Thermal-swing Extraction of Cadmium(II) by Thermosensitive Polymer Gel Crosslinked with Encapsulating Hexadentate Ligand

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(Received May 11, 2007; CL-070514; E-mail: takeshit@res.titech.ac.jp)

Thermal-swing extraction of Cd^{II} with a thermosensitive gel, poly(*N*-isopropylacrylamide) (NIPA) crosslinked with an encapsulating ligand, *N*,*N*,*N*′,*N*′-tetrakis(4-propenyloxy-2-pyridylmethyl)ethylenediamine (TPPEN), was examined. Cd^{II} was extracted in the gel swollen at 5 °C and released from the gel shrunken at 40 °C. The difference in the distribution ratios of Cd^{II} between these temperatures was more than 30 times.

Solvent extraction is one of important separation techniques in the chemical industry and is applicable widely to the separation of metals, the removal of environmental pollutant, the recovery of biochemical materials, etc. In a solvent extraction process, however, a large amount of chemicals is supplied to both the scrubbing and back-extraction processes. The used chemicals must be decomposed harmlessly or reused after purification from the viewpoint of environmental protection. By the introduction of process to reuse the chemicals, the further consumption of resources will be avoided. The use of chemicals should be suppressed as low as possible for the sustainable development of chemical industry.

The authors propose a new extraction technique called thermal-swing extraction, in which a thermosensitive gel copolymerized with functional ligands is prepared and the extraction and elution of object material are controlled by the conformational change of these functional ligands with the volume phase transition of thermosensitive gel. Therefore, the object material can be recovered without adding new chemicals. The consumption of chemicals can be reduced substantially by introducing the thermal-swing extraction technique. For example, the concept of thermal-swing extraction can be realized by a *N*-isopropylacrylamide (NIPA) gel copolymerized with a functional ligand monomer. Previously, some NIPA gels copolymerized with a phosphoric acid ester and a BTP [2,6-di(3-vinylbenzyl-1,2,4-triazol-5-yl)pyridine] were synthesized and the thermal-swing extraction of heavy metals such as lanthanide, actinide, and transient elements was tested.[1–3] The recent extraction tests of Cd^{II} using the NIPA–BTP gel indicated that the thermal-swing extraction was attained successfully and the extractability of BTP was controlled in principle by the temperature response of gel. However, the difference in the distribution ratios of Cd^{II} between the swelling state (5 °C) and the shrinking one (40 °C) was only 4 times. In this performance, it is difficult to establish a practical thermal-swing extraction process.

For the increase in the difference of extractability between high and low temperatures, the conformation of functional ligands introduced in the gel should be changed substantially with temperature. The use of TPEN [*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine] as a functional ligand instead of BTP was considered to get the clear conformational change with temperature. TPEN is a hexadentate ligand with 6 nitrogen donors and encapsulates a metal ion.[4–7] Four pyridyl groups in TPEN are flexible and the steric conformation of 6 nitrogen donors may be changed easily by the volume phase transition of thermosensitive gel. Figure 1 shows the concept of thermal-swing extraction process using a thermosensitive gel with an encapsulating ligand such as TPEN.

A TPEN derivative combining propenyloxy group to four pyridyl groups, TPPEN [*N*,*N*,*N*′,*N*′-tetrakis(4-propenyloxy-2-pyridylmethyl)ethylenediamine] was synthesized to introduce TPEN in a thermosensitive gel. TPPEN was synthesized easily by reacting ethylenediamine and 2-chloromethyl-4-propenyloxypyridine (the molar ratio of 1:4) in an aqueous solution of pH 8 for 10 d and was purified by a silica-gel column. The synthesis scheme was shown in Figure 2. NIPA and TPPEN (molar ratio = 80:1) were dissolved in *N*,*N*-dimethylformamide (DMF) and copolymerized at 60 °C for 18 h by the redical polymerization method using 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator.

The gel obtained was washed several times by pure water. DMF and unreacted compounds were removed from the gel. After drying, the gel was crashed and sieved in the range of 100 to 150 μm. 2 mL of gel particles was packed in a measuring

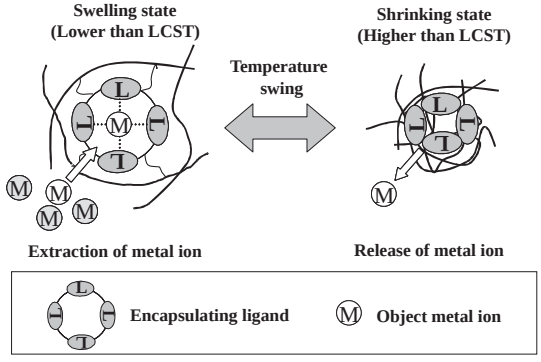

Figure 1. Concept of thermal-swing extraction.

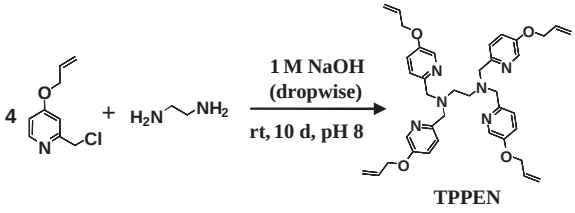

Figure 2. Synthesis scheme of TPPEN.

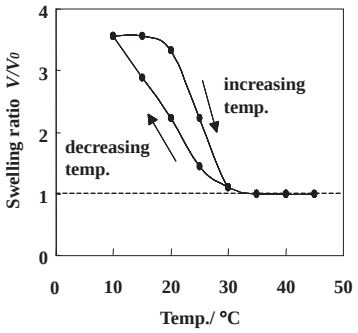

Figure 3. Temperature response of swelling ratio of NIPA–TPPEN gel.

cylinder and 15 mL of pure water was added. The volume change of gel with temperature was measured from the height change of packed bed of gel particles.[8] Figure 3 shows the volume change of NIPA–TPPEN gel with temperature. The ordinate represents the volume of packed gel (V) normalized with that at 45 °C (V_0). At 45 °C, the NIPA–TPPEN gel is in the shrinking state, because of the dehydration of NIPA.[8] Temperature was changed stepwise and maintained until the swelling equilibrium of gel was attained. The gel volume is not changed in the temperature range higher than LCST (lower critical solution temperature), which is evaluated as 34 °C from the volume change curve. This value is the same as that for pure poly-NIPA. The gel volume increased with decreasing temperature, namely the transformation of gel from the shrinking state to the swelling one. The NIPA–TPPEN gel shows obvious thermosensitivity. Furthermore, the hysteresis was observed for the volume change of gel. Generally, this phenomenon is observed for a polymer solution with tangled polymer chains. This means that the crosslinking degree of NIPA–TPPEN gel is low. The polymer network at the swelling state may have comparatively high flexibility.

Next, the extraction of Cd^{II} with the NIPA–TPPEN gel was tested. An aqueous solution containing 8.90×10^{-4} mol/L $Cd(NO_3)_2$ was prepared. Ionic strength and pH in the aqueous solution was adjusted as 0.01 and 2 to 6.5, respectively, by adding HNO_3 and $NaNO_3$. 5 mL of aqueous solution is entered in a vial and 0.1 g of dry gel were added. The vial was shaken vigorously for 1 h. In the preliminary tests, it was confirmed that the extraction equilibrium was reached within 1 h. After shaking, the concentration of Cd^{II} in the aqueous solution was measured by ICP-AES (inductively coupled plasma atomic emission spectrometry). The extraction temperature was adjusted to 5 °C (the swelling state) and 40 °C (the shrinking state). The distribution ratio of Cd^{II} was calculated from the experimental results and the mass balance of Cd^{II} between the gel and the aqueous solution.

Figure 4 shows the distribution ratios of Cd^{II} at 5 and 40 °C. Cd^{II} was little extracted at 40 °C. However, the extractability of gel was improved substantially by decreasing temperature to 5 °C. Then, the distribution ratio increased with increasing the pH value and showed about 300 at pH 5. This value corresponds to about 30 times of that at 40 °C. As mentioned above, the volume phase transition of thermosensitive gel is caused by the hydration of NIPA. This may be because the extractability of TPPEN is affected strongly by the conformational change of TPPEN with the volume phase transition, as shown in

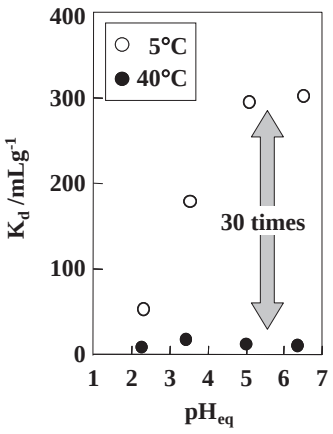

Figure 4. Change of distribution ratio of Cd^{II} with pH at 5 and 40 °C.

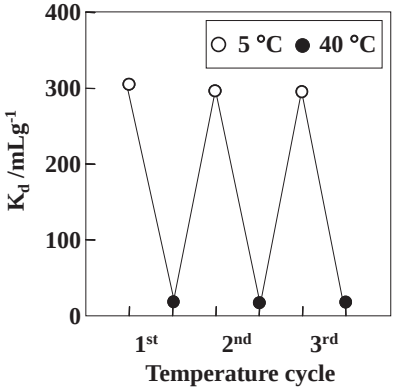

Figure 5. Thermal-swing extraction test. The extraction temperature was changed between 5 and 40 °C.

Figure 1. The extraction of Cd^{II} is controllable by the thermal-swing operation. Then, the extraction capacity of Cd^{II} with NIPA–TPPEN gel at 5 °C is evaluated as about 11 mg-Cd/g-dry gel, which is similar to that of ion-exchange resin and is sufficient for the design of practical process. Figure 5 shows the change of distribution ratio with the temperature swing between 5 and 40 °C. The extraction and release of Cd^{II} were repeated stably. Cd^{II} in the aqueous solution can be recovered by the thermal-swing operation. These results suggest that a practical thermal-swing extraction process can be established by a thermosensitive gel introducing an encapsulating agent, such as NIPA–TPPEN gel.

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Published on the web (Advance View) July 14, 2007; doi:10.1246/cl.2007.1032