Extraction of americium (III) by thermosensitive polymer gel copolymerized with acidic phosphorus compound

Kenji Takeshita*　Yoshio Nakano*　Tatsuro Matsumura**

A new gel-liquid extraction technique using a thermosensitive gel was proposed. The thermosensitive gel shows the conformational change of polymer network with temperature, which is known as the phase transition phenomena of gel. The extraction rate and equilibrium of Am(III) in an aqueous solution containing nitrate ion were measured batchwise by using a thermosensitive gel, N-isopropylacrylamide (NIPA) copolymerized with 2-methacryloyloxy- ethylacidphosphate (MR). The effects of the conformational change of polymer network on the extraction rate and equilibrium were discussed.

The distribution ratio of Am(III) showed a large value at higher than LCST (low critical solution temperature; 34℃) and was decreased by the phase transition of gel from shrinking to swelling with decreasing temperature. The extraction of Am(III) in the aqueous solution and the release of Am(III) extracted in the gel were repeated stably by the temperature swing operation between 40 and 3℃. The extraction mechanism of Am(III) was described simply as

$$Am^{3+} + 3R-OH = (R-O)_3 Am + 3H^+ \quad (R\text{-}OH: MR).$$

The equilibrium constant at the shrinking state (40℃) was more than 3 times of that at swelling state (3℃). The gel-phase diffusivity of Eu(III) used as a substitute of Am(III) was evaluated as the order of 10^{-12} m^2/s at either of 3 or 40℃, which was similar to those for practical extraction chromatographic resins. The temperature-response of gel for the extraction of Eu(III) was very excellent without delay even for the rapid temperature change at 10℃/min. These results suggest that the extraction and release of Am(III) in an aqueous solution can be controlled by the conformational change of polymer network of thermosensitive gel.

Keywords: extraction, extraction rate, gel, phase transition, thermosensitive gel, temperature swing, americium, N-isopropylacrylamide

感温性高分子ゲルを用いた新規なゲル／液抽出法を提案した．感温性ゲルは体積相転移現象を起こし，温度によってゲルの高分子ネットワーク構造が変化する．N-isopropylacrylamide (NIPA)に 2-methacryloyloxyethylacidphosphate (MR)を共重合した感温性ゲルを合成し，硝酸塩水溶液中の Am(III)抽出を行い，Am(III)抽出平衡及び抽出速度に対する高分子ネットワークの構造変化の影響を調べた．

ゲル/液間の Am(III)の分配比は LCST(下限臨界共溶温度;34℃)以上で大きな値を示し，温度低下に伴う収縮から膨潤へのゲルの体積相転移によって低下した． 3℃～40℃間の温度スイング試験を行ったところ，水溶液中の Am(III)の抽出と抽出された Am(III)の放出を安定して繰り返すことができた．Am(III)の抽出機構は共重合された MR (R-OH)に対して

$$Am^{3+} + 3R-OH = (R-O)_3 Am + 3H^+$$

と記述され，収縮状態(40℃)の抽出定数は膨潤状態(3℃)の 3 倍以上の値を示した．Am(III)の代替物質として Eu(III)を用いて，Eu(III)のゲル相内拡散係数を求めた．Eu(III)の拡散係数は 40℃，3℃いずれも $10^{-12}m^2/s$ のオーダーであり，実用的な抽出クロマト樹脂の値と同等であった．また，10℃/min の速い温度変化に対しても Eu(III)抽出容量はよい温度追従性を示した．これらの結果は感温性ゲルの高分子ネットワークの構造変化によって Am(III)抽出及び放出が制御できることを示唆している．

Keywords: 抽出,抽出速度,ゲル,感温性ゲル,相転移,温度スイング,アメリシウム, N-イソプロピルアクリルアミド

1 Introduction

Separation, isolation and purification of metal ion by solvent extraction are utilized widely in many industrial processes [1-3]. Metal ion forms the complex with extractant molecules and is extracted in an organic phase. The complex is decomposed by a stripping solution with different pH or ionic strength, in which the extracted metal ion is recovered. The use of a large amount of stripping solution causes the increase of industrial wastes. The development of new extraction technique to reduce secondary wastes is desired from the viewpoint of environmental protection. Such consideration is also important in the nuclear industry [4].

We proposed a gel-liquid extraction process using thermosensitive gel as a new technique to depress the generation of secondary wastes [4]. Thermosensitive gel shows the conformational change of polymer network with temperature, which is known as phase transition phenomena of gel [5]. If the extractant molecules are copolymerized in the thermosensitive gel, the complex formation between metal ion and extractant molecules is affected by the conformational change of polymer network with temperature. Then, the extraction capacity of metal ion may be controlled by the conformational change of polymer network in the gel, as shown in Fig.1 [4]. If the release of extracted metal ion to an aqueous solution is promoted by the conformational change of polymer network from shrinking to swelling, the amount of required stripping solution may be reduced.

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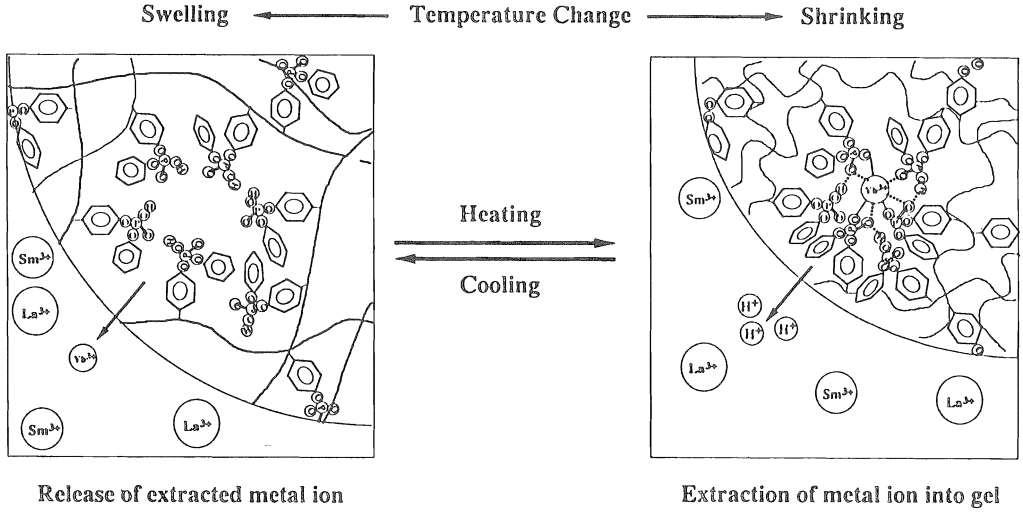


Fig.1 Extraction of metal ion by thermosensitive polymer gel copolymerized with acidic phosphorus compound

In this paper, the extraction behavior of Am(III) in an aqueous solution containing nitrate ions was measured batchwise in a stirred cell using a thermosensitive polymer gel, N-isopropylacrylamide (NIPA) copolymerized with an acidic phosphorus compound, 2-methacryloyloxyethylacidphosphate (MR), which shrinks and swells in water at temperature above and below the LCST (lower critical solution temperature) around 34℃, respectively [5-8]. The extraction mechanism for the extraction of Am(III) was evaluated by a slope analysis technique and the extraction constants at the shrinking and swelling states were compared. Temperature swing tests, in which the extraction operations at high and low temperature were repeated, were carried out and the stability of extraction behavior during the temperature swing operation was examined. The extraction rate of Eu(III) used as a substitute of Am(III) was measured and the intraparticle diffusion coefficients of Eu(III) at the shrinking and swelling states of gel were evaluated. From these results, the effects of the conformational change of polymer network on the extraction rate and equilibrium of Am(III) were discussed.

2 Experimental

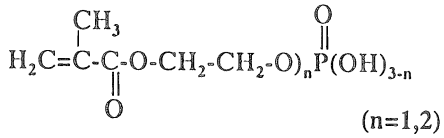
2.1 Preparation of thermosensitive gel

A copolymeric gel, N-isopropylacrylamide (NIPA : Kojin Co.LTD.) copolymerized with 2-methacryloyloxyethyl-acidphosphate (MR : Daihachi Kagaku Co.LTD.), was prepared. The chemical structures of NIPA and MR were shown in Fig.2. N,N'-methylenebis(acrylamide) (BIS : Wako Chemicals Co.LTD.) was used as a crosslinker and N,N'-azobis(isobutyronitrile) (AIBN : Kanto Chemical Co.LTD.) as an initiator. The mixture of these chemicals, which was adjusted as 350mmol NIPA, 350mmol MR, 7mmol BIS and 14mmol AIBN, was dissolved in 20cm^3 N,N-dimethylformamide (DMF : Wako Chemical Co.LTD). The DMF solution was purged with N_2 gas for 15 min, because of the removal of dissolved O_2 in the solution. The co-polymerization between NIPA and MR was carried out at 60℃ for 24h. NIPA was purified by recrystallization from hexane before use. Other chemicals were used without purification.

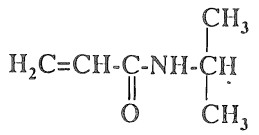
The NIPA-MR gel obtained was washed several times by pure water and dried *in vacuo* at 60℃. The dry gel was crashed and sieved in the range of 0.1 to 0.2 mm in diameter. In preliminary experiments, the swelling ratio of gel in water was measured over the range of 3 to 60℃. The swelling ratio of NIPA-MR gel decreased with increasing temperature. These results mean that the NIPA-MR gel is thermosensitive.

2.2 Temperature swing operation

The temperature swing tests were carried out over the temperature range of 3 to 40℃. Two solutions, an aqueous solution containing 6.7×10^{-9} mol/dm^3 (200Bq/cm^3) ^{241}Am(III) and a mixture of 4.4×10^{-10} mol/dm^3 (440Bq/cm^3) ^{152}Eu(III) and 2.5×10^{-9} mol/dm^3 (77Bq/cm^3) ^{241}Am(III), were prepared. The initial pH and ionic strength of these solutions were adjusted to 3.7 and 1 mol/dm^3, respectively, by adding HNO_3 and $NaNO_3$. Dry gel particles (0.08g) were added in 40cm^3 aqueous solution



2-methacryloyloxyethylacidphosphate (MR)



N-isopropylacrylamide (NIPA)

Fig.2 Chemical structures of NIPA and MR.

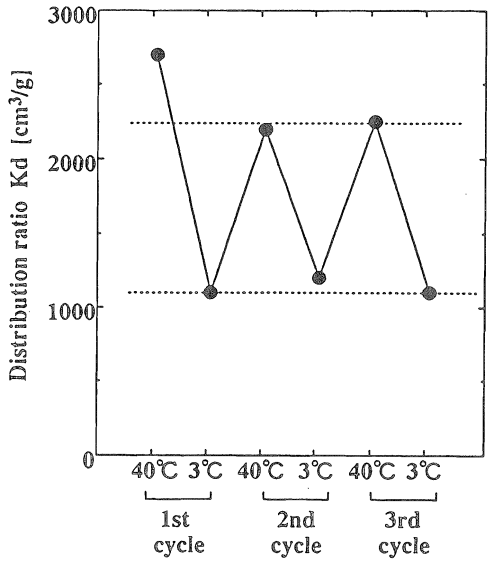


Fig.3 Thermal swing test for the extraction of Am(III). Initial pH and ionic strength was adjusted to 3.7 and 1.0 mol/dm^3, respectively.

at 40°C and the extraction equilibrium was attained by shaking vigorously for 1h. About 1cm^3 of solution was sampled by a syringe with a disposable filter (pore size 0.45μm). After that, the temperature of aqueous solution was decreased to 3°C and maintained for 1h. After about 1cm^3 of solution was sampled, the temperature was increased to 40 °C again. Such temperature swing operation was repeated 3 times. The concentrations of ^{241}Am(III) and ^{152}Eu(III) in the sample solution were evaluated from the count number of γ -ray measured by a Well-type Germanium Detector (EGPC115P15, Eurisys Mesures Co.LTD.). The concentration of hydrogen ion in the aqueous solution was measured by a pH meter (AUT-301, TOA Co.LTD.). From these results, the distribution ratio of metal ion between gel and aqueous solution, *Kd*, defined as

$$K_d = \frac{(C_0 - C)}{C} \frac{V}{W} \quad (1)$$

was calculated, where C_0, C, V and W denote the initial and equilibrium concentrations of metal ion, the volume of aqueous solution and the weight of dry gel, respectively.

2.3 Measurement of extraction rate

For the measurement of extraction rate, Eu(III) was used as a substitute of Am(III). The extraction rate of Eu(III) was measured batchwise in a stirred cell. An aqueous solution with 0.66 mmol/dm^3 of non-radioactive Eu(III) and 4.4x10^{-10} mol/dm^3 (440Bq/cm^3) of radioactive ^{152}Eu(III) was prepared. The initial pH and ionic strength of these solutions were adjusted over the range of 0.5 to 5 and to 1 mol/dm^3, respectively, by adding HNO_3 and $NaNO_3$. The aqueous solution (40ml) was stirred at 500 rpm and the extraction temperature was adjusted over the range of 3 to 40°C. Dry gel particles (0.08g) were added in the solution. At the prescribed time interval, about 1cm^3 of aqueous solution was sampled by use of a syringe with a disposable filter (pore size 0.45μm). The concentration of Eu(III) in the sample solution was evaluated from the count number of γ -ray of ^{152}Eu(III). From these results, the distribution ratio, *Kd*, was calculated.

3 Results and discussion

3.1 Temperature swing tests

Figure 3 shows the results of temperature swing test of Am(III) between 3 and 40°C. The NIPA-MR gel is swollen at 3°C and shrunken at 40°C. Am(III) is extracted at shrinking state and the extracted Am(III) is partly released to the aqueous solution by the phase transition from shrinking to swelling. The extraction amount at swelling state was decreased to about 40% of that at shrinking state. The swelling ratio of gel, defined as the ratio of the gel volume at the swelling state to that at the shrinking state, $V_{3°C}/V_{40°C}$, was 1.2. This value was much lower than that of ordinary NIPA gel, because of the hydrophilicity of MR. These results suggest that it is possible to control the extraction amount of Am(III) by the conformational change of polymer network with temperature, in spite that the change of gel volume is only 20%. If the swelling ratio increased with increasing the content of NIPA in the gel, the temperature swing behavior of Am(III) will be further improved. Note that the Kd values at shrinking and swelling states were repeated stably during the temperature swing operation. These results mean that the conformation of polymer network is reproducible by adjusting the temperature condition.

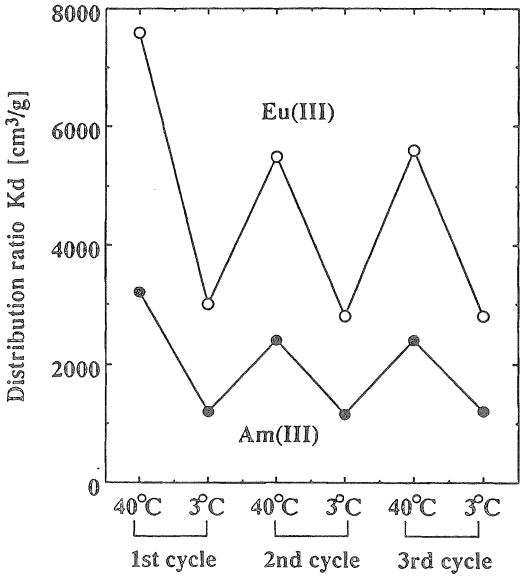


Fig.4 Thermal swing test for the binary extraction of Am(III) and Eu(III). Initial pH and ionic strength was adjusted to 3.7 and 1.0 mol/dm^3, respectively.

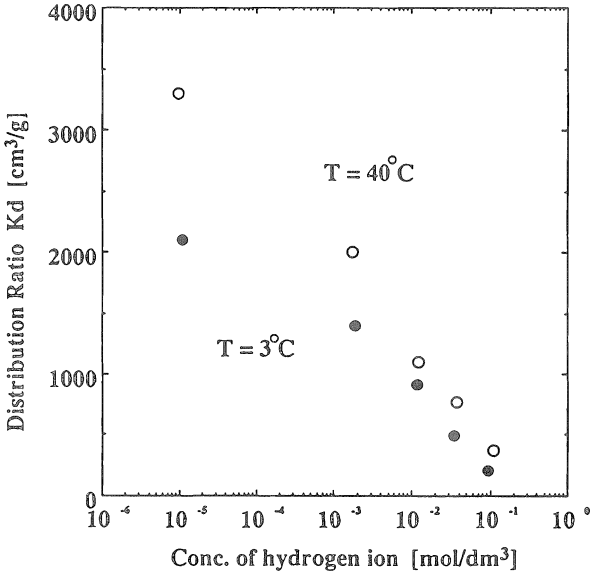


Fig.5 Change of Kd with the concentration of hydrogen ion in aqueous solution. Ionic strength was adjusted to 1.0 mol/dm³.

Figure 4 shows the results of temperature swing test using two components of Eu(III) and Am(III). The operating conditions were the same as those in Fig.3. The change of Kd with temperature was stable for either Eu(III) or Am(III). These results suggest that the concept of gel-liquid extraction is applicable to a multi-component extraction system.

3.2 Extraction mechanism of Am(III)

The effect of the conformational change of polymer network on the extraction behavior can be evaluated quantitatively by the comparison between the extraction constants of Am(III) at the shrinking and swelling states. Figure 5 show the dependence of Kd on the concentration of hydrogen ion in the aqueous solution at 40°C (shrinking state) and 3 °C (swelling state). The Kd value decreased with increasing the concentration of hydrogen ion. These results mean that the extraction of Am(III) proceeds by a cation exchange reaction between Am(III) and the phosphoryl group of MR. Assuming that the extraction mechanism of Am(III) is similar to those of lanthanide ions, which were shown in the previous paper [4], the stoichiometric equation for the extraction of Am(III) can be represented simply as

$$Am^{3+} + 3R-OH \rightleftarrows (R-O)_3Am + 3H^+ \qquad (2)$$

where R-OH denote the phosphoryl group of MR. Furthermore, the ion exchange reaction between sodium ion and MR,

$$Na^+ + R-OH \rightleftarrows R-O^-Na^+ + H^+ \qquad (3)$$

was considered. The extraction constants for Reactions (2) and (3) are defined as

$$K_{ex}^{Am} = \frac{[(R-.)_3Am][H^+]^3}{[Am^{3+}][R-OH]^3} \qquad (4)$$

$$K_{ex}^{Na} = \frac{[R-O^-Na^+][H^+]}{[Na^+][R-OH]} \qquad (5)$$

The K_{ex}^{Na} value was calculated from the pH data before and after the extraction experiments and was evaluated as $3\times10^{-3}$and 2.7×10^{-3} at 40 and 3°C, respectively. From the relation of $[Am^{3+}]_0 << [Na^+]_0$, the mass balance equation of MR (R-OH) is represented as

$$[R-OH]_0 = [R-OH] + \frac{K_{ex}^{Na}[Na^+][R-OH]}{[H^+]} \qquad (6)$$

where $[R\text{-}OH]_0$ denotes the total amount of MR copolymerized in the gel. Assuming that the ionic strength is kept constant during the extraction of Am(III), an apparent extraction constant, $K_{ex}^{Am'}$, can be defined as

$$K_{ex}^{Am'} = \frac{K_{ex}^{Am}}{(1+\beta_1[NO_3^-]+\beta_2[NO_3^-]^2)} = \frac{K_d[H^+]^3}{[R-OH]^3} \qquad (7)$$

where β_1 and β_2 denote the stability constants for the formation of nitrato complexes, $Am(NO_3)^{2+}$ and $Am(NO_3)_2^+$,

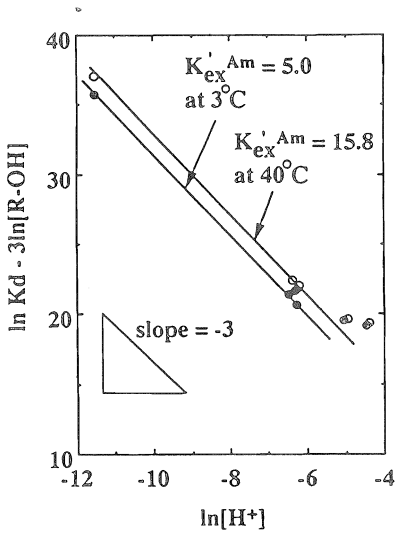


Fig.6 Slope analysis for the extraction of Am(III)

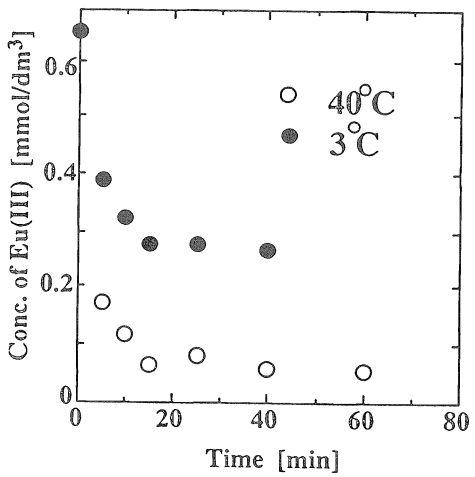


Fig.7 Time variation of the concentration of Eu(III) in aqueous solution. Initial pH and ionic strength was adjusted to 3.7 and 1.0 mol/dm³, respectively.

respectively. The relation between ($\ln K_d$-3ln[R-OH]) and ln[H^+] can be calculated from the experimental data of Fig.5 by using Eqs (6) and (7). The calculation results were shown in Fig. 6. The slopes of experimental data at 40°Cand 3°C were given as about -3 in the range of [H^+] < 10^{-2} mol/dm^3. These results indicate that the stoichiometric relation for the extraction of Am(III) can be described by Eq.(2). The difference between experimental data and solid line at the high acidic range may be due to increasing the hydrophobicity of gel by the undissociation of OH group in MR. Then, as shown in Fig.6, the thermosensitivity of gel is reduced by increasing the hydrohobisity of gel at the high acidic range. The apparent extraction constant, K_{ex}^{Am}', calculated by Eq.(7), was evaluated as 15.8 and 5.0 at 40 and 3°C, respectively. The K_{ex}^{Am}' value at the shrinking state was more than 3 times of that at the swelling state.

3.3 Evaluation of extraction rate

The extraction rate of metal ion into the thermosensitive gel is significant information to evaluate the extractability of gel-liquid extraction system. Figure 7 shows the extraction rate of Eu(III) at 3 and 40°C. Eu(III) was used as a substitute of Am(III). The concentration of Eu(III) in the aqueous solution decreased with increasing the operating time and the extraction equilibrium was reached within 20 min at both temperatures. The extraction rate of Eu(III) into the gel was evaluated by a mass transfer equation,

$$\frac{dq}{dt} = K(q^* - q) \tag{8}$$

where q and K denote the extraction amount of Eu(III) in the gel and the overall capacity coefficient, respectively. q^* means the extraction amount equilibrated with the concentration of Eu(III) in the aqueous solution. The intraparticle diffusivity of Eu(III) in the gel, De, is represented as

$$De = \frac{K \cdot d^2}{60} \tag{9}$$

by using K, where d denotes the diameter of gel [9,10]. Eq.(8) was solved numerically under the initial condition, q=0 at t=0. The De value, which was evaluated from the experimental results of Fig.7, was given as the order of 10^{-12} m^2/s at either 3 or 40°C. The diffusion rate of Eu(III) in the gel is similar to those for the practical extraction chromatographic resins, for example, SDB (styrene-divinylbenzene copolymer) resin swollen with DHDECMP [9,10].

Figure 8 shows the change of extraction amount of Eu(III) with increasing temperature. The increasing rate of temperature was given as 10°C/min as shown in the upper figure. The conformation of polymer network changes from swelling to shrinking with increasing temperature. The temperature-response of gel for the extraction of Eu(III) was very excellent without delay even for the rapid temperature change of 10°C/min.

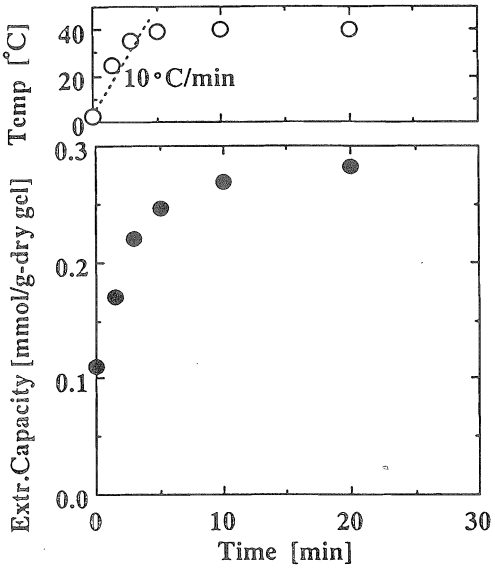


Fig.8 Change of the extraction amount of Eu(III) with increasing temperature at the rate of 10°C/min. Initial pH and ionic strength was adjusted to 3.7 and 1.0 mol/dm^3, respectively.

4 Conclusions

(1) The extraction of Am(III) can be controlled by the conformational change of polymer network with temperature. The conformation of polymer network is reproducible by adjusting the temperature condition. The extraction and release of Am(III) can be repeated stably by the temperature swing operation, which is operated at temperatures above and below LCST of gel.

(2) The extraction rate of Eu(III), which was used as a substitute of Am(III), is fast satisfactorily and the temperature-response of gel for the extraction of Eu(III) is very excellent without delay even for the rapid temperature change of 10°C/min.

(3) The extraction mechanism of Am(III) is represented as

$$Am^{3+} + 3R-OH \underset{\leftarrow}{\overset{\rightarrow}{}} (R-O)_3Am + 3H^+$$

at both the shrinking and swelling states. The extraction constant at the shrinking state is more than 3 times of that at the swelling state. The extraction and release of Am(III) in an aqueous solution can be controlled by the conformational change of polymer network with temperature.

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