

# Constant Correlation Factors between Temkin and Langmuir or Frumkin Adsorption Isotherms at Poly-Pt, Re, and Ni/Aqueous Electrolyte Interfaces

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## Abstract

The constant correlation factors between the Temkin and the Langmuir or the Frumkin adsorption isotherms of over-potentially deposited hydrogen (OPD H) for the cathodic H<sub>2</sub> evolution reaction (HER) at poly-Pt and Re/0.5 M H<sub>2</sub>SO<sub>4</sub> and poly-Ni/0.05 M KOH aqueous electrolyte interfaces have been experimentally and consistently found using the phase-shift method. At intermediate values of the fractional surface coverage ( $\theta$ ), *i.e.*,  $0.2 < \theta < 0.8$ , the Langmuir and Temkin adsorption isotherms of OPD H for the cathodic HER are correlated to each other even though the adsorption conditions or processes are different from each other. At the same range of  $\theta$ , correspondingly, the Frumkin and Temkin adsorption isotherms of OPD H for the cathodic HER are correlated to each other. The equilibrium constants ( $K_0$ ) for the Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) are consistently *ca.* 10 times greater than those ( $K$ ,  $K_0$ ) for the corresponding Langmuir or Frumkin adsorption isotherms ( $\theta$  vs.  $E$ ). The interaction parameters ( $g$ ) for the Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) are consistently *ca.* 4.6 greater than those ( $g$ ) for the corresponding Langmuir or Frumkin adsorption isotherms ( $\theta$  vs.  $E$ ). These numbers (10 times and 4.6) can be taken as constant correlation factors between the corresponding adsorption isotherms (Temkin, Langmuir, Frumkin) at the interfaces. The Temkin adsorption isotherm corresponding to the Langmuir or the Frumkin adsorption isotherm, and vice versa, can be effectively verified or confirmed using the constant correlation factors. Both the phase-shift method and constant correlation factors are useful and effective for determining or confirming the suitable adsorption isotherms (Temkin, Langmuir, Frumkin) of intermediates for sequential reactions in electrochemical systems.

**Keywords:** Constant correlation factors; Langmuir, Frumkin, and Temkin adsorption isotherms; Phase-shift method.

## 1. Introduction

In electrochemical systems, it is preferable to consider the adsorption isotherms (Langmuir, Frumkin, Temkin) of intermediates for sequential reactions rather than equations of the electrode kinetics and thermodynamics for intermediates, because the adsorption isotherms (Langmuir, Frumkin, Temkin) can be associated more directly with the atomic mechanisms of intermediate adsorptions.<sup>1-5)</sup> The adsorption isotherms (Langmuir, Frumkin, Temkin) are useful and effective for characterizing the relation, transition, and criterion between intermediates for sequential reactions, *e.g.*, under-potentially deposited hydrogen (UPD H) and over-potentially deposited hydrogen (OPD H) for the cathodic H<sub>2</sub> evolution reaction (HER), in electrochemical systems.<sup>6-8)</sup> Thus, there is a technological need for a fast, simple, and reliable technique to determine the suitable adsorption isotherms (Langmuir, Frumkin, Temkin) of intermediates for sequential reactions in

electrochemical systems.

Recently, we have experimentally and consistently found that the phase-shift method can be effectively used to determine the Langmuir or the Frumkin adsorption isotherms of UPD H and OPD H for the cathodic HER at noble and transition-metal/aqueous electrolyte interfaces.<sup>9-22)</sup> It appears that the phase-shift method, *i.e.*, a linear relationship between the behavior ( $-\phi$  vs.  $E$ ) of the phase shift ( $0^\circ \leq -\phi \leq 90^\circ$ ) for the optimum intermediate frequency and that ( $\theta$  vs.  $E$ ) of the fractional surface coverage ( $1 \geq \theta \geq 0$ ), is a useful and effective way to study the H adsorption sites and processes for the cathodic HER, the relation, transition, and criterion between UPD H and OPD H, the electrode kinetics and thermodynamics at these interfaces.

In this paper, we represent the constant correlation factors between the Temkin and the Langmuir or the Frumkin adsorption isotherms of OPD H for the cathodic HER at poly-Pt and Re/0.5 M H<sub>2</sub>SO<sub>4</sub> and poly-Ni/0.05 M KOH aqueous electrolyte interfaces using the phase-shift method. This aspect was overlooked or not well interpreted in our

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previously published papers.<sup>9-21)</sup> Both the phase-shift method and constant correlation factors are useful and effective for determining or estimating the suitable adsorption isotherms (Langmuir, Frumkin, Temkin) of intermediates for sequential reactions in electrochemical systems.

## 2. Experimental

### 2.1. The Phase-Shift Method

In electrochemical systems, the current-potential relationship is determined completely by the electrode potential ( $E$ ) dependence of the fractional surface coverage ( $\theta$ ) of intermediates. Thus, one can interpret that the electrode kinetic parameters for intermediates will depend on the corresponding adsorption isotherm ( $\theta$  vs.  $E$ ) of intermediates, which relates the surface concentration of intermediates to the bulk concentration of intermediates and to the electrode potential ( $E$ ).<sup>3)</sup>

A linear relationship between the behavior ( $-\phi$  vs.  $E$ ) of the phase shift ( $0^\circ \leq -\phi \leq 90^\circ$ ) for the optimum intermediate frequency and that ( $\theta$  vs.  $E$ ) of the fractional surface coverage ( $1 \geq \theta \geq 0$ ) of H (UPD H, OPD H) at noble and transition-metal /aqueous electrolyte interfaces has been suggested and verified or confirmed using cyclic voltammetric (CV), linear sweep voltammetric (LSV) or differential pulse voltammetric (DPV), and electrochemical impedance spectroscopic (EIS) techniques.<sup>13,14,20,21)</sup> The behavior ( $\theta$  vs.  $E$ ) of the fractional surface coverage ( $1 \geq \theta \geq 0$ ) of intermediates is well known as the electrochemical adsorption isotherm (Langmuir, Frumkin, Temkin). Note that the relation, transition, and criterion between UPD H and OPD H or the constant correlation factors between the corresponding adsorptions isotherms (Temkin, Langmuir, Frumkin) of H (UPD H, OPD H) cannot be effectively and consistently verified or confirmed using the other conventional methods.

### 2.2. Preparations

Taking into account  $H^+$  concentrations and effects of diffuse double layer and  $pH$ ,<sup>23)</sup> acidic and alkaline aqueous electrolytes were prepared from  $H_2SO_4$  (Sigma-Aldrich, reagent grade) and KOH (Alfa Aesar, reagent grade) with purified water (resistivity  $> 18 M\Omega cm$ ) obtained from a Millipore system. The 0.5 M  $H_2SO_4$  and 0.05 M KOH aqueous electrolytes were deaerated with 99.999% purified nitrogen gas for 20 min before the experiments.

A standard three-electrode configuration was employed using a saturated calomel electrode (SCE) reference electrode and a poly-Pt wire (Johnson Matthey, purity: 99.9985%, 1 mm diameter, estimated surface area *ca.* 1.01  $cm^2$ ), a poly-Re wire (Johnson Matthey, purity 99.97%, 1 mm diameter, estimated surface area *ca.* 0.96  $cm^2$ ), or a poly-Ni foil (Johnson Matthey, purity 99.994%, 0.5 mm thick, estimated surface area *ca.* 10.4  $cm^2$ ) working electrode. The poly-Pt and Re working electrodes were prepared by flame cleaning and then quenched and cooled in Millipore Milli-Q water and in air, sequentially. The poly-Ni working electrode was polished with alumina powder (0.3 and 0.05  $\mu m$ ) to a mirror-like finish and then was rinsed with the Millipore Milli-Q water

using an ultrasonic bath. A Pt wire (Alfa Aesar, purity: 99.95%, 1.5 mm diameter) was used as a counter electrode.

### 2.3. Measurements

The CV method was used to observe the UPD H peaks, which are useful and important for verifying the adsorption isotherm (Langmuir, Frumkin) of UPD H or OPD H at the interfaces. The DPV method was used to study the Tafel slopes at the interfaces. After the DPV experiments, the EIS method was used to study the relation between the phase-shift profile for the optimum intermediate frequency and the corresponding adsorption isotherm (Langmuir, Frumkin, Temkin) at the interfaces.

The CV and DPV experiments were sequentially performed using an EG&G PAR Model 273A potentiostat controlled with the PAR Model 270 software package. The EIS experiments were also sequentially performed using the same apparatus in conjunction with a Schlumberger SI 1255 HF Frequency Response Analyzer controlled with the PAR Model 388 or 398 software package. To obtain comparable and reproducible results, all measurements were carried out using the same preparations, procedures, and conditions at room temperature. The phase-shift method, experimental procedures, and data at the interfaces are described elsewhere.<sup>21)</sup>

## 3. Results and Discussion

We consider the constant correlation factors between the corresponding adsorption isotherms (Langmuir, Frumkin, Temkin) of OPD H for the cathodic HER at these interfaces as follows. First, we determine the Langmuir adsorption isotherm and then find the interaction parameter ( $g$ ) for the Frumkin adsorption isotherm based on the relevant experimental results, *e.g.*, the fractional surface coverage for the electrode potential, the phase-shift profile for the optimum intermediate frequency, *etc.* Finally, we derive and confirm the constant correlation factors between the Temkin and the Langmuir or the Frumkin adsorption isotherms.

### 3.1. Langmuir Adsorption Isotherm

The derivation of the practical form of the electrochemical adsorption isotherms (Langmuir, Frumkin, Temkin) of intermediates is described elsewhere.<sup>1-5)</sup> The Langmuir adsorption isotherm assumes that the electrode surface is homogeneous and that the lateral interaction effect is negligible. The practical form of the electrochemical Langmuir adsorption isotherm ( $\theta$  vs.  $E$ ) of H (UPD H, OPD H) for the cathodic HER can be expressed as:

$$[\theta/(1 - \theta)] = KC_H^+[\exp(-EF/RT)] \quad (1)$$

where  $\theta$  is the fractional surface coverage of H (UPD H, OPD H),  $K$  is the equilibrium constant for H (UPD H, OPD H),  $C_H^+$  is the  $H^+$  concentration in the bulk electrolyte,  $E$  is the electrode potential,  $F$  is the Faraday constant,  $R$  is the gas constant, and  $T$  is the absolute temperature. In Eq. (1),  $E$  is the actual electrode potential as measured against a stan-

dard reference electrode. In this paper, the standard reference electrode is a saturated calomel electrode (SCE). However, to clarify the hydrogen adsorption in the different aqueous electrolytes, all potentials are given in the reversible hydrogen electrode (RHE) scale.

Fig. 1 compares the experimentally determined Langmuir adsorption isotherm using the phase-shift method and the three numerically calculated Langmuir adsorption isotherms of OPD H for the cathodic HER at the poly-Pt/0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interface.<sup>22)</sup> Figs. 1A, B, and C show the three numerically calculated Langmuir adsorption isotherms ( $\theta$  vs.  $E$ ) corresponding to  $K = 1.3 \times 10^{-2}$ ,  $1.3 \times 10^{-4}$ , and  $1.3 \times 10^{-6}$ , respectively.

Fig. 2 compares the experimentally determined Langmuir adsorption isotherm using the phase-shift method and the

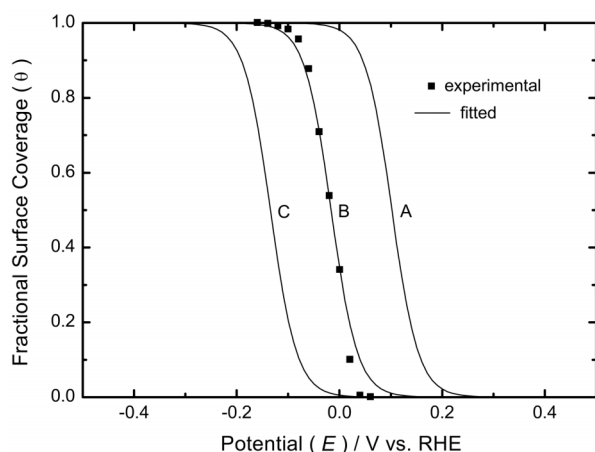


Fig. 1. Comparison of the experimentally determined Langmuir adsorption isotherm ( $\theta$  vs.  $E$ ) for  $K = 1.3 \times 10^{-4}$  and three numerically calculated Langmuir adsorption isotherms ( $\theta$  vs.  $E$ ) of OPD H for the cathodic HER at the poly-Pt/0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interface. (A)  $K = 1.3 \times 10^{-2}$ , (B)  $K = 1.3 \times 10^{-4}$ , and (C)  $K = 1.3 \times 10^{-6}$  (OPD H).

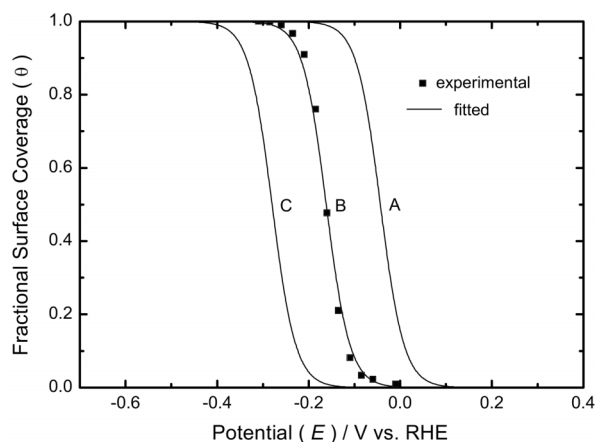


Fig. 2. Comparison of the experimentally determined Langmuir adsorption isotherm ( $\theta$  vs.  $E$ ) for  $K = 4.5 \times 10^{-7}$  and three numerically calculated Langmuir adsorption isotherms ( $\theta$  vs.  $E$ ) of OPD H for the cathodic HER at the poly-Re/0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interface. (A)  $K = 4.5 \times 10^{-5}$ , (B)  $K = 4.5 \times 10^{-7}$ , and (C)  $K = 4.5 \times 10^{-9}$  (OPD H).

three numerically calculated Langmuir adsorption isotherms of OPD H for the cathodic HER at the poly-Re/0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interface.<sup>21)</sup> Figs. 2A, B, and C show the three numerically calculated Langmuir adsorption isotherms ( $\theta$  vs.  $E$ ) corresponding to  $K = 4.5 \times 10^{-5}$ ,  $4.5 \times 10^{-7}$ , and  $4.5 \times 10^{-9}$ , respectively. As shown in Figs. 1 and 2, the Langmuir adsorption isotherm ( $\theta$  vs.  $E$ ) described in Eq. (1) is practically and definitively determined by the value of  $K$ . It has been experimentally and consistently verified or confirmed using the phase-shift method. The phase-shift method for determining the Langmuir adsorption isotherms of H (UPD H, OPD H) for the cathodic HER at noble metal (Pt, Ir, Au, Rh, Re, Pt-Rh alloy)/aqueous electrolyte interfaces is described elsewhere.<sup>10-12,14-22)</sup>

The shapes of the cyclic voltammograms of poly-Pt electrodes<sup>12,22)</sup> are similar to those of discal Pt(100) electrodes.<sup>11,24,25)</sup> Therefore, one can interpret that certain single-crystal faces dominate the poly-Pt electrode surfaces, and so the imperfection in the orientation and size of the same single-crystal face substrate is not practically serious for the Langmuir adsorption process. This implies that the surfaces of poly-Pt and Re electrodes can also be considered as homogeneous surfaces. In other words, as shown in Figs. 1 and 2, the Langmuir adsorption isotherm is applicable to the formation of OPD H at the poly-Pt and Re/0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interfaces. However, oxide layer formation or different single-crystal face substrates are serious considerations for the Langmuir adsorption process, and these should be considered inhomogeneous or heterogeneous surfaces. In this case, the Frumkin or the Temkin adsorption isotherm should be applied to the interfaces.

It is well known that UPD H and OPD H occupy different surface adsorption sites and act as two distinguishable electroadsorbed H species, while only OPD H can contribute to the cathodic HER.<sup>6-8)</sup> The Langmuir adsorption isotherm of H (UPD H, OPD H), *i.e.*, the equilibrium constant ( $K$ ) for H (UPD H, OPD H) described in Eq. (1), is useful and effective for characterizing the relation, transition, and criterion of UPD H and OPD H for the cathodic HER. For instance, the ranges of  $K$  for UPD H and OPD H at Pt electrode interfaces are *ca.* 1.9~2.7 and  $6.1 \times 10^{-6}$ ~ $2.1 \times 10^{-4}$ , respectively.<sup>11,12)</sup> Similarly, the ranges of  $K$  for UPD H and OPD H at Ir electrode interfaces are *ca.* 3.9 and  $9.9 \times 10^{-5}$ ~ $5.8 \times 10^{-4}$ , respectively.<sup>20)</sup> Note that the values of  $K$  for UPD H are much (*ca.*  $10^3$ ~ $10^5$  times) greater than those for OPD H. This implies that only OPD H can contribute to the cathodic HER. In other words, the absorption process of H for the cathodic HER at the interfaces depends strongly on UPD H.<sup>26)</sup> Consequently, one can interpret that the absorption of OPD H for the cathodic HER at the interfaces is negligible.

### 3.2. Frumkin Adsorption Isotherm

Considering an inhomogeneous electrode surface, the Frumkin or the Temkin adsorption isotherm should be applied to electrochemical systems. The Frumkin adsorption isotherm assumes that the electrode surface is inhomogeneous and that the lateral interaction effect is considerable.

The practical form of the electrochemical Frumkin adsorption isotherm ( $\theta$  vs.  $E$ ) of H (UPD H, OPD H) for the cathodic HER can be expressed as follows:

$$[\theta/(1 - \theta)] \exp(g\theta) = K_0 C_{H^+} [\exp(-EF/RT)] \quad (2)$$

$$g \equiv r/RT \quad (3)$$

$$K = K_0 \exp(-g\theta) \quad (4)$$

where  $g$  is the interaction parameter for the Frumkin adsorption isotherm,  $K_0$  is the equilibrium constant for H (UPD H, OPD H) at  $g = 0$ ,  $K$  is the equilibrium constant for H (UPD H, OPD H), and  $r$  is the rate of change of the standard free energy of H (UPD H, OPD H) with  $\theta$ , i.e.,  $0 \leq \theta \leq 1$ .

Fig. 3 compares the experimentally determined Frumkin adsorption isotherm using the phase-shift method and the three numerically calculated Frumkin adsorption isotherms of OPD H for the cathodic HER at the poly-Ni/0.05 M KOH aqueous electrolyte interface.<sup>13)</sup> Figs. 3A, B, and C show the three numerically calculated Frumkin adsorption isotherms ( $\theta$  vs.  $E$ ) corresponding to  $g = 0, 10$ , and  $20$  for  $K_0 = 0.13$ , respectively. As shown in Fig. 3, the Frumkin adsorption isotherm ( $\theta$  vs.  $E$ ) described in Eq. (2) is practically and definitively determined by the values of  $g$  and  $K_0$ . As  $g$  increases,  $\theta$  changes more slowly with  $E$ . For  $g = 10$  and  $K_0 = 0.13$  (Fig. 3B), using Eq. (4), the range of  $K$  is  $0.13 \geq K \geq 5.9 \times 10^{-6}$  with  $\theta$ , i.e.,  $0 \leq \theta \leq 1$ . Note that the Frumkin adsorption isotherm ( $\theta$  vs.  $E$ ) for  $g = 0$  and  $K_0 = 0.13$  (Fig. 3A) corresponds to the Langmuir adsorption isotherm ( $\theta$  vs.  $E$ ) for  $K = 0.13$ . By comparing Fig. 3B with Fig. 3A, one can interpret that the correlation between the Frumkin and the Langmuir adsorption isotherms is negligible. It has been experimentally and consistently verified or confirmed using the phase-shift method. The phase-shift method for determining the Frumkin adsorption isotherms of OPD H for the cathodic HER at noble and transition-metal (Pd, Ni)/aqueous electrolyte interfaces is described elsewhere.<sup>9,13)</sup>

### 3.3. Temkin Adsorption Isotherm

At intermediate values of  $\theta$ ,  $[\theta/(1 - \theta)]$  changes small with  $\theta$  compared to the changing of  $\exp(g\theta)$  in Eq. (2). Under the approximate conditions, the Temkin adsorption isotherm can be simply derived from the Frumkin adsorption isotherm described in Eq. (2). The practical form of the electrochemical Temkin adsorption isotherm ( $\theta$  vs.  $E$ ) of H (UPD H, OPD H) for the cathodic HER can be expressed as follows:

$$\exp(g\theta) = K_0 C_{H^+} [\exp(-EF/RT)] \quad (5)$$

Fig. 4 compares the experimentally determined Langmuir adsorption isotherm ( $\theta$  vs.  $E$ ) for  $K = 1.3 \times 10^{-4}$  (Fig. 1B) and the three numerically calculated Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) for  $K_0 = 1.3 \times 10^{-3}$  at the poly-Pt/0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interface. Figs. 4A, B, and C show, using Eq. (5), the three numerically calculated Temkin adsorption isotherms corresponding to  $g = 0, 4.6$ , and  $10$ ,

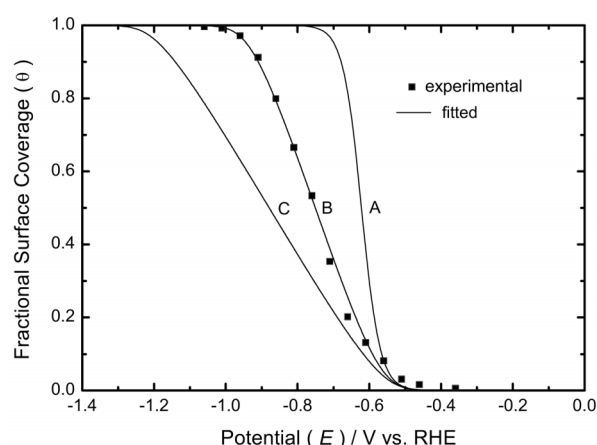


Fig. 3. Comparison of the experimentally determined Frumkin adsorption isotherm ( $\theta$  vs.  $E$ ) for  $g = 10$  and  $K_0 = 0.13$  and three numerically calculated Frumkin adsorption isotherms ( $\theta$  vs.  $E$ ) of OPD H for the cathodic HER at the poly-Ni/0.05 M KOH aqueous electrolyte interface. (A)  $g = 0$ , i.e., Langmuir adsorption isotherm, (B)  $g = 10$ , and (C)  $g = 20$  for  $K_0 = 0.13$ .

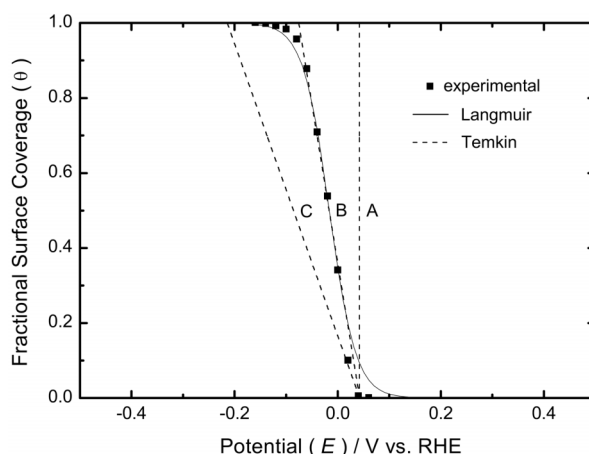


Fig. 4. Comparison of the experimentally determined Langmuir adsorption isotherm ( $\theta$  vs.  $E$ ) for  $K = 1.3 \times 10^{-4}$  (Fig. 1B) and three numerically calculated Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) for  $K_0 = 1.3 \times 10^{-3}$  at the poly-Pt/0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte interface. (A)  $g = 0$ , (B)  $g = 4.6$ , and (C)  $g = 10$  for  $K_0 = 1.3 \times 10^{-3}$  (OPD H).

respectively. For  $g = 4.6$  and  $K_0 = 1.3 \times 10^{-3}$  (Fig. 4B), using Eq. (4), the range of  $K$  is  $1.3 \times 10^{-3} \geq K \geq 1.3 \times 10^{-5}$  with  $\theta$ , i.e.,  $0 \leq \theta \leq 1$ . However, it should be noted that Fig. 4B shows a superposition or an overlapped region between the Langmuir and the Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) of OPD H at the range of  $\theta$ , ca.  $0.2 < \theta < 0.8$ . At  $0.2 < \theta < 0.8$ , using Eq. (4), the range of  $K$  is  $5.2 \times 10^{-4} > K > 3.3 \times 10^{-5}$ . At  $\theta = 0.5$ , it especially appears that the equilibrium constant ( $K = 1.3 \times 10^{-4}$ ) for the Temkin adsorption isotherm is the same as that ( $K = 1.3 \times 10^{-4}$ ) for the corresponding Langmuir adsorption isotherm. It is attributed to the rate of change of  $\theta$  vs.  $E$ , i.e.,  $\Delta\theta/\Delta E$  or  $d\theta/dE$ , which is maximized at  $\theta \approx 0.5$  and minimized at  $\theta \approx 0$  and  $1$ . The equilibrium constants ( $K$ ) for OPD H corresponding to the adsorption isotherms (Lang-

muir, Temkin, Frumkin) and  $\theta$  are summarized in Table 1.

Fig. 5 compares the experimentally determined Langmuir adsorption isotherm ( $\theta$  vs.  $E$ ) for  $K = 4.5 \times 10^{-7}$  (Fig. 2B) and the three numerically calculated Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) for  $K_0 = 4.5 \times 10^{-6}$  at the poly-Re/0.5 M  $\text{H}_2\text{SO}_4$  aqueous electrolyte interface. Figs. 5A, B, and C show, using Eq. (5), the three numerically calculated Temkin adsorption isotherms corresponding to  $g = 0, 4.6$ , and  $10$ , respectively. For  $g = 4.6$  and  $K_0 = 4.5 \times 10^{-6}$  (Fig. 5B), using Eq. (4), the range of  $K$  is  $4.5 \times 10^{-6} \geq K \geq 4.5 \times 10^{-8}$  with  $\theta$ , *i.e.*,  $0 \leq \theta \leq 1$ . Similarly, it should be noted that Fig. 5B also shows a superposition or an overlapped region between the Langmuir and the Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) of OPD H at the range of  $\theta$ , *ca.*  $0.2 < \theta < 0.8$ . At  $0.2 < \theta < 0.8$ , using Eq. (4), the range of  $K$  is  $1.8 \times 10^{-6} > K > 1.1 \times 10^{-7}$ . At  $\theta = 0.5$ , it especially appears that the equilibrium constant ( $K = 4.5 \times 10^{-7}$ ) for the Temkin adsorption isotherm is the same as that ( $K = 4.5 \times 10^{-7}$ ) for the corresponding Langmuir

adsorption isotherm. As stated above, it is attributed to the rate of change of  $\theta$  vs.  $E$ , *i.e.*,  $\Delta\theta/\Delta E$  or  $d\theta/dE$ , which is maximized at  $\theta \approx 0.5$  and minimized at  $\theta \approx 0$  and  $1$ . The equilibrium constants ( $K$ ) for OPD H corresponding to the adsorption isotherms (Langmuir, Temkin, Frumkin) and  $\theta$  are summarized in Table 2.

Fig. 6 compares the experimentally determined Frumkin adsorption isotherm ( $\theta$  vs.  $E$ ) for  $g = 10$  and  $K_0 = 0.13$  (Fig. 3B) and the three numerically calculated Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) for  $K_0 = 1.3$  at the poly-Ni/0.05 M KOH aqueous electrolyte interface. Figs. 6A, B, and C show, using Eq. (5), the three numerically calculated Temkin adsorption isotherms corresponding to  $g = 0, 14.6$ , and  $20$ , respectively. Under the Temkin adsorption conditions, as shown in Figs. 4-6,  $\theta$  changes linearly and more slowly with  $E$  than it does under the Langmuir adsorption conditions. For  $g = 14.6$  and  $K_0 = 1.3$  (Fig. 6B), using Eq. (4), the range of  $K$  is  $1.3 \geq K \geq 5.9 \times 10^{-7}$  with  $\theta$ , *i.e.*,  $0 \leq \theta \leq 1$ . However, it should be noted

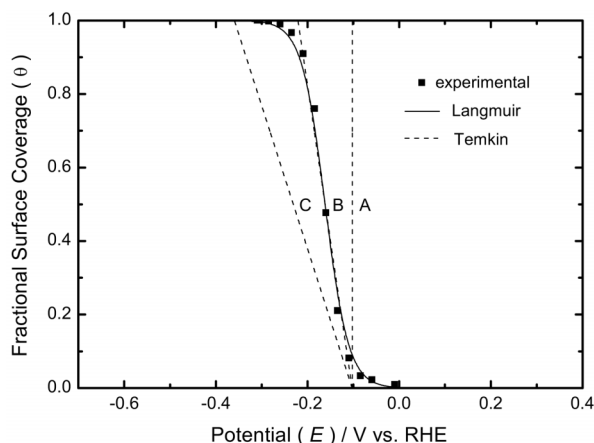


Fig. 5. Comparison of the experimentally determined Langmuir adsorption isotherm ( $\theta$  vs.  $E$ ) for  $K = 4.5 \times 10^{-7}$  (Fig. 2B) and three numerically calculated Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) for  $K_0 = 4.5 \times 10^{-6}$  at the poly-Re/0.5 M  $\text{H}_2\text{SO}_4$  aqueous electrolyte interface. (A)  $g = 0$ , (B)  $g = 4.6$ , and (C)  $g = 10$  for  $K_0 = 4.5 \times 10^{-6}$  (OPD H).

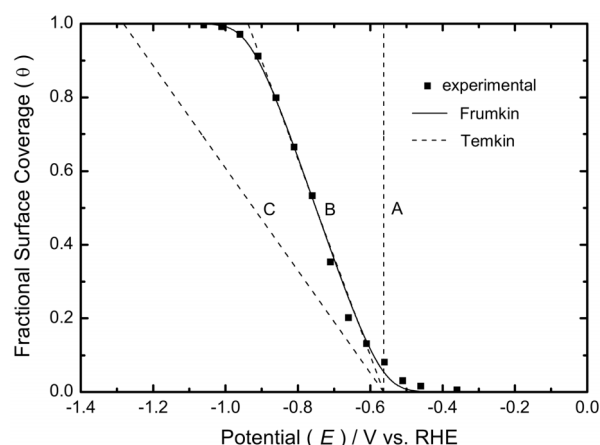


Fig. 6. Comparison of the experimentally determined Frumkin adsorption isotherm ( $\theta$  vs.  $E$ ) for  $g = 10$  and  $K_0 = 0.13$  (Fig. 3B) and three numerically calculated Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) for  $K_0 = 1.3$  at the poly-Ni/0.05 M KOH aqueous electrolyte interface. (A)  $g = 0$ , (B)  $g = 14.6$ , and (C)  $g = 20$  for  $K_0 = 1.3$  (OPD H).

Table 1. Comparison of the equilibrium constants ( $K$ ) for OPD H corresponding to the adsorption isotherms (Langmuir, Temkin, Frumkin) and fractional surface coverages ( $\theta$ ) at the poly-Pt/0.5 M  $\text{H}_2\text{SO}_4$  aqueous electrolyte interface.

Adsorption Isotherm	$K$	$K$	$K$
	$0 \leq \theta \leq 1$	$0.2 < \theta < 0.8$	$\theta = 0.5$
Langmuir ( $g = 0$ )	$1.3 \times 10^{-4}$	$1.3 \times 10^{-4}$	$1.3 \times 10^{-4}$
Temkin ( $g = 4.6$ )	$1.3 \times 10^{-3} \geq K \geq 1.3 \times 10^{-5}$	$5.2 \times 10^{-4} > K > 3.3 \times 10^{-5}$	$1.3 \times 10^{-4}$
Frumkin	-	-	-

Table 2. Comparison of the equilibrium constants ( $K$ ) for OPD H corresponding to the adsorption isotherms (Langmuir, Temkin, Frumkin) and fractional surface coverages ( $\theta$ ) at the poly-Re/0.5 M  $\text{H}_2\text{SO}_4$  aqueous electrolyte interface.

Adsorption Isotherm	$K$	$K$	$K$
	$0 \leq \theta \leq 1$	$0.2 < \theta < 0.8$	$\theta = 0.5$
Langmuir ( $g = 0$ )	$4.5 \times 10^{-7}$	$4.5 \times 10^{-7}$	$4.5 \times 10^{-7}$
Temkin ( $g = 4.6$ )	$4.5 \times 10^{-6} \geq K \geq 4.5 \times 10^{-8}$	$1.8 \times 10^{-6} > K > 1.1 \times 10^{-7}$	$4.5 \times 10^{-7}$
Frumkin	-	-	-

**Table 3. Comparison of the equilibrium constants ( $K$ ) for OPD H corresponding to the adsorption isotherms (Frumkin, Temkin, Langmuir) and fractional surface coverages ( $\theta$ ) at the poly-Ni/0.05 M KOH aqueous electrolyte interface.**

Adsorption Isotherm	$K$	$K$	$K$
	$0 \leq \theta \leq 1$	$0.2 < \theta < 0.8$	$\theta = 0.5$
Frumkin ( $g = 10$ )	$0.13 \geq K \geq 5.9 \times 10^{-6}$	$1.8 \times 10^{-2} > K > 4.4 \times 10^{-5}$	$8.8 \times 10^{-4}$
Temkin ( $g = 14.6$ )	$1.3 \geq K \geq 5.9 \times 10^{-7}$	$7.0 \times 10^{-2} > K > 1.1 \times 10^{-5}$	$8.8 \times 10^{-4}$
Langmuir	-	-	-

that Fig. 6B shows a superposition or an overlapped region between the Frumkin and the Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) of OPD H at the range of  $\theta$ , *ca.*  $0.2 < \theta < 0.8$ . At  $0.2 < \theta < 0.8$ , using Eq. (4), the range of  $K$  is  $7.0 \times 10^{-2} > K > 1.1 \times 10^{-5}$ . At  $\theta = 0.5$ , it especially appears that the equilibrium constant ( $K = 8.8 \times 10^{-4}$ ) for the Temkin adsorption isotherm is the same as that ( $K = 8.8 \times 10^{-4}$ ) for the corresponding Frumkin adsorption isotherm. The equilibrium constants ( $K$ ) for OPD H corresponding to the adsorption isotherms (Frumkin, Temkin, Langmuir) and  $\theta$  are summarized in Table 3.

#### 4. Conclusions

The Langmuir and Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) are correlated to each other even though the adsorption conditions or processes are different from each other. Correspondingly, the Frumkin and Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) are correlated to each other. The equilibrium constants ( $K_0$ ) for the Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) are consistently *ca.* 10 times greater than those ( $K$ ,  $K_0$ ) for the corresponding Langmuir or Frumkin adsorption isotherms ( $\theta$  vs.  $E$ ). Similarly, the interaction parameters ( $g$ ) for the Temkin adsorption isotherms ( $\theta$  vs.  $E$ ) are consistently *ca.* 4.6 greater than those ( $g$ ) for the corresponding Langmuir or Frumkin adsorption isotherms ( $\theta$  vs.  $E$ ). These numbers (10 times and 4.6) can be taken as constant correlation factors between the corresponding adsorption isotherms (Temkin, Langmuir, Frumkin) at the interfaces. The Temkin adsorption isotherm corresponding to the Langmuir or the Frumkin adsorption isotherm, and vice versa, can be effectively determined or confirmed using the constant correlation factors. This aspect was overlooked or not well interpreted in our previously published papers. The constant correlation factors can be experimentally and consistently determined or confirmed at the interfaces using the phase-shift method. Both the phase-shift method and constant correlation factors are useful and effective for determining or confirming the suitable adsorption isotherms (Temkin, Langmuir, Frumkin) of intermediates for sequential reactions in electrochemical systems.

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