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CHANGE OF MECHANISM OF THE HYDROGEN ELECTRODE REACTION WITH OVERPOTENTIAL

IV. Surface Coverage Effect

By

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Abstract

Analysis of the distribution of the reaction affinity among constituent steps of the hydrogen electrode reaction and the current *vs.* overpotential relation, reported previously, was extended taking the impeding effect of the surface coverage into consideration. The discharge-combination and the discharge-electrochemical desorption routes were treated assuming the LANGMUIR and FRUMKIN-TEMKIN adsorption isotherms for the reaction intermediate. The surface coverage term does not much influence the affinity distribution but the current *vs.* overpotential relations are significantly modified. Comparison with experiments on Ni and Rh suggests that the kinetically effective surface coverage of the hydrogen intermediate would be much smaller than that observed electrochemically.

1. Introduction

Mechanistic investigation of the hydrogen electrode reaction (*her*) on Rh, Ni and several other metals by means of the deuterium tracer technique^{1,2)} has revealed that no single step generally determines the overall reaction rate. Thus, the reaction is under coupled control and different rate-determining step (*rds*) may be expected under sufficiently separated experimental conditions, *eg.*, the overpotential. Indeed, change of the mechanism has been experimentally demonstrated in the chlorine electrode reaction on platinum group metals; the change takes place in the overpotential range of some 0.2 V.³⁾ Such a possibility of mechanism change with the reaction condition was then analyzed⁴⁻⁷⁾ and the equations derived were applied to interpretation of the "hydrogen pressure equivalent to hydrogen overpotential",⁶⁾ or of the change with overpotential of the electrolytic deuterium separation factor on Pt, Ni, or Au cathodes.⁷⁾

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The analysis was, however, made, as a first approach, with the approximation that the surface coverage with the reaction intermediate is sufficiently small as compared with the full coverage and/or has no significant effect upon the reaction kinetics.⁸⁻¹⁰ Evidences which support this attitude are: (A) Some polarization behaviors on Pt cathode¹⁰ suggest an insignificant impeding effect of hydrogen adsorbed on the electrode. (B) Experimental results² by means of an isotope tracer technique could well be accounted for without involving the "free surface fraction term." Nevertheless, the analysis is of limited applicability, as criticized later.¹¹ It is thus intended in the present paper to investigate the surface coverage effect. The analysis will be made with the LANGMUIR and the FRUMKIN-TEMKIN isotherms for the reaction intermediate adsorption.

2. Adsorption Isotherm

If the hydrogen adatoms are only the significant species adsorbed in *her*, the activity a_H may be expressed as,¹²⁻¹⁴

$$a_H = \frac{\theta_H}{1 - \theta_H} \exp \{u \theta_H\} \quad (1)$$

where θ_H is the surface coverage and u (in units of RT) represents the interaction energy among hydrogen adatoms at full coverage. Equation (1) with appreciable (usually positive) magnitude of u corresponds to the FRUMKIN-TEMKIN semilog adsorption isotherm in a wide range of θ_H (except near the limiting values $\theta_H \simeq 0$ or $\theta_H \simeq 1$), or the one with $u=0$ corresponds to the LANGMUIR isotherm.

The activity, hence the surface coverage, of hydrogen adatoms is not a simple function of overpotential in the present case where the system is under coupled control; it is determined by the steady-state condition that the net rates of the constituent steps must balance with each other.

3. Step Rates, Distribution of the Affinity, and the Overall Rate

The forward uni-directional rate v_{+s} of step s is expressed as,^{13,15}

$$v_{+s} = k_{+s} a_{I,s} / f_s^* \quad (2)$$

where $a_{I,s}$ is the activity of the initial system of the step, f_s^* is the activity coefficient of the activated complex and k_{+s} is a constant. Further, we may write,¹³

$$1/f_s^* = \Theta_{*(0)} \exp \{-u^* \theta_H\} \quad (3)$$

where $\Theta_{*(0)}$ is the probability that the adsorption site for the critical complex

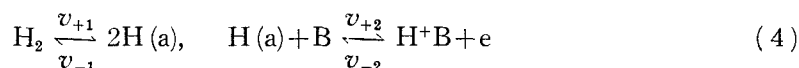
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is vacant and u^* (in units of RT) is the interaction energy between the critical complex and surrounding chemical species. Accordingly, f_s^* may be taken constant if the surface coverage with the reaction intermediate is sufficiently low or else if it is appreciable but has insignificant effect upon f_s^* , hence upon the reaction rate. We will consider below the case in which this is not necessarily acceptable.

Route A

(a) Step rate

Consider the discharge-combination route (Route A) of the *her*,



where (a) denotes an adsorbed state and $\text{B} = \text{H}_2\text{O}$ or OH^- . We may write for the two-site activated complex for step 1,

$$1/f_1^* = (1 - \theta_{\text{H}})^2 \phi \exp \{-2 \lambda_1 u \theta_{\text{H}}\} \quad (5)$$

where ϕ is a function of θ_{H} , usually not significantly deviating from unity,¹³ and $\lambda_1 \equiv u_1^*/2u$. Hence, using the approximation that $\phi = 1$, we have

$$v_{+1} = k_{+1} P_{\text{H}_2} / f_1^* = k_{+1} P_{\text{H}_2} (1 - \theta_{\text{H}})^2 \exp \{-2 \lambda_1 u \theta_{\text{H}}\}$$

and

$$v_{-1} = k_{-1} a_{\text{H}}^2 / f_1^* = k_{-1} \theta_{\text{H}}^2 \exp \{2(1 - \lambda_1) u \theta_{\text{H}}\}$$

where direct dependence of f_1^* of step 1 upon the electrode potential is assumed to be negligible. Defining

$$W \equiv \theta_{\text{H}} / \theta_{\text{H,eq}}, \quad Z \equiv (1 - \theta_{\text{H}}) / (1 - \theta_{\text{H,eq}}) \quad \text{and} \quad Q \equiv \exp \{u(\theta_{\text{H}} - \theta_{\text{H,eq}})\} \quad (6)$$

we may write

$$v_{+1} = v_{1,\text{eq}} Z^2 Q^{-2\lambda_1} \quad (7)$$

and

$$v_{-1} = v_{1,\text{eq}} W^2 Q^{2(1-\lambda_1)} = v_{1,\text{eq}} Z^2 Q^{-2\lambda_1} \gamma_{\text{H}}^2 \quad (8)$$

where

$$\begin{aligned} v_{1,\text{eq}} &= k_{+1} p_{\text{H}_2} (1 - \theta_{\text{H,eq}})^2 \exp \{-2 \lambda_1 u \theta_{\text{H,eq}}\} \\ &= k_{-1} \theta_{\text{H,eq}}^2 \exp \{2(1 - \lambda_1) u \theta_{\text{H,eq}}\} \end{aligned} \quad (9)$$

and (cf. (1))

$$\gamma_{\text{H}} \equiv a_{\text{H}} / a_{\text{H,eq}} = (W/Z) Q. \quad (10)$$

Similarly, assuming an analogous type of interaction effect upon f_2^* and denoting $u_2^*/u = \lambda_2$, we have

$$\begin{aligned} v_{+2} &= v_{2,\text{eq}} e^{\alpha_{+2} f \eta} W Q^{(1-\lambda_2)} \\ &= v_{2,\text{eq}} Z Q^{-\lambda_2} \gamma_H e^{\alpha_{+2} f \eta} \end{aligned} \quad (11)$$

and

$$v_{-2} = v_{2,\text{eq}} Z Q^{-\lambda_2} e^{\alpha_{+2} f \eta} e^{-f \eta} \quad (12)$$

where $\eta = -(\mu_e - \mu_{e,\text{eq}})/F$ is the overpotential, μ_e is the (electro-)chemical potential of electron in the electrode, $f \equiv F/RT$, α_{+2} denotes dependence of f_2^* , and hence of v_{+2} , upon η , and

$$\begin{aligned} v_{2,\text{eq}} &= k_{+2} \theta_{H,\text{eq}} \exp \{ (1-\lambda_2) u \theta_{H,\text{eq}} \} \\ &= k_{-2} (1-\theta_{H,\text{eq}}) \exp \{ -\lambda_2 u \theta_{H,\text{eq}} \}. \end{aligned} \quad (13)$$

The free energy change Δg_1 of step 1 at fixed hydrogen pressure is given (*cf.* eqs. (1) and (10)) by

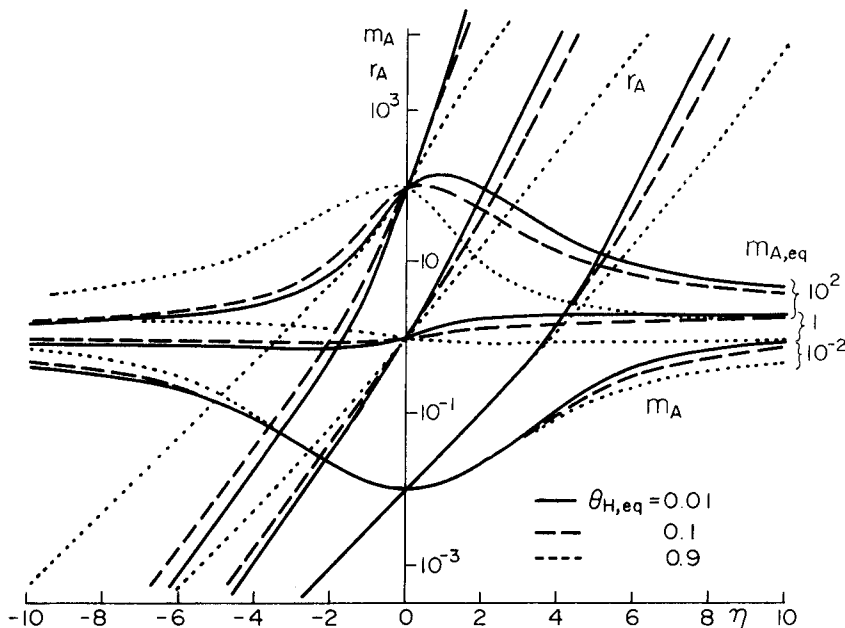


Fig. 1. Distribution of affinity to the constituent steps and dependence of r_A upon overpotential (Overpotential is given in units of $2.303 RT/F = 59 \text{ mV}$ (25°C))

Route A, FRUMKIN-TEMKIN isotherm ($u=5$), $m_{A,\text{eq}} = 10^{-2}$, 1, and 10^2 ; $\theta_{H,\text{eq}} = 10^{-2}$, 0.1, and 0.9.

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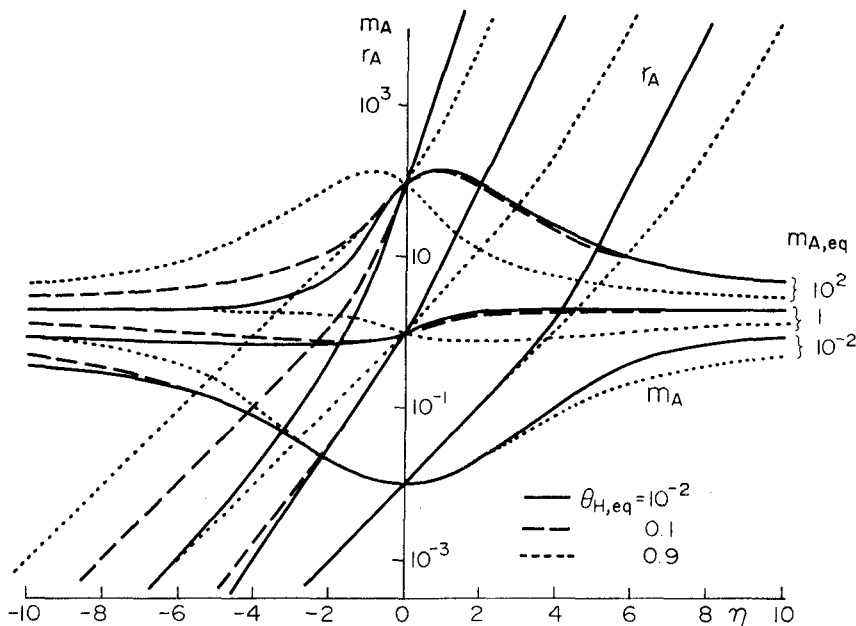


Fig. 2. Distribution of affinity to the constituent steps and dependence of r_A upon overpotential

Route A, LANGMUIR isotherm ($u=0$), $m_{A,eq}=10^2$, 1, and 10^{-2} ; $\theta_{H,eq}=10^{-2}$, 0.1 and 0.9.

$$\Delta g_1 = 2\mu_H - \mu_{H_2} = 2RT \ln \gamma_H = 2RT \ln WQ/Z \quad (14)$$

and that of step 2 with fixed solution composition,

$$\begin{aligned} \Delta g_2 &= \mu_{H+B} + \mu_e - \mu_H = -F\eta - RT \ln \gamma_H \\ &= -F\eta - RT \ln WQ/Z. \end{aligned} \quad (15)$$

(b) Distribution of the affinity among the constituent steps

The overall net rate V_A is given by the steady-state relation,

$$V_A = (v_{+1} - v_{-1})/\nu_1 = (v_{+2} - v_{-2})/\nu_2 \quad (16)$$

where $\nu_1 (=1)$ and $\nu_2 (=2)$ are the stoichiometric number of step 1 and 2, respectively. Accordingly, we have

$$\frac{v_{+2}}{2v_{+1}} = \frac{1 - \exp\{\Delta g_1/RT\}}{1 - \exp\{\Delta g_2/RT\}}. \quad (17)$$

Substitution of eqs. (7) and (11) into eq. (17) leads to

$$m_{A,eq} e^{\alpha_{+2}f\eta} \left[1 - \exp\left\{\frac{\Delta g_2}{RT}\right\} \right] = \frac{Z}{\gamma_H} Q^{(2-2\lambda_1)} \left[1 - \exp\left\{\frac{\Delta g_1}{RT}\right\} \right] \quad (18)$$

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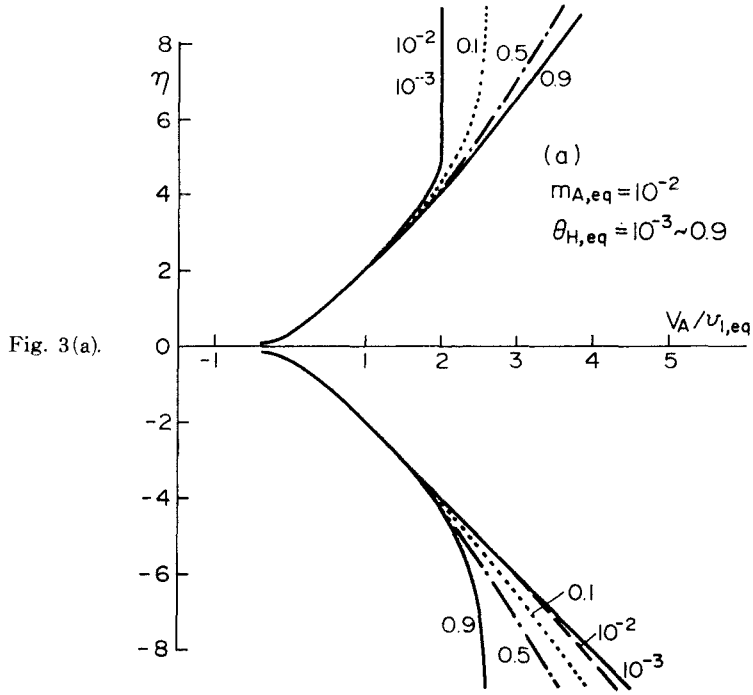


Fig. 3(a).

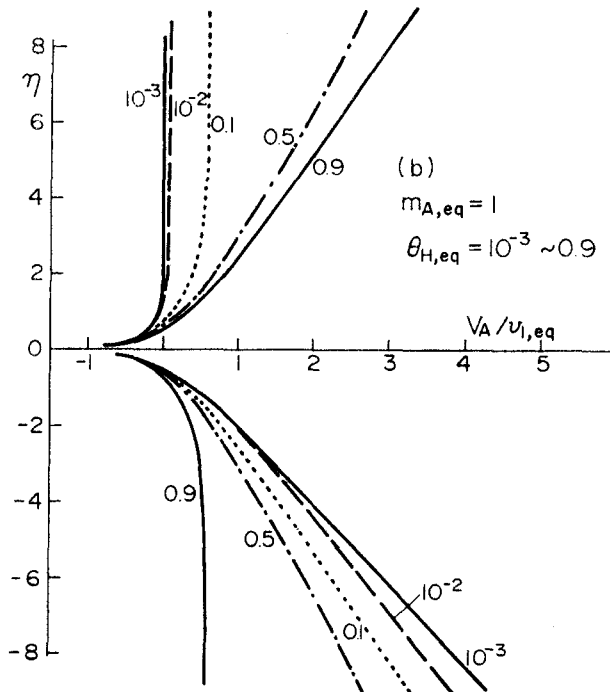


Fig. 3(b).

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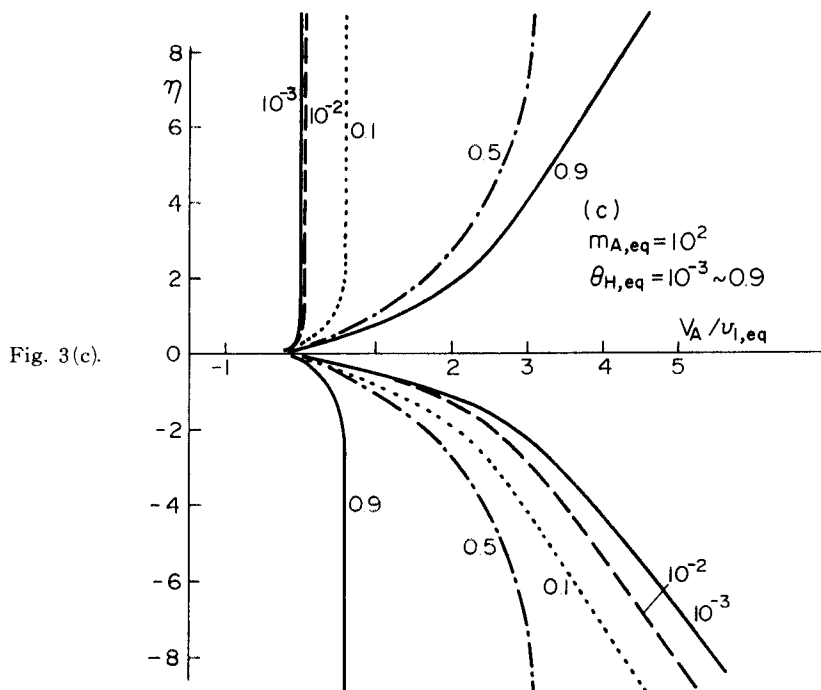


Fig. 3(c).

Fig. 3. Log current vs. overpotential relations (η is given in units of $2.303 RT/F = 59$ mV (25°C))

Route A, FRUMKIN-TEMKIN isotherm ($u/2.303 = 5$), $\theta_{H,eq} = 10^{-3} \sim 0.9$.
(a) $m_{A,eq} = 10^{-2}$, (b) $m_{A,eq} = 1$, and (c) $m_{A,eq} = 10^2$

where $m_{A,eq} \equiv v_{2,eq}/2v_{1,eq}$ ($= i_{0,2}/i_{0,1}$ in terms of step exchange c. d's.). Defining $m_A \equiv \Delta g_1/\Delta g_2$ and employing the relation^{5,6)}

$$v_1 \Delta g_1 + v_2 \Delta g_2 = \Delta G = -2F\eta \quad (19)$$

where ΔG is the overall free energy change, we obtain

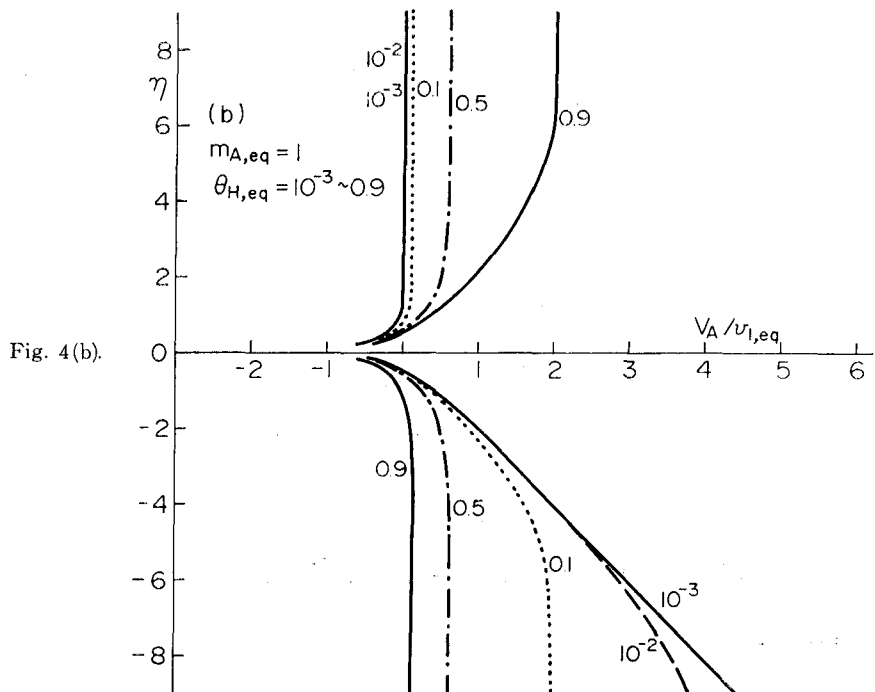
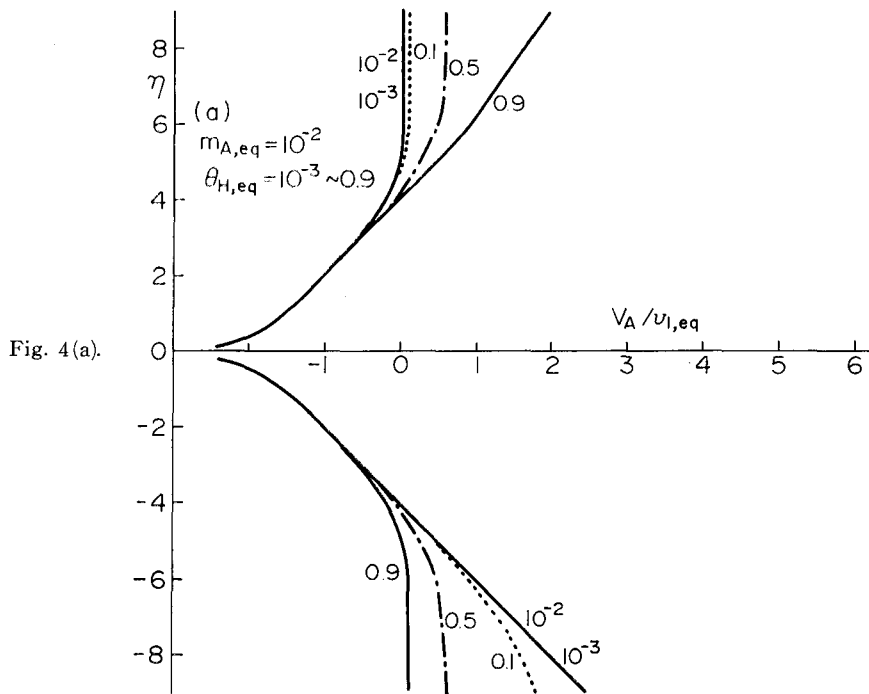
$$\frac{\Delta g_1}{RT} = -\frac{2m_A f\eta}{m_A + 2} \quad \text{and} \quad \frac{\Delta g_2}{RT} = -\frac{2f\eta}{m_A + 2}. \quad (20)$$

Referring to eqs. (14) and (20), eq. (18) is now rewritten as

$$m_{A,eq} e^{\sigma + i f \eta} \left[1 - \exp \left\{ -\frac{2f\eta}{m_A + 2} \right\} \right] \\ = ZQ^{(2_2 - 2\lambda_1)} \left[\exp \left\{ \frac{m_A f\eta}{m_A + 2} \right\} - \exp \left\{ -\frac{m_A f\eta}{m_A + 2} \right\} \right]. \quad (21)$$

FRUMKIN-TEMKIN isotherm

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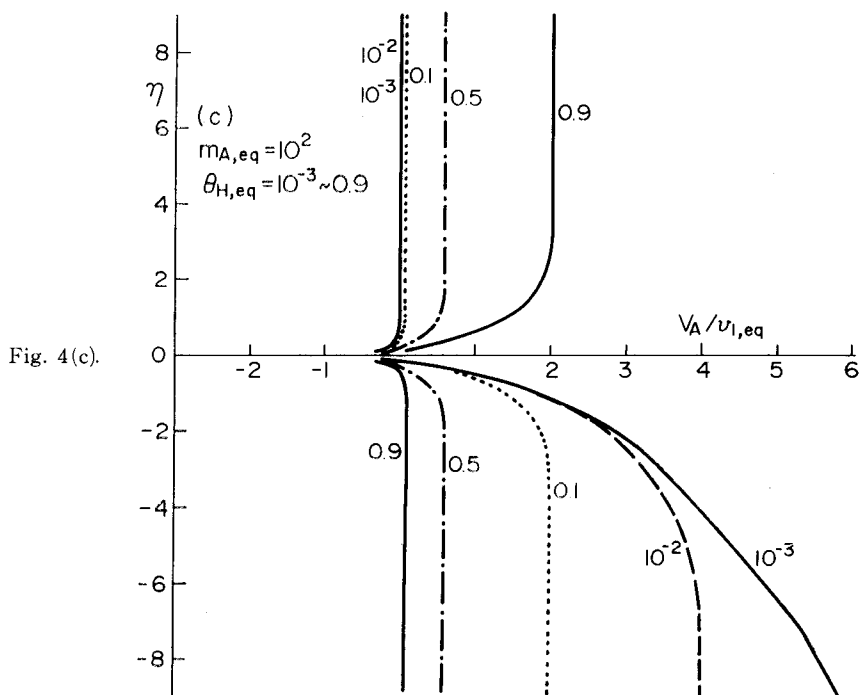


Fig. 4(c).

Fig. 4. Log current vs. overpotential relations
Route A, LANGMUIR isotherm ($u=0$), $\theta_{H,eq} = -3 \sim 0.9$.
(a) $m_{A,eq} = 10^{-2}$, (b) $m_{A,eq} = 1$, and (c) $m_{A,eq} = 10^2$.

Numerical values of m_A and θ_H at given η are readily obtained by solving eqs. (14) and (21) simultaneously, provided that u , $\theta_{H,eq}$, α_{+2} , $m_{A,eq}$ and λ 's are given. Calculations were carried out for the case $u/2.303=5$ (interaction energy = 28.4 kJ*), $\theta_{H,eq} = 10^{-3} \sim 0.9$, $m_{A,eq} = 10^{-2} \sim 10^2$, $\alpha_{+2} = 0.5$, and tentatively,¹⁷⁾ $\lambda_1 = \lambda_2 = 0.5$ (Fig. 1). It is seen that the m_A vs. η relation depends upon $\theta_{H,eq}$ but its general shape is analogous to the case where the surface coverage effect is neglected.^{5,6)} (The case of the "negative TEMKIN" was also calculated with $u/2.303 = -1$ but it often shows improbable behaviors. These are not presented in this report.)

LANGMUIR isotherm

Results of the calculation with the same set of parameter values except

*) This value was chosen in view of decrease of heat of adsorption (~ 40 kJ/mole) of hydrogen adatom with change of θ_H from zero to unity on Pt (and Rh) in aqueous solution.¹⁶⁾ Incidentally, such a decrease in the absorption heat with θ_H seems to be at variance with the "negative TEMKIN" occasionally reported in the literature.

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$u=0$ are plotted in Fig. 2.

(c) The net rate

Substituting eqs. (7), (8), (11), and (12) into eq. (16), we obtain

$$\begin{aligned} V_A &= v_{1,\text{eq}} Z^2 Q^{-2\lambda_1} [1 - \gamma_H^2] \\ &= (v_{2,\text{eq}}/2) Z Q^{-\lambda_2} e^{\alpha_{+2} f\eta} [\gamma_H - e^{-f\eta}] \\ &= \frac{1 - \gamma_H e^{-f\eta}}{(Q^{2\lambda_1}/v_{1,\text{eq}} Z^2) + (2\gamma_H Q^{\lambda_2}/v_{2,\text{eq}} Z) e^{-\alpha_{+2} f\eta}}. \end{aligned} \quad (22)$$

The ratio, r_A , of the two terms in the denominator of the *rhs* of eq. (22), which is equal to $v_{+2}/2v_{-1}$, is given, utilizing eqs. (8), (11), (14) and (20) and assuming $\alpha_{+2}=1/2$, by

$$\begin{aligned} r_A &= \frac{m_{A,\text{eq}}}{W} e^{\alpha_{+2} f\eta} Q^{-(1+\lambda_2-2\lambda_1)} \\ &= m_{A,\text{eq}} \frac{Q^{(2\lambda_1-\lambda_2)}}{Z} \exp\left\{\frac{1.5 m_A + 1}{m_A + 2} f\eta\right\}. \end{aligned} \quad (23)$$

This indicates that the rate of change of r_A with η is modified from that discussed previously⁵⁾ by the factor $Q^{(2\lambda_1-\lambda_2)}/Z$ which is however usually not very far from unity except at $\theta_{H,\text{eq}} \simeq 1$. Accordingly, it is seen from Figs. 1 and 2 that variation of r_A with η at large $\theta_{H,\text{eq}}$ is still fairly sharp. The mechanism change with reaction affinity (overpotential) is therefore readily anticipated.⁴⁾ The log current *vs.* overpotential relations are shown in Fig. 3 for the FRUMKIN-TEMKIN isotherm case and in Fig. 4 for the LANGMUIR case.

At sufficiently high anodic overpotentials, eq. (22) reduces to

$$V_A = v_{1,\text{eq}} Z^2 Q^{-2\lambda_1} \quad (\eta \gg RT/F). \quad (24)$$

Under the present condition, we may write $2v_{+1}=v_{+2}$, both the reverse rates being negligible. Then, using eqs. (7) and (11), we have

$$Z^2 = m_{A,\text{eq}} W e^{\alpha_{+2} f\eta} Q^{(1-\lambda_2+2\lambda_1)} \quad (25)$$

Hence, eq. (24) yields

$$V_A = \frac{v_{2,\text{eq}}}{2} W e^{\alpha_{+2} f\eta} Q^{(1-\lambda_2)} \quad (\eta \gg RT/F). \quad (26)$$

A similar relation for the LANGMUIR case was derived by ERENBURG¹⁸⁾: In a limiting case of $\theta_{H,\text{eq}} \simeq 1$, eq. (26) suggests that step 2 is rate-determining in the anodic region. However, it can be seen that the condition $W \simeq 1$ is not readily satisfied. For example, in the LANGMUIR case ($Q=1$) with $m_{A,\text{eq}}=1$, $\alpha_{+2}=1/2$, and $\theta_{H,\text{eq}}=0.95$ (or 0.99), we obtain from (25) that $W=$

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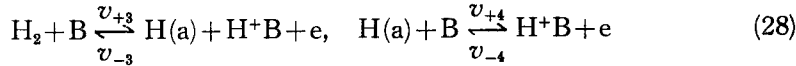
0.918 (0.982), 0.634 (0.969), and 0.239 (0.904) for $\eta=59, 118,$ and 236 mV, respectively. Thus, eq. (26) or (24) instead indicates that the overall rate expression involves kinetic parameters of both step 1 and 2. If $\theta_{H,eq}$ is large, the experimental Tafel line is therefore significantly modified by the variation of Z with η .

Similarly, at sufficiently high cathodic overpotentials, we have

$$\left. \begin{aligned} V_A &= -\frac{v_{2,eq}}{2} Z Q^{-\lambda_2} e^{-(1-\alpha_2) f \eta} \\ &= -v_{1,eq} W^2 Q^{2(1-\lambda_1)} \end{aligned} \right\} (-\eta \gg RT/F). \quad (27)$$

In this case, if $\theta_{H,eq} \simeq 1$, W and Q are both close to unity. Therefore, V_A may approach a limiting value, $v_{1,eq}$, as is also seen in the full analysis of the V_A vs. η relation (Fig. 3). This limit represents on the one hand the saturation value of the combination rate when θ_H approaches unity and on the other hand a sharp increase of $-\eta$ which is required to maintain a given current at step 2 with strongly diminished free surface area. Conversely, if $\theta_{H,eq} \ll 1$, the relation is fully given in terms of kinetic parameters of step 2.

Route B



(a) Step rates

Assuming one-site adsorption of the activated complex for these steps, we may write

$$1/f_s^* = (1 - \theta_H) \exp \{-\lambda_s u \theta_H\}. \quad (29)$$

The step rates at given solution composition are then written, with $\lambda_3 \equiv u_3^*/u$ and $\lambda_4 \equiv u_4^*/u$, as

$$v_{+3} = v_{3,eq} Z Q^{-\lambda_3} e^{\alpha_3 f \eta} \quad (30)$$

$$v_{-3} = v_{3,eq} W Q^{(1-\lambda_3)} e^{\alpha_3 f \eta} e^{-f \eta} = v_{3,eq} Z Q^{-\lambda_3} \gamma_H e^{-(1-\alpha_3) f \eta} \quad (31)$$

$$v_{+4} = v_{4,eq} W Q^{(1-\lambda_4)} e^{\alpha_4 f \eta} = v_{4,eq} Z Q^{-\lambda_4} \gamma_H e^{\alpha_4 f \eta} \quad (32)$$

and

$$v_{-4} = v_{4,eq} Z Q^{-\lambda_4} e^{-(1-\alpha_4) f \eta} \quad (33)$$

where

$$v_{3,eq} = k_{+3} (1 - \theta_{H,eq}) e^{-\lambda_3 u \theta_{H,eq}} = k_{-3} \theta_{H,eq} e^{(1-\lambda_3) u \theta_{H,eq}} \quad (34)$$

$$v_{4,eq} = k_{+4} \theta_{H,eq} e^{(1-\lambda_4) u \theta_{H,eq}} = k_{-4} (1 - \theta_{H,eq}) e^{-\lambda_4 u \theta_{H,eq}} \quad (35)$$

and with $m_B \equiv \Delta g_3 / \Delta g_4$,

$$\gamma_H \equiv a_H / a_{H,eq} = (W/Z) Q = \exp \{ -(m_B - 1) f\eta / (m_B + 1) \}. \quad (36)$$

(b) Distribution of the affinity

In the steady state the relation for the net rate,

$$V_B = v_{+3} - v_{-3} = v_{+4} - v_{-4} \quad (37)$$

must be satisfied. We then obtain,⁵⁾

$$\begin{aligned} m_{B,eq} Q^{(\lambda_3 - \lambda_4)} e^{(\alpha_{+4} - \alpha_{+3})f\eta} [e^{f\eta/(m_B+1)} - e^{-f\eta/(m_B+1)}] \\ = e^{m_B f\eta/(m_B+1)} - e^{-m_B f\eta/(m_B+1)} \end{aligned} \quad (38)$$

where

$$m_{B,eq} \equiv v_{4,eq} / v_{3,eq} \quad (= i_{0,4} / i_{0,3}). \quad (39)$$

Further, we have⁵⁾

$$m_B + 1 = 2f\eta / \ln \frac{m'_{B,eq} + e^{f\eta}}{m'_{B,eq} + e^{-f\eta}} \quad (40)$$

where

$$m'_{B,eq} = m_{B,eq} Q^{(\lambda_3 - \lambda_4)} e^{(\alpha_{+4} - \alpha_{+3})f\eta}. \quad (41)$$

These relations allow us to evaluate distribution of the affinity to the constituent steps. In case $\lambda_3 = \lambda_4$, the distribution is not influenced by the surface coverage term (cf. Fig. 3 in previous paper⁵⁾).

(c) The net rate

The net rate V_B is given as^{*)}

$$\begin{aligned} V_B &= v_{3,eq} Z Q^{-\lambda_3} e^{\alpha_{+3}f\eta} [1 - \gamma_H e^{-f\eta}] \\ &= v_{4,eq} Z Q^{-\lambda_4} e^{\alpha_{+4}f\eta} [\gamma_H - e^{-f\eta}] \\ &= Z [1 - e^{-2f\eta}] \left[\frac{1}{v_{3,eq} Q^{-\lambda_3} e^{\alpha_{+3}f\eta}} + \frac{1}{v_{4,eq} Q^{-\lambda_4} e^{(1+\alpha_{+4})f\eta}} \right]^{-1}. \end{aligned} \quad (42)$$

Referring to eqs. (31) and (32) we see that the ratio r_B of the two terms in the denominator of the *rhs* of eq. (42) is equal to v_{+4}/v_{-3} :

$$r_B \equiv m'_{B,eq} e^{f\eta} = v_{+4}/v_{-3}. \quad (43)$$

This has a tendency to change rapidly with η and $r_B \gg 1$ at $\eta \gg RT/F$ or $r_B \ll 1$ at $-\eta \gg RT/F$ unless $m_{B,eq}$ is extremely separated from unity. Accordingly, eq. (42) reduces at high anodic overpotentials to,

$$V_B = Z v_{3,eq} Q^{-\lambda_3} e^{\alpha_{+3}f\eta} \quad (\eta \gg RT/F) \quad (44)$$

*) Similar equations are reported elsewhere^{5,19)} for the case $Q=Z=1$.

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and at high cathodic overpotentials to

$$V_B = -Z v_{4,\text{eq}} Q^{-\lambda_4} e^{-(1-\alpha_+)\eta} \quad (-\eta \gg RT/F). \quad (45)$$

Substituting eqs. (30)~(35) and (41) into eq. (37), we obtain

$$Z = \left[1 - \theta_{\text{H,eq}} + \frac{\theta_{\text{H,eq}}}{Q} e^{-f\eta} \frac{e^{f\eta} + m'_{\text{B,eq}}}{e^{-f\eta} + m'_{\text{B,eq}}} \right]^{-1}. \quad (46)$$

If $\theta_{\text{H,eq}} \ll 1$, we have $Z \simeq 1$ independent of η , and we see from eqs. (44) and (45) that step 3 or 4 becomes rate-determining at large anodic or cathodic overpotentials, respectively.

The situation, however, becomes more involved if $\theta_{\text{H,eq}}$ is of significant magnitude. If $\theta_{\text{H,eq}}$ is taken to be close to unity, eq. (46) reduces to

$$Z \simeq Q \frac{e^{-f\eta} + m'_{\text{B,eq}}}{1 + m'_{\text{B,eq}} e^{-f\eta}} \quad (\theta_{\text{H,eq}} \simeq 1) \quad (47)$$

or from eq. (42)

$$V_B = \frac{Q}{\theta_{\text{H,eq}}} \frac{e^{-f\eta} + m'_{\text{B,eq}}}{1 + m'_{\text{B,eq}} e^{-f\eta}} [1 - e^{-2f\eta}] \cdot \left[\frac{1}{v_{3,\text{eq}} Q^{-\lambda_3} e^{\alpha_+ f\eta}} + \frac{1}{v_{4,\text{eq}} Q^{-\lambda_4} e^{(1+\alpha_+)\eta}} \right]^{-1}. \quad (48)$$

Accordingly, at high anodic overpotentials, we have

$$V_B = v_{4,\text{eq}} Q^{(1-\lambda_4)} e^{\alpha_+ f\eta} \quad (\theta_{\text{H,eq}} \simeq 1, m_{\text{B,eq}} \simeq 1, \eta \gg RT/F) \quad (49)$$

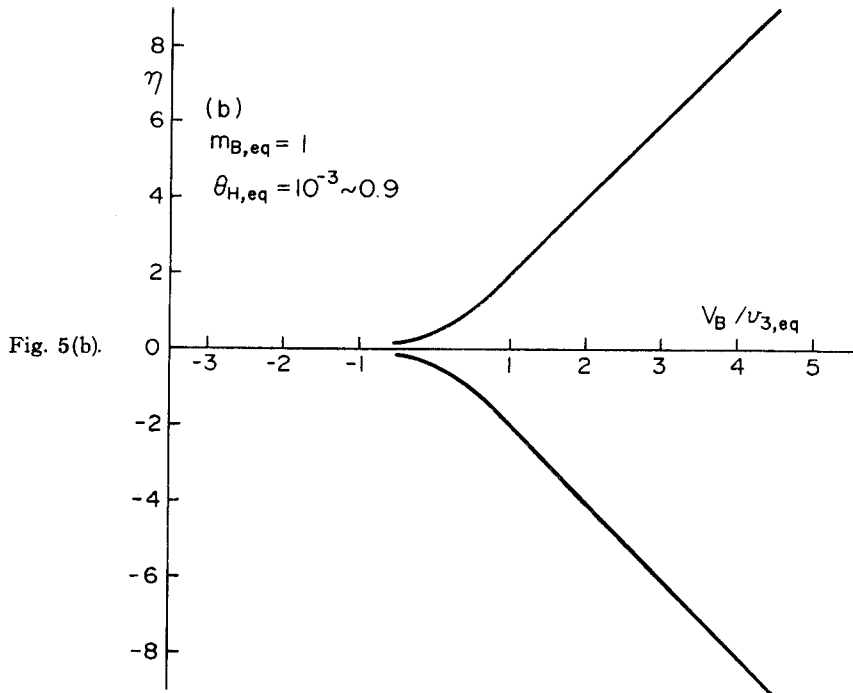
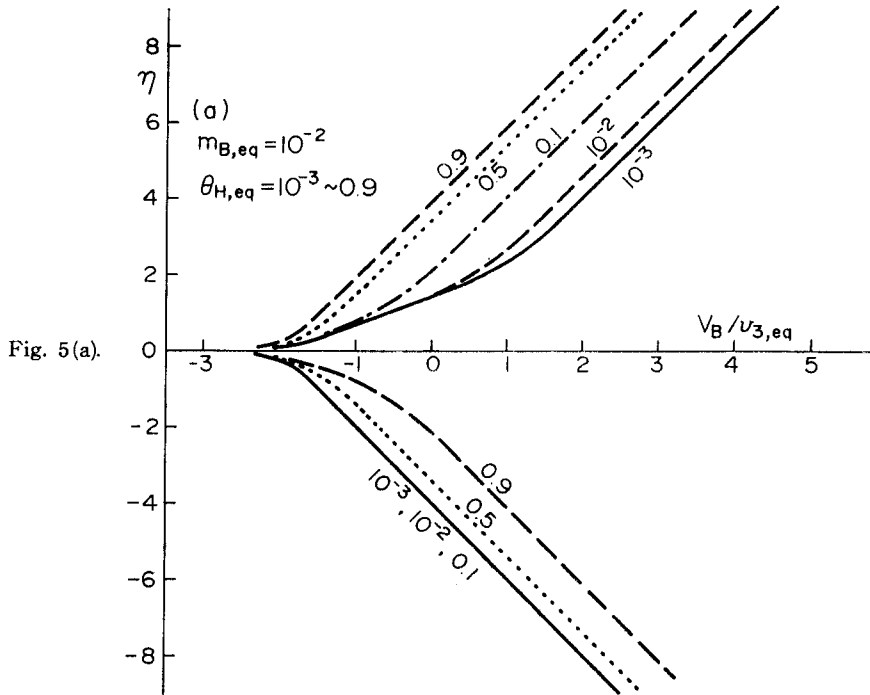
and at high cathodic overpotentials

$$V_B = -v_{3,\text{eq}} Q^{(1-\lambda_3)} e^{-(1-\alpha_+)\eta} \quad (\theta_{\text{H,eq}} \simeq 1, m_{\text{B,eq}} \simeq 1, -\eta \gg RT/F). \quad (50)$$

Comparison of eq. (44) with eq. (49) shows that the former is expressed in terms of Z and the reaction parameters of step 3 whereas the latter Q and those of step 4. The same argument applies to the comparison of eqs. (45) and (50).

Results of the calculation with $\theta_{\text{H,eq}} = 10^{-3} \sim 0.9$, $m_{\text{B,eq}} = 10^{-2}$, 1, and 10^2 , $\alpha_{+3} = \alpha_{+4} = 0.5$ and $\lambda_3 = \lambda_4 = 0.5$ are shown in Fig. 5 for the LANGMUIR and in Fig. 6 for the FRUMKIN-TEMKIN isotherm ($u/2.303 = 5$) case. The m_{B} vs. η and r_{B} vs. η relations are not shown as they are unchanged from those obtained previously after neglecting the surface coverage effect.⁵⁾ Thus, distribution of the affinity to the constituent steps is not influenced by the surface coverage term. However, even under high affinity values, the V_B vs. η relation generally involves kinetic parameters of both the steps and accordingly position of the relation is shifted with different values of $\theta_{\text{H,eq}}$.

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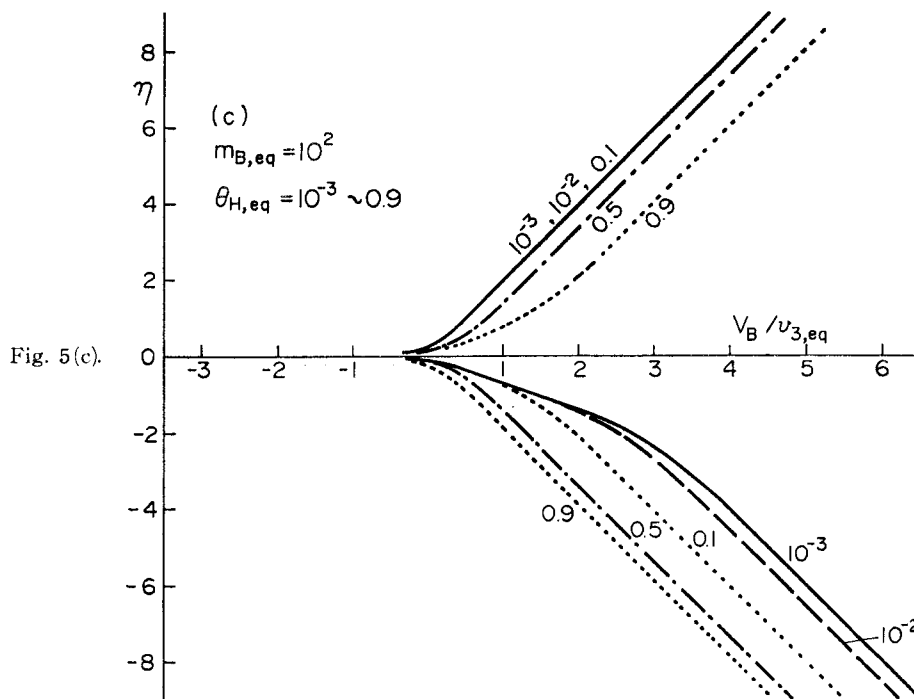


Fig. 5. Log current vs. overpotential relations
Route B, LANGMUIR isotherm ($u=0$), $\theta_{H,eq}=10^{-3}\sim 0.9$.
(a) $m_{B,eq}=10^{-2}$, (b) $m_{B,eq}=1$, and (c) $m_{B,eq}=10^2$.

Comparison of Figs. 5 and 6 reveals that the V_B vs. η relations for the LANGMUIR and FRUMKIN-TEMKIN adsorption isotherms are analogous (no difference exists at $m_{B,eq}=1.0$, cf. Fig. 5 b).

It is widely accepted that change of the (cathodic) TAFEL slope from 39 mV at low overpotentials to 118 mV at high overpotentials is one of characteristics of the slow-HEYROVSKY mechanism. (This behaviour is generally reproduced in the present calculation as seen in Fig. 5 c and 6 b for the LANGMUIR and FRUMKIN-TEMKIN case, respectively.) As well known, the break of the Tafel line has often been explained in terms of θ_H approaching unity: It has been argued that the lower TAFEL slope is a result of doubled contributions of the overpotential to the rate of the HEYROVSKY process, one through variation of θ_H with η in a Nernstian sense (because of the rapid VOLMER process) and the other through a direct effect upon the rate of step 4. With negative increase of η , it has been claimed, the higher slope is reached because θ_H would eventually approach unity and hence the former term would become ineffective.

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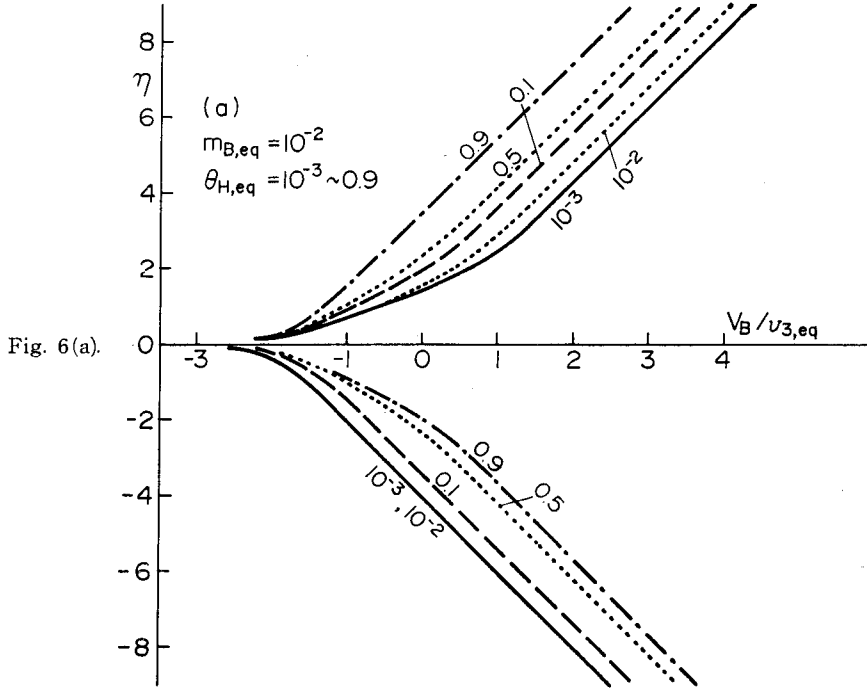


Fig. 6(a).

It should be noted that the present analysis does not support this view of θ_H being close to unity at the break. Table 1 shows rough values of $-\eta$ beyond which the TAFEL line attains 118 mV slope (read from Fig. 5c and 6 b) and of θ_H calculated at each point. It is seen that in both the LANGMUIR and FRUMKIN-TEMKIN cases $\theta_{H, \text{break}}$ is not generally close to unity.

The limiting value of θ_H at sufficiently high overpotentials is easily evaluated. At, *eg*, $\eta \rightarrow -\infty$, we see from eq. (40) $m_{B, -\infty} \rightarrow 1$. Under the same condition, v_{-3} must be equal to v_{-4} or from eqs. (31), (33) and (36), assuming $\lambda_3 = \lambda_4$ and $\alpha_{+3} = \alpha_{+4}$, we have

$$\begin{aligned} m_{B, \text{eq}} = \gamma_{H, -\infty} &= \left(\frac{WQ}{Z} \right)_{-\infty} \\ &= \left\{ \frac{\theta_H}{1 - \theta_H} \frac{1 - \theta_{H, \text{eq}}}{\theta_{H, \text{eq}}} \exp [u(\theta_H - \theta_{H, \text{eq}})] \right\}_{-\infty}. \end{aligned} \quad (51)$$

In the LANGMUIR case where $u=0$, therefore, we find

$$\theta_{H, -\infty} = \left[\frac{1 - \theta_{H, \text{eq}}}{m_{B, \text{eq}} \theta_{H, \text{eq}}} + 1 \right]^{-1}. \quad (52)$$

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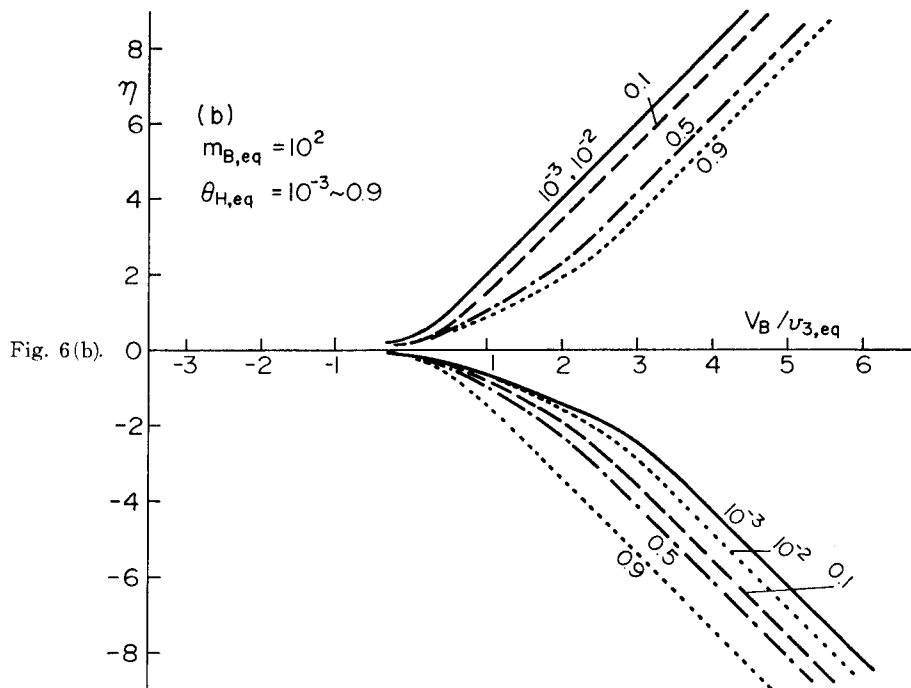
**Fig. 6.** Log current vs. overpotential relationsRoute B, FRUMKIN-TEMKIN isotherm ($u/2.303=5$), $\theta_{H,eq}=10^{-3}\sim 0.9$.(a) $m_{B,eq}=10^{-2}$ and (b) $m_{B,eq}=10^2$.Curves for $m_{B,eq}=1$ are the same as those shown in Fig. 5b.

TABLE 1. Approximate cathodic overpotential value, $-\eta_{break}$, beyond which the TAFEL line attains 118 mV slope and the corresponding surface coverage at the break, $\theta_{H,break}$ (γ is given in units of $2.303 RT/F \approx 59$ mV)

$\theta_{H,eq}$	10^{-3}	10^{-2}	0.1	0.5	0.9
(a) LANGMUIR case, $m_{B,eq}=10^2$					
$-\eta_{break}$	3	2.5	1.5	1	0.5
$\theta_{H,break}$	0.008	0.43	0.73	0.90	0.96
(b) FRUMKIN-TEMKIN case, $m_{B,eq}=10^2$ and $u/2.303=5$					
$-\eta_{break}$	3	2.5	2.5	2.5	1.5
$\theta_{H,break}$	0.005	0.14	0.34	0.77	0.98

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For example, if $\theta_{H,eq}=10^{-2}$ and $m_{B,eq}=10^2$, then $\theta_{H,-\infty}\simeq 0.5$. Further, $\theta_{H,-\infty}$ must be still smaller than this figure in the FRUMKIN-TEMKIN case with positive u ; thus $\theta_{H,-\infty}=0.157$ in case $\theta_{H,eq}=10^{-2}$, $m_{B,eq}=10^2$ and $u/2.303=5$. In these cases, therefore, θ_H can never attain the value of unity. Yet, because of the steady state requirement that θ_H attains a limiting value at overpotentials beyond a certain limit, the Tafel slope reaches the value of 118 mV.

Discussion

Common to Route A and B, the expression for the overall rate under high affinity condition is solely given in terms of kinetic parameters of the step which is located at the up-stream of the reaction, provided that θ_H is sufficiently small as compared with unity. We may then call the step rate-determining. However, if θ_H is of significant magnitude, the expression involves kinetic parameters of the down-stream step as well. Particularly, in Route B, if $\theta_{H,eq}$ is very close to unity and if the LANGMUIR isotherm is applicable, the expression may involve the kinetic parameters of the down stream step alone.

It has been shown that such behaviors are due to contributions from the "free surface fraction term," $Z\equiv(1-\theta_H)/(1-\theta_{H,eq})$: Although the up-stream step is now irreversible, Z , and hence the resultant rate, of the reaction in the steady-state depends upon the rates of both the constituent steps. In fact, in case $\theta_{H,eq}\simeq 1$, Z receives greater influences from kinetic parameters of the down-stream step, as already discussed by ERENBURG.^{11,20} The question of which step under what criteria should be called rate-determining may become to some extent a matter of convention. For example, we may define the *rds* as such a step that variation of exchange rate of the step in question will result in the variation by practically the same extent of the overall reaction rate. If this criterion should be accepted, the down-stream as well as the up-stream step may play the rate-determining role depending upon the value of $\theta_{H,eq}$.

In spite of this seemingly reasonable way of definition of the *rds*, it does not appear to be completely satisfactory. Consider the electrolytic hydrogen isotope separation factor, *eg*, in Route A. It may be a common understanding that the separation factor experimentally observed represents that of the *rds*. If two steps in Route A are both irreversible, *eg*, in the anodic region, we have $2v_{+1}=v_{+2}\gg v_{-1}, v_{-2}$. Then, the anodic separation factor is determined solely by that of step 1 and there should be no significant influence of that of step 2 because, v_{-1} being negligible, the isotopes that have passed through step 1 must eventually go to the final products.

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The separation factor in the anodic direction of step 2 will only exhibit such an influence that isotopic composition of H(a) is automatically adjusted so that the numbers of isotopes passed through step 1 per unit time become equal to those through step 2.

Quantitatively, the separation factor S_+ of the overall anodic reaction, eg, for protium/deuterium may be expressed as^{7,22)}

$$S_+ = s_{+1} \frac{s_{+2}/s_{-1} + r(\text{H})}{1 + r(\text{H})} \quad (53)$$

$$r(\text{H}) = v_{+2}(\text{H})/2v_{-1}(\text{H}) \quad (54)$$

where s_{+1} etc. represent separation factor in v_{+1} etc. and $v_{+2}(\text{H})$ etc. represent the partial step rate of v_{+2} for H alone, etc. It can be shown that $r(\text{H}) \equiv v_{+2}(\text{H})/2v_{-1}(\text{H}) \gg 1$ at high anodic overpotentials,⁷⁾ or we may expect $S_+ = s_{+1}$. It seems therefore more appropriate to say that step 1 is now rate-determining, although there may be a case in which the rate equation experiences stronger effects of step 2.

Comparison of the current-overpotential relations calculated above with those experimentally reported is of interest. Among various rate vs. overpotential relations depicted above, those obtained with Route A on the basis of the FRUMKIN-TEMKIN isotherm with relatively low $\theta_{\text{H,eq}}$ value generally well simulate observed behaviors of Ni,^{2,21)} Rh,²⁾ etc.. Others with high $\theta_{\text{H,eq}}$ (>0.5), with negative u , or those obtained on the basis of the LANGMUIR isotherm (except the cases of very low $\theta_{\text{H,eq}}$) and all of the Route B case are not in accordance with the general shape observed in experiments. It is therefore unlikely from experimental point of view that in those cases the $(1-\theta_{\text{H}})$ term has a decisive influence upon the reaction kinetics.

Thus, experimental current vs. overpotential relation on these metals reported in the literature could reasonably be simulated on the basis of Route A with low $\theta_{\text{H,eq}}$ values in terms of either FRUMKIN-TEMKIN or LANGMUIR adsorption model. On the other hand, it is true that, eg, on Rh and Pt, potential sweep experiments revealed that $\theta_{\text{H,eq}}$ should be close to unity in the potential range concerned.²³⁾ This might indicate^{9,10)} that surface coverage with hydrogen adatoms, at least that detected by means of an electrochemical technique, does not significantly impede the *her*.

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