Polymer Bulletin 45, 425–429 (2000)

Polymer Bulletin

Poly(*N*-vinylpyrrolidone) as metal ion liquid-liquid extractant

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Received: 7 September 2000/Revised version: 14 September 2000/Accepted: 14 September 2000

SUMMARY

Poly(N-vinylpyrrolidone) (PVP) was investigated as a novel extracting agent. The metal ion extraction properties for Cu(II), Co(II), Ni(II), Cd(II), Zn(II), Pb(II), Hg(II), Cr(III) and Fe(III) were investigated using the liquid-liquid solvent extraction technique (bath method). The metal ion interactions with the polymer were determined as a function of the pH as well as the kinetic characteristic and stripping.

For copper ions pH 4 was the optimum extracting pH value, and the 2M hydrochloride acid was better than nitric acid as a stripping agent.

INTRODUCTION

Metal-chelating and ion exchange polymers have been used for the metal separation and recovery from dilute solution such as industrial fluid and wastewater. Apart from insoluble crosslinked polymer reagents containing ligands, *e.g.*, amino, ammonium, phosphoric acid, carboxylic acid, and amidoxime (1-8), water-soluble functional polymers have been investigated for the removal of metal in the homogeneous phase (5, 9-17). By using these polychelatogens in combination with membrane filtration, higher efficiency and selectivity of membrane separations can be achieved. This method, based on the retention of certain metal ions by a membrane which separates low molecular mass compounds from macromolecular complexes on the ions, is called liquid-phase polymer-based retention (LPR) (18-20).

Recently, the interaction of water-soluble poly(acrylic acid) with Np(V) has been studied as extractant by solvent extraction method with TTA and 1,10-phenantroline in isoamyl alcohol. The apparent formation constant $ß_{app}$ was determined at several pH (between 5 and 8), and ionic strength (0.1 and 1.0 M of $NaClO_4$ and NaCl). The obtained values ranged from 1.7 to 3.0 The metal ion interaction was attributed to the multidentate coordination of carboxylic groups to NpO_2 ion and also to electrostatic attraction between cations and negatively charged polyacrylate ion (21).

It is well known that PVP shows complexion ability for some metal ions (22), but no systematic attempt has been made in order to study its properties as an extractant agent of metal ions by using the liquid – liquid extraction procedure (batch method).

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The goal of this paper is to investigate the metal ion binding ability of PVP through a novel liquid – liquid extraction by using kerosene–octanol mixture (6:4, v/v). This paper reports the solvent extraction behavior of copper and other metal ions using PVP in kerosene-octanol phase (6:4).

EXPERIMENTAL PART

Reagents and solutions:

All reagents were of analytical reagent grade and were used without further purification. Standard solutions and dilutions were prepared in deionized water that was further purified using Fistream III Glass Still, a high-purity water device (Barnstead, England).
Stock standard solutions (1000 µg/mL) of each cation at different pH values were prepared by dissolving $CuCl_2 \cdot 2H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 2H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $ZnCl_2$, $Pb(NO_3)_2$, $HgCl_2$, Fe_2O_3, $Cr(NO_3)_3 \cdot 9H_2O$ from Merck (Darmstadt). NaOH, HCl and HNO_3 were from Merck. The pH of the solutions was adjusted to a particular value by using NaOH, HCl or HNO_3 solutions.
Poly(N-vinylpyrrolidone) (PVP) M_n 25.000-30.000 (Merck, Darmstadt). Kerosene, benzene, n-octanol, n-decanol, and n-dodecanol (Aldrich) were used.

Measurements:

The residual metal concentrations in the aqueous phase were measured by atomic absorption spectrometry (AAS) (Perkin Elmer Analyst 100).
The pH measurements were carried out in a Beckman pH-meter (Model 4500). Stirring was performed in a mechanical shaker (Thys 2 MLW). Capped test tubes (20 mL) were used for extraction experiments.

General extraction procedure:

The procedure was based on solvent extraction technique. The ratio of the volumes of the aqueous phase and the organic phase was maintained at 2:1. The total volume of the aqueous phase was made up to 10.0 mL containing 10 µg/mL of a metal ion at a determined pH. The solution was transferred into a capped test tube and shaken at 20°C, atmospheric pressure, c.a. 760 mmHg and 300 rpm of stirring intensity with 5.0 mL of the solvent phase, as described above, for 10 minutes. The two layers were allowed to settle for 10 minutes. The aqueous phase was then separated and an aliquot of 5.0 mL was diluted to 25.0 mL in order to perform the analysis of the remaining metal ion by AAS. The amount of the metal ion in the solvent phase was estimated by material balance.

Stripping procedure:

The loaded organic with copper at pH 4.0 was stripped with hydrochloric acid or nitric acid at different concentrations. The mixture was shaken for 10 minutes. The aqueous phase was separated and the copper ions were analyzed by AAS.

RESULT AND DISCUSSION

Solubility of PVP.

Solubility of PVP in a mixture of organic solvents was assayed, immiscible with an aqueous phase, so that a fast separation of the phases was achieved. In this context, n-octanol, n-decanol, n-dodecanol were used for dissolution of PVP and benzene and kerosene as modifiers. The most successful binary mixture, according to the main objectives, that is a short time for phase separation, absence of emulsions and an appropriate solubility of PVP, was octanol – kerosene (4:6, v/v). Octanol must not be over 40% due to its high viscosity, which difficults the mass transfer of a species from one phase to another. Consequently, the solvent phase was prepared by dissolving the PVP (0.4 g/L) in four volumes of n-octanol and then mixing with six volumes of kerosene.

Effect of pH on degree of extraction (Batch method).

The extraction of several metal ions with PVP was performed at different pH, but at a constant extractant (0.4 g/L) and metal ion (10 µg/mL) concentrations. As shown in Table 1 the extraction of copper(II) and nickel(II) increases as pH is increased.

Table 1. Extraction of metal ions (%) as a function of pH.

pH	Cu(II)	Ni(II)	Co(II)	Cd(II)	Zn(II)	Pb(II)	Hg(II)	Fe(III)	Cr(III)
0	0.8	1.0	3.5	0.5	0.2	0.2	0.0	0.0	0.0
1	1.0	1.0	3.8	1.0	0.1	0.2	0.0	0.0	0.0
2	1.0	1.0	3.9	1.5	0.2	0.5	0.0	0.0	0.0
3	1.2	1.0	3.9	3.0	1.0	0.3	0.0	0.0	0.0
4	53	5.2	3.3	0.5	1.0	0.5	0.0	*	*
5	48	9.8	4.0	5.2	1.1	0.5	0.0	*	*
6	*	37	12	17	1.0	*	*	*	*
7	*	*	*	17	*	*	*	*	*

* To avoid the precipitation or gel formation, not all of the metal ions were investigated up to pH 7.0

The optimum extraction for copper(II) was reached at pH 4.0 (53%) and for nickel at pH 6.0 (37%), cadmium at pH 7.0 (17%), cobalt at pH 6.0 (12%). All the other metal ions considered were not extracted significantly (lower than 10%). Consequently, kinetic and stripping parameters were determined for copper only due to their higher extraction percentage. Therefore, pH 4.0 was selected as optimum for subsequent work.

Kinetic characteristics of the extraction process:

The contact time varied from 2 min to 16 min. This kinetic test for the extraction of copper(II) at optimum pH indicated the distribution ratio reached a constant value within 2.0 minutes of shaking. The same behavior was observed for Ni(II) (see Fig. 1). It is very fast considering that the reaction is occurring in two phases. Nevertheless, the contact time was kept for 10 minutes in all the experiments.

Stripping assays:

This study was carried out to choose an appropriate stripping agent solution. For this purpose the organic extract was stripped with hydrochloric acid and nitric acid (0.5 – 8.0 M). The volume ratio of the aqueous phase to the organic phase was maintained at 1:2 respectively. For both stripping agent solutions, the increasing concentration of the acid increased the stripping of copper(II) (see Table 2). Hydrochloric acid 2.0 M stripped 95 % of copper, after one step, being higher than nitric acid at the same concentration.

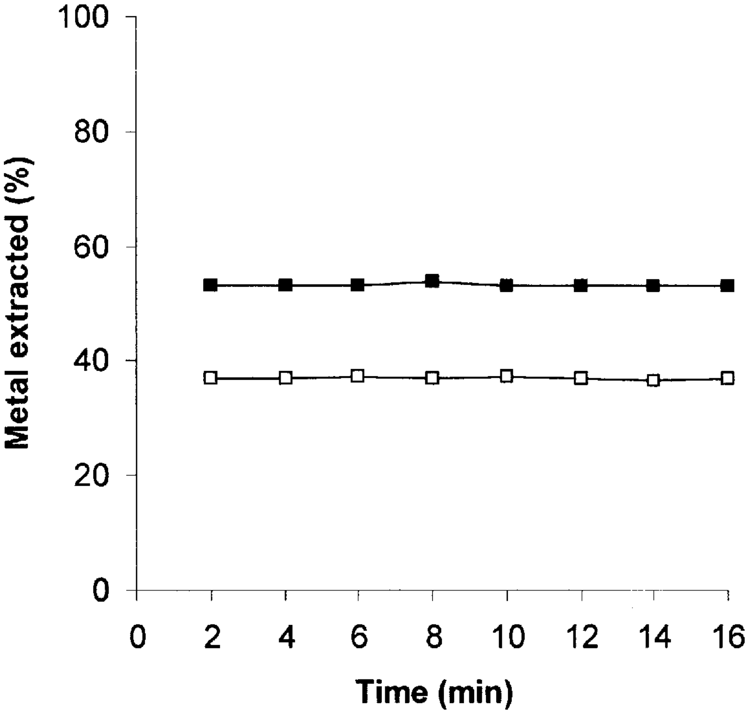

Figure 1. Determination of equilibration time for copper(II) at pH = 4.5 (■) and for Ni(II) at pH =6.0 (□).

Table 2. Copper(II) stripping (%) with hydrochloric acid and nitric acid at different concentrations.

[Acid] M	HCl	HNO_3
0.5	78	58
1.0	92	75
2.0	95	77
4.0	95	84
8.0	32*)	88

*) Emulsion formation

CONCLUSIONS

The relevance of this paper is the report of a novel application of poly(N-vinylpyrrolidone) as an extracting agent using the liquid-liquid solvent extraction. The best organic solvent for PVP was the kerosene-octanol mixture (6:4, v/v). This polymer retain around 50% of Cu(II) ions and is very selective up to pH 4.0 for all the metal ions investigated.

Only Ni(II) ions are retained over 35% at pH 6.0 but at this pH Cu(II) ions were not tested due to precipitation of the corresponding hydroxide.

ACKNOWLEDGMENTS

The authors thank financial support from FONDECYT Líneas Complementarias (Grant No 8990011).

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