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The Analytical Application of Sulfur Analogues of β-Diketones. II. The Separation of Mercury(II), Cobalt(II), and Zinc(II) as Their STTA (1,1,1-Trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one) Complexes by Extraction Chromatography

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The behavior of trace amounts of mercury(II), cobalt(II), and zinc(II) in liquid-liquid extraction have been investigated with 1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one in cyclohexane, and the results applied to the separation of the three metals as their STTA complexes by extraction chromatography. A chromatographic column in which 10^{-3} M STTA in cyclohexane supported on Kel-F(poly-trifluorochloroethylene) powder was the stationary phase has been employed throughout this work. After the metal ions had been retained on the column by passing a sample solution of pH 5.5—6.0 through the column, the zinc(II) was eluted with an aqueous solution of pH 5.0 and then the mercury(II) was eluted with 1M hydrochloric acid. Last of all, since the cobalt had been caught so tightly on the column that it could not be removed even with concentrated hydrochloric acid, acetone was poured down the column in order to wash down all the organic phase together with the cobalt. The relation between the extraction chromatography and the liquid-liquid extraction in batches has been discussed with regard to the metal-STTA system under the same conditions.

In recent years, extraction chromatography has received increasing interest as a powerful technique in the separation of various metal ions.[1] In this chromatography, the stationary phase is an organic extractant held on an inert support, while the mobile phase is a sample solution itself or an aqueous solution adjusted to an adequate condition. By this attractive method, it is possible to separate effectively inorganic compounds despite their low separability; further, it is a means of clarifying the extraction mechanism of the separation process. Because the extraction and back-extraction may recur many times throughout the chromatographic process, the separation of the difficultly-separable compounds can be achieved. The process is closely related to the ordinary batch extraction, so the optimum conditions for the chromatographic separation may be predicted from the distribution ratio (of the compound) given by the liquid-liquid extraction of the same system.

In extraction chromatography, the extraction systems involving ion association have been frequently applied, but the chelate extraction systems only rarely. For example, dithizone, TTA (thenoyltrifluoroacetone), and α-hydroxyoxime have been used in the extraction chromatography of several metal ions: In,[2,3] Zn,[4,5] and Hg,[6] by dithizone, some radio isotopes,[7] by dithizone; Fe–Co,[8] by dithizone; alkaline earth,[9] by TTA; alkali metals,[10] by TTA; Am–Ce–La,[11] by TTA and Cu,[12] by α-hydroxyoxime.

In this investigation, the behavior of trace amounts of mercury(II), cobalt(II), and zinc(II) in solvent extraction with STTA in cyclohexane has been examined in detail; in consequence, the separation of these metals has been achieved by extraction chromatography under the optimum conditions established by the present authors.

Experimental

Apparatus. A glass chromatographic column used was of 1 cm in diameter and 20 cm in length, with a coarse glass frit and a stopcock on the bottom and a separation funnel as an eluent reservoir on the top. The effluent was collected in fractions by means of a Toyo Kagaku Sangyo fraction collector, Model E–E, holding 200 tubes. The scintil-

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2) T. B. Pierce and P. F. Peck, *Analyst*, **86**, 580 (1961).
3) D. Mapper and J. R. Fryer, *ibid.*, **87**, 297 (1962).
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6) T. B. Pierce and P. F. Peck, *Anal. Chim. Acta*, **26**, 557 (1962).
7) F. Sebesta, *ibid.*, **7**, 41 (1971).
8) V. Spevackova and M. Krivanek, *Radiochem. Radioanal. Lett.*, **3**, 63 (1970).
9) I. Akaza, This Bulletin, **39**, 980 (1966).
10) D. A. Li, *J. Chromatogr.*, **26**, 342 (1967).
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lation counter, the pH meter, the shaking machine, and the spectrophotometer were ordinary ones.

Materials. The Daiflon-300 (trade name of polytrifluorochloroethylene) moulding powder, which is non-inflammable, exceptionally stable, and resistant to temperature as well as to chemicals, was purchased from Daikin Kogyo KK. The material was dried at 80 °C, stored in a silica gel desiccator, and then ground with a mixing grinder; the particles were then collected between 42 to 80 mesh by sieving them through screens. The STTA was synthesized by a modification by the present authors of the method reported by Berg and Reed.[13] The chlorides of such radioisotopes as ^{60}Co, ^{203}Hg, and ^{65}Zn were purchased from the Radiochemical Centre, Amersham, England, and from the New England Nuclear Corp., U.S.A. The cyclohexane was purified by distillation. All the other reagents were reagent-grade materials and were used without further purification.

Extraction. Extraction was carried out for a buffered solution containing a radioactive tracer (in a concentration of a few ppm); the solution was made to have 0.1 M acetic acid (in the acidic region) or 0.1 M boric acid (in the basic region), and its pH was adjusted to an appropriate value with a 0.1—1 M hydrochloric acid or a 0.1—1 M sodium hydroxide solution. Five or ten milliliters of this solution and an equal volume of 10^{-3} M STTA in cyclohexane were put in a 30-ml glass-stoppered centrifuge tube and shaken by means of a shaking machine (300 rpm in an amplitude of 4 cm) for 2—60 min at room temperature (25—29 °C). After centrifugation, an 3-ml aliquot of each phase was pipetted out into a test tube (14 mm in diameter), and the radioactivity was counted with the NaI(Tl) scintillation counter. The pH of the aqueous phase after the extraction was again measured.

Back Extraction. A 5-ml aliquot of an organic phase which had been prepared by the standard extraction procedure was shaken with a 5-ml portion of an aqueous solution adjusted to the desired pH for 2—60 min at room temperature.[14] The distribution was determined as in the case of the extraction.

Preparation of the Column and the Procedure in Extraction Chromatography. To 5 g of Kel-F powder of 42—80 mesh, a 20-ml portion of a solution containing 10^{-3} M STTA in cyclohexane was added; the mixture was then stirred in a small 100-ml beaker until it became homogeneous. Then, a 10-ml portion of distilled water adjusted to the desired pH and pre-equilibriated with a small portion of the 10^{-3} M STTA cyclohexane solution was added, and finally the mixture was allowed to stand for an hour.

After the excess of STTA-cyclohexane solution had been taken off by decantation, the mixture was poured into a column which had been filled with an eluting solution; the voids were eliminated by gently pressing the column with a glass rod. During the course of this manipulation, the stop cock was opened a little to make the eluting solution flow through the column spontaneously. Then, the stop cock was closed and the column was again filled with the eluting solution. These procedures were repeated so as to prevent the loss of the cyclohexane solution. The chromatographic column bed thus prepared (20 cm in height) was washed with 200 ml of pre-equilibrated water coming from the reservoir fitted at the top of the tube in order to eliminate the excess organic solution. Two milliliters of a solution containing a trace amount of radioisotopes were then poured onto the column, the metals were retained on the column by passing through an aqueous solution of pH 5.5—6.0 at a flow rate of 0.2 ml/min, and then the metals were released from the column by passing through at 0.5 ml/min, the eluting solution adjusted to the desired condition. The effluent was collected in 5-ml fractions by means of the automatic fraction collector, and the chromatographic behavior of the metals was examined by counting the radioactivity of each fraction.

Theoretical

Solvent Extraction. In the extraction system of divalent metal(M^{2+})–HR(STTA)–diluent(cyclohexane), the net distribution ratio of a metal, D, and that of the back-extraction, D^*, are generally described as follows:

$$D = \frac{(MR_2)_0}{\sum_{m=0}(MR_m^{(2-m)+}) + \sum_{i=0}(M(OH)_i^{(2-i)+}) + \sum_{j=0}(MX_j^{(2-j)+})} \quad (1)$$

$$D^* = 1/D \quad (2)$$

where ( ) and ( )$_0$ designate the concentration of chemical species in the aqueous phase and in the organic phase respectively, and where $M(OH)_i^{(2-i)+}$ and $MX_j^{(2-j)+}$ indicate the metal hydroxocomplexes and the water-soluble complexes formed with a masking agent, etc. The percentage of extraction, $\%E$, and the percentage of back-extraction, $\%E_{Back}$ were calculated by means of the following equations:

$$\%E = \frac{D}{(V/V_0)+D} \cdot 100 \quad (3)$$

$$\%E_{Back} = 100 - \%E \quad (4)$$

where V and V_0 are the volumes of the aqueous and the organic phase respectively.

Extraction Chromatography. The partition on the column, based on the theory of Martin and Synge,[15] seems to correspond to the counter-current system consisting of a series of plates. It has been demonstrated that the distribution ratio of metals in the extraction chromatography, D**, can be related by the following equation[15,16]:

$$D^{**} = \frac{V_m - V^*}{V_0^*} \quad (5)$$

where V_m is the volume of the eluate 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. In extraction chromatography, the extraction and the back-extraction of metals between the organic phase and the aqueous phase should be repeated many times; the $\%E$ and the $\%E_{Back}$ of metals in the column can be expressed by the following equation:

$$\%E = \frac{D^{**}}{(V^*/V_0^*)+D^{**}} \cdot 100 = \left(1 - \frac{V^*}{V_m}\right) \cdot 100 \quad (6)$$

If the extraction equilibrium is ideal and is attained

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15) A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, **35**, 1358 (1941).
16) H. B. F. Dixon, *J. Chromatogr.*, **7**, 467 (1962).

rapidly at any interval under certain extraction conditions, it may be established that $D=1/D^*=D^{**}$ and that $\%E=100-\%E_{Back}$ between the solvent extraction and the extraction chromatography.

Results and Discussion

The symbols in all the figures, A→O and O→A respectively, denote the extraction and the back-extraction of chemical species.

Distribution of STTA. The STTA in cyclohexane showed its absorption maximum at 365 nm and a molar absorption coefficient of 1.90×10^4.[13] The absorption spectra of STTA in cyclohexane and in an aqueous phase after the shaking of 10 ml of the 10^{-3} M STTA cyclohexane solution with 10 ml of an aqueous solution of pH 6.0 are shown in Fig. 1. The content of STTA in the aqueous solution was estimated by conventional spectrophotometry to be

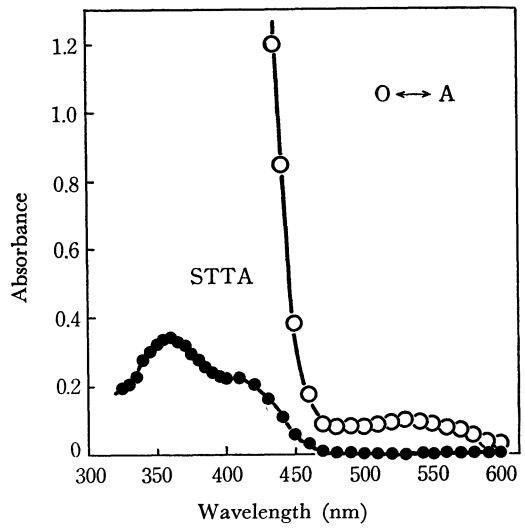

Fig. 1. Absorption spectra of STTA in the aqueous and the organic phase.
Organic phase: 10 ml of 10^{-3} M STTA in cyclohexane.
Aqueous phase: 10 ml of aqueous solution of pH 6.0.
Shaking time: 30 min.
—●— Aqueous phase, —○— Organic phase

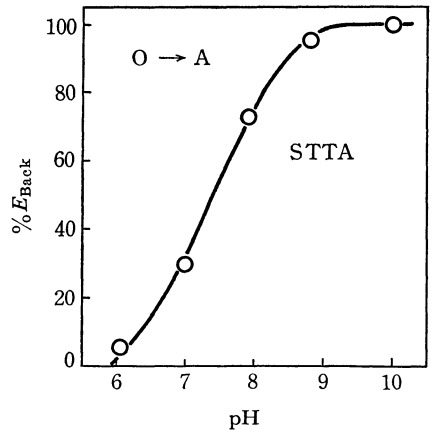

Fig. 2. Dependence on pH of the back-extraction of STTA.
Organic phase: 10 ml of 10^{-3} M STTA in cyclohexane.
Aqueous phase: 10 ml of aqueous solution of various pH.
Shaking time: 30—60 min.

3×10^{-5} M. The percentage of the back-extraction of STTA in cyclohexane as a function of the pH is shown in Fig. 2. The STTA was found to transfer itself partially into an aqueous solution from the cyclohexane phase at pH 6.0 and completely above pH 9.5. In the column extraction, an aqueous solution containing the metal ion to be extracted is always in contact with the fresh organic solvent on the column; the STTA in the organic phase will gradually dissolve in the aqueous phase and will be taken away from the extraction systems. Therefore, the eluting solutions should be pre-equilibrated with the STTA cyclohexane solution. The STTA was stable in both the aqueous and the organic phases for at least 10 hours under the present experimental conditions.

Liquid-liquid Extraction of Mercury(II), Cobalt(II), and Zinc(II). The extraction and the back-extraction of trace amounts of mercury(II), cobalt(II), and zinc(II) by 10^{-3} M STTA in cyclohexane were carried out; the results are shown in Fig. 3 as a function of the pH of the aqueous phase. It is enough to keep the concentration of 10^{-3} M STTA in cyclohexane to achieve the quantitative extraction of trace amounts of these metal ions in the acidic regions.[13,14] The extraction curves, show that the quantitative extractions of these metals are attained above pH 1.0 (Hg), pH 4.5 (Co), and pH 6.0 (Zn) respectively. The back-extractions of Hg and Zn from the organic phase were complete below pH 0 (1 M HCl) and pH 3.5 respectively, while that of Co is impossible in any pH region as has been described in the preceding paper.[13] The curves of the extraction and back-extraction of Hg and Zn obtained in the present extraction system were identical, indicating that the extraction equilib-

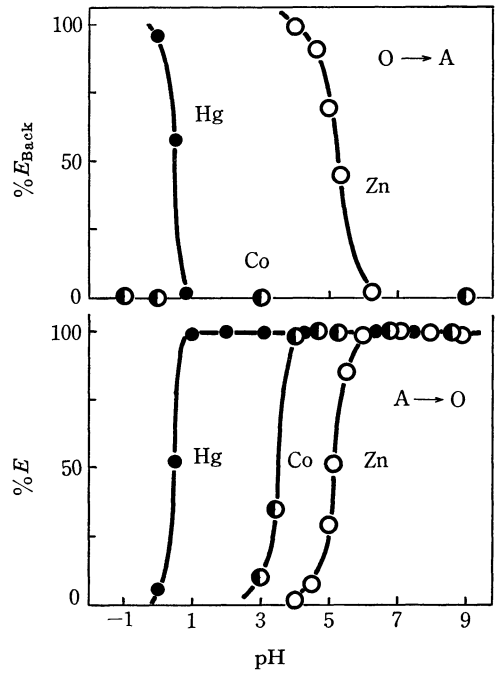

Fig. 3. Extraction and back extraction behavior of mercury(II), cobalt(II), and zinc(II)-STTA complexes as a function of pH.
Metal: —●— Hg(II), —◐— Co(II), —○— Zn(II)
Shaking time: 15 min.

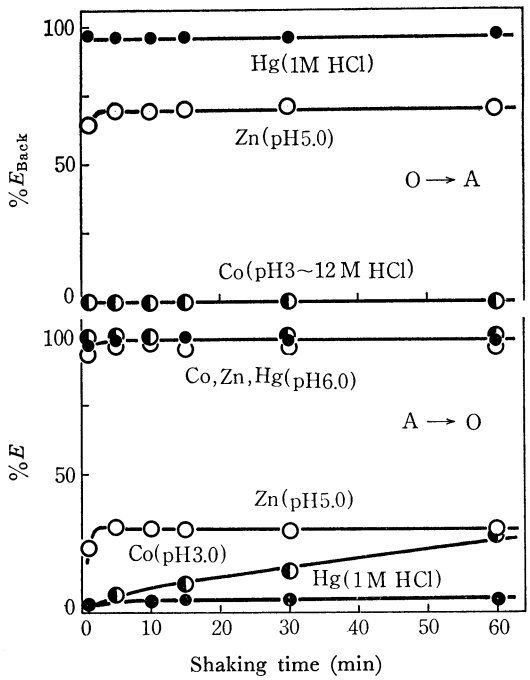

Fig. 4. Extraction and back-extraction behavior of mercury(II), cobalt(II), and zinc(II)-STTA complexes as a function of shaking time.
Metal: —●— Hg(II), —◐— Co(II), —○— Zn(II)

rium is reached within 30 minutes. The extraction and the back-extraction curves in Fig. 4 also demonstrate that the time required to reach the equilibrium is within 5 minutes in the extraction of the STTA chelates of Hg and Zn. The extraction of Co is quite rapid at pH 6.0, while it is quite show at pH 3.0, as can be seen in Fig. 4. The optimum pH for the extraction of Co into the STTA–cyclohexane seems to be above pH 5.5. However, the back-extraction of cobalt did not occur at all with any hydrochloric acid solution.[13] The extraction of cobalt(II) seemed to be accompanied by a transformation of the $Co(STTA)_2$ into an inert complex such as $Co(STTA)_3$.[14] The ratio of the volume of the stationary phase to the mobile phase in the extraction chromatography was 2.6 : 1, so the effect of the volume of the aqueous and organic phases in batch extraction was studied. When the volume of the aqueous phase was kept at 5 ml, when that of the volume of the organic phase of 10^{-3} M STTA in cyclohexane was varied from 5 ml to 15 ml, and when the $\%E$ and the $\%E_{Back}$ of metals were measured after every extraction, almost the same results were obtained in each case, as Figs. 3 and 4 show.

The Volume of the Stationary Phase. The volume of the stationary phase was determined by the following three methods: 1) In an Erlenmyer flask fitted with a glass stopper, 20 ml of a cyclohexane solution, 10 ml of distilled water, and 5 g of Kel–F powder were mixed together for a few minutes, and then the mixture was allowed to stand for one hour at room temperature. The unadsorbed solvent was subsequently drained through a small glass filter into a measuring cylinder placed in a slightly evacuated vessel. The difference between the volume of the cyclohexane solution initially taken and that measured in the cylinder showed the volume of the solvent adsorbed on the Kel–F. 2) Twelve milliliters of a cyclohexane solution, 10 ml of an eluting solution, and 5 g of Kel–F were put in a vessel with a stopper; the mixture was mixed well until it became homogeneous, and then it was allowed to stand for one hour. The slurry was then poured into the column tube and gently packed with a glass rod so as to be homogeneous. The column was then washed with 200 ml of the eluting solution at the flow rate of 2—3 ml/min, after which the excess of the solvent on the column was brought down into a receiver and the volume of the released solvent was measured by means of a measuring cylinder. The difference between the volume of the organic solvent initially taken and that of the released showed the volume of the stationary phase in ml. 3) The organic solution remaining on the column was completely taken out by passing 50 ml of acetone through the column, followed by washing with 100—150 ml of the eluting solution. All of the effluent was collected in a 250 ml flask fitted with a glass stopper, and shaken by hand so as to separate the two phases clearly. The volume of this organic phase seems to be the volume of the stationary phase of the column. The average of the values determined by the three methods was 9.3 ml for the stationary phase.

The Volume of the Mobile Phase. The space volume of the mobile phase of the column was determined by the elution of a ^{60}Co tracer in 0.1 M hydrochloric acid. The column bed was prepared in a glass tube as has been described above, and the eluting solution was drained until the liquid surface came just to the top of the column bed. One drop of a 0.1 M HCl solution containing ^{60}Co in a tracer quantity was placed at the top of the column bed, and the solution was eluted with the 0.1 M hydrochloric acid solution at the flow rate of 0.12 ml/min. Each five-drop portion (0.3 ml) of the effluent was collected in a test tube, and its radioactivity was counted by means of a NaI(Tl) scintillation counter. The volume of the eluting solution to the maximum peak of the elution curve of ^{60}Co appears to indicate the volume of

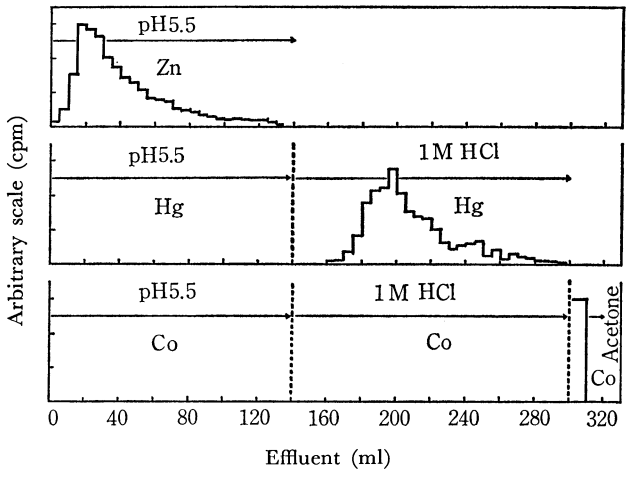

Fig. 5. Individual elution behavior of a trace amount of mercury(II), cobalt(II), and zinc(II) on a 10^{-3} M STTA-cyclohexane-Kel-F column.

the mobile phase in the column. The mean value of the mobile phase, as determined by the present method was 3.6 ml.

Chromatographic Behavior of Mercury(II), Cobalt(II), and Zinc(II). The chromatographic behavior of each metal ion was examined by loading 2 ml of a test solution containing only its radioactive tracer after it had been adjusted to pH 5.5. The results are shown in Fig. 5, in which Zn(II) is found to be completely eluted with 140 ml of the eluting solution of pH 5.5, while Hg(II) and Co(II) did not appear in the effluent under these conditions. When the eluting solution of 1 M HCl was passed through the column, Hg(II) was released in 160—300 ml of the effluent, while all of the cobalt was strongly held in the stationary phase as it was. The cobalt was not eluted even with a concentrated HCl solution, as could have been predicted from the extraction behavior. Therefore, the cobalt was finally washed down as metal chelates in cyclohexane by passing acetone through the column.

Mutual Separation of Mercury(II), Cobalt(II), and Zinc(II) from a Mixed Solution. Taking advantage of the results of the chromatographic behavior of an individual ion, the separation of the three metal ions from the mixed solution was carried out; the elution scheme is shown in Fig. 6. The cobalt was retained entirely on the column, while the zinc(II) was completely eluted with an aqueous solution of pH 5.0, and the mercury(II), with a 1 M HCl solution. Last of all, the cobalt was collected as metal chelates in the cyclohexane solution by passing acetone through the column. The average recovery for the three metal ions was 99.9%.

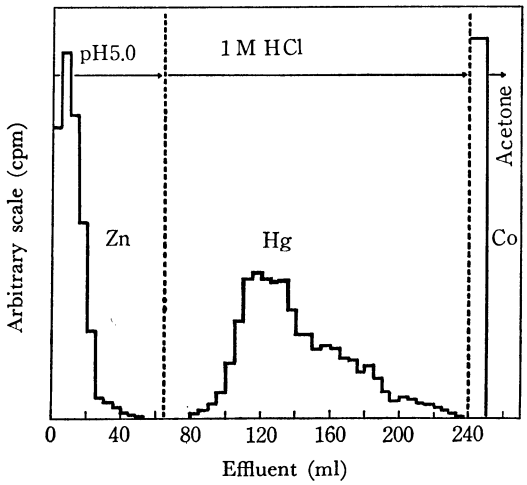

Fig. 6. Mutual separation of a trace amount of mercury-(II), cobalt(II), and zinc(II) from the mixed solution on a 10^{-3} M STTA-cyclohexane-Kel-F column.

TABLE 1. $\%E$ AND $\%E_{Back}$ OF MERCURY(II), COBALT-(II), AND ZINC(II) OBTAINED FROM THE EXTRACTION AND ELUTION CURVES

Metal	Acidity	Liquid-liquid extraction			Extraction chromatography
		$\%E$	$\%E_{Back}$		$\%E$
			Found	Calc.	
Zn	pH 5.5	85.0	26.0	15.0	79.4
Hg	1 M HCl	4.5	96.2	95.5	93.7
Co	12 M HCl	0.0	not back extracted		not eluted

The Relation of the Extraction Chromatography to the Liquid-liquid Extraction. The precentage of extraction ($\%E$) and the percentage of back-extraction ($\%E_{Back}$), as obtained from the liquid-liquid extraction and the extraction chromatography of the metals, are given in Table 1. The $\%E$ of zinc(II) which was obtained by means of liquid-liquid extraction differs somewhat from the value estimated by means of extraction chromatography, while that of mercury-(II) is quite different in the two methods. Moreover, the $\%E_{Back}$ of Zn(II) and Hg(II) deviated a little from the theoretical values. These facts indicate that the ideal extraction equilibrium was not strictly established in either the batch or column extraction of the metal–STTA–cyclohexane system. A similar phenomenon has been observed in alkali earth metal–TTA–MIBK systems.[9] This apparent 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 processes.