Dissociation Rates of Weak Acids Using Sinusoidal Hydrodynamic Modulated Rotating Disk Electrode Employing Koutecky-Levich Equation

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The hydrogen evolution reaction of HCOOH, CH₃COOH, and C₂H₅COOH solutions consists of two different reduction processes depending on the evaluation of potential region; (1) independent reduction of RCOOH and (2) simultaneous reduction of RCOOH and H₂O. The reduction of each carboxylic acid generates an apparent convective diffusion-controlled limiting current. The first achievement of the present study is that by using a rotating disk electrode (RDE) and a sinusoidal hydrodynamic modulated-rotating disk electrode (SHM), it was elucidated that the additive property of the reduction currents of RCOOH and H₂O was not effective, and the convective-diffusion current was successfully distinguished from the total current. The second achievement is the successful analysis of the rotation-speed dependency of the limiting current in RDE and SHM using a modified theory of the Koutecky-Levich equation. The slopes of the plots for each carboxylic acid increased in the following sequence: RDE, SHM (p = 0.05), and SHM (p = 0.24), which is consistent with the theory. The dissociation rates of the carboxylic acids and the reverse recombination rate were calculated.

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The dissociation rates of various carboxylic acids have previously been determined by applying the modified Koutecky-Levich relation on the rotational-speed dependency of the limiting current for H⁺ reduction at the rotating disk electrode (RDE). The dissociation rates determined in the previous study were apparently consistent with the results obtained using other methods. However, we now raise an elementary question about the procedure used for determining the H⁺-reduction limiting current, which is the basis of the Koutecky-Levich analysis. Based on sinusoidal hydrodynamic modulation (SHM) study, we conclude that the potential-dependent limiting current associated with H⁺-reduction in dilute acid solutions contains a significant potential-dependent current associated with OH⁻ generated simultaneously from the supporting electrolyte. The present SHM analysis of dilute HCl solution and an uncharged weak acid solution, such as formic, acetic, or propionic acid solutions, clearly demonstrates a pure convective diffusion-controlled potential region in addition to that associated with OH⁻. It is demonstrated that the “limiting” H⁺-reduction current for formic, acetic, and propionic acids varies considerably with the potential, and pure convective diffusion-controlled potential region could not be determined from the RDE data. Thus, it is likely that the previous studies by other researchers based on RDE have somewhat dealt with this issue. This fundamental issue exists for both RDE and SHM data. The present approach for determining the acid dissociation rates requires appropriate choice of an electrode potential that excludes the effect of OH⁻ in the convective diffusion-layer.

In this study, we also derive a linear approximation of SHM, as well as the RDE theory for determining the rate of dissociation of an uncharged weak acid, and apply it to the current SHM data for carboxylic acids. Detailed theory is presented in the Appendix section.

Experimental

Hydrochloric acid, formic acid, acetic acid, and propionic acid (all Fisher Certified ACS grade) were selected as target analytes. The analyte solutions comprised 1 mol dm⁻³ KCl (supporting electrolyte), a mixture of 1 mol dm⁻³ KCl and 0.75 × 10⁻³ mol dm⁻³ HCl, and one of the three carboxylic acids dissolved in 1 mol dm⁻³ KCl. The weak acid solutions examined comprised 1.5 mmol dm⁻³ formic acid with 0.02 mol dm⁻³ sodium formate, 2.7 mmol dm⁻³ acetic acid with 0.03 mol dm⁻³ sodium acetate, and 2.0 mol dm⁻³ propionic acid with 0.02 mol dm⁻³ sodium propionate. All solutions were prepared with pure water obtained from a Milli-Q Reagent Grade Water System (Milli-Q Corp.) and deoxygenated by using high purity nitrogen gas.

A platinum disk electrode of 0.23 cm radius was used for the SHM study. All measurements were carried out under nitrogen atmosphere.

Detailed experimental procedures, including fundamental results of SHM, have been described elsewhere. Modulated current and corresponding phase shifts were recorded according to the procedures outlined below because of the slow response of the lock-in amplifier and of the electrode to the reactant. A Pt electrode was potential cycled between +0.8 V (vs. SCE), and −0.95 V at a scan rate of 6 V min⁻¹ during measurements. The electrode potential was then maintained at a prescribed value during its cathodic scanning. After several seconds when the lock-in amplifier output showed a steady value, the modulated current and the phase shift were recorded. The rotation speed dependency of the disk current in the RDE was measured between 500 and 8400 rpm. Measurements of the rotation speed dependency of the modulation current in the SHM analysis were performed at a constant p-value of either 0.05 or 0.24. The corresponding modulation frequencies were 1–7 Hz for p = 0.05 (center speed between 1200 rpm and 8400 rpm), and 2–30 Hz for p = 0.24 (center speed between 500 rpm and 7500 rpm). Because the modulation amplitude of the rotator varied slightly depending on the center rotation speed and the modulation frequency, the applied modulation amplitude for constant input modulation amplitude (1 rpm⁻¹) was experimentally calibrated in advance of the measurements. The true concentration was monitored based on the time dependency of the limiting current in situ, given that the concentration of HCl and the carboxylic acids decreased slightly during the measurement. This concentration monitoring was necessary because a small decrease in the limiting current was found to affect the data analysis of the present SHM study.

As detailed below, the additive property of the hydrogen evolution current of HCl and carboxylic acids and that of the background hydrogen evolution current, i.e., the current ascribed to H₂O did not hold owing to the buffer reaction of OH⁻ and HCl or RCOOH, and the apparent limiting current region expanded with increasing rotation speed. On the other hand, present authors could found a potential region that was controlled solely by convective diffusion by using SHM. Based on this data, the limiting current measured at which the
modulated limiting current was maximum. The current was considered to be a convective diffusion-controlled limiting current. The RDE limiting current and the limiting current SHM were measured at −0.78 V vs. SCE for formic acid and −0.79 V vs. SCE for acetic acid and propionic acid. In each case, the RDE currents observed at these stated potentials were considered to be the correct limiting current. Herein, the conditions used to obtain the present results are specified in the legend of each figure.

The respective temperatures of the test solutions were 20°C for hydrochloric and formic acids and 25°C for acetic and propionic acids.

**Results and Discussion**

This study is organized into two segments dealing with the hydrogen evolution of dilute acid in aqueous solution. Initially, a qualitative evaluation of the mechanism of hydrogen evolution from dilute carboxylic acids is presented based on the SHM method. Subsequently, the dissociation rates of carboxylic acids were determined using either RDE or SHM employing the Koutecky-Levich equation based on the qualitative evaluation of SHM.

**Part 1: RDE and SHM response in dilute carboxylic acid solutions: failure of the additive property of partial currents in hydrogen evolution.**—The current-potential curve of the hydrogen evolution reaction of a dilute solution of a strong acid or a weak acid overlaps with that of the solvent water. The assumption of the additive property of these two hydrogen evolution currents does not hold as shown below and this fact suggests the presence of some anomaly within the overlapping current-potential region. The origin of this anomaly was conclusively resolved using SHM measurement, as presented in this section.

**Reduction of water.**—The reduction of water at the platinum electrode in aqueous neutral electrolyte solutions, e.g. in KCl, is described as follows:

\[
H_2O + e^- = 1/2H_2 + OH^- \tag{1}
\]

The reaction is largely kinetically controlled even in the negative potential regions that are ordinarily accessed during cyclic voltammetry because mass transfer of H_2O is not important in reaction 1. Thus, the total current, \(i_t\), equals the potential dependent kinetic current \(i_k\).

\[
i_t = i_k \tag{2}
\]

**Reduction of a strong acid and carboxylic acids.**—The electrochemical reduction of a partially dissociated, uncharged weak acid (HB in eqn. 3) is conventionally described as the kinetically controlled dissociation of the weak acid. The overall reaction is:

\[
HB + e^- = 1/2H_2 + B^- \tag{3}
\]

The reaction consists of initial dissociation:

\[
HB = H^++ B^- \tag{4}
\]

and subsequent electron transfer:

\[
H^++ e^- = 1/2H_2 \tag{5}
\]

Reaction 4 is perturbed by the buffer reaction 6 because of the formation of OH\(^-\) in reaction 1 at the interfacial region (the reaction layer).

\[
HB + OH^- = B^- + H_2O \tag{6}
\]

In the case of a strong acid, reaction 1 is perturbed by:

\[
H^++ OH^- = H_2O \tag{7}
\]

The Koutecky-Levich model\(^1\) assumes that at potentials that correspond to those for a limiting hydrogen ion reduction current the rate of dissociation of the weak acid can be measured, given that there is no hydrogen ion at the electrode surface to prompt the back reaction, i.e. the reverse of reaction 4. Thus appropriate plots of the identified limiting currents vs. the square root of the RDE rotation speed may be used to yield the rate of dissociation of HB.

Figure 1 shows schematic current-potential curves for the hydrogen evolution reaction of a carboxylic acid. The curve shown in Fig. 1A corresponds to the regime in which the rate of reaction 6 is extremely slow. In this case, the currents due to reaction 1 and 3 conform to the additive property of currents. The curve in Fig. 1C shows the regime in which reaction 6 is infinitely fast. In this case, the additive property of currents does not hold, and the apparent limiting current region is...
expanded to a more negative potential region as expounded below. Figure 1B shows the intermediate case.

Figures 1(A′)–1(C′) show the corresponding SHM current-potential curves. In this figure, the current due to reaction 1 is totally kinetically controlled and reaction 3 is totally convective-diffusion controlled. In the case of 1A′, the modulated limiting current region expands to negative potential irrespective of reaction 1. On the other hand, the SHM current must decrease in the more negative potential region of the current rise of reaction 1 (dotted line) if reaction 6 becomes fast (1B′ and 1C′).

Figure 2 shows the schematic current-potential curve of the RDE for the hydrogen evolution of HCl or carboxylic acids, assuming that reaction 6 or 7 is infinitely fast. The limiting current region is expanded to the more negative potential region with increasing rotation speed. Previous experimental results for the carboxylic acids clearly demonstrated that the observed curves were largely consistent with this schematic curve.3

SHM study of hydrogen evolution.—In SHM study, it is expected that the convective diffusion-controlled current can be extracted from the total current and distinguished from the kinetically controlled current, as stated above. In addition, the phase difference between the sinusoidal modulation of the rotation speed and the resulting modulation current increases as the irreversibility of the electron transfer process increases, i.e. as the rate of the electron transfer process decreases.3,13,14

Strong acid.—The experimental SHM and RDE curves for the reduction of the solvated proton present in a strong acid solution (e.g. HCl) are shown in Fig. 3. The RDE curve 1 in Fig. 3A shows an apparent limiting current. On the other hand, the modulated current curve (closed circles in Fig. 3B) shows a limiting current up to the potential at which the current rise due to H2O reduction (curve 2 in Fig. 3A) is observed, whereas the modulated current decreased at more negative potential irrespective of the apparent flat limiting current in the RDE. The phase shift measured using SHM (open circles in Fig. 3B) was characterized by a maximum near the half-wave potential, which reached the flat limiting region, and decreased owing to the increase in the electron transfer rate.14 The phase shift subsequently increased again corresponding to a decrease in the modulated current, indicative of the buffer reaction (eqn. 7) apart from convective-diffusion. Although no theoretical analysis of the subsequent increase of phase shift has been presented, the anomaly in the SHM current and phase shift obviously suggests the presence of a chemical process following the electron transfer process, H2O + e− = 1/2 H2 + OH− and H+ + OH− = H2O.

Carboxylic acids.—SHM analysis of weak acids can be challenging as illustrated in Figs. 4–6 that show the i-E curve of the RDE and the modulated current and phase shift curves of the SHM for formic, acetic, and propionic acids, respectively. No well-defined limiting current region was observed in the SHM for any of the carboxylic acids, whereas a maximum in the modulated current and a minimum in the phase shift were observed. In other words, the experimental “limiting currents” in RDE did not have an evident potential independent region.

The phenomena observed for the carboxylic acids as well as the strong acid can be interpreted as follows: solvated proton reduction produces a potential dependent kinetic current, iD, characteristic of the electrode material. As the potential becomes more negative, e.g. at the platinum electrode, a convective diffusion-controlled limiting current, iD,lim, appears to be reached. When using RDE this current conforms to the Levich equation15 for pure convective-diffusion controlled current and produces an unpredicted SHM response (Fig. 3B).

As the potential becomes more negative after reaching the modulation limiting current, the OH− produced by the kinetically controlled reduction of water (eqn. 1) will react with dissolved H+ in the interfacial region adjacent to the electrode via the extremely fast diffusion-controlled process, eqn. 7 or eqn. 8. This reaction reduces the flux of H+ reaching the electrode surface exactly by the flux of OH− that is produced in reaction 1. Consequently, the cathodic current due to reaction 3 or 5 is decreased by an amount equal to the cathodic current

Figure 2. Schematic RDE current-potential curve of hydrogen evolution reaction of weak acid when buffer reaction “HB + OH− = B− + H2O” is infinitely fast. Solid line: rotation speed dependency and additive property of currents between BH and H2O. Broken line: background hydrogen evolution current ascribed to H2O.

Figure 3. A: Current-potential curve of RDE in (1) {1 mol dm−3 KCl + 3/4 mmol dm−3 HCl}, (2) {1 mol dm−3 KCl}. Scan rate 1 V min−1. B: SHM current-potential curve in {1 mol dm−3 KCl + 3/4 mmol dm−3 HCl}. Closed circle: modulation current, open circle: phase shift. Electrode Pt, rotation speed 2,500 rpm, modulation frequency 10 Hz, modulation amplitude: 0.164 rad1/2 s−1/2, temp. 20°C. Solid arrow in A indicates potential at which iD or ΔΔi vs. ω01/2 relation was measured.
 accompanying reaction 1, and an apparent constant limiting current, \(i_{D, \text{lim}}\), is observed. This current is the sum of the currents arising from reaction 3 and reaction 5 rather than solely from reaction 1. If only reaction 3 was operative, the SHM current would be constant across the same potential region as the RDE current (Fig. 1(A)).

Reaction 3 predominates at less negative potentials where reaction 1 is less important. However, at the most negative potentials only reaction 1 is possible given that all \(H^+\) ions in the interfacial region arising from reaction 1 are converted to water by reaction with \(OH^-\) according to reaction 6 or 7. At the potential where the magnitude of the flux of \(OH^-\) from eqn. 1 equals the convective diffusion-controlled flux of \(H^+\), the interfacial region is identical to a bulk electrolyte solution that does not contain any acid. This potential depends on the magnitude of \(i_{D, \text{lim}}\) and determines the value of the potential in the supporting electrolyte solution at which

\[i_k = i_{D, \text{lim}}\]  

[8]

Consequently, the point at which the potential becomes more negative than this value marks the onset of the current-potential \(i - E\) curve, and subsequent points correspond to the \(i - E\) curve observed in the absence of a strong acid or carboxylic acids, but superimposed on the limiting current.

The current at the arrow points indicated in Figs. 4–6 is not a 100% convective diffusion-controlled limiting current. The difference between the convective diffusion-controlled limiting current (theoretical) and the observed current is shown as \(A_{\text{obs}}/A_{\text{theor}}\) in Table 1. In the case of a strong acid, we can select the potential at which 100% convective diffusion-controlled limiting current is achieved. However, the curves for the carboxylic acids suggest that a 100% diffusion-controlled limiting current region cannot be achieved. At the potential marked by the arrow, it was found that the limiting current and the modulated current could be determined within an error of 10%, and mostly better than 5%.

**Part 2: \((K/C)^{1/2}\) and dissociation rate of carboxylic acids measured using RDE and SHM** — It is suggested that the apparent limiting current region of the hydrogen evolution reaction of the strong acid and carboxylic acids could not be ascribed simply to the convective-diffusion controlled process based on the qualitative SHM measurement, as shown in Figs. 4–6. We note that \(i_k\) depends only on the potential, not on convective-diffusion, whereas \(i_{D, \text{lim}}\) depends on the RDE rotational speed in the limiting current-potential region according to the Levich equation. \(^{15}\) Thus, \(i_{D, \text{lim}}\) can be extracted from the slope of a plots of the total current vs. the square root of the rotational speed for various potentials. This can be accomplished by using cyclic voltammetry to identify whether there was a current in the experimental limiting current region, in which water reduction was negligible. On the other hand, a cyclic voltammogram acquired using SHM provides a direct means of separating these two processes and identifying the potential region; above this region, the reduction of \(H^+\) is convective diffusion-controlled and is free of the complications associated
curves in Figs. 4B–6B; the potentials are shown in Figs. 4A–6A indicated by bold arrows. At potentials more negative than that indicated by the arrow point, the current inevitably contains a contribution from the buffer reaction (eqn. 1 followed by eqn. 6). In addition, the current also exhibits rotation speed dependency as schematically illustrated in Fig. 1B. For comparison, the potential at which the limiting current was determined to evaluate the dissociation rates of carboxylic acids by Gostisa-Mihelcic is indicated by a dotted-line arrow in Fig. 5A.

The current at the stated potential used in the literature must involve a remarkable amount of kinetic current that is dependent on the rotation speed. The overall reaction scheme is postulated to proceed as follows. The electron transfer process is simple and the chemical process is considered to be first order according to the theoretical convenience.

Theory for determining dissociation rates of carboxylic acids.—The detailed theory of SHM for the electron transfer reaction preceded by a chemical process is presented in the Appendix section.

Selection of the appropriate potential for determining (K/kf)1/2.—Because the Koutecky-Levich plot is based on the assumption of a potential-independent limiting current region, the plot cannot be used without addressing the issue of the appropriate potential region as described above. The appropriate potential for measuring the dissociation rates of carboxylic acids can be determined from the SHM curve in Figs. 4B–6B; the potentials are shown in Figs. 4A–6A indicated by bold arrows. At potentials more negative than that indicated by the arrow point, the current inevitably contains a contribution from the buffer reaction (eqn. 1 followed by eqn. 6). In addition, the current also exhibits rotation speed dependency as schematically illustrated in Fig. 1B. For comparison, the potential at which the limiting current was determined to evaluate the dissociation rates of carboxylic acids by Gostisa-Mihelcic is indicated by a dotted-line arrow in Fig. 5A.

The current at the stated potential used in the literature must involve a remarkable amount of kinetic current that is dependent on the rotation speed.

The equilibrium constant K for eqn. 9 is expressed as:

\[
K = \frac{[X]}{[O]}
\]

where \(k_f\) and \(k_b\) are the pseudo first-order rate constants for the forward and backward reactions in eqn. 9, respectively. K is the apparent equilibrium constant in the case of carboxylic acids, and is equal to [RCOOH]/[H+] at a constant p-value, and constant modulation amplitude in \(\omega_o^{1/2}\); the modified and normalized equation for SHM is as described in eqn. A67 (see Appendix).

\[
\frac{\Delta I_{\text{shm,kl}}}{\Delta I_{\text{shm,l}}} = 1 - 0.554 \left( \frac{1}{I_X(\infty)} + r_1 \right) W (K/k_f)^{1/2} \omega_o^{1/2}
\]

where

\[
W = v^{-1/6} D_X O^{-5/6} D_O^{-1/2} D_X^{3/2}
\]

If \(r_1 = 0\), eqn. 60 will coincide with that of the RDE and with the Levich equation.

\[
\frac{i_{\text{shm,kl}}}{i_{\text{shm,l}}} = 1 - 0.554 \left( \frac{1}{I_X(\infty)} \right) W (K/k_f)^{1/2} \omega_o^{1/2}
\]

The most important test of the applicability of the SHM analysis to the fast chemical reaction preceding electron transfer is the evaluation of the slope of the \(i_{\text{shm,kl}} / i_{\text{shm,l}}\) (in the case of RDE) or \(\Delta I_{\text{shm,kl}} / \Delta I_{\text{shm,l}}\) (in SHM) vs. \(\omega_o^{1/2}\) plot. If the slopes follow the order, SHM (p = 0.24) > SHM (p = 0.05) > RDE, and the estimated (K/kf)1/2 is similar for the three measurements, the adequacy of the SHM study can be established.

| Acid    | p-value | Theo | Obs | \(A_{\text{obs}}/A_{\text{theor}}\) | Phase shift deg |
|---------|---------|------|-----|----------------------------------|-----------------|
| HCl*    | 0.05    | 0.988 | 0.991 | 1.003                           | −10.9          | −12          | 1.1          |
| HCOOH*  | 0.05    | 0.953 | 0.934 | 0.98                            | −17.7          | −18          | 0.3          |
| CH₃COOH**| 0.05   | 0.971 | 0.955 | 0.98                            | −17.9          | −19          | 1.1          |
| C₂H₅COOH**| 0.05  | 0.965 | 0.947 | 0.98                            | −19.1          | −21          | 1.9          |
| HCl*    | 0.24   | 0.813 | 0.817 | 1.005                           | −48.3          | −50          | 1.7          |
| HCOOH*  | 0.24   | 0.625 | 0.579 | 0.91                            | −69.7          | −77          | 7.3          |
| CH₃COOH**| 0.24 | 0.621 | 0.586 | 0.94                            | −70.2          | −73          | 2.8          |
| C₂H₅COOH**| 0.24 | 0.597 | 0.587 | 0.98                            | −72.6          | −75          | 2.4          |

*Measured at 20°C.  **Measured at 25°C.
The experimental conditions used here and in the literature suggests the adequacy of the SHM study.

Table II shows the physicochemical parameters used for the SHM analysis and the $r_i$ values for the three carboxylic acids in 1 mol dm$^{-3}$ KCl. These physicochemical parameters were used to evaluate ($K/k_i$)$^{1/2}$, $k_i$, and $k_o$ according to eqn. A63. The normalized $i_{o}(0)/i_{o}(1/2)$ plots for RDE and normalized $\Delta i_{o}(0)/\Delta i_{o}(1/2)$ vs. $\omega_1^{1/2}$ plots are shown in Figs. 7–9 for the three carboxylic acids, based on eqns. A67 and A68. The regression equations corresponding to Figs. 7–9 are summarized in Table III. The most important evidence of the adequacy of the study is the increase in the slopes in Figs. 7–9 according to the order: RDE < SHM ($p = 0.05$) < SHM ($p = 0.24$) for each carboxylic acid, which is consistent with the theoretical prediction based on eqns. A67 and A68. The conformance of the qualitative order to theory suggests the adequacy of the SHM study.

The slopes evaluated herein were compared with those from the previous study. The experimental conditions used here and in the literature suggests the adequacy of the SHM study.

### Table II. Physicochemical properties for calculation of kinetic parameters.

| Carboxylic acid | $v$ (in p)$^{21}$ | $I(\infty)$ | $r_i$ | $S_r^{**}$ | $D_{RCOOH}$ $^{1,22}$ (cm$^2$ s$^{-1}$) | $K_{dim}$ $^{1,23}$ (dm$^3$ mol$^{-1}$ s$^{-1}$) |
|-----------------|------------------|-------------|-------|------------|----------------------------------|----------------------------------|
| HCOOH           | $1.01 \times 10^{-2}$ | 0.9243      | 1.02  | 2.23       | $718 \times 10^{-5}$              | $3.8 \times 10^{-5}$ (20°C)      |
| CH$_3$COOH      | $0.882 \times 10^{-2}$ | 0.9239      | 1.02  | 2.24       | $733 \times 10^{-5}$              | $2.7 \times 10^{-5}$ (25°C)      |
| C$_2$H$_5$COOH  | $0.882 \times 10^{-2}$ | 0.9224      | 1.05  | 2.30       | $880 \times 10^{-5}$              | $2.1 \times 10^{-5}$ (25°C)      |

*1 mol dm$^{-3}$ KCl.

**Calculated from viscosity, density and diffusion coefficient.

### Table III. Regression curves of normalized $i_{o}$ vs. $\omega_1^{1/2}$ plots (RDE) and normalized $\Delta i_{o}$ vs. $\omega_1^{1/2}$ plots (SHM).

| Acids          | Method | $p$  | Regr. curve | Std. error in slope (%) |
|----------------|--------|------|-------------|-------------------------|
| HCOOH          | RDE    | -    | 1 - 0.00100 $\omega_1^{1/2}$ | 6.6                     |
|                | SHM    | 0.05 | 1 - 0.00139 $\omega_1^{1/2}$ | 4.0                     |
|                | SHM    | 0.24 | 1 - 0.00243 $\omega_1^{1/2}$ | 3.1                     |
| CH$_3$COOH     | RDE    | -    | 1 - 0.00116 $\omega_1^{1/2}$ | 11.8                    |
|                | SHM    | 0.05 | 1 - 0.00247 $\omega_1^{1/2}$ | 4.2                     |
|                | SHM    | 0.24 | 1 - 0.00429 $\omega_1^{1/2}$ | 9.5                     |
| C$_2$H$_5$COOH | RDE    | -    | 1 - 0.00115 $\omega_1^{1/2}$ | 17                      |
|                | SHM    | 0.05 | 1 - 0.00205 $\omega_1^{1/2}$ | 7.4                     |
|                | SHM    | 0.24 | 1 - 0.00391 $\omega_1^{1/2}$ | 3.6                     |

Figure 7. Normalized $i_{o}(0)/i_{o}(1/2)$ plot (o), normalized $\Delta i_{o}(0)/\Delta i_{o}(1/2)$ vs. $\omega_1^{1/2}$ plots for RDE and normalized $\Delta i_{o}(0)/\Delta i_{o}(1/2)$ vs. $\omega_1^{1/2}$ plots are shown in Figs. 7–9 for the three carboxylic acids, based on eqns. A67 and A68. The regression equations corresponding to Figs. 7–9 are summarized in Table III. The most important evidence of the adequacy of the study is the increase in the slopes in Figs. 7–9 according to the order: RDE < SHM ($p = 0.05$) < SHM ($p = 0.24$) for each carboxylic acid, which is consistent with the theoretical prediction based on eqns. A67 and A68. The conformance of the qualitative order to theory suggests the adequacy of the SHM study.

The slopes evaluated herein were compared with those from the previous study. The experimental conditions used here and in the literature suggests the adequacy of the SHM study.

Figure 8. Normalized $i_{o}(0)/i_{o}(1/2)$ plot (o), normalized $\Delta i_{o}(0)/\Delta i_{o}(1/2)$ vs. $\omega_1^{1/2}$ plot for $2.7$ mmol dm$^{-3}$ CH$_3$COOH $+$ 0.03 mol dm$^{-3}$ CH$_3$COONa in 1.0 mol dm$^{-3}$ KCl. Electrode Pt, modulation amplitude 0.164 rad$^{1/2}$ s$^{-1/2}$, temp. 25°C.

Figure 9. Normalized $i_{o}(0)/i_{o}(1/2)$ plot (o), normalized $\Delta i_{o}(0)/\Delta i_{o}(1/2)$ vs. $\omega_1^{1/2}$ plot for $2.0$ mmol dm$^{-3}$ C$_2$H$_5$COOH $+$ 0.02 mol dm$^{-3}$ C$_2$H$_5$COO$^{-}$Na in 1.0 mol dm$^{-3}$ KCl. Electrode Pt, modulation amplitude 0.164 rad$^{1/2}$ s$^{-1/2}$, temp. 25°C.
The dissociation and recombination rates of HCOOH calculated from the experimental slope and apparent dissociation constant were respectively $4.83 \times 10^5$ s$^{-1}$ and $1.28 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$. These values were one order smaller than those reported previously.$^{4,6}$ The origin of the discrepancy between the results of the present study and those of the previous ones is not clear, although the present study was theoretically self-consistent in terms of RDE and SHM. The dissociation rate, $k_d$, and the recombination rate, $k_b$, calculated for CH$_3$COOH and C$_2$H$_4$COOH were a few times higher than that reported in the previous study$^{4,6}$ and that of the diffusion-controlled second-order reaction.$^{16}$ The discrepancy can be attributed to the physicochemical values used and the several theoretical approximations. In particular, the value of the apparent dissociation constant, $K$, was used twice for the calculation process.

### Conclusions

Theoretical and experimental evaluation of the application of SHM to the electrode reaction with a preceding chemical reaction was established in the present study. The potential utility of SHM was adequately demonstrated through application to the hydrogen evolution reaction of carboxylic acids. The reaction current that could not be detected in the ordinary current-potential curve was readily apparent using SHM. The prospective application of SHM to the fast electrode reaction was also suggested; it is the subject of an ensuring study on the hydrogen evolution reaction of a strong acid and Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$. The data also suggested that SHM should be used in addition to RDE for analysis of the electrode reaction based on the Koutecky-Levich equation. However, it should be noted that successful application of RDE and SHM to the hydrogen evolution reaction requires careful experimental check of various physicochemical parameters. Otherwise, a rigorous discussion on the rate of kinetic parameters such as the dissociation rate, $k_d$, and the reverse recombination rate, $k_b$, is deemed inappropriate.

### Appendix

**Current-potential Curve and $\Delta k_d/k_b$ Relation of the Electrode Process with a Preceding Chemical Reaction in SHM**

**General:** The electrode reaction of interest is

$$\text{HCOOH} = \text{RCOO}^- + \text{H}^+ \quad [A1]$$

$$\text{H}^+ + e^- = \text{1/2H}_2 \quad [A2]$$

where $R = \text{H, CH}_3$, or $\text{C}_2\text{H}_4$ in this study. If $[\text{RCOO}^-] \gg [\text{RCOOH}]$, reaction $A1$ can be considered as pseudo first-order. In this study, $[\text{RCOO}^-] \approx 10[\text{RCOOH}]$; thus, we consider an electron transfer system with a preceding first-order or pseudo first-order chemical reaction designated by the scheme:

$$\frac{k_f}{k_R} \frac{X_{\text{RCOO}^-}}{K} \quad [A3]$$

### Table IV. $(K/k_f)^{1/2}$ values estimated from experimental slope, and calculated $k_f$ and $k_b$

| Acids    | $p$   | RDE | SHM | $(K/k_f)^{1/2}$ (average) | $K^*$ | $k_f$ (s$^{-1}$) | $k_b$ (dm$^3$ mol$^{-1}$ s$^{-1}$) |
|----------|-------|-----|-----|--------------------------|-------|-----------------|----------------------------------|
| HCOOH    | 0.05  | -   | -   | 0.0285 ± 0.0050          | 53    | $4.83 \times 10^5$ | $1.28 \times 10^9$               |
|          | 0.24  | -   | -   | 0.0270                   | -     | -               | -                                |
| CH$_3$COOH | 0.05  | -   | -   | 0.0436 ± 0.0040          | 1111  | $3.46 \times 10^6$ | $1.28 \times 10^{11}$           |
|          | 0.24  | -   | -   | 0.0477                   | -     | -               | -                                |
| C$_2$H$_4$COOH | 0.05  | -   | -   | 0.0404 ± 0.0037          | 910   | $2.88 \times 10^6$ | $1.37 \times 10^{11}$           |
|          | 0.24  | -   | -   | 0.0441                   | -     | -               | -                                |

$^a$Calculated from $K_{\text{diss}}$ and concentration of RCOO-$.
where $K$ is an apparent equilibrium constant of species $X$ and $O$, $k_f$ and $k_r$ are the forward and reverse rate constants that relate to $K$, as shown by eqn. A4. In this study, $X$ is electro-inactive $ROOH$, $O$ is $H^+$, and $R$ is $H_2$. All species must be soluble in solution.

For this process, the system of the convective diffusion equation at the disk electrode is given by:

$$\frac{\partial C_X}{\partial t} = D_X \frac{\partial^2 C_X}{\partial z^2} - \frac{\partial}{\partial z} \left( k_f (C_X - K C_O) \right)$$  \hspace{0.5cm} [A6]

$$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial z^2} + \frac{\partial}{\partial z} \left( k_r (C_X - K C_O) \right)$$  \hspace{0.5cm} [A7]

$$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial z^2} - \frac{\partial}{\partial z} \left( C_R \right)$$  \hspace{0.5cm} [A8]

where $w$ is the normal component of time dependent fluid velocity obtained in a previous study\(^{17}\) on SHM (eqns. (21) and (22)) using the results of Sparrow and Gregg\(^{17}\):

$$w_a = g w_0 + \left( 1 + \frac{\epsilon_0}{\epsilon_0(1 + v_0 \sin \theta)} \right)$$  \hspace{0.5cm} [A9]

where $\epsilon_0$ is the dimensionless distance and is equal to $(\omega_0 v_0)^{1/2} z$.

Based on precedent\(^{17}\), the steady-state sinusoidal solution, which neglects the transients is then sought. The boundary conditions are given by:

$$\begin{align*}
    z &\rightarrow \infty: \quad C_X + C_O = C^*, \quad C_X / C_O \rightarrow K, \quad C_R \rightarrow 0 \\
    z & = 0: \quad D_X \frac{\partial C_X}{\partial z} / b = 0
\end{align*}$$  \hspace{0.5cm} [A11]

Introducing unknown functions, according to Koutecky\(^{16}\) and Dogonadze\(^{19}\):

$$f = (D_X C_X + D_O C_O) / D_{X0} = C_X + C_O + (D_X - D_O) g / (K D_X + D_O)$$  \hspace{0.5cm} [A13]

$$g = C_X - K C_O$$  \hspace{0.5cm} [A14]

where

$$D_{X0} = (D_O + K D_X) / (1 + K)$$  \hspace{0.5cm} [A15]

We have

$$\frac{\partial f}{\partial t} = \left( D_{X0} \frac{\partial^2 f}{\partial z^2} - \frac{\partial f}{\partial z} \right) = -D_{X0} \frac{\partial g}{\partial z}$$  \hspace{0.5cm} [A16]

$$\frac{\partial^2 g}{\partial z^2} = \frac{k_f (1 + K) D_{X0}}{D_x D_{X0}} - \frac{\partial}{\partial z} \left( \frac{D_{X0}}{D_X + D_O} \right)$$  \hspace{0.5cm} [A17]

Here we assume that the homogeneous reaction $A3$ proceeds so fast that the thickness of the reaction layer, in which the deviation from equilibrium is found, is very low. The terms on the right hand sides of eqns. A16 and A17 are then considered zero. Thus, we have

$$\frac{\partial f}{\partial t} = \left( D_{X0} \frac{\partial^2 f}{\partial z^2} - \frac{\partial f}{\partial z} \right)$$  \hspace{0.5cm} [A18]

$$\frac{\partial^2 g}{\partial z^2} = \frac{k_f (1 + K) D_{X0}}{D_x D_{X0}} g$$  \hspace{0.5cm} [A19]

with the boundary conditions

$$\begin{align*}
    z &\rightarrow \infty: \quad f \rightarrow C^*, \quad g \rightarrow 0 \\
    z & = 0: \quad D_{X0} \frac{\partial g}{\partial z} = i (n F S), \quad D_{X0} g / (1 + K) = -K i (n F S)
\end{align*}$$  \hspace{0.5cm} [A11']

Equation A19 is solved as:

$$g = \frac{\epsilon_0 / (n F S) K}{k_f (1 + K) D_{X0} / D_o} \exp \left[ \frac{k_f (1 + K) D_{X0}}{D_o} \right]$$  \hspace{0.5cm} [A20]

As stated above, the steady-state sinusoidal solution must be found, which may have the form

$$f = C_X^0 \left[ \cos (\omega t) + \epsilon (\omega_0 \epsilon_0 \cos \sigma t + \omega_0 \sin \sigma t) + \cdots \right]$$  \hspace{0.5cm} [A21]

Following the procedure described in the previous papers\(^{12,13}\) and using the dimensionless variable

$$\xi = z / \delta$$  \hspace{0.5cm} [A23]

with

$$\delta = \sqrt{3 D_t (1 / \omega_0)^{1/2} / 0.51023}$$  \hspace{0.5cm} [A24]

produces a set of ordinary differential equations.

$$u_{n+1} - (b_{X0} w / D_{X0}) u_n = 0$$  \hspace{0.5cm} [A25]

$$u_{n+1} - (b_{X0} w / D_{X0})(u_{n+1} + a_0 u_n) = (b_{X0}^2 \sigma / D_{X0}) v_n$$  \hspace{0.5cm} [A26]

$$v_{n+1} - (b_{X0} w / D_{X0})(u_{n+1} + a_0 u_n) = -(b_{X0}^2 \sigma / D_{X0}) u_n$$  \hspace{0.5cm} [A27]

$$v_0'' - (b_{X0} w / D_{X0}) v_0' = 0$$  \hspace{0.5cm} [A28]

$$v_{n+1} - (b_{X0} w / D_{X0})(v_{n+1} + a_0 v_n) = -(b_{X0}^2 \sigma / D_{X0}) v_n$$  \hspace{0.5cm} [A30]

These equations have the same form as those in Ref. 13 (eqns. A1-A6). The expressions for $k_{X0} w / D_{X0} b_{X0}$, $a_0$, and $b_{X0}$ are also given by eqns. A7-A10.

The current through the disk electrode relates to the fluxes and concentrations of the species at the electrode surface by:

$$i / n F S = D_t (C_0 / b z) / \delta = (k_f (C_0 / b z) / \delta = k_f (C_0 / b z) / \delta = k_f (C_0 / b z) / \delta = k_f (C_0 / b z) / \delta)$$  \hspace{0.5cm} [A31]

where $k_f$ and $k_r$ are electrochemical rate constants.

Using eqns. A13, A14, and A20-A22 and rearranging, we have

$$i / n F S = i_{iow} / n F S + \Delta \delta \cos (\theta - \phi) / n F S + \cdots$$

$$i_{iow} / n F S + \Delta \delta \cos (\theta - \phi) / n F S + \cdots = (D_{X0} C^* / b_{X0} w) / v_0 + d_0 \cos (\theta - \phi) / n F S + \cdots$$

$$= (\cos (\theta - \phi) / n F S) v_0 + d_0 \cos (\theta - \phi) / n F S + \cdots$$

where

$$Q = \frac{D_t K}{D_{X0} (1 + K) \left[ k_f (1 + K) D_{X0} / D_o \right]^{1/2}}$$  \hspace{0.5cm} [A33]

Thus, we have the boundary conditions for eqns. A25-A30.

$$u_1 (0) = (b_{X0} / n F S D_{X0} C^*) v_{iow}, \quad u_1 (\infty) = 1$$  \hspace{0.5cm} [A34]

$$v_0 (0) = (b_{X0} / n F S D_{X0} C^*) v_{iow}, \quad v_0 (\infty) = 0$$  \hspace{0.5cm} [A35]

$$u_{n+1} (0) = (b_{X0} / n F S D_{X0} C^*) (i_{iow} / \epsilon_0), \quad u_{n+1} (\infty) = 0$$  \hspace{0.5cm} [A36]

$$u_{n+1} (0) = (b_{X0} / n F S D_{X0} C^*) (i_{iow} / \epsilon_0), \quad u_{n+1} (\infty) = 0$$  \hspace{0.5cm} [A37]

$$v_0 (0) = (b_{X0} / n F S D_{X0} C^*) (i_{iow} / \epsilon_0), \quad v_0 (\infty) = 0$$  \hspace{0.5cm} [A38]

$$v_0 (0) = (b_{X0} / n F S D_{X0} C^*) (i_{iow} / \epsilon_0), \quad v_0 (\infty) = 0$$  \hspace{0.5cm} [A39]
The solutions of eqns. A25 and A28 with A34 and A35 are given by

\[ n_0(\xi) = 1 - (b_{20}/nFS D_{20}) C_0 \int_{0}^{\xi} (I_{p}(\xi_{0}) - I_{c}(\xi_{0})) \, d\xi \]  

where

\[ I_{p}(\xi) = \int_{0}^{\xi} \exp \left[ -\xi - 0.8843 S_{1}^{-1/2} \xi - 0.3933 S_{1}^{-2/2} \xi^{6} \right] d\xi \]  

For the limiting current region, \( \xi \rightarrow \infty \), \( I_{p}(\xi) \) can be described as follows according to the numerical calculation by Newman.

\[ I_{p}(\xi) = 0.89294 + 0.26610 S_{1}^{-1/3} + 0.12960 S_{1}^{-2/3} \]  

Current-potential curve and limiting current of RDE: Substituting eqns. A40 and A41 into A32 and rearranging the resultant equation gives the current-potential relation.

\[ i_{sw}/nFS = \frac{k_{j}}{1 + \omega(1 + \omega_{k})} \]  

Equation A44 can be rewritten in a more explicit form

\[ i_{sw} = \frac{k_{j}}{1 + \omega_{1/2}} \]  

\[ \times \frac{0.554(A_{16}/n^{1/2} \omega_{1/2}^{1/2} / \omega^{1/2})^{1/2} + \left[ \omega_{1/2}^{1/2} \right]^{1/2} \omega_{1/2}^{1/2} + \left[ \omega_{1/2}^{1/2} \right]^{1/2} \omega_{1/2}^{1/2} \omega_{1/2}^{1/2}}{1 + \omega(1 + \omega_{k})} \]  

where

\[ k_{j} = k_{j0}(1 + K)^{1/2} \]  

\[ \zeta = (nF/RT) [E - (E^{1/2})] \]  

\[ D' = D_{20}^{1/2} \]  

Letting \( k_{j} \rightarrow \infty \) and \( k_{b} \rightarrow 0 \) in the limiting current region, we have the expression for the kinetic limiting current, suffixed by \( k_{b} \):

\[ i_{sw} = \frac{k_{j0}}{1 + \omega_{1/2}} \]  

\[ \times \frac{0.554(A_{16}/n^{1/2} \omega_{1/2}^{1/2} / \omega^{1/2})^{1/2} + \left[ \omega_{1/2}^{1/2} \right]^{1/2} \omega_{1/2}^{1/2} \omega_{1/2}^{1/2}}{1 + \omega(1 + \omega_{k})} \]  

Equation A50 can be rearranged to a useful form to determine \( k_{j} \):

\[ \frac{i_{sw}}{i_{sw_{0}}} = \frac{0.554(A_{16}/n^{1/2} \omega_{1/2}^{1/2} / \omega^{1/2})^{1/2} + \left[ \omega_{1/2}^{1/2} \right]^{1/2} \omega_{1/2}^{1/2} \omega_{1/2}^{1/2}}{1 + \omega(1 + \omega_{k})} \]  

Equation A53 was modified in this study multiplying by \( \alpha_{1/2}^{1/2} \), and dividing \( i_{sw} \) to get:

\[ \frac{i_{sw}}{i_{sw_{0}}} = 1 - \frac{0.554(A_{16}/n^{1/2} \omega_{1/2}^{1/2} / \omega^{1/2})^{1/2} + \left[ \omega_{1/2}^{1/2} \right]^{1/2} \omega_{1/2}^{1/2} \omega_{1/2}^{1/2}}{1 + \omega(1 + \omega_{k})} \]  

Equations A53 and A54 are coincident with the Levich equation because \( \lambda(\infty) \approx 0.92 \) as calculated below, and 0.954!/\( \infty \approx 1.6 \).

Current-potential curve of SHM: For the modulated current, the mathematical deviation and the results obtained for the current-potential curves in the previous report can be used in this case with a slight change of the meaning of \( \lambda \). Here, we use the suffix \( k \) to indicate the existence of chemical reaction. In this case,

\[ \frac{k_{j}}{k_{j0}} \frac{e^{\lambda/2} (1 + \epsilon_{1/2})}{D_{20} (1 + \Omega_{k})} = \frac{0.554(A_{16}/n^{1/2} \omega_{1/2}^{1/2} / \omega^{1/2})^{1/2} + \left[ \omega_{1/2}^{1/2} \right]^{1/2} \omega_{1/2}^{1/2} \omega_{1/2}^{1/2}}{1 + \omega(1 + \omega_{k})} \]  

It is necessary to assume \( D_{20} = D_{0} \) for elucidation of the half-wave potential (eqn. A49). This equation gives the modulated current-potential curve in the presence of a chemical reaction.

The ratio of the kinetic current with a preceding chemical reaction to the simple diffusion-controlled limiting current can be obtained as follows:

\[ \frac{i_{kl}}{i_{kl0}} = r_{1} \left( \frac{A_{kl}}{A_{kl0}} \right)^{1/2} \]  

or

\[ \frac{A_{kl}}{A_{kl0}} = \Delta_{kl}/\Delta_{kl0} \left( 1 + \left( \frac{r_{1}}{r_{2}} \right)^{1/2} \right) \]  

where \( r_{1} \) and \( r_{2} \) are numerically computable values, which depend on \( p \) and \( S \). For \( 0 < \rho < 1 \) and \( 100 < S < 2100 \),

\[ r_{1} = 1.521 p^{0.51} S^{0.169} \]  

\[ r_{2} = 0.941 \]  

Equation A57 gives the relation between the modulated current and the potential, however, it must be solved by numerical calculation for quantitative purpose.

Limiting current of SHM: Equations A58 and A59 that appeared in reference 13 were deduced based on the numerical calculation, and differ slightly from the analytical functions. Thus, these equations were modified in this study to coincide with the analytical functions and Levich’s relation,

\[ r_{1} = 1.521 p^{1/2} S^{1/6} \]  

\[ r_{2} = 1 \]  

The factor 1.521 must be slightly changed, and 1.52 will be used in the following discussion. In addition, the limiting current in the RDE (eqn. A54) is modified in this study to facilitate comparison with the result of SHM, described as follows. In the case of carboxylic acids, the rate of dissociation into \( H^{+} \) and \( RC-O^{+} \) is very fast, and the \( \alpha_{1/2} \) dependency of \( i_{sw} \) is small; moreover, \( i_{sw} \) ≃ \( i_{sw0} \), and

\[ \frac{i_{sw}}{i_{sw0}} = 1 - \frac{0.554(A_{16}/n^{1/2} \omega_{1/2}^{1/2} / \omega^{1/2})^{1/2} + \left[ \omega_{1/2}^{1/2} \right]^{1/2} \omega_{1/2}^{1/2} \omega_{1/2}^{1/2}}{1 + \omega(1 + \omega_{k})} \]  

This approximation results in a slight underestimation in the calculation of the slope of the \( i_{sw} \) vs. \( \omega_{1/2} \) plot.

When a chemical reaction is operative, the convective-diffusion limiting current in SHM is obtained if \( \lambda' \rightarrow \infty \) in eqn. A55.

\[ \frac{k_{j}}{k_{j0}} \frac{e^{\lambda/2} (1 + \epsilon_{1/2})}{D_{20} (1 + \Omega_{k})} = \frac{0.554(A_{16}/n^{1/2} \omega_{1/2}^{1/2} / \omega^{1/2})^{1/2} + \left[ \omega_{1/2}^{1/2} \right]^{1/2} \omega_{1/2}^{1/2} \omega_{1/2}^{1/2}}{1 + \omega(1 + \omega_{k})} \]  

Using eqns. A50, A57, and A61, we have:

\[ \frac{\Delta_{kl}/\Delta_{kl0} \left( 1 + \left( \frac{r_{1}}{r_{2}} \right)^{1/2} \right)}{1 + \left( \frac{r_{1}}{r_{2}} \right)^{1/2}} \]  

Expressing the rotation-speed and dissociation-coefficient independent term as \( W \),

\[ W = v^{1/6} D_{0}^{1/6} \]  

and in the case of a large \( K(\gg 1) \), such as for the carboxylic acids treated here:

\[ K / (k_{j} (1 + K))^{1/2} \approx (K / k_{j})^{1/2} \]
Eqn. A62 can be simplified as:

\[
\frac{\Delta \omega_{\text{p.i}}}{\Delta \omega_{\text{el}}} = \frac{1}{1 + \left[0.5540/(f/k)\right] W \left(K/k_f\right)^{1/2} \omega_0^{1/2}}
\]

\[
\Delta \omega_{\text{el}} = \frac{1}{1 + 0.5540 f/W \left(K/k_f\right)^{1/2} \omega_0^{1/2}}
\]

[A65]

For a large (k/k_f)^{1/2} (i.e. small W/(k/k_f)^{1/2}) of about 10^{-3}, such as in the dissociation of carboxylic acids (see text.), the first and second terms of the right-hand side in eqn. A65 can be approximated using the relation: 1/(1 + x) ≃ 1 - x (for x < 1), and hence, I_0(X_o,\infty) ≃ I_0(\infty).

\[
\frac{\partial \omega_{\text{p.i}}}{\partial \omega_{\text{el}}} = \frac{1}{1 - \left[0.5540/(f/k)\right] W \left(K/k_f\right)^{1/2} \omega_0^{1/2}}
\]

\[
\times \left[1 - \left[0.5540 f/W \left(K/k_f\right)^{1/2} \omega_0^{1/2}\right]\right]
\]

[A66]

\[
\Delta \omega_{\text{el}} = 1 - 0.5540 \left(\frac{1}{f/k} + r_l\right) W \left(K/k_f\right)^{1/2} \omega_0^{1/2} + 0.5540 r_l f/W \left(K/k_f\right)^{1/2} \omega_0^{1/2}
\]

In the case of small W, the W^2 term can be neglected, and eqn. A66 will be reduced to:

\[
\frac{\partial \omega_{\text{p.i}}}{\partial \omega_{\text{el}}} = 1 - 0.554 \left(\frac{1}{f/k} + r_l\right) W \left(K/k_f\right)^{1/2} \omega_0^{1/2}
\]

[A67]

The corresponding equation for the RDE using the parameter W (eqn. A54) is:

\[
\frac{\partial \omega_{\text{p.i}}}{\partial \omega_{\text{el}}} = 1 - 0.554 \left(\frac{1}{f/k} + r_l\right) W \left(K/k_f\right)^{1/2} \omega_0^{1/2}
\]

[A68]

It was found from eqns. A67 and A68 that the slope of \(\Delta \omega_{\text{p.i}}/\Delta \omega_{\text{el}}\) vs. \(\omega_0^{1/2}\) plot must be larger than that of the \(\omega_{\text{el}}/\Delta \omega_{\text{el}}\) vs. \(\omega_0^{1/2}\) plot because of the term \(r_l\), and it was also suggested that the slope increases with increasing \(p\)-value. Further approximation of \(D_{\text{GO}}\) ≃ \(D_X\) and \(l_\text{GO} \geq l_\text{X}\) is employed to fit the experimental data to account for the experimental data based on these two equations. It should be noted that only the \(K/k_f\) value can be calculated from the RDE or SHM experiment, and other data regarding \(K\) are necessary to deduce the \(k_f\) value.

Equations A67 and A68 suggest the potential of SHM. The slope of \(\Delta \omega_{\text{p.i}}/\Delta \omega_{\text{el}}\) vs. \(\omega_0^{1/2}\) is more strongly augmented by the \(r_l\) term in the case of SHM than that of RDE, and increases with increasing \(p\)-value (eqn. A58). This \(p\)-value dependency serves as a reliable evidence of an operative chemical reaction. The increase in the slope with increasing \(p\)-value must reflect the rate of the chemical process preceding electron transfer, and the rate can be estimated from the slope of either \(\Delta \omega_{\text{p.i}}/\Delta \omega_{\text{el}}\) or \(\Delta \omega_{\text{el}}/\Delta \omega_{\text{el}}\) vs. \(\omega_0^{1/2}\). Thus far, we have estimated the rate of the preceding chemical reaction only from the slope of \(\Delta \omega_{\text{el}}/\Delta \omega_{\text{el}}\) vs. \(\omega_0^{1/2}\). The \(p\)-value dependency of the slope of the plot based on SHM should afford highly reliable information on the preceding chemical reaction. It should be noted that eqns. A67 and A68 have a certain degree of error based on the continuing approximations, and the resultant rate constant inherently deviates from that estimated by other procedures such as the relaxation methods.

**List of Symbols**

- \(K\): concentration ratio of carboxylic acid to \(H^+\): \(K = [RCOOH]/[H^+]\)
- \(k_f\): chemical rate constant of dissociation of RCOOH in \(s^{-1}\)
- \(k_b\): recombination rate constant of RCOO\(^-\) and \(H^+\) in \(dm^{-3}\) \(mol^{-1}\) \(s^{-1}\)
- \(k_f\): forward electrochemical rate constant in eqn. A5
- \(k_b\): reverse electrochemical rate constant in eqn A5
- \(\Delta\): diffusion-coefficient term with a preceding chemical reaction
- \(W\): rotation-speed and dissociation-coefficient independent term
- Other symbols are similar to those in Ref. 13.

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