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The Analytical Application of Sulfur Analogues of β-Diketones. V. Some Aspects of the Extraction Behavior of STTA (1,1,1-Trifluoro-4-(2-thienyl)-4-mercapto-3-buten-2-one) Complexes and Their Adducts with TOPO

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The solvent extraction of trace amounts of various metal ions with STTA (1,1,1-trifluoro-4-(2-thienyl)-4-mercapto-3-buten-2-one) in the presence or in the absence of TOPO (tri-*n*-octylphosphine oxide) has been investigated. The results are as follows: (a) The apparent extraction constant of each metal–STTA chelate in cyclohexane, log K, increases, and their pH $_{1/2}$ values decrease, in the order of: Cd(II)-In(III)-Zn(II)-Fe(III)-Ni(II)-Ag(I)-Bi(III)-Co(II)-Pb(II)-Cu(II)-Hg(II). This order was found to hold also in the back-extraction, except for cobalt, which was not back-extracted even with 1—12 M HCl. The other metals, Au(III), and Pd(II), could also be extracted as their STTA chelates. (b) The kind of the solvent has an effect to the lowest pH value where the metal STTA chelates begin to be extracted; the lowest pH is shifted to a higher value in the order of: C_6H_{12}, CCl_4, MIBK, C_6H_6, and $CHCl_3$. (c) The distribution coefficient, P_r, and the enol dissociation constant, K_a, of STTA were log $P_r=2.99$ (10^{-3} M STTA in cyclohexane-0.1 M $NaClO_4$-pH 1.0) and log $K_a=-4.38$ (10^{-4} M STTA in 0.12 M HCl, 0.1 M CH_3COOH (pH 4.5) and 0.1 M NaOH-C_2H_5OH (1/5, v/v) solution) at 20 °C. (d) The extraction equilibrium of Zn seemed to be rapid, that of Ni showed its rate-determining step to be the formation of $Ni(STTA)^+$, and that of Co seemed to be accompanied by a transformation of $Co(STTA)_2$ to $Co(STTA)_3$. (e) In the metal–STTA(0.001 M)–TOPO(0.01 M)–cyclohexane system, the $|\Delta pH_{1/2}|$ was found to be 0.45 for Ni, 1.95 for Zn, and 0.25 for Co. The Co–STTA–TOPO chelate could be back-extracted to some degree with 1 M HCl. The extracted species were ascertained to be $Zn(STTA)_2$, $Zn(STTA)_2TOPO$, $Ni(STTA)_2$, $Co(STTA)_2$, $Co(STTA)_3$, and $Co(STTA)_2TOPO$. The stability constant of $Zn(STTA)_2$ TOPO was found to be 6.05.

A new chelating reagent, STTA (1,1,1-trifluoro-4-(2-thienyl)-4-mercapto-3-buten-2-one), was first prepared by Chaston *et al.*[1] and by Berg and Reed;[2] it has since been used for chelating and for the extractive photometric determination of metals.[3] The present authors have aimed to develop further analytical usages of STTA, and several reports have been published: on the spectrophotometric determination of cobalt(II),[4] the separation of Hg(II), Co(II), and Zn(II) by extraction chromatography,[5] the separation of Co(II), Ni(II), Cu(II), Zn(II), Hg(II), Pb(II), and Cd(II) by thin-layer chromatography,[6] and the separation of Ni(II) and Co(II) by a back-extraction process.[7] In the present work, a number of factors affecting the liquid-liquid extraction of trace amounts of various metal ions with STTA in the presence or in the absence of TOPO (tri-*n*-octylphosphine oxide) have been studied. The application of the solvent extraction techniques to the study of the kinetics of metal-chelate formations in Zn, Ni, and the Co–STTA–TOPO–cyclohexane system has also been examined.

Experimental

Materials. The STTA was synthesized by the reaction of hydrogen sulfide with TTA in absolute ethanol in the presence of hydrogen chloride.[4] The guaranteed-grade reagents of TTA (thenoyltrifluoroacetone) and TOPO-(tri-*n*-octylphosphine oxide) were obtained from Dojindo Co., Ltd. The chlorides or the nitrates of the radioisotopes, ^{110m}Ag, ^{207}Bi, ^{144}Ce, ^{115m}Cd, ^{60}Co, $^{152,154}Eu$, ^{59}Fe, ^{203}Hg, ^{114m}In, ^{54}Mn, ^{63}Ni, ^{210}Pb, ^{46}Sc, ^{124}Sb, and ^{65}Zn, were purchased from the Radiochemical Centre (England), the New England Nuclear Corporation (U.S.A.), and the Union

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[1] S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickeles and J. S. Shannon, *Aust. J. Chem.*, **18**, 673 (1965).

[2] E. W. Berg and K. P. Reed, *Anal. Chim. Acta*, **36**, 372 (1966).

[3] T. Honjo and T. Kiba, *Bunseki Kagaku*, **21**, 676 (1972).

[4] T. Honjo and T. Kiba, This Bulletin, **45**, 185 (1972). (Part I).

[5] T. Honjo and T. Kiba, *ibid.*, **46**, 1694 (1973). (Part II).

[6] T. Honjo and T. Kiba, *ibid.*, **46**, 3768 (1973). (Part III).

[7] T. Honjo, T. Unemoto, and T. Kiba, *Bunseki Kagaku*, in press. (Part IV).

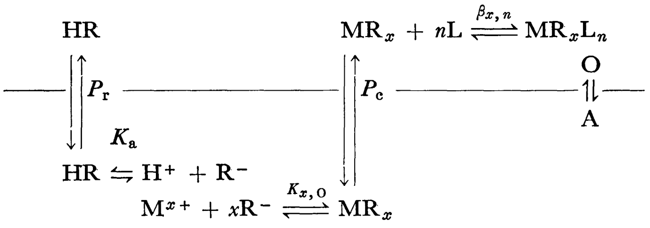
Carbide Corporation (U.S.A.). The non-radioactive metal salts of Al, Au, Be, Cu, Pd, Pt, Ru, Sn, Te, Tl, UO_2, and VO_2, and the other reagents were all reagent-grade materials.

Extraction. The experimental procedures were almost the same as have previously been described.[4-7] The extractions were performed between 5 or 10 ml of an aqueous solution containing individual metal ions and the same volume of an organic solution containing STTA or STTA and TOPO. The aqueous solution was made up to 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 a desired value with 0.1—1 M NaOH or 0.1—1 M HCl. The concentration of the STTA in the organic phase was 0.001 M, and various amounts of TOPO were added. After the two phases had been shaken for from 5 min to 2 hr at 20 °C, the distribution of the metal in question was determined radiometrically or spectrophotometrically. The pH of the aqueous phase was checked again after the extraction.

Back-extraction. After the extraction, the back-extraction of the metals from the organic phase was performed with an aqueous solution with a pH value appropriate to the desired condition. The distribution of the metals was determined as in the case of the extraction.

Theoretical

When a metal ion M^{x+}, reacts with STTA (abbreviated as HR) and is extracted as the neutral chelate, MR_x, and forms the adduct compounds, MR_xL_n, with an organic base, L, such as TOPO, the overall extraction processes can be written as in the following scheme:



The equilibrium relations can be expressed by the following equations, in which $K_{x,0}$ means the extraction constant; D, the distribution ratio of the metal; $pH_{1/2}$, the pH of the half-extraction and % E, the percentage of extraction in each extraction or back-extraction, ( ) and $(\ )_0$ designate the aqueous and the organic phases respectively.

Extraction (A→O) aqueous to organic

$$M^{x+} + xHR(org) \rightleftharpoons MR_x(org) + xH^+ \tag{1}$$

$$K_{x,0} = (MR_x)_0(H^+)^x/(M^{x+})(HR)_0{}^x \tag{2}$$

$$pH_{1/2} = -1/x \log K_{x,0} - \log(HR)_0 \tag{3}$$

$$D = (MR_x)_0/(M^{x+}) = K_{x,0}(HR)_0{}^x/(H^+)^x \tag{4}$$

$$\%\ E = 100D/((V/V_0) + D) \tag{5}$$

Back-extraction (O→A) organic to aqueous

The inverse of Eq. (1):

$$D_B = 1/D \tag{6}$$

$$\%\ \text{Back}\ E = 100 - \%\ E \tag{7}$$

Synergism

$$M^{x+} + xHR(org) + nL \rightleftharpoons MR_xL_n(org) + xH^+ \tag{8}$$

$$K_{x,n} = (MR_xL_n)_0(H^+)^x/(M^{x+})(HR)_0{}^x(L)_0{}^n \tag{9}$$

$$^*pH_{1/2} = -1/x \log K_{x,n} - \log(HR)_0 - n/x \log(L)_0 \tag{10}$$

$$D^* = ((MR_x)_0 + (MR_xL_n)_0)/(M^{x+}) = K_{x,n}(HR)_0{}^x(L)_0{}^n/(H^+)^x \tag{11}$$

$$D^*/D = 1 + \sum_1^n \beta_{x,n}(L)_0{}^n \tag{12}$$

where $\Delta pH_{1/2}$ is the shift of $pH_{1/2}$ from the extraction without the organic base.

$$\Delta\, pH_{1/2} = {}^*pH_{1/2} - pH_{1/2} = -1/x \log \beta_{x,n}(L)_0{}^n \tag{13}$$

If these three assumptions are fulfilled, all the above equations are valid: 1) the metal concentration is negligibly small compared to the total concentration of STTA; 2) the distribution coefficient of STTA is fairly high, but the acid dissociation is considerably low in the pH region investigated, and 3) the formation of hydroxo complexes can be ignored in the same pH region.

Results and Discussion

In all the figures, A→O means the transfer of the metals from the aqueous phase to the organic phase, and O→A, the so-called back-extraction from the organic phase to the aqueous phase.

Distribution and Dissociation of STTA. The apparent distribution coefficients between water and cyclohexane, and the enol dissociation constant of STTA, were determined spectrophotometrically using the method of Uhlemann and Muller.[8] The following values were obtained: $\log P_r = 2.99$ (10^{-3} M STTA in cyclohexane–0.1 M $NaClO_4$–pH 1.0) and $\log K_a = -4.31$ (10^{-4} M STTA in 0.12 M HCl, 0.1 M CH_3COOH (pH 4.5) and 0.1 M NaOH–C_2H_5OH (1/5, v/v)solution) at 20 °C. The $\log K_a (-8.64)$ of TTA[9] in 74.5 vol.% dioxane at 30 °C is smaller than that (-7.05) of STTA under the same conditions.[10] The apparent distribution coefficient of TTA between *n*-hexane and an aqueous solution at the ionic strength of 0.1 M ($HClO_4 + NaClO_4$) at 25 °C has been described as 0.68.[11] Therefore, the extraction of metals with STTA may be expected to occur n a lower pH region than that with TTA, and only a very small excess of the reagent over the stoichiometrical quantity is needed. Hence, a number of metals can be extracted without any interference by hydrolysis.

Extraction and Back-extraction. The pH dependence of the extractability of metals with 0.001 M STTA in cyclohexane was examined; the extraction curves and the back-extraction curves are compared in Fig. 1 for the first-transition elements, such as Fe, Co, Ni, and Cu. The range of the back-extraction of Fe, Ni, and Cu shifts to a somewhat lower pH than that of the extraction; that is, in the regular extraction its equilibrium seems to be unattainable within only 30 min. The back-extraction of the cobalt-STTA chelate was impossible. The pH-dependence of the

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[8] E. Uhlemann and H. Muller, *Anal. Chim. Acta*, **41**, 311 (1968).

[9] J. L. Rosenstreich and D. E. Gddberg, *Inorg. Chem.*, **4**, 909 (1965).

[10] S. H. H. Chaston and S. E. Livingstone, *Aust. J. Chem.*, **19**, 2035 (1966).

[11] T. Wakahayashi, S. Oki, T. Omori and N. Suzuki, *J. Inorg. Nucl. Chem.*, **26**, 2255 (1964).

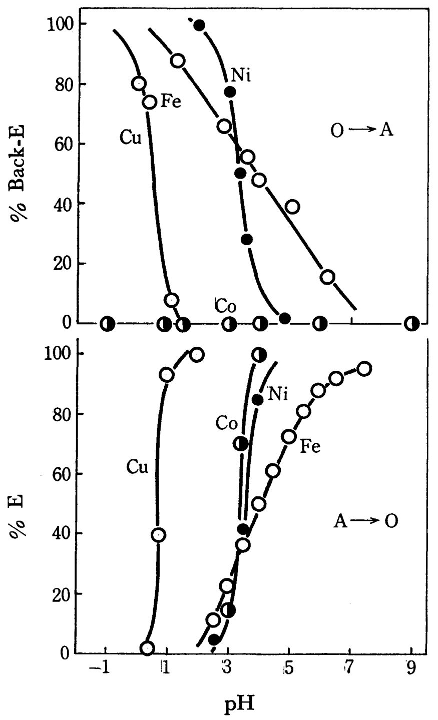

Fig. 1. The effect of pH on the extraction and the back-extraction of trace amounts of Fe(III), Co(II), Ni(II), and Cu(II)-0.001 M STTA-cyclohexane system.

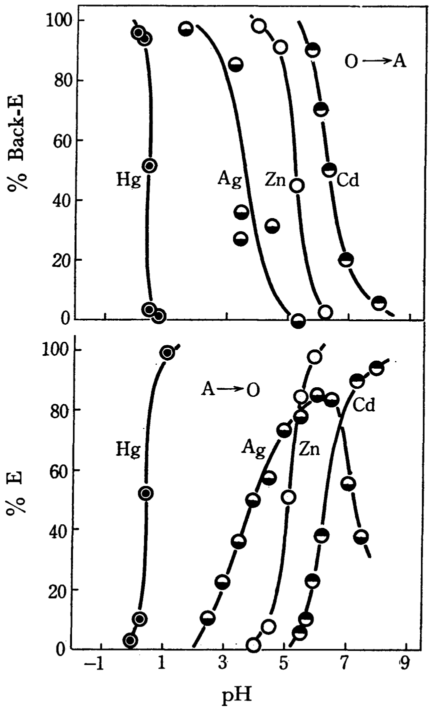

Fig. 2. The effect of pH on the extraction and the back-extraction of trace amounts of Zn(II), Cd(II), Hg(II), and Ag(I)-0.001 M STTA-cyclohexane system.

extractions of Ag and Zn family elements involving Zn, Cd, and Hg with 0.001 M STTA–cyclohexane is shown in Fig. 2. The extraction curves and the back-extraction curves are exactly symmetrical with regard to each other. The pH range of the back-extraction of Ag is somewhat lower than that of the extraction.

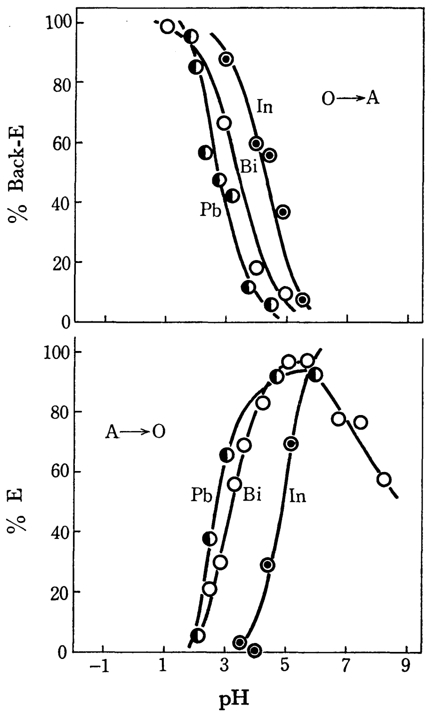

Fig. 3. The effect of pH on the extraction and the back-extraction of trace amounts of In(III), Pb(II), and Bi(III)-0.001 M STTA-cyclohexane system.

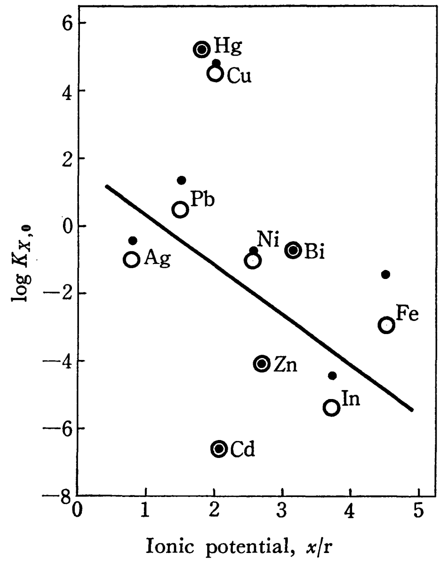

Fig. 4. The apparent extraction constant, log $K_{x,0}$, in the metal-STTA-cyclohexane systems as a function of the ionic potential. The values of the apparent extraction constants, log $K_{x,0}$ was as follows:

	Ag	Bi	Cd	Co	Cu	Fe
A→O (○)	−1.0	−0.75	−6.6	−0.6	4.5	−3.0
O→A (●)	−0.5	−0.75	−6.6	—	4.8	−1.5

	Hg	In	Ni	Pb	Zn
A→O (○)	5.2	−5.4	−1.0	0.50	−4.1
O→A (●)	5.2	−4.5	−0.8	0.80	−4.1

The extraction curves of In, Pb, and Bi are shown in Fig. 3; the pH range of the extraction for Bi is almost the same as that of the back-extraction curve, but in In and Pb the extraction and the back-extraction are somewhat different. The free energy of the formation of a complex between a metal ion and an organic reagent may be expressed as:

$-\Delta G=RT\log K=\text{const.}\times \text{pH}_{1/2}=\text{const.}\times x/r,$[12]

where x is the charge and r is the crystal radius of the metal ion. In Fig. 4, the extraction constants, $K_{x,0}$, of the extractable chelates are plotted as a function of the ionic potentials. The results show that the apparent extraction constants for the STTA chelates tend to decrease with an increase in the ionic potential of the metals. Similar results have been obtained in acetylacetone,[13,14] benzoylacetone,[15] and the β-isopropyltropolone chelate system;[16] that is, in all the $\text{pH}_{1/2}$ decreases in the ionic radii or the ionic potential. The stability of the complex of the first-transition elements follows Irving and Williams' order of stability,[17] that is, Zn<Cu>Ni, regardless of the nature of the coordination ligand. In the solvent extractions of the STTA chelates of these metals, a similar sequence is observed. Since the STTA is an oxygen-sulfur-donating ligand, it has a marked tendency to form a covalent bond. The contribution of dπ—dπ interactions seems to be responsible for this relationship. The discrepancy in the extraction constants between the extraction and the back-extraction indicates that a 30-min contact is insufficient to establish the extraction equilibrium. As the organic solvent plays an important role in the extration of the metal ions with any chelating reagent, various solvents were examined in the present study; cyclohexane was found to extract the cobalt STTA chelate at the lowest pH among the solvents, followed by CCl_4, MIBK, C_6H_6, and $CHCl_3$, in that order.[4] Experiments were also made on the extraction of trace amounts of zinc with 0.001 M STTA in cyclohexane, benzene, and MIBK. The extractability of the zinc chelate at a constant pH was found to be the same by either cyclohexane and benzene, but it was poor by MIBK, as is shown in Fig. 5. In general, the extractability of the cobalt and zinc STTA chelates is remarkable when

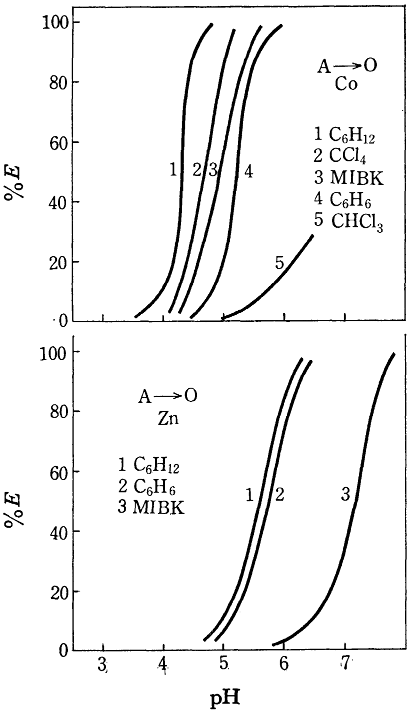

Fig. 5. The effect of the diluent on the extraction of trace amounts of Zn(II) and Co(II) with 0.001 M STTA in a various organic solvent.

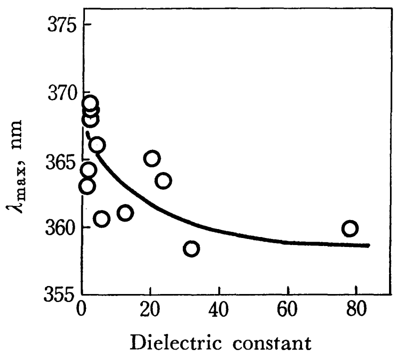

Fig. 6. The effect of the dielectric constant of the diluent on the wavelength of the absorption maximum, λ_{max}, of STTA. The values of wavelength of the absorption maximum, λ_{max}, was as follows:
1: Carbon disulfide (378.0), 2: Benzene (369.0) 3: Xylene (368.5) 4: Carbon tetrachloride and cyclohexane (365.0) 5: n-Hexane (363.0) 6: Chloroform (366.0) 7: Ethyl acetate (360.5) 8: Methyl isobutyl ketone (361.0) 9: Acetone (365.0) 10: Ethanol (363.5) 11: Methanol (358.5) 12: Water (pH 8.0) (360.0)

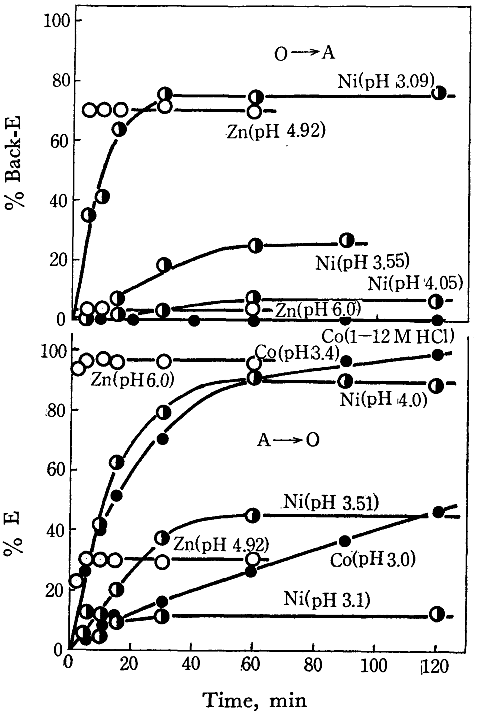

Fig. 7. The rates of the extraction and the back-extraction of trace amounts of Zn(II), Ni(II), and Co(II)-0.001 M STTA-cyclohexane system at different pH values.

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[12] D. Dyrssen, *Svensk Kem. Tidskr.*, **68**, 212 (1956).

[13] T. Shigematsu and M. Tabuchi, *Bull. Inst. Chem. Res., Kyoto Univ.*, **39**, 35 (1961).

[14] W. B. Brown, J. F. Steinbach, and W. F. Wagner, *J. Inorg. Nucl. Chem.*, **13**, 119 (1960).

[15] J. Stary and E. Hladky, *Anal. Chim. Acta*, **28**, 227 (1963).

[16] D. Dyrssen, "Extraction of Metal Ions with β-Isopropyl tropolone," Trans. Roy. Inst. Technol, No 188 Stockholm, 1962.

[17] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, **1953**, 3192.

using solvents of a small dielectric constant and a lower solubility of water. These facts show that the extracted chelates are stable and have no significant dipole moment. Therefore, the dipole interaction of the chelates with the diluent can scarcely play any appreciable role in the extraction process. Figure 6 shows the relationship between the absorption maximum of STTA in various solvents and the dielectric constants of the solvents. The STTA solution exhibits a typical absorption band, varying with the dielectirc constant and with the hydrogen-bonding ability of the solvents. This change in the absorption band is generally called the blue shift; its intensity becomes stronger with an increase in the dielectric constant of the solvent. This indicates that the interaction between STTA and the more polar solvent, *e.g.*, the hydrogen bonding or the dipole-dipole interaction, takes place in the solution; it may be one of the most important factors in the decrease of the extractability of cobalt and zinc STTA chelates.

Kinetics of Extraction and Back-extraction. The effects of the pH on the extraction and the back-extraction rate of trace amounts of cobalt, nickel, and zinc with 0.001 M STTA in cyclohexane are shown in Fig. 7. The extractions were carried out under vigorous shaking, for the extent of the extraction is independent of the shaking rate. The extraction of Zn seemed to be rapid, but that of Ni seemed to require about 60 min to reach its extraction equilibrium. Cobalt was not back-extracted, not even with 1—12 M HCl. The experimental results show that the extraction rate of the chelate compounds is a function of the pH and that it usually increases with an increase in the pH under the same conditions. If we assume that the slowest stage in the Ni–STTA–cyclohexane extraction system is due to the first-step formation of the chelate compound, the rate of the extraction of nickel, $-\mathrm{d(Ni^{2+})/dt}$, can be shown to obey the following equation in view of the general rate expression[18] for formation of metal chelates:

$$-\frac{\mathrm{d(Ni^{2+})}}{\mathrm{d}t} = k(\mathrm{Ni^{2+}})(\mathrm{R^-}) \tag{14}$$

$$= k(\mathrm{Ni^{2+}})\frac{K_a}{P_r}\frac{(\mathrm{HR})_0}{(\mathrm{H^+})} \tag{15}$$

$$\log(1-\%\ E/100) = -\frac{k}{2.303}\frac{K_a}{P_r}\frac{(\mathrm{HR})_0}{(\mathrm{H^+})}t \tag{16}$$

$$\log(\log 100/(100-\%\ E)) = \mathrm{pH}+\log(\mathrm{HR})_0+\log t+\mathrm{const.} \tag{17}$$

where:

$$(\mathrm{Ni^{2+}})_{\mathrm{initial}} = (\mathrm{Ni^{2+}}) + (\mathrm{NiR_2})_0$$

$$D = (\mathrm{NiR_2})_0/(\mathrm{Ni^{2+}}),\quad \%\ E = 100D/(1+D) \tag{18}$$

$$\text{Then,}\quad (\mathrm{Ni^{2+}}) = (\mathrm{Ni^{2+}})_{\mathrm{initial}},\ (1-\%\ E/100) \tag{19}$$

As is shown in Fig. 8, the $\log(1-\%E/100)$ *vs.* time plot is linear for 30 min at a constant pH. Moreover, the $\log(\log 100/(100-\%E))$ *vs.* pH plot shows a straight line with the slope of unity. These facts indicate that the rate-determining step in the Ni–STTA–cyclohexane extraction system is controlled by the formation of $\mathrm{Ni(STTA)^+}$. Similar phenomena have also been observed in Zn, Ni, and the Co–dithizone–chloroform system.[19] The rate of the transfer of the neutral species from the aqueous to the organic phase is a dominant factor in the extraction in Zn-acetylacetone, benzoylacetone, and the dibenzoylmethane–chloroform system.[20] In all cases, the displacement of water molecules coordinated to a metal ion may also play an important role in the chelate-formation rate. In addition, the rate of extraction depends on the nature of the metal ion, the partition coefficient and the dissociation constant of the organic reagent, and the pH. If we postulate that the slowest stage in the Co–STTA–cyclohexane extraction system is due to a transformation of $\mathrm{Co(STTA)_2}$ to $\mathrm{Co(STTA)_3}$, the rate of the extraction of cobalt, $\mathrm{d(CoR_3)}/\mathrm{d}t = -\mathrm{d(Co^{2+})}/\mathrm{d}t$ may be described approximately by the following equation:

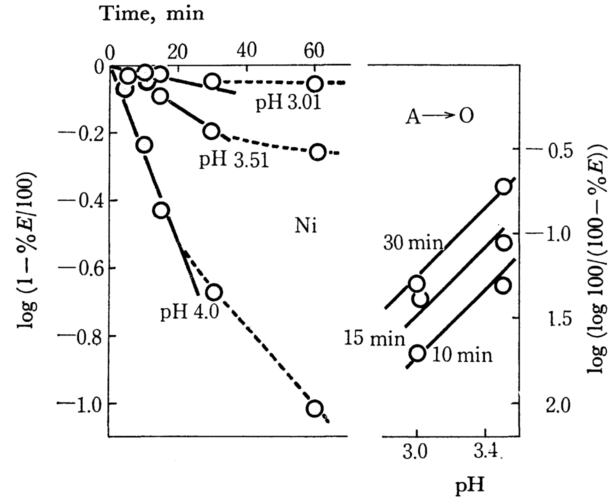

Fig. 8. The kinetics of the extraction of trace amounts of Ni(II) with 0.001 M STTA in cyclohexane at different pH values and time.

$$\frac{\mathrm{d(CoR_3)}}{\mathrm{d}t} = -\frac{\mathrm{d(Co^{2+})}}{\mathrm{d}t} = k(\mathrm{CoR_2})(\mathrm{HR})_0 \tag{20}$$

$$= k(\mathrm{Co^{2+}})\frac{KP_cK_a}{P_r^3}\frac{(\mathrm{HR})_0^3}{(\mathrm{H^+})^2} \tag{21}$$

$$\log(1-\%\ E/100) = -\frac{k}{2.303}\frac{KP_cK_a^2}{P_r^3}\frac{(\mathrm{HR})_0^3}{(\mathrm{H^+})^2}t \tag{22}$$

$$\log(\log 100/(100-\%\ E)) = 2\,\mathrm{pH} + 3\log(\mathrm{HR})_0 + \log t + \mathrm{const.} \tag{23}$$

As is shown in Fig. 9, the $\log(1-\%E/100)$ *vs.* time plot is linear at a constant pH. Moreover, the plots of $\log(\log 100/(100-\%E))$ *vs.* pH have a slope of 2, and the $\log(\log 100(100/(100-\%E)))$ *vs.* $\log(\mathrm{HR})_0$ plots give a straight line with a slope of 3, as is shown in Fig. 10. These facts indicate that the assumption of the extraction mechanism of cobalt is vaild.

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[18] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, **1949**, 1841.

[19] H. Freiser, "Solvent Extraction Chemistry," North-Holland, Amsterdam, (1967) p. 85.

[20] G. K. Schweitzer and J. R. Rimstidt, Jr, *Anal. Chim. Acta*, **27**, 389 (1962).

Synergistic and Antagonistic Effect in the Presence of TOPO. In the Ni and Zn–STTA(0.001 M)–TOPO(0.01 M)–cyclohexane systems, $|\Delta pH_{1/2}|$ was found to be 0.45 for Ni and 1.95 for Zn respectively. The logarithm of the distribution ratios of Zn and Ni is linearly related to the pH. The slope of the straight lines becomes 2, indicating that the extracted species can be written as $Zn(STTA)_2$ and $Ni(STTA)_2$ respectively. As is shown in Fig. 11, a straight line with a slope of 1 is obtained when log D^*/D values are plotted against $\log(TOPO)_0$ in the case of the Zn–STTA–TOPO–cyclohexane system. This fact indicates that one molar TOPO reacts with one molar Zn-STTA chelate to form the Zn(STTA)TOPO adduct in cyclohexane. The stability constant of the adduct was estimated to be log $\beta_{x,1}=6.05$. From the stability constant of the adduct of $Zn(TTA)_2TOPO$, log $\beta_{x,1}=6.47$,[21] under the same conditions, it may be

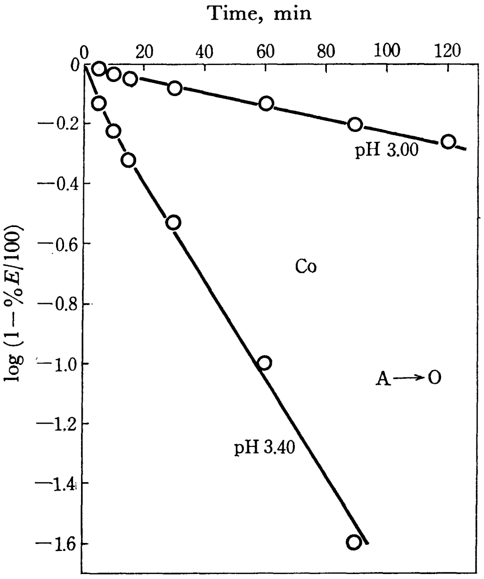

Fig. 9. The kinetics of the extraction of trace amounts of Co(II) with 0.001 M STTA in cyclohexane at different pH values and time.

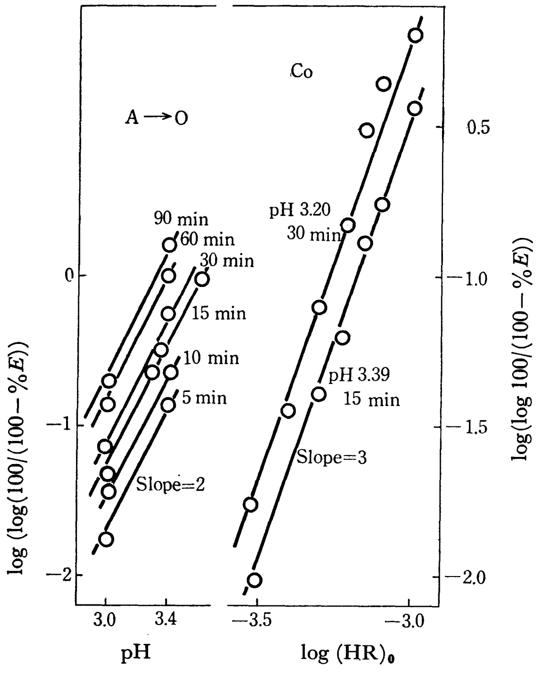

Fig. 10. The kinetics of the extraction of trace amounts of Co(II) with 0.001 M STTA in cyclohexane at different pH values and STTA concentration.

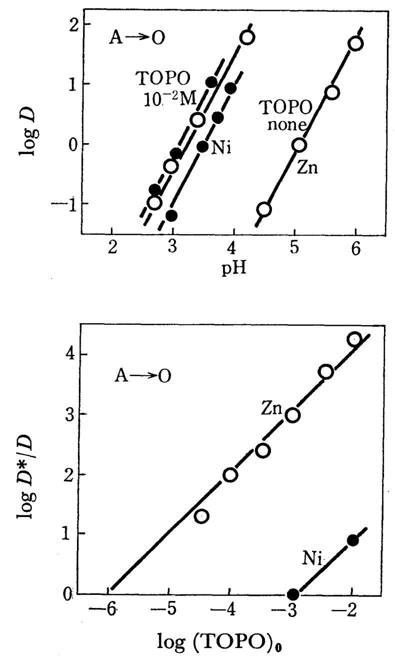

Fig. 11. The variation of the distribution ratio of trace amounts of Zn(II) and Ni(II) with 0.001 M STTA in cyclohexane in the presence or the absence of TOPO as a function of pH or TOPO concentration.

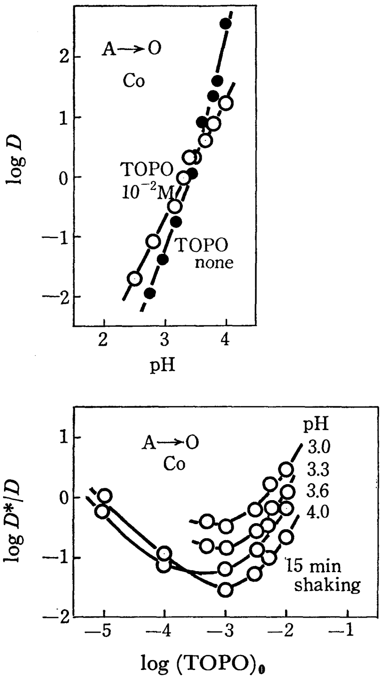

Fig. 12. The variation of the distribution ratio of trace amounts of Co(II) with 0.001 M STTA in cyclohexane in the presence or absence of TOPO as a function of pH or TOPO concentration.

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21) T. Honjo, M. Horiuchi and T. Kiba, This Bulletin, in press.

expected that TOPO forms more stable adducts with the $Zn(TTA)_2$ chelate than with the $Zn(STTA)_2$ chelate. As the extraction constants of $Zn(TTA)_2$ and $Zn(STTA)_2$ are $\log K_{x,0}=-8.33$[22] and -3.49 respectively, the general concept that the extraction constant of the chelates increases, while the stability constant of the adducts decreases,[23] is also the case for the metal–TTA and STTA–cyclohexane systems. The donor π-bond formation between the d-electrons of the metal and the sulfur of the STTA, bringing about the stabilization of the chelate, may play an important part. The Ni-STTA chelate ambiguously forms its adduct with TOPO. In the cobalt–STTA(0.001 M)–TOPO(0.001 M)–cyclohexane system, $|\Delta pH_{1/2}|$ was found to be 0.25. The slope in Fig. 12 of the log D against pH plot at a constant STTA(0.001 M) increases steeply up to 2 to 4 as the extraction pH becomes higher. Moreover, the plots of log D *vs.* $\log(STTA)_0$ at a constant pH give straight lines with a slope of 4, as is shown in Fig. 13. However, in the extraction of cobalt in the presence of 0.001 M TOPO, the log D *vs.* pH plots show straight lines with slopes of 2. As is shown in Fig. 12 the $\log D^*/D$ *vs.* $\log(TOPO)_0$ plots give concave curves including an antagonistic effect. The effect becomes more remarkable as the extraction is done at a higher pH, and appears most pronouncedly on the extraction of cobalt with STTA in the presence of 0.001 M TOPO. The effects of pH, of the extraction time, and of the TOPO concentration on the extraction and the back-extraction of the metal–STTA–TOPO–cyclohexane system are shown in Fig. 14. The cobalt STTA chelates extracted in the presence of 0.001—0.01 M TOPO could be back-extracted with 1 M HCl to a certain extent. However, when the concentration of TOPO becomes lower than 0.001 M, the cobalt chelate can not be back-extracted even with 1—12 M HCl. As can be seen in Fig. 14, the back-extraction of cobalt is controlled by the shaking time, the pH value, and the TOPO concentration. In the presence of 0.01 M TOPO, the back-extraction of cobalt with 1 M HCl decreases as the shaking time becomes longer and as the pH values increase. In general, the back-extractability of cobalt decreases with a decrease in the TOPO concentration. The Ni and Zn chelates extracted in the presence of TOPO are readily back-extracted with 1 M HCl. In the presence of 0.01 M TOPO, the extraction rate of zinc is rapid, while tha of Ni is somewhat slower than in the absence of TOPO In the extraction of cobalt in the presence of 0.01 M TOPO, the extraction increases greatly for 30 min and then more gradually. In the Co–STTA–TOPO–cyclohexane system, when the dominant species are CoR_2L, (which is back-extractable with 1 M HCl), CoR_3 (which is not back-extracted even with concentrated HCl), and Co^{2+}, the distribution ratio of cobalt in the extraction, D, may be written as follows:

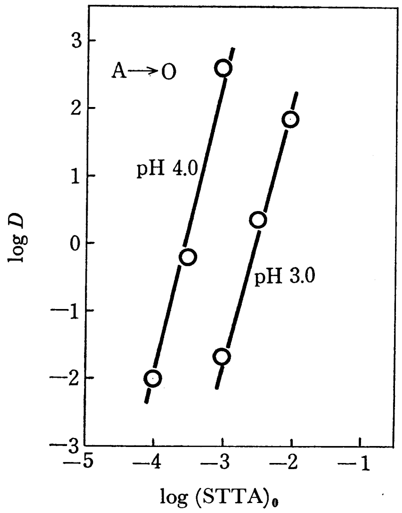

Fig. 13. The variation of the distribution ratio of trace amounts of Co(II) with STTA at definite pH values as a function of STTA concentration.

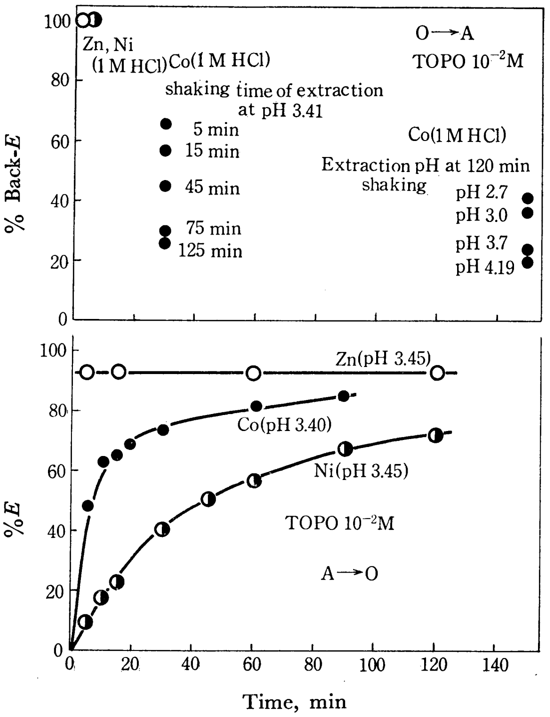

Fig. 14. The rates of the extraction and the back-extraction of trace amounts of Zn(II) and Ni(II)-0.001 M STTA-cyclohexane system in the presence or the absence of TOPO at different pH values or time.

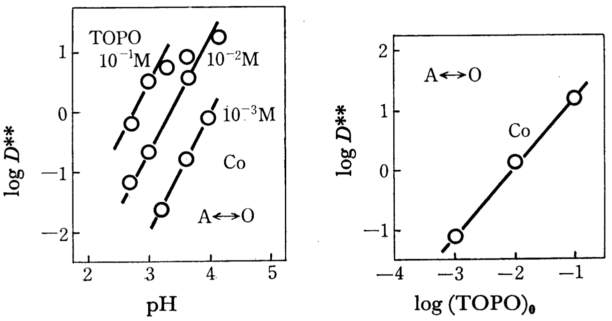

Fig. 15. The variation of the distribution ratio of trace amounts of Co(II)-0.001 M STTA-TOPO-cyclohexane system as a function of pH or TOPO concentration.

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[22] H. M. N. H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, **27**, 1359 (1965).

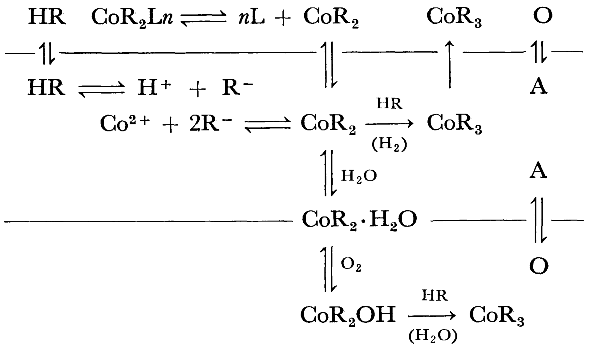
[23] T. Honjo and T. Shigematsu., *Kagaku* (Kyoto), **23**, 708 (1968).

$$D = \frac{(\mathrm{CoR_2L})_0 + (\mathrm{CoR_3})_0}{(\mathrm{Co^{2+}})}, \quad D_\mathrm{B} = \frac{(\mathrm{CoR_2L})_0}{(\mathrm{CoR_3})_0} \tag{24}$$

$$D^{**} = \frac{(\mathrm{CoR_2L})_0}{(\mathrm{Co^{2+}})} = \frac{D}{1+1/D_\mathrm{B}} = \frac{K\beta_{x,1}P_\mathrm{c}K_\mathrm{a}^2}{P_\mathrm{r}^2}\,\frac{(\mathrm{H})_0^2(\mathrm{L})_0}{(\mathrm{H^+})^2} \tag{25}$$

$$\log D^{**} = 2\,\mathrm{pH} + 2\log(\mathrm{HR})_0 + \log(\mathrm{L})_0 + \mathrm{const.} \tag{26}$$

Now, when terms such as D_B and D^{**} are used to explain the extraction behavior, the log D^{**} *vs.* pH plot shows a straight line with a slope of 2 at a constant concentration of TOPO, and the log D^{**} *vs.* log(TOPO)$_0$ plot shows a slope of unity at a constant concentration of STTA as is shown in Fig. 15. These facts suggest that the extracted cobalt compounds are $\mathrm{CoR_2L}$ and $\mathrm{CoR_3}$ respectively. From these experimental facts, the extraction mechanism of the cobalt(II)–STTA–TOPO–cyclohexane system may be expressed as follows:



The other evidence of the formation of $\mathrm{CoR_2}$, $\mathrm{CoR_2L}$ and $\mathrm{CoR_3}$ is as follows: 1) the existence of the first absorption band near 500 nm in the solution of the cobalt–STTA chelate ($\mathrm{CoR_3}$); 2) the cobalt–STTA chelate crystal prepared by the ordinary extraction was the diamagnetic ($\mathrm{CoR_3}$); 3) the silica gel thin-layer chromatograms of the extracted cobalt–STTA chelates at high concentrations give two spots, one corresponding to $\mathrm{CoR_2}$(R_f=0.29), and the other, to $\mathrm{CoR_3}$ (R_f=0.35), using carbon tetrachloride as the developing solvent; 4) a part of the cobalt-STTA chelates extracted in the presence of TOPO can be back-extracted with 1—12 M HCl, and the back-extracted cobalt behaves as a divalent ion ($\mathrm{CoR_2L}$). At present time, it should be considered that the irreversible extraction behavior of Co-STTA chelates is due to the inert nature of the trivalent cobalt complexes. The transformation of $\mathrm{Co(STTA)_2}$ to $\mathrm{Co(STTA)_3}$ may occur both in the aqueous and the organic phases, or at the interface of the two phases, by means of a certain interaction between $\mathrm{Co(STTA)_2}$ and STTA in the presence of oxygen and water. However, further investigations of these questions will be necessary before we reach any final conclusion.