



An extraction study of gallium, indium, and zinc with mixtures of *sec*-octylphenoxyacetic acid and primary amine N1923

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ARTICLE INFO

Article history:

Received 12 March 2011

Received in revised form 12 May 2011

Accepted 14 May 2011

Available online 23 May 2011

Keywords:

Extraction

Gallium(III)

Indium(III)

Zinc(II)

sec-Octylphenoxy acetic acid

Primary amine N1923

ABSTRACT

A synergistic extraction system consisting of *sec*-octylphenoxy acetic acid (CA12, H₂A₂) and primary amine N1923 (B) for gallium(III), indium(III), and zinc(II) has been developed from chloride medium. Synergistic and antagonistic effects are observed for the title metals at low and high CA12 concentration ratios, respectively. On the basis of the distribution ratios, the values of the separation factors are calculated and used for the discussion of the selectivities between gallium(III)/indium(III) and zinc(II). The synergistic extraction of zinc(II) with the mixtures has been investigated with the methods of slope analysis and constant mole. The synergistic adduct has been determined together with the equilibrium constant and thermodynamic constants.

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1. Introduction

Although solvent extraction has the drawback of employing considerable amounts of organic solvents, it is still one of the most important techniques for the separation of rare metals [1]. As it is well known, gallium and indium have attracted much attention because of their applications in semiconductor materials. However, there is no ore containing gallium and/or indium as major components, and a significant source is zinc refinery residue [2]. Solvent extraction has been applied to the separation of gallium and indium from the residue. Among the various systems, organophosphorus extractants are most often used [2–6]. Methyl isobutyl ketone (MIBK) [7], carboxylic acids [8,9], amines or ammonium salts [10–12], quinolines [13,14], and β -diketones [15] have also found their applications for this goal.

In order to improve the extraction efficiency and the extraction selectivity, synergistic extraction of gallium and/or indium has attracted much attention. In recent years, many synergistic extraction systems have been developed. The mutual mixtures of organophosphorus acids, neutral organophosphorus extractants, carboxylic acids, amines or ammonium salts, quinolines, dichlorophenols, and β -diketones have been reported by many authors [16–19]. For instance, Choi and Ohashi [18] have studied the large synergistic effect of 3,5-dichlorophenol (HDPC) in the extraction of

gallium with 2-methyl-8-quinolinol derivatives (HA). The extractability of gallium with HA has been remarkable enhanced upon the addition of HDPC. The compositions of gallium–HA complexes in the presence of HDPC is assigned to be Ga(DCP)₂·HDPC.

Carboxylic acids have been applied as extractants for many metals, among which *sec*-octylphenoxy acetic acid (CA12) has been recently developed by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Its applications in the extraction of gallium and/or indium have been investigated by some authors [20–22]. Zhang et al. [20] systematically investigated the extraction and separation of gallium, indium, and thallium with CA12, *sec*-nonylphenoxy acetic acid (CA100), and naphthenic acid (NA). A possible mechanism of the extraction is discussed based on the distribution equilibria of gallium, indium, and thallium as a function of the concentration of extractants and the concentration of hydrogen ion in aqueous phase. The separation of the three elements from one another and from alloys with CA12 has also been discussed. In our previous work [1], the extraction of gallium and indium has been investigated with CA100 and trialkyl amine (N235), *N,N*-di(1-methylheptyl) acetamide (N503), tributyl phosphate (TBP), and trialkyl phosphine oxide (Cyanex923). The only synergistic system, CA100 + N235, is studied in detail for the extraction stoichiometry of indium and separation feasibility for gallium and indium.

Primary amine N1923, having two branched carbon chains with the structure of R₁R₂CHNH₂, is an important basic extractant produced by Shanghai Institute of Organic Chemistry, Chinese Acad-

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emy Sciences. It has been recognized as having the following advantages: easy preparation, low solubility in water, high separation factors for some metal ions such as rare earths, and low stripping acidity [23]. However, N1923 is seldom applied to the extraction of gallium and indium, especially from other media except sulfuric acid solutions [10].

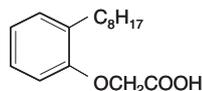
Since gallium and indium often exist in zinc refinery residue, it is of interest to study the extraction and separation of them. In this work, the extraction of gallium, indium, and zinc with mixtures of CA12 and primary amine N1923 has been investigated. Different extraction effects are studied and considered for the separation of the metals. For zinc, effects of several parameters, such as pH, extractant concentrations, and temperature have been studied. The extraction stoichiometry is obtained based on these data.

2. Experimental

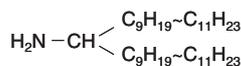
2.1. Reagents and apparatus

Ga₂O₃ and In₂O₃ obtained from Aladdin Reagents were used to prepare stock solutions of Ga(III) and In(III) by dissolving the oxides in 20% HCl, respectively. Stock solutions of Zn(II) was directly prepared with ZnCl₂ (Aladdin Reagents, China). All work solutions were obtained by appropriate dilution of the standardized stock solutions. All the initial metal concentrations were maintained at 1.0×10^{-3} mol L⁻¹. Ionic strengths were kept at 0.3 mol L⁻¹ with NaCl ($\mu = 0.3$ mol L⁻¹). pH values of the solutions was adjusted by the addition of HCl or NaOH solutions. All other reagents were of analytical reagent grade.

CA12 and N1923 were purchased from Shanghai Rare-Earth Chemical Co., Ltd., China with the following structures.



CA12



N1923

Both of the extractants were used without further purification and dissolved in *n*-heptane.

A TU 1810 ultraviolet–visible spectrophotometer (Beijing Purkinje General Instruments Co., Ltd., China) was employed for the determination of the metal ions. A PHS-3C pH meter was used for pH measurements (Shanghai Rex Instruments Factory, China).

2.2. Procedures

Unless otherwise stated, 5 mL aqueous and 5 mL organic solutions were mixed and shaken for 30 min at 293 ± 1 K. After the split of the phases, the concentrations of Ga(III)/In(III) and Zn(II) were determined spectrophotometrically with 4-(2-pyridylazo)-resorcinol (PAR) and 2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene sodium salt (Zincon) as the indicator, respectively. The wavelengths for the determinations are 505 nm (Ga), 510 nm (In), and 620 nm (Zn), respectively. The concentrations of the metal ions in the organic phase were obtained by mass balance. Distribution ratios (*D*) were calculated by $D = [M]_{(o)}/[M]_{(a)}$, where $[M]_{(o)}$ and $[M]_{(a)}$ represented the concentrations of the metal ions in the organic and aqueous phase, respectively.

3. Results and discussion

3.1. Extraction effects

Figs. 1–3 show the extraction of Ga³⁺, In³⁺, and Zn²⁺ with CA12 + N1923. X_{CA12} denotes the concentration ratio of CA12 in

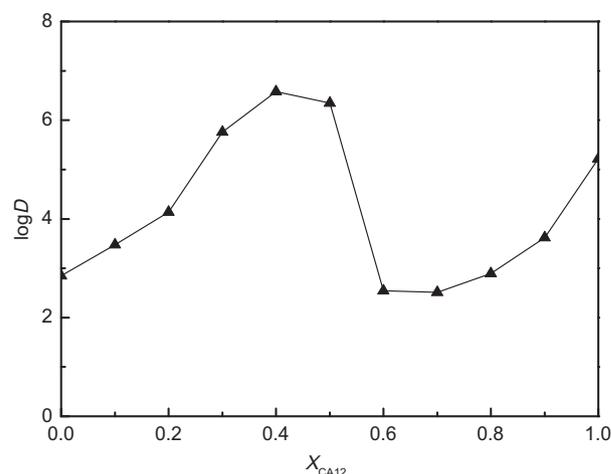


Fig. 1. Extraction of Ga³⁺ with CA12 + N1923. $[Ga^{3+}] = 1.0 \times 10^{-3}$ mol L⁻¹, pH 3.0, $\mu = 0.3$ mol L⁻¹, $C_{CA12} + C_{N1923} = 0.05$ mol L⁻¹.

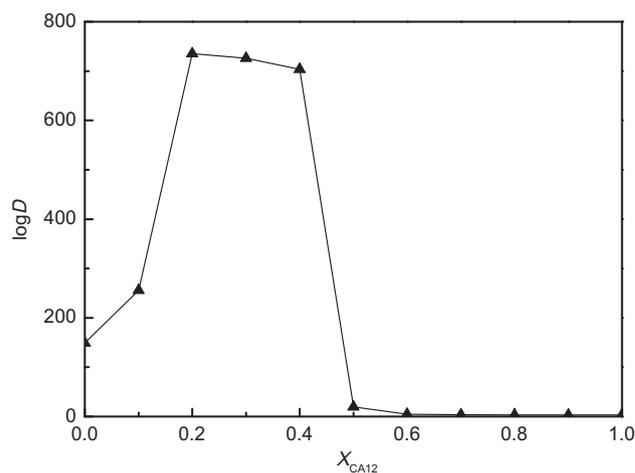


Fig. 2. Extraction of In³⁺ with CA12 + N1923. $[In^{3+}] = 1.0 \times 10^{-3}$ mol L⁻¹, pH 3.0, $\mu = 0.3$ mol L⁻¹, $C_{CA12} + C_{N1923} = 0.05$ mol L⁻¹.

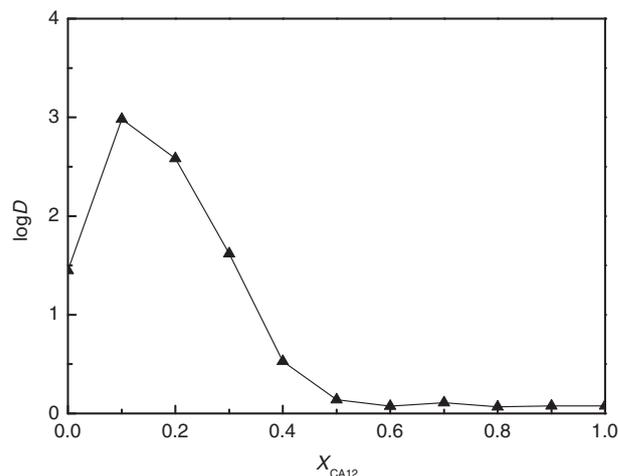


Fig. 3. Extraction of Zn²⁺ with CA12 + N1923. $[Zn^{2+}] = 1.0 \times 10^{-3}$ mol L⁻¹, pH 3.0, $\mu = 0.3$ mol L⁻¹, $C_{CA12} + C_{N1923} = 0.05$ mol L⁻¹.

the organic phases calculated by $C_{CA12}/(C_{CA12} + C_{N1923})$. Synergistic enhancement coefficient, *R*, is often used to evaluate whether a mixing system has synergistic extraction or not [24].

Table 1
Synergistic enhancement coefficients of Ga³⁺, In³⁺, and Zn²⁺ with CA12 + N1923.

X _{CA12}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Ga ³⁺	1.1	1.2	1.6	1.7	1.6	0.6	0.6	0.6	0.7
In ³⁺	1.9	6.1	6.9	7.7	0.3	0.1	0.1	0.1	0.2
Zn ²⁺	2.3	2.2	1.6	0.6	0.2	0.1	0.2	0.2	0.4

$$R = \frac{D_{\text{mix}}}{D_A + D_B} \quad (1)$$

where D_{mix} , D_A , and D_B denote the distribution ratios when metal ions are extracted with the mixed extractant and the single extractant, A and B, respectively. The R values are calculated and listed in Table 1, indicating that synergistic effects are replaced by antagonistic effects with increasing X_{CA12} values.

It is interesting to note that the mixtures have synergistic effects on all the three metal ions at low concentration ratios of CA12. However, antagonistic effects are found at high X_{CA12} values. The reason why such effects exist is not very clear. There have been some reports about the synergistic or antagonistic extraction mechanism. For instance, when neutral electron donors are used as the synergist, an explanation about the synergism is that the hydrophobicity of extracted chelates is increased because of formation of an adduct in an organic phase [25]. However, there is not a generally shared view about the synergistic or antagonistic mechanism. It is difficult to understand the complete extraction mechanism and expect the extraction effects because three extraction processes, i.e., the synergistic/antagonistic extraction and the extraction with single extractant, exist simultaneously and determine the final extraction effects.

3.2. Separation of Ga³⁺, In³⁺, and Zn²⁺ with CA12 + N1923

Separation factors are often used to describe the separation ability of metal ions, which can be expressed as follows:

$$\beta = \frac{D_M}{D_N} \quad (2)$$

where D_M and D_N are the distribution ratios of M and N under the same experimental conditions.

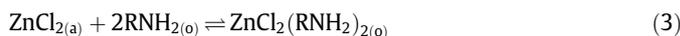
Table 2 shows the β values of Ga³⁺, In³⁺, and Zn²⁺ in N1923–heptane and CA12 + N1923 systems. Compared with single N1923 extractant, higher separation factors cannot be obtained at most N1923 concentration ratios (X_{N1923}) in CA12 + N1923 system. However, it should be noted that when X_{N1923} is 0.6, the selectivity between Ga³⁺/In³⁺ and Zn²⁺ is greatly enhanced, especially between In³⁺ and Zn²⁺. Such a result implies that there is potential for the separation of Ga³⁺ and In³⁺ from zinc solutions with mixtures of CA12 and N1923.

3.3. Synergistic extraction of Zn²⁺ with mixtures of CA12 and N1923

The extraction of Zn²⁺ with CA12 has been studied in detail by Wang et al. [26]. In their work, CA12 was treated with several steps before employed to extract Zn²⁺. CA12 was firstly purified with NaOH, HCl successively and washed with H₂O. The purified CA12 was then ammonized with NH₃·H₂O mixed with NaCl. In the pres-

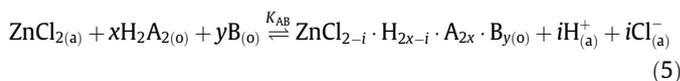
ent study, the extraction ability of Zn²⁺ with CA12 is negligibly small compared with N1923 and CA12 + N1923, which can be clearly seen from Fig. 3. Therefore, the extraction of Zn²⁺ with CA12 will not be considered for subsequent stoichiometry studies.

Several papers have been reported for the extraction of Zn²⁺ from chloride medium with N1923, e.g., Le et al.'s work [27]. The following extraction reactions can be expressed when N1923 as received and N1923 after acidified are employed:



In the present study, both the extractants are employed as received. Therefore, Eq. (3) can be used to express the extraction stoichiometry.

When the mixtures of CA12 (H₂A₂) and N1923 (B) are used as the extractant of Zn²⁺, the following reaction can be proposed:



The equilibrium constant K_{AB} can be expressed as,

$$K_{\text{AB}} = \frac{[\text{ZnCl}_{2-i} \cdot \text{H}_{2x-i} \cdot \text{A}_{2x} \cdot \text{B}_{y(\text{o})}]_{(\text{o})} [\text{H}_{(\text{a})}^+]^i [\text{Cl}_{(\text{a})}^-]^i}{[\text{ZnCl}_{2(\text{a})}]_{(\text{a})} [\text{H}_2\text{A}_{2(\text{o})}]_{(\text{o})}^x [\text{B}_{(\text{o})}]_{(\text{o})}^y} \\ = \frac{D_{\text{AB}} \left(1 + \sum_{i=1}^4 \beta_i [\text{Cl}^-]^i \right) [\text{H}_{(\text{a})}^+]^i [\text{Cl}_{(\text{a})}^-]^i}{\beta_2 [\text{Cl}^-]^2 [\text{H}_2\text{A}_{2(\text{o})}]_{(\text{o})}^x [\text{B}_{(\text{o})}]_{(\text{o})}^y} \quad (6)$$

If Y is described as,

$$Y = \frac{1 + \sum_{i=1}^4 \beta_i [\text{Cl}^-]^i}{\beta_2 [\text{Cl}^-]^2} \quad (7)$$

the distribution ratio D_{AB} of the mixing system should be:

$$\log D_{\text{AB}} = x \log [\text{H}_2\text{A}_{2(\text{o})}]_{(\text{o})} + y \log [\text{B}_{(\text{o})}]_{(\text{o})} + \log K_{\text{AB}} - \log Y + ipH \\ - i \log [\text{Cl}^-]_{(\text{a})} \quad (8)$$

In the present study, the concentration of Cl⁻ is fixed at 0.3 mol L⁻¹, the stability constants of ZnCl_i are as: log β_1 = 0.43, log β_2 = 0.61, log β_3 = 0.53, log β_4 = 0.20 [28]. logY is thus calculated as 0.79. [H₂A₂]_(o) and [B]_(o) can be determined as follows:

$$[\text{H}_2\text{A}_{2(\text{o})}]_{(\text{o})} = C_{\text{H}_2\text{A}_2} - C_{\text{Zn}^{2+}} \times \frac{x D_{\text{AB}}}{1 + D_A + D_B + D_{\text{AB}}} \quad (9)$$

$$[\text{B}_{(\text{o})}]_{(\text{o})} = C_B - C_{\text{Zn}^{2+}} \times \frac{2 D_B + y D_{\text{AB}}}{1 + D_A + D_B + D_{\text{AB}}} \quad (10)$$

To examine the composition of extracted complexes in CA12 + N1923 system, the distribution ratios are investigated at a series of experiments. Firstly, i is determined by the plots of logD versus pH when the initial concentrations of CA12 and N1923 are fixed. Results are shown in Fig. 4, giving an i value of about 2.0. Secondly, x and y are determined by the plots of logD_{AB} – ipH versus log[H₂A₂]_(o) or log[B]_(o) when initial pH and concentration of the other extractant are kept constant. Results in Fig. 5

Table 2
Separation factors of Ga³⁺, In³⁺, and Zn²⁺ in N1923 and CA12 + N1923 systems.

X _{N1923}	Ga ³⁺ /Zn ²⁺					In ³⁺ /Zn ²⁺				
	0.2	0.4	0.6	0.8	1.0	0.2	0.4	0.6	0.8	1.0
N1923	16.0	8.1	4.7	3.1	2.0	515.2	292.5	198.6	138.1	102.8
CA12 + N1923	43.8	33.9	12.4	1.6	2.0	52.4	60.8	1327.2	284.9	102.8

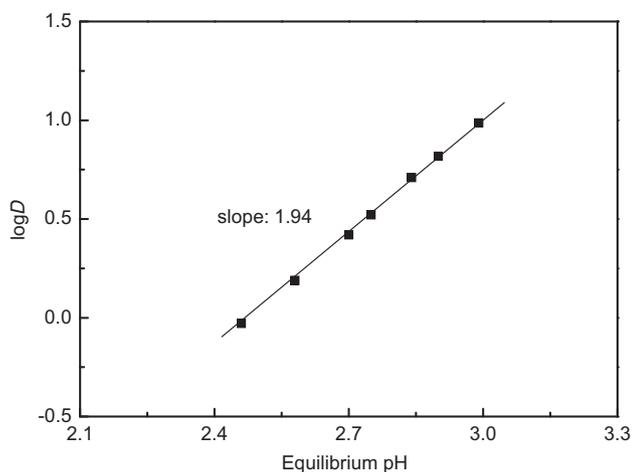


Fig. 4. Influence of pH on the extraction of Zn^{2+} with CA12 + N1923. $[Zn^{2+}] = 1.0 \times 10^{-3} \text{ mol L}^{-1}$, $\mu = 0.3 \text{ mol L}^{-1}$, $C_{CA12} = 0.005 \text{ mol L}^{-1}$, $C_{N1923} = 0.045 \text{ mol L}^{-1}$.

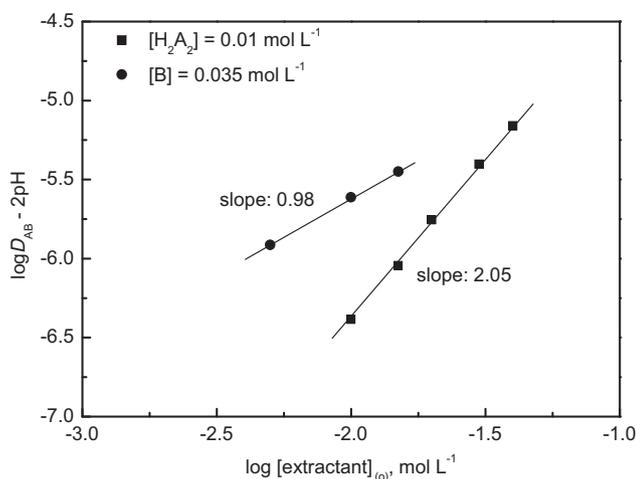


Fig. 5. Influence of extractant concentration on the extraction of Zn^{2+} with CA12 + N1923. $[Zn^{2+}] = 1.0 \times 10^{-3} \text{ mol L}^{-1}$, pH 3.0, $\mu = 0.3 \text{ mol L}^{-1}$.

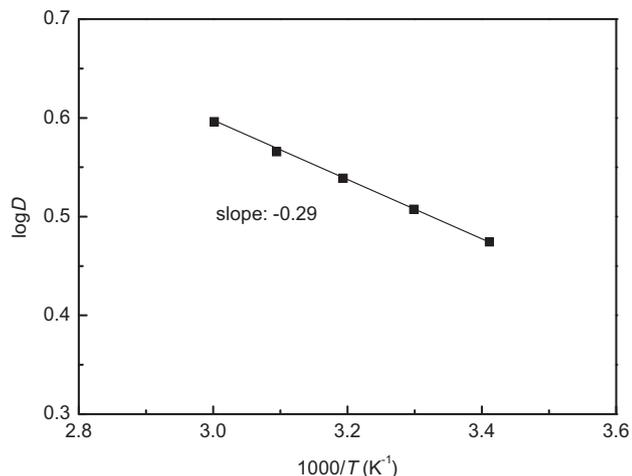
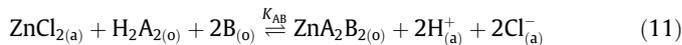


Fig. 6. Influence of temperature on the extraction of Zn^{2+} with CA12 + N1923. $[Zn^{2+}] = 1.0 \times 10^{-3} \text{ mol L}^{-1}$, pH 3.0, $\mu = 0.3 \text{ mol L}^{-1}$, $C_{CA12} = 0.005 \text{ mol L}^{-1}$, $C_{N1923} = 0.045 \text{ mol L}^{-1}$.

indicate that x and y are about 1.0 and 2.0, respectively. Based on these results, the following reaction can be expressed for the synergistic extraction:



$\log K_{AB}$ can thus be calculated as -0.63 ± 0.02 based on Eq. (8).

Temperature is a very important factor in extraction experiments. In order to investigate the influence of temperature on the extraction of Zn^{2+} with CA12 + N1923, the plots of $\log D$ versus $[1000/T(K)]$ have been determined in a range of 293–333 K. As shown in Fig. 6, a line with a slope of -0.29 has been obtained, according to which the change of enthalpy of the reaction, ΔH , can be calculated using Van't Hoff equation [29]:

$$\frac{\Delta \log D}{\Delta \frac{1}{T}} = \frac{-\Delta H}{2.303R} \quad (12)$$

The change of Gibbs free energy, ΔG , and the change of entropy, ΔS of the system at 293 K can be obtained as:

$$\Delta G = -RT \ln K \quad (13)$$

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} \quad (14)$$

ΔH , ΔG , and ΔS can be calculated as 5.6 kJ mol^{-1} , 3.5 kJ mol^{-1} , and $7.3 \text{ J mol}^{-1} \text{ K}^{-1}$. The sign of ΔH is “+”, indicating that the synergistic extraction process is endothermically driven. The sign of ΔS is also “+”, which is in accordance with the theory of increasing of entropy from the view of statistics.

4. Conclusions

In the present work, the extraction of Ga(III), In(III), and Zn(II) with mixtures of CA12 and N1923 has been studied. The extraction effects change from synergistic to antagonistic ones with increasing CA12 concentration ratios. The mixtures can enhance the selectivity between Ga(III)/In(III) and Zn(II) at a proper concentration ratio of CA12 and N1923. The stoichiometry of Zn(II) extraction with the mixtures has been studied in detail and the extracted complex is determined as ZnA_2B_2 . Thermodynamic constants have also been investigated, illustrating that the synergistic extraction of Zn(II) with the mixtures is an endothermic one.

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