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Thermoresponsive gels incorporating di- or tetrathioether units for the separation of metal ions

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Polymer extraction using the copolymers of poly(N-isopropylacrylamide) and monoazapolythioether derivatives for noble metal ions and counter anions such as picrate ion were examined. One of the reagent containing thioether unit, 9-aza-3,6,12,15-tetrathiaheptadecane (ATH) or 6-aza-3,9-dithiaundecane (ATU) were synthesized by the reaction between bis(2-chloroethyl) amine hydrochloride and related thiols in alkarine solution. The monomer unit 9-acryloyl-9-aza-3,6,12,15-tetrathiaheptadecane or 9-acryloyl-6-aza-3,9-dithiaundecane were synthesized. Reagents synthesized were isolated by NMR spectra. The polymerization reaction was performed with N,N-dimethylform-amide as a solvent and αα'-azobisisobutyronitrile as the initiator. The molar ratio of the monomers N-isopropylacrylamide and 9-acryloyl-ATH were varied in a range between 20:1and 150:1 in feed. The resulting products were precipitated in double distilled water and washed for two or three days then evaporated. The polymer synthesized (ATH-NIPAAm) were dissolved in an aliquot volume of water. The sulfur atom concentration of the solution was determined by ICP-AES. The copolymer incorporating monoazadithioether unit were synthesized as same synthetic routes. The extraction behaviour of metal ions were clarified with those of with the copolymer incorporating monoaza-tetra-thioether units.

When the temperature of the solution containing the copolymer increases, the phase transfer occurred and lipophilic species might be absorbed into the polymer phase and separated from the aqueous phase. As the polymer contains the monoaza-polythioether unit, metal ion which is familiar with thioether group may be coordinated with the thioether groups in the polymer chain. Then, the metal ion might be transfered into the polymer phase with an appropriate anion to compensate the charge. The use of anion such as picrate, nitrate and perchlorate ion was effective for extraction of silver ion from the aqueous phase into the polymer phase.

Biography

Kenji Chayama has completed his Ph.D at the age of 32 years from Kobe University. He was awarded The Japan Society for Analytical Chemistry Award for Younger Researchers (1994). He has synthesized more than 50 new reagents which has polythioether groups and published more than 50 papers in journals related to Analytical Chemistry.

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