

Solvent Extraction of Metals Using Chelating Extractants

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Introduction:

Solvent extraction enjoys a favored position among the separation techniques because of its ease, simplicity, speed and wide scope. A further advantage of the extraction methods over widely used precipitation methods lies in the cleaner separations. The extraction of metal chelates plays an important role because of its speed, versatility, simplicity and selectivity. The amount of metal separated can be determined by some standard technique. Recently a number of hydrometallurgical routes have emerged as potential methods for the processing of lean grade ores and reserves. The ammonia leaching system is a preferred one amongst them, the reason being, in most of the cases iron, manganese etc., are rejected and the desired elements such as nickel, copper and cobalt are present in the leach liquor following amine complexing.

Due to inadequate reserves of strategically important metals in India, priority has always been given to the search of new resources. The polymetallic sea nodules available in Indian Ocean constitute one such untapped reserve which could meet the country's requirements for unlimited period for cobalt, nickel and copper, if they are processed economically in future.

Literature Review:

In the recent years the use of hydroxyoxime type extractants in solvent extraction processes for base metals, particularly for copper from acid leach liquors, has been described in the literature [1]. Less attention has been paid to their application to other metals and to ammoniacal media.

Chelating extractants are those which contain two or more donor groups capable of forming complexes with metal ions. Although such reagents have been used in analytical and inorganic chemistry in the past, they have been far expensive for use on industrial scale.

During the last decade the commercial availability of copper selective chelating reagents, as extractants in solvent extraction processing of copper containing leach liquors, has provided a particular stimulus to use of solvent extraction as a hydrometallurgical process. Commercially available chelating extractants are, at present limited to the following types a series of substituted 2-hydroxy benzophenone oximes (ACORGA), substituted 2-hydroxy acetophenone oximes (SME) and substituted 8-hydroxy quinolines (KELEX). Most of the above extractants were developed for the specific extraction of copper from acidic leach liquors as well as from alkaline solutions.

Recently the range of chelating extractants has been extended by the introduction of reagents from shell, SME-529 (2-hydroxy 5-nonyl acetophenone oxime) and Acorga, who market P-17 (2-hydroxy 5-nonyl benzoylphenone oxime) and P-1 (2-hydroxy 5-nonyl benzaldehyde oxime).

Nyman and Hummelstedt have studied the extraction of nickel and cobalt from acidic media with hydroxyoximes [2] and published a flow sheet based upon a mixture of LIX-70, Versatic 911 and Dinonylnaphthalenesulphonic acid. Hummelstedt and co-workers have also investigated the chemistry of nickel and cobalt extraction from acidic media with mixtures of KELEX-100 and Versatic 911 [3].

Flett and West have investigated the extraction of nickel at low pH by mixture of LIX-63 and carboxylic acids [4] and have reported very slow stripping kinetics, a phenomenon studied further by Flett, Cox and Heels [5]. However, little has been published on the chemistry of nickel

extraction from ammoniacal media especially under conditions of practical leaching processes where relatively high metal loading and high ionic strength exists, eg. Sherrit Gordon Process [6] where ammonium sulphate concentrations upto 4 mol dm⁻³ can be encountered.

Characteristics which make SME-529 a better extractant than LIX-64N have already been reported in the literature [7]. Extraction of copper does not show appreciable change with the variation in the pH of aqueous solution. Nickel extraction of 10% SME-529 vary significantly with pH, the higher extraction takes place at lower ammonia content of the solution. SME-529 extracts copper in preference to nickel from their mixed solutions leaving cobalt (III) in the raffinate. Co-extraction of nickel and copper by SME-529 and their selective stripping with precise control of acid content in the electrolyte is a possible option to separate these metals from ammoniacal leach liquor of sea nodules.

Experimental work:

The experimental work is divided into three parts;

- 1) Preparation and characterization of chelating extractants
- 2) Analysis of metal uptake by the extractants and
- 3) Study of preference of extraction of metal from the mixture of different metals.

ISSN 0976-9714

1) Preparation and Characterization of Chelating Extractants:

The chelating extractants chosen for the present study were basically o-hydroxyoximes. They were prepared first by Friedel Craft's reaction followed by oxime formation.

All the chelating extractants prepared were basically o-hydroxyoximes. All the chelating extractants were prepared by preparing the corresponding ketone first and then oximating it with hydroxylamine hydrochloride. The ketones were prepared by Friedel Craft's Acylation of corresponding phenol and different acyl halides. The catalyst used is a Lewis acid. Since the well known Lewis acid i.e. Aluminium chloride (AlCl₃) did not give satisfactory results, therefore another Lewis acid viz., Zinc chloride (ZnCl₂) was used. This catalyst gave the desired products in lesser time and also, the yield was comparatively better than previous time when other catalyst was used.

Synthesis of 2-Hydroxy 5-Nonyl Benzophenone 1:

Scheme 1:

A mixture of p-nonyl phenol (0.02 moles, 5 ml), benzoic acid (0.03 moles, 4 gms), fused zinc chloride (0.11 moles, 15 gms) and phosphorus oxychloride (40 ml) was stirred at room temperature under anhydrous conditions for 24 hours and then poured over ice with stirring. The brownish oily product was extracted with ether, washed with water and dried over anhydrous sodium sulphate. The extract was evaporated to give colourless solid. The product **1** obtained was purified by crystallization using petroleum ether, (4gms, 78%). Melting Pt-110° C. I.R, >C=O (1760 cm⁻¹), -OH (3000 cm⁻¹).

Synthesis of 2-Hydroxy 5-Nonyl Benzophenone Oxime 2:

Scheme 1:

A mixture of 2-hydroxy 5-nonyl benzophenone (0.02 moles, 5gms) sodium acetate (0.05 moles, 4gms), hydroxylamine hydrochloride (0.11 moles, 7gms) and pyridine (0.06 moles, 5 ml) was refluxed in ethanol (35 ml) with constant stirring for 31 hours. Then the reaction mixture was poured into crushed ice and acidified with concentrated hydrochloride acid till pH was around 6.

It was then extracted with ether, washed with water and dried over anhydrous sodium sulphate. The extract evaporated to give shiny needles. The product **2** thus obtained was purified by crystallization using petroleum ether and dried in vacuum to yield (4.5gms, 85.71%) of the product. M. Pt- 116°C. I.R.: >C=N (1700 cm⁻¹), -OH (3000 cm⁻¹).

Synthesis of 2-Hydroxy 5-Nonyl Acetophenone 3:

Scheme 2:

A Mixture of P-nonyl phenol (0.02 moles, 5 ml), Acetic acid (0.03 moles, 2.1 ml), fused zinc chloride (0.11 moles, 15 gms) and phosphorous oxychloride (40ml) was stirred at room temperature under anhydrous conditions for 24 hours and poured over ice with stirring. The brownish oily product was extracted with ether, washed with water and dried over anhydrous sodium sulphate. The product **3** thus obtained was purified by column chromatography (ethyl acetate : pet ether, 5%) and dried in vacuum to yield (4 ml, 74.5%) of the product. Boiling Pt - above 200°C.

I.R.: >C=O (1700 cm⁻¹), -OH (3000 cm⁻¹), NMR: (60 MHz, CDCl₃), -COCH₃ (2.2 d, 3H-singlet).

ISSN 0976-9714

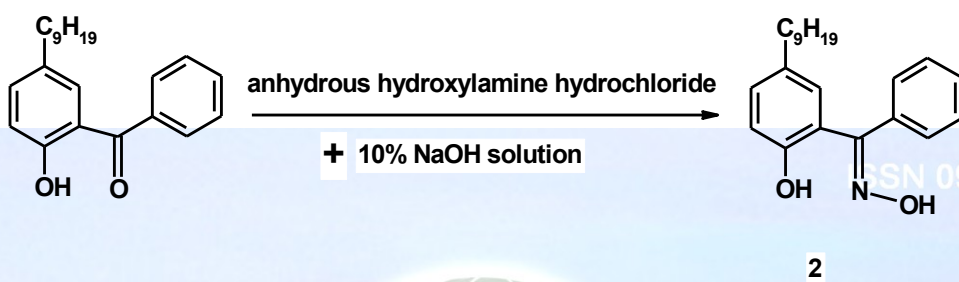
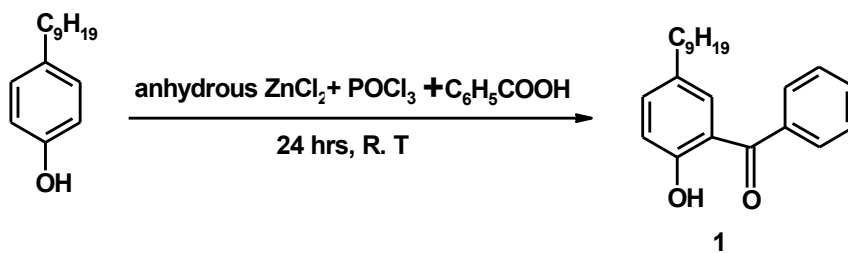
Synthesis of 2-Hydroxy 5-Nonyl Acetophenone Oxime 4:

Scheme 2:

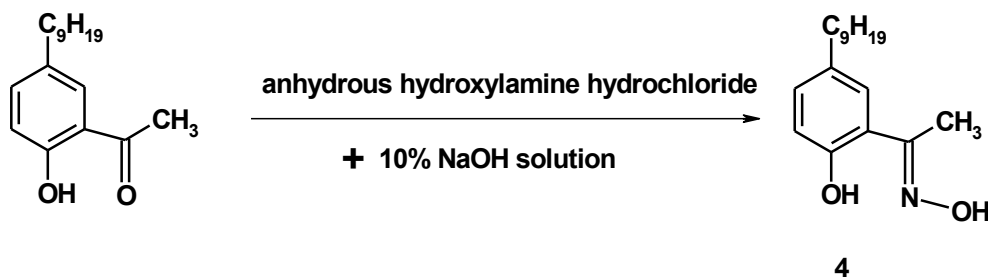
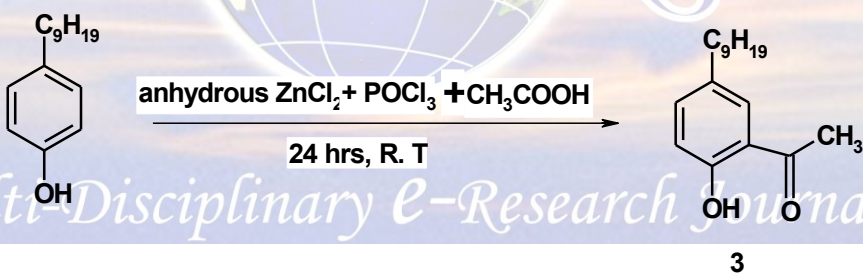
A mixture of 2-hydroxy 5-nonyl acetophenone (0.02 moles, 3 ml), ethanol (50ml), water (50ml) and hydroxylamine hydrochloride (0.11 moles, 7 gms) was stirred at a low temperature (below 30°C) for half an hour. Then 10% sodium hydroxide solution (0.125 moles, 25 ml) was added drop wise so as to keep the temperature below 30°C and was stirred for 4 hours. The reaction mixture was poured in ice and acidified with concentrated hydrochloric acid to obtain a pH of 6. It was then extracted with dichloromethane, washed with water and dried over anhydrous sodium sulphate. The extracted was evaporated to give reddish brown viscous liquid and dried in vacuum to yield product **4** (3.2 gms, 95%) of the product. B.P.-above 200°C. I.R.: >C=N (1700 cm⁻¹), -OH (3000 cm⁻¹).

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Scheme 1:



Scheme 2:



Analysis of Metal Uptake by the Extractants:

The chelating extractants characterized by different spectroscopic methods for their structure and purity were tested for the metal extraction by chelate formation. Due to inadequate reserve of strategically important metal in India. Priority has been always given to the search of new resources. The polymetallic sea nodules available in Indian Ocean constitute on such untapped reserve which could meet the country's requirements for unlimited period for nickel, copper and cobalt if they are processed economically in future. The non ferrous metals which are abundant in the manganese sea nodules are cobalt, copper and nickel. The salts of these were taken individually as well as in the mixture from in various composition and concentration. The extractants used were dissolved in kerosene (B.P range 273-285 °C) which had aromatic content (as tested by reduction by hydrogenation method) of about 25%. The concentration of the extractant taken was 1% wt/vol throughout the analytical experiment.

Study of Preference of Extraction of Metal from the Mixture of Different Metals:

2-Hydroxy 5-nonyl benzophenone oxime (LIX-65N) was found to extract preferentially cobalt and then copper. Cobalt once extracted by the chelating extractant can not be stripped easily. Cobalt is in the cobaltous state (II) in the aqueous phase. It's extraction by the extractant can be prevented by oxidizing it to cobaltic state (III) by passing air into the aqueous phase. Cobalt (III) is thus left in the raffinate as it cannot be extracted. This is required to be done since there are greater chances of cobalt occupying most of the extractant positions, resulting in the low extraction of copper and nickel.

2-Hydroxy 5-nonyl acetophenone oxime (SME-529) was found to have good extraction capacity than 2-hydroxy 5-nonyl benzophenone oxime (LIX-65N). The equilibrium time for SME-529 was less (2mins) as compared with that of LIX-65N (10 mins). SME-529 extracted the metals more quantitatively than LIX-65N. This can be explained on the basis of the presence of two aromatic rings and easy dimerization of both the isomers of LIX-65N due to hydrogen bonding. In the case of SME-529, presence of methyl group at the ortho position to the hydroxyl group prevents easy dimerisation of the two isomers and results in better extraction of the metals as compared with the LIX-65N.

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In loving memory of my beloved guide Mr. K. D. Deodhar

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