Complexation Properties of the Chelating Resin Functionalized with Iminodiacetic Acid. Application to Column Separation of Molybdenum and Tungsten

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A chelating polymer resin having iminodiacetic acid (IDA) as the functional group has been prepared for the selective adsorption of oxo-molybdenum(VI) or oxo-tungsten(VI). The ¹³C- and ¹H-NMR spectra of these IDA complexes have been studied in the pH range of 4–7 to elucidate the complexation properties of the functional group. The NMR study in the homogeneous system suggests that the IDA forms a 1:1 complex with Mo^{VI} and W^{VI} in the pH region 4–7. The peak integration of coordinated acetate signals indicates that the complex formation of IDA is much favorable with Mo^{VI} than with W^{VI}. A selective adsorption of Mo^{VI} over W^{VI} has been realized by the chelating resin having an IDA group. A mutual separation of Mo^{VI} and W^{VI} has been demonstrated by the IDA resin in a column system.

Keywords Chelating resin, iminodiacetate, complexation property, molybdenum, tungsten, column separation

Highly purified molybdenum and tungsten have become tremendously important in industries. Since the chemical properties of molybdenum and tungsten are very similar^{1,2}, their mutual separation usually requires tedious procedures. For the separation of metals, there is a growing interest in the use of hydrometallurgical techniques, including solvent extraction³ and ion-exchange processes.^{4,5} Ion-exchange methods are being applied to the analytical separation of molybdenum and tungsten;⁵ still the selectivity of the conventional anion-exchangers toward anionic oxo-molybdenum(VI) and oxo-tungsten(VI) ions is not sufficiently high to allow their clear separation.

Chelating polymer resins containing a highly selective complexing group are one of the attractive candidates for the metal separation procedure because of their high selectivity and operational convenience.⁶ The selectivity of the chelating resin is mainly attributed to the nature of the chelating reagent fixed on the polymer support. Iminodiacetic acid (IDA) is the most popular functional group for a chelating resin that can form stable complexes with metal ions of high valency. We have measured the ¹H- and ¹³C-NMR spectra of IDA in the presence of molybdenum(VI) or tungsten(VI) to elucidate the ligand selectivity toward these metal ions. A part of the work has been reported briefly.⁷ This is the full detailed paper dealing with the NMR study, preparation of the chelating resin, adsorption characteristic of the resin and the application to the column separation of molybdenum(VI) and tungsten (VI).

Experimental

Materials

Reagent grade Na₂MoO₄·2H₂O and Na₂WO₄·2H₂O were used for the preparation of metal ion stock solutions. Analytical grade iminodiacetate and diethyliminodiacetate were used without further purification. All other reagents and solvents were analytical grade.

IDA resin was prepared according to the following procedure. A suspension of chloromethylated styrene-10%-divinyl benzene copolymer beads (macroreticular type; surface area, 7.3 m² g⁻¹; mean pore diameter, 720 Å; Cl, 17.1%; 30–60 mesh) (25 g) and diethyliminodiacetate (47.6 g) in 270 cm³ of dioxane was refluxed for 24 h under stirring. The resin beads were filtered off and were washed with ethanol. To the resin beads a 250 cm³ of 1 M (M=mol dm⁻³) sodium hydroxide solution was added and the suspension was refluxed for 24 h. The beads were filtered off, washed with water and then immersed in 2 M hydrochloric acid overnight. After being washed with water, the resin beads were transferred to a Soxhlet extractor, extracted with ethanol, and then dried *in vacuo*. The yield of the IDA resin was 33.5 g. The nitrogen content of the IDA resin was 4.2% (ligand content was 3.0 mmol/g-resin).

Adsorption capacity

Equilibrium adsorption capacity (amount of metal ion adsorbed on one gram of the resin) was determined in a batchwise technique with the metal ion always being in excess over the resin capacity. Typically, 100 mg of dry resin was added to 100 cm³ of metal ion solution (5×10⁻³

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M) of various pH. After the solution was shaken for 2 d at 25°C, the equilibrium pH and the amount of metal ion remaining in the solution were determined. The capacity of the resin was calculated by the difference observed between the initial and the final metal ion concentration.

Measurements

The metal ion concentration was determined by an inductively coupled plasma atomic emission spectrometer, Seiko Model SPS-1200A. The ^1H -NMR and ^{13}C -NMR spectra were measured in D_2O by a Varian VXR-300 spectrometer with sodium 3-(trimethylsilyl)propanesulfonate as the internal standard. A digital pH meter, TOA Model HM-18E, was used for the pH measurements. The pH values of solutions were adjusted with phosphate buffer in the pH range of 6–8, with acetate buffer in the pH range of 3–5 and with hydrochloric acid below 3.

Adsorption rate

The adsorption rate of the metal ion was determined in a batchwise experiment. One gram of dry resin was swollen with water and was added to 100 cm^3 buffered metal ion solutions (5×10^{-4} M) of various pH values. While stirring, small portions of the samples were withdrawn at appropriate intervals and the metal ion concentration was determined.

Distribution coefficient

In a solid ion exchanger such as polymer chelating resin, the distribution coefficient is defined as⁸

$$K_d = \frac{\text{amount of metal ion per g of dry resin}}{\text{amount of metal ion per cm}^3 \text{ of solution}}$$

The equilibrium distribution coefficient of metal ion was determined under a batchwise procedure. One gram portion of dry resin was added to a 100 cm^3 buffered metal ion solution (1×10^{-3} M). After shaking for seven days at 25°C, the equilibrium pH and the amount of metal ion remained in the solution were determined. The K_d value was calculated according to the formula given above.

Column-breakthrough experiments

Column separation of Mo^{VI} and W^{VI} was typically carried out as follows: Five grams of resin was swollen with water and then poured onto a glass column (ϕ 1.0 cm). The column was conditioned with 0.5 M acetate buffer (pH 5) prior to use. Equimolar amounts of Mo^{VI} and W^{VI} (5×10^{-3} M each) were passed through the column continuously at a rate of 1 $\text{cm}^3 \text{ min}^{-1}$. The effluent was fractionated into 20 cm^3 portions and the amount of the metal ions was determined. The adsorbed Mo^{VI} and/or W^{VI} was liberated from the column by elution with 1 M sodium hydroxide solution. The solution coming out of the column was fractionated again and the amount of metal ions was determined.

The column was ready to use again after washing first with dilute hydrochloric acid, then with water.

Results and Discussion

NMR study

One of the characteristic features of oxo-molybdenum(VI) and oxo-tungsten(VI) is that they change their chemical form depending on pH of the solution as well as on the concentration of metal ion.⁹ This makes the separation of Mo^{VI} and W^{VI} quite difficult by anion exchange methods. In basic media, the major species are mononuclear MoO_4^{2-} and WO_4^{2-} , but they tend to form polynuclear anions in acidic media. Mononuclear MoO_4^{2-} begins to form at pH higher than 5, while that of W^{VI} exists at a much higher pH region.¹⁰

The ^{13}C -NMR spectra of IDA were measured at pH 6 in D_2O with the presence of equimolar amount of Mo^{VI} or W^{VI} (Fig. 1). Iminodiacetic acid gives two ^{13}C -NMR

Fig. 1 The ^{13}C -NMR spectrum of iminodiacetic acid and the spectra measured in the presence of equimolar amounts of Mo^{VI} and W^{VI} at pH 6 in D_2O .

Fig. 2 Schematic structure of the IDA complex, $[\text{MO}_3(\text{IDA})]^{2-}$ ($\text{M}=\text{Mo}, \text{W}$).

Fig. 3 The intensity ratio of signals due to acetate protons as a function of pH for the equimolar mixture of Mo^{VI} , W^{VI} and IDA. The intensities of each species i.e., IDA- Mo^{VI} , IDA- W^{VI} complexes and free IDA were calculated by the peak integration of the acetate protons. The concentration of IDA, Mo^{VI} and W^{VI} were 0.2 M, 0.1 M and 0.1 M, respectively. The spectra were measured in D_2O .

peaks corresponding to the acetate carbons. These two peaks shift 6.9 and 6.5 ppm down the field upon addition of an equimolar amount of Mo^{VI} . The peaks for the free IDA almost disappeared due to complete complexa-

tion.¹¹ Four ^{13}C peaks corresponding to free and coordinated acetate groups were observed in the presence of W^{VI} . The ^1H -NMR spectra of the IDA- Mo^{VI} and IDA- W^{VI} solution show quartet peaks corresponding to the typical AB pattern of the coordinated acetate protons¹² at pH 4–7. The clear quartet peaks suggest the formation of fixed chelating ring of rigid conformation. Only the structure given in Fig. 2 can explain the observed couplet. Thus, at this pH region IDA forms a 1:1 complex with Mo^{VI} in which two acetate arms of IDA coordinate symmetrically to the MoO_3 core. In case of W^{VI} , on the other hand, free IDA protons were observed as the major peak, along with the small quartet peaks of the coordinated acetate protons. In agreement with the results of ^{13}C -NMR spectra, the intense peak of free acetate protons in ^1H -NMR suggests less favorable complexation of IDA with W^{VI} . The ^1H -NMR spectra of equimolar mixture of Mo^{VI} , W^{VI} and IDA were measured at various pH values. The peak intensity of the free and complexed acetate signals was plotted as a function of pH (Fig. 3). The peak intensity of the coordinated acetate protons is always larger in the presence of Mo^{VI} than that in the presence of W^{VI} . Thus the IDA forms a metal complex with Mo^{VI} rather than with W^{VI} in the pH range measured.

Equilibrium adsorption capacity

On the basis of NMR studies, the chelating resin having IDA group looks promising for the preferential uptake of Mo^{VI} rather than W^{VI} . The adsorption capacity vs. pH profile of the IDA resin is shown in Fig. 4. The adsorption of Mo^{VI} is much more favorable than that of W^{VI} . We observed that the adsorption of Mo^{VI} is always accompanied with the increase in pH of the solution suggesting that protons are withdrawn from the solution upon coordination. The maximum capacity for Mo^{VI} is 2.2 mmol g^{-1} , which is less than the estimated content of the functional group of the IDA resin (3.0 mmol g^{-1}). The IDA resin appeared to form a 1:1 complex with Mo^{VI} , in analogy with the solution phase.

Fig. 4 Equilibrium adsorption capacity of the IDA resin for Mo^{VI} and W^{VI} as a function of pH. IDA resin, 0.1 g; metal concentration, 5×10^{-3} M (100 cm^3).

Fig. 5 Time courses for the adsorption of Mo^{VI} and W^{VI} with the IDA resin. IDA resin, 1 g; metal concentration, 5×10^{-4} M (100 cm^3); pH, 4.5.

On the contrary, the capacity of W^{VI} is remarkably lower than that of molybdenum in the pH range 4–5.5. The capacity slightly increased at acidic pH region. Practically no adsorption of Mo^{VI} nor of W^{VI} takes place at basic pH region. In fact adsorbed Mo^{VI} and W^{VI} were readily liberated from the resin on treatment with 1 M sodium hydroxide solution.

Adsorption rate

Although the equilibrium capacity and the distribution coefficients are of fundamental importance in characterizing the chelating resin, the rate of adsorption is extremely important from a practical point of view. The time-courses of Mo^{VI} and W^{VI} adsorption on IDA resin were examined at pH 4.5. The result is given in Fig. 5. At pH lower than 3, the adsorptions of both Mo^{VI} and W^{VI} were slow, and the equilibrium was not attained even after 2 h. At pH around 4–5, the adsorption of Mo^{VI} was fast and the equilibrium was attained in 50 min, while that of W^{VI} required much more time. At pH higher than 6, the adsorption for Mo^{VI} was fast initially, and started to slow down after 20 min, but very slow adsorption of W^{VI} was observed. These results show that the pH region around 4–5 is most favorable for the separation of Mo^{VI} and W^{VI} .

Distribution coefficient

The distribution coefficients of Mo^{VI} and W^{VI} with the IDA resin were examined as a function of pH. The results are given in Fig. 6. The $\log K_d$ vs. pH curves clearly imply that the adsorption of Mo^{VI} by the IDA resin is always superior to that of W^{VI} . This is in good accordance with the results of NMR studies. The large difference of K_d value in the pH range of 4–5.5 suggests the possibility of the column separation of two metal

Fig. 6 The distribution coefficient of Mo^{VI} and W^{VI} with the IDA resin. IDA resin, 1.0 g; metal concentration, 1×10^{-3} M (100 cm^3).

Fig. 7 The column breakthrough profile for the separation of Mo^{VI} and W^{VI} . Bed resin, 5 g (19.6 cm^3); pH, 5; buffer, 0.5 M acetate buffer; metal ion feed, 5×10^{-3} M each; flow rate, $1 \text{ cm}^3 \text{ min}^{-1}$.

ions. The large K_d values for Mo^{VI} at pH 4–5.5 indicate that Mo^{VI} is adsorbed nearly completely on the IDA resin. The Mo^{VI} can be retained in the resin as the mononuclear complex with IDA group, in analogy with homogeneous solution. Therefore, facile dissociation of polynuclear species into mononuclear ones may take place in the presence of IDA resin to form 1:1 complexes with the functional group. Complexation of W^{VI} with IDA group is less favorable, presumably due to the higher stability of polynuclear species in the solution.^{9,10} The K_d vs. pH profile indicates that the complex formation of IDA group both with Mo^{VI} and W^{VI} is unlikely in basic media because the base hydrolysis should compete with the complexation.¹³

Column separation of molybdenum(VI) and tungsten(VI)

In the batch experiments, the IDA resin showed an apparent selectivity toward Mo^{VI} over W^{VI} at pH values

ranging from 4 to 6. This suggests the efficient separation of the two metal ions. We have examined the selective retainment of Mo^{VI} by the column system. A solution of given pH containing equimolar amounts of Mo^{VI} and W^{VI} was continuously passed through the column; the metal ions in the effluent were determined. The pH of the feed solution is one of the most important parameters, since it greatly affects the separation efficiency. Figure 7 shows typical breakthrough curves at pH 5.0. The retained metal ions were quantitatively released from the column by elution with 1 M sodium hydroxide solution. The optimum pH value for successful separation is around 5: the amount of Mo^{VI} retained in the resin is much larger and the leaking of W^{VI} is faster than that under any other pH conditions. At higher pH, both metals quickly appeared out of the column without effective adsorption. Thus the efficiency of the column separation was most favorably operated at around pH 5.0.

In conclusion, the ^{13}C - and ^1H -NMR spectroscopic study in homogeneous solution provided important information about the complexation behavior of IDA with Mo^{VI} and W^{VI} . IDA forms a 1:1 complex ($[\text{MO}_3(\text{IDA})]^{2-}$) with MO_3 ($\text{M}=\text{Mo}, \text{W}$) core in the pH range of 3–8. The coordination of IDA toward Mo^{VI} is much more favorable than that with W^{VI} . The chelating resin having IDA group revealed a higher adsorptibility of Mo^{VI} over W^{VI} at pH 4–6. An efficient separation of Mo^{VI} and W^{VI} was achieved by the column packed with the IDA resin. Thus, iminodiacetate was demonstrated to be an useful functional group of the chelating resin for the selective separation of Mo^{VI} from W^{VI} .

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