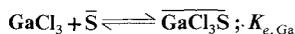


EXTRACTION EQUILIBRIA OF GALLIUM(III) AND THALLIUM(III) WITH DIHEXYL SULFIDE FROM HYDROCHLORIC ACID

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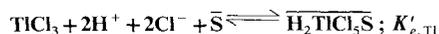
Key Words: Extraction, Equilibrium, Dihexyl Sulfide, Gallium(III), Thallium(III), 1,2-Dichloroethane, Hydrochloric Acid

The extraction equilibria of gallium(III) and thallium(III) from hydrochloric acid with dihexyl sulfide (DHS = \bar{S}) in 1,2-dichloroethane were measured at 303 K to examine the effects of the concentrations of hydrochloric acid and dihexyl sulfide. The stoichiometric relation of the extraction reaction of gallium(III) was found to be:



where the equilibrium constant was evaluated as $K_{e,\text{Ga}} = 1.9 \times 10^2 \text{ dm}^3/\text{mol}$.

Extraction of thallium(III) was found to be expressible by the following two stoichiometric relations for low and high concentration regions of hydrochloric acid, respectively.



where the equilibrium constants were evaluated as $K_{e,\text{Tl}} = 4.0 \times 10^6 \text{ (dm}^3/\text{mol)}^4$ and $K'_{e,\text{Tl}} = 1.6 \times 10^5 \text{ (dm}^3/\text{mol)}^5$.

Introduction

Solvent extractions of gallium(III) and thallium(III) from hydrochloric acid have been investigated with various kinds of extractant: tributylphosphate (TBP),^{1,5,10} trioctylphosphine oxide (TOPO),¹⁰ di-(2-ethylhexyl)phosphoric acid (D2EHPA)¹⁰ and high-molecular weight amines such as trioctylamine (TOA)¹⁰ and trioctylmethyl ammonium chloride (TOMAC).¹⁰ Sato *et al.*¹⁰ investigated the extraction of gallium(III) from hydrochloric acid with TBP and TOPO, and concluded that it is extracted as the complexes $\text{GaCl}_3(\text{H}_2\text{O}) \cdot 2\text{TBP}$ and $\text{GaCl}_3 \cdot \text{TOPO}$, respectively. They further investigated with dihexyl sulfoxide (DHSO) in benzene¹¹ and found that gallium(III) is extracted as the complexes $\text{GaCl}_3 \cdot 2\text{DHSO}$ and $\text{GaCl}_3 \cdot \text{DHSO}$ in the low and high loading regions of gallium(III), respectively. In the extraction from hydrochloric acid with 100% TBP, however, Reznik *et al.*^{6,7} deduced that hydrogen tetrachlorogallate HGaCl_4 is extracted into organic phase by measuring the molar ratio of chloride ion to gallium(III) extracted in organic phase.

Recently, Reddy *et al.*⁸ conducted a quantitative investigation of extraction equilibria of thallium(III) from hydrochloric acid with dialkyl sulphoxides (DASO) and found the extracted complex to be

$\text{HTlCl}_4 \cdot 2\text{DASO}$ by slope analysis. The above-mentioned extractants, TBP, TOPO, DHSO and DASO, are those containing oxygen as a donor atom.

It is well known that thallium(III) is one of the typical "soft acids," as is thallium(I). Chlorides of gallium(III) and indium(III) are also classified as "soft acids" while their aqua-cations are typical "hard acids." Consequently, thallium(III) and gallium(III) or indium(III) chlorides are expected to be much more effectively and selectively extracted by sulfur-containing extractants, typical "soft bases,"¹³ compared with extractants containing nitrogen or oxygen as the donor atom.

As mentioned above, some studies have been carried out on extractions of gallium(III) and thallium(III) with extractants containing nitrogen or oxygen as donor atoms and the extracted species have been clarified. However, only a few studies² have been conducted on extractions with extractants containing sulfur as a donor atom. From the viewpoint mentioned above, the authors conducted a fundamental study on the distribution equilibria of gallium(III) and thallium(III) from hydrochloric acid with dihexyl sulfide (DHS = \bar{S}) in the present work. The concentration dependency of the reactant species on the distribution ratio of these metals was examined in order to clarify the composition of the extracted species and to evaluate the extraction equilibrium constants.

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1. Experimental

1.1 Reagents

The commercial extracting reagent SFI-6, produced and marketed by Daihachi Chemical Industry Co., Ltd., Japan, was used as a dihexyl sulfide. Since the purity of the commercial extractant is above 98%, it was used as received without further purification. The organic phase was prepared by diluting this reagent with 1,2-dichloroethane to the required concentration. Hydrochloric acid solutions containing gallium(III) were prepared by dissolving metallic gallium (99.99%) in concentrated hydrochloric acid followed by dilution with deionized water. The aqueous thallium(III) solution was prepared by dissolving thallium(III) chloride in hydrochloric acid solution. The initial concentrations of both metals were about 5×10^{-3} mol/dm³.

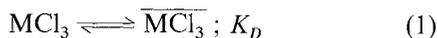
1.2 Measurement of extraction equilibria

Hydrochloric acid solutions containing gallium(III) or thallium(III) were allowed to attain equilibrium with an equal volume of the organic solution of DHS in a 0.1 dm³ stoppered glass flask by shaking the two phases for 24 hours for gallium(III) and 1 hour for thallium(III) in a thermostated water-bath maintained at 303 K. It was ensured by preliminary experiments that the equilibrations were attained within these times for each metal. After equilibration, the two phases were separated and the metal content in each phase was determined as follows. Gallium(III) concentration in the aqueous phase was determined by titration with EDTA using TAR (4-(2-thiazolylazo)-resorcinol) as an indicator according to the procedure proposed by Yamada *et al.*¹⁴⁾ and that in the organic phase was determined in a similar manner after stripping with 0.1 mol/dm³ hydrochloric acid. The thallium(III) concentration in the aqueous phase was determined by atomic absorption spectrochemical analysis using a Nippon Jarrell-Ash model AA-782 spectrophotometer. The concentration in the organic phase was determined in a similar manner after stripping with 0.1 mol/dm³ aqueous EDTA solution. The concentration of hydrochloric acid in the aqueous phase was determined by titration using phenolphthalein as an indicator.

2. Results and Discussion

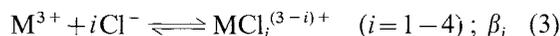
2.1 Physical partition of gallium(III) and thallium(III) between the diluent and hydrochloric acid

The physical partition of trivalent metals (M³⁺) such as Ga(III) and Tl(III) between the diluent and hydrochloric acid is described as follows:



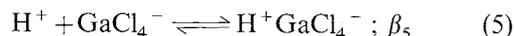
$$K_D = \frac{[\overline{\text{MCl}_3}]}{[\text{MCl}_3]} \quad (2)$$

In an aqueous solution containing chloride ion, trivalent metal ions form chloro-complexes as follows:



$$\beta_i = \frac{[\text{MCl}_i^{(3-i)+}]}{[\text{M}^{3+}][\text{Cl}^-]^i} \quad (4)$$

Furthermore, it is necessary to take into account the formation of the ion-pair described by Eq. (5) in the high-concentration region of hydrochloric acid in the case of the partition of gallium(III).⁴⁾



In case the metal content in the aqueous phase is very low, the concentration of hydrogen ion is nearly equal to that of chloride ion and consequently the concentration of the neutral complex, [MCl₃], can be represented by Eq. (6), taking account of the equilibria expressed by Eqs. (4) and (5).

$$[\text{MCl}_3] = \frac{\beta_3[\text{Cl}^-]^3}{1 + \sum_{i=1}^4 \beta_i[\text{Cl}^-]^i + \beta_4\beta_5[\text{Cl}^-]^5} C_{\text{Mw}} = \alpha_3 C_{\text{Mw}} \quad (6)$$

where

$$\alpha_3 = \frac{\beta_3[\text{Cl}^-]^3}{1 + \sum_{i=1}^4 \beta_i[\text{Cl}^-]^i + \beta_4\beta_5[\text{Cl}^-]^5} \quad (7)$$

C_{Mw} denotes the total concentration of metal (M) in the aqueous phase.

Therefore, the distribution ratio, D , is expressed by Eq. (8) from Eqs. (2) and (6).

$$D = \frac{[\overline{\text{MCl}_3}]}{C_{\text{Mw}}} = K_D \alpha_3 \quad (8)$$

The logarithm of Eq. (8) gives

$$\log D = \log \alpha_3 + \log K_D \quad (9)$$

The experimental results of the extraction of gallium(III) are plotted according to Eq. (9) as shown in **Fig. 1**. In this calculation, the following values^{4,12)} were used as the stability constants of the chloro complex of gallium(III): $\beta_1 = 2.29 \times 10^{-1}$, $\beta_2 = 6.60 \times 10^{-3}$, $\beta_3 = 1.26 \times 10^{-4}$, $\beta_4 = 1.82 \times 10^{-7}$, $\beta_5 = 7.94 \times 10^1$.

Obviously, the plotted points lie on a straight line of slope 1 as expected from Eq. (9). From the intercept of this straight line with the ordinate, the value of the distribution coefficient, K_D , was evaluated as $K_D = 1.58$.

On the other hand, thallium(III) was extracted by the diluent only in a negligibly small amount.

2.2 Extraction equilibria of gallium(III) and thallium(III) with the extractant

In general, trivalent metals such as gallium(III) and

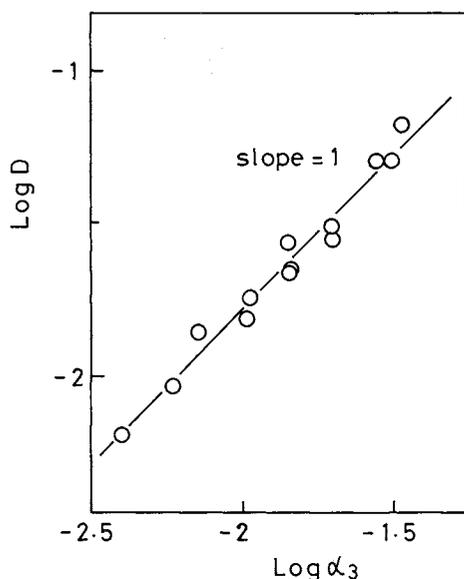


Fig. 1. Relation between $\log D$ and $\log \alpha_3$ in the extraction of gallium(III) ($C_{B0} = 0$).

thallium(III) are considered to be extracted by neutral solvating extractants from hydrochloric acid according to the following stoichiometric relation accompanied by ion-pair formation:⁹⁾



where \bar{S} denotes the extractant in the organic phase. The equilibrium constant, $K_{e,M}$, for the above reaction is given by Eq. (11).

$$K_{e,M} = \frac{[\overline{H_jMCl_{(3+j)}S_n}]}{[MCl_3][H^+]^j[Cl^-]^j[\bar{S}]^n} \quad (11)$$

Since the initial concentration of the extractant is much higher than the metal concentration under the present experimental conditions, the concentration of the unreacted extractant, $[\bar{S}]$, may be approximated by its initial concentration, C_{B0} . Further, since the hydrogen ion concentration is nearly equal to the chloride ion concentration as mentioned earlier, the distribution ratio is ultimately described by Eq. (12) from Eqs. (6) and (11).

$$\log D = \log(\alpha_3[Cl^-]^{2j}) + n \log C_{B0} + \log K_{e,M} \quad (12)$$

In the low concentration region of chloride ion, α_3 for gallium(III) may be approximated as follows:

$$\alpha_3 \approx \beta_3[Cl^-]^3 \quad (13)$$

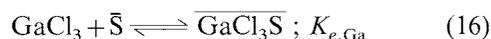
In this region, the logarithm of the distribution ratio is approximately expressed by Eq. (14) from Eqs. (12) and (13).

$$\log D \approx (2j+3) \log[Cl^-] + a \quad (14)$$

where

$$a = n \cdot \log C_{B0} + \log(\beta_3 K_{e,M}) \quad (15)$$

Figure 2 shows the effects of hydrochloric acid concentration on the distribution ratio of gallium(III) for various initial concentrations of DHS, C_{B0} . As is evident from this figure, the distribution ratio, D , increases with increasing hydrochloric acid concentration. In the low concentration region of hydrochloric acid, the plotted points give straight lines of slope 3. This suggests that $j=0$ in Eq. (14). In addition, the values of a , defined by Eq. (15), were obtained for each C_{B0} and plotted against $\log C_{B0}$ to evaluate the number of the molecules of the solvated extractant in the extracted complex, n , and the equilibrium constant, $K_{e,M}$, as shown in Fig. 3. Evidently, the points plotted in Fig. 3 lie on a straight line of slope 1, which suggests $n=1$ in Eq. (15); that is, gallium(III) is coordinately solvated by one molecule of DHS in the organic phase. Therefore, the stoichiometric relation of this extraction reaction is expressed as follows:



The extraction equilibrium constant, $K_{e,Ga}$, was evaluated as $K_{e,Ga} = 1.9 \times 10^2 \text{ dm}^3/\text{mol}$. The solid lines in Fig. 2 are the calculated results according to Eqs. (7) and (12) using the evaluated value of $K_{e,Ga}$. The calculated curves are in good agreement with the experimental results. Further, the molar ratio of gallium(III) to chloride ions in the organic phase was measured after stripping by 0.1 mol/dm^3 nitric acid to make sure the constituent of the extracted species in the organic phase. It was found to be about 1 : 3 over the whole concentration regions of hydrochloric acid. The extracted species, $GaCl_3S$, is the same with that observed in the extraction with TOPO or DHSO as mentioned earlier. However, compared with the extractants containing oxygen as a donor atom like TBP, TOPO and DHSO, the distribution ratio in the extraction with DHS is rather low against the expectation mentioned earlier.

Figure 4 shows the effects of the hydrochloric acid concentration on the distribution ratio of thallium(III) for various concentrations of DHS, C_{B0} . As shown in Fig. 4, the distribution ratio, D , decreases with increasing acid concentration, and exhibits minimum at the hydrochloric acid concentration of about 3 mol/dm^3 . Beyond this acidity, it increases with further increase in acid concentration.

Further rearrangement of Eq. (12) gives Eq. (17).

$$\log(D/\alpha_3) = 2j \cdot \log[Cl^-] + a' \quad (17)$$

where

$$a' = n \cdot \log C_{B0} + \log K_{e,M} \quad (18)$$

α_3 was calculated using the stability constants³⁾ of thallium(III)-chloro complexes as follows: $\beta_1 = 1.26 \times 10^8$, $\beta_2 = 3.98 \times 10^{13}$, $\beta_3 = 6.31 \times 10^{15}$, $\beta_4 = 1.0 \times$

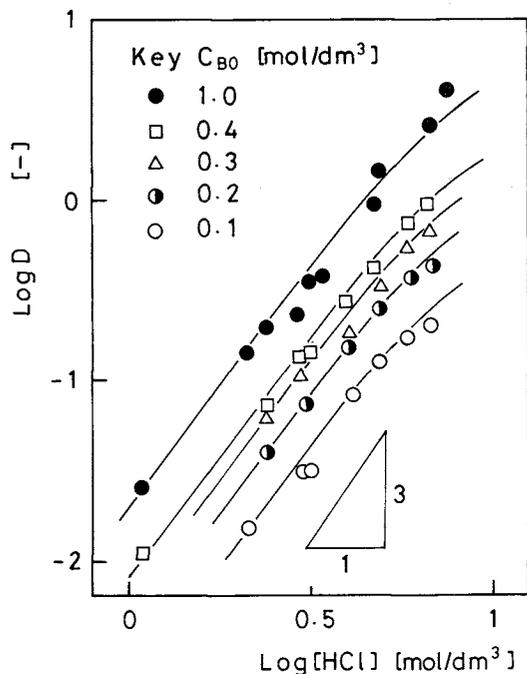


Fig. 2. Effects of hydrochloric acid concentration and C_{B0} on the distribution ratio of gallium(III).

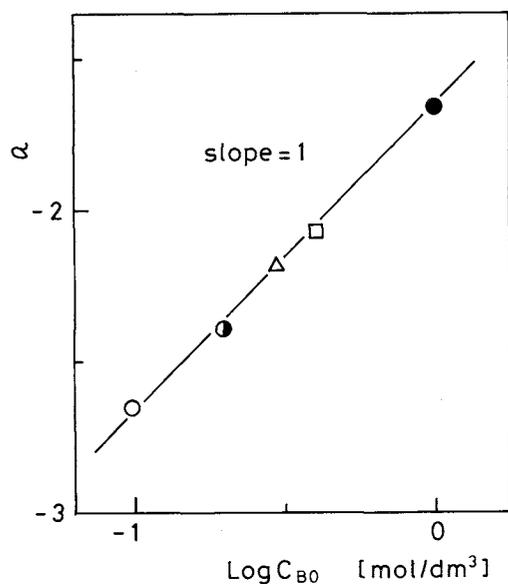


Fig. 3. Relation between α and $\log C_{B0}$ in the extraction of gallium(III).

10^{18} , $\beta_5 = 1.26 \times 10^{20}$, $\beta_6 = 7.94 \times 10^{21}$.

Figure 5 shows the plots of the experimental results according to Eq. (17). In the low concentration region of hydrochloric acid, the plotted points lie on straight lines with a slope of 2 for various concentrations of DHS. This suggests that $j=1$ from Eq. (17), that is, thallium(III) is extracted as the species, HTlCl_4S_n , from Eq. (10). On the other hand, in the high concentration of hydrochloric acid, the plotted points lie on straight lines with a slope of 4, which suggests that $j=2$, that is, thallium(III) is extracted as the

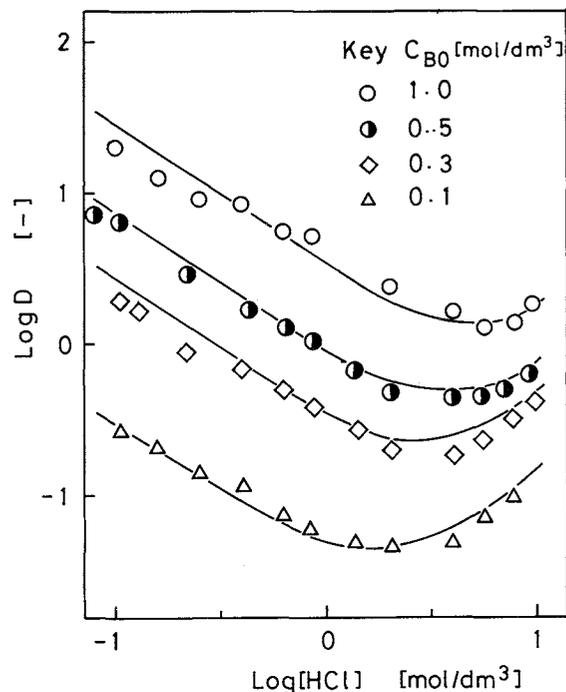


Fig. 4. Effects of hydrochloric acid concentration and C_{B0} on the distribution ratio of thallium(III).

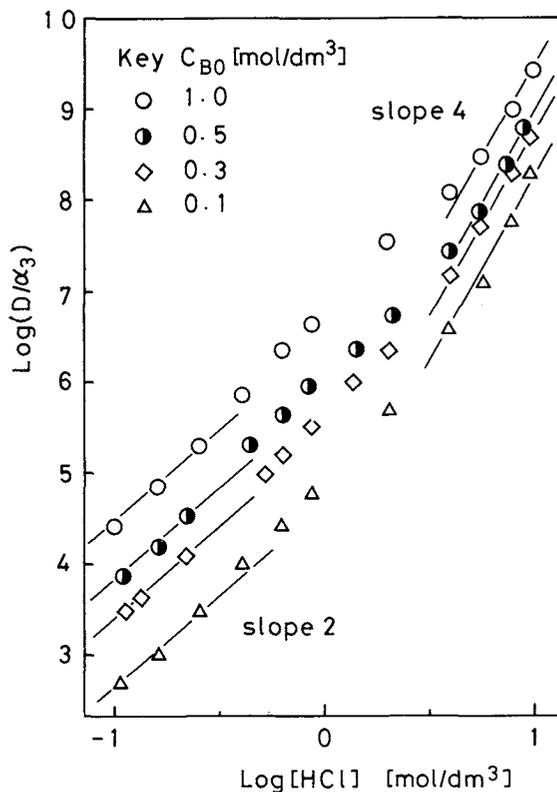
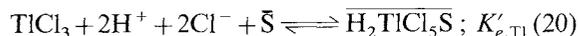


Fig. 5. Relation between $\log(D/\alpha_3)$ and $\log[HCl]$ in the extraction of thallium(III).

species $\text{H}_2\text{TlCl}_5\text{S}_n$. In order to make sure the constituent of the extracted species, the mole ratio of thallium(III) to chloride ions in the organic phase were measured after stripping by 0.1 mol/dm³ aque-

ous EDTA solution. It was found to be about 1 : 4 and 1 : 5 in the low and high concentration regions of hydrochloric acid, respectively.

The values of a' defined by Eq. (18) were evaluated for each C_{B0} , in the both concentration regions of hydrochloric acid. In Fig. 6, the values of a' are plotted against $\log C_{B0}$. Obviously, the plotted points lie on straight lines of slopes 2 and 1, for the low and high concentration regions of hydrochloric acid, respectively. Therefore, the stoichiometric relations of the extraction reactions of thallium(III) from hydrochloric acid are described by Eqs. (19) and (20) in the low and high concentration regions of hydrochloric acid, respectively.



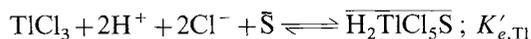
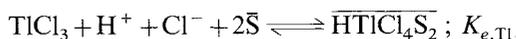
The extraction equilibrium constants for the reactions of Eqs. (19) and (20) were evaluated as $K_{e,\text{Tl}} = 4.0 \times 10^6 (\text{dm}^3/\text{mol})^4$ and $K'_{e,\text{Tl}} = 1.6 \times 10^5 (\text{dm}^3/\text{mol})^5$, respectively.

The solid lines in Fig. 4 are the calculated results according to Eqs. (11), (19) and (20) using the values evaluated above. The calculated results are in good agreement with the experimental results.

One of the extracted species, $\overline{\text{HTlCl}_4\text{S}_2}$, is the same with that observed in the extraction with DASO by Reddy *et al.*⁸⁾ as mentioned earlier. As to the distribution ratio, DHS provides higher distribution ratio than DASO, the extractant containing oxygen as a donor atom, in the low concentration region of hydrochloric acid while DASO provides higher distribution ratio in the high concentration region of hydrochloric acid.

Conclusion

Extraction equilibria of gallium(III) and thallium(III) with dihexyl sulfide in 1,2-dichloroethane from hydrochloric acid were studied at 303 K. Thallium(III) was not extracted with pure 1,2-dichloroethane but gallium(III) was extracted by the physical partition of GaCl_3 . It was clarified that gallium(III) and thallium(III) are extracted with the extractant according to the following extraction reactions:



The equilibrium constants of these reactions are evaluated as follows: $K_{e,\text{Ga}} = 1.9 \times 10^2 \text{ dm}^3/\text{mol}$, $K_{e,\text{Tl}} = 4.0 \times 10^6 (\text{dm}^3/\text{mol})^4$ and $K'_{e,\text{Tl}} = 1.6 \times 10^5 (\text{dm}^3/\text{mol})^5$.

Compared with the extractants containing oxygen

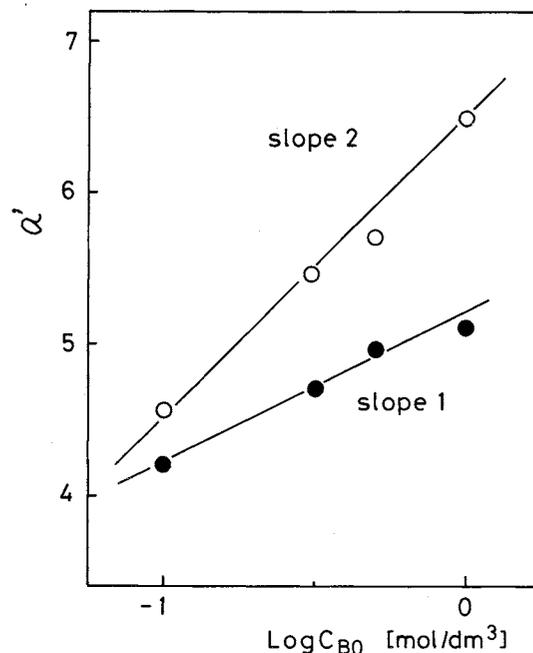


Fig. 6. Relation between a' and $\log C_{B0}$ in the extraction of thallium(III). Keys: Open, low-concentration region of hydrochloric acid; Filled, high-concentration region of hydrochloric acid.

as a donor atom, DHS did not always provide higher distribution ratio in the extraction of thallium(III) and provided rather lower distribution ratio in the extraction of gallium(III).

Acknowledgment

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Nomenclature

C_{B0}	= initial concentration of dihexyl sulfide in organic phase	[mol/dm ³]
C_{Mw}	= concentration of metal (M) in aqueous phase	[mol/dm ³]
D	= distribution ratio	[—]
K_D	= partition constant of metal (MCl_3) into organic phase defined by Eq. (2)	[—]
$K_{e,M}$	= equilibrium constant of metal species, M, defined by Eq. (11)	[(dm ³ /mol) ^{2j+n}]
j	= stoichiometric coefficient defined by Eq. (10)	[—]
n	= stoichiometric coefficient defined by Eq. (10)	[—]
α_3	= fraction of chloro complex, MCl_3	[—]
β_i	= stability constant of i -th chloro complex	[(dm ³ /mol) ⁱ]

<Superscript>

— = organic phase

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EFFECTS OF COUPLING METHOD AND LIGAND CONCENTRATION ON ADSORPTION EQUILIBRIUM IN IMMUNO-AFFINITY CHROMATOGRAPHY

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Key Words: Biochemical Engineering, Purification, Adsorption, Affinity Chromatography, Immunoaffinity

The effects of ligand concentration and coupling method on the adsorption equilibrium in immuno-affinity chromatography were studied by use of polyclonal anti-BSA antibody and F_{ab} fragments. Immobilized IgG and F_{ab} fragments showed similar adsorption behavior, and the adsorption equilibrium was not affected by the coupling method or the concentration of immobilized ligands. However, the binding ratio, defined as the ratio of mole antigen adsorbed to mole binding site, depended on the coupling method and decreased with increasing ligand concentration.

Introduction

Immuno-affinity chromatography, which utilizes the biological interaction between antigen and antibody, is expected to have high potential in purification of biologically active materials, because this interaction is highly specific and strong and a specific antibody against a biological material can generally be raised by immunization. A knowledge of the behavior of immobilized antibodies against antigens is essential for effective application of immuno-affinity chromatography to purification.

In the previous work⁴⁾ the effects of pH, ionic strength and anion species on the adsorption equilibrium were studied. From the engineering viewpoint, the effectiveness of utilization of antibodies for adsorption and the adsorption capacity of the immobilized antibodies affect the economic feasibility of immuno-affinity chromatography. Therefore, in the present work the effects of immobilization method and antibody concentration on the molar ratio of

adsorbed antigen to immobilized binding-sites on support beads were studied by use of bovine serum albumin (BSA)-anti-BSA.

1. Experimental

1.1 Materials

Bovine serum albumin (BSA, Cohn fraction V 96-99% BSA, molecular weight 66,000, Nakarai Chemicals Ltd.), papain (25 units/mg, from papaya latex, Sigma Chem. Co.), protein-A (from *Staphylococcus aureus*, Pierce Chem. Co.) and FITC-IgG (Cappel Lab. Inc.) were used. As support beads activated CNBr- and CH-Sepharose 4B (made of agarose, diameter 60-140 μm , Pharmacia Fine Chemicals) and Formyl Cellulofine (made of cellulose, diameter 105-210 μm , Chisso Co., Ltd.) were used. The chemicals used were of reagent grade.

1) Anti-BSA antibody The antisera against BSA used were raised in rabbits. A mixture of equal volumes of a BSA solution (1.5 mg in 1 cm^3 saline) and complete Freund's adjuvant (1 cm^3 each) were injected into rabbits. After one month booster injections were given with 1.5 mg BSA dissolved in

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