

## Determination of Stability Constants Using Electrochemical Methods for the Complex Formation of Platinum and Palladium with Polyelectrolytes

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**Abstract** : The complexation of platinum and palladium with synthetic polyelectrolytes was studied.

The successive and overall stability constants of Pd(II) with PEI and 2PVP were obtained by potentiometric titration. Because of the slow equilibrium time, the potentiometric titrations were performed using the home-made automatic titrator in order to analyze the complexations according to the modified Bjerrum method.

The complex formation constant of Pt(IV) with 2PVP, measured by differential pulse polarography, was calculated from the peak currents that were obtained in non-complexing media and in solution containing 2PVP.

**Keywords** : Polyelectrolyte, Palladium, Platinum, Potentiometric Titration, Differential Pulse Polarography.

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### 1. Introduction

The isolation of the desired species from a mixture is a challenging and important step in analytical process. The separation methods using precipitation and complex formation are used widely because of high selectivity and recovery rate.

The synthesis and use of synthetic polyelectrolytes have grown rapidly in the last twenty years. This can be attributed to increasing awareness of the economic

benefits derivable from the use of these versatile molecules[1].

Our laboratory has intended to develop the method using polyelectrolytes for the recovery of metal ions from aqueous solution. For this purpose, the complex formation ability of polyelectrolyte for Pd(II) and Pt(IV) was investigated by potentiometric titration and differential pulse polarography.

## 2. Theory

### 2.1 Potentiometric Titration

Polymeric electrolytes, commonly called polyelectrolytes, are high polymer molecules having ionizable groups as part of their repeating unit. The systematic investigation of the physical chemistry of polyelectrolytes was initiated in the first of a series of important papers by Kern[2,3].

In general, the titration curves of the monobasic acids fit the well-known equation of Henderson-Hasselbalch.

$$pH = pK_a - \log \frac{1-\alpha}{\alpha} \quad (1)$$

However, Kern[4] and Katchalsky[5] experimentally found that in the case of polyelectrolytes the slope of the titration curve is larger than unity. Accordingly, the titration curves of the polyelectrolytes are empirically described by the modified Henderson-Hasselbalch equation.

$$pH = pK_a - n \log \frac{1-\alpha}{\alpha} \quad (2)$$

From his experiments, Kern tentatively concluded that  $n$  is an index of the intramolecular electrostatic interaction, being dependent upon the separation between ionized groups. The dependence of  $pK_a$  and  $n$  values on concentration, ionic strength, and structure was verified for typical polyelectrolytes by the later investigators.

It must be emphasized that the Kern-Katchalsky equation (eq. (2)) is strictly empirical. Actually the correction for the electrostatic contribution to the free energy of ionization should be additive. Hartley and Roe[6] obtained an equation for potentiometric titrations of colloidal systems, which implies the possibility of determining the electrostatic potential  $\psi$  at the surface of the polyelectrolyte.

$$pH = pK_a - \log \frac{1-\alpha}{\alpha} + 0.4343 \frac{e\psi}{kT} \quad (3)$$

Overbeek[7], and Katchalsky and Gillis[8] identified

$\psi$  with the differential of the electrostatic energy  $F_e$  of the ionized polyelectrolytes to  $v$  [9].

$$e\psi = \frac{\partial F_e}{\partial v} \quad (4)$$

$$F_e = \int \psi c_l dq \quad (5)$$

Since log-log plots are quite insensitive, it is possible to approximate the equation (3) with the equation (2), and thus introduce a very significant simplification in the empirical characterization of electrostatic interaction in the acid base behavior of polyacids[10].

The method used to calculate complexation constants from the pH data was based on the Bjerrum's method[11]. Gregor[12], Mandel and Leyte[13], and Scatchard[14] modified the Bjerrum's method considering the characteristic of polyelectrolytes.

The average number of ligands bound per metal ion present in all forms ( $\bar{n}$ ) is defined as

$$\bar{n} = \frac{[P]_t - [P] - [P \cdot H^+]}{[M]_t} \quad (6)$$

where  $[P]_t$  denotes the total unit concentration of the polyelectrolytes,  $[P]$  that of free P,  $[P \cdot H^+]$  that of the protonated P ion, and  $[M]_t$  that of the metal. In equation (6),  $[P \cdot H^+]$  can be determined by the following mass balance.

$$[P \cdot H^+] = [P]_t(1-\alpha) - [H^+] \quad (7)$$

In the case of simple acids,  $[P]$  is simply determined by the set of dissociation constants. In the case of a polyelectrolyte, however, the relation between  $[P \cdot H^+]$ ,  $[P]$  and  $[H^+]$  is less simple since it is governed by an almost continuously varying dissociation "constant". A relationship

$$K_a = K_0 \exp(-\Delta F_e / kT) \quad (8)$$

should hold where  $K_0$  is an intrinsic dissociation constant and  $\Delta F_e$  is the free energy change due to the displacement of the proton to infinity against the field of all charges on the molecule. For a constant polyelectrolyte and salt concentration, the term in equation (9) involving the free energy change should be a function of the degree of charging  $Z$  only.  $Z$  is

the ratio of charged to uncharged groups, *i. e.*,

$$Z = \frac{[P]_t - [P]}{[P]} \quad (9)$$

Therefore,

$$K_a = K_0 \cdot f(Z) \quad (10)$$

It has shown empirically that over a wide range of  $\alpha$ ,  $f(Z)$  can be expressed as  $(1/Z)^m$  where  $m$  is a constant[2,4,5]. In a simple titration  $[P]_t - [P] = [P \cdot H^+]$  and  $Z$  becomes  $[P \cdot H^+]/[P]$ . Equation (10) then takes the form

$$K_a = \frac{[H^+][P]}{[P \cdot H^+]} \left(\frac{1}{Z}\right)^m = [H^+] \left(\frac{[P]}{[P \cdot H^+]}\right)^n \quad (11)$$

where  $n = m + 1$ . Some theoretical justification for equation (11) has been provided by Katchalsky and Gillis[8].

It is now assumed that the occurrence of chelation does not in itself alter the dissociation relations of the acid, *i. e.*, that the first part of equation (11) still holds.

However,  $1/Z$  is now no longer equal to  $[P]/[P \cdot H^+]$ . Equation (11) will then take the form

$$K_a = \frac{[H^+][P]}{[P \cdot H^+]} \left(\frac{[P]}{[P]_t - [P]}\right)^{n-1} \quad (12)$$

The equation is then solved for the only unknown  $[P]$  through an iterative procedure. Values of  $[P \cdot H^+]$  and  $[P]$  are determined by equation (7) and (12), and  $\bar{n}$  can be obtained by introducing these values to equation (6). Plots of  $\bar{n}$  versus  $p[P]$  give a formation curve, from which a successive stability constant  $k_n$  is determined[11].

$$\log k_n = -\log [P]_{n=n-1/2}^- = p[P]_{n=n-1/2}^- \quad (13)$$

Thus, the overall stability constant  $\beta_N$  is given by

$$\beta_N = \prod_{n=1}^N k_n \quad (14)$$

## 2.2 DPP(Differential Pulse Polarography)

For voltammetric applications, the notion of the lability and inertness of complexes can be

envisaged[15].

In the case of an inert system, complex is not dissociated during measurement time and, does not contribute to the current.  $i_p^L$  is then a direct measure of the free metal ion remaining in solution and  $E_p^L = E_p$  (superscript L means the complexing media).

In the labile system, with  $D_{ML} = D_M$ , all complexes are dissociated and diffusion is not affected by ligand, since  $D_{ML} = D_M$ , so then  $i_p^L = i_p$ . However, contrary to the previous case  $\Delta E_p = E_p - E_p^L > 0$  and it is a measure of the thermodynamic stability of the complex.

For slowly dissociating complexes, an intermediate situation holds.

The complex formation reaction is expressed as follows.



For the inert complex,

$$k_d \ll \frac{DK[L]}{D_m \pi t_m} \quad (16)$$

This relationship has been discussed by Davidson[16] and van Leeuwen[17].

If the dissociation of the complex is so slow that it is negligible during the measurement time, the complex can be considered as a chemical species completely independent of the free metal ion. The shape of the polarogram for complexing media will then be the same as for a non-complexing media.

$$E_p = E_p^L \quad (17)$$

$$\frac{i_p^L}{i_p} = \frac{[M]}{[M]_i} = \frac{1}{\alpha} \quad (18)$$

Since the complex is not dissociated at the electrode, the condition  $[L]_0 = [L]$  will be realized even if  $[L]_t$  is not much larger than  $[M]_t$ . And measurement of  $\alpha$  by using equation (18) does not depend on the reversibility of the redox couple, since only the peak current,  $i_p$ , is used. The formation constant for the inert complex can be obtained from the peak currents

in non-complexing media and complexing media.

$$\frac{[ML]}{[M]} = \frac{i_p}{i_p^0} - 1 \quad (19)$$

In the aqueous solution, ligand L is bound with proton as well as the metal ion.

$$[L] = [L]_f \alpha_L \quad (20)$$

So,

$$K = \frac{[ML]}{[M][L]} = \left( \frac{i_p}{i_p^0} \right) \frac{1}{[L]_f \alpha_L} \quad (21)$$

$\alpha_L$  is calculated by Henderson-Hasselbalch equation.

### 3. Experimental

#### 3.1 Chemicals and Reagents

All polyelectrolytes were supplied from Polysciences, Inc., U.S.A.. The polyelectrolytes studied were polyethyleneimine[PEI] (M. W. = 10,000), poly(2-vinyl pyridine)[2PVP] (M. W. = 200,000), poly(4-vinyl pyridine)[4PVP] (M. W. = 300,000), poly(N-vinyl pyrrolidone)[PVPn] (M. W. = 40,000).

The platinum group metals, PdCl<sub>2</sub> (Inuishi Precious Metals Co., Ltd., Japan) and PtCl<sub>4</sub> (Aldrich Chemical Co., Inc., U.S.A.), were used as received. All other chemicals used in this work were AR grade. Mercury was purchased from Quicksilver. Deionized water was used throughout.

#### 3.2 Apparatus

It takes many hours for polyelectrolytes to equilibrate, because it get tangled in the solution. It often takes 24-48 hours to complete a titration. Therefore, an automatic titrator was prepared to save manual operations involved in titration.

An home-made automatic titrator consisted of a personal computer, a solenoid valve, a photo-counter, and a pH meter. The addition of the titrant is

controlled by the personal computer through the solenoid valve, and the photo-counter detects the amount of the titrant added which is saved in the personal computer. — When pH remains unchanged during the given time (30 minutes), the PC directs the signal to open the solenoid valve, and saves the pH value of the solution titrated.

I/O Board (Interface Card) was made up of two 8255 I/O element and the data acquisition board of ICL 7109 A/DC. The personal computer was a IBM compatible PC 286 AT. The pH meter was a model 801A (Orion, U.S.A.), and the glass electrode was a ROSS combination electrode model 81-03 (Orion, U.S.A.). The PTFE solenoid valve (cat. no. L-01367-70) of Cole Parmer, U.S.A., was used. This instrument was operated by C language.

A polarograph (EG&G PARC Model 174A) with a static mercury drop electrode (EG&G PARC Model 303A SMDE) and an X-Y recorder (Allen Datagraph Model 920E) were used for the polarographic measurements.

#### 3.3 Procedure

Polyelectrolyte, dissolved in a standard hydrochloric acid solution, was titrated by a sodium hydroxide solution while metal ion concentration is successively increased. The ionic strength was kept constant with a neutral salt, NaCl.

The mixture solution of Pt(IV) and 2PVP was fixed at pH 2.20 by hydrochloric acid and sodium hydroxide solutions. The ionic strength was kept constant with a neutral salt, NaCl. Polarograms were obtained from solutions of Pt(IV) in the absence and presence of 2PVP.

### 4. Results and Discussion

#### 4.1 Potentiometric Titrations

A potentiometric titration method was employed in order to determine complex formation constants of polyelectrolytes with Pd(II). Fig. 1 shows typical titration curves of PEI aqueous solution titrated with NaOH solution in the absence and presence of Pd(II) ions (PdCl<sub>2</sub>) at μ=1.0. As the metal ion concentration increased, the titration curves shifted downward due to the complex formation of Pd(II) ion with nitrogen atoms of PEI. As the metal ion concentration exceeds that for curve 4 of Fig. 1, the titration mixture began to precipitate.

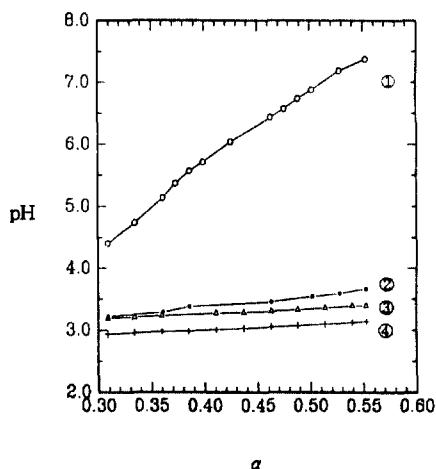


Fig. 1 Titration curves of PEI. [PEI] = 2.475 × 10<sup>-3</sup> M; 50.00 mL of μ=1.0 (NaCl) with 0.0159 M NaOH: ① no metal ion present ② [Pd<sup>2+</sup>] = 5.04 × 10<sup>-4</sup> M ③ [Pd<sup>2+</sup>] = 7.33 × 10<sup>-4</sup> M ④ [Pd<sup>2+</sup>] = 1.38 × 10<sup>-3</sup> M

Fig. 2 shows the so-called Henderson-Hasselbalch plots of the simple neutralization curve 1 of Fig. 1, whose equation is expressed as follows.

$$pH = pK_a - n \log \frac{1-\alpha}{\alpha}$$

The polyelectrolytes have two inflection points as observed in Fig. 2. This behaviors reflect the difference of the degree of chain flexibility with respect to the pH change. In the low pH range,

nitrogen atoms of PEI are protonated and the strong electrostatic repulsion among neighboring ammonium groups makes the chain rigid. However, the chain is flexible in the high pH range. Therefore, in Fig. 2 the slope of the curve(n) was changed because of the changed electrostatic interaction.

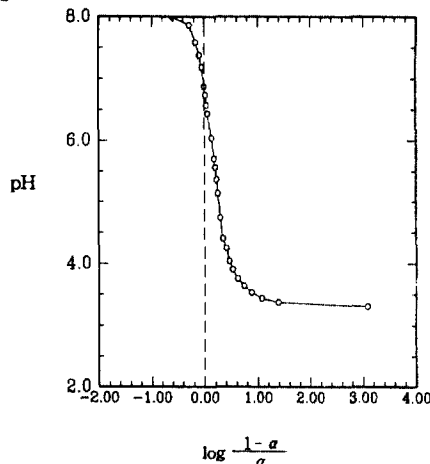


Fig. 2 Plots of pH vs log((1-α)/α) for 2.475 × 10<sup>-3</sup> M PEI (μ = 1.0 NaCl)

In the case of 2PVP, the same types of curves were shown.

Because 4PVP began to precipitate beyond the pH 4, titration cannot be continued. In the case of PVPn, the pH of the titration mixture did not change as the metal ion concentration increased. Therefore, it was considered that PVPn does not form the complex with Pd(II) ion at this condition.

The n values and pK<sub>a</sub>'s are listed in Table 1.

Table 1. The pK<sub>a</sub> and n Values of PEI, 2PVP, and PVPn

	PEI	2PVP	4PVP
pK <sub>a</sub>	6.86	4.23	2.92
n	6.80	2.19	1.74

From the results in Table 1, it is obvious that PEI (n=6.80) is a polyelectrolyte showing relatively strong interactions in neighboring ammonium groups on the

polyelectrolyte chain in comparison with 2PVP( $n=2.19$ ).

The complex formation constants of Pd(II) with PEI and 2PVP have been evaluated according to the modified Bjerrum's method[11,12]. The average number of ligands bound per metal ion present in all forms ( $\bar{n}$ ) is expressed as a function of the free ligand concentration to give the formation curve of the system (Fig. 3).  $\bar{n}$  is defined as

$$\bar{n} = \frac{[P]_t - [P] - [P \cdot H^+]}{[M]_t}$$

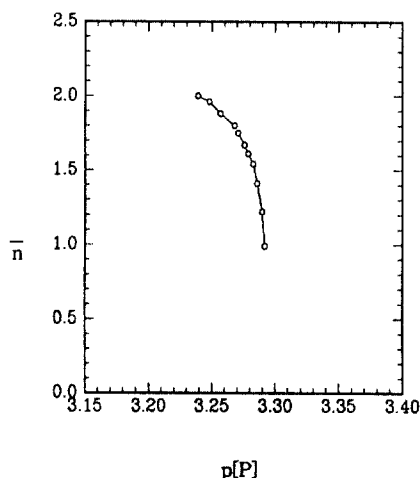


Fig. 3 Formation curve for PEI complex with Pd(II)

From Fig. 3, the successive complex formation constants  $k_n$  and overall complex formation constant  $\beta_n$  of the complexes of Pd(II) with PEI were determined. In the case of 2PVP, those constants were obtained by the same procedure.

Table II. Complex Formation Constants of PEI and 2PVP for Pd(II) at 25 °C with  $\mu=1.0$  (NaCl)

	$\log k_1$	$\log k_2$	$\log \beta$
PEI	3.29	3.28	6.57
2PVP	3.69	3.63	7.32

The complex formation constants of 2PVP are larger than those of PEI. This is probably due to the

enhanced flexibility of 2PVP, since it has coordinating nitrogen atoms linked to the side chain.

#### 4.2 DPP (Differential Pulse Polarography)

Because platinum forms inert complexes with nitrogen containing polyelectrolytes[11], the complexation constants of Pt(IV) with the polyelectrolytes cannot be determined by potentiometric titration. During titration of complexes, various reactions, e.g., acid-base equilibrium, dissociation of polyelectrolytes, and complex formation, etc., mutually affect each other. When equilibrium is disturbed by another addition of a titrant, the pH of the solution should be measured. However, due to the inertness of platinum complex, it takes a lot of time to reach equilibrium. Therefore, it takes many hours to complete a titration, and it is difficult to judge whether pH is at equilibrium. This makes data inaccurate. Consequently, the complexation of Pt(IV) with polyelectrolyte was studied by the differential pulse polarography(DPP).

In DPP, the sensitivity is increased relative to that attainable by linear sweep polarography because the sampling period is located at the end of the pulse, at which capacitive current is minimal.

The voltammetric signal resulting from the oxidation or reduction of an ion or compound may be influenced by all the solution chemical reactions that are involved. That is, when the metal ions formed complex with ligand, the position of the peak on potential axis and the peak current depend on the characteristics of the dissociation reaction. Interpretation of inert complex is easy. The degree of lability of a system is a relative notion which depends on the time interval,  $t_m$ , used to measure the voltammetric signal.  $t_m$  can be considered as the time allowed for the complex to diffuse to the electrode, to

dissociate and to be reduced during the signal recording period (e. g. during an DPP pulse). The rate of dissociation being independent of the time of measurement,  $t_m$ , the same system would be considered inert by a fast method (e. g. DPP) and labile (e. g. linear sweep polarography). Because the rate of diffusion is inversely proportional to  $t_m$ , the shorter  $t_m$  let the dissociation rate see slower relative to the diffusion. Therefore, DPP has been employed[15].

In the voltammetry, adsorption of compounds is an important factor that makes data inaccurate. Adsorption can be minimized by diminishing the preconditioning period as much as possible. This is possible in DPP by working at short preconditioning period. Therefore, life time of Hg drop was shortened. SMDE (static mercury drop electrode) was used, the scan rate was 10 mV/sec, and the purge time was 12 minutes.

In the DPP curve of Pt(IV) at pH 2.20, the catalytic hydrogen waves presumably arose by the decrease in the hydrogen overpotential on the active centers of metallic platinum group metals reduced and deposited on the surface of the mercury electrode[20]. So the peak current was considered as mixed current of the reduction of Pt(IV) and hydrogen catalytic current.

The calibration curve for Pt(IV) was made ( $i_p = [2.07 \times 10^6]C + 1.8 \mu A$ ; C = concentration of Pt(IV) at pH 2.20  $\mu=0.5$  NaCl). As the concentration Pt(IV) was increased to ca.  $7 \times 10^{-5}$  M or more, hydrogen gas bubbles were generated vigorously at the surface of the SMDE. The catalytic peak became irregular and was not reproducible at higher concentrations because of vigorous evolution of hydrogen bubbles at the surface of the SMDE.

Fig. 4 shows DPP curves of the mixture of Pt(IV) and 2PVP, increasing the concentration of 2PVP.

Sodium chloride was used as supporting

electrolyte. The chloride ion forms complex with Pt(IV). In general, the metal ion-ligand complex is reduced at more negative potential than the "free" metal ion. The 0.5 M of chloride eliminated interference by overlapping polarographic peaks of Pt(IV) and 2PVP.

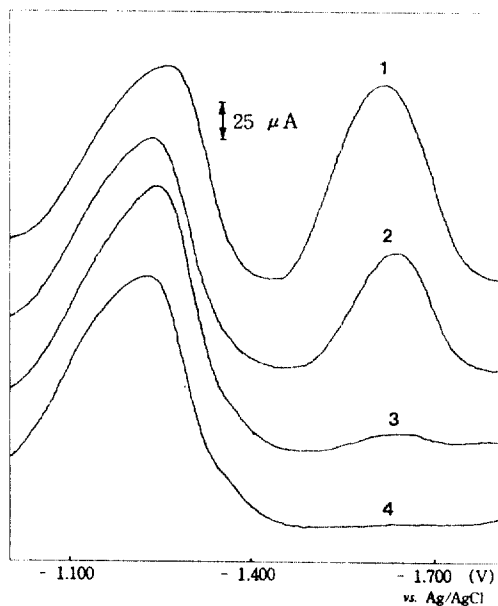


Fig. 4 DPP curves of Pt(IV) ( $[Pt^{4+}] = 9.00 \times 10^{-4}$  M) with (1)  $3.972 \times 10^{-3}$  M (2)  $7.532 \times 10^{-3}$  M (3)  $1.120 \times 10^{-3}$  M (4)  $1.495 \times 10^{-2}$  M of 2PVP; electrolyte, 0.5 M NaCl; drop time, 0.5 sec.; initial potential, -0.8 V; scan rate 10 V/sec; modulation amplitude, 50 mV; purge time, ca. 12 min.

The formation constant of Pt(IV)-2PVP complex is as follows.

Table III. The Formation Constant of Pt(IV)-2PVP Complex

$[Pt(IV)]_t$ (M)	$[2PVP]_t$ (M)	$i_p$ ( $\mu A$ )	$[Pt(IV)]$ (M)	$\log k_1$
$9.00 \times 10^{-4}$	$3.98 \times 10^{-3}$	130.00	$6.039 \times 10^{-5}$	4.52
	$7.53 \times 10^{-3}$	71.25	$3.338 \times 10^{-5}$	4.51
	$1.12 \times 10^{-2}$	11.25		
	$1.74 \times 10^{-2}$	0.00		

$\alpha_L$  was calculated by Henderson-Hasselbalch equation.

### Conclusions

The potentiometric titration using a home-made automatic titrator was performed to analyze the complexation of Pd(II) with polyelectrolytes. The complex formation constant of Pd(II) with 2PVP ( $\log \beta = 7.32$ ) was larger than that with PEI ( $\log \beta = 6.57$ ). This is probably due to the enhanced flexibility of 2PVP, since it has coordinating nitrogen atoms linked to the side chain.

In the case of Pt(IV), the complexation constants with the polyelectrolytes cannot be determined by potentiometric titration, because Pt(IV) forms inert complexes with the polyelectrolytes. In the polarography,  $\Delta E_p = E_p - E_p^L$  is a measure of the thermodynamic stability of the complex which may be a useful information in recovery of metal ions using membrane. The complex formation constant of Pt(IV) with 2PVP ( $\log k_1$ ) was 4.52.

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