# Synergism in the Liquid-Liquid Extraction and the Extraction Chromatography of Manganese(II), Cobalt(II), and Zinc(II) in the Thenoyltrifluoroacetone-Trioctylphosphine Oxide-Cyclohexane Extraction System

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The synergism appearing in the liquid-liquid extraction and the extraction chromatography of trace amounts of manganese(II), cobalt(II), and zinc(II) has been investigated with TTA (thenoyltrifluoroacetone) in various solvents with or without TOPO (tri-*n*-octylphosphine oxide). For example, the $pH_{1/2}$ of the extraction of Co(TTA)$_2$ differed with the solvent used; it was, for example, 4.1 for nitrobenzene, 4.6 for cyclohexane, and 5.2 for benzene, when examined with 0.1 M TTA. When 0.01 M TOPO was present under the same conditions, the above values became 3.3, 2.4, and 3.1 respectively. The synergism was thus found to become more effective as a less polar solvent was used. The extraction constants of the three metals with only 0.1 M TTA–cyclohexane increases in the order of Mn(II)–Zn(II)–Co(II); however, when 0.001 or 0.01 M TOPO was present, all the extraction curves of the three metals became identical, even in the acidic region of pH 1—4. The overall stability constants of the adducts, M(TTA)$_2$–(TOPO)$_n$, increased in the order of Zn(II)–Co(II)–Mn(II), unlike the case of M(TTA)$_2$. The adducts were found to have two TOPO for Mn(II) and Co(II), but only one for Zn(II). The extraction equilibria were found to be attained within two minutes. Unlike as in the batch extraction, the column-extraction chromatography gave a dissimilar order of the extractability of three metals (Zn(II)–Mn(II)–Co(II)) when 0.1 M TTA–cyclohexane was the stationary phase on Kel-F in the presence of TOPO. The mutual separation could not be achieved among these metals in the presence of TOPO, and the synergism was found to be rather unfavorable for the separation of metals. The relation between the batch extraction and the extraction chromatography was also discussed briefly on the basis of the distribution data obtained.

The synergistic effect has been known to bring about a considerable enhancement of the extractability of metals in the liquid-liquid extraction of metal-$\beta$-diketonates in the presence of TOPO (tri-*n*-octylphosphine oxide); this effect can be attributed to the adduct formation between the metal chelates and TOPO.[1-5] Under the synergism, metal ions can usually be extracted quantitatively even in a lower pH region, but the distribution ratios of individual ions become so close to each other that the attempt of the mutual separation of metals by the batch extraction ends in failure. The extraction chromatography of inorganic compounds involving the metal chelates has recently been developed as a powerful separation technique,[6-8] in it the extraction and the back-extraction are repeated many times on so-called theoretical plates. A delicate separation can be expected through the use of this process. Taking advantage of this technique, Cvjetićanin studied the synergism appearing in the reversed-phase partition (extraction) chromatography of Am(III), Ce(III), and La(III) on paper treated with TTA and TOPO;[9] he found the adduct formation of M(TTA)$_3$(TOPO)$_2$, which appeared also in the liquid-liquid extraction of the same metal-chelate-solvent system. Aly and Raieh investigated the synergism in the extraction chromatography of the TTA-DBDECP-(Celite) system and clarified the factors affecting the column performance for separating Eu(III) from Sm(III) and Cm from Cf.[10] Since the same extraction process is generally used in both batch and column extractions, the extraction mechanism can be elucidated from both of the above techniques, as has been described by the present authors in connection with the system of Zn(II), Hg(II), and Co(II)–STTA–cyclohexane-(Kel-F),[11] and that of Ag(I), Bi(III), Cd(II), and Zn(II)–TOA–carbon tetrachloride(Kel-F).[12]

In the present paper we will describe the behavior of trace amounts of Mn(II), Co(II), and Zn(II) in the liquid-liquid extraction as well as in the extraction chromatography with TTA in the presence or the absence of TOPO, and will compare the results obtained by the two methods. The utility of the synergism in the extraction chromatography, the mutual separation of the metals, and the mechanism of the adduct formation will then be discussed further.

## Experimental

*Apparatus.* Hitachi-Horiba M-3 and M-4 pH meters; a shaking machine, Type V-S, of the Iwaki Co.; a centrifuge machine of the Kubota Co.; a well-type scintillation counter of the Kobe Kogyo Co.; a 200-channel pulse-height analyzer, type EDS-34208A, of the same company; a chromatographic glass tube, 10×300 mm, with a fritted glass filter; a fraction collector, Toyo SF-200 A.

*Materials.* The radioisotopes, $^{54}$Mn, $^{60}$Co, and $^{65}$Zn as chloride in a hydrochloric acid solution, were supplied by the New England Nuclear Corp. and the Radio Chemical Center, and were used as the tracers. The purity of each tracer was checked from its $\gamma$-spectra ($^{60}$Co: 1.17, 1.33; $^{65}$Zn: 1.12; $^{54}$Mn: 0.85 MeV) by the 200-channel pulse-height analyzer. TTA (thenoyltrifluoroacetone) and TOPO (tri-*n*-octylphosphine oxide), GR-grade reagents, were purchased from the Dojindo Co. Kel-F 300 moulding powder, the trade name of polytrifluorochloroethylene, was obtained from the Daikin Kogyo Co. The cyclohexane, benzene, and nitrobenzene were all purified by distillation. All the other reagents were of a GR grade and were employed without further purification.

*Extraction and Back Extraction.* The experimental procedure was the same as has previously been described.[2-5,11,12]

To a 10 ml portion of an aqueous solution containing a few ppm of metals, sodium acetate (0.1 M) (for the acidic region) or boric acid (0.1 M) (for the basic region) were added, after which the pH of the solution was adjusted to a desired value. A 10 or 30 ml portions of an organic solvent containing TTA (0.1 M) and varying amounts of TOPO were then added. Both phases were placed in a 50 ml glass-stoppered centrifuge tube and agitated by the shaking machine for from one to three hours at 20 °C. After centrifugation a 2 ml portion of each phase was pipetted out into a test tube, and the $\gamma$-activity of each portion was measured with the NaI(Tl) well-type scintillation counter. The distribution ratio of the metals was calculated from the counting rate of both phases. The pH of the aqueous phase was checked again after the extraction. The back extraction was carried out by shaking a 5 ml or 10 ml portions of the organic phase containing the extracted metal chelates with an aqueous solution of the desired acidity. Then a 1 or 3 ml portion was pipetted out of both phases into a test tube and the back distribution ratio was determined as in the case of the extraction.

*Extraction Chromatography.* All the aqueous solutions and organic solvents containing TTA should be pre-equilibrated before use. A 150 ml portion of 0.1 M sodium acetate solution which had been adjusted to pH 4.5 was shaken with a 20—30 ml portion of 0.1 M TTA–TOPO–cyclohexane for an hour. After discarding the organic solution, a 20 ml portion of the aqueous solution was taken out and was agitated with 30 ml of a new 0.1 M TTA–TOPO–cyclohexane solution for an hour. Then 20 ml of the organic solution was taken out, poured onto 5 g Kel-F powder (42—80 mesh), and allowed to stand for two hours. On the other hand, 200—250 ml of a 0.1 M sodium acetate solution, adjusted to the desired pH, was agitated with 30—40 ml of 0.1 M TTA–TOPO–cyclohexane for an hour to prepare the eluting solution. The procedure for preparing the column was the same as has previously been described.[11,12] A buffer solution of pH 4.5 was placed in the column tube, and 1—2 ml of the 0.1 M TTA–TOPO–cyclohexane was poured in. A slurry of TTA–TOPO–cyclohexane–Kel-F powder was then dropped into the tube in small portions. After every addition the slurry in the column tube was stirred with a sharp-pointed glass rod and gently pressed with the other, flat end of the same rod under a slow flow of the eluting solution. The stop-cock was then closed, and the column was filled again with the eluting solution. This operation was repeated about ten times until all the slurry made from 5 g Kel-F had been poured into the tube. Thereafter, a separating funnel was fitted at the top of the column tube; from it 100 ml of a buffer solution of pH 4.5 was passed through to wash down the excess unabsorbed organic solvent through the completely opened cock at the bottom of the tube.

The column bed thus prepared was $10\times200$ mm. The fraction collector was placed below the column tube and operated so as to collect each 10 ml portion of the eluate.

When the liquid surface came to the upper surface of the column bed, 1 ml of the sample solution was poured onto the bed. The sample solution containing a radioactive tracer had been buffered to pH 4.5. Then, 2—3 ml of the buffer solution was repeatedly poured onto the column and flowed through the column. By this treatment, all the metal ions could be completely retained on the column. A separating funnel containing a buffer solution with pH 4.5 was fitted on the column tube, and the column was washed with 100 ml of the solution. The eluting solution was then passed through from another separating funnel newly-fitted on the tube at the rate of 0.5 ml/min. From each 10 ml fraction of the eluate, a 3 ml portion was pipetted out in a test tube and the radioactivity was measured by means of the well-type scintillation.

## Theoretical

*Liquid-Liquid Extraction.* The extraction constant of a metal chelate, $K$; the pH of the half extraction, $pH_{1/2}$, and the stability constant of the metal chelate adduct, $\beta_n$, can be calculated from the data obtained by the following equations:

$$D = (MR_2)_0/(M^{2+}) \quad (1)$$

$$K = (MR_2)_0(H^+)^2/(M^{2+})(HR)_0^2 \quad (2)$$

$$\log K = \log D - 2\log(HR)_0 - 2pH \quad (3)$$

$$pH_{1/2} = -\log K/2 - \log(HR)_0 \quad (4)$$

$$D^* = \{(MR_2)_0 + \sum_1^n (MR_2L_n)_0\}/(M^{2+}) \quad (5)$$

$$\beta_n = (MR_2L_n)_0/(MR_2)_0(L)_0^n \quad (6)$$

$$\log D^*/D = \log(1+\beta_n(L)_0^n) \quad (7)$$

where $D$ and $D^*$ are the distribution ratios in the absence and in the presence of the organic base, TOPO; M stands for metal, HR for $\beta$-diketone, and L for TOPO; the parentheses designate the concentration of the chemical species in the aqueous phase and in the organic phase with the suffix 0.

*Extraction Chromatography.* The distribution of metals can be derived from the data obtained by the column-extraction chromatography by employing the following equations:

$$D = (V_m - V^*)/V \quad (8)$$

$$D^* = (V_m^* - V^*)/V \quad (9)$$

$$\log D^*/D = \log(V_m^* - V^*)/(V_m - V^*) \quad (10)$$

where $V_m$ and $V_m^*$ are the volumes of the effluent necessary to reach the maximum concentration of the eluted metal ion in the absence and in the presence of TOPO; $V^*$ is the volume of the mobile phase in the column, and $V$ that of the stationary phase.

## Results and Discussion

*Liquid-Liquid Extraction in the TTA–TOPO–Solvent System.* The liquid-liquid extraction was carried out for a trace amount of Co(II) with 0.1 M TTA in various solvents *i.e.* cyclohexane, benzene, and nitrobenzene, in the presence of 0.01 M TOPO as well as in the absence of the base. The results are shown in Fig. 1.

From the figure it can be seen that the $pH_{1/2}$ of cobalt extraction differs among the solvents, from 4.1 for nitrobenzene, and 4.6 for cyclohexane to 5.2 for benzene. All the straight lines with a slope of about 2 also show that the extractions proceed almost ideally, but a slight deviation from the integer suggests the formation of some water-soluble complexes in the extraction process.

On the other hand, when the same extraction was carried out in the presence of 0.01 M TOPO, the extractability of the metals is remarkably enhanced by the adduct formation and the $pH_{1/2}$ shifts lower with

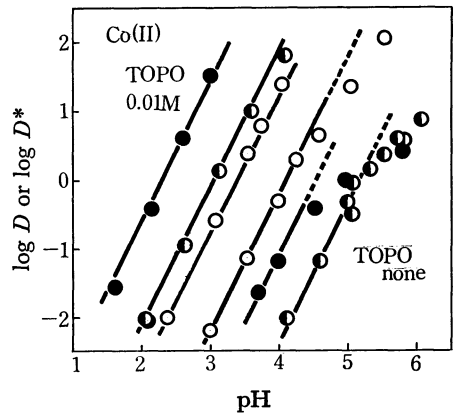


Fig. 1. Solvent effect on the extraction of a trace amount of Co(II) with 0.1 M TTA in various diluents in the presence and in the absence of 0.01 M TOPO.
Diluent: —●— cyclohexane, —◐— benzene, —○— nitrobenzene

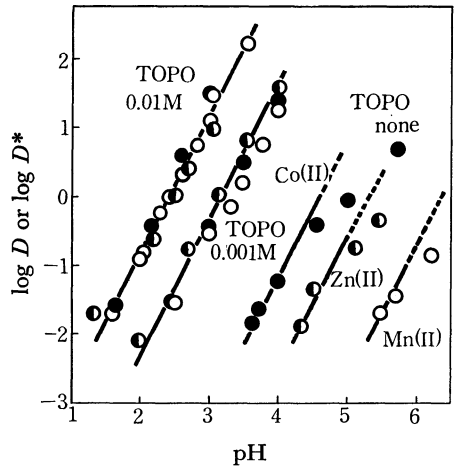


Fig. 2. Liquid-liquid extraction of a trace amount of Mn(II), Co(II), and Zn(II) with 0.1 M TTA in the presence and in the absence of 0.001 M and 0.01 M TOPO in cyclohexane.
Metals: —○— Mn(II), —◐— Zn(II), —●— Co(II)

the net shifts of 0.8 for nitrobenzene, 2.1 for benzene, and 2.2 for cyclohexane. In general, the synergistic effect by TOPO is more effective in the case of a solvent with a smaller dielectric constant and a lower solubility of water.[1,3]

Therefore, cyclohexane was preferred for the synergistic study of the extraction because a distinct effect seems to be obtained by employing this solvent. With 0.1 M TTA in cyclohexane, the extraction of a trace amount of Mn(II), Co(II), and Zn(II) was carried out in the presence of 0.001 M or 0.01 M TOPO or in the absence of the base. The results are summarized in Fig. 2 as the log D *vs.* pH plots, in which the slope of the straight lines is apt to deviate lower than 2 because of the formation of a certain water-soluble complex, such as a hydroxo- or charged one, while in higher concentrations of TOPO the $pH_{1/2}$ shifts lower until all the lines for the three metals coincide with each other on one straight line, as can be seen when 0.01 M

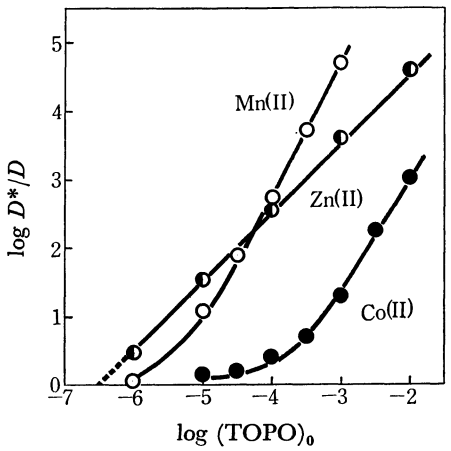


Fig. 3. Variation of the distribution ratio of a trace amount of Mn(II), Co(II), and Zn(II) with the concentration of TOPO.
Metals: —○— Mn(II), —◐— Zn(II), —●— Co(II)

TOPO is applied.

The synergistic effect by TOPO thus seems effective on metal ions in the order of Co(II)–Zn(II)–Mn(II); finally, the differences in the distribution ratio among the three metals disappear when a sufficient amount of TOPO is added. Another effect of TOPO can be seen in Fig. 3, in which $\log D^*/D$ *vs.* $\log(TOPO)_0$ plots for three metals are drawn. The slope of the line gives the number of the adduct molecule bound to the TTA-chelate, indicating an $MR_2L_2$-type adduct for Mn(II) and Co(II), and an $MR_2L$-type one for Zn(II). The stability constants of the adducts were obtained by analyzing the plots in Fig. 3 by means of the curve-fitting method.[1–5] The stability of a metal chelate is said generally to increase with the ionic potential of the metal, while that of the adduct decreases conversely.[13]

Table 1. Apparent extraction constant of TTA chelates, log $K$ and the stability constant of their adduct with TOPO, log $\beta_n$

| Complex extracted | log $K$ | log $\beta_1$ | log $\beta_2$ |
|---|---|---|---|
| $Mn(TTA)_2(TOPO)_2$ | −10.7 | 5.70 | 10.80 |
| $Co(TTA)_2(TOPO)_2$ | −7.2 | 4.18 | 7.40 |
| $Zn(TTA)_2(TOPO)$ | −8.6 | 6.47 | |

A similar tendency can also be observed in the present results; log $K$ and log $\beta_n$ are summarized in Table 1, in which it can be seen that the apparent extraction constants increase in the order of Mn(II)–Zn(II)–Co(II), the first and the overall stability of the adducts in the order of Co(II)–Mn(II)–Zn(II) and Zn(II)–Co(II)–Mn(II), respectively. The time needed for the attainment of the extraction equilibrium had also been ascertained to be within two minutes whenever 0.1 M TTA–cyclohexane and 0.001 M or 0.01 M TOPO are employed at pH 3—4.

*Extraction Chromatography in the TTA–TOPO–Cyclohexane System.* The volume of the stationary phase on the column was determined as follows; the stationary phase consisting of TTA–TOPO–cyclohexane supported

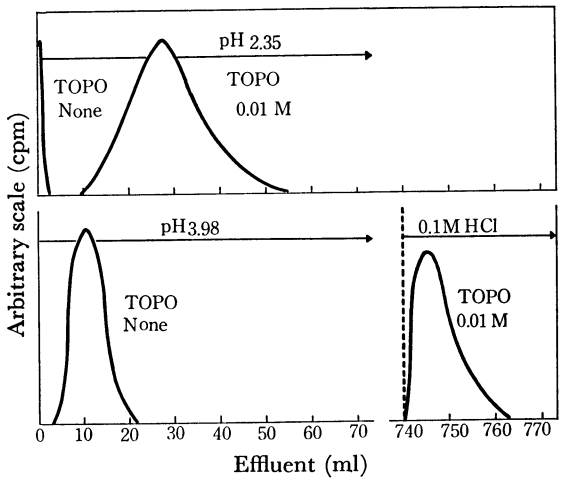


Fig. 4. Chromatograms of a trace amount of Co(II) on 0.1 M TTA–cyclohexane (Kel-F) column in the presence and in the absence of 0.01 M TOPO.

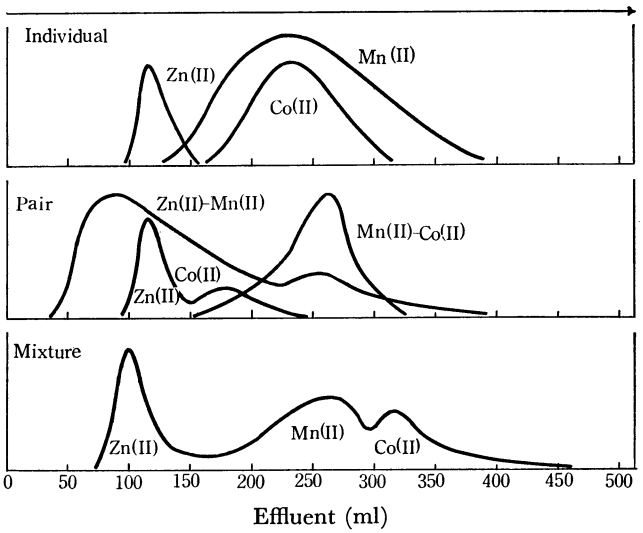


Fig. 5. Chromatograms of a trace amount of Mn(II), Co(II), and Zn(II) on 0.1 M TTA–cyclohexane (Kel-F) column in the presence of 0.01 M TOPO. pH=3.6.

on Kel-F was washed down by passing 20—30 ml of acetone through the column; the washings were received in a 200 ml measuring flask, 50—60 ml of distilled water was added, and the content was shaken by hand. After standing for a day, the separated cyclohexane solution was transferred into a graduated cylinder, and its volume was measured after every experiment. 5.8 ml was obtained as the mean value of the stationary-phase volume. The volume of the mobile phase on the column was determined as follows: one drop of 0.1 M hydrochloric acid containing a $^{60}Co$ tracer (20000 cpm/ml) was put on the top of the column bed and much water pre-equilibrated with a TTA–TOPO–cyclohexane solution was passed through the column at the flow rate of 0.5 ml/min; each 0.31 ml fraction of the effluent was taken in a test tube, and the $\gamma$-activity was counted; the elution curve was prepared for the counting rate against the effluent volume; the volume required to reach the maximum counting rate was estimated as the volume of the mobile phase (2.7 ml was obtained in this case). In order to investigate how to make the synergistic effect appear in extraction chromatography, the Co(II)–TTA–cyclohexane system was first tested with and without TOPO, since the synergistic effect had been known to depend on the concentration of the organic base.[1] The results are shown in Fig. 4 as the elution curves from the 0.1 M TTA–cyclohexane(Kel-F) column as well as from the 0.1 M TTA–0.01 M TOPO–cyclohexane(Kel-F) column, with eluting solutions of various pH's. When a sample solution of pH 4.5 was passed through the column, the Co(II) was retained completely on the column in both cases and was then eluted by eluting solutions. Without TOPO, Co(II) could be eluted instantly with the eluting solution of pH 2.35 into the first fraction of 2.3 ml; nevertheless, with the eluting solution of pH 4.0 it was eluted somewhat later, as its elution peak appeared around 10 ml of the effluent. On the other hand, with TOPO the elution feature changed remarkably, as the elution peak with the eluting solution of pH 2.35 appeared around 30 ml of the effluent, while with the eluting solution of pH 4.0 Co(II) did not appear in the effluent after as much as 740 ml of the eluting solution had been passed through the column.

Therefore, Co(II) had to be released from the column by passing 0.1 M hydrochloric acid through. The extraction chromatography was examined with a column of 0.1 M TTA–0.01 M TOPO–cyclohexane–(Kel-F) for Mn(II), Co(II), and Zn(II) individually, and also for mixtures of them. After the metals had been retained on the column by passing through sample solutions of pH 4.5, the metals were eluted with the eluting solution of pH 3.6. In Fig. 5, the chromatograms of the individual metal ions, of the mixtures of two ions, and of a mixture of three ions are illustrated. As some overlap of the elution curves can be seen for Mn(II) and Co(II), even in the case of the independent tests, the separation of each metal ion seems to be difficult except for that of Zn(II) from the mixture.

Table 2. Comparison of the distribution ratio, $D^*$, obtained by batch and chromatographic extraction

| Ions | | D* | |
|---|---|---|---|
| | | Extraction chromatography | Batch extraction |
| | Mn | 40.9 (98.9) | 499 (99.8) |
| | Co | 40.9 (98.9) | 322 (99.7) |
| | Zn | 15.9 (97.2) | 81 (98.8) |
| Mn–Co | Mn | 44.4 (99.0) | |
| | Co | 44.4 (99.0) | |
| Mn–Zn | Mn | 40.1 (98.9) | |
| | Zn | 15.1 (97.0) | |
| Co–Zn | Co | 29.7 (98.5) | |
| | Zn | 19.4 (97.7) | |
| Mn–Co–Zn | | | |
| | Mn | 45.2 (99.0) | |
| | Co | 54.7 (99.2) | |
| | Zn | 17.6 (97.4) | |

The values in the blacket are the percent extraction, % E, of metals.

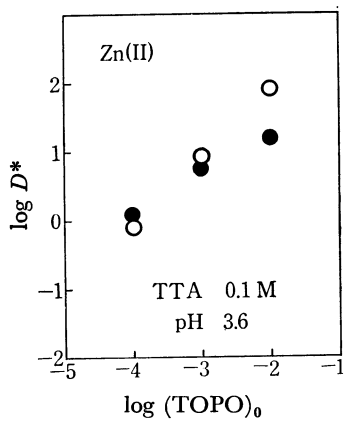


Fig. 6. Distribution ratio of a trace amount of Zn(II) with 0.1 M TTA in cyclohexane as a function of TOPO concentration obtained by batch and chromatographic extraction.
Batch extraction: —○—
Extraction chromatography: —●—

Moreover, it can also be seen that the elution peaks of the ions do not always coincide, especially when there is a wide gap between the individual ion-peak and that obtained in the mixture of two ions. The delayed appearance of the peaks of Mn(II) and Co(II) from the mixture of the three metals seems to be due to the competition of the chelate formation among metals or to some kinetic disposition of each chelate. In coclution, the synergistic effect is not favorable to the separation of metals.

*Relation between Extraction Chromatography and the Liquid-Liquid Extraction.* The distribution ratios of the three metals are summarized in Table 2 in the case of both the batch extraction and the extraction chromatography; some discrepancy can be noticed. The effect of the TOPO concentration on the Zn(II)–TTA–TOPO–cyclohexane system is shown in Fig. 6, in which the distribution is found to increase with the concentration of TOPO; the values are in quite good agreement with each other, whether they are determined by batch extraction or by extraction chromatography. If some discrepancy seems to exist between them, it might be caused by the difference in the process between the batch extraction and the chromatography; in the former the equilibrium could be reached after shaking the two phases, but in the chromatography the contact time of the two phases and the kinetic properties of the complex formation, as well as the rate of the release from the organic phase, back-extraction, might be an important factors in providing an elution curve.

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