

An Extraction Study of Gallium and Indium from Chloride and Sulphate Media with Sec-Nonylphenoxy Acetic Acid in Kerosene

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ABSTRACT: *The distribution of gallium(β) and indium (β) between hydrochloric or sulphuric acid solution with sec-nonylphenoxy acetic acid(CA-100) in kerosene has been investigated under various conditions. CA-100 is a new organocarboxylic extractant, which has been shown to be efficient for gallium(β) and indium(β) whereas germanium(γ), which was not extracted. The extraction system is studied as a function of initial pH, equilibration time, CA-100 concentration and aqueous ionic media(Cl^- and SO_4^{2-}). Extraction mechanism is discussed on the basis of slope-analysis method, constant molecular series method and saturation capacity method. It was found that sec-nonylphenoxy acetic acid was extracted into the organic phase by formation of the MA_3HA species from chloride media and in the form of MA_3 from sulphate media.($M=Ga$ and In) The equilibrium equations are proposed on the basis of the results that obtained.*

KEY WORDS: *Sec-nonylphenoxy acetic acid, Gallium(β), Indium(β), Solvent extraction.*

INTRODUCTION

Currently, increasing interests in environmental protection, energy saving as well as process optimization

and continuous progress in fundamental chemistry have produced an important development of new chemical

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separation techniques. The need of more specific from both ecological and economic aspects has led to the development in the synthesis of new extractants. Gallium(β) and indium (β) are indispensable rare metals in manufacture of electronic products. Using of them in semi-conducting products as photovoltaic cells and computers has generated interest in finding an electronic process for their recovery. Due to the increasing demand from gallium(β) and indium (β) in electronic industry, the recovery of gallium(β) and indium (β) from different primary and secondary sources are of great importance. Solvent extraction is now widely accepted as a process for the preconcentration and separation of gallium (β) and indium (β) from aqueous solutions in hydrometallurgical [1-4]. In recent years, several researchers have studied fundamental extraction behaviors and mutual extraction separation of gallium (β) and indium (β) with many kinds of extractants either from acidic or alkaline solutions [5,19]. These extractants include hydroxyquinoline derivatives, high molecular weight amines, organophosphorus compounds and carboxylic acids and so on. These researches have significantly enriched theory of solvent extraction and improved the selectivity and efficiency of extraction and separation process.

Bhattacharya B., et al. [7] studied the extraction equilibrium of gallium(β) with LIX 26 (alkyl substituted 8-hydroxyquinoline) in n-decanol as a moderator and kerosene as diluent. It was reported that extracted species is in the GaL_3 form.

H_3thba (Tris(2-hydroxybenzyl)amine) is a tripod quadridentate ligand having one tertiary amine-N and three phenolate-O donor atoms. Recently, *Ramunas J. M., et al.* [8] studied complexation equilibria between H_3thba and Ga^{3+} , In^{3+} and Fe^{3+} . It was found that H_3thba can form stable $\text{Ga}(\text{thba})$ and $\text{Fe}(\text{thba})$ complexes in ethanolic solution but that $\text{In}(\text{thba})$ cannot be formed because of its low stability. Because of synthesis of H_3thba requires many complicated steps, *Hirayama N. et al.* [9] investigated selective extraction of gallium from aluminum and indium using more easier synthesis of H_3tdmba (tris(2-hydroxy-3,5-dimethylbenzyl)amine) and H_3tcmba (tris(5-chloro-2-hydroxy-3-methylbenzyl) amine) as extractants. It was concluded that extractive separation of Ga^{3+} from Al^{3+} and In^{3+} in H_3tcmba system can be performed easier than in H_3tdmba . And the extractability was increased with the increase of ligand acidity.

They also evaluated that the extracted Ga^{3+} species was in the form of trigonal bipyramidal $\text{Ga}(\text{tdmba})(\text{H}_2\text{O})$ in H_3tdmba using chloroform as extraction solvent.

Acidic organophosphorous compounds are among the most promising extractants known for extraction of gallium and indium. *Zeng Dongming et al.* successfully separated indium and iron from smelting residue by technique of low acid leaching and solvent extraction with P204 [10]. Many researchers investigated multistage countercurrent extraction of indium from simulation experiments with D2EHPA (di-2-ethyl-hexylphosphoric acid) in sulfuric acidic solutions by different diluents [11-13]. Nearly complete separation of indium and gallium accomplished by a two-stage extraction. Other investigations reported on extraction of gallium [14] and indium [15] with PC-88A(2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester).

Extractants of carboxylic acid type, although not as widely used as their organo-phosphorus counterparts, have found some application in the hydrometallurgical processing of metals. For example, they have been employed in the separation of gallium and indium by supported liquid membranes containing 2-bromodecanoic acid as carrier [16], the extraction of zirconium and hafnium with versatic acid 10 [17], the extraction of rare earths and yttrium with high molecular weight carboxylic acids [18].

CA-100 as a new reagent for the extraction of rare metals has been studied in our laboratory [5, 19]. Studies indicate that CA-100 has several advantages including stable composition, low solubility in aqueous phase, non-toxic, high extraction efficiency. The purpose of this paper is to investigate the difference of extraction behavior and extraction mechanisms of gallium(β) and indium (β) from chloride and sulphate media using CA-100 as an extractant.

EXPERIMENTAL SECTION

Apparatus

A digital pH meter model pHs-3C with combined electrode was used for pH measurements. A model 722 spectrophotometer was used for the spectrophotometric determination of gallium and indium. HZ-8201K constant-temperature shaker was used for keeping temperature constant.

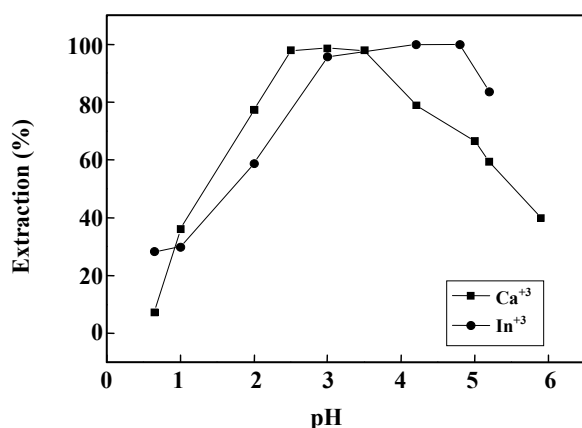


Fig. 1: Effect of initial pH on percentage extraction of gallium(β) and indium(β) from chloride media (Ga^{3+} : $7.80 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, In^{3+} : $2.90 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, CA-100: $4.60 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$).

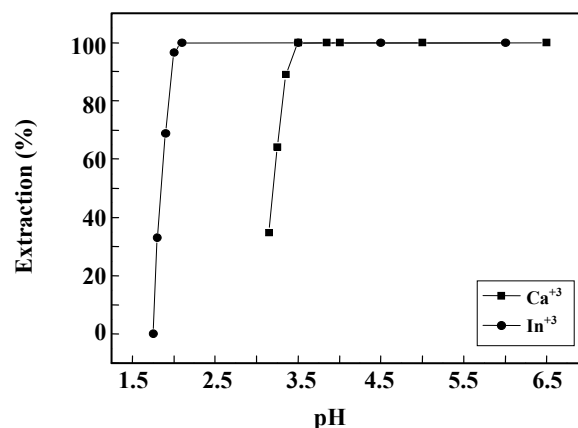


Fig. 2: Effect of initial pH on percentage extraction of gallium(β) and indium(β) from sulphate media ($1.60 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1} Ga^{3+}$ was extracted with $1.00 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1} CA-100$ in kerosene; $1.61 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1} In^{3+}$ was extracted with $3.83 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1} CA-100$ in kerosene from sulphate media).

Materials

CA-100 was supplied by Shanghai Institute of Organic Chemistry. CA-100 was washed alternatively with 1:1 HCl and distilled water until no chlorides were observed. By two phase potentiometric titration with $0.1 \text{ mol}\cdot\text{L}^{-1}$ NaOH, the concentration of CA-100 was found to be $1.60 \text{ mol}\cdot\text{L}^{-1}$. All other concentrations of CA-100 were prepared by appropriate dilutions of the standardized stock solutions with kerosene.

The stock hydrochloric solutions of gallium(β) and indium (β) were prepared by dissolving Ga_2O_3 and In_2O_3 in 1:4 HCl, respectively. The stock sulphuric solution of gallium(β) was prepared by dissolving Ga_2O_3 in $9 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 and the stock sulphuric solution of indium (β) was prepared by dissolving $In_2(SO_4)_3$ in distilled water at pH=2. All other concentrations of gallium(β) and indium (β) were prepared by appropriate dilutions of the standardized stock solutions. All other chemicals used were of analytical grade.

Procedure and method

All distribution equilibria studies were carried out at $288 \pm 2 \text{ K}$ with aqueous to organic phase ratio of 1:1. The ionic strength of aqueous phase was kept constant at $0.2 \text{ mol}\cdot\text{L}^{-1}$ using NH_4Cl . An aliquot of 5 mL of extractant in kerosene was equilibrated with same volume of aqueous gallium(β) and indium(β) solution in a 50 mL separating funnel. After the phase separation the pH of

aqueous phase was measured with pH meter. The concentrations of gallium and indium in aqueous phase were determined spectrophotometrically with 4-(2-pyridylazo)-resorcinol (PAR) at 505 and 510 nm. The concentrations of gallium and indium in organic phase were obtained by mass balance.

RESULTS AND DISCUSSION

Effect of initial pH

The effect of initial pH on the percentage extraction of gallium(β) and indium(β) by CA-100 in kerosene from chloride and sulphate media were ascertained (keeping other parameters constant). As shown in Figs. 1 and 2, in general, with the pH values rising, the percentage extraction of gallium(β) and indium(β) in both media increased. The extraction of gallium(β) was quantitative in the pH range 2.50-3.50 and that of indium(β) in the pH range 4.20-4.80 with CA-100 from chloride media. In contrast, gallium(β) and indium(β) were quantitatively extracted with CA-100 from sulphate media in the wide pH range 3.50-6.50 and 2.10-6.00, respectively (Fig. 2.). In this part, we also studied the effect of initial pH on extraction percentage of germanium(χ) with CA-100 in kerosene from chloride and sulphate media, it was found that germanium(χ) was not extracted in the pH range 0.65-6.50. So gallium(β) and indium(β) may easily separate from germanium(χ) according to initial pH.

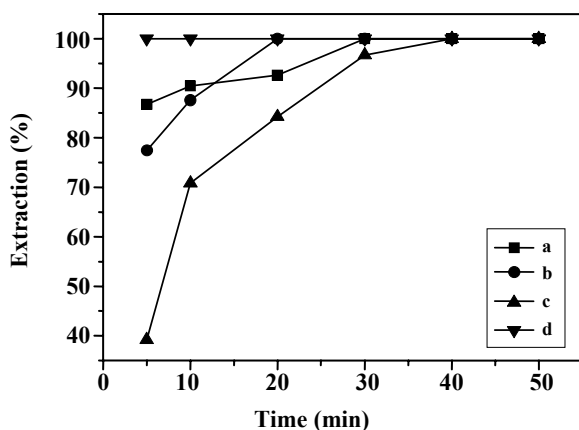


Fig.3. Effect of time on percentage extraction of gallium(β) and indium(β). (a: $7.80 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \text{ Ga}^{3+}$ was extracted with $3.04 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ CA-100 at pH 3.00 from chloride media in kerosene; b: $2.90 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \text{ In}^{3+}$ was extracted with $0.46 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ CA-100 at pH 4.800 from chloride media in kerosene; c: $1.60 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \text{ Ga}^{3+}$ was extracted with $1.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ CA-100 at pH 3.50 from sulphate media in kerosene; d: $1.61 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \text{ In}^{3+}$ was extracted with $3.83 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ CA-100 at pH 3.50 from sulphate media in kerosene).

Variation in extraction time (keeping other parameters constant) showed that quantitative extraction need 30min for gallium(β) and 20min for indium(β) from chloride media and 40min for gallium(β) and 5min for indium(β) from sulphate media. And prolonged extraction had no adverse effect (Fig. 3).

Effect of CA-100 concentration

Gallium(β) and indium(β) were extracted with various concentration of CA-100 at appropriate initial pH values (Figs. 4 and 5). As is expected, the percentage extraction of gallium(β) and indium(β) from both media increased with the increasing of the CA-100 concentration. The extraction of gallium(β) and indium(β) were quantitatively extracted with $3.07 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ and $1.53 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ CA-100 respectively from chloride media. And it indicates that gallium(β) and indium(β) were quantitatively extracted when concentration of CA-100 was over 40 and 50 times than that of gallium(β) and indium(β) respectively. Whereas, from sulphate media the extraction of gallium(β) and indium(β) were quantitative with $1.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ and $3.83 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ CA-100 which was 60 and 20 times than concentration of gallium(β) and indium(β) respectively.

Effect of aqueous ionic media

Various tests were carried out in order to determine the influence of the aqueous ionic media on the extraction of gallium(β) and indium(β) by CA-100 (keeping other parameters constant). As seen in Table 1., the effects of Cl^- on percentage extraction of gallium(β) and indium(β) indicate that the extraction of these two elements have almost no change when Cl^- concentration increase in a large wide range, so we proposed that Cl^- can't take part in extraction reaction from chloride media. However, percentage extraction of gallium(β) and indium(β) greatly decreased with increasing of the $\log[\text{SO}_4^{2-}]$ values. This indicates that SO_4^{2-} took part in the extraction reaction.

Proposed extraction mechanism

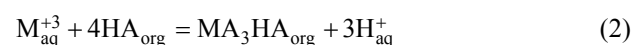
The distribution coefficient for gallium and indium from chloride and sulphate media is defined as

$$D = \frac{[\text{M}]_{(\text{org})}}{[\text{M}]_{(\text{aq})}} \quad (1)$$

org: the concentration of M in the organic phase under equilibrium conditions

aq: the concentration of M in the aqueous phase under equilibrium conditions

The stoichiometries of the complexes of metal ions extracted by CA-100 in kerosene from chloride media were investigated by the slope-analysis method (Figs. 6,7). It was observed that the plot of $\log D$ vs. pH values is linear with slope 2.7 for gallium(β) and 2.9 for indium(β), confirming that three protons were released during a cation exchange reaction. The plot of $\log D - 3\text{pH}$ against $\log[\text{HA}]$ is linear with slope is 3.7 for gallium(β) and 3.8 for indium(β), confirming that four extractant molecules take part in the reaction. And Cl^- doesn't take part in the reaction according to Table 1. Hence the probable extracted species of gallium(β) and indium(β) with CA-100 in kerosene from chloride solution is MA_3HA and the extraction reaction can be expressed as follows:

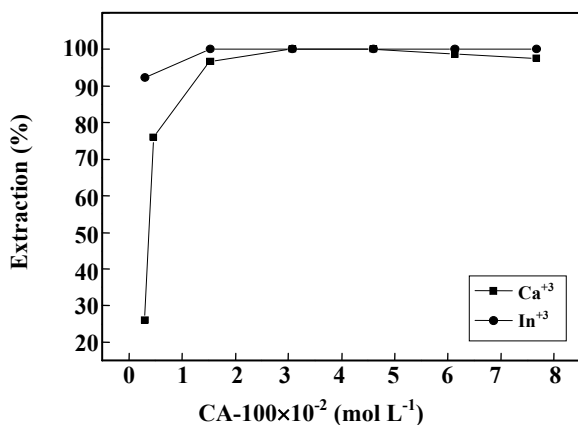
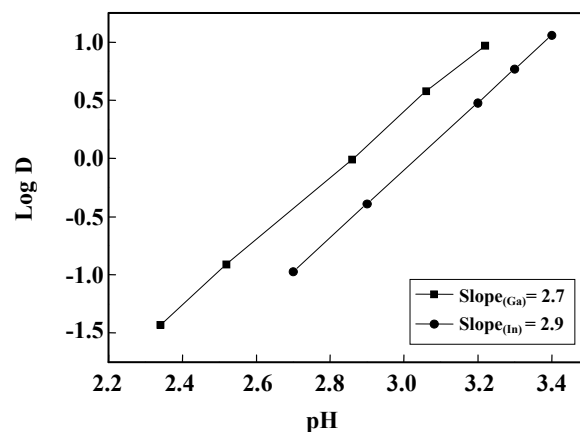
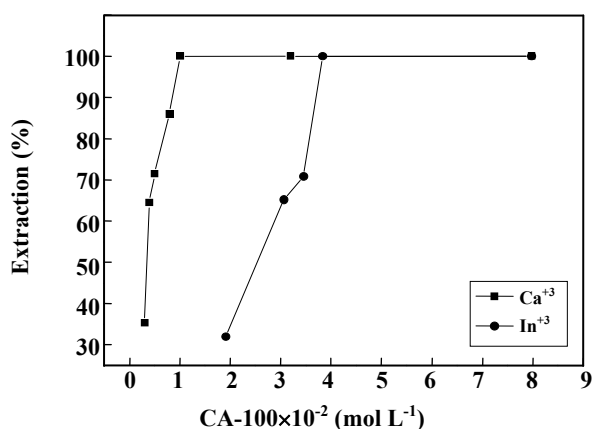
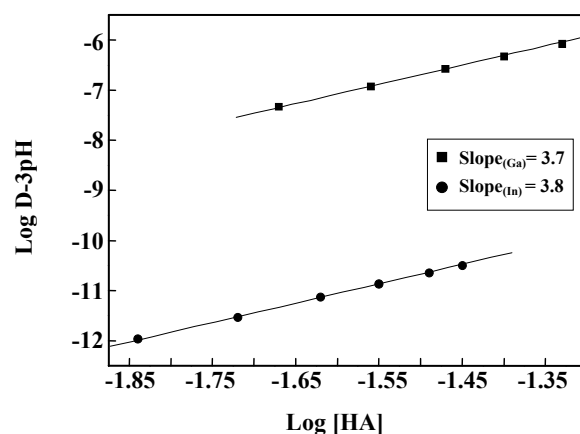


(M: Ga or In, HA:CA-100)

The compositions of extracted species from sulphate media were evaluated by $\log D$ against pH (Fig.8.), $\log D$ against $\log[\text{HA}]$ (Fig.9.) and also $\log D$ against $\log[\text{SO}_4^{2-}]$ (Fig.10.). The slopes were, respectively, 3.1, 3.01 and -0.94 for gallium(β), close to 3, 3, -1; 2.9, 3.3, and -0.91

Table 1: Effect of aqueous ionic media on percentage extraction of gallium(β) and indium(β).

Log[Cl ⁻]	-0.6990	-0.7956	-0.9208	-1.0969	-1.3979
E, %	36.10	36.06	36.12	36.08	36.11
pH 1.00		Ga ³⁺ : $7.80 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$		CA-100: $4.60 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$	
Log[Cl ⁻]	-0.6990	-0.7956	-0.9208	-1.0969	-1.3979
E, %	30.00	30.01	30.05	30.02	30.00
pH 1.00		In ³⁺ : $2.90 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$		CA-100: $4.60 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$	
Log[SO ₄ ²⁻]	-0.6990	-0.7956	-0.9208	-1.0969	-1.3979
E, %	18.31	20.81	26.77	39.76	50.00
pH 3.25		Ga ³⁺ : $1.60 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$		CA-100: $1.00 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$	
Log[SO ₄ ²⁻]	-0.6990	-0.7956	-0.9208	-1.0969	-1.3979
E, %	20.11	22.68	30.08	35.63	51.56
pH		In ³⁺ : $1.610 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$		CA-100: $3.83 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$	

Fig. 4: Effect of CA-100 concentration on percentage extraction of gallium(β) and indium(β) from chloride media (Ga³⁺: $7.80 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, pH 3.00; In³⁺: $2.90 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, pH 4.80).Fig. 6: Relationship between $\log D$ and pH of Ga³⁺ and In³⁺ extracted with CA-100 in kerosene from chloride media (D : the distribution coefficient for gallium or indium, following the same).Fig. 5: Effect of CA-100 concentration on percentage extraction of gallium(β) and indium(β) from sulphate media (Ga³⁺: $1.60 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, pH 3.50; In³⁺: $1.61 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, pH 4.50).Fig. 7: Relationship between $\log D-3\text{pH}$ and $\log[\text{HA}]$ of Ga³⁺ and In³⁺ extracted with CA-100 in kerosene from chloride media.

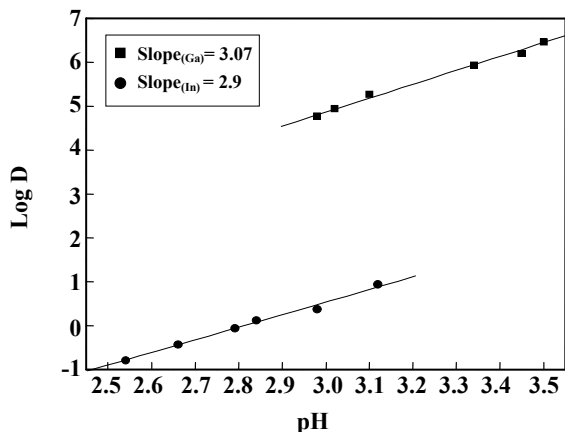


Fig. 8: Relationship between $\log D$ and pH of Ga^{3+} and In^{3+} extracted with CA-100 in kerosene from sulphate media.

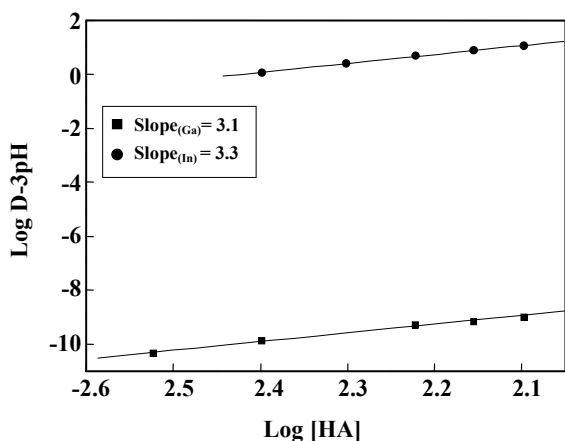


Fig. 9: Relationship between $\log D-3\text{pH}$ and $\log[\text{HA}]$ of Ga^{3+} and In^{3+} extracted with CA-100 in kerosene from sulphate media.

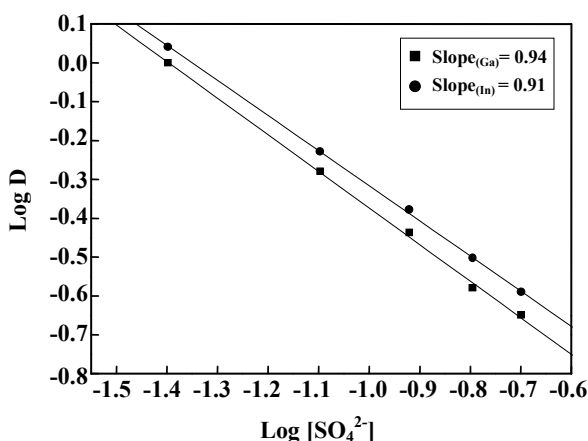
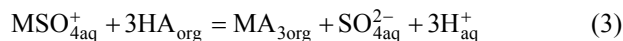


Fig. 10: Relationship between $\log D$ and $\log[\text{SO}_4^{2-}]$ of Ga^{3+} and In^{3+} extracted with CA-100 in kerosene from sulphate media.

for indium(β), close to 3, 3, -1. It confirmed that three protons were released during a cation exchange reaction and three extractant molecules take part in the reaction, in the same time one SO_4^{2-} ion were released. The possible mechanism of extraction from sulphate media can be written as:



(M:Ga or In, HA:CA-100)

To further elucidate the mechanism of the solvent extraction systems, constant molecular series method and saturation capacity method were also used to determine extraction mechanism. The results of constant molecular series method show that at the maximum extraction capacity the molecular proportion of gallium(β) is 0.20 and that of indium(β) is 0.21 from chloride media. And that is 0.27 for gallium(β) and 0.26 for indium(β) sulphate media. That is to say, the balanceable concentration ratio of CA-100 against metal equals 4 for chloride media and 3 for sulphate media. It also validates that extractant molecules taking part in the reaction is 4 and 3 from chloride media and sulphate media respectively. And the results of saturation capacity method from chloride media and sulphate media proved that the ratio of the concentration of CA-100 to the concentration of gallium(β) is 3.32:1 and 3.40:1 and that of the concentration of CA-100 to the concentration of indium(β) is 3.14:1 and 3.22:1 respectively. All the data are close to 3 which indicate that the mole ratio of metal ions to complex is 3:1. The results agree well with that reported using slope-analysis method.

CONCLUSIONS

From the above results it is observed that gallium(β) and indium(β) is extracted with CA-100 in kerosene by a cation exchange mechanism. The extracted species in the organic phase is MA_3HA for chloride media and MA_3 for sulphate media. The behavior of gallium(β) and indium(β) with CA-100 in kerosene from both media are high efficient, for quantitative extraction pH range from chloride media was narrow and the selection was good. However, CA-100 is easily emulsible from chloride media and it is preferred to extract and separate gallium(β) and indium(β) by CA-100 in kerosene from sulphate media.

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