

Interpolyelectrolyte Complex of Poly(2-vinylpyridinium chloride) and Poly(sodium phosphate)

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ABSTRACT: A polyelectrolyte complex (PEC) was formed by mixing aqueous solutions of the polyanion poly(sodium phosphate) with the polycation poly(2-vinylpyridinium chloride). Conductometric and potentiometric titrations indicated the electrochemical end point of each titration. In all cases the end point occurred at a unit molar ratio of polyanionic to polycationic groups that was approximately one. The stoichiometry was also confirmed by analysis of the supernatant liquid in conjunction with the weights of the initial components and complex. An analysis showed that the starting materials were regenerated after dissolution of the complex with a 2M HCl solution. The interaction of the bivalent cupric ions with PEC were also investigated. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 3022–3028, 2002; DOI 10.1002/app.2332

Key words: poly(2-vinylpyridinium chloride); polyelectrolyte complex; poly(sodium phosphate); characterization

INTRODUCTION

Many interpolymer complexes are formed between two polymers containing interacting groups (e.g., cationic–anionic polymers or hydrogen-bond donor–acceptor polymers). The formation and structure of the polyelectrolyte complex (PEC) were shown to depend on several factors such as the chemical structures of both polymers, their chain lengths, and their environments such as the solvent and temperature.^{1–7} PEC formation between two oppositely charged polymeric molecules in solution was actively studied during the last three decades.⁸ The strong electrostatic interaction that exists between the two polyions leads to precipitation of the PEC from the solution. The nature of the precipitate can be varied easily by changing the composition of the complex. Knowledge of the compositions is important because it affects the nature and the properties of

the complex. There are many systems that can form interpolymer complexes, and they have already found wide applications in technology and medicine.²

The PECs involving poly(vinylpyridine) derivatives are interesting. There are some reports in the literature on the stoichiometry of PEC involving poly(vinylpyridine) as the polycation component.^{9–13} The molecular structure of the polycation is found to have an influence on the stoichiometry of the complexes. Poly(sodium phosphate) (PSP) is interesting because it is not an organic polymer and is, rather unusually, one of the few anionic polymers of the integral type.

The intention of this article is to investigate PEC formation and reaction stoichiometry upon mixing two polysalts in aqueous solution.

EXPERIMENTAL

Materials

Unquaternized poly(2-vinylpyridine) (P2VP) was purchased from Polyscience Ltd. This polybase

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was converted to the polysalt poly(2-vinylpyridinium chloride) (P2VPHCl) by the addition of a stoichiometric amount of standardized aqueous hydrochloric acid followed by evaporation and drying in a vacuum oven at 313 K. The degree of quaternization of 97% was yielded by both a gravimetric method and a volumetric procedure.¹⁴

The PSP was purchased from Aldrich Chemical Co. The measured value of the limiting viscosity number in 0.415M aqueous NaBr at 298 K ($2.60 \text{ dm}^3 \text{ kg}^{-1}$), in conjunction with the Mark-Houwink constants,¹⁵ gave a molecular weight of $2.77 \times 10^3 \text{ g mol}^{-1}$. All other materials were analytical grade and distilled deionized water was used.

Methods

Formation and Separation of PEC

Two series of PECs were prepared by mixing 0.30M PSP and P2VPHCl solutions; the molarity was in moles of monomer units per cubic decimeter. The mole fractions of phosphate units in the feed were 0.1, 0.3, 0.5, 0.7, and 0.9. In series 2 the order of addition was reversed. Before mixing the solutions were clear, but after mixing the precipitates formed immediately. After isolation of the precipitates by centrifugation, they were washed repeatedly with distilled water and dried to a constant mass *in vacuo* at 343 K.

UV Analysis of Supernatant Liquids

The supernatant liquid associated with each PEC from series 1 and series 2 was analyzed by a Shimadzu UV-160 A spectrometer. P2VPHCl has an absorbance peak at 263 nm ($\lambda_{\text{max}} = 263 \text{ nm}$), at which wavelength the PSP does not absorb. The absorbance of standard solutions of P2VPHCl, having concentrations between 10^{-4} and 10^{-5} M , was measured at this wavelength and was found to obey the Lambert-Beer Law, the extinction coefficient having a derived value of $319 \text{ m}^2 \text{ mol}^{-1}$.

The supernatant liquid and washings from each reaction were collected and made up to a known volume with distilled deionized water. It was possible to determine the PEC composition from the concentration of P2VPHCl detected in the supernatant liquids.

Characterization

Differential scanning calorimetry (DSC) measurements were made with a Perkin Elmer DSC 6 in-

strument. Indium and zinc standards were used to calibrate the temperature and thermal scale. The measurements to determine the glass-transition temperatures (T_g) were carried out in a N_2 atmosphere at a heating rate of $10^\circ \text{ min}^{-1}$. In order to avoid differences in thermal history, all the samples were subjected to the same thermal treatment.

The IR spectra were recorded on a Mattson 1000 FTIR spectrometer; 20 scans were signal averaged with a resolution of 4 cm^{-1} . Samples were prepared by dispersing the compounds in KBr and compressing the mixture to form disks.

Conductometric and Potentiometric Titrations

Conductometric titrations were performed using an ATI Orion model 162 conductivity meter, and pH measurements were made using a WTW pH 526 pH meter. The reactions were carried out by slow dropwise addition of titrant to the solution with rapid stirring. The solutions were maintained at constant temperature. The P2VPHCl salts are more acidic in aqueous solution than PSP, and because changes in pH during titration affect the conductance of the reaction mixture, it is expedient to measure the pH and conductance together.

Suppression of PEC Formation

Various volumes of standard aqueous NaCl solution were included in a fixed volume of standard aqueous P2VPHCl in order to visually assess whether or not the PEC precipitate was produced by subsequent addition of standard PSP.

Interaction between PEC and Cu(II)

The maximum loading capacity of PEC was investigated by using batch and column procedures. A Shimadzu UV-160A spectrometer was used to determine the concentration of Cu(II). A stock solution (267 mg/10 mL) of Cu(II) was made from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ has an absorbance peak at 806 nm ($\lambda_{\text{max}} = 806 \text{ nm}$). The absorbance of standard solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ having concentrations between 5×10^{-2} and $1 \times 10^{-3} \text{ M}$ was measured at this wavelength and found to obey the Lambert-Beer law, because the extinction coefficient had a derived value of $119 \text{ dm}^2 \text{ mol}^{-1}$. In the batch technique, 0.137 g of dried PEC (1:1) was dispersed in 5 mL of Cu(II) solution in a polyethylene vessel and shaken for 1–12 h. After shaking for 12 h the concentration of copper in the supernatant was directly determined by UV spectroscopy. The maximum

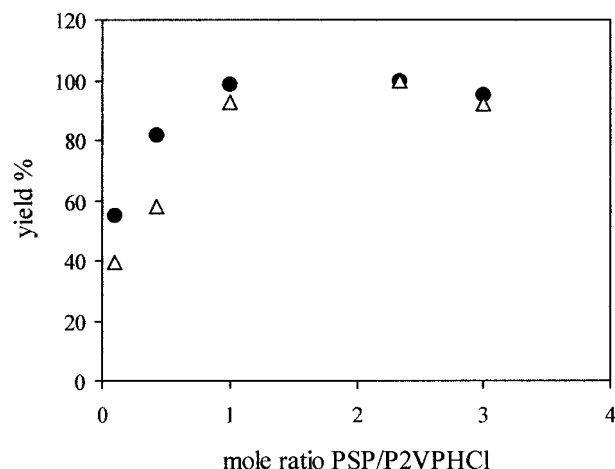


Figure 1 The relation between the complex yield and the mole ratio (PSP/P2VPHCl).

loading capacity of the PEC with respect to Cu(II) was calculated by using the Lambert–Beer Law. The loaded PEC was separated from the supernatant solution by filtration. The loaded PEC without treatment with any solvents was dried at 353 K, and the IR spectrum of the sample was recorded on a FTIR spectrometer. In the column technique a small polyethylene column (0.5-cm i.d., 5.0-cm height) was filled with 0.233 g of dried PEC (1:1). The sample was passed through the column. In the eluent the Cu(II) was determined by UV spectroscopy.

Breakdown of PEC

Ten milliliters of 2M HCl was added to 0.389 g of dried PEC (1:1), and the breakdown accompanied

by dissolution at room temperature was assessed visually. When dissolution did occur, the breakdown products were determined analytically.

RESULTS AND DISCUSSION

Gravimetric Analysis of PEC

It is known that interpolymer complexes, which are the reaction products of two oppositely charged polyelectrolytes combined through their Coulombic forces, can be obtained by mixing aqueous solutions of the component polymers. The PEC composition was determined by assuming that complete a stoichiometric reaction and total counterion release occurred. Figure 1 shows the precipitation yields of PEC formed by mixing the polyanion (PSP) solution with the polycation (P2VPHCl) solution. We can see that PEC is formed stoichiometrically. The excess of polymer does not take part in further formation of the complex. This situation does not depend on the order of addition.

UV Analysis of Supernatant Liquids

The PEC compositions determined from UV analysis of the supernatant liquids in series 2 are represented in Table I. The concentration of unreacted 2VPH⁺ was detected in the supernatant liquid and each PEC composition was obtained as follows using UV analysis: the weight of 2VPH⁺ units in the supernatant liquid was subtracted from the weight in the feed mixture to yield the weight of 2VPH⁺ present in the complex; and this

Table I PEC Compositions Determined from UV Analysis of Supernatant Liquids

Mole Ratio (PSP/P2VPHCl)	$m_{\text{PEC(weighed)}}$	m_{P2VPH^+}			m_{PSP} in PEC	χ_{P2VPH^+}
		In Supernatant	Initially	In PEC		
Series 1 PSP Titrant						
0.1	0.0188	0.2748	0.2866	0.0118	7.022×10^{-3}	0.556
0.3	0.0842	0.1664	0.2229	0.0565	0.0277	0.603
0.5	0.1690	0.0582	0.1592	0.1010	0.0680	0.525
0.7	0.1033	0.0291	0.0955	0.0664	0.0369	0.572
0.9	8.7×10^{-3}	0.0275	0.0318	4.3×10^{-3}	4.4×10^{-3}	0.421
Series 2 P2VPHCl Titrant						
0.1	0.0138	0.2782	0.2866	8.44×10^{-3}	5.36×10^{-3}	0.540
0.3	0.0607	0.1879	0.2229	0.0350	0.0257	0.504
0.5	0.1614	0.0631	0.1592	0.0961	0.0653	0.522
0.7	0.1047	0.0313	0.0955	0.0642	0.0404	0.542
0.9	0.0117	0.0252	0.0318	6.62×10^{-3}	5.08×10^{-3}	0.492

weight was subtracted from the actual weight of the PEC (W_a) to provide the mass of phosphate units present in the precipitate, allowing the mole fraction of 2VPH^+ ($X_{2\text{VPH}}$) in PEC to be determined. Table I shows that the composition of PEC is independent of the order of addition, and for all feed mixtures the reaction stoichiometry is very close to 1:1. The slight departures from the 1:1 stoichiometry are probably due to the errors associated with transference losses. In the present work the average value of the ratio of cationic to anionic groups in the complex is 1.12.

Characterization

The DSC method was used to obtain values of 395 and 540 K¹⁵ for the glass-transition temperatures of P2VPHCl and PSP, respectively. The measured value of the T_g for the complex (1:1) was 405 K. The T_g of the complex was lower than the weight-averaged value of the component polyelectrolytes.

MacKnight et al. investigated the interaction between the acid form of sulfonated polystyrene and poly(ethyl acrylate-co-4-vinylpyridine) by FTIR.¹⁶ They explained that pyridine ring vibration modes shift to a higher wavenumber upon the formation of the complex. It is known that P2VP has a pyridine ring vibration mode at 1591 cm^{-1} . The peak at 1632 cm^{-1} is attributed to the ring-stretching mode of the pyridinium cation.^{17,18} Figure 2 shows the spectra of PSP, P2VPHCl, and PEC. The spectrum of PSP (Fig. 2, spectrum a) is characterized by the following bands: the bands at 1298 and 1196 cm^{-1} can be assigned to asymmetric stretching vibrations of PO_2 . The bands at 1170 and 1093 cm^{-1} can be attributed to symmetric stretching vibrations of PO_2 . The bands observed at 887 or 759 and 528 cm^{-1} are attributed to asymmetric stretching vibrations and symmetric stretching vibrations of P-O-P, respectively.¹⁹ In spectrum b in Figure 2 the bands at 1632 and 1555 cm^{-1} can be assigned to a ring stretching vibration of the pyridinium cation. Spectrum c in Figure 2 is that of PEC. The main spectral features of PEC are as follows:

1. the presence of pyridinium cation ring stretching vibrations at 1632 and 1555 cm^{-1} ; PO_2 symmetric stretching vibration modes at 1170 and 1093 cm^{-1} ; asymmetric stretching vibration modes of P—O—P at 887, 759, and 728 cm^{-1} .
2. the disappearance of asymmetric stretching vibration modes of PO_2 at 1298 cm^{-1} .

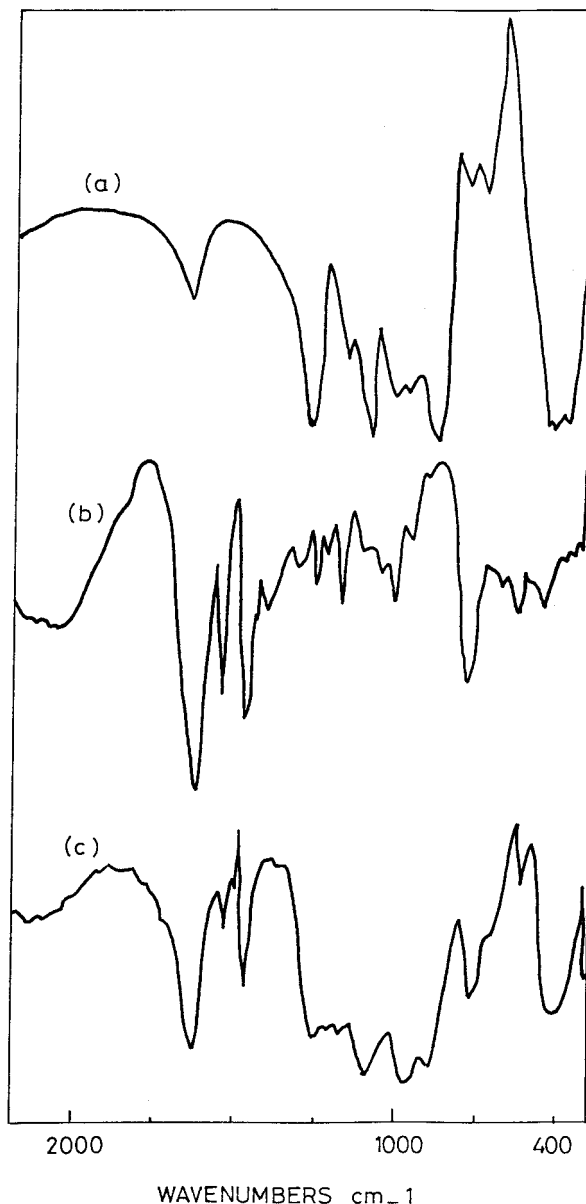


Figure 2 The IR spectra of PSP (spectrum a), P2VPHCl (spectrum b), and PEC (spectrum c).

These points suggest the existence of an intermolecular association between the two constituent polymers.

Conductometric and Potentiometric Titrations

The use of conductance measurements to examine the reaction between oppositely charged polyions depends on the change in concentration of species of different equivalent conductances. Conductometric titration techniques were used by other workers to investigate the stoichiometry of PEC

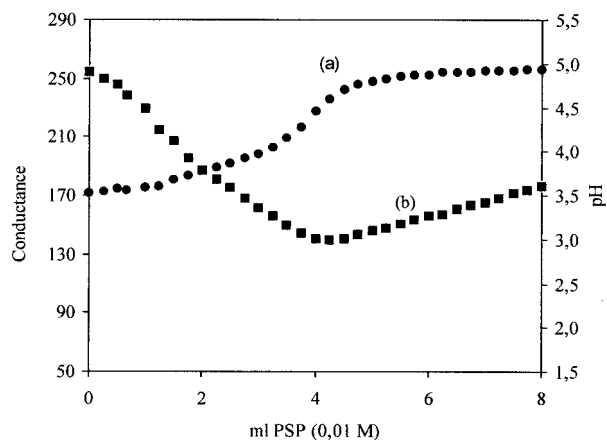


Figure 3 Potentiometric (curve a) and conductometric (curve b) titrations of 35 mL of 1×10^{-3} M P2VPHCl with 1×10^{-2} M PSP.

formation between polyelectrolytes.^{20–22} Tsuchida et al. showed that, in titrations between two polysalts, the conductance rises at a constant rate to the end point because of the release of small mobile counterions into solution. After the end point there is no further release of counterions and the excess of titrant comprises polyelectrolyte. Hence, the resultant rise in conductance becomes less rapid. Therefore, the end point of the reaction is clearly observed as an inflexion point on the conductance curve and the ratio of anionic to cationic units may be calculated.^{21,22}

Incremental Addition of PSP to P2VPHCl

Figure 3 shows the results of conductometric and potentiometric titrations for the addition of 1×10^{-2} M PSP to 35 mL of 1×10^{-3} M P2VPHCl. There were a few features of note. The conductance falls until the end point; after the end point the conductance begins to rise. The pH of the solution rises steadily during titration, and the pH rises more quickly in the region of end point. The plot shows that the end point occurs at a unit mole ratio 1.14 ± 0.03 .²³ P2VPHCl is a salt of a weak base and a strong acid; the initial pH of a 1×10^{-3} M P2VPHCl solution would be expected to be smaller than 7. In fact, the value is 3.53. At pH 3.53 not all of the 2VP will be ionized to $2VPH^+$ sites because the pK_a value of P2VP is 4.4.²⁴ Ionized 2VP units are unable to participate in Coulombic interaction with anionic phosphate moieties. Consequently, as the titration proceeds, PEC is formed with some of the 2VP groups present in the unionized form. However, the in-

teraction between the ionized $2VPH^+$ and polyphosphate present in the complex lowers the positive charge density around the unionized 2VP units, which in turn facilitates the ionization of 2VP groups. This ionization occurs, causing H^+ from the solution to be consumed; the pH of the solution rises and, because the conductivity of H^+ ions is at least 3 times greater than that of the counterions released into solution, the conductance of the solution falls. The end point of this titration is observed when the complexation between PSP and P2VPHCl is complete. After the end point, the pH and the conductance of the solution rise because of the excess PSP.

Incremental Addition of P2VPHCl to PSP

Figure 4 presents the potentiometric and conductometric titration curves when 1×10^{-2} M P2VPHCl is added to 35 mL of 1×10^{-3} M PSP. The following features are notable: the conductance rises steadily until the end point is reached, after which the conductance rises more quickly; and the pH falls rapidly near the end point. At the start of the experiment the pH of the 1×10^{-3} M PSP solution is 5.79, and the pH of 1×10^{-3} M P2VPHCl is 3.53; therefore, the P2VPHCl solution is more acidic than the PSP solution. The addition of P2VPHCl to the PSP solution results in the formation of PEC and a decrease in the pH of the solution. This decrease in the pH can only be due to the release of H^+ ions into the solution,

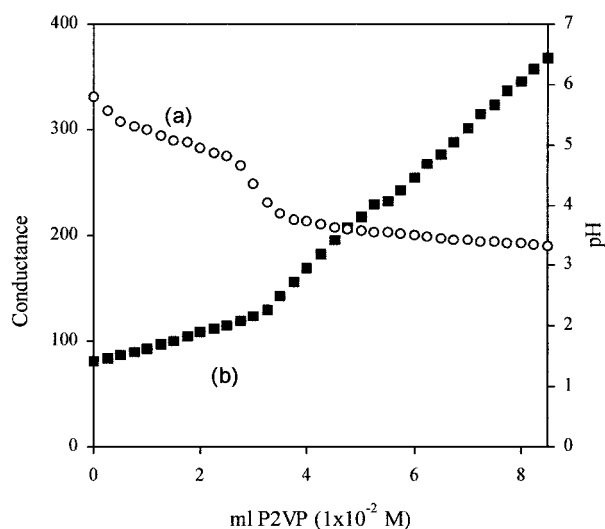


Figure 4 Potentiometric (curve a) and conductometric (curve b) titrations of 35 mL of 1×10^{-3} M PSP with 1×10^{-2} M P2VPHCl.

which were previously associated with 2VP sites in the titrant. The end points occur at a unit molar ratio of 1.17 ± 0.02 . After the end point the addition of excess titrant causes the pH of the solution to fall and the conductance of the solution to increase.

Breakdown and Suppression of PEC Formation

An attempt to suppress PEC formation was made using NaCl. In PEC formation the NaCl is eliminated. The role of added NaCl is to suppress PEC formation by the common ion effect. Additionally, although the precursors are dissociated, masking of their charges by NaCl reduces the interaction between the polyelectrolytes. With regard to suppression of PEC formation, the solutions each comprised 2 mL of 0.2M aqueous precursors. The concentration of aqueous NaCl contained within the aqueous P2VPHCl was 4.7M and the volumes of NaCl solution used were 1.0, 1.5, 2.0, and 2.5 mL. Precipitate formation was observed when the volume of the NaCl solution was 1.0 mL. When 1.5 mL of NaCl was used, complete clarity was obtained after 24 h. At the two higher salt concentrations, when 2.0 and 2.5 mL of NaCl solution was used, suppression of PEC formation was obtained after 3 h and 15 min, respectively.

Ten milliliters of 2M HCl solution was added to 0.389 g of dried PEC (1:1). After breakdown the resultant solution was neutralized (pH \sim 7) with NaOH to yield a precipitate. The precipitate was isolated by centrifugation. The precipitate was washed repeatedly with distilled deionized water. The supernatant liquid and washings were collected and made up to 50 mL with distilled deionized water. The precipitate was dissolved in ethanol. The UV spectrum of this solution was identical to that of the original P2VP in ethanol. Ten milliliters of supernatant liquid was taken and acidified with HNO₃ and then ammonium molybdate solution was added to it. The immediate formation of a yellow precipitate verified the presence of phosphate.¹⁴ The breakdown products having been identified qualitatively, their contents were analyzed quantitatively. The UV spectroscopy and volumetric techniques¹⁴ were used for quantitative determination of P2VP and PSP, respectively. P2VP has an absorbance peak at 208 nm in ethanol. The absorbance of standard solutions of P2VP, having concentrations between 1×10^{-4} and 1×10^{-5} M, was measured at this wavelength and was found to obey the Lambert-Beer law, the extinction coefficient having a de-

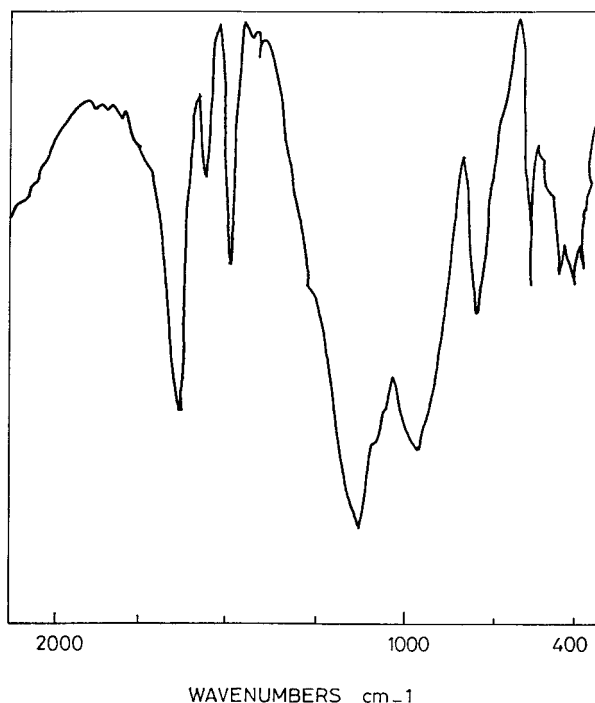


Figure 5 The IR spectrum of PEC-Cu(II).

rived value of $240.5 \text{ m}^2 \text{ mol}^{-1}$. Quantitative determinations showed that PEC contains 0.184 g of P2VP and 0.205 g of PSP, which means that the mole ratio of PSP to P2VP is 1.15.

Interaction between PEC and Cu(II)

The loading capacity of the resin is 186.2 mg Cu²⁺/g PEC. The quantitative (40.61%) retention of Cu(II) was investigated by using the column technique. PEC can be an appropriate resin for separation of Cu(II).

Polymers containing chelating groups have been widely used for concentration, separation, and extraction of metal ions. In this work the interaction between Cu(II) and PEC was also investigated. Figure 5 shows the IR spectrum of the PEC-Cu(II) sample. The IR spectrum of the PEC-Cu(II) was compared to that of PEC (Fig. 2, spectrum a). The vibrations at 1632, 1555, and 1503 cm⁻¹ were also obtained for PEC-Cu(II). The ring stretching modes of the pyridinium cation do not shift. As explained, the strong band at 1632 cm⁻¹ can be attributed to quaternized pyridine ring vibrations. The P—O—P stretching vibrations obtained at 887 cm⁻¹ for PEC (Fig. 2, spectrum c) disappeared in the spectrum of PEC-Cu(II) (Fig. 5). The vibrations at 1093 cm⁻¹ decrease in intensity with the presence of Cu(II) in the complex

while the C—C—C band at 631 cm^{-1} becomes narrower and intense. The PSP and P2VPHCl both have a band at 1170 cm^{-1} . This band can be assigned to CH stretching vibrations of P2VPHCl¹⁸ and symmetric stretching vibrations of PO₂ for PSP. The 1170 cm^{-1} band becomes less intense in spectrum c in Figure 2. A strong band at 1144 cm^{-1} is observed for PEC-Cu(II). This band also appeared as a result of a shift from 1170 to 1144 cm^{-1} . The IR bands for P2VP and its complex with CuCl₂ were investigated by other workers.¹⁸ They found that the band that was assigned to CH stretching vibrations of P2VPHCl shifted to 1165 cm^{-1} when P2VPHCl was complexed with CuCl₂.

Potentiometry and conductometry were also used to investigate the interaction between Cu(II) and PEC. Thirty-five milliliters of $1 \times 10^{-3}\text{ M}$ PSP was titrated with $1 \times 10^{-2}\text{ M}$ P2VPHCl in the presence of $1 \times 10^{-3}\text{ M}$ Cu(II).

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