NOVEL SYNTHESIS, CHARACTERIZATION OF
N-*n*-octylcyclohexylamine (N-*n*-OCA) AND APPLICATIONS

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ABSTRACT:

The reagent N-*n*-octylcyclohexylamine(N-*n*-OCA) high molecular weight amine using cyclohexylamine and octyl bromide in acetonitrile at room temperature. The synthesized N-*n*-Octylcyclohexylamine (N-*n*-OCA) is characterized by NMR spectrum and GC- MS data. The N-*n*-octylcyclohexylamine used as analytical extractant for the extraction, separation and determination of Cr(VI), Cd(II) and Pb(II). N-*n*-OCA is an ion-pair reagent forming a neutral complex. The optimum extraction conditions were determined from a critical study of effect of acid, concentration of N-*n*-OCA, equilibrium time, study of solvents, loading capacity, and stripping. Stoichiometry of the extracted ion-pair complex determined by slope ratio method.

Keywords: Synthesis of N-*n*-OCA; Characterization of N-*n*-OCA.

SOLVENT EXTRACTION BY HIGH MOLECULAR WEIGHT AMINES:

Amines are one of the most commonly known classes of solvent extraction technology, having been used industrially for the recovery of many metals. Organic solutions of high molecular weight amines and amines salts have been shown to be excellent extractant for mineral acids, many organic acids and complex metal acids from aqueous solutions. The analytical radio chemist and process development chemist have been found the technique valuable for a wide verity of separations.

Smith and page [1] first reported that the acid binding properties of high molecular weight amines and amines depend on fact that acid salts of these bases are, in general, essential insoluble in water but rapidly soluble in organic

solvents, such as chloroform, xylene, toluene, kerosene or 1,2-dichloroethane. The extraction reactions are of the following ion association type.

[1] The organic solvent containing amines can extract an a aqueous acid to form an amine salt in the organic phase:

$$[RR'NH]_{(org)} + H^+_{(aq)} + A^-_{(aq)}\square \quad [RR'NH_2^+A^-]_{(org)} \tag{1}$$

Where,

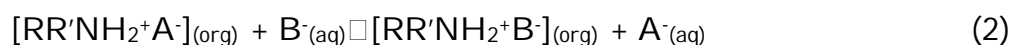RR'NH = A high molecular weight secondary amine.

A⁻ = Anion of either a single acid or a complex metal acid.

aq = Aqueous phase.

org = Organic phase.

In alkaline solution, the extraction is reversed.

[2] An amine salt in the organic phase can undergo anion exchange with an ion in the aqueous phase:
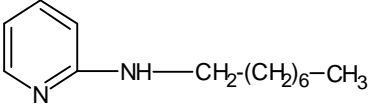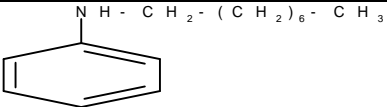
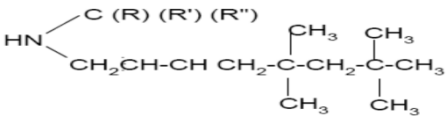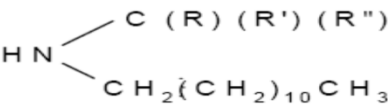$$[RR'NH_2^+A^-]_{(org)} + B^-_{(aq)}\square[RR'NH_2^+B^-]_{(org)} + A^-_{(aq)} \tag{2}$$
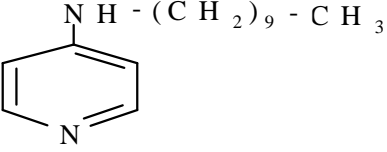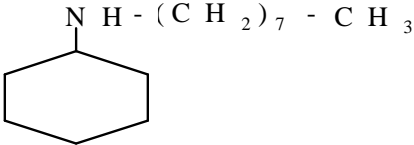
The order of reference in the amine organic solution is similar to that in anion exchange resin- ClO_4^- ・ NO_3^- ・ Cl^- ・ HSO_4^- ・ F^- [2].

The high molecular weight amines are often referred to as "liquid anion exchangers". In general, a strongly analogy has been found between liquid anion exchanger in liquid-liquid extraction with high molecular weight amines and solid anion exchange resin. The ion exchange resins in solid form packed in column have been employed in various separations containing bases. However, this separation suffers from several limitations, in short cycle, back wash requirement of fixed bed is a problem so. Also the dilution phenomenon the loss of reagent, the avoid volume in the interstices of bed of solid ion exchange also create difficulty. On the converter, in the solvent extraction with high molecular weight amine all difficulty associated with the use of ion exchange mitigated, the solvent extraction with high molecular weight amines facillated selective transfer of solute between the organic and aqueous phase. The organic phase containing high molecular weight amine is completely anhydrous in contrast to the useful ion exchange resin. The latter are normally highly hydrated during the process.

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The most common liquid ion exchange, high molecular weight secondary amines used for solvent extraction [3-8] study of metal as listed as follow.

The common high molecular weight secondary amines

| Sr. No	Secondary amine	Amine structure
1	2-Octylaminopyridine (2-OAP)	
2	N-*n*-octylaniline	
3	Amberlite LA-1 [N-dodecyl(trialkylmethyl) amine]	
4	Amberlite LA-2 [N-lauryl(trialkyl-methylamine)]	
5	N-*n*-decylaminopyridine	
6	Adogen 283	$C_{26}H_{55}N$
7	N-*n*-octylcyclohexylamine (N-*n*-OCA)	

METHODOLOGY:

Chemicals:

Cyclohexylamine[s. d. fine-chem, A. R grade], acetonitrile (s. d. fine-chem), octyl bromide (s. d. fine-chem), acetone, dichloromethane (DCM) and xylene, are used in the synthesis of N-*n*-octylcyclohexylamine.

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Synthesis of N-*n*-octylcyclohexylamine (N-*n*-OCA):

Cyclohexylamine (10 mL, 8.65 mole) and octyl bromide (10 mL, 11.18 mole) were mixed in 20 mL acetonitrile at room temperature. The reaction mixture was warmed and stirred for 2 h. The amorphous white product was precipitated. The product was filtered through Whatmann filter paper no 1 and washed with acetone. The compound was dried and weighed [2].

Cyclohexylamine   Octyl bromide

Room temp

(3)

N-*n*-octylcyclohexylamine (N-*n*-OCA)
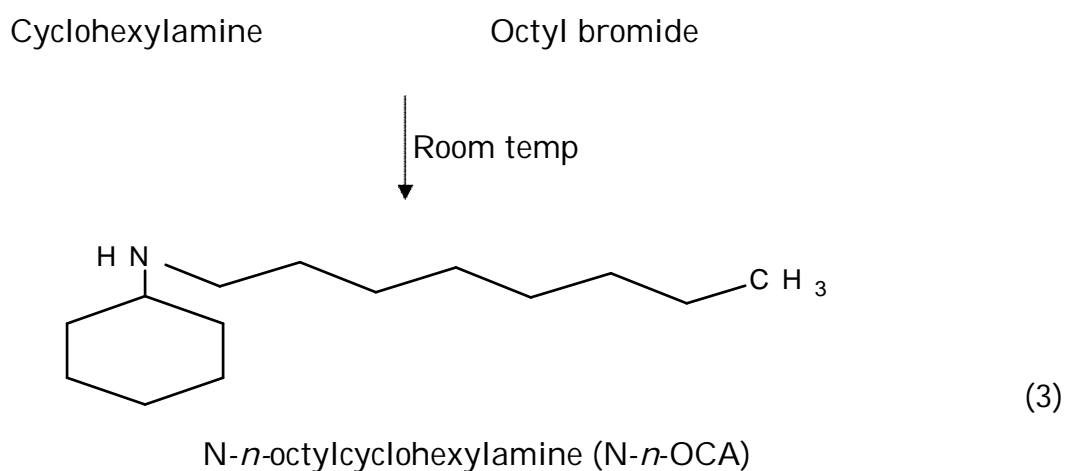
Characterization of N-*n*-octylcyclohexylamine:

The percentage yield of N-*n*-octylcyclohexylamine is 75 and melting point of reagent is 188-195°C.

Thin layer chromatography (TLC):

Thin-layer chromatography technique is used to monitor the reaction. In TLC, spot of reactant and reaction mixture were made on TLC plate. It was run in dichloromethane (DCM) and placed in UV chamber after drying, the formation of single spot on reaction mixture side clearly indicates the formation of product N-*n*-octylcyclohexylamine (Fig. 1) which was confirmed further by spectral analysis.

UV-VIS Absorption spectra:

The absorption spectrum of N-*n*-OCA in xylene showed that the N-*n*-OCA exhibit sharp absorption spectra at λ_{max} 350.0 and 355.0 nm (Fig. 2).
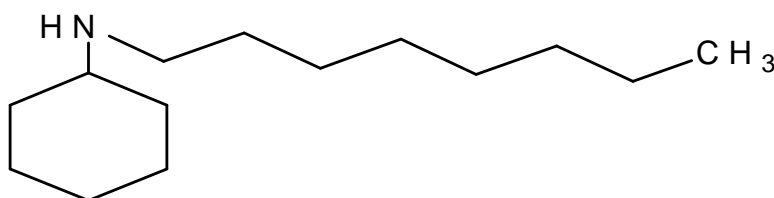
GC- MS data spectra:

Finally the structure of the reagent was confirmed by GC-MS analysis which is in good agreement with the proposed structure. Molecular peak at 211 clearly showed that formation of desired product by condensation reaction at room temperature (Fig. 3).

NMR Spectrum of N-*n*-octylcyclohexylamine:

The ^{1}H NMR spectrum of N-*n*-octylcyclohexylamine exhibited a triplet at δ 0.893 due to methyl proton of n-octyl side chain. The singlet appeared at δ 8.86 confirmed the presence of -NH proton. The presence of twelve methylene group protons appeared as multiplet in the range of δ 1.25 - 3.03(Fig. 4).

The molecular structure of N-*n*-octylcyclohexylamine is given as below,

Figures

Fig. 1 Thin-layer chromatography(TLC) of N-*n*-octylcyclohexylamine
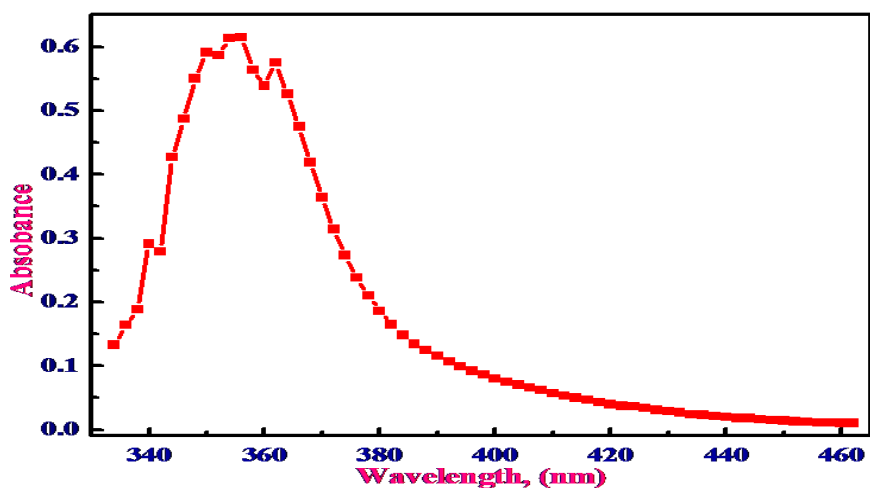
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Fig. 2 UV-VIS Absorption spectra of N-*n*-octylcyclohexylamine (0.001 M)
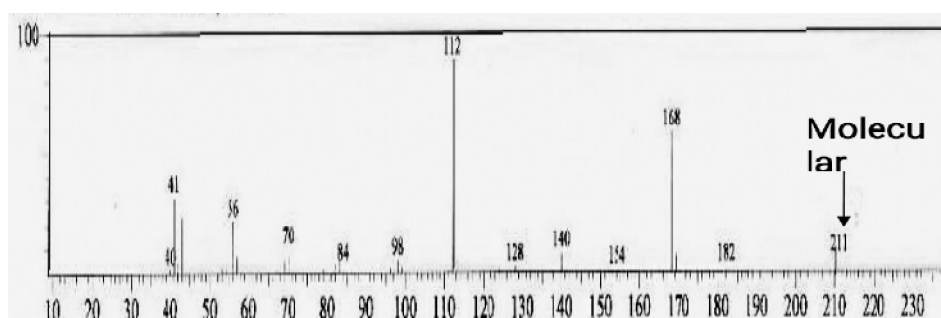
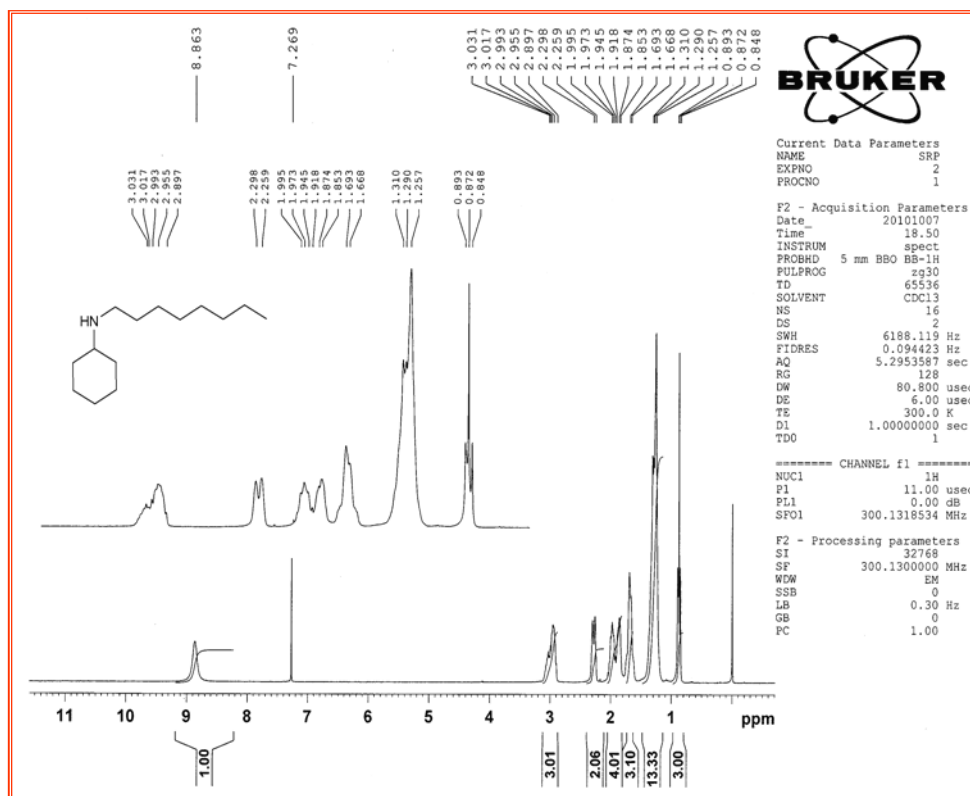
Fig. 3 GC- MS data spectra of N-*n*-octylcyclohexylamine

Fig. 4 NMR Spectrum of N-*n*-octylcyclohexylamine

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The previously reported solvent extraction methods of mercury(II):

Solvent extraction is one of the most important and widely used selective method for the separation of mercury(II) from different aqueous solutions. Recently, high molecular weight amines (HMWA) have considered being as powerful extractant for separation and extraction of many elements. The extraction separation and determination of mercury(II) using high molecular weight amine extractants is well known reported methods. Liquid-liquid extraction and separation of mercury(II) with succinate media from 2-octylaminopyridine (2-OAP) [9] in chloroform at pH 9.5 was reported. The solvent extraction of mercury(II) by using n-octylaniline [10] in chloroform with hydrochloric acid medium has been carried out. The extracted organic phase of mercury(II) was stripped with 1.5 M ammonia and estimated complexmetrically with EDTA using eriochrome-black-T as an indicator. The selective extraction of mercury(II) from aqueous solution with 2-chloroacetamide [11] in dimethylformamide (DMF) as a solvent has been investigated. The quaternized resin [poly(4-vinyl pyridine)] can be regenerate by stripping of the sorbed mercury(II) with hot acetic acid. Liquid-liquid extraction of mercury(II) by tertiary amines, trioctylmethylammonium chloride (aliquat 336) [12] was the efficient anion exchanger for mercury(II) with halide silver nitrate media [13]. The selective separation of mercury(II) from various metal ions using aliquat 336-S [14] with acetic acid solution has been given. Liquid-liquid extraction of mercury(II) with hydrochloric acid media by trioctylamine (TOA), and trioctyl methyl ammonium chloride (TOMAC) [15-16] has been carried out under different condition by Sato and his coworkers. The extraction efficiency of mercury (II) was higher in TOMAC than TOA. N-octyl methane sulfonamide (OMSA) [17] as a analytical extractant has been applied for extraction and separation of mercury(II) from aqueous solution and percentage of extraction of mercury(II) was found upto 82.2 %.

Extraction separation of methyl mercury(II) from human teeth and biological samples by diethyldithiocarbamate (DDC) [20] in hydrochloric acid was carried out and determined by electrothermal atomic absorption spectrometry (ET-AAS). Liquid-liquid microextraction of mercury(II) by ionic

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liquid methyltrioctylammoniumthiosalicylate [19] in ethanol was presented and estimated with cold vapour generation atomic absorption spectrometry(CV-AAS). Liquid-liquid extraction of inorganic mercury(II) at room temperature by using ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate [C4tmsim][PF6] as a solvent and o-carboxyphenyldiazoamino-p-azobenzene as an extractant (CDAA) [20] was reported. Back extraction of mercury(II) with sodium sulphide solution was carried out and determined by cold vapor atomic absorption spectrometry (CV-AAS). The separation of mercury(II) from tissue of broiler chicken by cloud point extraction using a complexing agent ammonium 0,0-diethyldithiophosphate (DDTP) and non-ionic surfactant triton X-114 [21] was determined with cold vapor atomic absorption spectrometry (CV-AAS). The extraction of ultra-trace amount methyl, phenyl, and inorganic mercury(II) from environmental and biological samples by triton X-114 [22] was given. Sequential cloud point extraction of mercury(II) with ammonium pyrrolidinedithiocarbamate (APDC) and octylphenoxypolyethoxyethanol (Triton X-114) [23] was carried out. The relative standard deviation (RSD) was 3.6 % and recovery of spiked sample was 93.2-108.7 %. Mercury(II) was determined with inductively coupled plasma-optical emission spectrometry (ICP-OES). The extraction of mercury(II) with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol [Hg(II)-(5-Br-PADAP)] complex [24] at pH 9.2 mediated by non-ionic surfactant polyethyleneglycolmono-p-nonylphenylether (PONPE 5) from water samples was studied. The cloud point extraction of mercury(II) with 3-nitro benzaldehydethiosemicarbazone (3-NBT) [27] from water samples was carried out and determined inductively coupled plasma-atomic absorption spectrometry (ICP-AAS). Extraction separation of methylmercury and ethylmercury from petroleum samples was carried out by using tetramethylammonium hydroxide (TMAH) [25] with 5 min equilibration time and estimated by high performance liquid chromatography with cold vapor generation atomic fluorescence spectrometry (HPLC-CV-AFS). Separation of mercury(II) by solid phase extraction from water and fish samples using dowexoptiporeV-493 [26] and sodium dodecyle sulphate-coated magnetite nanoparticles (SDS-coated Fe3O4NPs) [27] as a new extractant was reported. Separation and determination

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of mercury(II) from natural water with on-line solid phase extraction using C18SPE mini cartridge modified with sodium diethyldithiocarbamate (DDTC) [31] has been investigated. The solid phase extraction of mercury(II) in rice, canned tuna fish, tea leaves by using ethylene glycol bis-mercaptoacetate modified 3-(trimethoxysilyl)-1-propanethiol [28] was reported. Solid phase extraction of mercury(II) with sulphuric acid by diphenylthiocarbazone [29] complex on an alumina column was carried out and determined by spectrophotometrically. Cloud-point extraction of mercury(II) with hydrochloric acid media by dithizone [30] and triton-100 as solvent was investigated. The extraction of mercury(II) from aqueous solution by a batch equilibrium technique using 1,5-diphenylcarbazide (DPC) [31] functionalized sol–gel silicas (DPCSG) at pH 6 has been given. A highly selective method was developed for separation of mercury(II) by 2-[(2-sulfanylphenyl)ethanimidoyl]phenol [32] on an agarose membrane was studied. Extraction of ultra-trace amount of mercury(II) by using octadecyl silica membrane by hexathia-18-crown-6-tetraone [33] was determined with cold vapour atomic absorption spectrometry (CV-AAS).

The developed method is an effective extraction and removal of mercury(II) from associated metal ions with hydrochloric acid medium by using N-n-OCA. The method was optimizing various parameters like effect of acid, concentration of extractant (N-n-OCA), equilibrium time, effect of solvent, strippant study, loading capacity of the extractant, effect of aqueous to organic volume ratio and stoichiometry of formed $HgCl_4^{2-}$ species. The utility was checked by extraction of mercury(II) from diverse ions, binary mixture of associated metal ions, multicomponent mixture and ayurvedic samples.

Analysis of mercury(II) from ayurvedic samples

Mercury(II) = 100 μg   Hydrochloric acid = 0.4 M

N-*n*-OCA = 10 mL 0.05 M in xylene   Equilibrium time = 3 min

Aqueous: organic volume ratio = 2.5:1 Strippant = 4 M NH_3 (3×10 mL)

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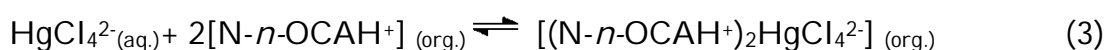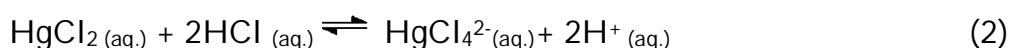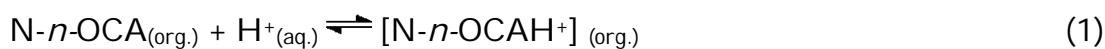| Ayurvedic samples	Hg(II) found by proposed method*µg/gm	Hg(II) found by ICP-OES µg/gm	Recovery * (%)	R.S.D, (%)
SmrutiSagar Rasa	236.80	237.0	99.6	0.4
Arogyavardhini	32.44	33.61	99.5	0.5
MahawatVidhvhans Rasa	132.81	133.52	99.7	0.3
Vasantkusumkar Rasa	81.67	82.73	99.4	0.6

*Average of five determinations
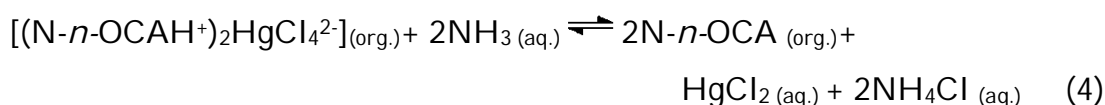
masked by 10mg EDTA

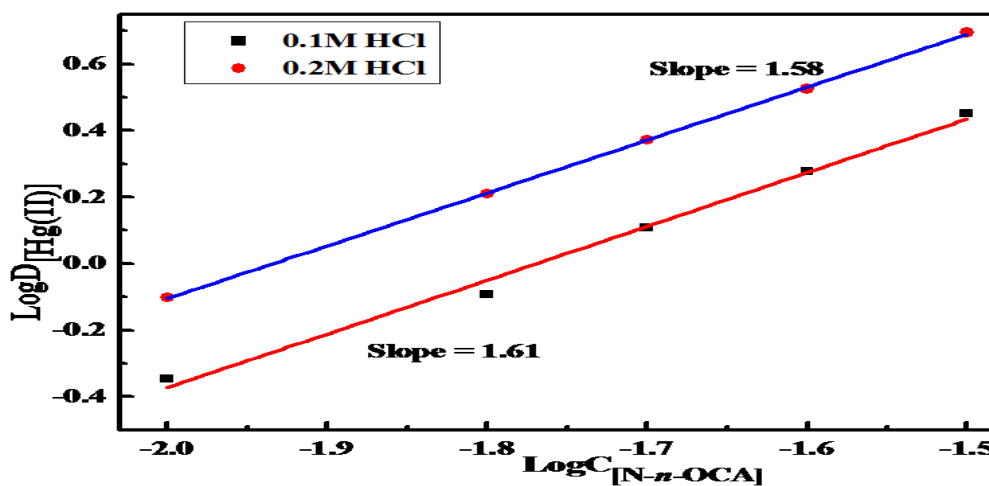**Composition of the extracted species by slope analysis method:**

Log-Log plot of distribution ratio of mercury(II) versus N-*n*-OCA and chloride concentration were used to determine stoichiometry of the extracted species. The graph of Log $D_{[Hg(II)]}$ vs Log $C_{[N-n-OCA]}$ having straight line with slope values 1.61 and 1.58, (Fig. 5) at 0.1 M and 0.2 M hydrochloric acid, respectively. The graph of Log $D_{[Hg(II)]}$ vsLog $C_{[HCl]}$ at 0.01 M and 0.02 M N-*n*-OCA give straight line graph with slope values 3.72 and 3.75, respectively (Fig. 6). The stoichiometry of mercury(II): N-*n*-OCA was found to be 1:2 and mercury(II): HCl was found to be 1:4. Hence the overall stoichiometry of the extracted species was 1:4:2 (metal: acid: extractant). The extraction proceed via ion-pair formation of cationic species [N-*n*-OCAH$^+$] and anionic species [HgCl$_4$$^{2-}$].

The possible extraction mechanism

N-*n*-OCA$_{(org.)}$ + H$^+$$_{(aq.)}$ ⇌ [N-*n*-OCAH$^+$] $_{(org.)}$ (1)

HgCl$_2$ $_{(aq.)}$ + 2HCl $_{(aq.)}$ ⇌ HgCl$_4$$^{2-}$$_{(aq.)}$+ 2H$^+$ $_{(aq.)}$ (2)

HgCl$_4$$^{2-}$$_{(aq.)}$+ 2[N-*n*-OCAH$^+$] $_{(org.)}$ ⇌ [(N-*n*-OCAH$^+$)$_2$HgCl$_4$$^{2-}$] $_{(org.)}$ (3)

Stripping mechanism

[(N-*n*-OCAH$^+$)$_2$HgCl$_4$$^{2-}$]$_{(org.)}$+ 2NH$_3$ $_{(aq.)}$ ⇌ 2N-*n*-OCA $_{(org.)}$+

HgCl$_2$ $_{(aq.)}$ + 2NH$_4$Cl $_{(aq.)}$ (4)

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Composition of the extracted species by slope analysis method Log D$_{[Hg(II)]}$vs Log C$_{[N-n-OCA]}$ plot.

Mercury(II) = 100 μg; Solvent = Xylene; Equilibrium time = 3min; Hydrochloric acid = 0.4 M; Aqueous: organic volume ratio = 2.5:1; Strippant = 4 M NH$_3$ (3×10 mL)

Composition of the extracted species by slope analysis method

　　Log D$_{[Hg(II)]}$ vs Log C$_{[HCl]}$ plot.

Mercury(II) = 100 μg; Solvent = Xylene; Equilibrium time = 3min; Hydrochloric acid = 0.4 M; Aqueous: organic volume ratio = 2.5:1; Strippant = 4 M NH$_3$ (3×10 mL)

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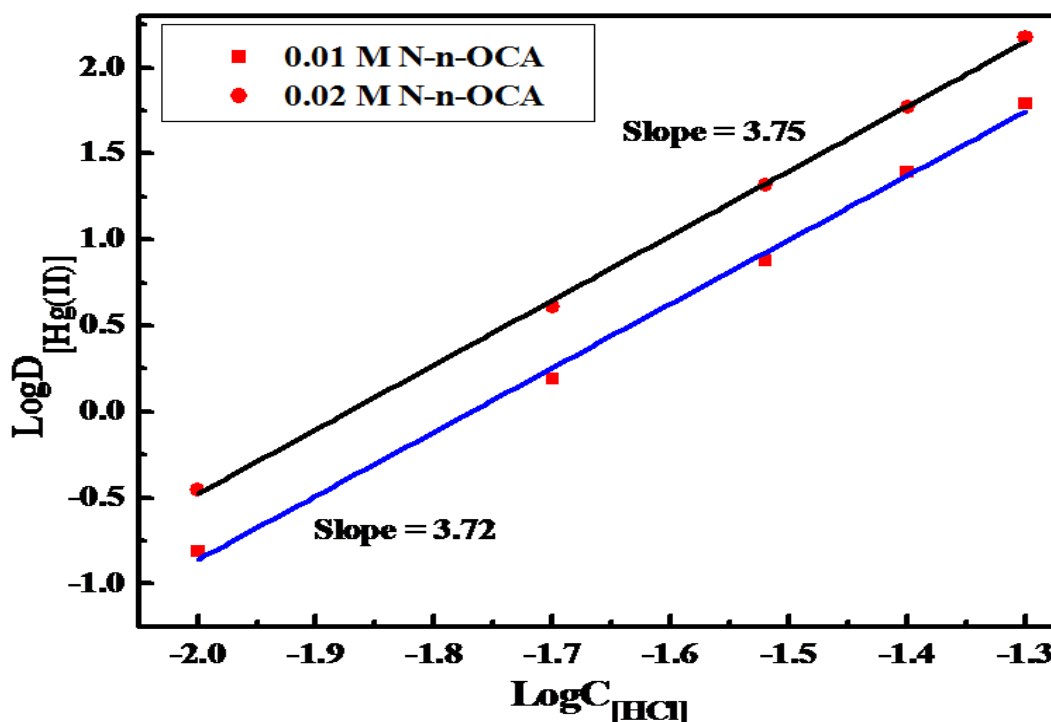
Extraction separation of thallium(III) from thallium(I):

The extraction separation of thallium(III) using high molecular weight amine N-*n*-octylcyclohexylamine (N-*n*-OCA) in xylene from aqueous hydrochloric acid solution at room temperature has been systematically investigated. The optimization of extraction conditions such as acid concentration, N-*n*-OCA concentration, equilibrium time, effect of solvent, strippant study, loading capacity of the N-*n*-OCA for thallium(III) ion have been presented. The extracted thallium(III) from organic phase was back stripped successfully by 7.0 M ammonia(3×10 mL). The stoichiometry of the extracted species was found to be 1:4:1 (metal: acid: extractant). The method was successfully applied to remove of thallium(III) from real samples such as diverse ions,associated metal ions, synthetic mixtures and sequential separation of thallium(III) from thallium(I) by using N-*n*-octylcyclohexylamine.
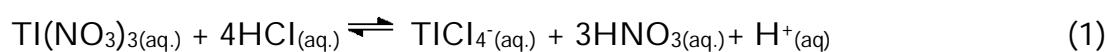
Nature of the extracted species:

The stoichiometry of extracted complex species was determined by plotting Log D vs Log C the conventional slope analysis method. The graph of Log $D_{[Tl(III)]}$vs Log $C_{[N-n-OCA]}$ at fixed concentration of hydrochloric acid at 0.1 and 0.2 M were found linear and having slope 1.16 and 1.25, respectively (Fig. 5). Which indicates that one mole of N-*n*-OCA reacts with thallium(III). The plot of Log $D_{[Tl(III)]}$vs Log $C_{[HCl]}$ at fixed N-*n*-OCA (0.01 and 0.02 M) were linear and having slope 3.78 and 3.76, respectively. Which indicates that four mole of hydrochloric acid react thallium(III) to form $TlCl_4^-$ species (Fig. 6). Hence the stoichiometry was found to be 1: 4: 1 (metal: acid: extractant).

The overall anion exchange reaction can be expressed as follow in presence of hydrochloric acid medium.

Extraction Mechanism:

In the presence of hydrochloric acid the thallium nitrate changes to $TlCl_4^-$ ion [65, 66].

$$Tl(NO_3)_{3(aq.)} + 4HCl_{(aq.)} \rightleftharpoons TlCl_{4\ (aq.)}^- + 3HNO_{3(aq.)} + H^+_{(aq)} \tag{1}$$

$$N\text{-}n\text{-}OCA_{(org.)} + HCl_{(aq.)} \rightleftharpoons [N\text{-}n\text{-}OCAH^+Cl^-]_{(org.)} \tag{2}$$

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The anion exchange mechanism is,

$$TICl_{4\ (aq.)}^{-} + [N\text{-}n\text{-}OCAH^{+}Cl^{-}]_{(org.)} \rightleftharpoons [N\text{-}n\text{-}OCAH^{+}\,TICl_{4}^{-}]_{(org.)} + Cl_{(aq.)}^{-} \qquad (3)$$
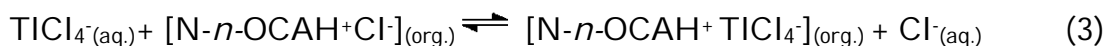
Stripping with 7 M NH₃ solution (3×10 mL)

$$[N\text{-}n\text{-}OCAH^{+}\,TICl_{4}^{-}]_{(org.)} + NH_{3(aq.)} \rightleftharpoons N\text{-}n\text{-}OCA_{(org.)} + TICl_{3(aq.)} + NH_{4}Cl_{(aq.)} \quad (4)$$
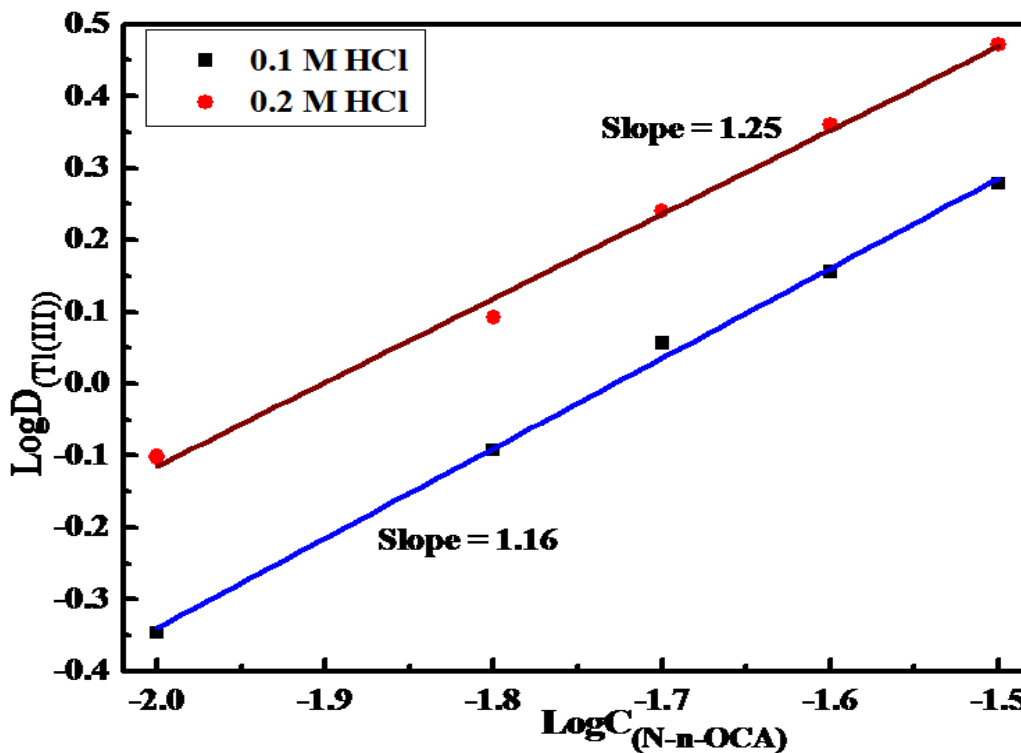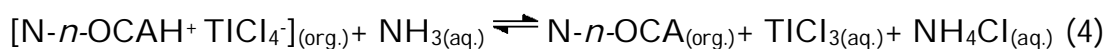
Fig.5 Composition of the extracted species by slope analysis method

Log D$_{[TI(III)]}$vs Log C$_{[N\text{-}n\text{-}OCA]}$

Thallium(III) = 100 µg; Solvent = Xylene; Equilibrium time = 5 min; Hydrochloric acid = 0.1 & 0.2 M; Aqueous: organic volume ratio = 2.5:1; Strippant = 7 M NH₃ (3×10 mL)

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