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Liquid–liquid extraction of divalent transition metal ions with a novel bis-β-ketoester extraction reagent

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ABSTRACT

Solvent extraction is a very effective method for the separation of metal ions. N,N′-bis(2-hydroxyphenylmethyl)-N,N′-bis(2-pyridylmethyl)-1,2-ethanediamine derivatives have been researched for solvent extraction of metal ions. In this study.

We synthesized a bis-β-ketoester ligand and evaluated its selectivity in extracting divalent transition metal ions. The ligand, hexane-1,6-diyl bis (4,4,4-trifluoro-3-oxobutanoate) (H_2hdfob or H_2L) was synthesized in one step by transesterification of ethyl 4,4,4-trifluoroacetoacetate with 1,6-hexanediol. The multidentate ligand H_2hdfob successfully extracted divalent transition metal ions into its organic phase.

The relationship between $\log D$, which is a distribution ratio (D), and pH or $\log[H_2L]_o$ exhibited linear relationships with slopes of approximately $+2$ and $+1$, respectively. Based on these results, we proposed a mechanism of extraction with H_2hdfob. Extraction with tetradentate H_2hdfob provides a new method for enhancing selectivity of divalent metal ions, in comparison to other bidentate ligands.

1. Introduction

There have been reported many methods to collect and separate the metal ions such as ion-exchange techniques, solvent extraction methods and more.

Liquid–liquid (or solvent–solvent) extraction techniques are relatively easier to carry out and provide a good selectivity. The improvements of extractability have been reported [1,2]. For effective extraction of metal ions from the aqueous phase to an organic phase, the extractability of the metal ions is frequently enhanced by complexation with chelating ligands such as phosphates, β-diketones, or oximes [3–5].

Steric and electronic effects, and ion size recognition of the ligands are used to improve the selectivity of extractant [6,7].

Synergistic extraction, i.e., the use of a neutral ligand with the main extractant, is employed to improve the extractability in the solvent extraction system [6].

This bis-β-ketoester compound H_2hdfob was synthesized by a transesterification reaction using trifluoromethyl acetoacetate, and 1,6-hexanediol. Acid dissociation constant was regulated by trifluoromethyl group of the β-ketoester.

pK_a value of H_2hdfob was controlled by the electronic influence of the terminal functional groups, and the coordination space was regulated by the alkyl chain. In this study the synthesis of a bis-β-ketoester compound serving as a new ligand for the extraction of divalent metal ions was researched.

2. Material and methods

Ethyl 4,4,4-trifluoroacetoacetate, 1,6-hexanediol, transition metal salts, and other chemicals used in the experiments were purchased from Tokyo chemical industry Co., Ltd. The measurement of pH was conducted using a HM-60 pH meter (TOA-DKK Corporation, Japan) equipped with a glass electrode, after calibrating with two standards. Matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI TOF-MS) was performed on an Autoflex 3 smart beam (Bruker Daltnics, Germany).

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were used by employing JEOL-ECX400P (400 MHz) (JEOL, Japan), and inductively coupled argon plasma atomic emission spectroscopy (ICP-AES) was used by employing SPS1700, R, V, VR (Seiko Instruments Inc., Japan).

2.1. Synthesis of H_2hdfob

Derivatives of H_2hdfob were synthesized by transesterification according to the scheme shown in Fig. 1. Ethyl 4,4,4-trifluoroacetoacetate (30.0 g, 163 mmol) was heated with 1,6-hexanediol (10.6 g, 89.7 mmol) at 368 K for 20 h. The mixture was distilled under vacuum (4 mmHg) at 415 K to yield the bis-β-ketoester,

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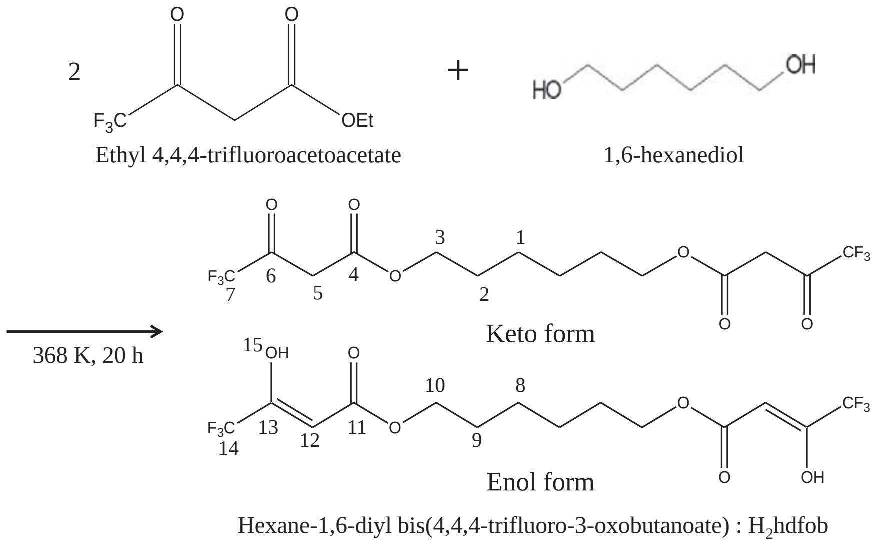

Fig. 1. Synthesis of hexane-1,6-diyl bis(4,4,4-trifluoro-3-oxobutanoate).

Table 1
^{1}H and ^{13}C NMR details of H_2hdfob.

^{1}H NMR (400 MHz, $CDCl_3$)	δ 1.4–1.5 (m, 4H (1)(8)), 1.6–1.7(m, 4H (2)(9)), 3.75(s, 0.5H (5)), 4.22(t, J=6.0, 3H (10)), 4.28(t, J=6.0, 1 (3)), 5.64(s, 0.75H (12)), 11.8(br.s, 0.75H (15))
^{13}C –NMR (100 MHz, $CDCl_3$)	δ 25.2, 28.2, 36.6, 37.7, 65.4, 65.8, 92.14, 92.5, 92.8, 93.1, 117.9, 119.9, 120.8, 121.0, 122.6, 123.6, 123.9, 126.4, 159.1, 159.5, 159.9, 160.2, 171.5

hexane-1,6-diyl bis(4,4,4-trifluoro-3-oxobutanoate) (H_2hdfob, 43%). In this experiment, it was added in excess of 1,6-hexanediol to react completely with ethyl 4,4,4-trifluoroacetoacetate. The compound was characterized using IR, ^{1}H NMR and ^{13}C NMR (Table 1).

2.2. *Determination of log K_D and pK_a by liquid–liquid titration method [8,9]*

The organic phase (solv. $CHCl_3$) containing 0.01 mol dm^{-3} H_2hdfob and aqueous (containing 0.1 mol dm^{-3} sodium perchlorate) phases were mixed in a separatory funnel, and shaken for 5 min. Then, it was titrated using 17.95 mmol sodium hydroxide solution, and pH of aqueous phase was determined.

2.3. *Extraction of divalent transition metal ions*

In a 50 cm^3 centrifuge tube, 20 cm^3 of an organic phase (solv. $CHCl_3$) containing 0.01 mol dm^{-3} H_2hdfob was equilibrated with 20 cm^3 of an aqueous phase containing 0.1 mol dm^{-3} sodium perchlorate, 1.0×10^{-2} mol dm^{-3} acetate buffer or Good's Buffer (pH 3–7) and 1.0×10^{-4} mol dm^{-3} transition metal ion (Co^{2+}, Ni^{2+}, Cu^{2+}, or Zn^{2+}). After shaking for 20 h at 298 ± 1.0K, the mixture reached an equilibrium. The two phases were separated by centrifugation, and then the pH and metal concentration of the aqueous phase were measured. The organic phase (solv. $CHCl_3$) was back-extracted with HCl solution (1 mol dm^{-3}). Concentration of metal ions in the aqueous phase and in back extracted HCl solution was measured by inductively coupled argon plasma atomic emission spectroscopy (ICP-AES). The pH value of the aqueous phase was measured by a pH meter.

2.4. *Analysis by MALDI-TOF-MS*

Solution of methanol containing H_2hdfob (0.01 mol dm^{-3}) was added to an aqueous solution of the metal acetate (0.2 mol dm^{-3}), then each metal was complexed with the ligand – H_2hdfob. A solution of sodium hydroxide (0.01 mol dm^{-3}) was slowly added to this mixture, and the precipitated metal complex was filtered and dried. After recrystallization, these complexes were analyzed by MALDI-TOF-MS in the negative mode using 1,1,4,4-Tetraphenyl-1,3-butadiene as the matrix.

3. Results and discussion

3.1. *Characterization of H_2hdfob*

An analysis of the IR spectrum of H_2hdfob shows the presence of hydroxyl and carbonyl groups, as observed from the absorbance at 3428 cm^{-1} and 1713 cm^{-1}, respectively. The details of the ^{1}H NMR and ^{13}C NMR spectra of H_2hdfob are listed in Table 1. Both the keto and the enol forms of H_2hdfob are observed. The resonances at δ 3.75 and 4.28 in the ^{1}H NMR can be assigned to the protons on carbons 3 and 5 of the keto form, whereas the protons observed at δ 4.22, 5.64 and 11.8 represent the protons on carbons 10 and 12, and the acidic enol proton 15 of the enol form (Fig. 1). It is evident from the proton spectrum, that in the chloroform H_2hdfob predominantly exists in the enol form. All the other proton and carbon resonances are in agreement with the keto–enol structures described in Fig. 1. Thus, the structure of the acidic bis-β-ketoester ligand is confirmed.

3.2. *Determination of log K_D and pK_a*

When the reaction is in equilibrium between two phases, then the distribution constant K_D and acid dissociation constant K_a can be described as follows:

$$(K_D - 1)/K_a = (a - b)/b[H^+] \qquad (1)$$

where "a" is the concentration of acidic compounds dissolved into an organic phase, and "b" is the concentration of sodium hydroxide.

Eq. (1) exhibits the changes into formulas as represented by the following Eq. (2):

$$\log b = \log\{1/(K_D+1)[H^+]/K_a+1\} \qquad (2)$$

Fig. 2 shows the relationships between log b and $[H^+]$ of the aqueous phase. This plots were made by curve-fitting, and from which K_D and K_a were obtained to give log $K_D=4.34$ and $pK_a=5.04$ ($R^2=0.995$).

3.3. *Extraction of transition metal ions with H_2hdfob*

The extraction experiment was carried out by the synthesis of H_2hdfob which was introduced into two fluoro methyl group contained in the extractant. The extraction reagent, H_2hdfob, has a large acid dissociation constant and a distribution constant. It was employed for the extraction of the four transition metals.

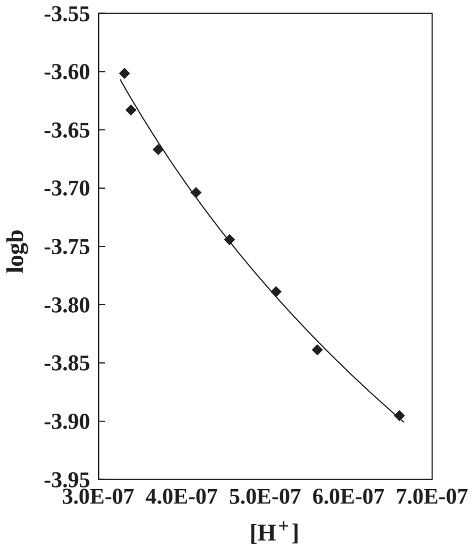

Fig. 2. Log b vs $[H^+]$ plots H_2L:0.01 mol dm^{-3}; b: concentration of $[OH^-]$.

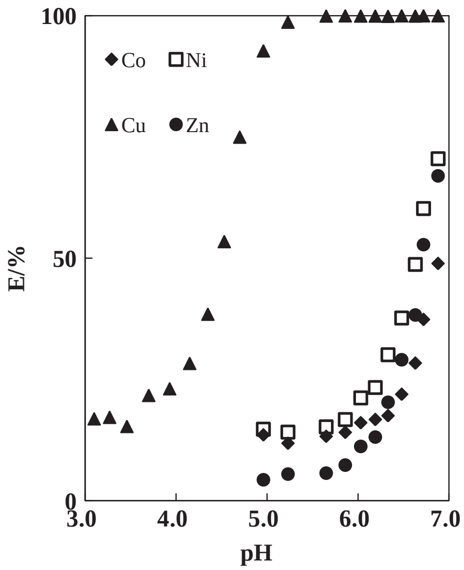

Fig. 3. Extraction ratio (E %) of transition metal ions with H_2hdfob; divalent transition metal ions (M^{2+}):1.0 × 10^{-4} mol dm^{-3}; H_2L:0.01 mol dm^{-3}; ClO_4^-:0.1 mol dm^{-3}.

The extraction ratio (E %) of the transition metal ions with H_2hdfob is shown in Fig. 3as a function of pH of the aqueous phase equilibrated with an organic phase.

Table 2
pH at which 50% of metal ions are extracted.

	H_2hdfob	TTA [10]	HQ [10]
Co^{2+}	6.74	4.10	3.21
Ni^{2+}	6.46	5.00	2.38
Cu^{2+}	4.47	1.38	1.51
Zn^{2+}	6.58	–	3.30

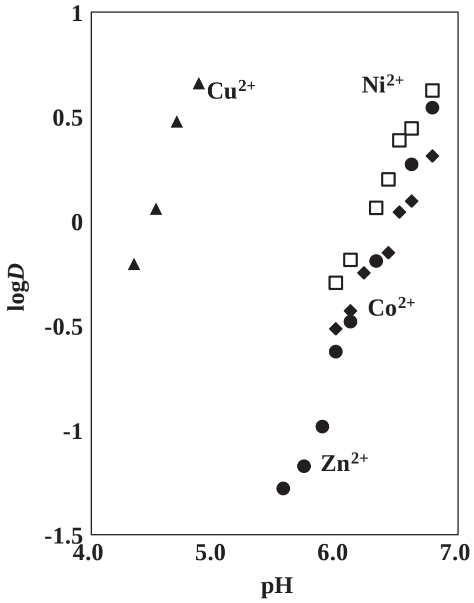

Fig. 4. Log D vs pH plots: divalent transition metal ions (M^{2+}):1.0 × 10^{-4} mol dm^{-3}; H_2L:0.01 mol dm^{-3} (Cu^{2+}), 0.03 mol dm^{-3} (Co^{2+}, Ni^{2+}, Zn^{2+}); ClO_4^-:0.1 mol dm^{-3}; slopes: $Co^{2+}=1.0$, $Ni^{2+}=1.2$, $Cu^{2+}=1.7$, and $Zn^{2+}=1.7$.

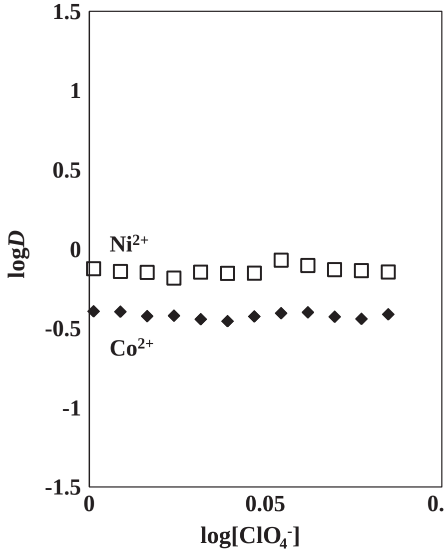

Fig. 5. Log D vs log$[ClO_4^-]$ plots: divalent transition metal ions (M^{2+}):1.0 × 10^{-4} mol dm^{-3}; H_2L:0.01 mol dm^{-3}; pH:4.5 (Cu^{2+}), and 6.5 (Co^{2+}. Ni^{2+}, Zn^{2+}).

Fig. 3 suggests that H_2hdfob has high a selectivity to Cu^{2+}, and it shows same extraction reactions for Co^{2+}, Ni^{2+}, and Zn^{2+}. The maximum value of extraction for Cu^{2+} is almost 100% (Fig. 3).

Table 2 shows the pH when 50% of the metal ions were extracted into the organic phase with each extraction reagent. From the data in Table 2, it can be observed that the selectivity of Cu^{2+} using H_2hdfob is higher than that of the other ligands such as 8-quinolinol (HQ) and thenoyltrifluoroacetone (TTA) [10].

When the transition metal M^{2+} is extracted with H_2L, the overall extraction equilibrium and the extraction constant (K_{ex}) of transition metals can be described as follows:

$$M^{2+} + H_2L_o \rightleftarrows ML_o + 2H^+ \tag{3}$$

$$K_{ex} = [ML]_o[H^+]^2/[M^{2+}][H_2L]_o \tag{4}$$

$$\log K_{ex} = \log D - 2pH - \log[H_2L]_o \tag{5}$$

where the subscripts "o" denote the species in the organic phase, D is the distribution ratio of the metal ions [11–18]. In Fig. 4, when H_2hdfob was used as the extractant, the relationship between $\log D$ and pH was linear with a slope of approximately $+2$, whereas the slopes for Co^{2+} and Ni^{2+} were approximately $+1$.

This result indicates that 2 protons are involved in the complexation reaction of Cu^{2+} or Zn^{2+} with H_2hdfob, whereas, in the reaction between Co^{2+} or Ni^{2+} with H_2hdfob, only one proton is involved with the probable involvement of a counter anion (in this case ClO_4^-). However, the plot of $\log D$ for Co^{2+} or Ni^{2+} shows no dependence on $[ClO_4^-]$ (Fig. 5). The involvement of ClO_4^- as a counter ion in the reaction between Co^{2+} or Ni^{2+} and H_2hdfob requires a slope of $+1$ between $\log D$ and $\log[ClO_4^-]$. The absence of such a dependence, rules out the involvement of ClO_4^- ion in the extracted species. Thus, it is likely that the $M(OH)^+$ form of the transition metals Co^{2+} and Ni^{2+} undergoes complexation with H_2hdfob.

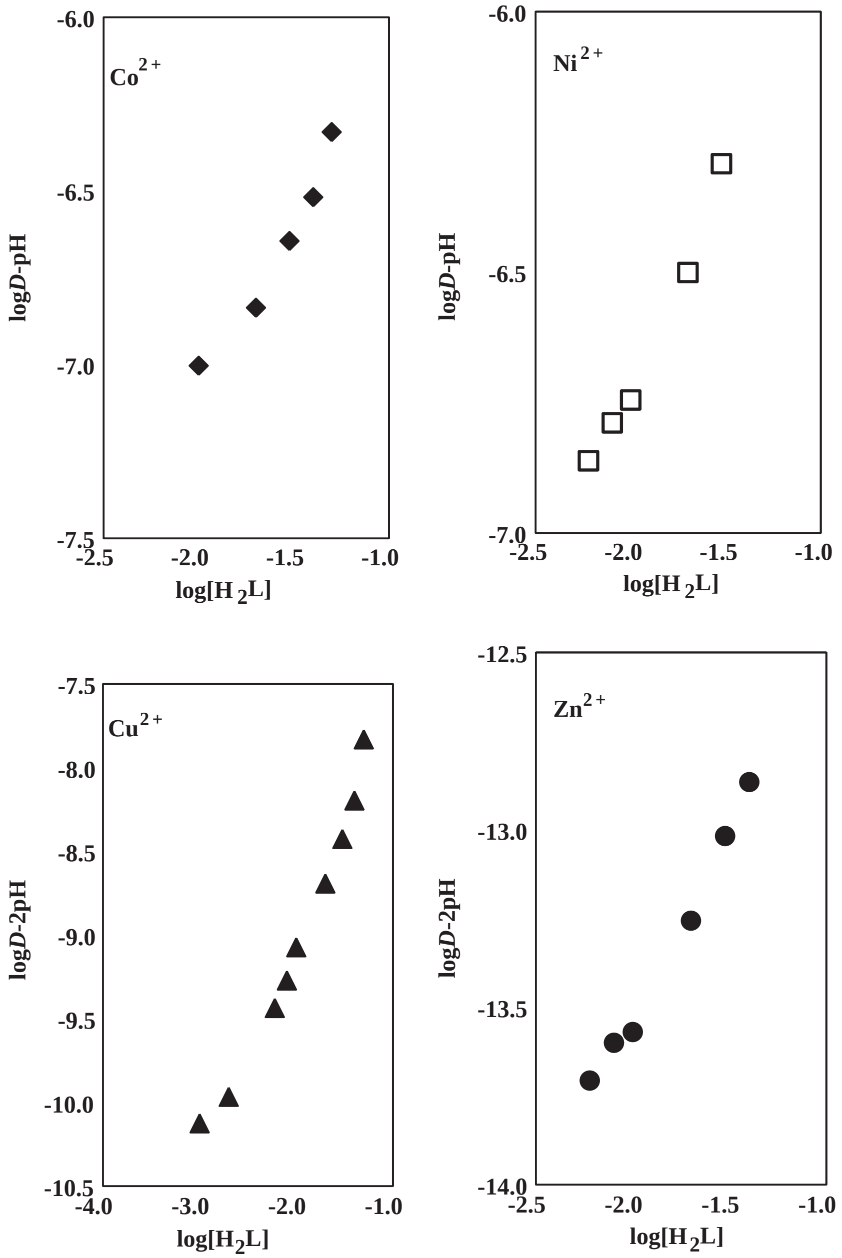

Fig. 6. Log D vs $\log[H_2L]_o$ plots: divalent transition metal ions (M^{2+}):1.0×10^{-4} mol dm^{-3};ClO_4^-:0.1 mol dm^{-3}; pH:4.5 (Cu^{2+}), 6.5 (Co^{2+}. Ni^{2+}, and Zn^{2+}) ;slopes: Co^{2+}=0.93, Ni^{2+}=0.81, Cu^{2+}=0.97, 2.1, and Zn^{2+}=1.0.

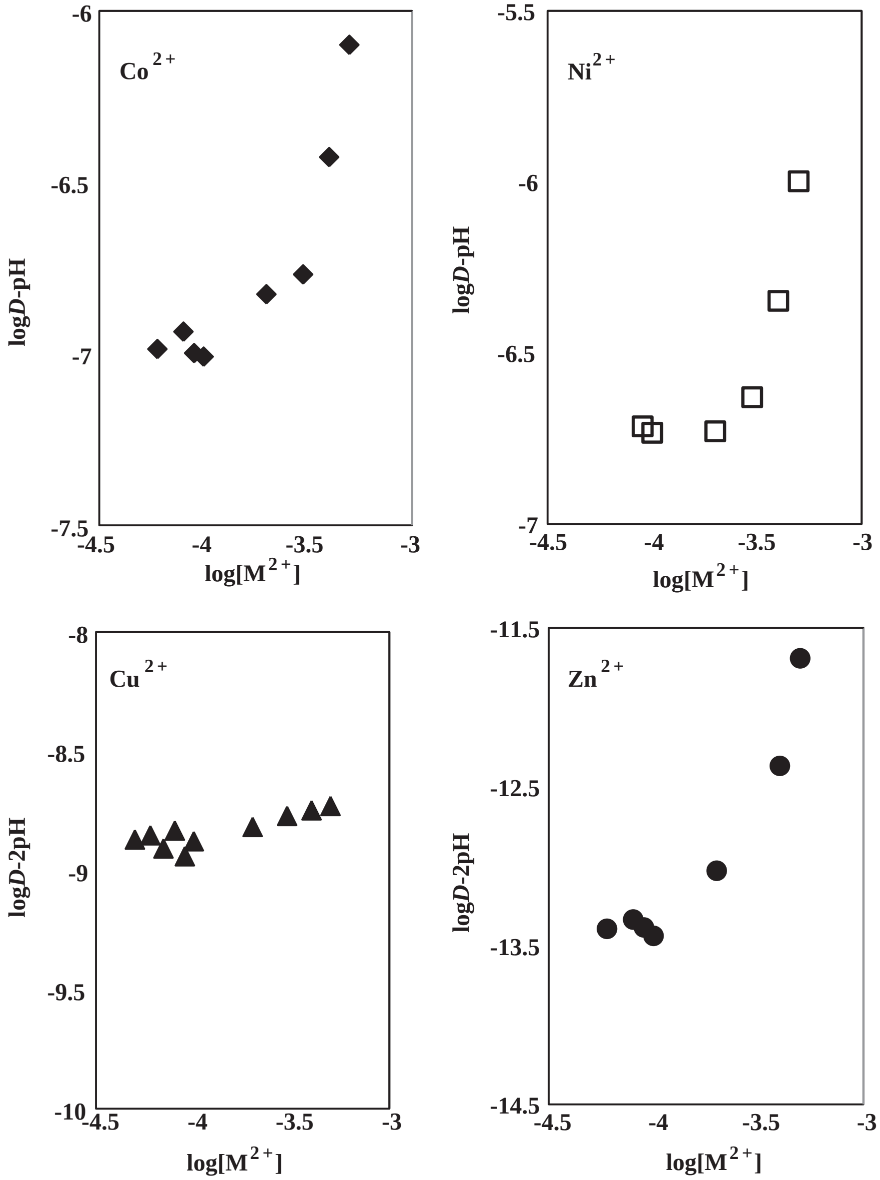

Fig. 7. Log D vs log$[M^{2+}]$ plots: H_2L:0.01 mol dm^{-3}; ClO_4^-:0.1 mol dm^{-3}; pH:4.5 (Cu^{2+}), and 6.5 (Co^{2+}. Ni^{2+}, Zn^{2+}).

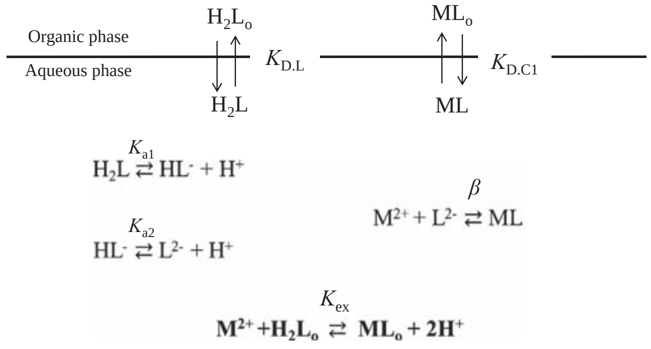

Fig. 8. Extraction mechanism for Cu^{2+} or Zn^{2+} with H_2hdfob: M^{2+} (Cu, Zn):1.0 × 10^{-4} mol dm^{-3}; H_2L(H_2hdfob):0.01 mol dm^{-3}; ClO_4^-:0.1 mol dm^{-3}.

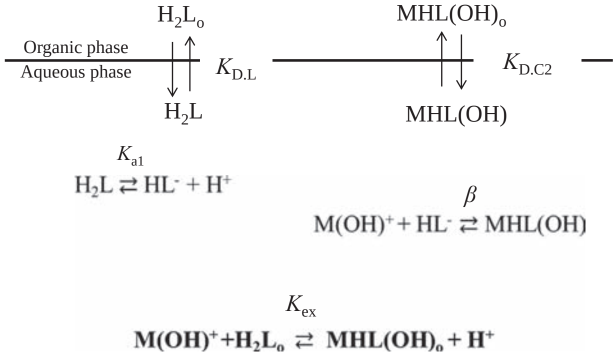

Fig. 9. Extraction mechanism for Co^{2+} or Ni^{2+} with H_2hdfob: M^{2+} (Co, Ni): 1.0 × 10^{-4} mol dm^{-3}; H_2L(H_2hdfob):0.01 mol dm^{-3}; ClO_4^-:0.1 mol dm^{-3}.

Next, the relationship between log D and the concentration of the ligand was evaluated. The log D vs log$[H_2L]$ plots for Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} are shown in Fig. 6. While, the slopes for Co^{2+}, Ni^{2+}, and Zn^{2+} are approximately +1, the slope for Cu^{2+} is approximately +1 or +2, depending on the concentration of H_2hdfob. These results indicate that in this extraction process, all the metal ions produce mononuclear complexes with H_2hdfob. With Cu^{2+}, at a higher concentration of the ligand, more complex reactions have been observed.

Further evaluation of the dependence of log D on log[M^{2+}] shows that log D varies significantly at higher concentrations of Co^{2+}, Ni^{2+}, and Zn^{2+}. Under these extraction conditions all metal ions become mononuclear complexes (Fig. 7). These results confirm the validity of Eqs. (3–5).

3.4. *Extraction mechanism of divalent transition metal ions by H_2hdfob*

When concentration of metal ion was 1.0×10^{-4} mol dm^{-3} and ligand was 0.01 mol dm^{-3}, extraction mechanism of divalent transition metal ions using H_2hdfob appeared as shown in Figs. 8 and 9. In the case of Cu^{2+} or Zn^{2+} (Fig. 8), the divalent metal with ligand H_2hdofb leads to the formation of a 1:1 metal–ligand complex. The dissociation of the acidic protons from the H_2hdfob occurs in the aqueous phase, and the resulting bis-β-ketoester dianion forms a complex with the divalent metal giving rise to a neutral complex. This neutral complex is then rapidly partitioned into the organic phases.

In the case of Co^{2+} or Ni^{2+} (Fig. 9), a monovalent metal hydroxide ion reacts with the ligand where one of the protons is dissociated. Such a complexation formed the 1:1 metal–ligand neutral complex. This neutral complex is then rapidly distributed into organic phase, quickly.

Bis pyrazolone derivatives using extraction and complex formation of metal ions had been described [7]. The length of alkyl chain have an implication for complex formation of metal ions using a bis-bidentate ligand such as H_2hdfob and bis-pyrazolone which had been reported in a previous work. In that work, the relationship between the complex form and the length of alkyl chain was shown. The length of the alkyl chain (hexane in H_2hdfob) acts as a link between the two bidentate acetoacetate groups as same as bis pyrazolone.

Table 3
Calculated and measured m/z values of the metal–ligand complexes.

	Measurement m/z	Calculated m/z					
		M^{2+}:L^{2+}:H_2O			$M(OH)^+$:HL:H_2O		
		1:1:0	1:1:1	1:1:2	1:1:0	1:1:1	1:1:2
Co^{2+}	485.3	451.0	469.0	487.0	469.0	487.0	505.0
Ni^{2+}	490.2	450.0	468.0	486.0	468.0	486.0	504.0
Cu^{2+}	454.1	455.0	473.0	491.0	473.0	491.0	509.0
Zn^{2+}	490.1	456.0	474.0	492.0	474.0	492.0	510.0

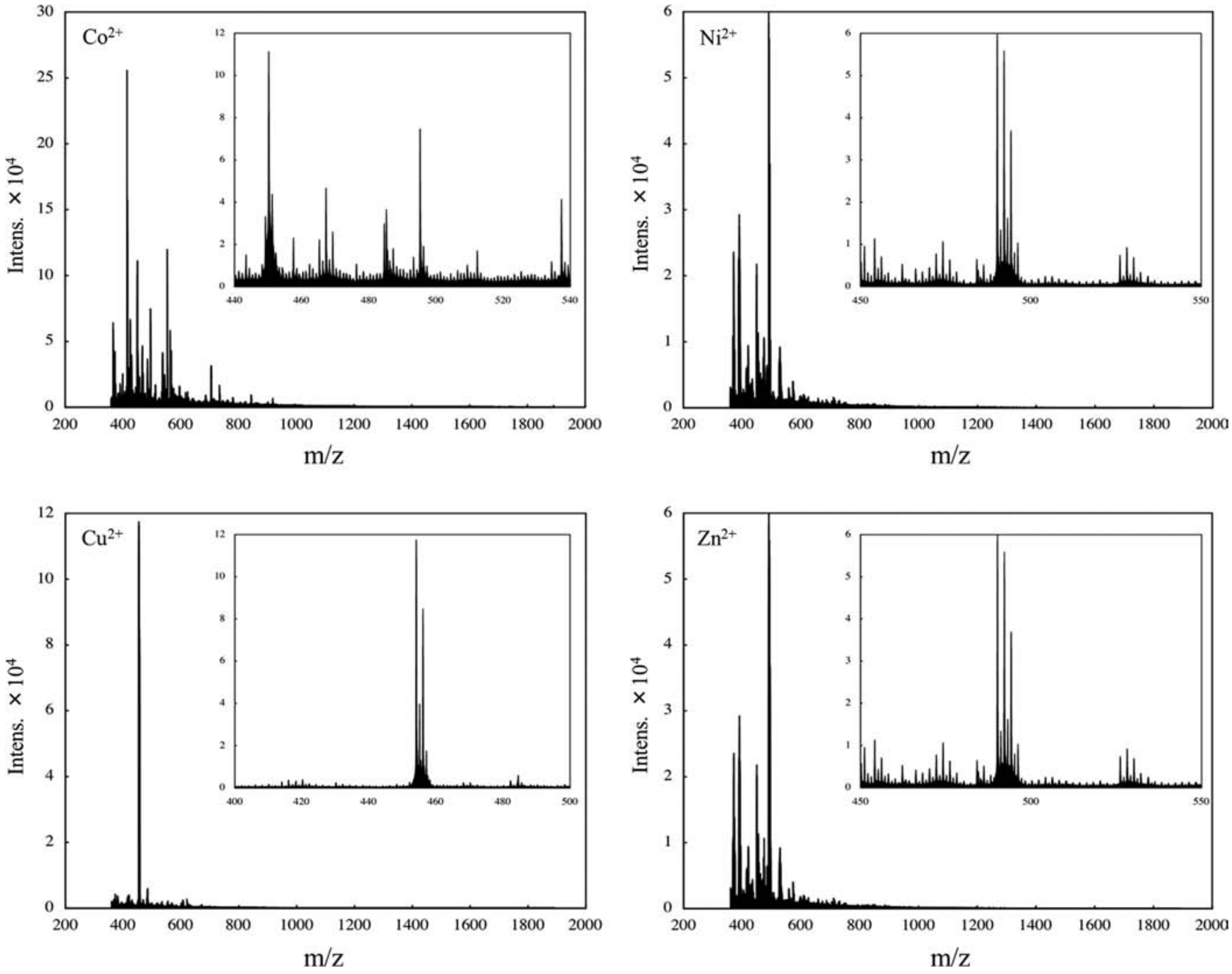

Fig. 10. MALDI-TOF-MS of metal–H_2hdfob complexes: divalent transition metal ions (M^{2+}):0.2 mol dm^{-3};H_2L:0.01 mol dm^{-3};matrix: 1,1,4,4-tetraphenyl-1,3-butadiene.

3.5. *MALDI-TOF-MS analysis of metal–H_2hdfob complexes*

The transition metals, other than zinc, formed colored complexes with H_2hdfob. While the complex H_2hdfob and Zn^{2+} is white, the colors of the complexes formed as Co^{2+}, Ni^{2+}, and Cu^{2+} are red, green and dark blue. The MALDI-TOF-MS analysis of these complex was shown in Fig. 10 and Table 3. A comparison of the observed and calculated m/z values indicates that all the complexes are 1:1 metal–ligand complexes, although they are hydrated to different levels (Table 3). And the multinuclear complexes were not produced in this state.

In the cases of Co^{2+}, Ni^{2+}, and Zn^{2+}, the complexes have two molecules of water; and this hydration prevents to distribute into organic phase. While, in case of Cu^{2+}, the complex has no molecules of water.

It is thus understood that the selectivity of Cu^{2+} using H_2hdfob was higher than that of other divalent transition metal ion (Table 2).

4. Conclusion

The synthesized ligand hexane-1,6-diyl bis(4,4,4-trifluoro-3-oxobutanoate) (H_2hdfob) has a higher selectivity for Cu^{2+} than that of the other divalent transition metal ions, i.e., Co^{2+}, Ni^{2+} and Zn^{2+} ions. In all extracted species, the metal-to-ligand ratios are 1:1. However, the nature of the complexed metal in these complexes is different. For the complexes with Cu^{2+} and Zn^{2+}, the divalent metal is involved in the complexation reaction, whereas in the case of Co^{2+} and Ni^{2+}, the metal hydroxides $M(OH)^+$ participate in the complexation reaction.

The results suggest that the formation of the neutral complexes with H_2hdfob is dependent on the concentration of the metal ions and the ligand.

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