

Recovery of Pd(II), Pt(IV), and Rh(III) Using Polyelectrolytes

You-Sean Lee[†], Hoosung Lee, and Koo-Soon Chung

Department of Chemistry, Sogang University, Seoul, 121-742, Korea.

[†]*Mass Spectrometry Group, Korea Basic Science Institute, Taejeon, Korea.*

Abstract : Two methods, precipitation and ultrafiltration, were applied in order to recover platinum group metals(PGM) by complexing them with water-soluble polyelectrolytes, e.g., polyethyleneimine [PEI], poly(2-vinylpyridine) [2-PVP], poly(4-vinylpyridine) [4-PVP], and poly(styrene sulfonic acid) [PSSA].

In the precipitation method, the PGM-polyelectrolyte complex that was formed by mixing first with polybase, e.g., 4-PVP at pH 1 was precipitated by further mixing with polyacid, e.g., PSSA. However, the recovery of PGM obtained by this method was not quantitative (less than 70%). The "sandwiching" binding between the metal anions and two polyelectrolytes was examined by X-ray photoelectron spectroscopy(XPS). The XPS studies indicated that the PGM atom was bound with the acidic and basic polyelectrolyte via its oxygen and nitrogen atom, respectively.

The recovery of PGM using polyelectrolyte was further studied by ultrafiltration method as follows : The PGM ions, complexed at pH 1 with polyelectrolyte, allowed the application of membrane filtration by virtue of the great differences in molecular weights between PGM and other low molecular weight species. By applying this method, Pd and Pt (ca. 10^{-4} M) were selectively separated almost quantitatively from coexisting metal ions, e.g., Cu^{2+} and Ni^{2+} . The EPR spectra and viscosity measurements indicated that these polyelectrolytes were not bound to Cu^{2+} and Ni^{2+} ions at this pH, which provided the basis for selective separation of PGM(Pd, Pt and Rh) from these coexisting ions.

Keywords : recovery of PGM, metal/polyelectrolyte complexes, ultrafiltration

1. Introduction

Mazzarelli[1] and Jellinek[2,3] reported that Rh, Cr, and Pd could be precipitated from solution anionic complexes of metals such as Au, Pt, Ru, by adding first polyethyleneimine followed by

polygalacturonic acid, "sandwiching" the metallic anions between the two polyelectrolytes.

Shkinev and Spivakov[4-7] suggested a new method for the preconcentration of metal ions in aqueous solution called liquid - phase polymer - based retention(LPR). This method is based on the ability of water-soluble polymeric reagents to form metal-polymer complexes and subsequent separation of these complexes from low molecular-weight species by membrane filtration. As a result, it can be shown that polyethyleneiminemethylthiourea(PTU) quantitatively retains several divalent metals such as Cu^{2+} , Hg^{2+} , Pt^{4+} , Pd^{2+} , Au^{3+} , Ag^+ from chloride solution at pH 1.

Use of chemically inert solid membranes makes it possible to achieve separations in the homogeneous phase, and these processes are easily handled and automated. To date, membrane separation processes such as ultrafiltration, reverse osmosis are becoming increasingly popular in industry.

The present work is concerned with the application of these techniques to the recovery of metallic anions, in particular, platinum group metals. The binding behaviors of various metals including PGM with polyelectrolytes were studied by EPR spectroscopy and viscosity measurements. In ultrafiltration method the factors which influenced the retention of the PGM and the basis for selective separation of the PGM from coexisting ions were discussed.

2. Experimental

2.1 Materials and reagents. Polyelectrolytes studied were poly(ethylencimine)[PEI], poly(2-vinylpyridine) [2-PVP], poly(4-vinylpyridine) [4-PVP], and poly(styrene sulfonic acid)[PSSA]. PEI, 2-PVP, 4-PVP, and PSSA were obtained from Polysciences Inc.. Platinum(IV) chloride (PtCl_4) was obtained from Fluka, and palladium(II) chloride (PdCl_2) from Inuicho Precious Metals. Rhodium(III)

chloride (RhCl_3) and ammonium hexachloroiridate (IV) [$(\text{NH}_4)_2\text{IrCl}_6$] were purchased from Strem Chemicals, cupric(II) chloride(CuCl_2) and nickel(II) chloride (NiCl_2) from Alfa Products. A sample of anode slime that obtained from an electrolytic copper refinery was used.

2.2 Infrared spectroscopy. Metal-polyelectrolyte complexes precipitated in the ratio of [polyelectrolyte]/[metal] = 1 were characterized by FT-IR. Infrared spectra were recorded on DIGILAB FT-80 spectrophotometer from BIO-RAD Inc. as KBr pellet.

2.3 Electronic spectroscopy. Soluble metal - polyelectrolyte complexes obtained in the ratio of [polyelectrolyte]/[metal] = 6 were investigated by electronic spectra. These spectra were recorded on Shimadzu Model UV-240 spectrophotometer.

2.4 Electron paramagnetic resonance spectroscopy. Copper chelate was obtained by mixing to molar ratio of 1/10 for Cu to polyelectrolyte. It was essential to maintain a low Cu^{2+} concentration in order to prevent the broadening of EPR lines by dipolar interaction. EPR spectra were measured with Bruker ER-200E spectrometer operating at 9.3GHz. Spectra at 77K were taken in a liquid nitrogen Dewar flask inserted in the EPR cavity.

2.5 X-ray photoelectron spectroscopy. The "sandwiching" binding between the metal anions and two polyelectrolytes was studied by X-ray photoelectron spectroscopy. XPS spectra were acquired with ESCA LAB MK II (VG SCIENTIFIC Ltd) spectrometer.

2.6 Viscosity behavior. The specific viscosity of the polymer solutions was measured with an Ostwald type viscometer at various pH values [24°C , $\mu = 1.0(\text{NaCl})$]

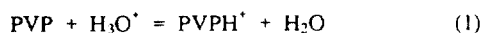
2.7 Precipitation method. When metal and

polyelectrolyte were mixed to molar ratio of 1/1 for metal to polyelectrolyte at pH 1, the gelatinous precipitates were obtained. The PGM complexes which were formed by adding first polybase, e.g., poly(4-vinylpyridine) at pH 1 were precipitated by the further addition of polyacid, e.g., poly(styrene sulfonic acid). These precipitates were filtered with sintered glass filter and the filtrate was analyzed for metal to examine the ratio of metal removal. Atomic absorption spectrophotometer (Varian Techtron Model 1200) was used to analyze the content of metal in the filtrate.

2.8 Ultrafiltration method. When metal and polyelectrolyte were mixed to molar ratio of 1/10 for metal to polyelectrolyte, metal-polyelectrolyte complexes were soluble. The sample solution was filtered using a ultrafiltration cell and PM 10 membrane filter(molecular weight cut-off 10,000 daltons, Amicon Co.), under 30 Psi N₂ pressure. The sample solution was continuously stirred during the filtration to prevent concentration polarization, gel formation and fouling. The filtrate was analyzed for metals to examine the ratio of metal retention using Atomic absorption spectrophotometer(Varian Techtron Model 1200) and ICP.

3. Result and discussion

3.1 Metals-polyelectrolytes binding. 2-PVP and 4-PVP are very weak polyelectrolyte with no hydrophilic chain. However, when dissolved by an acid, 2-PVP and 4-PVP are protonated according to equation (1).



At high pH where ionization decreases, the relative proportion of hydrophobic portion increases.[8] 2-PVP and 4-PVP precipitates at pH above 4.2.

The PGM was precipitated from solution by adding equal amount of 2-PVP at pH 1. However,

when the amount of 2-PVP was increased, the PGM did not precipitate by adding 2-PVP and the solution became transparent and viscous. It was assumed that PVP was bound to PGM ions in place of proton in equation (1), and the solubilities of metal-polyelectrolyte complexes were dependent upon the ratio of [polyelectrolyte]/[metal].

The binding between the PGM ions and 2-PVP was studied by infrared and electronic spectroscopy. The infrared spectra of PGM/2-PVP complex precipitated at pH 1 was compared to that of 2-PVP as shown in Fig. 1. The region of particular interest is that of the pyridine ring vibration. For the PGM/2-PVP complexes, vibrations at 1435 cm⁻¹ and 1574 cm⁻¹ decrease in intensity. A new band

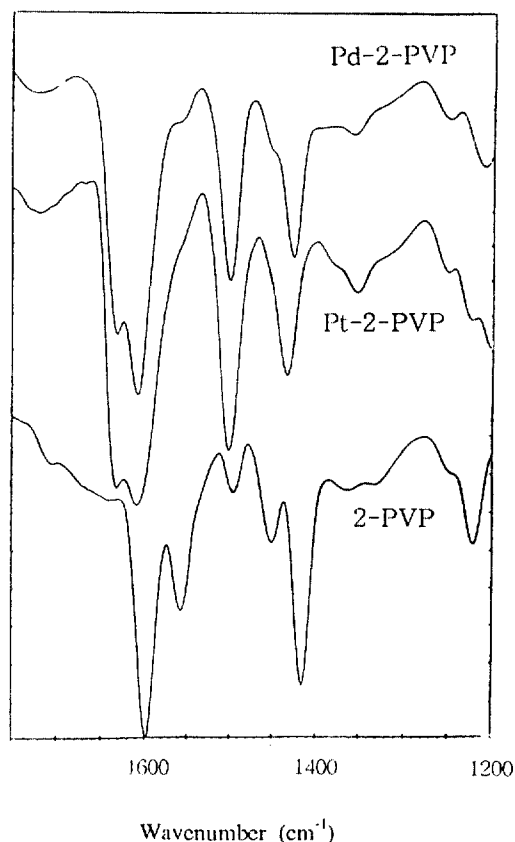


Fig. 1 FT-IR spectra of metal/2-PVP complexes in KBr pellet. Molar ratio [Metal]:[2-PVP] = 1:1.

at 1537 cm^{-1} may be attributed to quarterized pyridine ring vibration.[9,10] Shifting toward higher frequency of the band, which may be assigned to C=N stretching vibration is attributed to complex formation. These observations indicate coordination through the N atom of 2-PVP. The electronic spectra indicate Pd/4-PVP binding in the transparent and viscous PGM solution with 4-PVP (Fig. 2).

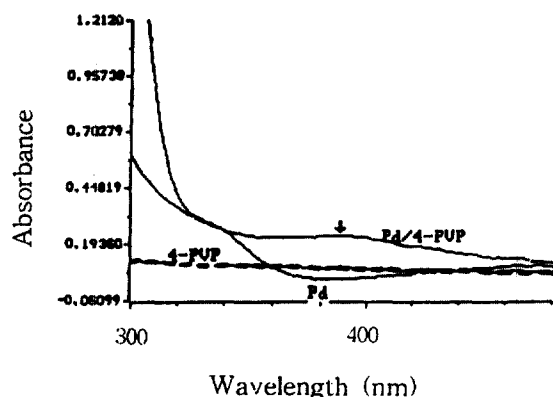


Fig. 2 UV-Visible spectrum of Pd/4-PVP complexes at pH 1.

Molar ratio [Pd]:[4-PVP] = 1:6

3.2 pH dependence of metals-polyelectrolytes binding. The stability constants of Table 1 [11] determined by potentiometric titration indicate that the binding between metal ions such as Cu and Ni and polyelectrolytes may be strong. However, these metals did not precipitate from solution by adding 2-PVP or 4-PVP at pH 1. These results suggest that metals-polyelectrolytes binding does not take place at this pH.

EPR spectra for CuCl_2 solution and sample solution mixed to molar ratio of 1/10 for Cu to polyelectrolytes at various pH are shown in Fig. 3. The range of values for the g and A values measured in this study is within the range expected for Cu^{2+} bonded to four ligands in an approximately

Table 1. Stability constants(β) of metal-polyelectrolyte complex formation.

	Log β				
	Pd	Ir	Rh	Cu	Ni
PEI	6.28	6.36	6.23	10.78	10.44
2-PVP	7.25	6.93	7.09	13.97	13.23
4-PVP	8.45	7.66	7.32		

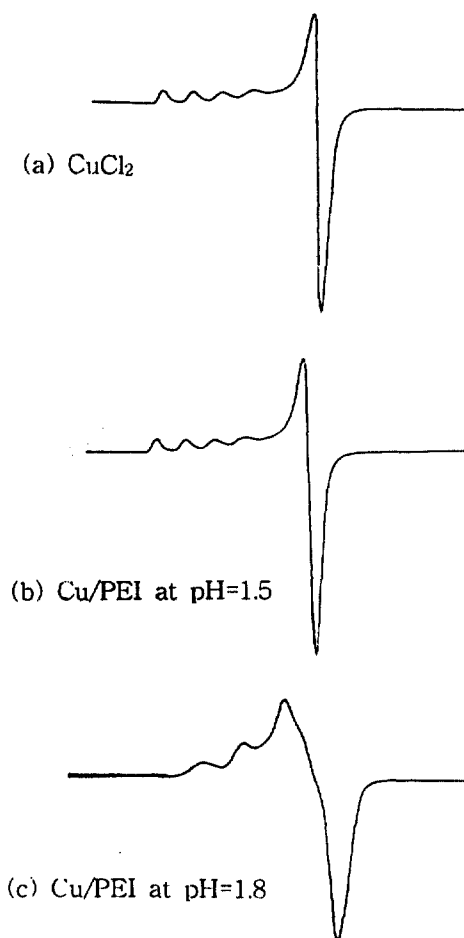


Fig. 3 EPR spectra of Cu/PEI complexes.

square-planar configuration[12]. The shape and position of the signal in Cu/PEI solution began to change at pH 1.8. In this case the signal due to the parallel orientation is somewhat shifted to the higher magnetic field and its fine structure constant A decreases. It may be said that the structure of CuCl_2 is probably distorted toward a tetrahedral structure [13,14]. In case of Cu/2-PVP and Cu/4-PVP solution only the shape of peak began to change at pH 2.6. These results indicate that Cu^{+2} ions begin to be bound to each polyelectrolytes at specific pH value.

A similar result was also obtained by viscosity measurements. The viscosities of 0.25 M 4-PVP solution and sample solutions mixed to molar ratio of 1/10 for metals to 4-PVP with various pH are plotted in Fig. 4. This figure shows that specific viscosity of 0.25 M 4-PVP solution increases sharply with addition of Cu^{+2} at pH 2.6 and Ni^{+2} at pH 4.0. This sharply increased specific viscosity demonstrates that Cu^{+2} and Ni^{+2} begin to bind to 4-PVP at pH 2.6 and pH 4.0, and the intermolecular chelations take place at narrow pH range[15-18].

3.3 Precipitation method. The complex of Pd(II) with each of several polybases, i.e., PEI, 2-PVP, 4-PVP can be precipitated, respectively by adding polyacid such as PSSA as shown in Table 2, but only about 29 to 71% of the Pd/polyelectrolyte complex at pH 3.2 is precipitated. By evaluating the precipitation ratios for various systems, simultaneous addition of both acidic and basic polyelectrolyte permits a better precipitation of metal ion compared with that obtained by either polyelectrolyte alone. This result may be attributable to the "sandwiching" complex of Pd ion and ligand i.e., the two polyelectrolytes.

The "sandwiching" binding of the metal anions and two polyelectrolytes was studied X-ray photoelectron spectroscopy.(Table3) The XPS spectra of the N(1s) and O(1s) transitions provide information about the electronic processes in these

complexes. The N(1s) transition of 4-PVP was found at 398.5 eV in this study whereas the N(1s) transition of pyridine was reported at 398.6 eV by Nolberg et al.[19] Upon complexation, this value

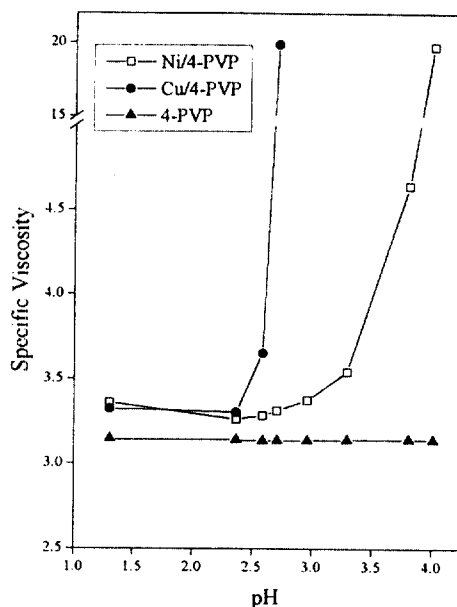


Fig. 4 pH-dependence of the specific viscosity of 0.25M 4-PVP solutions containing 0.025M metal ions in the presence of NaCl(1.0M) at 22°C.

Table 2. Percentage of Pd precipitated by various polyelectrolytes.

	Pd precipitated(%)	
	pH 1.0	pH 3.2
PEI	7.4	29.0
PEI + PSSA	34.2	48.6
2-PVP	26.4	47.2
2-PVP + PSSA	41.3	50.3
4-PVP	49.5	56.7
4-PVP + PSSA	64.8	71.2

Molar ratio [metal] : [polyelectrolyte] = 1 : 1
Concentration of metals, basic polyelectrolytes (PEI, 2-PVP, 4-PVP), and acid polyelectrolytes(PSSA) were 5×10^{-4} M, respectively.

Table 3. XPS results for various metal/poly-electrolyte complexes.

	N(1s)		O(1s)	
	BE(eV)	shift(eV)	BE(eV)	shift(eV)
4-PVP	398.6	0.0	-	-
Pd/4-PVP	399.7	1.1	-	-
Pt/4-PVP	400.5	1.9	-	-
Ir/4-PVP	401.0	2.4	-	-
PSSA	-	-	533.0	0.0
Pd/4-PVP/PSSA	399.4	0.8	531.3	-1.7
Pt/4-PVP/PSSA	400.7	2.1	530.9	-2.1

shifts to higher energies. The N(1s) transition is observed at 400.7 eV for the Pt/4-PVP/PSSA complex without an increase in peak width, indicating that partial charge transfer from the nitrogen lone pair to platinum has occurred.[10,20] This observation was also similar to that found in the case of the O(1s) transition. The O(1s) transition of PSSA was found at 533 eV whereas the O(1s) of Pt/4-PVP/PSSA was found at 530.9 eV. This chemical shift indicates that platinum is bound to not only polybase but also polyacid.

3.4 Ultrafiltration method. To avoid incorrect evaluations of the following results, preliminary experiments were performed to detect the retention of free species of metal ions and ligand. The retention of PGM ions occurred only when high pH's are reached and can be attributed to the precipitation of hydroxylated species. However, the retention of 2-PVP and 4-PVP occurred above 99.9%. Thus the concentration of PGM ions in the filtrate which was filtered through PM 10 membrane (molecular weight cut-off 1000 daltons) represents the concentration of free PGM ions.

Most membrane separators are not equilibrium process but rate process. The transfer of metal(M) across the membrane can be considered to result from three consecutive process, i.e., diffusion of complex ML, chemical dissociation of ML, and

transfer of free metal M across the membrane. The diffusion of ML in solution can be neglected because the sample solution was continuously stirred during the filtration in ultrafiltration. Under this condition, definition of labile and inert complexes depends on the value of k_c (chemical dissociation rate constant) relative to k_m (transfer across the membrane rate constant). Complexes are labile if J_w (flux of solvent) is small ($k_c \gg k_m$) and inert if J_w is large ($k_c \ll k_m$). [21] In the case of labile complex for constant J_w , as M is filtered, chemical equilibria may shift during the separation stage. As a result, it is possible that M exists in the filtrate under the condition in which free metals are absent.

The retention ratio of each metal investigated at various concentration ratio of polyelectrolyte to PGM is shown in Table 4. The retention of palladium and platinum occurs above 99.9 % at molar ratio of 3/1 for 4-PVP to metal. Nearly complete retention of these metal indicates that the complexes of these metal and 4-PVP is inert under the experimental conditions of 30 Psi N_2 pressure.

Sample solution in the molar ratio of 1/10 for metals to 4-PVP were ultrafiltered at various pH as shown in Fig. 5. Nearly complete retention of palladium and platinum occurred above pH 0.6. The retention of copper and nickel occurred only at pH values are 2.6 and 4. These observations are in accord with that estimated from EPR experiments and viscosity measurements. Thus, the PGM can be selectively separated from the coexisting metal cations, e.g., Cu^{2+} and Ni^{2+} ions under pH 2.5.

The amount of various metals in a sample of anode slime that obtained from an electrolytic copper refinery determined by ICP, and the retention ration(%) of metals by 4-PVP were investigated at pH 0.6.(Table 5) The retention ratio(%) of metals by 4-PVP were determined from amount of metals in filtrate and in retentate. The retentate with metals/4-PVP complexes and free 4-PVP by adding HNO_3 and H_2O_2 was treated with wet ashing for the elimination of 4-PVP, thus the amount of metals in retentate was determined by

ICP. As a result, trace amounts PGM and gold were selectively recovered by applying this method which permits pre-concentration of these metal from coexisting base metals. The recovery(%) of metals in retentate was not 100% for the loss of metals during preliminary treatment process.

Table 4. Retention(%) of various metals by 4-PVP.

[M]:[P] ratio	Retention(%) at pH = 1.2				
	Pd	Pt	Rh	Cu	Ni
1:1	58.21	53.65	-	0	0
1:3	99.9	99.9	-	0	0
1:5	99.9	99.9	23.4	0	0
1:10	99.9	99.9	32.5	0	0

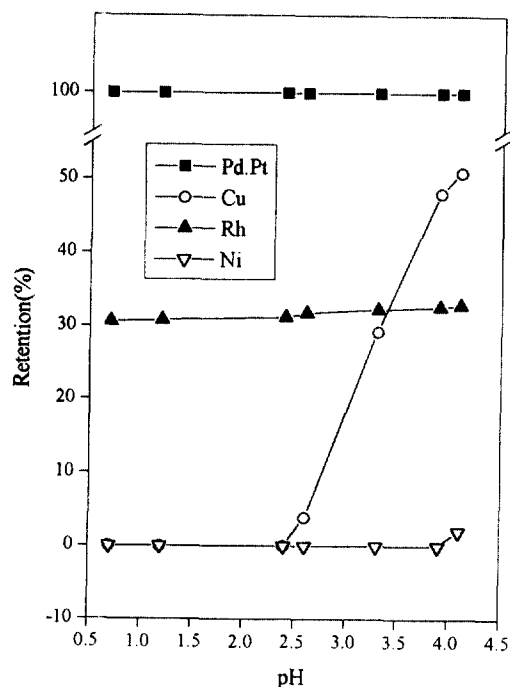


Fig. 5 Retention of metal ions by 4-PVP at different pH values.

Concentration of metals : 5×10^{-4} M.

Molar ratio [Metal]:[4-PVP] = 1 : 10.

Table 5. The recovery of PGM in an anode slime. (electrolytic copper refinery)

Metals	Sample* (mg)	Recovery	
		filtrate(%)	retentate(%)
Pd	0.3593	0.00	86.72
Pt	0.0388	0.00	92.90
Au	0.0494	0.00	93.21
Cu	0.0093	99.36	0.00
Fe	0.0081	100.7	0.00

Conc. of 4-PVP : 5×10^{-3} M

* 1.872g of anode slime in 1L of 0.2M HCl

4. Conclusions

The ultrafiltration method for the pre-concentration of trace metals shows the recovery ratio of PGM much higher than the precipitation method. Trace amounts PGM and gold in a sample of anode slime that obtained from an electrolytic copper refinery were selectively recovered by applying this method which permits pre-concentration of these metal from coexisting base metals, i.e., Cu and Ni under pH 2.5, because Cu^{+2} and Ni^{+2} begin to bind with 4-PVP at pH 2.6 and pH 4.0, respectively. Nearly complete retention (>99.9%) of Pd and Pt is due to the inertness of the complexes of these metals and 4-PVP under the present experimental conditions.

Acknowledgment

The authors are very grateful for the financial support from the Korea Science and Engineering Foundation (89-0312-04).

References

1. R. A. A. Muzzarelli, "Natural Chelating Polymers" Pergamon Press, Oxford, Chap. 6 (1973).

2. H. H. G. Jellinek and M. D. Luh, *J. Polymer Sci., A-1*, 2444 (1969).
3. H. H. G. Jellinek and S. P. Sangal, *Water Res.*, 6, 305 (1972).
4. K. E. Geckeler, V. M. Shkinev, and B. Ya. Spivakov, *Separation and Purification Methods*, 17(2), 105-140 (1988).
5. V. M. Shkinev, G. A. Vorob'eva, B. Ya. Spivakov, K. E. Geckeler, and E. Bayer, *Sep. Sci. Technol.*, 22, 2165 (1987).
6. V. M. Shkinev, V. M. Gomolitskii, B. Ya. Spivakov, K. E. Geckeler, and E. Bayer, *Talanta* 36(8), 861-863 (1989).
7. K. E. Geckeler, E. Bayer, B. Ya. Spivakov, V. M. Shkinev, and G. A. Vorob'eva, *Anal. Chim. Acta.*, 189, 285 (1986).
8. E. Selegny, M. Mandel and U. P. Strauss, " *Polyelectrolytes ; Charged and reactive Polymers* ", D. Reidel Press, Boston U. S. A., 195-205 (1972).
9. A. M. Lyons, M. J. Vasile, E. M. Pearce, and J. V. Waszczak, *Macromolecules*, 21(11), 3125 (1988).
10. L. A. Belfiore, A. T. N. Pires, Y. Wang, H. Graham, and E. Ueda, *Macromolecules*, 25, 1411-1419 (1992).
11. J. W. Park, thesis for M.Sc. degree, Sogang University, 1990.
12. S. Schlick, *Macromolecules*, 19, 192 (1986).
13. H. Nishikawa and E. Tsuchida, *J. Phys. Chem.* 79, 2072 (1975).
14. E. J. Goethals, " *Polymeric amines and ammonium salts* " Pergamon Press, 357-416 (1979).
15. J. W. Park, K. H. Choi, and K. K. Park, *Bull. Kor. Chem. Soc.*, 4(2), 68 (1983).
16. J. W. Park, M. O. Park and K. K. Park, *Bull. Kor. Chem. Soc.*, 5(3), 108 (1984).
17. S. Kobayashi, M. Tokunoh, T. Saegusa, and F. Mash, *Macromolecules*, 2357-2361 (1985).
18. S. Kobayashi, K. Hiroishi, M. Tokunoh, and T. Saegusa, *Macromolecules*, 20, 1496-1500 (1987).
19. R. Nordberg, et al., *Arkiv. Kemi.* 28, 257 (1968).
20. W. Liang, J. Lei and C. R. Martin, *Synthetic Metals*, 52, 227-239 (1992).
21. J. Buffle, " *Complexation reactions in aquatic systems : an analytical approach* " John Wiley & Sons, Chap. 10 (1988).