Effects of Pretreatment of Platinum Surface on the Adsorption of Iodine from Aqueous Solutions

by

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Abstract

Three kinds of platinum surface, *i.e.* oxidized platinum surface, reduced platinum surface and partially reduced platinum surface were prepared to adsorb iodine from acidic aqueous potassium iodide solutions. It was found that the oxidized platinum surface adsorbed more iodine than both the reduced platinum surface and the partially reduced platinum surface under the same conditions studied.

When the adsorption temperature was raised increases in adsorption capacity and adsorption rate were observed for the oxidized platinum surface, but very little effect was observed for the reduced and the partially reduced platinum surface.

The effect of nitrogen on the adsorption of iodine onto platinum surface was also investigated.

Introduction

Controversial arguments have been postulated on the adsorption behavior of iodine onto platinum surface from aqueous solutions. Some workers reported that only a monolayer adsorption would be obtained when iodine was adsorbed on the reduced platinum surface¹⁾²⁾³⁾. Osteryoung *et al.* postulated that iodine but not iodide is adsorbed on platinum surface⁴⁾⁵⁾. Nevertheless, in a recent study the same authors reviewed their results and concluded that both iodine and iodide are adsorbed on platinum surface but only the iodine displays electrochemical activity in the vicinity of the reversible iodide-iodine potential⁶⁾. Schuldiner *et al.*⁷⁾ and others⁸⁾ have suggested that iodide is oxidized to iodine by sorbed oxygen in platinum and adsorbed on platinum surface. Although some additional work have been reported in the literature⁹⁾¹⁰⁾, it seems that much more work have to be done to understand the behavior of adsorption of iodine on platinum surface, which is suitable for carrierfree preparation of I-131²⁾.

The present work was carried out to study the effects of the pretreatment of platinum surface on the adsorption of iodine from dilute aqueous solution of iodide. The platinum surface was treated at various polarization potentials for different periods of time. The oxidized surface was also prepared by oxidizing agents for comparison. The effects of adsorption temperature on the capacity of adsorption and rate of adsorption were also studied. Finally, the influence of nitrogen atmosphere on the adsorption of iodine onto platinum surface was also investigated.

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Experimental

1. Material

Radiotracer: I-131 was used as tracer in this work, Carrier-free I-131 was obtained from the Radioisotope Laboratory of the National Tsing Hua University.

Potassium iodide solution: The C.P. grade potassium iodide was used to prepare the stock solution ($2.5 \times 10^{-6} M$), which was stored in a dark bottle and placed in a cool dark place.

Platinum: The platinum wire was made in spiral form and one of its ends was sealed into a glass tube. The diameter of the platinum wire was 1.1 mm and the length was 11.4 cm, in the result its apparent surface area was 3.9 cm^2 .

All the other chemicals used in this experiment were of C.P. grade and used without further purification.

2. Potentiostat and thermostat

The modified Lingane's constant potential device was used throughout this work. The sensitivity with respect to change in electrode potential was about 1 mV. and the instantaneous deviation from the control point was not more than $\pm 10 \text{ mV}$. A saturated calomel electrode was used as a reference electrode.

The temperature of adsorption was controlled within $\pm 0.1^\circ \text{C}$ using the Acme thermostat.

3. Pretreatment of platinum surface

(A) Cleaning of platinum surface: In order to obtain unique platinum surface for adsorption experiment the platinum spiral was subjected to the following cleaning process before pretreatment:

(1) The adsorbed iodine was desorbed by cathodic polarization in 0.1% sodium sulfite solution at -1.0 V vs S.C.E. for 30 minutes.

(2) The platinum spiral was then anodically polarized in $1N \text{ H}_2\text{SO}_4$ solution at 1.5 V vs S.C.E. for 1 minute.

(3) Finally, the platinum spiral was cathodically polarized in $1N \text{ H}_2\text{SO}_4$ solution at -0.7 V vs S.C.E. for 10 minutes. Step (2) was found to be very effective to remove trace of residual iodine on the platinum surface. This step is necessary, because the residual iodine is rather tightly adsorbed on the platinum surface and can not be removed even after treated by step (1) for several hours. Step (3) was used to remove any platinum oxide previously formed in step (2). The platinum surface cleaned by this process, though it might cause adsorption of hydrogen to some extent, was then used for further pretreatment as described below.

(B) Pretreatment of platinum surface by electrochemical method: The cleaned platinum surface was treated by anodic or cathodic polarization at room temperature, A 3.0 cm^2 platinum foil was used as an auxiliary electrode during each polarization.

(1) "Oxidized" platinum surface: The cleaned platinum surface was anodized in $1N \text{ H}_2\text{SO}_4$ solution at different potentials for different periods of time.

(2) "Reduced" platinum surface: The cleaned platinum surface was cathodized in $1N \text{ H}_2\text{SO}_4$ solution at different potentials for different periods of time.

(3) "Partially reduced" platinum surface: The cleaned platinum surface was anodized at $0.5 \sim 2.0 \text{ V vs S.C.E.}$ for 10 minutes and subsequently cathodized at -0.3 V

vs, S.C.E. for 2 minutes. The potential was chosen so that the electrode adsorb hydrogen at least extent according to Kolthoff and Tanaka¹¹⁾.

(C) Pretreatment by chemical method.: The oxidized platinum surface can also be prepared by chemical method. The cleaned platinum surface was dipped into the acidic solutions of strong oxidizing agents for predetermined time to make oxidized platinum surface as shown below¹¹⁾.

<u>Oxidizing agents</u>	<u>Time of dipping</u>
0.1N K ₂ Cr ₂ O ₇ in 1N H ₂ SO ₄	15 min.
0.1% KMnO ₄ in 1N H ₂ SO ₄	5 min.
0.1M Ce(SO ₄) ₂ in 0.5N H ₂ SO ₄	15 min.
0.1M Ce(SO ₄) ₂ in 0.5N H ₂ SO ₄	18 hours

4. General procedure for the adsorption measurements

(A) Adsorption of iodine in the aerated system. A 40 ml tube was used as the adsorption vessel which was placed in a water bath regulated at desired temperature by Acme thermostat. Twenty ml. of 2.5×10^{-6} M potassium iodide was placed in the adsorption vessel and a small amount of iodide form carrier-free I-131 was added as a tracer. The solution was then made 1N with respect to H₂SO₄. The pretreated platinum surface was dipped into the solution to adsorb the iodine. At predetermined time interval, the platinum was taken out, washed very thoroughly with distilled water*), and put into PVC tube for radioactivity measurement with NRD well type scintillation counter using NaI(Tl) crystal. The amount of iodine adsorbed on the platinum surface was estimated by the following formula.

$$I_{ad} = \frac{A_{ad}}{A_t} \times \frac{C}{S}$$

where

I_{ad} : Amount of iodine asorbed on the platinum surface per unit surface area.

A_{ad} : Radioactivity of iodine adsorbed on the platinum surface.

A_t : Total radioactivity of I-131 initially added to the potassium iodide solution.

S : Apparent surface area of platinum surface.

C : Initial concentration of potassium iodide in the solution.

(B) Adsorption of iodine under nitrogen atomosphere: A 30 ml glass vessel with a gas inlet and outlet was used as the adsorption vessel. Twenty ml of 2.5×10^{-6} M potassium iodide solution was placed in the vessel and a small amount of carrier-free I-131 was added as a tracer. After the solution was made 1N with respect to H₂SO₄, the oxygen free nitrogen gas was slowly bubbled through the solution for half an hour during the platinum spiral had been dipped into the solution for adsorption. Even each time when the platinum spiral was taken out for radioactivity measurement, the nitrogen gas was allowed to bubble through the solution to prevent redissolving of oxygen in the solution. The rest of the procedure was entirely the same as described before.

Results and Discussion

1. Adsorption of iodine onto oxidized platinum surface.

Effects of pretreatment anodic potential on the capacity and the rate of adsorption.

* It has been corformed that careful jet out of a washing bottle containing distilled water was enough to drive away radioactive iodide even from the site of glass seal of platinum wire.

Platinum surface treated with different anodic potentials (0.5~2V *vs.* S.C.E.) was used to adsorb iodine from $2.5 \times 10^{-6} M$ potassium iodide solution prepared in $1 N H_2SO_4$ at $25^\circ C$. The results are summarized in Fig. 1. It was observed that the higher the anodization potential used for pretreatment of the platinum surface, the higher the capacity of adsorption was obtained. This trend is rather straight forward, because it is generally believed that platinum oxide formed on the platinum surface by anodic polarization increases with the increase in anodic potential¹²⁻¹⁵.

Concerning the rate of adsorption, it is noteworthy to point out that the higher the

Fig. 1. Adsorption of iodine on oxidized *Pt* surface at $25^\circ C$. Anodization for 10 min; $\times$: 2.00V, Δ : 1.50V, $\circ$: 1.00V, ∇ : 0.50V.

Fig. 2. Adsorption of iodine at different temperatures on oxidized *Pt* surface pretreated with anodic potential at 2.00V *vs.* S.C.E. for 10 min. ∇ : $50^\circ C$, $\circ$: $45^\circ C$, Δ : $40^\circ C$, $\times$: $25^\circ C$.

pretreatment anodic potential for is applied to the platinum electrode, the slower is the rate of adsorption. This is probably due to the fact that the platinum oxide forms rather tight structure on treatment with high anodic potential or strong oxidizing agent¹⁵⁾¹⁶⁾ and that it is more difficult to interact with iodide.

Effect of temperature of adsorption on the capacity and the rate of adsorption.

Fig. 2 shows the effects of temperature of adsorption on the capacity and the rate of adsorption for the platinum surface anodized at 2.0V *vs.* S.C.E. for 10 minutes. It is clear that both the capacity and the rate of adsorption increase as the temperature of adsorption is raised from 25°C to 50°C. This may be due to the fact that the interaction between the iodide and platinum oxide are enhanced at higher temperatures. In an attempt to obtain more detailed informations the platinum surface pretreated with different anodic potentials (0.5 V-2.0V *vs.* S.C.E.) was used to adsorb iodine at 45°C, and the results are summarized in Fig. 3. By comparing Fig. 1 and Fig. 3, it is very interesting to note that both the rate and capacity of adsorption are sharply increased by raising the temperature of adsorption.

Fig. 3. Adsorption of iodine on oxidized Pt surface at 45°C. Anodization for 10 min.
○ : 2.00V, ▽ : 1.50V, △ : 1.00V, × : 0.50V.

Fig. 4. Adsorption of iodine on oxidized Pt surface at 45°C. Anodized at 2.00V *vs.* S.C.E. × : 5 min., ○ : 10min., △ : 20 min., ▽ : 60 min., ● : 300 min.

Effects of pretreatment time on the capacity of adsorption.

The platinum surface was anodized at 2.0V *vs.* S.C.E. for different period of time and used to study the effects of pretreatment time on the adsorption of iodine at 45°C. As is shown in Fig. 4, it was observed that highest adsorption capacity was obtained for the platinum surface pretreated for ten minutes. Longer period of pretreatment gives lower adsorption capacity. Fig. 5 shows the effects of temperature on the adsorption of iodine onto platinum surface pretreated for one hour at the anodic potential 2.0 V *vs.* S.C.E.. The difference in adsorption capacity at the temperature range 35°C~60°C was not significant. Thus the longer period of anodic polarization at high potential (2.0 V *vs.* S.C.E.) gives rather tight oxide structure as well as the constant amount of platinum oxide¹⁴⁾.

Fig. 5. Adsorption of iodine at different temperatures on oxidized *Pt* surface pretreated at 2.00V *vs* S.C.E. for 60 min. $\times$: 60°C, ∇ : 45°C, $\circ$: 35°C, $\triangle$: 25°C.

Fig. 6. Adsorption of iodine on chemically oxidized *Pt* surface at 45°C.

$\circ$: 0.1M $\text{Ce}(\text{SO}_4)_2$ in 0.5N H_2SO_4 for 18 hrs.
 $\triangle$: 0.1M $\text{Ce}(\text{SO}_4)_2$ in 0.5N H_2SO_4 for 15 min.
 ∇ : 0.1% KMnO_4 in 1N H_2SO_4 for 5 min.
 $\times$: 0.1M $\text{K}_2\text{Cr}_2\text{O}_7$ in 1N H_2SO_4 for 15 min.

Fig. 7. Adsorption of iodine on reduced *Pt* surface.

$\circ$: clean *Pt* surface at 45°C.
 $\triangle$: clean *Pt* surface at 25°C.
 $\times$: cathodized at -0.70V *vs* S.C.E. for 180 min., at 25°C.

Effects of pretreatment with different chemical oxidizing agents on the capacity of adsorption.

Platinum oxide can be formed on the platinum surface by chemical method¹¹⁾¹⁶⁾¹⁷⁾. Kolthoff and Tanaka¹¹⁾ have prepared platinum oxide with various oxidizing agents and measured the amount of platinum oxide by polarography. In this work

several strong oxidizing agents was selected to treat the platinum surface for the adsorption of iodine. The results are summarized in Fig. 6. It is found that the platinum surface treated with ceric sulfate for 18 hours in acidic solution gives the highest adsorption capacity. However, the platinum surface treated with oxidizing agent in general gives lower adsorption capacity than that treated by high anodic polarization.

2. Adsorption of iodine on reduced platinum surface

In order to compare the capacity of adsorption the reduced platinum surface was prepared by cathodic polarization under various conditions and used for adsorption of iodine. The results are summarized in Fig. 7. It can be seen in the Fig. 7 that the amount of iodine adsorbed by the reduced platinum surface is lower compared to the cleaned platinum surface.

The increase in the time of cathodic polarization shows no marked effect on the capacity of adsorption. Raising temperature of adsorption also has little effect on the capacity of adsorption, which trends are very much different from those of the oxidized platinum surface. The trend of negative effect for iodine adsorption can be seen by cathodization, which makes hydrogen to be adsorbed on the electrode surface.

3. Adsorption of iodine on the partially reduced platinum surface.

Fig. 8 shows the adsorption of iodine onto the partially reduced platinum surface pretreated by anodization at the potential range 0.5~2.0V *vs.* S.C.E. for 10 minutes and subsequently by cathodization at 0.3 V *vs.* S.C.E. for 2 minutes. It is apparent that the capacity of adsorption of the partially reduced platinum surface is slightly greater than that of reduced platinum surface. (cf. Fig. 7 and 8). Nevertheless, its rate of adsorption is much faster and reaches adsorption saturation almost within one hour. There is also no temperature effect on the capacity of adsorption.

4. Adsorption of iodine under the nitrogen atmosphere.

Both the reduced platinum surface and the oxidized platinum surface were used to adsorb the iodine from the $2.5 \times 10^{-6} M$ potassium iodide solution prepared in 1N H_2SO_4 at 25°C. The oxygen dissolved in the solution was expelled by bubbling through oxygen free nitrogen gas and the adsorption of iodine onto platinum surface was carried out under the nitrogen atmosphere throughout the whole experiment. As is shown in Fig. 9, both the capacity and the rate of adsorption for the reduced surface are decreased rather sharply compared to those of oxidized platinum surface. The capacity of adsorption of oxidized platinum surface obtained under the nitrogen atmosphere showed little difference from that of in the aerated system. (c.f. Fig. 1) It is interesting to point out that the adsorption of iodine on the platinum surface may be mainly dependent on the platinum oxide in sulfuric acid which functions as an oxidizing agent in the course of adsorption.

Fig. 8. Adsorption of iodine on partially reduced Pt surface.
 ○ : anodized at 2.00V, adsorption at 45°C.
 △ : anodized at 2.00V, adsorption at 25°C.
 ▽ : anodized at 1.50V, adsorption at 25°C.
 ● : anodized at 0.50V, adsorption at 25°C.

Fig. 9. Adsorption of iodine in the nitrogen gas atmosphere at 25°C.
 × : reduced *Pt* surface cathodized at $-0.70V$ vs S.C.E. for 180 min.
 ○ : oxidized *Pt* surface anodized at $1.00V$ vs S.C.E. for 10 min.
 △ : oxidized *Pt* surface anodized at $2.00V$ vs S.C.E. for 10 min.

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水溶液からヨウ素を吸着する白金表面の前処理効果

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太い白金線端をガラス管にシールし、 3.9cm^2 の面積上に、ヨウ化カリウムの硫酸酸性溶液からヨウ素が吸着する様子をしらべた。白金表面は、まづ一定の陰性、陽性の分極化によつて清浄にしたのち、なお所定の酸化、還元及び部分的還元処理を施した。酸化には、薬品による酸化処理の場合も比較の対象とした。吸着後の白金表面のヨウ素の分析は、 ^{131}I のガンマ線を用いシンチレーション計数によつて行つた。

一定時間、溶液中に浸漬してのち白金表面を水洗したとして、一般にヨウ素の吸着は酸化前処理白金においてでは、還元処理のものよりも多いことがわかつ

た。そして、吸着時の液温を上げると、吸着容量及び吸着速度は共に上るが、その程度も、酸化処理白金の場合に著しく、還元処理のものや部分的還元処理のものでは、ほとんど効果が見受けられなかつた。

なお吸着試験溶液に窒素を通じ、溶液酸素を追出したものについての試験も行つた。還元処理白金では脱気しない場合に比して著しく吸着量が減少し、酸化処理のものでは、さほどもなかつた。このことから、溶液酸素は吸着途上でもその酸化力によつて吸着を助けるものと考えられる。