



Synergistic extraction study of indium from chloride medium by mixtures of *sec*-nonylphenoxy acetic acid and trialkyl amine

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ABSTRACT

The extraction of gallium(III) and indium(III) from chloride medium with mixtures of *sec*-nonylphenoxy acetic acid (CA100) and other organic extractants, including trialkyl amine (N235), *N,N*-di(1-methylheptyl) acetamide (N503), tributyl phosphate (TBP), and trialkyl phosphine oxide (Cyanex923) in *n*-heptane, has been studied. Synergistic effects are only found when indium(III) is extracted with mixtures of CA100 and N235. The synergistic extraction stoichiometry of indium(III) with CA100 + N235 is studied with the methods of slope analysis and continuous variations. The extracted complex, equilibrium constants, and thermodynamic functions are determined. Moreover, the different extraction behavior of gallium(III) and indium(III) have been applied to discuss the separation of gallium(III) and indium(III).

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1. Introduction

In recent years, gallium(III) and indium(III) have emerged as important strategic metals as they are vital for the electronic industry [1]. For example, gallium(III) and indium(III) are used as semiconductor materials such as InP or GaAs. However, there are no discrete reserves of gallium(III) and indium(III), and their global distributions are very sparse. Since the use of these metals is likely to increase in the near future and also the two metals show similar chemical behavior, sincere efforts have been made to recover gallium(III) and indium(III) from leaner sources, namely ores and wastes.

Liquid–liquid extraction has been applied to the practical separation and recovery of gallium(III) and indium(III) [2]. A variety of extractants have been studied for this goal, such as acidic organophosphorus extractants [1,3–6], neutral organophosphorus extractants [7–11], high molecular weight amines [12–14], carboxylic acids [15–19]. However, processes that could separate gallium(III) and indium(III) from mixed solutions are complicated and the complexity of these processes make the application for practical operation difficult. For example, Gupta et al. reported that the use of carboxylic acids and high molecular weight amines had limitations [7], such as long equilibration time, addition of modifier, and loss of extractant due to aqueous miscibility or the need for rigid control of phase variables. Alkyl-phosphorus

compounds namely tributyl phosphate (TBP) and trioctylphosphine oxide (TOPO) require high reagent concentration or long extraction time [7]. Consequently the ongoing discussion highlights the emerging interest towards the recovery of gallium(III) and indium(III) from different types of leaner sources.

As a branch of liquid–liquid extraction, synergistic extraction has several advantages. It not only enhances the extraction efficiency, but also improves the selectivity significantly in some cases, which attracts more and more attention of separation scientists. In synergistic systems, the extracting ability of the mixture exceeds the sum of the extracting abilities of its components. A few types of synergistic extractants were used in the separation and recovery of gallium(III) and indium(III) [9,13]. For instance, Yamada et al. studied the synergistic extraction of gallium(III) from aqueous perchlorate solutions into toluene with mixtures of 2-thenoyltrifluoroacetone (HTTA) and TOPO [9]. A synergistic enhancement of the extraction was found when TOPO was added. The extracted adduct was found to be in the form of $\text{Ga}(\text{TTA})_3(\text{TOPO})_2$.

Carboxylic acids, although not as widely used as their organophosphorus counterparts, have found some applications in the hydrometallurgical processes of base metals. *Sec*-nonylphenoxy acetic acid (CA100) and *sec*-octylphenoxy acetic acid (CA12) have been recently developed by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The extraction of gallium(III) and indium(III) with CA100 and CA12 has been reported elsewhere [15–19]. In our previous work, several studies have been developed about the extraction of rare earths with a mixing system containing CA100 or CA12 [22–25]. The separation abilities of rare

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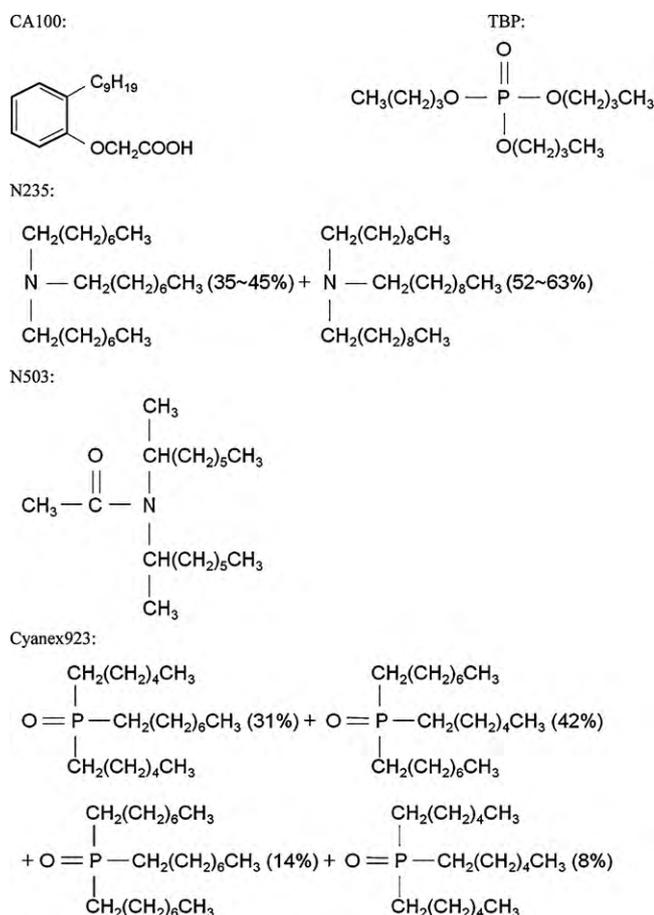


Fig. 1. The extractants' chemical structures.

earths are greatly improved, which leads us to explore some new mixing systems including CA100 to see whether it can enhance the extraction and separation abilities of other metals.

In the present study, the extraction of gallium(III) and indium(III) with mixtures of CA100 and four organic extractants, TBP, N235, N503, Cyanex923 (hereafter abbreviated as C923), has been investigated. The structures of the employed extractants are shown in Fig. 1. The effects of several parameters, such as pH, extractant concentrations, and temperature have been studied. Furthermore, the separation of gallium(III) and indium(III) with the mixtures is considered.

2. Experimental

2.1. Reagents and apparatus

CA100, N235, and N503 were purchased from Shanghai Rare-Earth Chemical Co., Ltd., China. TBP was obtained from Shanghai Organic Reagent Company, China. C923 was supplied by Cytec Canada Inc. All of the extractants were used without further purification and dissolved in *n*-heptane to the required concentrations.

Stock solutions of Ga(III) and In(III) were prepared by dissolving Ga₂O₃ and In₂O₃ in 1:4 HCl, respectively. They were analyzed by titration with a standard solution of EDTA with xylenol orange as an indicator. All work solutions of Ga(III) and In(III) were prepared by appropriate dilution of the standardized stock solutions. All the initial metal concentrations were maintained at 1.0×10^{-3} mol L⁻¹. The pH of the aqueous phase was adjusted by the addition of HCl or NaOH solutions. All extraction experiments were performed at constant ionic strength with NaCl ($\mu = 0.3$ mol L⁻¹). All other reagents were of analytical reagent grade.

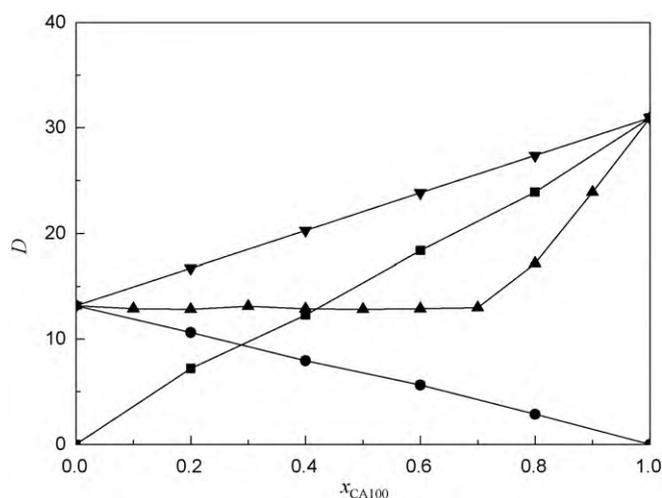


Fig. 2. Extraction of Ga³⁺ with CA100, N235, and CA100+N235. [Ga³⁺] = 1.0×10^{-3} mol L⁻¹, pH = 3.0, $\mu = 0.3$ mol L⁻¹, $C_{CA100} + C_{N235} = 0.05$ mol L⁻¹. (■) D_{CA100} , (●) D_{N235} , (▲) $D_{CA100+N235}$, (▼) $D_{CA100} + D_{N235}$.

A pH-3C digital pH meter was employed for pH measurements (Shanghai Rex Instruments Factory, China). The concentrations of Ga(III) and In(III) were determined by spectrophotometry using a Cintra 10e spectrophotometer (GBC Scientific Equipments, Australia).

2.2. Extraction procedures

Equal volumes (5 mL each) of aqueous and organic solutions were mixed and shaken for 30 min at 293 ± 1 K unless otherwise stated. 30 min was determined to be sufficient for equilibrium attainment in preliminary experiments. The solutions were then settled and separated by gravity. After the split of the phases, the concentrations of Ga(III) and In(III) in aqueous phase were determined spectrophotometrically with 4-(2-pyridylazo)-resorcinol (PAR) at 505 nm (Ga) and 510 nm (In), respectively. The concentrations of Ga(III) and In(III) in organic phase were obtained by mass balance. Distribution ratios (D) were calculated from these concentrations.

3. Results and discussion

3.1. Extraction of Ga³⁺ and In³⁺ with mixtures of CA100 and N235, N503, TBP, C923

Fig. 2 shows the distribution ratios of Ga³⁺ when extracted with CA100, N235 and their mixtures, respectively. The sum of D_{CA100} and D_{N235} , $D_{CA100} + D_{N235}$, calculated based on Xu et al.'s method [26] is also shown. x_{CA100} represents the mole fraction of CA100 in the organic phases ($x_{CA100} = C_{CA100} / (C_{CA100} + C_{N235})$). It can be seen that the mixtures of CA100 and N235 do not have synergistic effects on Ga³⁺.

Fig. 3 shows the distribution ratios of In³⁺, D_{CA100} , D_{N235} , $D_{CA100+N235}$, and $D_{CA100} + D_{N235}$. There are evident synergistic effects on the extraction of In³⁺ with the mixtures of CA100 and N235. According to Xu et al.'s theory [26], the synergistic enhancement coefficient can be calculated as

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

where D_{mix} , D_A and D_B represent the distribution ratios when In³⁺ is extracted by CA100 + N235, CA100, and N235, respectively. R can be calculated as 1.54.

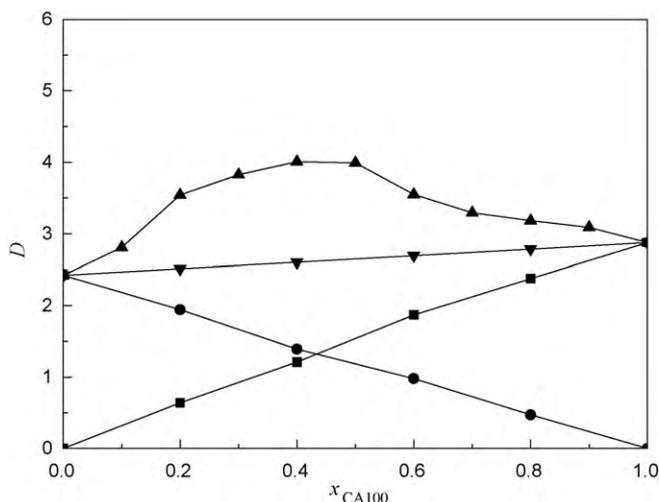


Fig. 3. Extraction of In^{3+} with CA100, N235, and CA100+N235. $[\text{In}^{3+}] = 1.0 \times 10^{-3} \text{ mol L}^{-1}$, $\text{pH} = 3.0$, $\mu = 0.3 \text{ mol L}^{-1}$, $C_{\text{CA100}} + C_{\text{N235}} = 0.05 \text{ mol L}^{-1}$. (■) D_{CA100} , (●) D_{N235} , (▲) $D_{\text{CA100+N235}}$, (▼) $D_{\text{CA100} + D_{\text{N235}}}$.

The extraction of Ga^{3+} and In^{3+} with mixtures of CA100 and N503, TBP, C923 is also investigated. Results show that all the mixtures do not have evident synergistic effects on Ga^{3+} and In^{3+} . The reason why a mixing system has synergistic or antagonistic effect is not clear so far. There have been several reports about the extraction mechanism of metal ions with mixtures of two extractants. For instance, Zhang et al. [27] have studied the extraction of cadmium and zinc with mixtures of di-(2-ethylhexyl)-monothiophosphoric acid and trioctylamine in toluene. By conductance titration, infrared spectrum (IR) and nuclear magnetic resonance spectrum (NMR), the two extractants are confirmed to form an electrolyte of ion-pairs. However, there is no generally shared view about the ion-pairs mechanism. An important question is that how the ion-pairs are bound to the central metal ions is not clear [28]. In addition, there are arguments about which kind of extraction effects may be brought by such ion-pairs [29]. Except conductance titration, IR and NMR techniques, a method of varying initial metal concentration in the aqueous phase has been developed by Reddy and Kumar to determine the extracted compound to be mononuclear or binuclear species [30].

Although it is difficult to understand the complete extraction mechanism and expect the extraction effects, it is possible to obtain synergistic or antagonistic effect and apply this effect to the separation of metal ions by controlling experimental conditions, such as the ratio of the two extractants. In the present work, the separation factors between Ga^{3+} and In^{3+} , $D_{\text{Ga}}/D_{\text{In}}$, have been obtained as shown in Table 1. Compared with single CA100 system, only CA100+C923 mixtures have higher separation ability of Ga^{3+} and In^{3+} at the mole fraction of CA100 of 0.8 ($x_{\text{CA100}} = 0.8$). This is because of the phenomenon that CA100+C923 mixtures have weak synergistic effect on Ga^{3+} but antagonistic effect on In^{3+} when x_{CA100} is 0.8. All other mixtures do not have such abilities when used for the separation of Ga^{3+} and In^{3+} compared with CA100 extrac-

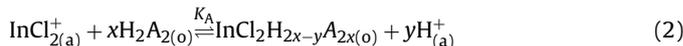
tant. Therefore, CA100+C923 can be considered for the separation of the two metal ions at the appropriate ratio of the extractants.

3.2. Synergistic extraction of In^{3+} with mixtures of CA100 and N235

3.2.1. Extraction of In^{3+} with single CA100 system

The extracted complex of In^{3+} by CA100 from sulfate aqueous solution has been reported as InA_3 [19]. However, to the best of our knowledge, there are no reports about the extraction stoichiometry of In^{3+} with CA100 from chloride medium. Cheng et al. studied the extraction of $\text{In}(\text{III})$ with petroleum sulfoxides (PSO), indicating that $\text{In}(\text{III})$ was extracted as $\text{InCl}_3 \cdot 2\text{PSO}$ when $[\text{H}^+]$ was lower than 1.00 mol L^{-1} but $\text{HInCl}_4 \cdot 3\text{PSO}$ when $[\text{H}^+]$ was higher than 2.00 mol L^{-1} [20]. Bao et al. also reported that Cl^- participated in the extraction of $\text{In}(\text{III})$ when TOPO was selected as the extractant. The extracted compound was determined as $\text{HInCl}_4 \cdot 2\text{TOPO}$ [11].

In the present work, the concentration of Cl^- was fixed at 0.3 mol L^{-1} , the stability constants of InCl_i are as: $\beta_1 = 41.69$, $\beta_2 = 275.42$, $\beta_3 = 50.12$, $\beta_4 = 39.81$ [21]. β_2 is greater than β_1 and β_3 , indicating that the species InCl_2^+ predominates. Therefore, the following reaction can be proposed for the extraction of In^{3+} with CA100:



The relationship between the distribution ratio D_A and the extraction constant K_A can be described as follows:

$$D_A = \frac{[\text{InCl}_2\text{H}_{2x-y}\text{A}_{2x}]_{(o)}}{[\text{InCl}_2^+]_{(a)}} \quad (3)$$

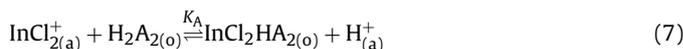
$$K_A = \frac{[\text{InCl}_2\text{H}_{2x-y}\text{A}_{2x}]_{(o)}[\text{H}^+]_{(a)}^y}{[\text{InCl}_2^+]_{(a)}[\text{H}_2\text{A}_2]_{(o)}^x} = \frac{D_A(1 + \sum_{i=1}^4 \beta_i[\text{Cl}^-]^i)[\text{H}^+]_{(a)}^y}{\beta_2[\text{Cl}^-]^2[\text{H}_2\text{A}_2]_{(o)}^x} \quad (4)$$

where

$$Y = \frac{1 + \sum_{i=1}^4 \beta_i[\text{Cl}^-]^i}{\beta_2[\text{Cl}^-]^2} \quad (5)$$

$$\log D_A = x \log[\text{H}_2\text{A}_2]_{(o)} + \log K_A - \log Y + y\text{pH} \quad (6)$$

At constant ionic strength, Y is constant. At fixed In^{3+} concentration, CA100 concentration and ionic strength, the effects of pH on the extraction of In^{3+} with CA100 have been investigated. The plots $\log D_A$ versus pH are shown in Fig. 4, giving a straight line with a slope of about 1.0. Accordingly, at fixed In^{3+} concentration, pH value, and ionic strength, the effects of CA100 concentration on the extraction of In^{3+} are also investigated. As shown in Fig. 5, the slope of the plot of $\log D_A - \text{pH}$ versus $\log[\text{H}_2\text{A}_2]_{(o)}$ has been determined to be around 1.0. Therefore, the extraction reaction of In^{3+} from chloride medium with CA100 can be expressed as



The average of $\log K_A$ is calculated to be -0.63 ± 0.03 .

Table 1
Separation factors of Ga and In with CA100+N235, CA100+N503, CA100+TBP, and CA100+C923 systems.

	x_{CA100}					
	0	0.2	0.4	0.6	0.8	1
CA100+N235	5.43	3.62	3.21	3.62	3.59	10.76
CA100+N503	2.41	2.35	2.33	2.78	3.56	4.53
CA100+TBP	0.34	1.22	3.21	6.75	11.77	12.3
CA100+C923	5.19	5.18	5.18	7.78	11.57	9.64

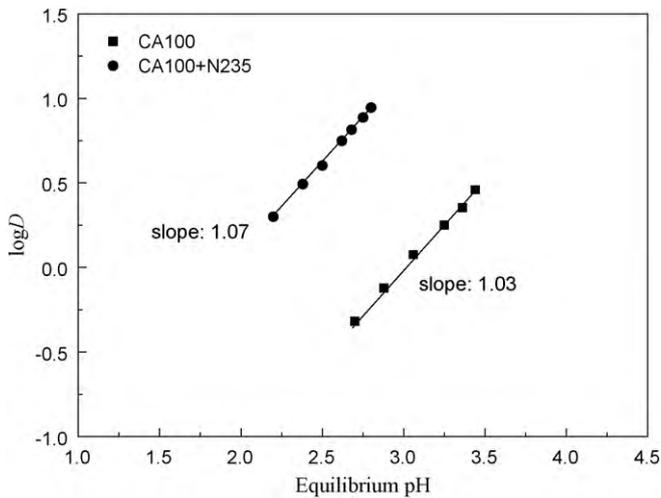
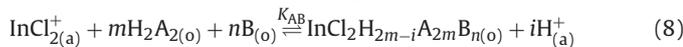


Fig. 4. Effect of pH on the extraction of In^{3+} with CA100 and CA100+N235 systems. $[\text{In}^{3+}] = 1.0 \times 10^{-3} \text{ mol L}^{-1}$, $\mu = 0.3 \text{ mol L}^{-1}$. (■) Single CA100 system: $C_{\text{CA100}} = 0.05 \text{ mol L}^{-1}$; (●) CA100+N235 system: $C_{\text{CA100}} = 0.02 \text{ mol L}^{-1}$, $C_{\text{N235}} = 0.03 \text{ mol L}^{-1}$.

3.2.2. Extraction stoichiometry of In^{3+} with mixtures of CA100 and N235

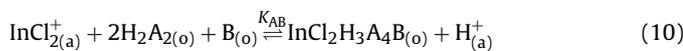
If the synergistic extraction of In^{3+} with mixture of CA100 and N235 from chloride medium is expressed as



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

$$\log D_{\text{AB}} = m \log [\text{H}_2\text{A}_2]_{(o)} + n \log [\text{B}]_{(o)} + \log K_{\text{AB}} - \log Y + ip\text{H} \quad (9)$$

The effects of pH on the extraction of In^{3+} are investigated at fixed concentrations of CA100, N235, and ionic strength. The results are also shown in Fig. 4, giving a straight line with a slope of about 1.0. Similarly, when pH, ionic strength, and the concentration of one extractant are fixed, the plots of $\log D_{\text{AB}} - \text{pH}$ versus the concentration of the other extractant are obtained as shown in Fig. 6. The plots are linear with slopes of about 2.0 and 1.0 for $\log [\text{H}_2\text{A}_2]_{(o)}$ and $\log [\text{B}]_{(o)}$, respectively. Therefore, the synergistic extraction can be rewritten as



The value of $\log K_{\text{AB}}$ can be thus be calculated to be 3.36 ± 0.04 .

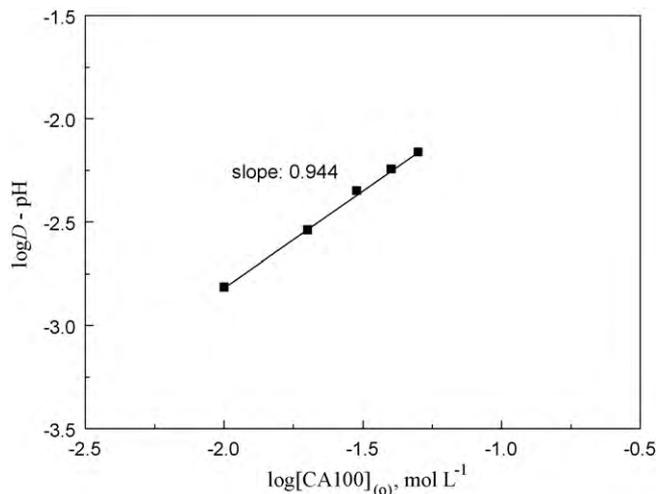


Fig. 5. Effect of CA100 concentration on the extraction of In^{3+} with single CA100 system. $[\text{In}^{3+}] = 1.0 \times 10^{-3} \text{ mol L}^{-1}$, $\mu = 0.3 \text{ mol L}^{-1}$, $\text{pH} = 3.0$.

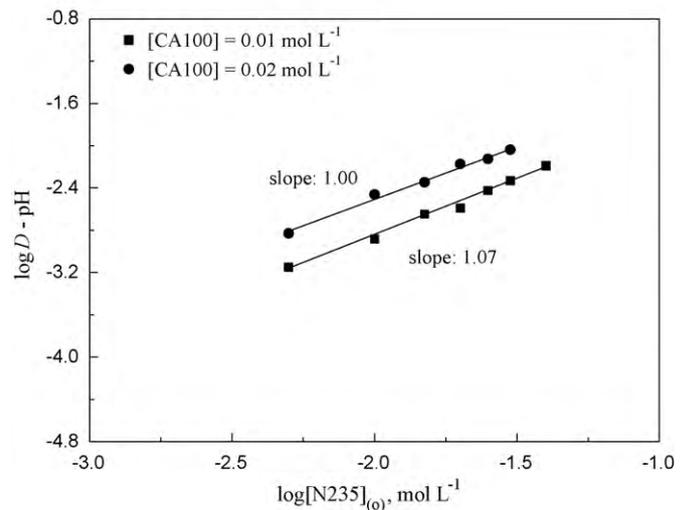
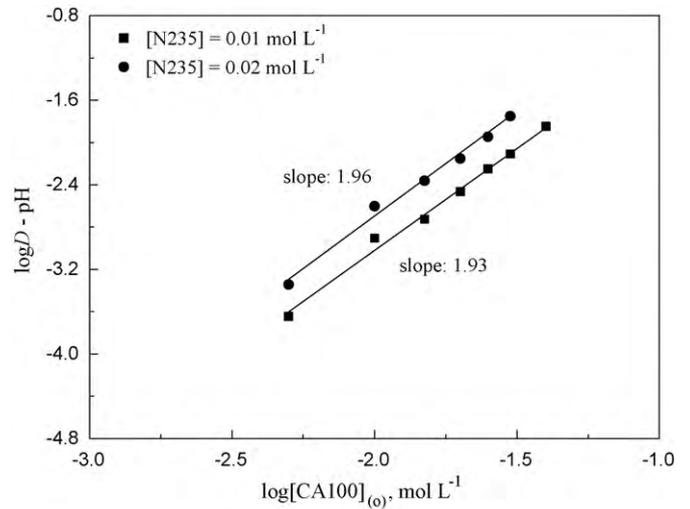


Fig. 6. Effect of extractant concentration on the extraction of In^{3+} with mixtures of CA100 and N235. $[\text{In}^{3+}] = 1.0 \times 10^{-3} \text{ mol L}^{-1}$, $\mu = 0.3 \text{ mol L}^{-1}$, $\text{pH} = 3.0$.

3.3. Influence of temperature on the extraction of In^{3+} with mixtures of CA100 and N235

The influence of temperature on the extraction of In^{3+} with CA100 + N235 has been studied at fixed pH, ionic strength, and concentrations of CA100 and N235. Plots of $\log D$ versus $[1000/T \text{ (K)}]$ are shown in Fig. 7. It can be seen that the distribution ratio of In^{3+} increases with increasing experimental temperatures. The change of enthalpy (ΔH), the change of Gibbs free energy (ΔG), and the change of entropy (ΔS) can thus be obtained as the following:

$$\frac{\Delta \log D}{\Delta(1/T)} = \frac{-\Delta H}{2.303R} \quad (11)$$

$$\Delta G = -RT \ln K \quad (12)$$

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} \quad (13)$$

ΔH can be determined from the slope of Fig. 7, whereas ΔG and ΔS can be calculated from Eqs. (12) and (13) for $T = 293 \text{ K}$ and $K = 10^{3.36}$. The values of ΔH , ΔG , and ΔS can be obtained as 3.12 kJ mol^{-1} , $-18.86 \text{ kJ mol}^{-1}$, and $74.97 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The sign of ΔH in CA100 + N235 system is positive, indicating that the synergistic procedure is endothermically driven.

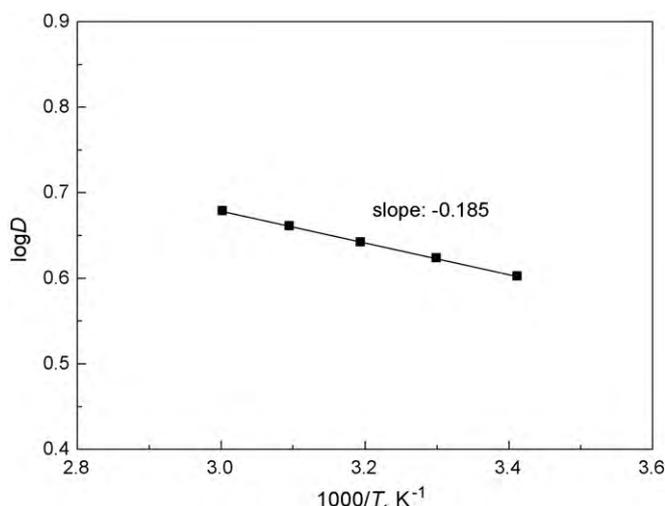


Fig. 7. Effect of experimental temperature on the extraction of In^{3+} with CA100+N235. $[\text{In}^{3+}] = 1.0 \times 10^{-3} \text{ mol L}^{-1}$, $\text{pH} = 3.0$, $\mu = 0.3 \text{ mol L}^{-1}$, $C_{\text{CA100}} = 0.02 \text{ mol L}^{-1}$, $C_{\text{N235}} = 0.03 \text{ mol L}^{-1}$.

4. Conclusions

In the present work, the mixtures of CA100 with N235, N503, TBP, C923 are applied to the extraction of gallium(III) and indium(III) from chloride medium. The mixtures exhibit different extraction effects on gallium(III) and indium(III). Compared with single CA100 system, only CA100 + C923 mixtures have higher separation ability of Ga^{3+} and In^{3+} at the mole fraction of CA100 of 0.8 ($\chi_{\text{CA100}} = 0.8$). All other mixtures do not have such abilities when used for the separation of Ga^{3+} and In^{3+} compared with CA100 extractant. Therefore, CA100 + C923 can be considered for the separation of the two metal ions at the appropriate ratio of the extractants. The mixtures of CA100 (H_2A_2) and N235 (B) have evident synergistic effects on In^{3+} from chloride medium. The extracted complexes with CA100 and CA100 + N235 are determined as $\text{InCl}_2\text{HA}_{2(o)}$, and $\text{InCl}_2\text{H}_3\text{A}_4\text{B}$, respectively. The synergistic extraction is an endothermic one.

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