\right] \qquad \text{when } t > t_0, \tag{7}$$

where

$$p = [1 - \exp(-k_m A/Q)]Q/V,$$

and Q is the volumetric flow rate. Then Eq. 8 is derived by mathematical analysis similar to that in a rotating electrode system.

$$\zeta = \frac{iA(2t_0 - t)/2VF + k_m A C_0\{1 - \exp[-p(t-t_0)]\}/pV}{iA(t-t_0)/VF - k_m A C_0\{1 - \exp[-p(t-t_0)]\}/pV}. \tag{8}$$

$i_L < i$ at $t=0$: Substituting t_0 and C_0 with 0 and C_i, respectively, ζ is given by Eq. 8.

Table 1 shows the experimental values of product-selectivity (ζ) obtained in the galvanostatic electrolysis of *p*-methylbenzaldehyde using the flow cell. Here a dimensionless parameter (q) is used instead of t. $q=1$ means that the charge passed for 1 mol of substrate is 96485 coulombs. The relation between q and t is given by

$$t = qVFC_i/iA. \tag{9}$$

As expected from Eq. 8, ζ decreases with an increase in t (i.e. q). On the other hand, ζ increases with an increase in k_m and the effect of Q is attributed to this. However, the correlation between k_m and Q (or Re) for the flow cell used is unknown, hence a numerical method similar to that in a rotating electrode system was used to calculate k_m's and their calculated values were also shown in Table 1. Then the following correlation is established:

Table 1. Product-Selectivity ζ (Hydrodimer/Hydromonomer) for the Reaction of *p*-Methylbenzaldehyde (Initial Concentration: 0.08 mol dm^{-3}) in a Parallel Plate Electrode–Flow Cell System and k_m Calculated by Newton's Method. $q = iAt/VFC_i$

Q/cm^3 min^{-1}	i/mA cm^{-2}	q	Exptl ζ	Calcd k_m/cm s^{-1}
150	8.0	0.2	1.06	0.000851
150	8.0	0.3	0.885	0.000860
150	8.0	0.4	0.739	0.000869
200	10.0	0.4	0.660	0.00106
250	12.0	0.2	1.05	0.00128
250	12.0	0.3	0.904	0.00130
250	12.0	0.4	0.774	0.00132
300	8.0	0.4	13.30	0.00138
300	10.0	0.4	3.40	0.00144
400	12.0	0.2	6.10	0.00160
400	12.0	0.3	4.33	0.00165
400	12.0	0.4	3.14	0.00170

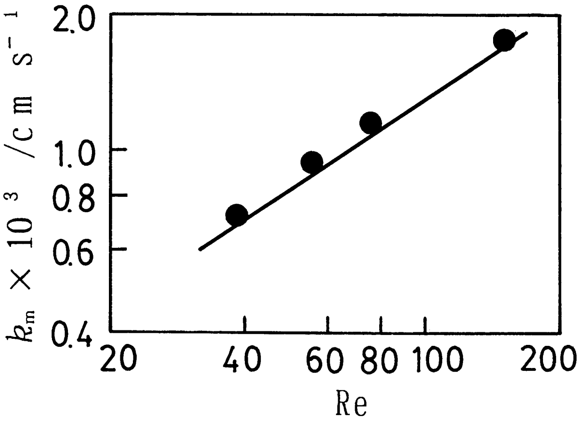


Fig. 2. Mass-Transfer coefficients (k_m) in a parallel plate electrode–flow cell system. $Re=d_eu/\nu$. Straight line: Eq. 10. Plot: Obtained from Eq. 7.

$$k_m = 5.84 \times 10^{-5}\, Re^{0.67}\ (\text{cm s}^{-1}), \qquad (10)$$

where $Re=d_eu/\nu$, u is the linear velocity, and d_e=0.58 cm is the equivalent diameter of the flow cell.

The validity of Eq. 10 must be examined by comparing with other methods based on different principles. In stead of the information of mass transport from polarization curves (Eq. 1), Eq. 7 was used for this purpose.[8] From the relation of C and t, k_m was derived. The straight line in Fig. 2 comes from Eq. 10. Although k_m's calculated from Eq. 7 are somewhat larger than those of Eq. 10, the difference (4—8%) between them is rather small. Accordingly, the application of this mathematical reaction model to the electroreduction of *p*-methylbenzaldehyde is proven reasonable in the flow cell system.

However, flow in a range of $Re<1000$ is expected to be laminar. The experimental k_m's are larger than those of a correlation for laminar flow,[9] and the power in Eq. 10 indicates that the flow under our operating conditions is in a transition state from laminar flow to turbulent flow. It must be considered that the entrance effect introduces a measure of uncertainty into the prediction of mass-transfer rates in this type of electrolysis system.[10]

From the above discussion we conclude that the product-selectivity is itself an index of mass transport in some electrolytic systems, and mass-transfer coefficients can be estimated theoretically and experimentally in pratical parallel plate flow cell systems as well as in rotating electrode systems used for laboratory study. Furthermore, it is suggested that theoretical prediction of product-selectivity is possible by means of appropriate cell design.

References

1) H. V. K. Udupa, G. S. Subramanian, K. S. Udupa, and K. Katarajan, *Electrochim. Acta,* **9**, 313 (1964).
2) P.-C. Cheng, T. Nonaka, and T.-C. Chou, *Bull. Chem. Soc. Jpn.,* **64**, 1911 (1991).
3) For example: D. E. Danly, *Chem. Ind.* (*London*), **1979**, 439.
4) A. E. Dustan and F. B. Thole, *J. Chem. Soc.,* **95**, 1556 (1909).
5) M. Eisenberg, C. W. Tobias, and C. R. Wilke, *J. Electrochem. Soc.,* **101**, 306 (1954).
6) N. R. K. Vilambi and D.-T. Chin, *J. Electrochem. Soc.,* **134**, 2501 (1987).
7) M. K. Kishinevskii and T. S. Kornienko, *Soviet Electrochem.,* **25**, 737 (1989).
8) R. M. Spotnitz, R. F. Kreh, J. T. Lundquist, and P. T. Press, *J. Appl. Electrochem.,* **20**, 209 (1990).
9) D. J. Pickett and B. R. Stanmore, *J. Appl. Electrochem.,* **2**, 151 (1972).
10) J. M. T. Clark, F. Goodridge, and R. E. Plimley, *J. Appl. Electrochem.,* **18**, 899 (1988).