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Adsorption Behavior of Various Metal Ions in Nitrite Medium and Separation of Some Metals by Anion Exchange

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Abstract

The purpose of this work is to investigate the adsorption behavior of various metals ions and the possibility of their separation in nitrite medium by anion exchange. Distribution coefficients of about 40 metals from nitrite solution onto a conventional anion exchanger (IRA-900) and a new type anion exchanger (AR-01) containing benzimidazoles as functional group were systematically measured. Based on the different adsorbability, some metal pairs such as Zn(II)/Cd(II) and Ga(III)/In(III) in NaNO₂-HNO₃ solution, were successfully separated from each other by column chromatography.

1 Introduction

As an efficient separation method of metal ions in solution, ion exchange technology has found wide applications in analytical chemistry, water treatment, metallurgical and radiochemical separation during the past decades. Anion exchange behavior of most metal ions in many kinds of aqueous media including chloride, nitrate, sulfate, fluoride, carbonate and the combination of these media have been extensively studied.[1,2] However, until now very little attention has been given to the anion exchange of metal ions in nitrite medium. It was reported that some metal ions can form anionic nitro-complexes in nitrite medium.[3] In our previous work, we investigated the adsorption and separation behavior of the three typical transition metals of Co(II), Ni(II) and Cu(II) in nitrite solution with a commercial anion exchanger, Amberlite IRA-900 and a novel silica-based anion exchanger, AR-01.[4] It was found that successful separations of Co(II) from Ni(II), and Cu(II) from Ni(II) were achieved by column chromatography based on their different adsorbability.

In this study, to evaluate the adsorption behavior of various metal ions from nitrite medium onto anion exchanger, distribution coefficients of about 40 metal ions in the aqueous solutions containing 0-3 M ($M=\text{mol/dm}^3$) NaNO₂ and 0.1 M HNO₃ were measured systematically with the anion exchangers of IRA-900 and AR-01. Furthermore, separation behavior of some typical metal pairs such as Zn(II)/Cd(II) and Ga(III)/In(III) was demonstrated by column chromatography based on their different adsorbability.

2 Experimental

2.1 Materials

The structure and property of the anion exchangers are shown in Table 1. The bead diameter of IRA-900 is

450-550 μm and the capacity is 4.2 eq/kg-resin. AR-01 is a new type of anion exchanger prepared in our laboratory. It consists of the macroreticular resin embedded in porous silica particles with a mean particle size of 50 μm . The resin contains N-methylbenzimidazole (weak-base) and N,N'-dimethylbenzimidazolium (strong-base) groups as exchange sites. The total exchange capacity and strong-base capacity are 3.4 eq/kg-resin and 2.0 eq/kg-resin, respectively.

2.2 Batch Adsorption

The sample solutions containing a metal were prepared by dissolving its nitrate salt in HNO_3 - NaNO_2 solution. About 1 g of anion exchanger and 20 cm^3 of a sample solution containing 10 mM of metal ion, 0.1 M HNO_3 and 0-3 M NaNO_2 , were mixed in a glass flask. The flask was placed in the shaking water bath maintained at 298 K and was shaken for 2 hours. Then the solution was separated from the anion exchanger by filtration and the metal concentrations in the solution were analyzed by ICP-AES. The anion exchanger was washed and then dried at 333 K in vacuum for 12 hours. The distribution coefficient (K_d) was calculated by Eq.(1).

$$K_d = \frac{C_0 - C_s}{C_s} \times \frac{V_s}{W_R} \quad (\text{dm}^3/\text{kg-resin}) \quad (1)$$

where C_0 and C_s denote the metal concentration in the aqueous phase before and after adsorption, respectively. W_R indicates the weight of the dry resin (kg) and V_s indicates the volume of the aqueous phase (dm^3).

2.3 Column Separation

Separation experiments were conducted using a Pyrex-glass column with 10 mm internal diameter and 500 mm length. The column and the throughput solutions were kept at 298 K. 30 cm^3 of a sample solution containing 6-10 mM of metal ions, 0.5 M NaNO_2 and 0.1 M HNO_3 was fed to the column at flow rate of 0.3 dm^3/h . Then washing and eluent solutions were supplied to the column at the same flow rate, successively. The effluent from the column was collected by auto-fractional collector in 10 cm^3 aliquots and analyzed by ICP-AES.

3 Results and Discussion

3.1 Adsorption Behavior

The effects of NaNO_2 concentration on distribution coefficients of various metals onto IRA-900 are shown in Fig. 1 to Fig. 3. Note that the metal ions except Mo(VI) and Cd(II) showed almost no or very weak adsorption on the anion exchanger without NaNO_2 . However, the adsorption of In(III), Co(II), V(V), Cd(II), Mo(VI), Ga(III), Zn(II), Cu(II), Cu(I), Ag(I), Pb(II), Cr(III) and Al(III) increased significantly with increasing nitrite concentration and the K_d of some ions showed a maximum value at around 1 M NaNO_2 (Fig. 1 and Fig. 2). On the other hand, the metals such as Li(I), Ca(II), Sr(II), and the trivalent rare earths exhibited almost no or only slight adsorption over 0-3 M NaNO_2 and the K_d values are less than 4 dm^3/kg (Fig.3). From the results of K_d measurement, the adsorbability of the metal ions from nitrite solution onto anion exchanger can be summarized as follows:

- (1) Strong adsorption ions ($K_d > 100$): In(III), Co(II), V(V), Cd(II), Mo(VI), U(VI), Ru(III).

Table 1 Structure and property of the anion exchangers

Anion exchanger	AR-01	IRA-900
SEM image
Functional group	4-(1-Methylbenzimidazole-2-yl)phenyl 4-(1,3-Dimethylbenzimidazolium-2-yl)phenyl	Quaternary ammonium
Bead diameter (μm)	37-74	450-550
Resin content (%)	24.4	100
Support	SiO_2	—
Total capacity (EC) (meq/g-resin)	3.4	4.2
Strong base capacity N4 (meq/g-resin)	2.0	4.2

- (2) Moderate adsorption ions ($K_d=20-100$): Zn(II), Cu(II), Cu(I), Ag(I), Pb(II), Cr(III), Ga(III), Al(III).
- (3) No or very weak adsorption ions ($K_d<5$): Ni(II), Mn(II), alkali metals, alkaline earths and rare earths.
- (4) Some metal ions such as Fe(II), Fe(III), Sn(IV), Hg(I), Hg(II) and Zr(IV) were found to precipitate in the nitrite solution probably due to hydrolysis reactions.

Fig.1 Effect of nitrite concentration on the adsorption of Mo(VI), V(III), Cd(II), In(III) and Co(II) on IRA-900

Fig.2 Effect of nitrite concentration on the adsorption of Ga(III), Zn(II), Cu(II), Cu(I), Ag(I), Pb(II), Cr(III) and Al(III) on IRA-900

Fig.3 Effect of nitrite concentration on the adsorption of Li(I), Sr(II), Ca(II) and trivalent rare earths on IRA-900

Fig.4 Effect of nitrite concentration on the adsorption of Ga(III), In(III), Zn(II) and Cd(II) on AR-01

Fig.4 illustrates the K_d values of Ga(III), In(III), Zn(II) and Cd(II) from nitrite solution onto AR-01 as a function of NaNO_2 concentration. As seen, the adsorption of these metal ions was significantly promoted by increasing NaNO_2 concentration and the adsorption behavior is similar to the results shown in Fig. 1 and Fig. 2. On the other hand, the K_d value of In(III) is much higher than that of the same group element, Ga(III), and the separation factor (SF) between In(III) and Ga(III) is 10-20 at 0.5-1 M NaNO_2 . Similarly, the adsorption of Cd(II) is stronger than Zn(II) and the SF for Cd(II)/Zn(II) is about 10.

In nitrite solution, some metal ions can form anionic nitro-complexes and show adsorbability on an anion exchanger. The complex formation and adsorption reactions of metal ions in nitrite medium can be expressed as

Where m , n and R denote the charge number of metal ion, the coordination number of nitro-complexes and the fixed-ionic-group of anion exchanger, respectively. The adsorbability of metal ions is considered to depend on their complexation ability with NO_2^- . In many cases of anion exchange for metal complexes, a maximum adsorption is observed in a certain ligand concentration based on the equilibria of complex formation and the competitive adsorption of anionic ligand.[5,6] As shown in Fig. 1, Fig. 2 and Fig. 4, the maximum K_d values of some metals were observed at around 1 M nitrite.

3.2 Separation behavior of some metal pairs

From the above K_d measurement results, it was found that some metal pairs of the same group such as Ga(III)/In(III), Zn(II)/Cd(II) and Co(II)/Ni(II) show significantly different adsorbability from nitrite solution onto an anion exchanger. This indicates that efficient separation between these metal pairs can be expected by column chromatography. In our previous studies, it was found that compared to IRA-900, AR-01 shows faster adsorption-elution kinetics and higher stability in nitric acid medium.[4,7,8] In this work, the separations of Ga(III) from In(III) and Zn(II) from Cd(II) were attempted by using AR-01 packed column.

Fig. 5 shows the results of the separation experiment for a sample solution containing 6 mM Ga(III), 10 mM In(III), 0.5 M NaNO_2 and 0.1 M HNO_3 by an AR-01 packed column. As can be seen, Ga(III) leaked out the column firstly with the sample solution and the first part of 0.1 M HNO_3 eluent solution. The In(III) was strongly adsorbed and then eluted off effectively by 0.1 M HNO_3 , showing a sharp elution peak. Successful separation between Ga(III) and In(III) was achieved. A separation experiment for a sample solution containing 9-10 mM Zn(II) and Cd(II), 0.5 M NaNO_2 and 0.1 M HNO_3 was carried out by using the AR-01 packed column, and the results are presented in Fig. 6. As seen, compared to Cd(II), the adsorption of Zn(II) was weaker and leaked out the column firstly. Cd(II) was completely adsorbed and efficiently eluted off by 0.1 M HNO_3 . Perfect separation between Zn(II) and Cd(II) was obtained.

Fig. 5 Results of separation experiment for a Ga(III)-In(III) containing nitrite solution by AR-01 column

Fig. 6 Results of separation experiment for a Zn(II)-Cd(II) containing nitrite solution by AR-01 column

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