Adsorption of Divalent Transition Metal Ions with a Chelating Agent on Octadecyl Silica Gel

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This investigation looked at the extraction ability of divalent transition metal ions onto an octadecyl silica gel (C18g) with a 4,4-trifluoro-1-(2-thienyl)-1,3-butadione (TTA) chelating agent. A method of retaining TTA onto C18g (TTA-C18g) was developed in order to adsorb the metal ions. The difference in the half-adsorption and half-extraction pH values between transition metals Ni^{2+} - Co^{2+} was found to be 0.7 in this system. This is better than previously published results of 0.3 for the conventional extraction method using TTA in nitrobenzene. More than 96% of the metal ions in aqueous solution could be adsorbed onto TTA-C18g. Our system, which has no organic phase, can achieve a better removal or separation of transition metal ions than the conventional solvent-extraction methods using TTA in toluene or nitrobenzene.

(Received July 5, 2004; Accepted August 31, 2004)

The 4,4,4-trifluoro-1-(2-thienyl)-1,3-butadione (TTA) used in toluene solvent-extraction (SE) technique is known to be one of the most effective methods to remove or separate toxic metal ions.¹ We have developed a new solvent-extraction method to efficiently remove metal ions using an octadecyl silica gel (C18g) together with TTA (SE-C18g).² This method showed an increase in the extraction ability of the metal ions compared with SE. The extraction mechanism of this system involves to adsorption of the extracted metal chelate in the organic phase onto C18g.³ Because the adsorption reaction is affected by the affinity of C18g to the solvent, it is necessary to use a lower polarity organic solvent, such as toluene. A system has been developed that has no organic solvent, by retaining the TTA molecule directly onto C18g (TTA-C18g). However, the new TTA-C18g particles were found to aggregate together in the aqueous solution due to their hydrophobicity. Hence, a quantitative analysis of metal ion adsorption could not be performed. To prevent aggregation, the C18g particle size was increased. Larger TTA-C18g particles are less likely to aggregate, and are considered to have better adsorption ability. This paper reports on a new method to remove and separate metal ions, without the use of organic solvents, by using large TTA-C18g particles.

Experimental

Reagents and apparatus

The starting materials were silica gel (Wako Pure Chemical

Industries, 1 – 2 mm particle size) and TTA (Dojindo Laboratories). All other reagents were of analytical grade. Deionized water was prepared by a MilliQ Gradient A10 MILLIPORE and used throughout.

An inductively coupled argon-plasma atomic emission spectrometry (ICP-AES, VARIAN VISTA-PRO) apparatus was used to determine to metal ion concentration in aqueous solution. The pH values of aqueous solutions were measured by a pH meter (HORIBA F-21) equipped with a glass electrode.

Preparation of TTA-C18g

Silica gel was crushed and sieved to a size of 0.50 – 1.0 mm. The C18g was synthesized according to a published method.⁴ In order to synthesize TTA-C18g, 50 cm³ of toluene containing 0.5 mol dm⁻³ TTA was added to 10 g of C18g. After standing for 24 h at 277 K, the mixed solution was filtered, washed with deionized water and dried at room temperature under a vacuum.

Adsorption experiment of divalent transition metal ions

Aqueous solutions were prepared containing 1.0 × 10⁻⁴ mol dm⁻³ metal ions (Co^{2+} , Ni^{2+} or Cu^{2+}), 0.1 mol dm⁻³ sodium perchlorate and 2.0 × 10⁻² mol dm⁻³ of a buffer agent (chloroacetic acid or acetic acid). A 20 cm³ aliquot of each solution, along with 0.3 g of TTA-C18g, was put into a 50 cm³ stoppered glass tube. In the case of Co^{2+} , to prevent to oxidation of Co^{2+} to Co^{3+} , 1.0 × 10⁻² mol dm⁻³ ascorbic acid was added to the solution as a reductant. The stoppered glass tubes were shaken a few times each day to reach to reaction equilibrium (within 36 h) at 298 K. After the reaction was complete, the mixed solutions were filtered. The concentration of metal ions in the aqueous solutions was determined by ICP-AES and the pH value of the aqueous phase was measured.

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Fig. 1 Adsorption of divalent transition metal ions as a function of to pH with silica gel, C18g and TTA-C18g. Silica gel: ■, Co²⁺; ▲, Ni²⁺; ●, Cu²⁺. C18g: ◇, Co²⁺; ▽, Ni²⁺; ×, Cu²⁺. TTA-C18g: □, Co²⁺; △, Ni²⁺; ○, Cu²⁺.

Fig. 2 Distribution coefficient of divalent transition metal ions (□, Co²⁺; △, Ni²⁺; ○, Cu²⁺) as a function of to pH with TTA-C18g. The slopes of these lines are +2.

Results and Discussion

As described in the introduction, since C18g particles aggregated due to hydrophobicity in the aqueous phase, it was impossible to use normal C18g as a carrier of the TTA chelating agent. TTA-C18g made from the conventional-size C18g (< 0.053 mm) did not quantitatively adsorb the metal ions in the aqueous solution. We successfully synthesized large particles (0.5 – 1.0 mm) of TTA-C18g, which prevented particle aggregation. Meanwhile, silica gel that had not bonded with an octadecyl group was not able to retain TTA molecules. The amount of TTA retained on C18g was found to be 0.19 ± 0.01 mmol g⁻¹. This value was the average of three measurements via the flask combustion method.⁵

Since divalent metal ions (Co²⁺, Ni²⁺, Cu²⁺) were used for this study, the reaction equation can be expressed as

where HR and M²⁺ represent the TTA retained on C18g and the divalent transition metal ion, respectively. The subscript C18g denotes the species on the solid phase. The distribution coefficient (K_d) was calculated for Eq. (1) as follows:

K_d = moles metal ion per 1 g of TTA-C18g/moles metal ion per 1 cm³ of solution. Figure 1 shows a plot of to adsorption percentage of metal ions onto silica gel C18g and TTA-C18g,

Table 1 The pH_{1/2} values of divalent transition metal ions (M²⁺) with TTA-C18g, SE and SE-C18g systems

M ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺
TTA-C18g	4.5	3.8	2.5
SE ^{a*}	5.5	5.2	2.8
SE-C18g ^{b**}	— ^c	— ^c	2.7

a. Aqueous phase (1 cm³): 1.0×10^{-5} to 1.0×10^{-4} mol dm⁻³ M²⁺ and 0.1 mol dm⁻³ KNO₃. Organic phase (5 cm³): nitrobenzene containing 0.01 mol dm⁻³ of TTA. *See Ref. 7.

b. Aqueous phase (10 cm³): 1.0×10^{-4} mol dm⁻³ M²⁺ and 0.1 mol dm⁻³ NaNO₃. Organic phase (10 cm³): cyclohexane containing 0.01 mol dm⁻³ of TTA. C18g (< 0.053 meshes): 0.5 g. **See Ref. 3.

c. —: not extracted.

versus pH of the aqueous solutions. Figure 1 shows that the TTA-C18g has the ability to adsorb metal ions, whereas the silica gel and C18g have no adsorption ability in this pH range. Figure 2 gives plots of log K_d versus pH for the aqueous solutions. The solid lines in this figure show plots with a slope of +2. From these results, the reaction is well expressed by Eq. (1) for the divalent ion systems studied. As can be seen in Fig. 2, the adsorption selectivity in this system is Cu²⁺ > Ni²⁺ > Co²⁺. The stability constant (β_2) can be defined for Eq. (1) as follows:

$$\beta_2 = [MR_2]/[M^{2+}][R^-]^2. \quad (2)$$

The stability constants have been reported to be log β_2 = 16.3, 15.3 and 14.9 for Cu²⁺, Ni²⁺ and Co²⁺, respectively.⁶ The selectivity of our system is in agreement with the order of the stability constant of the above metal ions with TTA.

Table 1 gives the pH values of the half-extraction and half-adsorption (pH_{1/2}) for the TTA-C18g, SE and SE-C18g systems. The results given in the table show that Co²⁺ and Ni²⁺ could not be extracted by the SE-C18g method using the lower polarity solvent, toluene. These metal ions were extracted in the SE system using TTA in nitrobenzene, with higher polarity. The maximum value of adsorption for Co²⁺ was 96% (Fig. 1). The values for Cu²⁺ and Ni²⁺ were more than 96% in the TTA-C18g system.

The difference in to pH_{1/2} value for the TTA-C18g system between Ni²⁺-Co²⁺ was 0.7, whereas that of the SE system was only 0.3. This result shows that our TTA-C18g system has better mutual selectivity for Ni²⁺-Co²⁺ than the SE system using TTA in nitrobenzene.

This new method has the advantage of a chelating agent that can be used effectively to remove metal ions from an aqueous solution without organic solvents. It can be expected in a reduction of the amount of toxic solvent used.

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