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Solvent extraction determination of metals with high molecular weight secondary amine

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Abstract

In the present work, a high molecular weight secondary amine extractant, N-n-octylcyclohexyl amine was explored for extraction of refractory metals molybdenum, tungsten and lanthanide elements lanthanum and cerium. The effect of acidity, extractant and metal concentration, equilibrium time, aqueous to organic volume ratio, solvents, strippants were studied critically to establish optimum conditions to achieve quantitative extraction of metal ions. The extraction was found to be quantitative with 0.05 M concentration of N-n-octylcyclohexylamine in dichloromethane and xylene (1:4) from acidic media. After back extraction of metals with suitable strippant, they were determined spectrophotometrically.

Keywords: Solvent extraction, Molybdenum (VI), Tungsten (VI), Lanthanum (III), Cerium (IV), N-n-octylcyclohexylamine

1. Introduction

One of the most widely used and popular separation techniques in analytical chemistry is solvent extraction, also known as liquid-liquid extraction. Its simplicity, speed and applicability at tracer and microgram concentrations of metal ions make it popular for analytical separations. Frequently only a separatory funnel is required in the process. It is completed only in few min. The method can be used in a broad range of concentrations. High Molecular Weight Amines (HMWA's), known as liquid anion exchangers, has become increasingly popular in recent years for study of the metal complexes. The solvent extraction with HMWA facilitates the selective transfer of solute molecules between the organic and aqueous phase. Liquid anion exchangers generally consist of primary or secondary or tertiary amines as well as quaternary ammonium ions. As primary amines are having greater solubility, they are used less frequently than secondary amines.

Molybdenum is found in the earth's crust to the extent of 1.2 ppm by weight [1]. It is mostly utilized as a hardening agent in alloys. At least 85% consumption of Mo is for making Iron-base alloys. Addition of molybdenum to alloy steel improve its hardness. When it is added to stainless steel, corrosion resistance, strength at elevated temperature and weldability get improved. Besides this, it is used in a variety of electronic devices, comprising tubes, contacts, electrodes, transducers, transistors and rectifiers. The refractory nature of molybdenum makes it good for certain critical rocket and missile parts [2]. Molybdic oxide and various molybdates are important catalysts and also act as activators and promoters of other catalysts in many petroleum and organic chemical reactions. Molybdenum is important in the life processes of plants and animal.

Tungsten occurs in the earth's crust with an average abundance as $5\times10^{-4}\%$ by weight. Ferrous alloys consume 40% of the tungsten mined. Tungsten improves high temperature strength and hardness when added in iron or steel. Radiation shields are made from high density tungsten-copper-nickel alloys. Many drilling applications are carried by tungsten carbide. The filaments in incandescent lights are the most common application for tungsten. Phosphors include calcium, barium, and magnesium tungstate. Tungsten compounds are applied for making welding rods, X-ray targets, lead wires, power tube cathodes and distributor points for cars and aeroplanes. Tungsten compounds have the potential to be used as primary catalysts or catalyst promoters.

The main sources of minerals of the lanthanides are USA, China, Australia and India. About 5000 tons of La and 13000 tons of the lanthanides are produced annually. Mischmetal (50% Ce, 40% La, 7% Fe, 3% other metals) is added to steel to improve its strength and workability. It is also used in Mg alloys and in small amounts as 'lighter flints. Crooke's lenses use La_2O, which absorbs UV rays to provide protection. Cerium oxide is used as a coating in self-cleaning ovens and to polish glass. Cerium salts are used for both cotton dyeing and qualitative analysis. They serve as catalysts as well. Cerium oxides are utilized in gas mantles. Colour TV tubes use different lanthanide oxides as phosphors [2].

The literature survey reveals the use of N-n-octylcyclohexyl amine for extraction, separation of some metals. Micro amounts of Pb(II) was determined by using N-n-octylcyclohexyl amine where a neutral complex with formula $[\text{N-n-OCAH}^+\text{PbCl}_3^-]$ was formed in hydrochloric acid medium. The metal: Chloride: Extractant species found on slope analysis method was 1:3:1 [3]. An extractive determination of Cd(II) with N-n-octylcyclohexyl amine was extended for analysis of diverse ions, binary separations, multicomponent mixtures, alloy samples and separation of Cd(II) cigarette tobacco sample [4]. A concentration range of 0.4 M-0.7 M hydrochloric acid quantitatively extracts Cr(VI) with 0.05 M N-n-octylcyclohexyl amine in xylene. The proposed method is having relative standard deviation of 0.09 with respect to calibration range of 0.2 to 0.8 $\mu g\ mL^{-1}$ [5]. The sequential separation of Se(IV) and Te(IV) with N-n-octylcyclohexyl amine extractant was carried out by a procedure based on difference in acidity. The study of thermodynamic functions in the extraction, indicates endothermic reaction process and increase in percentage extraction with increasing temperature [6]. N-n-octylcyclohexyl amine was used for solvent extraction of Ge(IV) from 8.4 M - 9.6 M hydrochloric acid medium. The loading capacity of reagent towards Ge(IV) was observed to be 0 to 3 mg [7]. The extraction of Hg(II), Tl(III) with N-n-octylcyclohexyl amine from hydrochloric acid medium was reported [8].

In the present work, we report the use of N-n-octylcyclohexyl amine as an extractant for refractory metals such as molybdenum and tungsten and lanthanide elements such as lanthanum and cerium.

2. Experimental

2.1 Apparatus

The absorbance study was done using a Systronics digital spectrophotometer model 104 with 1cm quartz cells while Systronics pH-meter model 802 was used for pH measurements. An analytical balance with 0.001 gm accuracy was used to carry weighing operations.

2.2 Reagents

2.2.1 Preparation of extractant

The extractant was prepared by refluxing one mole of cyclohexyl amine and one mole of bromooctane in presence of solvent acetonitrile at room temperature with constant stirring for 3 hours [9].

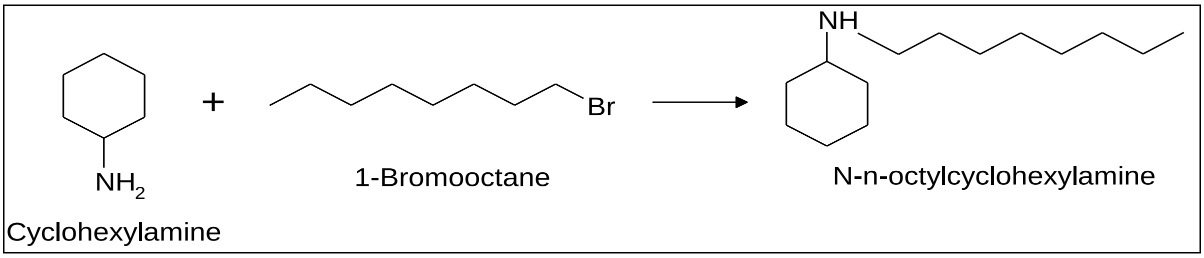

Fig 1: A 0.05 M solution of the extractant N-n-octylcyclohexylamine was prepared in dichloromethane and xylene (1:4)

2.2.2 Metal ion solutions

- **Molybdenum (VI) solution:** Exactly 1.838 g of ammonium heptamolybdate (A.R. grade) was dissolved in 1000 mL of double distilled water with a few milliliters of ammonia solution to prepare a stock solution (1 mg/mL) of Mo(VI), which was then standardized using the oxine [10] method.
- **Tungsten (VI) solution:** Exactly 1.790 g of sodium tungstate (A.R. grade) was dissolved in 1000 mL of double distilled water to prepare a stock solution (1 mg/mL) of W(VI). Reported gravimetric method was used to standardize W(VI) solution [11].
- **Lanthanum (III) solution:** Exactly 1.173 gm of lanthanum oxide was dissolved in 5 mL hot hydrochloric acid (1:1) and diluted to 1000 mL with distilled water to prepare a stock solution (1 mg/mL) of La(III) and then standardized [10].
- **Cerium (IV) solution:** Exactly 4.275 g of ceric ammonium sulphate was dissolved in 1 L water containing 2 mL of concentrated sulphuric acid to give 1 mg/mL of Ce(IV) stock solution which was standardized titrimetrically [11].
- The working solutions of metal ions were prepared by appropriate dilution and used throughout the experimentation.

2.2.3 Other reagents

The solutions of stannous chloride dihydrate (7%, 10%) were prepared in 1 M hydrochloric acid. 10% and 20% Solutions of potassium thiocyanate were prepared in double distilled water. 1% Ferrous ammonium sulphate solution was prepared by dissolving in double distilled water. Triethanolamine, 200 mL of 15% (W/V), is mixed with 160 mL of 1 M nitric acid and 40 mL of water, adjusted pH 7.2 (± 0.1) with dilute ammonia and nitric acid to produce a Triethanol amine buffer solution (pH 7.2). The aqueous solution of Arsenazo I (0.05% W/V) was prepared and used for the spectrophotometric determination of La(III). Acetate buffer (pH 3.42**)** was prepared by taking 190 mL of 0.2 M acetic acid and then mixing with 10 mL of 0.2 M sodium acetate solution. The aqueous solution of Arsenazo III (0.05%) was prepared and used for the spectrophotometric determination of Ce(IV) as a chromogenic reagent.

3. Solvent extraction determination procedure for metal ions

3.1 Solvent extraction of Molybdenum (VI)

An aliquot of solution containing 40 µg of Mo(VI) was mixed with hydrochloric acid to give final concentration of 1.5 M in a total volume of 10 mL. The solution was then transferred to a 125 mL separatory funnel and shaken for 5 min with 10 mL of 0.05 M of N-n-octylcyclohexylamine in dichloromethane and xylene (1:4). The organic phase was separated and equilibrated with three 10 mL portions of 1 M ammonia solution to back extract Mo(VI). The back extractants were combined and shaken with 5 mL of xylene to remove the traces of dissolved amine and used to determine Mo(VI) as follows: The aqueous phase was neutralized by the addition of 2 mL concentrated hydrochloric acid, followed by the addition of 1 mL of 1% ferrous ammonium sulphate and 3 mL of 10% potassium thiocyanate solution. After mixing 3 mL of 10% stannous chloride was added and solution was diluted to 25 mL with doubly distilled water. The red colored Mo-thiocyanate complex was extracted with 10 mL of isoamyl alcohol by shaking for 30 s. The two layers were allowed to settle and organic layer was separated and dried with anhydrous sodium sulphate and absorbance was measured at 470 nm against blank prepared in the similar manner [12]. The amount of Mo(VI) was computed from a calibration curve.

3.2 Solvent extraction of Tungsten (VI)

An aliquot of solution containing 200 µg of W(VI) was mixed with hydrochloric acid to give the final concentration of 0.1 M in a total volume of 10 mL. The solution was transferred into 125 ml separatory funnel and shaken for 5 min with 10 mL 0.05 M N-*n*-octylcyclohexylamine in dichloromethane and xylene (1:4). The organic phase was separated and equilibrated with two 10 mL portions of 1 M ammonia to back extract W(VI). The back extracts were combined and shaken with 5 mL xylene to remove the traces of dissolved amine.

The back extractants were evaporated to moist dryness and the residue was leached with water, followed by addition of 1 M hydrochloric acid, 0.8 mL 20% potassium thiocyanate and 6 mL of 7% stannous chloride solution. It was made 10 mL using standard volumetric flask and diluting with double distilled water. After 15 min the complex was extracted with 10 mL methyl isobutyl ketone (MIBK). The two layers were allowed to settle and the organic layer was separated and dried over anhydrous sodium sulphate. The absorbance was measured at 400 nm against the reagent blank prepared in the similar manner [12].

3.3 Solvent extraction of Lanthanum (III)

An aliquot of solution containing 200 µg of La(III) was used for all the experimental studies. The aqueous phase containing La(III) was maintained at 0.0075 M sodium succinate and pH was adjusted to 13.0 with dilute hydrochloric acid and sodium hydroxide solution, diluted to 25 mL and transferred to 125 mL separatory funnel. A 10 mL of 0.05 M N-*n*-octylcyclohexylamine in dichloromethane and xylene was added to the funnel, equilibrated for 5 min and the two phases were allowed to separate. La(III) from the organic phase was stripped with 0.5 M acetic acid (3 × 10 mL). La(III)-containing stripped solution was evaporated to wet dryness and added with water. To this solution 2 mL of 0.05% arsenazo I was added, the pH was adjusted to 7.2 (± 0.1) by adding 5 mL of triethanolamine buffer solution. The absorbance was measured at 575 nm using the reagent blank solution [12].

3.4 Solvent extraction of Cerium (IV)

An aliquot containing 50 µg of Ce(IV) was transferred into a 125 mL separatory funnel. A sodium succinate (0.0075 M) was added in aliquot and pH was adjusted to 6.0 with dilute hydrochloric acid and sodium hydroxide solution by maintaining the total volume of 25 mL. Then the aliquot was shaken for 5 min with 10 mL of 0.05 M N-n-octylcyclohexylamine in xylene. After separation of two phases, Ce(IV) was stripped from organic phase by shaking with three 10 mL portions of 0.5 M acetic acid. Ce(IV) content in stripped phase was determined spectrophotometrically by using Arsenazo III method at λmax = 660 nm [12].

4. Results and Discussion

4.1 Effect of acidity

The liquid-liquid extraction studies of Mo(VI) and W(VI) were carried out from different hydrochloric acid concentrations with 10 mL of 0.05 M N-n-octylcyclohexylamine. Hydrochloric acid is the acid, forming stable ion-pair complex with Mo(VI) or W(VI). It was found that extraction of Mo(V) was quantitative in the hydrochloric acid concentration range of 1.0 M to 2.5 M and that of W(VI) is 0.075 M-1.0 M. Further extraction studies of Mo(VI) were carried out by using 1.5 M hydrochloric acid and that of W(VI) by using 0.1 M concentration of acid.

Extraction studies of La(III) and Ce(IV) were carried out from different concentrations of sodium succinate with extractant. The quantitative extraction of La(III) as well Ce(IV) occurs in the range of 0.006 M to 0.008 M sodium succinate. A concentration of 0.0075 M was maintained throughout the study. For extraction of La(III) and Ce(IV), the pH study from pH 1 to 14 shows quantitative extraction in pH range 12.0-13.5 for La(III) and 5.0-6.5 for Ce(IV) respectively at fixed succinate concentration. A pH of 13.0 and 6.0 was maintained for La(III) and pH 6.0 for Ce(IV).

4.2 Effect of extractant concentration

Required concentration of N-n-octylcyclohexylamine for quantitative removal of metal ions from aqueous phase was studied in the range of 0.01 M-0.1 M concentration of N-n-octylcyclohexylamine. The extraction of metals was found to be quantitative in the range of 0.04 M-0.07 M. A concentration of 0.05 M was kept throughout the study for ensuring complete extraction.

4.3 Effect of equilibrium period

Extraction of ion-pair complex was quantitative with equilibrium time of 2-7 min. To ensure complete extraction, 5 min period was recommended. After 7 min, the percentage extraction decreases due to breakdown of ion-pair complex.

4.4 Effect of aqueous to organic volume ratio

A study of variation of aqueous to organic phase volume ratios from 1:1 to 10:1 showed ratio of 1:1 showed quantitative extraction for Mo(V) and W(VI) and ratio of 2.5:1 for La(III) and Ce(IV) respectively.

4.5 Effect of solvent:

Extraction of each of the metals with 0.05 M N-n-octylcyclohexylamine was studied with solvents like benzene, xylene, toluene, chloroform, dichloromethane, kerosene, amyl acetate, amyl alcohol. The extractant was primarily found to be partially soluble in most of solvents. It is soluble in dichloromethane. The percentage of extraction found with 0.05 M concentration of N-n-octylcyclohexylamine in dichloromethane is much less. But when N-n-octylcyclohexylamine was dissolved in minimum quantity of dichloromethane and diluted with xylene at ratio of 1:4, quantitative extraction of metals occurs. The other diluents like benzene, toluene, chloroform, amyl acetate, amyl alcohol, n-butanol showed incomplete extraction.

4.6 Strippant study

The various concentrations of acids and bases were tested for stripping of metal ions from loaded organic phase. Among the strippants like nitric acid, ammonia, potassium hydroxide, sodium hydroxide, acetic acid, only ammonia gave quantitative stripping of Mo(VI) and that for W(VI) with three 10 mL portions of 1 M ammonia. The back stripping of La(III) or Ce(IV) occurs with three 10 mL portions of 0.5 M acetic acid.

4.7 Extractant loading capacity

The maximum loading capacity of extractant for 10 mL 0.05 M solution in dichloromethane-xylene at 1.5 M hydrochloric acid was found to be 75 µg of Mo(VI) and 300 µg of W(VI) at 0.1 M hydrochloric acid. The metal loading capacity of extractant from succinate media was found to be 250 µg of La(III) and 60 µg of Ce(IV) respectively.

Table 1: Summarizes the extraction conditions of metalions

Metalion	Extractant	Acid	Metalion	Eq. period	Aq: Org volume ratio	Strippant
Mo(VI)	0.05 M N-n-Octylcyclohexylamine in Dichloromethane-xylene	1.5 M HCl	40 µg	5 min	1:1	1 M ammonia
W(VI)		0.1 M HCl	200 µg			
La(III)		0.0075 M Sodium succinate	200 µg		2.5:1	0.5 M Acetic acid
Ce(IV)		0.0075 M Sodium succinate	50 µg			

Conclusion

The extractant N-n-octylcyclohexylamine extracts refractory metals, Mo(VI) and W(VI) and lanthanide elements, La(III) and Ce(IV). The quantitative extraction Mo(VI) and W(VI) was achieved by using hydrochloric acid medium while La(III) and Ce(IV) quantitatively extracted from succinate media. Low reagent concentration is required for quantitative recovery of metal ions. The developed methods are very simple, selective, reproducible and rapid; requires less time for separation and determination.

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