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Prediction of Product-Selectivity in an Electroorganic Process by Mathematical Modeling of Reaction Mechanism. A Rotating Cylinder Electrode System

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A mathematical mechanism model is developed for the electroreduction of carbonyl compounds in an acidic solution and shows that the formation ratio of hydrodimeric to hydromonomeric products, i.e. the product-selectivity, depends on substrate concentration, mass transfer coefficient and current density. Model calculations are in agreement with experimental results from the electroreduction of *p*-methylbenzaldehyde using a rotating cylinder cathode and explain a drastic effect of mass transport on the product-selectivity.

Product-selectivity control has been a significant subject in electroorganic synthesis. Saveant and coworkers[1–8] extensively studied modes of product distribution in preparative scale electrolysis from a theoretical aspect, but only few experimetal approaches were insufficiently made.[4–6] Wendt[9] also suggested an importance of mass transport in the product distribution of electroorganic processes with few experimental data. On the other hand, some other workers[10–13] reported experimental results that product-selectivity and/or yield were influenced by mass transport, without any theoretical considerations. For purposively designing practical electroorganic processes on the basis of prediction of product-selectivity, it is recommended that studies are harmoniously made from both theoretical and experimental aspects.

Recently we also reported that the ratio of hydrodimeric to hydromonomeric products in the electroreduction of carbonyl compounds, e.g. benzaldehyde and acetophenone, could be varied drastically by controlling mass transport conditions, such as substrate concentration, flow rate in a parallel plate flow cell and rotating speed of a rotating cylinder electrode.[14] Thus, it is aimed in this work to evaluate the product-selectivity by mathematical modeling and demonstrate how the product-selectivity can be controlled.

However, considerable hydrogen evolution[15] and formation of hydroquinonoid-dimers[16–18] in the reduction of acetophenone and benzaldehyde, respectively, might make very difficult the mathematical analysis of reaction model. In this work, therefore, *p*-methylbenzaldehyde was used as a starting compound which has an adequately low reduction potential and is blocked by a methyl group at the *p*-position to be prevented from the formation of the hydroquinonoid-type dimers.[16] In fact, using *p*-methylbenzaldehyde, current efficiencies and material balances are high enough (>90%) for mathematical analysis.

In general, mass transport conditions can be controlled using either a rotating electrode batch cell or a parallel plate flow cell. Although the availability of the latter for industrial processes, of course, is much greater than the former, in this work the former was preferably used because of easier and more accurate mathematical treatment of mass transport phenomena. Furthermore, because quantitative analysis of products was required in this work, a rotating cylinder electrode with a large area was chosen instead of a rotating disc one used commonly for voltammetric studies.

Experimental

Materials. The method of Grimshaw and Ramsey[19] was employed for preparation of the hydrodimer samples: *dl*-(mp 159—160 °C, from ethanol–water) and *meso*-1,2-bis(*p*-methylphenyl)-1,2-ethanediol(mp 143—144 °C, from benzene). All other reagents used were analytical GR grade without further purification.

Electrolytic Cell. The cathode was a Pb solid cylinder, 5 cm in length and 0.5 cm in diameter. The cylindrical Pb sheet anode, 6.5 cm in depth and 5.6 cm in diameter, was separated from the cathode by a ceramic diaphragm in a beaker type batch cell. The rotating cathode was rotated at 250 to 1500 rpm by a variable speed motor (Yanagimoto RP-3).

Procedure. The electrolyte was 0.25 M H_2SO_4 solution containing 50% v/v ethanol, unless stated otherwise. A saturated calomel electrode was used as reference electrode and the electrolyte was deaerated with nitrogen prior to the measurement of polarization curves. For preparative electrolysis, pre-electrolysis was carried out for ca. 15 min. All the electrolyses were carried out at 25±2 °C. Throughout this paper 1 M=1 mol dm^{-3}.

Analysis. The products were routinely analysed using HPLC. The mobile phase was a mixture of acetonitrile and 0.1% aqueous phosphoric acid with a volume ratio of 30:70. The column was a Utron S-C 18 reversed-phase column (Chromato Packings Center) and peaks for the products were detected by UV absorbance at 254 nm.

Results and Discussion

The reaction mechanism for the electroreduction of aromatic carbonyl compounds depends on pH, and the generally accepted scheme in acidic media is as follows:[20]

$$\mathrm{ArCOR + H^+ \rightleftarrows Ar\overset{+}{C}(OH)R} \qquad \text{(I)}$$

$$Ar\overset{+}{C}(OH)R + e \xrightarrow{k_1} Ar\dot{C}(OH)R \qquad \text{(II)}$$

$$Ar\dot{C}(OH)R + e \xrightarrow{k_2} Ar\bar{C}(OH)R \qquad \text{(III)}$$

$$Ar\bar{C}(OH)R + H^+ \xrightarrow{\text{fast}} ArCH(OH)R \qquad \text{(IV)}$$

$$2Ar\dot{C}(OH)R \xrightarrow{k_D} ArRC(OH)C(OH)RAr \qquad \text{(V)}$$

In order to theoretically calculate the product-selectivity, a general relationship between k_2 and k_D must be mathematically written. Thus, it is our first goal to obtain Eq. 21 along with Eqs. 10 and 22. At the second stage, for a special case Eq. 27 is obtained along with Eqs. 31 and 32.

Let X_b and X_s represent substrate X in bulk solution and at electrode surface, respectively. Thus, the mass-transfer process of ArCOR(S) and $Ar\overset{+}{C}(OH)R(S^*)$ from bulk solution to electrode surface can be expressed as follows:

$$S_b \xrightarrow{k_m} S_s \qquad \text{(VI)}$$

$$H^+{}_b \rightleftarrows H^+{}_s \qquad \text{(VII)}$$

$$S_s + H^+{}_s \overset{K_s}{\rightleftarrows} S^*{}_s \qquad \text{(VIII)}$$

$$S_b + H^+{}_b \overset{K_b}{\rightleftarrows} S^*{}_b \qquad \text{(IX)}$$

$$S^*{}_b \xrightarrow{k_m^*} S^*{}_s \qquad \text{(X)}$$

Recognizing that reactions VIII and IX are essentially at equilibrium, we can write

$$[S^*{}_b] = K_b[S_b][H^+{}_b], \qquad (1)$$

$$[S^*{}_s] = K_s[S_s][H^+{}_s], \qquad (2)$$

where K_b and K_s are the equilibrium constants between ArCOR(S) and $Ar\overset{+}{C}(OH)R(S^*)$ in bulk solution and at electrode surface, respectively. In strong acidic solution, $[H^+{}_s]$ and $[H^+{}_b]$ are assumed to be constant.

The steady-state material balance for S and S* is given by

$$k_1[S^*{}_s] = k_m([S_b]-[S_s]) + k_m^*([S^*{}_b]-[S^*{}_s]) = i_1/F, \qquad (3)$$

where k_m and k_m^* are the mass transfer coefficients of S and S*, respectively, k_1 is the rate constant for the formation of radical $Ar\dot{C}(OH)R$ (R_s), i_1 is the partial current density for the primary electron-transfer reaction (Eq. II), and F is the Faraday constant.

Suppose that k_m is equal to k_m^*, Eq. 3 becomes

$$k_1^*[C_s] = k_m([C_b]-[C_s]) = i_1/F \qquad (4)$$

where

$$[C_b] = [S_b] + [S^*{}_b],$$

$$[C_s] = [S_s] + [S^*{}_s],$$

$$k_1^* = k_1K_s[H^+{}_s]/(1+K_s[H^+{}_s]) = k^0{}_1 \exp(-b_1E).$$

b_1 and $k^0{}_1$ are the characteristic constants on the assumption of Tafel relationship, and E is electrode potential. It should be noted that $[C_b]$, substrate concentration before protonation, is readily measurable rather than $[S^*{}_b]$.

The radical(R) formed in the primary electron-transfer reaction then undergoes the second electron-transfer reaction (Eq. III) to form the hydromonomer ArCH(OH)R(HM) or is dimerized (Eq. V) to give the hydrodimer ArRC(OH)C(OH)RAr(HD).

$$V\mathrm{d}[HM]/A\mathrm{d}t = k_2[R_s] = i_2/F, \qquad (5)$$

$$k_2 = k^0{}_2 \exp(-b_2E), \qquad (6)$$

$$2V\mathrm{d}[HD]/A\mathrm{d}t = -D_R(\mathrm{d}[R]/\mathrm{d}x)_{x=0}, \qquad (7)$$

$$D_R(\mathrm{d}^2[R]/\mathrm{d}^2x) - v_x(\mathrm{d}[R]/\mathrm{d}x) - k_D[R]^2 = 0, \qquad (8\text{-a})$$

$$[R] = [R_s] \quad \text{at } x=0, \qquad (8\text{-b})$$

$$[R] = 0 \quad \text{as } x \to \infty, \qquad (8\text{-c})$$

where i_2 and k_2 are the partial current density and the rate constant for the second electron transfer reaction, respectively, k_D is the rate constant for the dimerization step, A is the cathode area, V is the volume of catholyte, D_R is diffusion coefficient of R, x is the distance from electrode, and v_x is the x-component of the fluid velocity vector.

Let us neglect the second term in Eq. 8-a, then we obtain Eq. 9 after satisfying the boundary conditions.[21]

$$[R] = \frac{6D_R/k_D}{(\sqrt{6D_R/(k_D[R_s])}+x)^2}. \qquad (9)$$

Substituting Eq. 9 into Eq. 7, one finds

$$2V\mathrm{d}[HD]/A\mathrm{d}t = k_3[R_s]^{3/2}, \qquad (10)$$

where

$$k_3 = (2k_DD_R/3)^{1/2}.$$

Since hydrogen evolution and other side reactions are negligible, we can write

$$i = i_1 + i_2, \qquad (11)$$

$$k_1^*[C_s] = k_2[R_s] + k_3[R_s]^{3/2}, \qquad (12)$$

where i is the total current density of electrolysis.

From these equations a simulation for predicting the product-selectivity may be accomplished if all the rate constants are available. The product-selectivity (ζ) is herein defined by

$$\zeta = \mathrm{d}[HD]/\mathrm{d}[HM] = k_3[R_s]^{1/2}/2k_2. \qquad (13)$$

The Determination of $k^0{}_1$ and b_1. Equation 4 can be rearranged as

$$i_1 = k_1^*k_m[C_b]F/(k_m+k_1^*), \qquad (14)$$

or

$$1/i_k = 1/i_1 - 1/i_L,$$

where the limiting current density (i_L) and kinetic current density (i_k) are defined as

$$i_L = k_m[C_b]F, \qquad (15)$$

$$i_k = k^0{}_1 \exp(-b_1E)[C_b]F, \qquad (16)$$

or

$$\ln(i_k) = \ln(k^0{}_1[C_b]F) - b_1E.$$

Potentiostatic electrolysis of *p*-methylbenzaldehyde at a potential where $i<i_L$, the hydromonomer (HM) is not found and the hydrodimer is a sole product, i.e. $i \fallingdotseq i_1$. Using experimental data from polarization curves (Fig. 1), i_k can be calculated from Eq. 14. A plot of Eq. 16 is presented in Fig. 2. The slope gives a value for b_1 of 26 V^{-1} and the intercept leads to a value for $k^0{}_1$ of 5.4×10^{-14} cm s^{-1}.

Values of $k^0{}_2$, b_2 and k_3. When the total current density is larger than i_L, i_1, and i_2 can be expressed as

$$i_1 = k_1{}^*[C_s]F \fallingdotseq i_L, \qquad (17)$$

$$i_2 \fallingdotseq i - i_L, \qquad (18)$$

Substitution of Eq. 18 into Eq. 5 gives

$$k_2[R_s] = (i - i_L)/F. \qquad (19)$$

Then from Eqs. 17, 19, and 12 we obtain

$$k_3[R_s]^{3/2} = (2i_L - i)/F. \qquad (20)$$

Combination of Eqs. 19 and 20 leads to

$$z = k_2{}^3/k_3{}^2 = (i - i_L)^3/F(2i_L - i)^2. \qquad (21)$$

From a plot of Eq. 22 (Fig. 3) b_2 is found to be 26 V^{-1} and $k^0{}_2$ can be determined from an intercept, provided k_D and D_R are known.

$$\ln(z) = \ln(k^0{}_2{}^3/k_3{}^2) - 3b_2E. \qquad (22)$$

However, any rate constant (k_D) for the dimerization in electroreduction of carbonyl compounds in acidic solutions has not been reported, while k_D in hydroxide solution is known to be in a range of 10^7—10^9 mol^{-1} s^{-1} cm^3.[21,22] Here, 10^8 mol^{-1} s^{-1} cm^3 is tentatively taken as k_D.

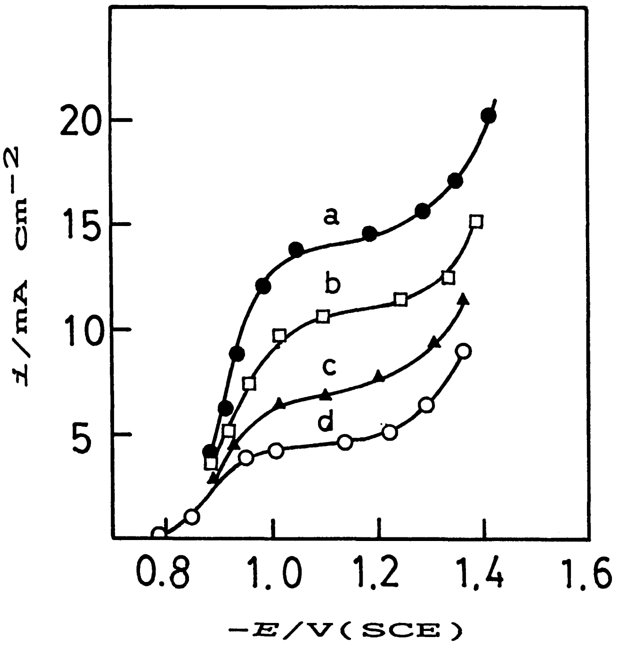

Fig. 1. Polarization curves for the reduction of *p*-methylbenzaldehyde (80 mM) at a rotating cylinder electrode in 0.25 M H_2SO_4/50% EtOH. Rotating speed, a: 1500, b: 1000, c: 500, d: 250 rpm.

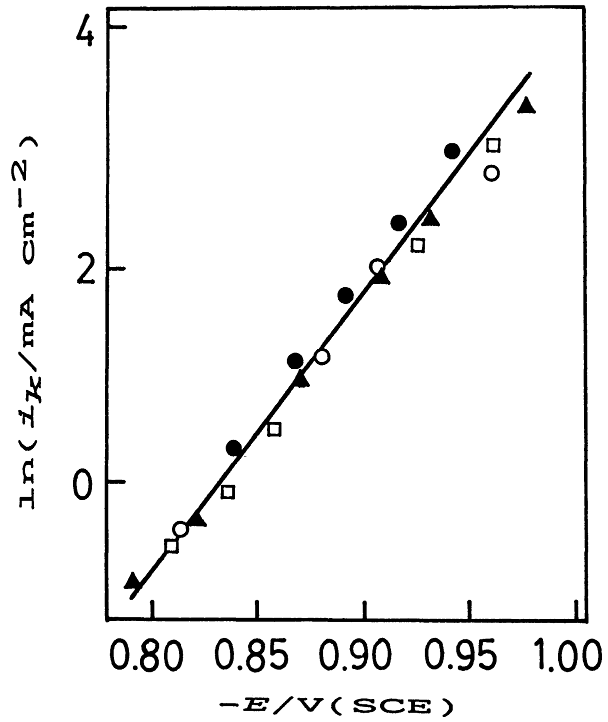

Fig. 2. The relation between i_k and E. Data from polarization curves at various rotating speed: 1500 (●), 1000 (□), 500 (△), and 250 rpm (○).

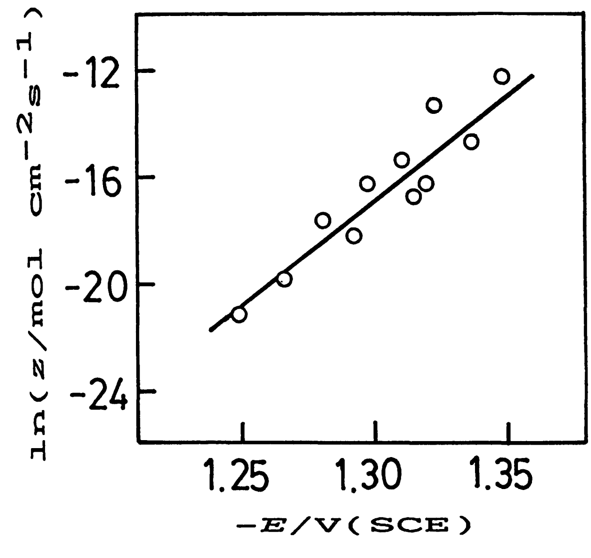

Fig. 3. The relation between $z(=k_2{}^3/k_3{}^2)$ and E. Data from polarization curves at 250 rpm.

Using Newton's method, E for a constant current operation can be solved for a set of k_m, $[C_b]$ and i, then ζ is calculated from Eqs. 4—13. Curve a in Fig. 4 shows the prediction of product-selectivity (ζ) for the galvanostatic reduction of *p*-methylbenzaldehyde at a rotating cylinder Pb electrode, using 10^{-3} cm s^{-1} as k_m, 80 mM as $[C_b]$, 10^{-5} cm^2 s^{-1} as D_R, 1.1×10^{-16} cm s^{-1} as $k^0{}_2$ and 10^8 mol^{-1} s^{-1} cm^3 as k_D. When either 10^7 or 10^9 mol^{-1}

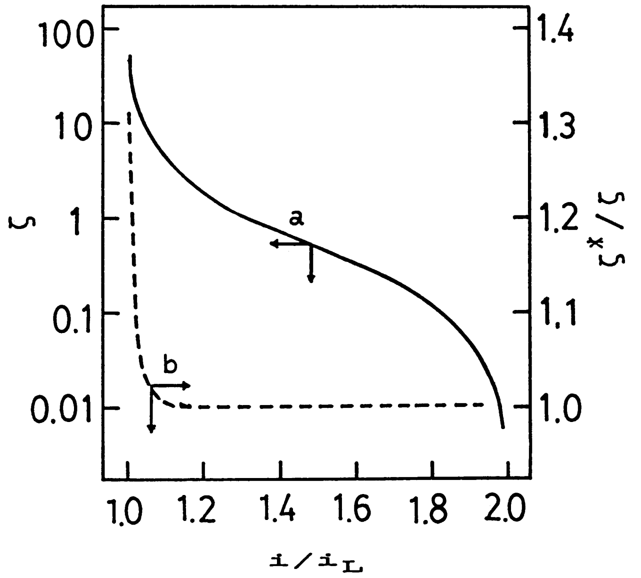

Fig. 4. Prediction of product-selectivity as a function of i/i_L. Curve a: Product-selectivity (ζ) calculated according to Eq. 4—13, using $k_1{}^0=5.4\times10^{-14}$ cm s^{-1}, $b_1=26$ V^{-1}, $k_2{}^0=1.1\times10^{-16}$ cm s^{-1}, $b_2=26$ V^{-1}, $k_D=10^8$ mol^{-1} s^{-1} cm^3, $D_R=10^{-5}$ cm^2 s^{-1}, $k_m=10^{-3}$ cm s^{-1}, $[C_b]=80$ mM. Curve b: Comparison between ζ and ζ^*.

s^{-1} cm^3 is taken as k_D, the difference of ζ from curve a is not regarded as significant for $i/i_L>1.04$.

Curve a suggests that the product-selectivity (ζ) can be drastically (ca. 10^4 times) changed by slightly (two times) varying the parameter i/i_L relating directly to mass transport. This should be noticeable from an aspect of product-selectivity control in synthetic electroorganic processes. However, an ambiguity might remain in calculation of curve a using k_D assumed. Therefore, another method, which is simpler and more convenient for predicting ζ, is developed to avoid this kind of problem. Two facts must be emphasized here: (1) When the total current density (i) is smaller than the limiting current density (i_L) of the primary electron-transfer reaction, the hydromonomer (HM) is not found and the the hydrodimer (HD) is the sole product. (2) When i exceeds the limiting current density ($2i_L$) for the two-electron reaction, the formation of HM and hydrogen evolution occur exclusively and HD is almost not formed. Hence, a mathematical evaluation for the product-selectivity is only necessary when i is between i_L and $2i_L$. In such a situation, i_1 is almost equal to i_L (Eq. 17) and Eqs. 19 and 20 are rewritten as follows:

$$V\mathrm{d}[\mathrm{HM}]/A\mathrm{d}t=i_2/F=(i-i_L)/F, \tag{23}$$

$$V\mathrm{d}[\mathrm{HD}]/A\mathrm{d}t=(2i_L-i)/2F. \tag{24}$$

Since i_L is a function of k_m and $[C_b]$ as presented by Eq. 15, the product-selectivity can be expressed as a function depending on the bulk concentration ($[C_b]$), total current density (i) and mass transfer coefficient (k_m),

$$\zeta^*=\mathrm{d}[\mathrm{HD}]/\mathrm{d}[\mathrm{HM}]=(2-i/i_L)/2(i/i_L-1)=f(k_m, [C_b], i). \tag{25}$$

Here ζ^* is used to distinguish from ζ, the product-selectivity calculated from Eq. 4—13. Curve b in Fig. 4 shows the comparison between ζ^* is and ζ. Although ζ^* is considerably larger than ζ when i/i_L is in the vicinity of unity, the difference is so small that ζ^* is almost equal to ζ when $i/i_L>1.1$. This implies that Eq. 25 can be used for predicting product-selectivity (ζ^*) in the electroreduction of carbonyl compounds, if k_m, $[C_b]$ and i are known.

For a batch electrolysis, $[C_b]$ and i_L decrease with the electrolysis time in the following ways.

$$-V\mathrm{d}[C_b]/A\mathrm{d}t=i/F \qquad \text{when } i_L>i, \tag{26-a}$$

$$-V\mathrm{d}[C_b]/A\mathrm{d}t=k_m[C_b]=i_L/F \qquad \text{when } i_L\leqq i. \tag{26-b}$$

Hence a relation between product-selectivity and time must be considered.

In stead of d[HD]/d[HM], the product-selectivity defined by Eq. 27 is used in the following discussion.

$$\zeta=[\mathrm{HD}]/[\mathrm{HM}]. \tag{27}$$

When $i_L>i$ at $t=0$: Let t_0 be the time that is required to decrease i_L to i, then we have

$$[C_{b,0}]=i/k_mF, \tag{28}$$

$$t_0=([C_{b,i}]-[C_{b,0}])VF/iA \tag{29}$$

where $[C_{b,i}]$ and $[C_{b,0}]$ are the substrate concentrations at $t=0$ and $t=t_0$, respectively.

Integration of Eq. 26-b gives

$$[C_b]=[C_{b,0}]\exp[-k_mA(t-t_0)/V]. \tag{30}$$

Then integration of Eq. 23 and 24, after substitution of Eq. 30 for $[C_b]$, yields:

$$[\mathrm{HM}]=iA(t-t_0)/VF-[C_{b,0}]\{1-\exp[-k_mA(t-t_0)/V]\}, \tag{31}$$

$$[\mathrm{HD}]=[C_{b,0}]\{1-\exp[-k_mA(t-t_0)/V]\}+iA(2t_0-t)/2VF. \tag{32}$$

When $i_L\leqq i$ at $t=0$: Let $t_0=0$, $[C_{b,0}]=[C_{b,i}]$, then Eqs. 31 and 32 can be applied to calculate ζ.

Prediction of ζ: Table 1 shows experimental values of the product-selectivity obtained in the galvanostatic electrolysis of p-methylbenzaldehyde at a rotating Pb cylinder electrode, compared with those predicted from Eqs. 27,31, and 32. Here, a dimensionless parameter, q, is used in stead of time. $q=1$ means that the charge

Table 1. Product-Selectivity (ξ) for the Reduction of p-Methylbenzaldehyde (Initial Concentration: 80 mM) at a Rotating Cylinder Pb Cathode

Run	ω/rpm	i/mA cm^{-2}	q[a]	ξ_{exp}	ξ_{calcd}
1	250	5	0.2	0.9	1.0
2	250	5	0.3	0.7	0.8
3	250	5	0.4	0.6	0.7
4	500	10	0.2	0.5	0.4
5	1000	10	0.2	2.5	5.3
6	1000	10	0.4	1.9	2.1

a) $q=iAt/[C_{b,i}]VF$.

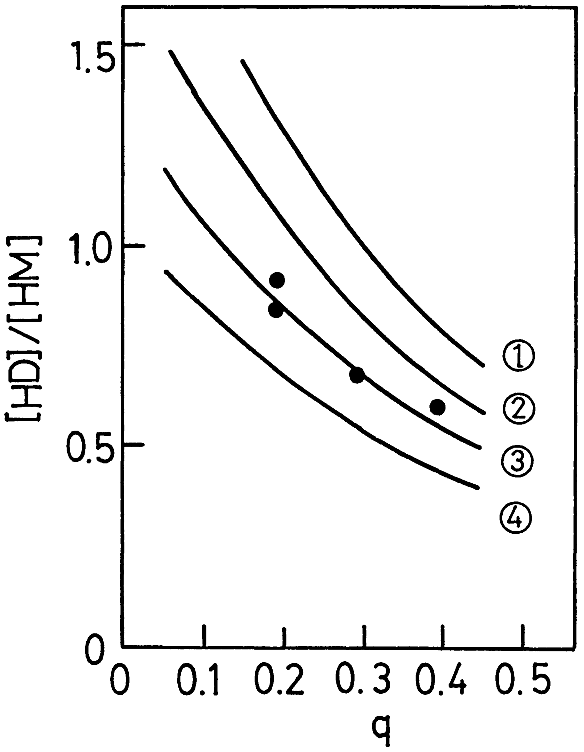

Fig. 5. Effect of charge passed ($q=iAt/[C_{b,i}]VF$) and mass transfer on product-selectivity at 5.0 mA cm^{-2} and 250 rpm. Mass transfer coefficients: ① 0.00055, ② 0.00053 (average mass transfer coefficient), ③ 0.00051, ④ 0.00049 cm s^{-1}.

passed for 1 mole of substrate is 96485 C. The relation between time and q is given by

$$t=q[C_{b,i}]VF/iA \tag{33}$$

Values of k_m's used in this model are determined from Fig. 1 at various rotating speeds. In general, both the two ζ 's are in good agreement. Bearing in mind that the model calculation is based on many assumptions, the result is encouraging. The prediction, of course, may become more accurate if we take hydrogen evolution into account.

Combination of Eqs. 27 and 31—33 gives theoretical curves of ζ vs. q as shown in Fig. 5. The mean mass transfer coefficient at 250 rpm is 0.00053 cm s^{-1} with a deviation of 5%. The theoretical curve is expected to be curve 2. Nevertheless, the measured values of ζ 's are very near to curve 3, calculated by using 0.00051 cm s^{-1} as k_m. The difference between the two k_m 's is rather small, therefore, the validity of this model is proved. It should also be noted that a slight change (5%) in mass transfer rate could lead to a considerable variation (20%) in ζ for the case in Fig. 5. Hence, this model is shown to be applicable to the electroreduction of p-methylbenzaldehyde and can explain why the ratio of hydrodimeric to hydromonomeric products in the electroreduction of benzaldehyde increases 20 times as the rotating speed increases from 250 to 1000 rpm.[14]

It is interesting that this model could be used in estimating k_m as implied in Fig. 5. The evaluation of mass transfer coefficient is important in designing a practical electrolytic cell, and the application of this model in a flow cell system is in progress. Finally, it must be emphasized again that the product-selectivity is itself an index of mass transport for some electrolytic systems.

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