Solvent extraction of chromium and copper using Schiff base derived from terephthaldehyde and 5-amino-2-methoxy-phenol

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Abstract Separation with solvent extraction of Cu$^{2+}$ and Cr$^{3+}$ from aqueous solution using [N,N'-p-phenylene bis (5-amino-2-methoxy-phenol)] as the new extractant has been studied. The Schiff base was synthesized by reaction of terephthaldehyde and 5-amino-2-methoxy-phenol. Schiff base has been characterized by elemental analyses, mass and IR spectral data. The Schiff base has been studied by liquid–liquid extraction toward the metal ions (UO$_2$$^+$) and d-metal ions (Hg$^{2+}$, Cu$^{2+}$ and Cr$^{3+}$) from aqueous phase to organic phase. The effect of chloroform and nitrobenzene as organic solvents on the metal chlorides extraction was investigated at 25 ± 0.1 °C by using flame atomic absorption. It was found that the extraction efficiency of ligand for metals is in the order Cu$^{2+}$ > Cr$^{3+}$. The extractability and selectivity of cations was evaluated as a function of relationship between distribution ratios of metal and pH. Cu$^{2+}$ showed the highest extractability and selectivity at pH 6.27. The effect of ionic strength and aqueous to organic phase on the extraction has been studied.

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1. Introduction

Chelate extraction is a very effective analytical separation method for the metal species in solution (Stary, 1964; Marcus and Kertes, 1969; Alegret, 1988; Tanaka and Akaiwa, 2000). Solvent extraction techniques are among the most studied method for the production and recovery of various metals ions from different sources because of its ease, simplicity, speed and wide scope. Solvent extraction of metal chelate complexes has been used as a separation method for a long time. Copper and chrome are both vital and toxic for many biological systems (Greenwood and Earnshow, 1984). Thus, the determination of trace amounts of Cu and Cr are becoming increasingly important because of the increased interest in environmental pollution. Flame and graphite furnace atomic absorption spectrometry and spectrophotometric methods provide accurate
and rapid determination of these metals in natural waters and wastewaters. Nevertheless, very frequently for the extremely low concentration of these metals in waters, a direct determination cannot be applied without their previous preconcentration and separation. The most widely used techniques for the separation and preconcentration of trace amounts are liquid-liquid extraction (Franson, 1995), precipitation, sorption (Bag et al., 2000a,b) solid phase techniques (Soylak et al., 2002) and chelating resins (Sung et al., 1997). Very often, both separation and preconcentration are required, and an advantage of solvent extraction is that both can be obtained in the same step. Recovery of metals from an aqueous phase with an organic phase that contains a metals selective chelating agent used has high distributions, coefficient and pH dependence in the system chosen. Reagent such as crown ethers, Schiff bases, oximes, amines and several phosphine oxides can be used as chelating agent (Rydberg et al., 1992). In this present paper, Schiff base derived from 5-amino-2-methoxy-phenol and terephthaldialdehyde has been reported. The ligand has been characterized on the basis of analysis of IR-spectra, mass spectra and elemental analyses. Therefore, combination of these also is a stiff structure but N and O donor atoms have possible development of novel extraction reagent having specific selectivity at various pH values.

2. Experiments

2.1. Reagents and apparatus

Chloroform, nitrobenzene, CuCl2·2H2O, CrCl3·6H2O, KCl, NaH2PO4 and NaOH, were the analytical grade reagents and were purchased from Merck. 5-Amino-2-methoxy-phenol and terephthaldialdehyde were obtained from Fluka. Distilled water was used in extraction experiments. The solvents were saturated with each other before use in order to prevent volume changes of the phases during extraction. The C, H and N were analyzed on a Carlo-Erba 1106 elemental analyzer. IR spectra were recorded on a Midac 300 instrument in KBr pellets. Mass spectra were recorded using a KRATOS MS50TC spectrometer. AA 929 Unicam Spectrometer was used for FAAS measurements with an air-acetylene flame. A pH meter (Metrohm 691 pH Meter) was also used. All extraction were performed by using a mechanical flask agitator in 50 cm³ stoppered glass flasks.

2.2. Ligand preparation

The preparation of ligand containing nitrogen and oxygen donor atoms is shown in Scheme 1. The structure of the new compound was characterized by a combination of IR and MS spectral data. The compound was synthesized according to the reported procedure (Reddy et al., 2008).

In a typical procedure, to a suspension of terephthaldialdehyde (1.34 g, 10 mmol) in 15 ml of aqueous methanol solution was added to a 15 ml solution of 5-amino-2-methoxy-phenol (2.78 g, 20 mmol) with stirring at 60 °C. The reaction mixture was continuously stirred for 30 min to separate the solid from reaction mixture and cooled. The solid was filtered and washed with diethyl ether. The corresponding product was recrystallized from methanol and found to be TLC-pure in chloroform and methanol mixture and dried under vacuum over P2O5. Yield% 97, m.p 236–238 °C. Elemental analysis found % (found atomic mass 376 amu), %, C: 70.1; H: 5.3; N: 7.4 for C23H20N2O4.

The electron impact spectrum of the ligand confirms the probable formula by showing a peak at 376 amu, corresponding to the macrocyclic moiety [C23H20N2O4], calculated atomic mass 376]. The series of peaks in the range i.e. 15, 42, 59, 76, 82, 104, 110, 172, 186, 262, 290, 314 amu etc., may be assigned to various fragments.

The advantages of synthetic procedure are: (1) the process is a simple one – step reaction involving inexpensive starting materials: (2) the process is shorter: (3) using water methanol (1:1) as solvent allows the formation of imine without the need for catalysis and (4) yield is high and the reaction is fast, and the product can be isolated by filtration.

2.3. Extraction procedure

Aqueous solutions containing 1.5 × 10⁻³ M metal chloride in appropriate buffer were equilibrated with equal volumes of the chloroform and nitrobenzene solutions of the ligand 4 × 10⁻⁴ M by shaking in a mechanical shaker at 25 °C. Optimum equilibration time was determined for this system. In most cases distribution equilibrium was attained in less than 120 min and a shaking time of 120 min. Theionic strength of the aqueous phase was 0.1 M KCl in all experiments except those in which the effect of ionic strength was studied. After agitation, the solutions were allowed to stand for 120 min. The copper(II) and chrome(III) concentrations of the aqueous phase were determined by FAAS, and that of the organic phase were calculated from the difference by considering the mass balance. The copper(II) and chrome(III) concentrations of the aqueous phase were determined by FAAS, and that of the organic phase from the difference by considering the mass balance. The pH of aqueous phase was recorded as equilibrium pH.

3. Results and discussion

The IR spectra of the free ligand exhibits various bands in the 3800–3100 cm⁻¹ region as due to stretching frequencies is in the 1509–1600 cm⁻¹ region. A full assignment of the IR spectra of Schiff bases is very difficult due to the extensive vibrational coupling in the molecules (Percy and Thornton, 1972; Turberville and Dutta, 1990; Yuzawa et al., 1993; Majerz et al., 2000; Ogunyana et al., 1999; Ambroziak et al., 2002; Fredman, 1961). The observed bands in the "fingerprint" region are a result of strongly mixed vibrations. Ligand displays a broad band at 3200–3400 cm⁻¹ due to n(O–H) vibrations of the phenolic hydroxyl. Very strong band near 1272 cm⁻¹ has been assigned to in-plane bending (O–H) vibrations of the ligand (Zamian and Dockal, 1996; Feliciano et al., 1999). The C=N stretching frequencies is in the 1509–1600 cm⁻¹ region as reported for similar ligands (Signorini et al., 1996; Condorelli et al., 1975; Ho et al., 1996).
3.1. Extraction of metal ions with Schiff bases

3.1.1. Effect of pH and solvents on the extraction of Cu(II) and Cr(III)

Various organic solvents as inert diluents were tested at a fixed pH containing equal amount of metal chloride and ligand solutions. The phase volume ratio was always maintained at 1:1 to avoid emulsion formation. The solvents, nitrobenzene and chloroform are same effective. The exact cause of this type of behavior is not known. The dielectric constant of medium has some contribution in the extraction process. However the only factor determining the extraction efficiency in the extraction process can be taken into account and a better term correlating the relative extraction order is solubility parameter (Zolezzi et al., 1999; Percy and Thornton, 1973; Downing and Urbach, 1969; Sekine and Hasegawa, 1976).

The results indicate that H2L in organic phase extracts efficiently Cu2+, Cr3+ aqueous phase containing 0.1 mol L⁻¹ KCl in the pH range of approximately 3–8.5 at 25°C.

In this research liquid–liquid extraction experiments were performed to examine the efficiency and selectivity of Schiff base in transferring metal ions (UO2⁺²) and d-metal ions (Hg2+, Cu2+ and Cr3+) from aqueous phase into chloroform. The results show that metals ions of UO2⁺² and Hg2+ are not extracted by Schiff base (E < 1%).

The percentage extraction (%E) of some metals into chloroform and nitrobenzene with Schiff base were plotted as a function of aqueous phase pH equilibrated with the organic phase in Fig. 1. The results are also expressed as distribution ratio (Table 1). The distribution ratio of cation may be represented by Eq. (1).

\[ D = \frac{[MLA]_{org}}{[M⁺]_{aq}} \]  

(1)

The degree of separation was determined in terms of ‘separation factor’ Sf defined as the ratio of D1 for the desired metal ion M1 to D2 for the contaminant metal ion M2;

\[ S_f = \frac{D_1}{D_2} \]  

(2)

The selected relative cation selectivity of Cu2+/Cr3+ was calculated from the distribution ratio of metal ion between the organic and aqueous phase as shown in Table 2.

The extractability and selectivity of cations were evaluated as a function of pH. The highest extractability and selectivity for Cu²⁺ among the other used cations such as Cr³⁺ was achieved at pH 6.2. The selectivity of H2L to Cu²⁺ over the Cr³⁺ is as follows Cu²⁺/Cr³⁺ = 58 for CHCl₃ and 41 for C₆H₅NO₂ (pH 6.2).

The extraction process may be represented by the equation:

\[ M_{(w)}^{2+} + H_2L_{(0)} \leftrightarrow ML_{(0)} + 2H_{(w)}^+ \]  

(3)

Where H₂L represents the extractant reagent and subscript (w) and (0) denotes the aqueous and organic phases, respectively.

The extraction mechanism corresponds to a cation exchange, in which a complex of stoichiometric formula (CuLₙ, CrLₙ) is formed in the organic phase liberating at the same time n mol H⁺ ions in aqueous phase. In this case, extraction constant (K_ext) can be expressed as follows;

\[ K_{ext} = \frac{[CuL]_{(w)} [H^+]_{(0)}^n} {[Cu^{2+}]_{(w)} [H_nL]_{(0)}} \]  

(4)

When CuL is the only extractable species and the metal is present in the aqueous phase predominantly as the cation Cu²⁺, the metal distribution ratio (D) and the extraction constant are related by

\[ \log D = \log K_{ext} + n \cdot \log [H_2L]_0 \]  

(5)

According to Eq. (5) a plot of log D against pH at constant 4 × 10⁻⁴ M of [H₄L] which will give straight line of slope is the number of hydrogen ions and intercept log [H₆L] + log K_ext (Fig. 2).

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**Table 1** Distribution ratio of cation between the organic and aqueous phases.

<table>
<thead>
<tr>
<th>pH</th>
<th>Cu²⁺ Distribution ratios of cations (D)</th>
<th>Cr³⁺ Distribution ratios of cations (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chloroform</td>
<td>Nitrobenzene</td>
</tr>
<tr>
<td>3.27</td>
<td>0.016</td>
<td>0.067</td>
</tr>
<tr>
<td>4.12</td>
<td>0.22</td>
<td>0.096</td>
</tr>
<tr>
<td>5.08</td>
<td>0.23</td>
<td>0.15</td>
</tr>
<tr>
<td>6.27</td>
<td>65.66</td>
<td>41.85</td>
</tr>
<tr>
<td>7.05</td>
<td>34.29</td>
<td>28.5</td>
</tr>
<tr>
<td>7.57</td>
<td>19.86</td>
<td>20.68</td>
</tr>
<tr>
<td>8.15</td>
<td>19.45</td>
<td>15.21</td>
</tr>
<tr>
<td>8.4</td>
<td>21.22</td>
<td>10.18</td>
</tr>
</tbody>
</table>

*a* Averages calculated for data obtained from three independent extraction experiments.

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**Figure 1** Effect of pH and Solvents on the extraction of [a] Cr(III), [b] Cu(II). [■] CHCl₃, [■] C₆H₅NO₂.
The effect of pH on the extraction of Cu$^{2+}$ and Cr$^{3+}$ ions from KCl media of ionic strength ($I = 0.1$ M) has been studied, the logarithm of the $D$ values obtained were plotted against the corresponding pH values. A straight line with a slope of about 2 and 0.68 was obtained at $I = 0.1$ of Cu$^{2+}$ and Cr$^{3+}$, respectively, as shown in Fig. 2. The values represent the number of hydrogen ions released during the formation of metal–ligand complex.

If the concentration of the extractants is constant and the hydrolysis in the aqueous phase as well as the polymerization in the organic phase occur to a negligible extent only, then the plots will be straight lines and their slopes will give the number of the ligands of the adducts.

Fig. 3 shows the evolution of log $[D]$ when increasing the concentration of ligand at constant metal chloride concentration with two different organic solvents. As seen from the plots, there is a linear relationship between log $[D]$ and log $[L]_{\text{org}}$, and the slope should be equal to the number of ligand molecules per cation in the extracted species. The slopes of lines are equal to 0.5 and 0.22 for dichloromethane and chloroform, respectively. Therefore, ligand forms a 2:1 $(L:M)$ complex with Cu$^{2+}$ and 3:1 $(L:M)$ complex with Cr$^{3+}$ for both solvents.

### 3.2. Effect of ionic strength on $E\%$

The effect of ionic strength was studied at constant pH, a plot of the $E\%$ values versus the corresponding ionic strength values. The data (Fig. 3) indicate that the $E\%$ value increases with the increasing in KCl. This is explained by the increase of the thermodynamic activity of the metal salt extracted and decrease in the activity of water as the ionic strength increase, this is shown in Fig. 4(a, b), which means that Cl$^-$ anion is functioning as salting out agent.

The effect of salt variation upon MCl$_{2.3}$ extraction by Schiff base was studied. The distribution ratio increases with the

### Table 2: The selected relative cation selectivities.

| pH  | Selectivity ($S$) | Cu$^{2+}$/Cr$^{3+}$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chloroform</td>
<td>Nitrobenzene</td>
</tr>
<tr>
<td>6.2</td>
<td>58</td>
<td>41.5</td>
</tr>
<tr>
<td>7.05</td>
<td>3.5</td>
<td>7.51</td>
</tr>
<tr>
<td>7.57</td>
<td>3</td>
<td>3.68</td>
</tr>
<tr>
<td>8.15</td>
<td>4.1</td>
<td>3.98</td>
</tr>
<tr>
<td>8.4</td>
<td>14</td>
<td>1.8</td>
</tr>
</tbody>
</table>

*a Relative cation selectivity determined by the distribution ratio of metal ion between the organic and aqueous phases.

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Figure 2. The plot of log $D$ vs. pH at constant $[\text{H}_2\text{L}]$ [a] Cu(II), [b] Cr(III). [■] CHCl$_3$, [■] C$_6$H$_5$NO$_2$.

Figure 3. The plot of log $D$ vs. log $[\text{H}_2\text{L}]$ at constant $[\text{H}_2\text{L}]$ [a] Cu$^{2+}$, [b] Cr$^{3+}$. [■] CHCl$_3$, [■] C$_6$H$_5$NO$_2$. 

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increase in salt concentration of KCl in ternary extraction system and this explained by the complexing ability of the anion.

3.3. Effect of aqueous to organic phase

Phase ratio \( A/O \) is one of the factors that affect the extraction efficiency. The extraction efficiency, \( E\% \) can be represented by

\[
E\% = \frac{D}{D + A/O} \times 100
\]

where \( D \) is the distribution ratio, \( A \) and \( O \) are the volumes of the aqueous and organic phases, respectively. Equation indicates that the extraction efficiency decrease with increasing \( A/O \) ratio. Fig. 4(c, d) shows the effect of \( A/O \) on percentage extraction which was satisfied by Eq. (6).

4. Conclusion

The Schiff base was synthesized and the extraction of the metal ions was examined. The high transfer of \( \text{Cu}^{2+} \) and \( \text{Cr}^{3+} \) ions from the aqueous phase to the Chloroform and nitrobenzene were observed with compound \((\text{H}_2\text{L})\) and results showed that the order of solvents is not changed. Also the results show that metals ions of \( \text{U}^{3+} \) and \( \text{Hg}^{2+} \) are not extracted by Schiff base.

The results indicate that \( \text{H}_2\text{L} \) in organic phase extracts efficiently \( \text{Cu}^{2+} \) and \( \text{Cr}^{3+} \) in aqueous phase containing 0.1 mol KCl in the pH range of approximately 5.5–8 and 6–8.2, respectively at 25°C.

The effect of ionic strength and aqueous to organic phase on the extraction has been studied. The extraction of \( \text{Cu}^{2+} \) and \( \text{Cr}^{3+} \) ions increases with the increase in ionic strength. Added to that results indicate that the extraction efficiency decrease with increasing \( A/O \) ratio.

The composition of extracted M-complexes for the ligand and their slopes values for the both solvents are given in Fig. 4. Ligand gives the 2:1 and 3:1 complexes with \( \text{Cu}^{2+} \) and \( \text{Cr}^{3+} \) respectively for the both solvents. The later studies will examine the effective transfer of these metals with Schiff base and study the structure of the formed complex.

References


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