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Formation of Two Chromium(Ⅲ) Dithiocarbamates from Cr(VI) in Solvent Extraction System and Origin of Oxygen Atom in Bis(1-pyrrolidinecarbodithioato)[1-pyrrolidinecarbothio (thioperoxoato)]chromium(Ⅲ)

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In order to explore the cause of a distinctive extraction behavior of Cr(VI) in the dithiocarbamate formation-solvent extraction systems, extracted chromium compounds were investigated and relationships between the formation of the compounds and the extraction behavior were studied. Chromatographic separation and spectroscopic analyses showed that two kinds of chromium(Ⅲ) dithiocarbamates (i.e. tris(1-pyrrolidinecarbodithioato)chromium(Ⅲ) and bis(1-pyrrolidinecarbodithioato)[1-pyrrolidinecarbothio(thioperoxoato)]chromium(Ⅲ)) were formed and extracted in an ammonium 1-pyrrolidinecarbodithioate (APCD)/diisobutyl ketone (DIBK) solvent extraction system. The two products comprised most of the extracted chromium. Concentrations of the two dithiocarbamates in extracts were determined using double wavelengths analysis. The dependence of concentration ratio of the two complexes on pH was also investigated. The results of the investigation clarified that a major extract obtained under high pH condition was the thioperoxo complex and that the percentage of the tris complex increased with decreasing pH. Furthermore, it was clarified that the unusual extraction behavior of chromate was distinguished by the formation of thioperoxo complex. In order to elucidate the formation mechanism of the thioperoxo complex, the origin of an oxygen atom in the molecule of the thioperoxo complex was determined with an isotope labeling technique. The labeling experiments clarified that the source of the oxygen atom of the complex molecule was chromate ion and that the oxygen atom was fixed to chromium atom prior to the rate determination step of the formation of the thioperoxo complex.

The dithiocarbamate ions have been used widely in analyses of many elements, because the ions form chelate complexes, which exhibit high extractabilities into organic solvents, with many kinds of metal ions. Recently, some bioactivities of the dithiocarbamate ions such as an inhibition of growth of cancer cells[1] and an effect on apoptosis of some types of cell[2] have become important in the fields of biology and medicine. Since these bioactivities significantly change with coexistence of some kinds of heavy metal ions, a relationship between the formation of the metal dithiocarbamates and the bioactivities has become of interest in recent years. Also in analytical chemistry, potentials of the dithiocarbamate formations for speciation of some elements enhance the values of the analytical methods based on the formations.[3–6]

The dithiocarbamate formation-solvent extraction systems have high potential for the speciation of Cr(Ⅲ) and Cr(VI). Because the toxicities of Cr(Ⅲ) and of Cr(VI) to the mammals differ considerably, these extraction systems are suitable for environmental analysis. In fact, some extraction systems have been applied for speciation of chromium in various samples such as fresh water and seawater.[7–12] However, there are noticeable discrepancies among the reported pH ranges for quantitative extraction of Cr(Ⅲ)[11,13] and of Cr(VI).[8,14] In order to resolve the discrepancies and to clarify a true pH effect on the extraction of chromium, the author and co-workers studied the effects of pH on the extraction of Cr(Ⅲ) and of Cr(VI) in APCD/DIBK system.[15] With due consideration for pH changes caused by chelating agent addition, we clarified the hidden true pH effect. The discrepancies among papers were because the discussions were based only on initial pH values. The extraction behavior of Cr(VI) was mainly dominated by pH after addition of chelating agent.[15] In the study, however, Cr(VI) exhibited some complicated behavior at pH values lower than 6 (in initial pH < 4) and the behavior could not be explained reasonably; extractability-pH curves had a valley at pH 4 (in initial pH 2) only within short shaking periods and the valley disappeared with elongation of the shaking time. This distinctive extraction behavior of Cr(VI) has not been observed in the extraction of the other transition metal ions. It is known that Cr(VI) makes two types of complexes in aqueous solution with the dithiocarbamate ions.[16] This formation of multiple complexes observed in reaction of Cr(VI) differs from the other metal ions. It is presumed that multiple complexes are also formed in dithiocarbamate-extraction systems and that the formation of the complexes is responsible for the distinctive behavior of Cr(VI).

The objects of this study are to identify extractable chromium compounds in the APCD/DIBK system and to elucidate a relationship between formation of the compounds and the distinctive extraction behavior. In addition, another object is to

determine the origin of the oxygen atom in the complex that is dominating the distinctive extraction behavior.

Experimental

Apparatus. An HM-30S glass electrode pH meter (TOA, Tokyo, Japan) was used for pH measurements. An SR-IIw vertical reciprocating shaker (TAITEC, Saitama, Japan) was used in extraction processes. IR spectra of chromium(III) complexes were measured with A-202 and IR-F IR spectrophotometers (Jasco, Tokyo, Japan). Determination of molar extinction coefficients of the complexes and determination of concentrations of the complexes in extracts were carried out with a Ubest-50 UV/VIS spectrophotometer (Jasco, Tokyo, Japan). An AA-782 atomic absorption spectrometer (Nippon Jarrell-Ash, Kyoto, Japan) was used for the measurement of chromium concentrations. A JMS-SX102A mass spectrometer (JEOL, Tokyo, Japan) was used for measurement of HPTLC-FABMS.

Reagents. All chemicals used were analytical-reagent grade or better. Doubly distilled water was used throughout. Solution of chelating agent was prepared daily by dissolving an APCD (Wako Pure Chemical Industries, Ltd., Osaka, Japan) in water. Including DIBK (Wako Pure Chemical Industries, Ltd., Osaka, Japan), all chemicals were used without further purification. ^{18}O-enriched H_2O (10 atom%) was purchased from ISOTECH Inc. (Miamisburg, OH). Wakogel C-300 (Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used for column chromatography and Kieselgel 60 HPTLC plate (Merck, Darmstadt, Germany) was used for HPTLC-FABMS.

Identification of Chromium Compounds Existing in Extract. A 25 mL of potassium dichromate solution (8×10^{-3} Cr mol/dm^3) was placed in an Erlenmeyer flask. With concentrated hydrochloric acid and water, the acidity of the solution was adjusted to pH 0 or 4, and volume of the solution was adjusted to ca. 225 mL. A 50 mL of DIBK and 25 mL of APCD solution (8×10^{-1} mol/dm^3) were added to the flask. The mixture was shaken for 5 or 30 min. After the extraction process, organic layer was separated from aqueous layer with a Whatman 1PS phase separator and the organic phase was vacuum dried to remove DIBK. The purple residue obtained was dissolved in a small amount of chloroform and the solution was chromatographed over silica gel. A mixture of *n*-hexane and chloroform (65:35 v/v) was used as eluent. Absorbance of the eluent was monitored at 254 nm to find and to separate constituents of the residue. All of the separated constituents were checked with AAS whether these contained chromium. For chromium-containing constituents, visible and IR spectrum measurements, conventional FABMS measurement and elemental analysis were carried out.

Determination of Concentration of Two Chromium Complexes in Extract. The extraction process was carried out in same manner as described above. The volume of each aqueous solution was reduced to one-tenth; 10 mL of DIBK was used.

Concentrations of tris complex and of thioperoxo complex in organic layer were determined using two wavelengths analysis, without separation of the two complexes; where "tris complex" is tris(1-pyrrolidinecarbodithioato)chromium(III) and "thioperoxo complex" is bis(1-pyrrolidinecarbodithioato)[1-pyrrolidinecarbothio(thioperoxoato)]chromium(III). Absorbances of DIBK phase were measured at 649.5 nm and at 705.8 nm for determination of the tris complex, and at 621.5 nm and at 677.5 nm for determination of the thioperoxo complex. Each set of the two wavelengths was a set of equiabsorptivity points of each complex. For example, calculation for the determination of tris complex was performed as below. The difference between the two absorbances measured at 649.5 nm and at 705.8 nm was divided by the difference between molar extinction coefficients of tris complex at the two wavelengths.

Introduction of Stable Isotope Label into Solvent Extraction System. Extraction conditions were changed from the above conditions, in order to reduce consumption of ^{18}O-enriched H_2O and to obtain high total abundance of the ^{18}O in whole extraction system. Chloroform was used as a solvent to facilitate the treatment of extract after extraction. In order to eliminate dissolved oxygen, all solutions were degassed with nitrogen gas before use.

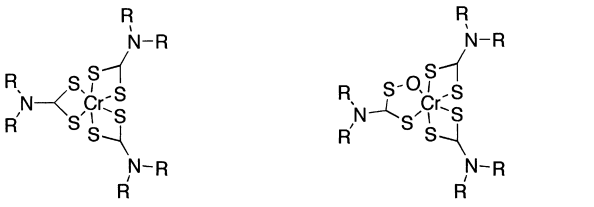
An 11 mL of ^{18}O-enriched H_2O or normal water was placed into a 50 mL Erlenmeyer flask. Then 0.5 mL of hydrochloric acid of appropriate concentration was added to adjust the pH of the content of flask and 10 mL of chloroform was added. A 0.5 mL of potassium dichromate solution (0.8 Cr mol/dm^3) and 0.5 mL of APCD solution (0.8 mol/dm^3) were added to the flask. The order of the addition of dichromate and APCD was permuted on occasions. Immediately after the additions, shaking was started. After the extraction period, the chloroform layer was separated with an 1PS phase separator, and the organic layer was washed with 10 mL of normal water before evaporation. The washed extract was dried at room temperature under a nitrogen atmosphere. Then the residue was served as a sample for HPTLC-FABMS measurement.

HPTLC–FABMS. The prepared extract sample was dissolved in small amounts of chloroform. The sample was spotted on an HPTLC plate and it was developed with chloroform. The plate was air-dried and was cut into suitable sizes to fit a probe of a mass spectrometer. Each plate was coated with 3-nitrobenzyl alcohol and was attached onto the probe. Resolution of a spectrometer was set to 3000 and the spectrometer was operated under standard conditions for positive ion measurement.

Results and Discussion

Identification of Chromium Compounds Existing in Extract. In order to identify the chromium compounds extracted into organic phase in APCD/DIBK system, extractions were carried out under four conditions that were combination of two initial pH conditions (0 and 4) and two extraction times (5 and 30 min). The extracts were chromatographed over silica gel column. The obtained results showed that, regardless of the difference in the conditions, all the extracts contained the same three components: these were two kinds of major chromium compounds (bluish purple and grayish purple) and one organic compound (yellow). A trace amount of the other chromium compound also eluted after the elution of the two chromium compounds. However, the amount of the minor chromium compound was negligibly small, about one-thousandth of the amounts of the major two compounds in chromium content. It was inferred from the results that the two chromium compounds obtained in this extraction system were the same types as the two dithiocarbamato complexes (Fig. 1) reported in aqueous solution.[17]

Conventional FABMS measurement, elemental analysis and visible and IR spectrum measurements were applied to the two obtained substances. FABMS measurements gave intense peaks at *m*/*z* 490 for the bluish purple substance and at *m*/*z* 506 for the grayish one. These mass spectra suggested that the blu-



tris(dialkylcarbamodithioato)-chromium(III)

bis(dialkylcarbamodithioato)-[dialkylcarbamothio(thioperoxoato)]-chromium(III)

Fig. 1. Two kinds of dithiocarbamato complexes formed from Cr(VI).

ish one was the tris complex and the grayish one was the thioperoxo complex.

Other analytical data of the bluish compound are shown below. IR (nujor cm^{-1}): 670, 756. Visible (DIBK) (λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 501.0 (1.24×10^3), 649.5 (1.22×10^3). Found: C, 36.61; H, 4.89; N, 8.55; S, 39.63; Cr, 10.50%. Calcd for $C_{15}H_{24}N_3S_6Cr$: C, 36.71; H, 4.93; N, 8.56; S, 39.21; Cr, 10.60%. Data of the grayish one are shown below. IR (nujor cm^{-1}): 402, 438, 501, 537, 665, 750, 759, 884, 957, 1155. Visible (DIBK) (λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 500.0 (8.39×102), 677.5 (1.08×10^3). Found: C, 35.50; H, 4.65; N, 8.30; S, 37.80; Cr, 10.35%. Calcd for $C_{15}H_{24}ON_3S_6Cr$: C, 35.55; H, 4.77; N, 8.29; S, 37.97; Cr, 10.26%.

The elemental analysis data agreed well with the values calculated for the two presumed complexes. Because there is no IR data and electronic spectra data for the two complexes, these measured data were compared with data of diethyldithiocarbamato complexes and of dimethyldithiocarbamato complexes,[17] which were corresponding to the two. From the wavelengths and wave numbers of the maximal absorption in the electronic spectra and the IR absorption band at 501 cm^{-1} which was assigned to Cr–O vibration, it was clarified that the bluish purple substance was tris(1-pyrrolidinecarbodithioato)chromium(III) and that the grayish purple substance was bis(1-pyrrolidinecarbodithioato)[1-pyrrolidinecarbothio(thioperoxoato)]chromium(III).

Concentration Ratio of Two Chromium(III) Dithiocarbamates in Extract. The identification showed that chromium existed as the two complexes in the DIBK phase after extraction, regardless of the difference in the extraction conditions. Although there is a little chromium compound besides the two complexes described above, these facts showed clearly that practically all of chromium existed as the two complexes in the organic phase. Concentration ratio of the two complexes in DIBK phase was determined under several pH conditions, in order to elucidate a relationship between extraction behavior of Cr(VI) which depended on pH and formation of the two chromium complexes. Both the complexes had two absorption bands in the visible region at ca. 500 nm and ca. 660 nm. Although the absorptivity at around 500 nm was enough to the determination of concentrations, the spectral difference between the two complexes was little and the yellow organic compound formed with the complexes also exhibited absorption at this region. Thus, absorbance measurements of DIBK phase for calculation of the concentrations were executed at 600–700 nm.

A typical result of the determination is shown in Fig. 2. Concentrations of the two complexes were plotted with total concentration of the two. The curve of the total chromium concentration has two peaks at initial pH 1 and 3 as the extraction behavior reported in the literature,[15] even though the concentration of chromate in this study was increased higher than the concentration in the literature to obtain enough absorbance. This extraction behavior was distinctive; it has not been observed within dithiocarbamate extraction systems of the other metal ions.

As shown in Fig. 2, tris complex was not formed significantly above initial pH 3 and the percentage of the complex in the total amount of the chromium compounds increased with increasing in acidity. On the other hand, thioperoxo complex was formed under all pH conditions. Although concentration ratios of the two complexes fluctuated measurably with shaking time, the pH-dependencies mentioned above did not change with shaking time. It is well known that the two complexes are formed in reactions between the dithiocarbamate ions and chromate ion and that the formation of the tris complex from chromate ion interferes with determination of Cr(III) in chromatographic simultaneous determination of Cr(III) and Cr(VI).[18–20] However, there is no investigation about the effect of pH on the formation of the two dithiocarbamato complexes, even in reactions in aqueous solution. This is the first report about the relationship between the concentration ratio of the two dithiocarbamato complexes and the reaction conditions. The concentration curve of thioperoxo complex obtained after a 2 min of shaking period had maxima at initial pH 1 and 3 (Fig. 2). The characteristics of the curve were faithfully reflected in the curve of the total chromium concentration. Although an essential cause of occurrence of the two maxima (or one valley at initial pH 2) could not be explained reasonably, it was clarified that the distinctive extraction behavior of Cr(VI) was due to the formation of thioperoxo complex. On the other hand, a concentration curve of the tris complex was also interesting. Although the tris complex is also formed in reaction between Cr(III) ion and dithiocarbamate ion, the formation of tris complex from Cr(III) is very slow and does not occur below initial pH 1.[15] The curve of tris complex in Fig. 2 showed

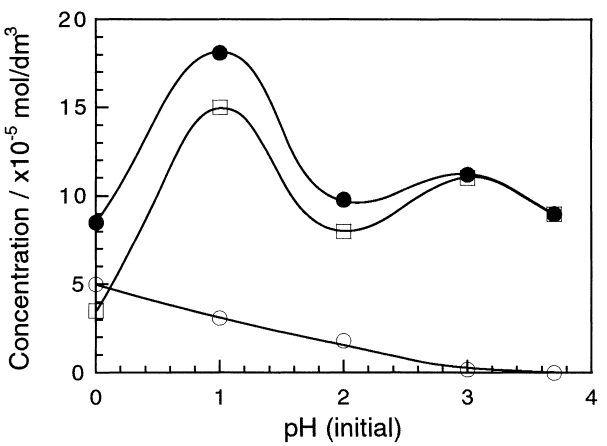


Fig. 2. Concentrations of two chromium complexes in the extracts. Shaking time: 2 min. ○: Tris complex, □: thioperoxo complex, ●: total chromium.

that tris complex was formed from Cr(VI) under highly acidic conditions within a short reaction time. These facts indicated that the formation mechanisms of the tris complex from Cr(III) and from Cr(VI) differ essentially.

Evaluation of Isotope Ratio of Oxygen Included in Bis(1-pyrrolidinecarbodithioato)[1-pyrrolidinecarbothio(thioperoxoato)]chromium(III). The above investigation clarified that the formation of the thioperoxo complex dominated the distinctive extraction behavior of Cr(VI). The thioperoxo complex contains a unique five-membered chelate ring, which includes one oxygen atom.[17] Therefore, to investigate the formation of the complex and of the unique ring structure is important for clarification of the distinctive behavior. However, there are only mentions of formation of disulfides as by-product in the reactions between Cr(VI) and dithiocarbamate ion[18,21,22] and there is no kinetic and/or mechanistic study on the reaction. Furthermore, there are not many compounds that contain the ring structure, and there are few references about the preparation of these compounds.[23–27] Thus, the formation mechanism of the oxygen including chelate ring was interesting not only from the viewpoint of clarification of the distinctive extraction behavior but also from the viewpoint of the uniqueness of the ring structure.

In order to determine the origin of the oxygen atom included in the thioperoxo complex, a stable isotope labeling technique was adopted in the following investigation. One of the most important matters in the labeling experiment was evaluation of the isotope composition of oxygen atom in the thioperoxo complex molecules. In this study, the evaluation was carried out based on change of pattern of isotope peaks. Then, to obtain a standard mass spectrum pattern of thioperoxo complex, a non-labeled thioperoxo complex was measured with HPTLC–FABMS preliminarily. The non-labeled extract was developed on an HPTLC-plate and the plate was attached to the probe of a mass spectrometer. Although the extract was separated clearly into each component, the shape of a peak-group that appeared around *m/z* 506, which corresponded to the molecular weight (MW) of thioperoxo complex, obviously differed from a pattern of calculated isotope peaks for the complex (Fig. 3). In order to find out the cause of the difference, FABMS measurement was carried out in high-resolution mode. Results of the HR-FABMS measurement showed that the major cause of the difference in pattern was formation of protonated molecular ions (i.e. MH^+). There was tendency that the rate of the formation of protonation increased with increasing in the amount of sample on a TLC-plate. Although high-resolution measurement is superior to low-resolution measurement in discrimination, all of isotope peaks cannot be resolved completely even with HR-measurements and it is difficult to apply HR-measurement to TLC–FABMS. Because TLC–FABMS is an effective analytical method for small amounts of mixture samples, if LR-TLC–FABMS had enough precision for this isotopic labeling experiment, it is more suitable for this study than HR-measurement.

If the obtained mass spectrum agreed with the calculated pattern, abundance of ^{18}O in thioperoxo complex can in principle be simply estimated based on an intensity ratio between intensities at *m/z* 506 and 508. However, the obtained spectrum disagreed with the theoretical pattern as described above. In order to estimate the precision of measurement of ^{18}O abundance in thioperoxo complex with presence of the protonation, a non-labeled extract was measured repeatedly. Results of the measurements showed that an intensity ratio at *m/z* 508 to at *m/z* 506 varied significantly between 46% and 50%; an RSD of the ratio was 1.95% ($n = 32$). The range of variation was not small as compared with abundance of ^{18}O in the purchased ^{18}O-enriched water (i.e. 10%).

Many masses of thioperoxo complex molecules are present as isotopic compositions. It was thought that all of the complex molecules protonated at a same rate regardless of the mass of the molecules within one measurement; thus both the complex molecules of MW ca. 507 and ca. 506 would form MH^+ in same rate at *m/z* ca. 508 and ca. 507. From the above, it was inferred that the fluctuation of intensity at *m/z* 508 caused from the protonation correlates closely with fluctuation at *m/z* 507.

The results of the repeated FABMS measurements ($n = 32$) are plotted in Fig. 4. Intensity ratios of *m/z* 508/506 strongly correlated (correlation coefficient = 0.91) with intensity ratios of *m/z* 507/506. A regression line for the data was calculated

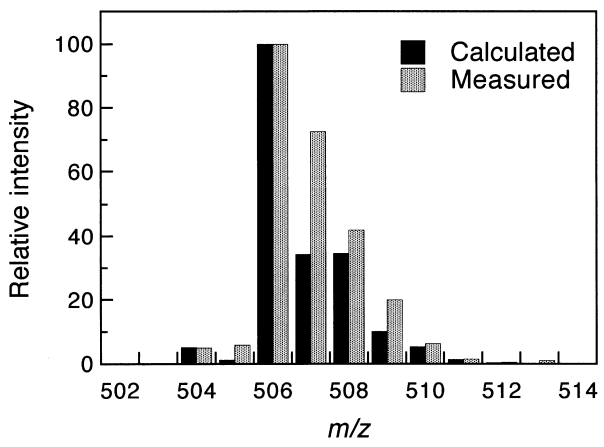


Fig. 3. Mass spectrum patterns of thioperoxo complex.

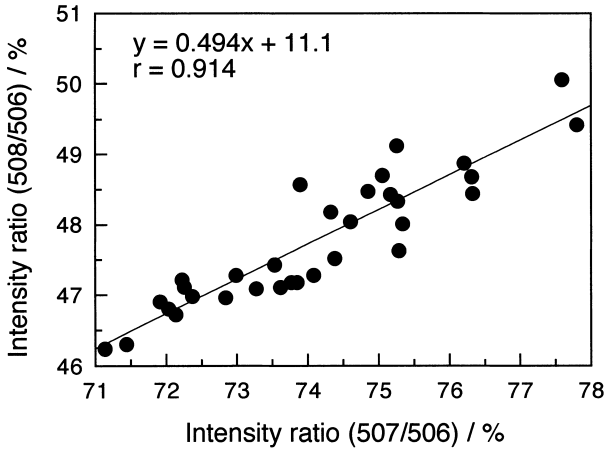


Fig. 4. Effect of formation of protonated molecular ion on intensity ratio. One non-labeled sample was used for all measurements.

and it is also drawn in the figure. Deviations of the data along the ordinate from the regression line were lower than ±1%, which was half of a deviation of without consideration of the correlation between the fluctuations. Because the ±1% deviation was small enough for this study, in the following, the abundance of ^{18}O in thioperoxo complex was evaluated with a deviation from the regression line along the ordinate.

Because abundances of thioperoxo complex molecule of MW ca. 504 and ca. 505 were small, signal intensity at *m/z* 506 and 507 would not be increased significantly by introduction of ^{18}O label. Thus the increasing in intensity at *m/z* 507 was fully attributable to the protonation of complex molecule of MW ca. 506.

Origin of Oxygen Atom in Bis(1-pyrrolidinecarbodithioato)[1-pyrrolidinecarbothio(thioperoxoato)]chromium(Ⅲ). Isotopic labeling experiments were carried out under some different conditions in pH, reaction time and order of additions of Cr(VI) solution and of APCD solution. Non-labeling extractions were also executed under the same conditions as control experiments. All extracts were developed with HPTLC and the TLC-plates were attached onto the probe of the mass spectrometer. Results of the labeling experiments are shown in Fig. 5. Solid lines in Fig. 5 are the regression line obtained above and broken lines are guides for estimation of the deviation from the regression line. Naturally, all data of the control experiments appeared along the regression line within the error limits. By contrast, all of the data obtained from labeled extraction showed unusually larger values in the intensity ratio *m/z* 508/506, than those obtained from the control. These large intensity ratios evidenced that the introduced ^{18}O labels were incorporated into the thioperoxo complex. In labeled extractions, addition of Cr(VI) solution prior to addition of APCD solution increased the ratio ca. 10% over the regression line (Fig. 5-a) and the inverted order in the additions increased them ca. 5.5% over (Fig. 5-b). The 10% and 5.5% of increases in the intensity ratio *m/z* 508/506 correspond to 9.1% and 5.2% of ^{18}O abundance in the thioperoxo complex in calculation respectively. Extent of these increases in abundance did not depend on the extraction conditions such as acidity or reaction time.

There were two probable sources of the oxygen atom in thioperoxo complex: those were water and chromate. Total abundance of ^{18}O in the labeled extraction system was 8.8%, because the labeled water (10 atom%) was diluted with a small amount of normal water that was contained in solutions of HCl, chromate and APCD. If water molecule or related species such as H_3O^+ had brought an oxygen atom directly into the complex molecule, ^{18}O would have been incorporated into the complex at rate of ca. 9% unexceptionally. However, some data showed partial (ca. 5% in ^{18}O abundance) incorporation of the label as described above. This fact indicated that the source of the oxygen atom in the thioperoxo complex was not water but it was the chromate ions (i.e. $Cr_2O_7^{2-}$ or $HCrO_4^-$).

It is known that exchange of oxygen atoms occurs between water and Cr(VI) species such as CrO_4^{2-}, $HCrO_4^-$ and $Cr_2O_7^{2-}$ in aqueous chromate solutions. Thus, it was thought that a cause of the incorporation of ^{18}O atom, which was originally labeled in water, into the complex was attributable to the oxygen exchange between the Cr(VI) species and water. That is,

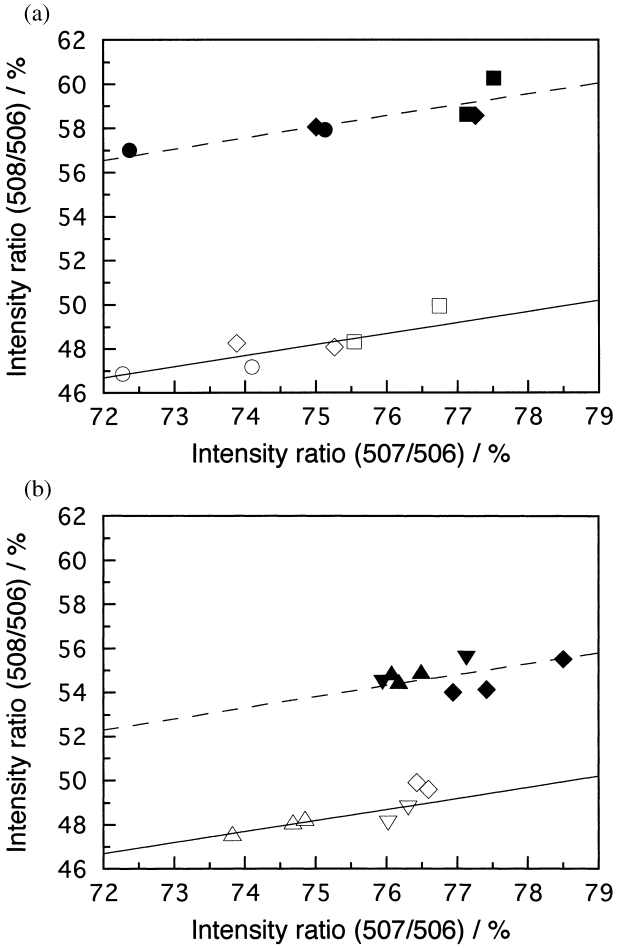


Fig. 5. FABMS-data of labeled samples. (a): Cr(VI) sol. was added prior to APCD sol., (b): APCD sol. was added prior to Cr(VI) sol. Open markers and closed markers correspond to non-labeled samples and labeled samples. Initial pH and reaction time: ●, 1.7 and 4 min; ◆, 2.9 and 4 min; ■, 4.5 and 4 min; ▲, 1.9 and 1 min; ▼, 1.9 and 10 min.

the circumstances of the ca. 9 and 5% increases in abundance of ^{18}O could be explained as the following. In the case of the addition of chromate prior to addition of APCD, a time gap between the addition of Cr(VI) solution and the addition of APCD allows the oxygen exchange to progress sufficiently. The sufficient exchange equalized abundances of ^{18}O in chromate ion and in water, even before the addition of APCD. Consequently, the equalized abundance (ca. 9%) reflected in the abundance in the resulting thioperoxo complex. On the other hand, in the case of the addition of chromate after the addition of APCD, the oxygen exchange and formation of thioperoxo complex began at the same time. Because rates of the isotope exchange and of the incorporation of oxygen atom were comparable, the two reactions progressed simultaneously and the partial incorporation (ca. 5%) was observed in the resulting complex. Although some investigators study the rates and mechanisms of the complicated exchange of oxygen under neutral and basic conditions,[28–30] unfortunately information about the rates and mechanisms under acidic conditions is scarce. Brasch et al. calculated theoretically the rate of loss of

isotopic oxygen label from monomeric chromate into water.[31] The calculated results indicated that more than 25% of the oxygen label was lost into water within 3 s after mixing at pH 3.[31] Because the rates were theoretical and were calculated under specific conditions in concentration of Cr(VI) and in ion strength, the rate data are not applicable to the results of this work directly. However, Brasch's data were consistent with the explanation described above.

It is interesting that all of the data obtained in the case of the posterior addition of chromate to addition of APCD exhibited practically same abundance (5.5%), regardless of differences in pH and in shaking time (Fig. 5-b). The amount of extracted thioperoxo complex was increased with elongation of shaking time under all pH conditions. For example, 10 min of extraction gave twofold and fivefold of the amounts compared with 1 min of extraction at pH 0 and 2 respectively. Although the amount of the extracted complex kept on increasing over 1–10 min, the effect of progress of the isotope exchange that finished within few seconds did not appear in the abundance of ^{18}O in the complex obtained under initial pH range 0–3 (Fig. 5-b). This fact indicated the followings. All oxygen atoms, which would be incorporated into thioperoxo complex molecules, were fixed to chromium atoms immediately after the mixing of chromate and APCD, in aqueous phase. The fixation of the oxygen atoms occurred prior to a rate-determining step in this complexation-extraction system. The time interval between the fixation of the oxygen atom and the extraction of thioperoxo complex indicates that a water-soluble intermediate was formed in this extraction system. Many studies on reduction of Cr(VI) to Cr(III) by organic compounds or by metal ions evidenced the existence of intermediates of Cr(V) or Cr(IV).[32–34] Rao et al. indicated that a relatively long-lived Cr(V) species was formed as an intermediate in the reaction between Cr(VI) and cysteine which contains –SH group.[35] This fact intimates that the intermediate formed in this extraction system is species of Cr(V) or of Cr(IV) as the intermediate observed in the reaction of cysteine.

It is well known that thiols are oxidized by Cr(VI) to disulfides.[36] Indeed, generation of disulfide was observed in reactions between Cr(VI) and dithiocarbamate ions;[18,21,22] it was thought that the yellow organic substance obtained in this work corresponds to a disulfide. Thus, dithiocarbamate ion acts not only as a ligand but also as a reducing agent in the reaction with Cr(VI). McAuley et al. determined overall reactions between Cr(VI) and some –SH containing substances as below.[37]

$$n\mathrm{H}^+ + 2[\mathrm{HCrO_4}]^- + 6\mathrm{RSH} \rightarrow 2\mathrm{Cr(III)} + 3\mathrm{RS{-}SR}$$

(RSH: penicillamine or glutathione)

Hydrogen chromate ion acts as reactant in the above reaction. This fact agrees with our results obtained from the study of the effect of pH on the dithiocarbamato complex formation–solvent extraction of Cr(VI).[15] Thus, there is great possibility that formation of tris(1-pyrrolidinecarbodithioato)chromium(III) from Cr(VI) occurs in the same manner as in the equation in which reduction of Cr(VI) to Cr(III) fully corresponds to oxidation of –SH group to S–S bond. On the other hand, the equation is inadequate to describe the formation of the thioperoxo complex. Since the thioperoxo complex molecule is electrically neutral, the thioperoxo ligand containing oxygen also bears charge -1 just as do the other two normal dithiocarbamato ligands; the charge of the oxygen atom in the thioperoxo ligand is apparently zero. Because the origin of the oxygen atom is in chromate ion, the atom is oxidized from O(−II) to O(0) through the thioperoxo complex formation. It is thought that the only atom existing in this extraction system that has oxidizing ability is the Cr(VI) atom. From the above, the followings are inferred. Two electrons in three electrons required in the reduction of Cr(VI) to Cr(III) are provided from the oxidation of the oxygen atom. One more electron is provided from the formation of the S–S bond. To establish the formation mechanisms of the unique thioperoxo complex, stoichiometric study especially on the formed disulfide and kinetic study including the water-soluble intermediate with flow techniques are required.

Conclusion

Extraction behavior of Cr(VI) in dithiocarbamate formation–extraction system is distinctive among the extraction behaviors of transition elements. In order to elucidate the cause of the distinctive behavior of Cr(VI), this study was carried out in APCD/DIBK extraction system. Specification of extracted chromium compounds was carried out firstly and a relationship between formations of the specified complexes and the distinctive extraction behavior was investigated. The conclusions were as follows.

(1) The extractable chromium species in APCD/DIBK extraction system were two dithiocarbamato complexes, i.e. tris(1-pyrrolidinecarbodithioato)chromium(III) and bis(1-pyrrolidinecarbodithioato)[1-pyrrolidinecarbothio(thioperoxoato)]chromium(III).

(2) Dependence of concentration ratio of the two complexes on pH was investigated. Only the thioperoxo complex was extracted above pH 3 and the percentage of the tris complex increased with increasing in acidity. Formation of the thioperoxo complex characterized the distinctive extraction behavior of Cr(VI) in the dithiocarbamate extraction systems.

(3) The origin of the oxygen atom in the thioperoxo complex was chromate ion $Cr_2O_7^{2-}$ or $HCrO_4^-$. Furthermore, it was clarified as new information about the thioperoxo complex formation that the fixation of the oxygen atom to chromium atom occurred prior to a rate-determining step in the formation of the thioperoxo complex and yielded a water-soluble intermediate.

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