Concentration of Some Transition Metal Chelates by Using Poly(N-isopropylacrylamide-co-4-vinylpyridine) as a Solid Adsorbent

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By utilizing a thermally reversible liquid-solid variation of poly(N-isopropylacrylamide-co-4-vinylpyridine), pyrrolidinedithiocarbamate complexes of transition metal ions such as Cu²⁺, Ni²⁺, Cd²⁺, Co²⁺, Fe³⁺, Mn²⁺, Pb²⁺, and Zn²⁺ could be successfully extracted into copolymer phase and the back-extraction of Mn²⁺ from a copolymer phase into EDTA aqueous solution was also established. (Received on August 8, 2001; Accepted on September 13, 2001)

A noble concentration method, in which tris(1,10-phenanthroline)iron(II) perchlorate (Fe(phen)₃(ClO₄)₂) and bis(2,4,6-tris(2-pyridyl)triazine)iron(II) perchlorate (Fe(TPTZ)₂(ClO₄)₂) could be successfully extracted from an aqueous solution to a copolymer phase by use of poly(N-isopropylacrylamide-co-4-vinylpyridine) (copoly(NIPAM/4VP)) as an adsorbent, has been developed recently. It was supposed that the better extractability of Fe(TPTZ)₂(ClO₄)₂ than Fe(phen)₃(ClO₄)₂ was attributed to the stronger hydrophobic interaction between pyridine ring in a copolymer and Fe(TPTZ)₂(ClO₄)₂.

Since chelate complexes are generally more hydrophobic compared to ion-pair complexes such as ferroin complex, by deducing the previously obtained result, it can be expected that copoly(NIPAM/4VP) would be able to extract the chelate complex with excellent extractability. Ammonium pyrrolidinedithiocarbamate(APDC) is one of the most well-known chelate extractants for transition metals and was, therefore, chosen as an extractant in this study in order to verify this expectation. And if it is possible to back-extract metals concentrated in the form of pyrrolidinedithiocarbamate(PDC) complex in a copolymer phase to an aqueous solution, the concentration of metals without using any organic solvents will put into practice. From this point of view, the possibility of back-extraction was also studied.

Finally, it was found that Zn²⁺, Cd²⁺, and Pb²⁺ were extracted into a copolymer with 100% extractability and Mn²⁺ was extracted with 65% extractability and that Cd²⁺, Pb²⁺, Zn²⁺, and Mn²⁺ in a copolymer phase were back-extracted into 0.01M EDTA solution with recovery of 40%, 40%, 70%, and 90%, respectively.

Experimental
Preparation of copoly(NIPAM/4VP)
N-Isopropylacrylamide(NIPAM) was generously donated by Kohjin Co. Ltd. and was used after recrystallization from acetone. 4-Vinylpyridine(4VP) was commercially available one and used without further purification, and 2,2'-azobisisobutyronitrile was used as an initiator after recrystallization from ethanol. Fourteen gram of combined NIPAM and 4VP in the weight ratio of 1:9 was added to 70 ml of tetrahydrofuran in a 100 ml vial and was sealed with a rubber cap and an aluminum seal after deaeration with N₂ for 15 min, followed by polymerizing by vigorously stirring at 65°C for 24 hr. Copolymer was obtained by adding the reactant solution into hexane, and was purified twice by precipitating in hexane from acetone solution.

Viscosity average molecular weight was determined by use of Ubbelohde viscosimeter and monomer composition was determined by comparing 1H peak intensities at δ 7.21(2H, α-position in pyridine ring and 1H in amido group) and δ 8.41(2H, β-position in pyridine ring) in 1H-NMR(270 MHz, CD3COCD3). For copolymers synthesized 4 times separately, the viscosity average molecular weight and monomeric composition of 4VP of were 2.7×10⁴±1.5×10³ and 8.8±0.01, respectively.

Reagents and apparatus Metal standard solutions were stored in polyethylene bottles and were arbitrarily mixed in the following combinations prior to use so that the concentration of each metal was exactly 1.0 mM; Cu-Co-Ni-Cd, Mn-Ni-Pb, and Cd-Fe-Zn. Other reagents and apparatus used in this study were same to those previously reported.

Extraction procedure Four milliliters of 3% APDC and 4 ml of 10% copolymer aqueous solutions were added to 40 ml of metal ion cocktail solution adjusted pH appropriately and the mixture was centrifuged at 40°C and 3000 rpm for 40 min. The supernatant solution was separated by decantation and was subjected to the determination of metal ion concentration by flame-AAS method. The percent extraction(EX(%)) was...
obtained by dividing the calculated metal ion concentration in the copolymer phase by the known total concentration in the aqueous solution. The remaining copolymer in the extraction vial was rinsed with chilled water several times and was redissolved in 4 ml of HCl solution or 4 ml of 0.01M EDTA solution adjusted pH appropriately. The resulted solution was centrifuged at 40°C and 3000 rpm for 40 min again and the supernatant solution obtained by decantation was subjected to the determination of metal ion concentration by flame-AAS method. The recovery of metal ion(R(\%)) was determined by the following equation.

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R(\%) = \frac{[\text{Metal ion}]_{\text{supernatant soln.}}}{[\text{Metal ion}]_{\text{known}} \times \text{EX}(\%) \times \text{Volume ratio (48ml/4ml)}}
\]

Results and Discussion

Lower critical solution temperature  Poly-NIPAM has a lower critical solution temperature (LCST) at 32°C. Since it was expected that LCST would change by copolymerizing [copoly(NIPAM/4VP)] = 1wt/v%.  ◆: at pH 2, ▲: at pH 10.

Fig. 2 The effect of pH on the metal concentration.  (a) Extraction of Mn^{2+}, Pb^{2+}, Co^{2+}, and Zn^{2+}; (b) Extraction of Ni^{2+}, Cu^{2+}, Cd^{2+}, and Fe^{3+}.—[Metal ion] = 0.4mM, [Copolymer] = 1wt/v%.

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\begin{align*}
\text{Fig. 1 The effect of temperature on the solubility of copoly(NIPAM/4VP).} \\
\text{◆: at pH 2, ▲: at pH 10.}
\end{align*}
\]
NIPAM with 4-VP, turbidities of 1% copolymer aqueous solutions adjusted at pH 2 and 10, respectively, were observed at 660nm by changing the temperature in a cell holder room at a rate of 0.2℃/min. As shown in Fig. 1, LCST at pH 2 was 36-40℃, while that at pH 10 was 27-31℃. Taking into account that pKa value of pyridinium ion is 5.22, this phenomena can be understood as follows: At pH 2, pyridinium ions in a molecule disturbed a coil-globule transition of copolymer molecule due to the electrostatic repulsion, which brought about a higher LCST than LCST of poly-NIPAM; While, hydorophobicity of pyridine ring accelerated a coil-globule transition of copolymer molecule at pH 10, which resulted in a lower LCST.

Effect of the amount of copolymer on the extraction The effect of the concentration of copolymer on the extraction was examined with Fe^{3+}, Cu^{2+}, and Ni^{2+} by changing the added amount of copolymer solution from 1ml(0.24%) to 4ml(0.91%) in the pH range of 2.3-7.1. It was found that these metals could be perfectly extracted to a copolymer phase irrespective of the copolymer concentration. However, the added amount of copolymer was set to 4ml just to make sure.

Effect of pH on the extraction Figure 2-a and 2-b show that seven transition metals other than manganese could be quantitatively extracted from aqueous solution to a copolymer phase in the wide pH range. Manganese, cadmium, and zinc were not extracted from the aqueous solution in HCl acidic region, therefore, the possibility of back-extraction from the copolymer phase containing PDC-complex to a HCl solution is present with these metals.

Recovery of metal ion In order to evaluate whether metal ions concentrated in a copolymer phase could be back-extracted into aqueous phase or not, metal ion extraction was carried out in the presence of 0.01M EDTA. The presence of EDTA disturbed extraction of Mn^{2+} severely in the wide pH range and extraction of Fe^{3+} and Co^{2+} in the pH range greater than 8 and greater than 6, respectively, while other metals were hardly affected with EDTA although the

Fig. 3 The effect of pH on the recovery of metal ion. (a) Recovery of Mn^{2+}, Pb^{2+}, Co^{2+}, and Zn^{2+}; (b) Recovery of Ni^{2+}, Cu^{2+}, Cd^{2+}, and Fe^{3+}. [Metal ion] = 0.1mM, [Copolymer] = 1wt/v%.


12345678910 111213
0 20 40 60 80 100
Recovery of metal ion, %

0 3 2 1 0
Recovery of metal ion, %

4 3 2 1 0
HCl (M)

4 3 2 1 0
HCl (M)
extractabilities equally decreased as pH increased in the pH range greater than 7. Incidentally, EDTA did not affect only the extraction of Cu\(^{2+}\) at all in all the pH region examined. Then, after extraction of metal ions into a copolymer, the precipitated copolymer containing the metal-PDC complex was shaken to redissolve with 4ml of HCl adjusted at various concentration or with 4ml of 0.01M EDTA solution adjusted at various pH (Fig. 3-a and -b). Only manganese and zinc showed comparatively high recovery with alkaline 0.01M EDTA solution and/or HCl solution, while other metals did not give satisfactory results.

The effect of the concentration of EDTA was examined with Mn\(^{2+}\) in order to improve the recovery. As can be seen from Fig. 4, the recovery of Mn\(^{2+}\) attained 100% at pH 5.2-7.1, when the concentration of EDTA raised to 0.05M. The extractability of Mn\(^{2+}\) was not very good (See Fig. 2, at pH 4.12, EX=65%), however, it had revealed by the present authors that the extractability of Mn\(^{2+}\) was fully governed by the concentration of APDC\(^{3,4}\), so that it is easy to improve the extractability of Mn\(^{2+}\) if only the concentration of APDC was increased sufficiently. On the other hand, the recoveries of other metals could not be remarkably improved by increasing the concentration of EDTA up to 0.1M.

In conclusion, seven transition metals other than Mn\(^{2+}\) could be perfectly extracted from aqueous solution to a copolymer phase in the wide pH range. As for Mn\(^{2+}\), it could be back-extracted from a copolymer phase to 0.05M EDTA solution with 100% recovery. As yet, based on the volume ratio of 10(40ml/4ml), the total concentration factor of 5.9 for Mn\(^{2+}\), that of 4.0 for Cd\(^{2+}\) and Pb\(^{2+}\), and that of 7.0 for Zn\(^{2+}\) were attained without using organic solvents at all for which harmful effects on environment are suspected.

References

![Fig. 4 Effects of pH and the concentration of EDTA solution on the extractability of Mn\(^{2+}\).](image-url)