BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3764—3767 (1973)

The Separation of Silver, Bismuth, Cadmium, and Zinc as Their Trioctylamine Complexes by Extraction Chromatography

Takaharu Honjo, Shigeru Ushijima, and Toshiyasu Kiba
Department of Chemistry, Faculty of Science, Kanazawa University, Marunouchi, Kanazawa, Ishikawa 920

(Received June 1, 1973)

The behavior of milligram amounts of silver, bismuth, cadmium, and zinc in liquid-liquid extraction has been studied with 20% trioctylamine (TOA) in carbon tetrachloride. The results have also been applied to the separation of the four metals as their TOA complexes by extraction chromatography. After passing a sample solution of 2 M HCl through a column (ϕ 1 cm×l 30 cm) consisting of a stationary phase of TOA-CCl_4 on Kel-F, the metal ions were retained and then eluted with 5.5 M HCl at the rate of 0.5—1 ml/min at 20±1 °C. Silver was found in 90—180 ml of the effluent; Bi was flowed down in 200—500 ml of the same effluent. The cadmium and Zn were held so firmly on the column that they could not be removed under the above conditions. Therefore, water was passed through to release these metals. Zinc was first flowed down with 0—50 ml, and then Cd, with 200—500 ml of water. When 5 M HNO_3 was used as the eluting solution instead of water, the Cd was immediately removed from the column. The percentage recovery of these metals in the extraction chromatography was estimated as 101% (Ag), 99% (Bi), 97% (Cd), and 94% (Zn) respectively. The distribution ratios of these metals, as obtained by the extraction chromatography of the TOA-carbon tetrachloride (Kel-F)-HCl system, were in quite good agreement with those obtained by the batch extraction.

For the past few years, the group separation of nineteen common cations (Fe, Hg, Sn, Ag, Bi, Zn, Cd, Sb, Cr, Al, Cu, Co, Ni, Pb, Mn, Mg, Ca, Sr, and Ba) has been attempted in the authors' laboratory by extraction chromatography with six different columns (TBP-(1), TOA, TBP-(2), AcAc, TTA-(1), TTA-(2)).[1] One of these columns consists of the 20% TOA–CCl_4–(Kel-F)–2 M HCl system; four metal ions, silver, bismuth, cadmium, and zinc, could be selectively held on this column. The present authors aimed to separate these retained metal ions from each other by passing a suitable eluting solution through the column. The TOA(trioctylamine) has been used as a powerful extractant of metals;[2] recently, however, this liquid ion-exchanger has been found also to be

---

[1] I. Akaza, T. Tajima, and T. Kiba, This Bulletin, **46**, 1199, (1973).

[2] T. Sato, *Kagaku to Kogyo*, **20**, 52 (1967).

suitable for the chromatographic separation of metals.[3] Cerrai and Testa have also achieved the mutual separation of Ni-Co-Fe by using a reversed-phase column of cellulose impregnated with TOA, with hydrochloric acid as the eluent.[4] The process of the extraction chromatography are closely related to the ordinary liquid-liquid extraction in batch, as has already been described by the present authors with regard to the Zn Hg, and Co–STTA–cyclohexane (Kel-F) system;[5] therefore, some basic investigations should be made into the behavior of milligram amounts of Ag, Bi, Cd, and Zn in solvent extraction with trioctylamine in carbon tetrachloride. The optimum conditions for the mutual separation of these metals by extraction chromatography could be predicted from the above results. The separation could be achieved successfully; the relation between the extraction chromatography and the liquid-liquid extraction was also considered.

Experimental

Apparatus. A chromatographic glass tube of ϕ 10 × 1 300 mm equipped with a fritted glass filter; a Toyo fraction collector, Type E-E, SF 200 A; a KM-type shaking machine, Type V-S, KK IWAKI, 280 stroke/min, a well-type scintillation counter, Kobe Kogyo Corp, Ten scaler SA-250; a 200-channel pulse-height analyser; an Expandmatic Beckman pH meter; a Hitachi Horiba M 5 pH meter.

Materials. The radioisotopes, Ag–110 m, Bi-207, Cd-115m, and Zn-65, were imported from the New England Nuclear Corp and The Radio Chemical Centre, and were used as the tracers. The tracer of Cd contained some radioactive impurities; therefore, it was purified by extraction with 20% TOA–CCl_4 from a 2 M HCl solution and by back-extraction with 5 M HNO_3. The purity of each tracer was checked by means of the 200-channel pulse-height analyser at every use. Each of the metal salts, such as $AgNO_3$, $Bi(NO_3)_3$-$5H_2O$, $Cd(NO_3)_2 4H_2O$, and $Zn(NO_3)_2 6H_2O$, was dissolved in a slightly acidic solution (pH 0.3—4.5) to 0.5 mg/ml. TOA (trioctylamine) of the GR grade was purchased from the Tokyo Kasei Co. Kel-F 300 moulding powder, the trade name of polytrifluorochloroethylene, was obtained from the Daikin Kogyo Co. The other reagents were reagent-grade materials.

Extraction and Back-extraction. Into a 50-ml centrifuge tube, 20% TOA in carbon tetrachloride (10 ml) and an aqueous solution (10 ml) containing 0.5 mg of a metal and trace amounts of its radioactive tracer were put together; the contents were then agitated with a shaking machine for 2—30 min at 20±1 °C. After centrifugation, a 3-ml portion was taken out of each phase into a test tube, the radioactivity was counted with the scintillation counter, and the distribution ratio of the metal was calculated. The back-extraction behavior of the metal was also examined by shaking the organic phase with an aqueous solution adjusted to a suitable acidity with HCl. Since the extraction equilibria involve the extraction of HCl along with the metal chloride,[6] the aqueous phase and organic phases were pre-equilibrated with each other to prevent any change in the acidity or in the concentration of the reagent during the extraction.

Preparation of the Column and the Extraction Chromatographic Procedure. The Kel-F was crushed by means of a grinding mixer, and particles of 42—80 mesh was collected by sieving through a screen. A 5.5-g portion of Kel-F and a 10-ml portion of 20% TOA in carbon tetrachloride, which had been pre-equilibrated with 2 M HCl, were put into an Erlenmyer flask fitted with a stopper; the contents were then shaken by hand so as to become homogeneous and subsequently allowed to stand overnight in a dark place. The product was then slurried with an eluting solution: the slurry was then packed, little by little, into a glass tube, which had previously been then filled with an eluting solution as has been described in the preceding paper.[5] The chromatographic column of a 20 × 2 cm bed was thus prepared simply, and the excess TOA solution was washed down from the column by passing through enough volume of 2 M HCl. In this case, the upper surface of the column should be covered with 2 M HCl to a depth of 1—2 cm. The eluting solution should have been previously saturated with the organic solution of the stationary phase; also, the sample solution should have the same acidity as the eluting solution. Each 1-ml portion of the stock solution, containing 0.5 mg of metal, was mixed with a 49-ml portion of 2 M HCl to prepare the test solution. To investigate the chromatographic behavior of the metals, a minute amount of the radioactive tracer was added to the stock solution; however, the total amount of the metal present in the solution might be taken as unvaried from 0.5 mg. From a separation funnel fitted to the top of the column, a 50-ml portion of the sample solution was flowed down through the column at the rate of 0.5—1 ml/min. After washing the column three times with 5—10 ml of 2 M HCl, 500—1000 ml of the eluting solution, adjusted to an adequate acidity of HCl, was put into a 1000-ml separation funnel and passed through the column at the rate of 0.5—1 ml/min. The eluate was subsequently divided into 5-ml fractions by means of a fraction collector. A 3-ml portion of the eluate was pipetted out of each 5-ml fraction into a test tube, and the radioactivity was counted by means of a NaI(Tl) well-type scintillation counter. All the experimental procedures were carried out in the thermostatic room at 20±1 °C. The Kel-F in the degraded column was taken out into a 200-ml beaker and washed two or three times with ethanol, water, 6 M HCl, acetone, and ether successively. Then the materials were air-dried, and the particles of a 42—80 mesh were collected by sieving them through a screen and were then used for further experiments.

Results and Discussion

Liquid-liquid Extraction of Silver, Bismuth, Cadmium, and Zinc. The extraction of milligram amounts of silver, bismuth, cadmium, and zinc with 20% TOA in carbon tetrachloride was investigated for aqueous solutions with varying concentrations of HCl. The back-extraction behavior of these metals was also investigated with 2—12 M HCl. As is shown in Fig. 1, about a 100% quantitative extraction of metals was achieved in 2—3 M HCl (Ag), 2—5 M HCl (Bi), 2—9 M HCl (Zn), and 2—10 M HCl (Cd). The back-extraction curves of Ag and Bi show shapes almost the reverse of those of the extraction, but Cd and Zn could not be back-extracted with 2—12 M HCl. It seemed strange that zinc has a relatively lower extractability in the acid region of 0—0.6 M, but can

---

[3] U. A. Th. Brinkman, G. De Vries, and E. Van Dalen, *J. Chromatogr.*, **22**, 407 (1966).

[4] E. Cerrai and C. Testa, *ibid.*, **6**, 443 (1961).

[5] T. Honjo and T. Kiba., This Bulletin, **46**, 1706, (1973).

[6] T. Kojima, H. Fukutomi, and H. Kakihana, *ibid.*, **42**, 875 (1969).

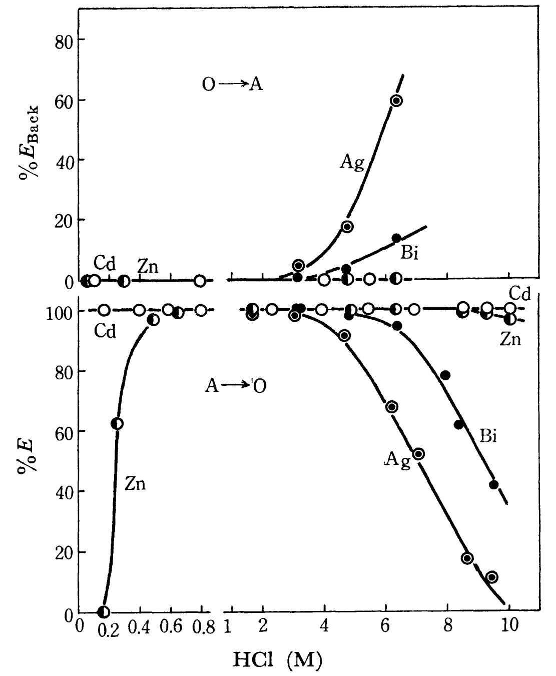

Fig. 1. The extraction and the back-extraction curves of Ag, Bi, Cd, and Zn with 20% TOA in carbon tetrachloride as a function of the acidity of HCl.

Metal: 0.5 mg/ml, Shaking time: 2—30 min, O→A: Back-extraction, A→O: Extraction.

not be back-extracted from the organic phase by shaking the organic phase with an aqueous solution in the same acid region. However, the volume ratio of the aqueous phase to the organic phase was increased; the Zn could be back-extracted 9% (4 : 1), 20% (8 : 1), and 84%(20 : 1) with 0.06 M HCl under shaking for 30 min, but when the volume of the aqueous phase was increased, the organic phase was remarkably in the emulsification state. The aqueous phase in a larger volume might promote the dissociation of the TOA–HCl complexes present in the organic phase as well as the stripping of HCl into the aqueous phase, resulting in a higher acidity of the aqueous solution. In a similar manner, the elution process may take place in the extraction column, where the mobile aqueous phase is always renewed and never again comes into contact with the same place in the stationary phases. On the other hand, as can be seen in Fig. 1, the extraction of Cd was near 100% from 0—2 M HCl; the back-extraction was also impossible under the same acidity. The difference in the behavior of Cd and Zn may be due to the difference in the stability constants of their chloro complexes,[7] the former being more stable than the latter. Nevertheless, in the case of cadmium the metal could be released from the TOA–CCl_4 column by passing it through plenty of water. As has been described above, the equilibria of the TOA–CCl_4 extraction system are affected by the acid concentration of the aqueous phase; therefore, the organic phase and the aqueous phase should be pre-equilibrated with each other in respect to hydrochloric acid. The time needed for the extraction equilibrium to be reached was ascertained to be within 2 min in the metal–20% TOA–CCl_4–HCl system.

The Volume of the Stationary Phase. In the preparation of the column, a simple previously-described method was used: a definite volume of a TOA–CCl_4 solution was held on Kel-F to make a slurry, and the slurry was put into the glass tube; then, the excess portion of the TOA-CCl_4 was washed down by passing 2 M HCl through the column. The difference between the volume of TOA–CCl_4 taken initially and that of the effluent seems to be the volume of the stationary phase in the column. The mean value after five determinations was 8.5 ml.

The Volume of the Mobile Phase. The volume of the mobile phase was determined by means of two methods. 1) The column bed was prepared as has been described above, and much 0.1 M sodium chloride solution saturated with TOA–CCl_4 was allowed to flow down until the effluent showed the same concentration of sodium chloride. After carefully washing the inside of the tube below the fritted glass filter with water, the 0.1 M sodium chloride solution occupying the pores of the column was flowed down by thoroughly washing the column with water pre-equilibrated with TOA–CCl_4. The sodium chloride in the washing liquid was determined by titrating it with a 0.1 M silver nitrate solution as usual. The value was estimated to be 5.45 ml. 2) One drop of a ^{60}Co tracer was put into the top of the column bed, and water pre-equilibrated with TOA–CCl_4 solution was passed through the column. The elution curve was obtained by taking 0.22-ml portions of the effluent and counting the radioactivity of each fraction. The volume of the effluent required to reach the maximum peak of the elution curve was the mobile phase. The value obtained by this method was 5.11 ml.

Mutual Separation of Silver, Bismuth, Cadmium, and Zinc from the Mixed Solution. The optimum acidity of the eluting solution was predicted from the liquid-liquid extraction behavior of the metals. As is shown in

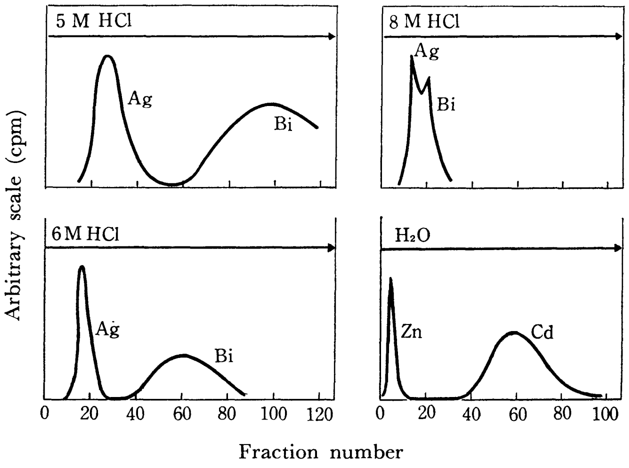

Fig. 2. The elution curves of Ag, Bi, Cd, and Zn retained on the column of 20% TOA-carbon tetrachloride-(Kel-F)-2 M HCl system.

Metal: 0.5 mg/ml, Flow rate: 0.5—1 ml/min, 1 fraction: 5 ml.

---

7) J. Bjerrum, G. Schwarzenbach, and L. G. Sillen, "Stability Constants," Spec. Publ. No. 7, Chemical Society, London (1958).

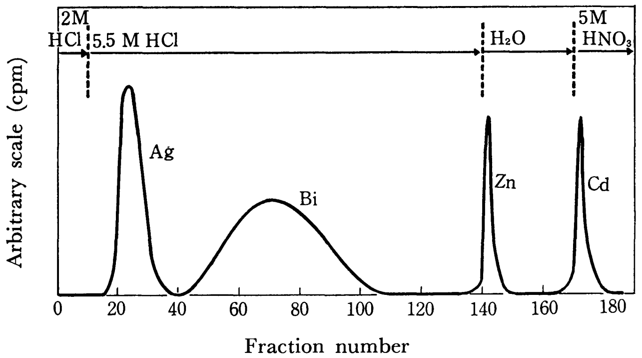

Fig. 3. The mutual separation of Ag, Bi, Cd, and Zn retained on the column of 20% TOA-carbon tetrachloride-(Kel-F)-2 M HCl system from a mixed solution.
Metal: 0.5 mg/ml, Flow rate: 1 ml/min, 1 fraction: 5 ml.

Fig. 2, silver was eluted with 100—225 ml of 5 M HCl, 50—100 ml of 8 M HCl, and 60—125 ml of of 6.5 M HCl at the flow rate of 0.5—1 ml/min. Bismuth was eluted with 325 ml of 5 M HCl, 50—150 ml of 8 M HCl, and 150 ml of 6.5 M HCl. The mutual separation of Ag and Bi could be expected using 5 M or 6 M HCl as an eluting solution, but Cd and Zn could not removed, not even with 2—12 M HCl, as had been predicted from the results of the batch extraction. However, Zn could be eluted with 50—100 ml of water after the elution of Ag and Bi with 5—6 M HCl and that of Cd with 5 M nitric acid. In conclusion, an optimum mutual separation diagram of Ag, Bi, Cd, and Zn in the 20% TOA–CCl_4–HCl system was established, as is given in Fig. 3. Silver and Bi were eluted with 90—180 ml and 200—500 ml of 5.5 M HCl successively. Then Zn was flowed down with 50—100 ml of water. In this case, the pH of the water effluent was found as low as 2. To shorten the eluting time, 5 M HNO_3 was passed through the column after separating Zn; thus, Cd was immediately eluted. The recovery of the metals was 101% (Ag), 99% (Bi), 94% (Zn), and 97% (Cd) respectively for each 0.5-ml portion of the metals.

The Relation of the Extraction Chromatography to the Liquid-liquid Extraction. The extraction and the back-extraction are repeated in the column many times in the process of the extraction chromatography. Therefore, the distribution ratios of the metals obtained by the batch extraction and by the extraction chromatography should be closely related with each other. If the extraction equilibrium is ideal and is attained rapidly at any interval under certain extraction conditions, the net distribution ratio of the metals in the extraction, D, that in the back-extraction, D^*, and the distribution of metals in the column extraction, D^{**}, will be related to the following equation:[1,2)]

$$D = \frac{(\text{Total metals})_0}{(\text{Total metals})} = \frac{1}{D^*} = D^{**} = \frac{V_m - V^*}{V_0^*}$$

where ( ) and ($)_0$ designate the concentrations of chemical species in the aqueous and in the organic phase respectively, where V_m is the volume of the effluent in relation to the maximum of the eluted metal concentration, where V^* is the volume of the mobile phase, and where V_0^* is that of the stationary phase.

TABLE 1. DISTRIBUTION RATIO OF METAL IONS WITH 20% TOA IN CARBON TETRACHLORIDE

	HCl (M)	By solvent extraction	By extraction chromatography
Ag	5	8.0 (6.6)	8.0
	5.5	3.3 (1.9)	3.5
	6	2.1 (1.1)	4.1
	8	0.5 (0.1)	1.7
Bi	5	18 (16)	55
	5.5	32 (12)	29
	6	24 (7.6)	28
	8	3.5 (1.9)	5.0
Zn	0.01	2.5	2.0
Cd	0.01	100	30

The values in the bracket were determined by analysing the back-extraction curves. Metal : 0.5 mg/ml

The values of the distribution ratio of the metals obtained by the batch extraction and the extraction chromatography are summarized in Table 1. The two values are in quite good agreement. The discrepancy may be caused by the differences in the contact times of the two phases and/or by the time-lag in the complex formation in the extraction and the back-extraction.

The authors wish to thank Dr. Ikuko Akaza for her helpful advice and discussion.