Solvent Extraction And Spectrophotomteric Determination Of Cu(Ii) With Dicyclohexyl - 18- Crown-6

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Received 25, September, 2012
Accepted 9, December, 2012

Abstract:
Liquid-Liquid Extraction of Cu(II) ion in aqueous solution by dicyclohexyl-18-crown-6 as extractant in dichloroethane was studied. The extraction efficiency was investigated by a spectrophometric method. The reagent form a coloured complex which has been a quantitatively extracted at pH 6.3. The method obeys Beer’s law over range from (2.5-22.5) ppm with the correlation coefficient of 0.9989. The molar absorptivity 1 × 10⁴ L mol⁻¹ cm⁻¹ of the stoichiometry of extracted complex is found to be 1:2. The proposed method is very sensitive and selective.

Key words: dicyclohexyl-18-crown-6, copper determination, Extraction Spectrophotometry.

Introduction:
Copper has many applications and its separation and estimation at trace level is of considerable importance. For determination of copper, various methods, including atomic absorption spectrophotometry, ion chromatography, anodic stripping analysis, inductively coupled plasma mass spectrometry have been used. Many of these methods are either time consuming or require complicated and expensive instruments. Determination by solvent extraction is fast and simple process. This method is based on differences in solubilities of element and their compounds in two immiscible liquid media. The method is usually used to remove metals from an aqueous solution. This requires organic solvent immiscible with water and appropriate ligands or complexing agent to form metal complexes.

Copper is one of the most important metals after iron. It is used in many fields such as industry, laboratory medicine, food, and beverage. Copper and its salts are highly toxic to lower organisms much more than man; however, it is an essential constituent of certain proteins. Its toxic effect is the main cause of Wilson’s disease. In plant physiology, it is essential as a component of number of different plant enzymes. It is one of the most harmful impurities in semiconductor materials. Several compounds are known to react with metal ions to give coloured complexes and have been employed for the quantitative extraction and spectrophotometric determination of metal at trace levels but no work seems to have been done using dicyclohexyl-18-crown-6 (DCH-18-Crown-6). Therefore, it was thought of interest to develop suitable methods for the determination of copper(II) with above reagent. The use of this reagent may prove to be advantageous. In the present paper, the extraction and

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spectrophotometric determination of copper (II) with dicyclohexyl-18-crown-6 (DCH-18-Crown-6) is proposed, which found to be simple, sensitive, rapid and precise.

Materials and Methods

All chemical reagents and solvent are standard analytical grade purchased from BDH. The stock solution of copper (II) mg ml\(^{-1}\) is prepared by dissolving a 3.928g of its sulphat penta hydrate in double distilled water containing 1 ml concentrated sulphuric acid. Solution is diluted to the desired concentration with double distilled water as required,(10\(^{-3}\) M) of the solution of extractants are prepared by dissolving appropriate (dicyclohexyl -18- crown - 6) in dichloroethane which was diluted to the desired concentration with dichloroethane.

Ammonia,dilute solution is used ( 1 drop of concentrated ammonia in 20 ml of double distilled water). The absorbance is measured by shimadzu uv-visible (160) spectrophotometer with 1 cm quartz cells. pH of aqueous phase is measured with pH meter, pw 9421, ( philips England ). All the solutions are freshly prepared daily.

Extraction Method

To 2.0 ml of aqueous solution containing 20 µg of metal ion solution in a 10 ml glass-stoppered tube .The pH is adjusted to 6.3 then 4ml of (dicyclohexyl-18- crown-6) as extractant in 1,2 dichloroethane solution is added and mixture is shaken mechanically at room temperature for 10 min. and allowed to separate . The metal ion concentration in aqueous phase is determined. The (Brownish-pale) coloured organic phase is separated and dried over silica gel to remove trace of water.

The absorbance of organic phase containing the complex is measured at(469nm) against a reagent blank.

Result and Discussion:

The reagent dicyclohexyl- 18-crown-6 form (Brownish-pale) coloured complex with Cu(II), which is extracted into organic phase.

The extraction of Cu(II) is studied over a wide range of experimental conditions . The results of various studies are discussed below.

Absorption spectrum

The absorption spectrum of Cu(II) dicyclo hexyl -18-crown-6 in dichoroethane (Fig 1 ) shows the maximum absorption at (469) nm the absorption due to reagent at this wave length is nearly negligible. Hence Extraction of copper (II) dicyclohexyl-18-crown-6-carried out at (469) nm all the
Fig(1) Absorption spectra Cu(II)DCH-18-crown-6 (Condition :Cu(11) 20µg, Dicyclohexyl-18-crown-6 (10^{-3}M) ,PH(6.3)

Influence of pH on extraction efficiency
Six different pH solutions ranging from pH( 4-9) are prepared for the extracting of Cu(II)-

**Fig ( 2) Extraction of Cu(II) as a Function of pH**

Choice of solvent

Various solvents dichloroethane, dichloromethane, chloroform, carbon tetra chloride and hexane are used for the extractuction of copper (II) dicylohexy 18crown -6 complex to investigate the suitability of solvents (Fig3). It is found that the extraction of copper(II)complex is quantitative in dichloroethane.
A linear relationship has been observed between log D and log ε. As the solvent is varied. The solvent can be arranged in the decreasing order of their extraction coefficients as dichloroethane > dichloromethane > chloroform > carbon tetra chloride > hexane. (Table 1). Hence dichloroethane is used for further extraction studies as it gave better and fast phase separation.

Table (1) Distribution percent values for extraction of copper by using DCH-18C-6 which are soluble in different Dielectric constant solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric constant (ε)</th>
<th>Log ε</th>
<th>Log D*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloroethane</td>
<td>10.4</td>
<td>1.0</td>
<td>1.3</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>8.1</td>
<td>0.9</td>
<td>1.2</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.80</td>
<td>0.68</td>
<td>0.76</td>
</tr>
<tr>
<td>carbon tetra chloride</td>
<td>2.3</td>
<td>0.36</td>
<td>0.45</td>
</tr>
<tr>
<td>Hexane</td>
<td>1.8</td>
<td>0.25</td>
<td>0.27</td>
</tr>
</tbody>
</table>

*Distribution ratio.

Effect of reagent volume

Various volumes of $1 \times 10^{-3} M$ reagent solution are added to the aqueous solution containing 40 µg of copper (II) at pH (6.3). The absorbance remained nearly constant when the volume of the reagent solution is 4ml.
Therefore 4 ml of $1 \times 10^{-3}$ M reagent was chosen as optimum.

**Beer’s range**

![Graph showing the effect of reagent volume on the extraction of Cu(II)]

**Fig (4) Effect reagent volume on the Extraction of Cu(II)**

Beer`s range A Calibration plot of absorbance against varying copper concentration and fixed dicyclohexyl-18--crown-6 concentration, gives linear graph in conc. Range (5-45) µg of copper

![Graph showing the calibration plot of Cu(II) DCH-18-Crown-6)]

**Fig (5) Calibration plot of Cu(II) DCH-18-Crown-6**

Absorbance = 0.02310 Conc. Cu (ug) - 0.018
Stoichoimetry of the complex

The composition of extracted species has been determined by slope analysis method. It shows that the composition of Cu(II) DCH-18-crown-6 complex is 1:2.

Effect of some cations and anions in Extraction

The effect of the various ions were investigated in order to find limit of these ions in the extraction of Cu(II). Interference was observed in the presence of ions at amounts mol/L⁻¹ (Table 3).
Table (3) effect of divalent ions on extraction.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Conc (mg ml(^{-1}))</th>
<th>D</th>
<th>E%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(^{2+})</td>
<td>(1.2 \times 10^{-4}) (15µg)</td>
<td>2</td>
<td>80%</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>(4.5 \times 10^{-4}) (57µg)</td>
<td>21</td>
<td>97%</td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>(5.4 \times 10^{-4}) (68µg)</td>
<td>15</td>
<td>96%</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>(3.7 \times 10^{-4}) (47µg)</td>
<td>20</td>
<td>97%</td>
</tr>
<tr>
<td>ClO(_4^{-})</td>
<td>(4.4 \times 10^{-4}) (55µg)</td>
<td>N.E</td>
<td>_____</td>
</tr>
</tbody>
</table>

E% Percentage Extraction  
N.E: No Extraction

Conclusion:
Reagent cyclohexyl-18-crown-6 provides a simple, rapid and accurate method for spectrophotometric determination of copper(II). It has advantages of high sensitivity selectivity and easy availability.

References:
الاستخلاص المذبي للنحاس بوساطة داي سايكلو هيكسل-18-كراون-6 وتعينه بتقنية المطيافية الضوئية

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الخلاصة:

تم استخدام طريقة الاستخلاص بالمذيب لتعين النحاس في الوسط المائي بطريقة لونية باستخدام الكاشف المذاب في الدايكلوروايثان والذي كون معقد ملون. استخلص في داله حامضي dicyclohexyl-18-crown-6 قانون بير وجد متطابقاً في مدى تراكيز (2.5-22.5) ملغ/لتر بمعامل ارتباط 0.9989 وامتصاصه مولارية 4.10 × 1 لتر مولٌ⁻¹ سمٌ⁻¹. ووجد أن المعقد المستخلص ذات تركيب محتمل هو (2:1).