CHAPTER-2

SYNTHESIS AND CHARACTERISATION OF n-OCTYLANILINE

2.1 Solvent extraction with some basic extractants

Solvent extraction by high molecular weight amine (HMWA) has become increasingly popular in recent years for studying metal complexes. These are known as “liquid anion exchangers” which uniquely combine some of the advantages of liquid-liquid extraction and ion exchange. It was further observed that the acid binding properties of HMWA depend on the fact that acid salts of these bases are essentially insoluble in water while they are readily soluble in hydrocarbon solvents [1].

High molecular weight primary, secondary, and tertiary amines that are organophilic weak bases are used for solvent extraction of anionic species in acidic aqueous solutions. The interaction of these extractants with the anionic species is mainly due to electrostatic forces, and in this sense they are similar to the ion-pair forming cationic extractants, such as tetraalkyl or tetraphenylammonium ions. However, the effectiveness of the extractants treated here in the extraction of anions is dependent on the hydrogen-ion concentration, and as they show a greater tendency to polymerize, the extraction equilibria are much more complicated.

These high molecular weight amines can be regarded as “liquid anion-exchangers” in the same way as the alkylphosphoric acids can be regarded as “liquid cation-exchangers.” This is because the extraction equilibria can, at least formally, be expressed by an ion-exchange reaction of anionic metal complexes in the aqueous phase with ligand anions combined with the extractant in the organic phase. However, it should be pointed out that, although these extractants are liquid anion-exchangers, it should not necessary to consider that only those chemical species in the aqueous phase that have a negative charge are extractable. It has often been found that an extraction of metal ions with these extractants is possible even when anionic complexes of the metal in the aqueous phase are negligible.
Since the extraction is mainly due to the formation of ion-pairs, it is dependent on the charge and the ionic size; and no specificity can be expected among ions of the same charge and similar size. However, these extractions can be used specifically for the separation of many metal ions because they form a variety of complexes with nitrate, halide, thiocyanate, sulfate and a number of other organic and inorganic ions. The ease of formation of anionic complexes of different metal ions with these ligands varies greatly and since only the anionic metal complexes are extractable with protonated amines, the distribution behavior of different metal ions in this type of solvent extraction system is quite different. For this reason, a very high specificity of extraction is obtained by using these extractants, provided that a suitable extractant and a suitable anionic ligand are employed and those proper experimental conditions are adopted for the given problem [2].

### 2.2 Amines and amine salts

There are three kinds of amines, namely, primary RNH$_2$, secondary RR’NH, and tertiary RR’R”N amines, in addition to quaternary ammonium ions, RR’R”N$. All these organic derivatives of ammonia can be used for solvent extraction of metal ions and other anions (some or all of the R, R’ and R” may be the same). However, since the lower molecular weight amines are very soluble in water, high molecular weight ones have been used for solvent extraction.

These three types of amines in the aqueous phase are weak bases; they can accept one further proton and form amine salts. The amine salts, R$_n$H$_{4-n}$N$^-$X$, dissociate in aqueous solutions, but they are present essentially as ion-pairs in non polar organic solvents. Thus, when an amine in a non-polar solvent is equilibrated with a basic and neutral aqueous solution, the amine in the organic phase remains unchanged; but when the aqueous solution is acidic, the amine in the organic phase becomes the salt of the amine and the acid. The extraction capacity of many amines of these three classes has been extensively
studied [3, 4] and several of them have been used for the extraction of metal complexes.

The basicity of primary and secondary amines in aqueous solutions is not greatly affected by the chain length. However, that of tertiary amines increases as the molecular weight decreases. The basicity of secondary amines in aqueous solution is somewhat higher than primary or tertiary amines. The basicity of these three classes of amines in organic solvents is different from that in aqueous solutions.

Due to the action of the hydrogen combined with the nitrogen atom, primary or secondary amines polymerize by forming hydrogen bonds with each other or with water and thus their solubility in organic solvents is somewhat lower than tertiary amines, which are completely miscible with non polar organic solvents if the molecular weight is not very high. Their solubility in water or polar solvents often shows the opposite tendency. However, since the solubility of amines is dependent not only on the basicity but also on the branching of the aliphatic chain and total molecular volume, a simple comparison of solubilities of primary, secondary and tertiary amines having the same alkyl group or similar molecular weights may not have any special meaning.

2.3 Common liquid anion exchangers

High molecular weight amine (HMWA) popularly known as liquid anion exchangers uniquely combine some of the advantage of liquid–liquid extraction and ion exchange. These are several general features, which are essential for an extraction, if it has to achieve the selective extraction of metal.

These are as follows.

- The ability to extract the metal at the desired acidity or pH.
- To be selective for the required metal.
Ease of formation of complex with metal of interest and high solubility of metal organic species in the organic phase.

Ease of recovery of the metal from the organic phase.

It must be stable throughout the principle stages of solvent extraction.

It is to be prepared in laboratory in large scale.

To have acceptable rates of extraction and stripping.

Regeneration of extractant for recycling in economical larger-scale process.

The high molecular weight amine systems were used for liquid-liquid extraction of many metals from different aqueous solutions.

High molecular weight amines have found very wide applications in the separation chemistry. The separations of metals were carried out from both mineral acid as well as organic acid by taking the advantage of the difference in the $K_D$ values of anionic complexes of metals. The basis for the separation devised was by exploiting the inability of some elements to form the complexes. The parameters which govern the formation of anionic complex are the effect of acidity, effect of salting out agents and stability of the complex.

Among the organic acids dicarboxylic acid such as oxalic, malonic, citric and tartaric acids and monocarboxlic acids such as succinic, salicylic have been extensively used as complexing ligand. The extraction depends on the pH, nature and the concentration of amine as well as that of the ligand. The extractions involving organic acids are more selective and specific.

The most common liquid-anion exchangers used for the solvent extraction studies of metal are given in the table 2.1.
Table 2.1  The common liquid anion exchangers

<table>
<thead>
<tr>
<th>Amine</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I) Primary amines</strong></td>
<td></td>
</tr>
<tr>
<td>a) n-octylaniline</td>
<td></td>
</tr>
<tr>
<td>b) Primene JMT (Trialkylmethylamine)</td>
<td>H₂N –C (R) (R’)(R’’)</td>
</tr>
<tr>
<td>c) Octadecylamine</td>
<td>CH₃(CH₂)₁₇NH₂</td>
</tr>
<tr>
<td><strong>II) Secondary amines</strong></td>
<td></td>
</tr>
<tr>
<td>a) 2-Octylaminopyridine</td>
<td></td>
</tr>
<tr>
<td>b) N-n-octylaniline</td>
<td></td>
</tr>
<tr>
<td>c) Amberlite LA-1 [N-dodecyl(trialkylmethyl) amine]</td>
<td></td>
</tr>
<tr>
<td>d) Amberlite LA-2 [N-lauryl(trialkyl-methylamine)]</td>
<td></td>
</tr>
<tr>
<td><strong>III) Tertiary amine</strong></td>
<td></td>
</tr>
<tr>
<td>a) TLA (Tri-n-lauryl amine)</td>
<td>N-[CH₂(CH₂)₁₀CH₃]₃</td>
</tr>
<tr>
<td>b) TOA (Tri-octylamine)</td>
<td>N-[CH₂(CH₂)₇CH₃]₃</td>
</tr>
<tr>
<td>c) TIOA (Tri-iso-octylamine)</td>
<td>N-[C₈H₁₇]₃</td>
</tr>
</tbody>
</table>
IV) Quaternary amines

a) Aliquat 336 S
(Trialkylmethyl-ammonium chloride)

\[ \text{[CH}_3\text{-N-(CH}_2\text{)}_{11}\text{(CH}_3\text{)}_3\text{]Cl} \]

b) Zephiramine
(Tetradecyldimethyl benzyl ammonium chloride)

2.4 Mechanism of extraction with liquid anion exchangers

The anionic complexes were best extracted by solid anion exchanger in column and batch experiments. On the same lines these negatively charged complexes were also quantitatively extracted by liquid anion exchangers or high molecular weight amines (HMWA). Such amines consisted of primary, secondary, tertiary and quaternary amines. The main interaction was due to electrostatic attraction leading to the formation of ion-paired complexes; however, extractability largely depends upon \([\text{H}^+]\) ion concentration. Many of them underwent polymerization after extraction. Even negligible concentrations of anionic species were extractable by them. Such extraction depended upon charge and size of the ion. With mineral acids, an array of negatively charged complexes of metals was formed. So also organic acids formed stable anionic complexes. The extraction is represented by an equation as,

\[
\text{RNH}_2\text{org} + \text{H}^+ \text{A}^-\text{aq} \iff [\text{RNH}_3^+\text{A}^-] \text{org} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2.1)
\]

The acid was extracted by amine to form salt in equation (2.1)

\[
[\text{RNH}_3^+\text{A}^-] \text{org} + \text{B}^-\text{aq} \iff [\text{RNH}_3^+\text{B}^-] \text{org} + \text{A}^-\text{aq} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2.2)
\]
In second stage the anionic species was extracted as ion-pair. In order to have quantitative extraction the amine must be compatible with the diluent. Further the ammonical cation of amine should not undergo hydrolysis [3-6]. Finally the phase separation must be rapid with no foam formation or generation of third phase. Primary and secondary amines formed hydrates. With increasing chain length primary amines readily dissolved in the organic solvents. The secondary amines rarely dissolved in polar solvents; tertiary amines dissolved best in the nonpolar solvents. Amines form homogeneous mixture with nonpolar solvents like aromatic hydrocarbons.

2.5 Preparation and characterization of n-Octylaniline

n-Octylaniline has been investigated as a group extractant for noble metals [7-11]. The fact that the n-octylaniline though now available commercially, is very expensive, prompted us to prepare it in laboratory.

Pohlandt [10] has reported that the effectiveness of n-octylaniline in extraction depends on its method of preparation. When it was prepared from n-octylbenzene by a procedure analogous to preparation of aniline from benzene [8], difficulties were encountered in the extractions owing to the formation of emulsions. A second method of preparation involving the reaction of chlorobenzene with octanoic acid in the presence of ammonia, followed by reduction, was also reported to give a product which formed emulsions in noble metal extractions. On the other hand when the reagent was synthesized from aniline and 1-octanol [10] in the presence of zinc chloride, emulsions were not encountered in the extraction resulting in greater efficiency. Another advantage of the method is that the reagent can be recovered and reused without loss of extraction efficiency. Thus we have prepared reagent by Pohlandt’s method from octanol and aniline.

2.5.1 Preparation of n-octylaniline

The reagent n-octylaniline was prepared by the method of Pohlandt’s [10]. In the method freshly distilled 1-octanol (210 gm, 1.6 mole), aniline (433
gm, 4.8 mole) and anhydrous ZnCl\textsubscript{2} (317 gm, 2.5 mole) were placed in the reaction vessel fitted with reflux condenser, thermometer and a Dean and Stark water separating device. An inert atmosphere was maintained by passing nitrogen gas over the reaction mixture during heating at a temperature of 225\textdegree{}C for 21 h. The reaction mixture was then cooled and treated with dilute H\textsubscript{2}SO\textsubscript{4} (120 gm/L) to form slurry. The vessel containing slurry was placed in crushed ice and the oily n-octylaniline was obtained by neutralization with ammonia. It was transferred to a separating funnel and layers were allowed to separate. Oily layer was removed and the aqueous layer washed with ether. The oil and ether extracts were combined, ether was evaporated and sodium hydroxide pellets were added to remove emulsified water. The yield of crude product was 70 \% based on the amount of aniline used. The product was purified before use for extraction by distillation under vacuum at temperature 101\textdegree{}C or on direct flame at temperature of 302\textdegree{}C as pale yellow liquid.

\[
\begin{align*}
\text{NH}_2 & \quad \text{n-C}_8\text{H}_{17}\text{OH} \\
\text{ZnCl}_2 & \\
\text{Aniline} & \quad \text{n-Octylaniline}
\end{align*}
\]

2.5.2 Characterization of n-Octylaniline

A) Characterization

a) Absorption spectra

The absorption spectrum of n-octylaniline in chloroform (1×10^{-4}M) shows that the extractant exhibits sharp absorption maxima at \(\lambda_{\text{max}}\) 320 and 340 nm with the molar extinction coefficient 1.106×10^{4} and 7.82×10^{3} L mol\textsuperscript{-1}cm\textsuperscript{-1}, respectively (Fig 2.1).
b) NMR Spectra

The purity of the n-octylaniline was confirmed by comparing its physical properties such as boiling point, refractive index, chemical composition and NMR spectra. Anal: Mol wt 205.34, Refractive index of n_25 = 1.5160, Density = 0.898 gm/cc, PMR (CCl_4); δ 0.8 (t,-CH_3); 1.2 (bs, -(CH_2)_6; 2.38 (t,ArCH_2); 3.30 (S,ArCH_2); 6.25 (d, J=9 Hz, Ar-H); 6.75 (d, J= 8 Hz, Ar-H). The chemical analysis of product gave C, 82.1; H, 11.4 whereas C_{14}H_{23}N requires C, 81.9 and H, 11.3 (Fig 2.2).

Depending on the impurities present, the colour of the reagent varied from light yellow to yellow red. Purification of the reagent by vacuum distillation showed enhancement with respect to solidify after extraction of metals. The organic phase had a tendency to solidify after extraction depending on the room temperature. Solidification was minimum when the amine was vacuum distilled. Hence, it is recommended that n-octylaniline should be distilled before use. It is soluble in most of organic solvent.
Fig. 2.1  UV-VIS spectrum of \( n \)-octylanilne (1 \( \times \) 10\(^{-4} \) M)
**Chapter 2**

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**Synthesis and Characterisation of n-Octylaniline**

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![NMR Spectrum of n-Octylaniline](image)

**Fig. 2.2 - NMR Spectrum of n-Octylaniline**

- **Spectrum No. 219**
- **Operator**: S.O.L
- **Sample No.**: 2
- **Submitted by**: S.S.S

### NMR Parameters

- $^1H$: 60-90 MHz
- $^{13}C$: 56-146 MHz

**Solvent**: Neat Liq.

- **Conc.**: —
- **Temperature**: —
- **Ref. std.**: TMS (EXT.)
- **Lock signal**: —
- **Sweep range**: 100
- **Sweep time**: 450
- **Filter**: 2
- **Offset**: —
- **H. Level**: 7
- **Sensitivity**: 1

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The diagram shows the NMR spectrum of n-Octylaniline with chemical shifts and intensity peaks indicated.
Chapter 2 – Synthesis and characterisation of n-octylaniline

References


