

# Prodigious Azocalix[4] Pyrrole Super-molecule: Effective Reagent for Liquid-liquid Extraction, Preconcentration and Transport of Cu(II) Ions

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**Abstract** A novel series of eight prodigious calix[4]pyrrole super-molecules bearing azo-moiety at the *meso* position of the macrocycle have demonstrated the ability for liquid-liquid extraction, preconcentration and transport of Cu(II) ions across a liquid membrane. Various significant extraction parameters such as effect of pH, effect of solvent and effect of reagent concentration were investigated which showed high affinity and selectivity towards Cu(II) in the presence of large quantities of associated metal ions. The wavelengths of maximum extraction ( $\lambda_{max}$ ) and molar absorptivity ( $\epsilon$ ) have also been determined. The stoichiometry of complex was evaluated by slope ratio method. The system obeys Beer's law over the range 0.5–10.0  $\mu\text{g mL}^{-1}$ . Liquid membrane transport studies of Cu(II) were carried out from source to the receiving phase under controlled conditions and a mechanism of transport is proposed. To check the validity of the proposed method, Cu(II) was analyzed in natural and ground water samples of Ahmedabad city, Gujarat, India.

**Keywords** Calix[4] Pyrrole, Azo-dyes, Copper, Liquid-liquid Extraction, Transport Study

## 1. Introduction

The design and synthesis of a variety of host molecules is a challenging topic in the field of molecular recognition chemistry because of the promising new functions of these novel compounds or the fantastic features attainable by forming supramolecular complexes from the host and guest molecules[1]. Synthetic chromo-ionophores that give rise to specific color changes on selective complexation with cations have attracted considerable attention as efficient spectrophotometric analytic reagents for the detection of particular species as well as the design of supramolecular devices having recognition and optical sensing functions[2-3]. Generally, the developments of most chromogenic reagents based on the supramolecular calixarenes have been achieved by attaching a chromogenic moiety/chelating moiety. There have been few reports wherein macrocycles such as calixarene[4], calixresorcinarene[5], thiacalixarene[6] and crown-ether[7] are used as components for the preparation of azo dyes but the research in the area of calix[4]pyrrole based dyes[8] is still in infancy.

Important positive and negative roles of trace heavy metal ions in human health are known[9]. Lot of studies[10] has been performed for the determination of trace metal

ions in various media including some body tissues and fluids, natural waters etc. Also the investigation of trace heavy metal contents in food samples including honey, vinegar, lemon juice, sour cream, yogurt, buttermilk, chocolate, cocoa, honey, molasses and other food samples are an important part of analytical chemistry[11].

Copper has received considerable attention owing to its uses in metallurgy and chemical industries. Copper is a gastrointestinal tract irritant, but it is generally not harmful to humans at low ( $\mu\text{g mL}^{-1}$ ) concentrations. In surface water, however, copper can be toxic to aquatic plants[12] and some fishes at concentrations of less than 1.0  $\mu\text{g mL}^{-1}$ . Thus, copper tends to be much more of an environmental hazard than a human hazard. Most environmental and biological samples generally contain copper at ng level. Many industrial waste water streams (such as those used in metal works, semiconductor, and copper industries, mining etc.) contain heavy metals which are of great environmental concern and must be removed prior to water discharge or water recycling[13]. Therefore, from the viewpoints of pollution, environmental chemistry, geochemistry, marine biology and analytical control in industrial, food, agricultural, pharmaceutical and clinical areas, it is necessary to establish a rapid, simple, sensitive and accurate procedure for the selective concentration of copper prior to its determination. Numerous techniques[14] for the separation and concentration of metal ions including evaporation of solvents, electro-deposition, surface adsorption, precipitation, ion exchange, ion exchange impregnated materials, immobilized

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reagents, electro-osmosis and flotation have been reported. Some of these techniques may be tedious, having limited concentration factors, lengthy and rigid conditions for the separation of solid adsorbents[15].

For the determination of copper, various instrumental methods[16,17] including UV Vis spectrophotometry, FAAS, ET-AAS, ICP-AES, ICP-MS, spectrofluorimetry, anodic stripping voltammetry and ion chromatography have been used. ET-AAS, ICP-MS, and anodic stripping voltammetry can be directly applied to the determination of copper at the  $\text{ng mL}^{-1}$  level. However, some of these methods are time-consuming, require complicated and expensive instruments, have complex operational conditions, are not free from various types of interference, and have high maintenance costs. Spectrophotometry still represents an attractive technique for the determination of metal ions in aqueous media because of its simplicity, being inexpensive and ready availability[18]. So, the development of a simple, sensitive and reliable method for the determination of copper is worthwhile. Although a lot of chromogenic reagents[19] for detection of transition metals have been reported, none of the reagents was prepared by attaching a chromogenic moiety such as azo ( $-\text{N}=\text{N}-$ ) functional group at the *meso*-position of a macrocyclic compound, such as calix[4] pyrrole. It is even more interesting and significant to develop a new type of calix[4]pyrrole based chromogenic reagent for detection of Cu(II).

Since we synthesized a series of novel eight azocalix[4] pyrrole dyes[20] and carried out very preliminary complexation studies with Cu(II), we thought it worth to extend our investigations to liquid liquid extraction, preconcentration and transport of Cu(II) across a liquid membrane in a non polar solvent. The extracted copper complexes have been determined simultaneously by spectrophotometry/flame atomic absorption spectrometry (FAAS)/inductively coupled plasma emission spectrometry (ICP-AES). Various parameters for the extraction have been studied. The validity of the proposed method is tested by analyzing this Cu(II) in natural and ground water samples of Ahmedabad city, Gujarat, India.

## 2. Experimental Section

### 2.1. Instruments and Measurements

UV-Vis absorption studies were carried out on a JASCO 570 UV/VIS/NIR spectrophotometer using 10mm quartz cells. All pH measurements were performed using an Elico digital pH meter, model L1 614, equipped with a combined pH electrode. A Chemito, flame atomic absorption spectrophotometer (FAAS), model 201, equipped with air-acetylene burner was used for the analysis under conditions recommended by the manufacturer. The analytical wavelength for Cu(II) was 324.8 nm. Inductively coupled plasma atomic emission spectrophotometer (ICP-AES), plasma scan model 710 was used for the determination of

trace metal content, only in those cases where concentration of metal ion was too low to be determined by spectrophotometry and FAAS.

### 2.2. Chemicals and Reagents

All the chemicals used were of analytical grade from E. Merck or BDH. All aqueous solutions were prepared with quartz distilled deionized water, which was further purified by a Millipore Milli-Q water purification system (Millipack 20, Pack name: Simpak 1, Synergy) throughout the entire study. The pH was adjusted with the following buffer solutions[21]:  $\text{PO}_4^{3-}/\text{HPO}_4^{2-}$  buffer for pH 2.0 and 3.0;  $\text{CH}_3\text{COO}^-/\text{CH}_3\text{COOH}$  buffer for pH 4.0 and 6.0;  $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$  buffers for pH 7.0 and 7.5. Standard copper stock solution ( $1000 \mu\text{g mL}^{-1}$ ) was prepared by dissolving 0.3805 g of copper nitrate [ $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ] in 100 mL water and was standardized spectrophotometrically[22]. Working solution was subsequently prepared by appropriate dilution of the stock solution.

The eight tetra functionalized azocalix[4]pyrrole dyes (Figure 1) were synthesized and characterized as per earlier reported method[20] and their stock solutions (0.1%) were prepared in *iso*-amyl alcohol. Working solutions were subsequently prepared by appropriate dilution of the stock solutions.

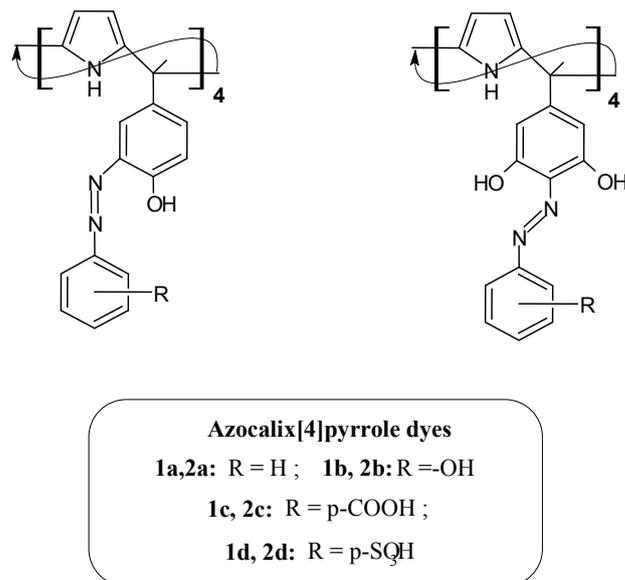


Figure 1. Tetra functionalized azocalix[4]pyrrole dyes (1a-d, 2a-d)

### 2.3. Sample Collection

The water samples from Sabarmati River were isokinetically collected in clean polyethylene bottles from locations near a thermal power station, Ahmedabad. The ground water samples were collected from the university area and Vatva industrial zone of Ahmedabad city, Gujarat, India.

### 2.4. General Procedure for the Liquid-Liquid Extraction of Cu(II)

An aliquot of sample solution containing 0.5-10  $\mu\text{g}$  of

Cu(II) was transferred into a 25 mL separatory funnel and desired 5 pH was adjusted with the appropriate buffer solutions in a total volume of aqueous phase of 10 mL. The mixture was shaken with 6 ml of 0.015 % reagents (azocalix[4]pyrrole dyes) in *iso*-amyl alcohol. The metal-reagent complex was extracted into the organic phase. To ensure complete recovery, the extraction was repeated with 2 mL of reagent solution; the organic extract was separated, dried over anhydrous sodium sulphate and transferred into a 10 mL volumetric flask. The combined extracts and washings were diluted to the mark (10 mL) with *iso*-amyl alcohol. The absorbance of the organic phase was measured at 540 nm.

The concentration of the metal ion extracted into the organic phase  $[Cu^{+2}]_{(org)}$  as complex was estimated by  $[Cu^{+2}]_{(org)} = [Cu^{+2}]_{(aq, int)} - [Cu^{+2}]_{(aq)}$ , where  $[Cu^{+2}]_{(aq, int)}$  is the initial concentration of the metal ion in the aqueous phase.

The percent extraction (%E), was calculated by Eq. (1)

$$\% E = \frac{[Cu^{+2}]_{(org)}}{[Cu^{+2}]_{(aq, int)}} \times 100 \quad (1)$$

The concentration of Cu(II) remaining in the raffinate was measured by spectrophotometry/FAAS/ICP-AES.

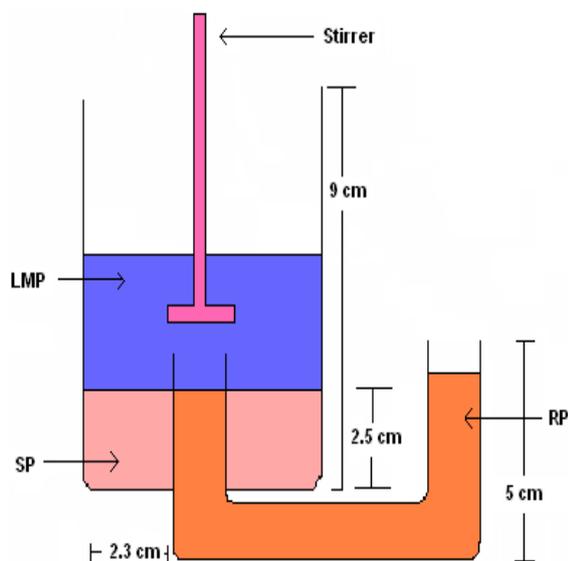


Figure 2. Apparatus for Transport Studies<sup>a</sup>

<sup>a</sup> Condition for transport studies: Source Phase (SP): 50 ml of  $0.58 \times 10^{-4}$  M Cu(II) containing 5 pH solution; Liquid Membrane Phase (LMP): 75 ml of  $1.167 \times 10^{-4}$  M *o*-APCRCPD (2b) in *iso*-amyl alcohol; Receiving Phase (RP): 50 ml, 1.0 M HCl.

## 2.5. Liquid Membrane Transport Studies

Transport of Cu(II) was carried out in a specially fabricated glass assembly (Figure 2). The reaction cell was 6.6 cm in inner diameter and 9.0 cm in height with a total capacity of 305 mL. U-tube (2.0 cm outer diameter, 20 cm length) was fused from the base of the cell. The height of the tube inside the cell was 4.0 cm from the basal plane. The whole assembly was kept in a thermostat maintained at

room temperature (30°C).

The transport experiments were performed with 50 ml of  $0.58 \times 10^{-4}$  M Cu(II) solutions at 5 pH as source phase and 50 ml, 1.0 M HCl as receiving phase. The liquid membrane consisted of 75 mL of  $1.167 \times 10^{-4}$  M *o*-APCRCPD (2b) in *iso*-amyl alcohol. The amount of copper transported from the source phase to the receiving phase was measured by FAAS/ICP-AES. The transport data were the average of 5 runs with an experimental error of less than 1.8%.

## 3. Results and Discussion

In order to obtain the optimum conditions for the maximum extraction efficiency of Cu(II) with the azocalix[4]pyrrole dyes (1a-d, 2a-d), different factors affecting this process have been studied.

### 3.1. Solvent Extraction and Spectrophotometric Determination of Cu(II) with Azocalix[4] Pyrrole Dye

#### 3.1.1. Spectral Characteristics of Cu(II)-Azocalix[4]-Pyrrole Dyes Complex

The synthesized azocalix[4]pyrrole dyes (1a-d, 2a-d) were used for the extraction and spectrophotometric determination of Cu(II). It has been seen that among all the synthesized azocalix[4]pyrrole dyes (1a-d, 2a-d), *o*-amino phenol based meso-tetra(methyl)meso-tetra(3,5-dihydroxy phenyl) calix[4]pyrrole dye [2b (*o*-APCRCPD)] was the most sensitive reagent for the Cu(II) ion (Table 1).

The complexation of Cu(II) with *o*-APCRCPD was studied under optimum conditions like pH, solvent, and reagent (*o*-APCRCPD) concentration. The maximum absorbance of the pinkish-red colored complex was measured at 540 nm and showed a bathochromic shift of 110 nm [540-430nm] from that of the reagent blank (Figure 3). The molar absorptivity was found to be  $7048 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The system obeys Beer's law in the range of 0.5-10  $\mu\text{g mL}^{-1}$ .

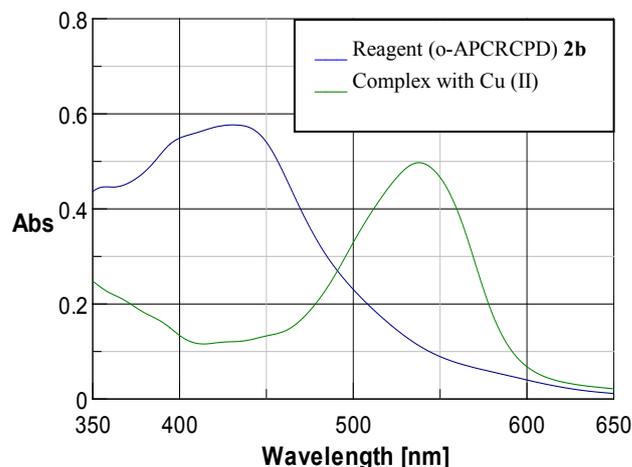


Figure 3. Comparative spectra of reagent (*o*-APCRCPD) 2b ( $1.167 \times 10^{-4}$  M) and its Cu(II) complex in *iso*-amyl alcohol

**Table 1.** Spectral characteristics of azocalix[4]pyrrole dyes for the extraction<sup>a</sup> of Cu(II)

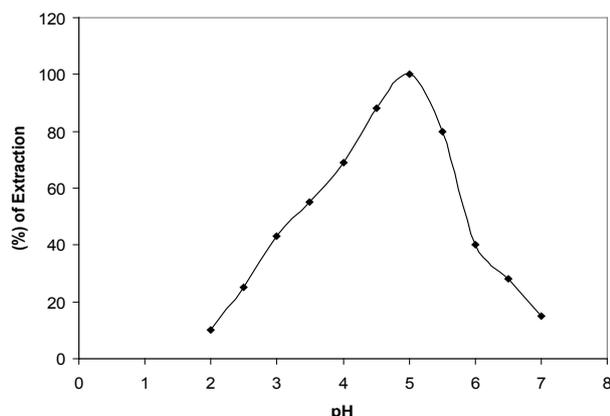
No.	Azocalix[4]pyrrole Dyes	$\lambda_{max}$ (nm)	Color of the Complex	Molar absorptivity ( $L mol^{-1} cm^{-1}$ )
1	Aniline based (4-hydroxy phenyl) calix[4]pyrrole dye ( <b>1a</b> )	533	Light red	4228
2	o-Aminophenol based (4-hydroxy phenyl) calix[4]pyrrole dye ( <b>1b</b> )	536	Pinkish red	5990
3	p-amino benzoic acid based (4-hydroxy phenyl) calix[4]pyrrole dye ( <b>1c</b> )	530	Light red	2748
4	Sulphanilic acid based (4-hydroxy phenyl) calix[4]pyrrole dye ( <b>1d</b> )	530	Light red	1762
5	Aniline based (3,5-dihydroxy phenyl) calix[4]pyrrole dye ( <b>2a</b> )	535	Light red	4933
6	o-Aminophenol based (3,5-dihydroxy phenyl) calix[4]pyrrole dye ( <b>2b</b> )	540	Pinkish red	7048
7	p-amino benzoic acid based (3,5-dihydroxy phenyl) calix[4]pyrrole dye ( <b>2c</b> )	530	Light red	3876
8	Sulphanilic acid based (3,5-dihydroxy phenyl) calix[4]pyrrole dye ( <b>2d</b> )	538	Light red	2819

<sup>a</sup> Extraction conditions: Cu(II): 4 mL, 25  $\mu g mL^{-1}$ ; pH 5; Reagent : 0.015 % Azocalix[4]pyrrole dyes; Solvent: *Iso*-amyl alcohol.

### 3.1.2. Effect of Variable on Extraction

The complexation of Cu(II) with *o*-APCRCPD was studied under optimum conditions of pH, shaking time, solvent and reagent (*o*-APCRCPD) concentration.

Effect of pH and shaking time: The pH of the medium is a highly significant factor in extraction process. A series of experiments were carried out to study the effect of pH on the liquid-liquid extraction of Cu(II) with reagent, *o*-APCRCPD in *iso*-amyl alcohol. Maximum extraction of copper-complex was obtained in pH range of 4.5-5.0 (Figure 4); at the lower and higher pH the extraction was incomplete. This may be because the reagent remains protonated at pH lower than 4.5 and hydrolysis of Cu(II) ion at pH higher than 5.5. So, pH 5.0 was chosen for the extraction of Cu(II).



**Figure 4.** Effect of pH on the extraction

The optimum shaking time was found to be 5-10 min., for quantitative extraction of Cu(II). The extraction was not affected by further shaking, indicating that the equilibrium state had been attained.

Solvents: The Cu(II)-*o*-APCRCPD complex was extracted with various solvents like ethyl acetate, chloroform, toluene, benzene, dichloromethane, carbon-tetrachloride and *iso*-amyl alcohol. *Iso*-amyl alcohol was found to be the most suitable solvent for quantitative extraction as compared to other solvents (Table 2).

Reagent (*o*-APCRCPD) concentration: The influence of *o*-APCRCPD was studied by extracting a fixed amount of Cu(II) with varying amounts of reagent (*o*-APCRCPD) at 5 pH. A 6 mL, of 0.015% *o*-APCRCPD was sufficient for the

quantitative extraction of Cu (II), where as the extraction was incomplete at the lower concentration of *o*-APCRCPD. The excess of the reagent had no adverse effect on the extraction of Cu (II).

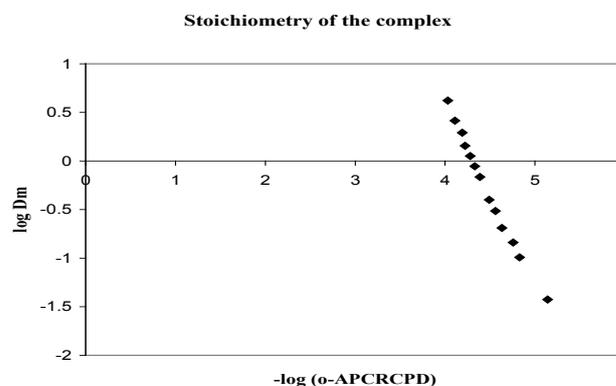
**Table 2.** Effect of solvents on the extraction<sup>a</sup> of *o*-APCRCPD – Cu(II) complex

Solvent	Dielectric constant	Molar absorptivity ( $L mol^{-1} cm^{-1}$ )	Extraction (%)
Toluene	2.30	-	-
Benzene	2.28	704	10
Carbon tetrachloride	2.20	1409	20
Dichloromethane	8.90	2466	35
Chloroform	4.80	2819	40
Ethyl acetate	6.40	4863	69
<i>Iso</i> -amyl alcohol	15.3	7048	100

<sup>a</sup> Extraction conditions: Cu(II): 4 mL, 25  $\mu g mL^{-1}$ ; Reagent : 0.015 % *o*-APCRCPD; pH: 5;  $\lambda_{max}$ : 540 nm.

### 3.1.3. Stoichiometry of the Extracted Complex

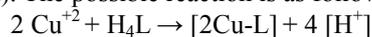
The composition of Cu(II) - *o*-APCRCPD complex extracted into *iso*-amyl alcohol has been studied by *slope-ratio method*[23] {plotting the graph of logarithm of distribution coefficient of the metal ( $\log D_m$ ) against the negative logarithm of the reagent concentration  $-\log$  (*o*-APCRCPD)}. The extraction is carried out by taking a fixed concentration of copper solution and varying amounts of reagent.



**Figure 5.** Plot of  $\log [D_m]$  against  $-\log$  (*o*-APCRCPD)

The plot of ( $\log D_m$ ) against  $-\log$  (*o*-APCRCPD) gave a straight line of slope 1.92 indicating that, the extracted species Cu(II): *o*-APCRCPD is in the ratio of 2:1 (M:L) (Figure 5). Thus, 1 mole of *o*-APCRCPD was required for 2

mole of Cu(II). The possible reaction is as follows:



Where  $\text{H}_4\text{L}$  represents four azo-moieties attached with the one mole of reagent (azocalix[4]pyrrole dye) and hence forms a 2:1(M:L) complex with Cu(II) in the solution.

To obtain more information about the nature of the extracted complex, attempts were made to isolate it from *iso*-amyl alcohol extract. The extract was evaporated to dryness. A known weight of the dry complex was digested with a perchloric and nitric acid mixture. It was centrifuged and after appropriate dilution the copper content was determined by FAAS/ICP-AES, which also conformed 2:1(M:L) complex.

### 3.1.4. Effect of Diverse Ions

To assess the usefulness of this method, the effect of foreign ions which often interfere on the extraction and spectrophotometric determination of Cu(II) were studied by adding a known amount of the metal-ion in to a solution containing 10 mL,  $3 \mu\text{g mL}^{-1}$  of Cu(II) and the general procedure for the liquid-liquid extraction was followed. Cu(II) was extracted in the presence of several other ions to determine the sensitivity and utility of the method.

Interference studies were performed by measuring the absorbance of the extracted organic-phase and aqueous phase by spectrophotometry/FAAS/ICP-AES. The tolerance limit was set as the amount of foreign ion causing a change of  $\pm 0.02$  in absorbance. It was observed that addition of 60-95 mg of Ca(II), Ag(I), Co(II), Ba(II), Zn(II), Mn(II), Pb(II), Ni(II), Hg(II), Cd(II),  $\text{UO}_2(\text{II})$ , Fe(III), Ga(III), La(III), Th(IV), Ce(IV) and Sr(II) do not interfere in the determination of Cu(II). The results are shown in Table 3.

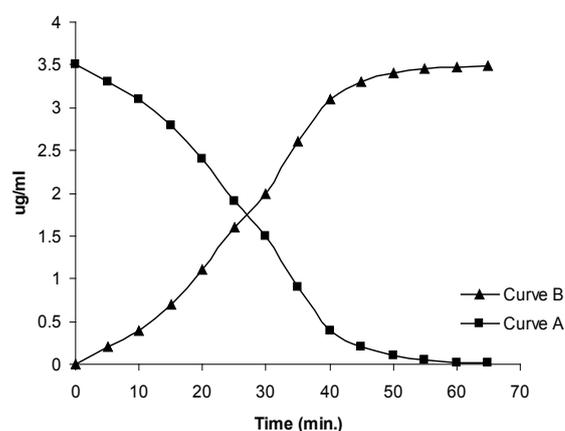
**Table 3.** Effect of diverse-ions on the extraction<sup>a</sup> of o-APCRCPD – Cu(II) complex

Various Ions Added as	Amount added (mg)	Recovery of Cu(II) ( $\mu\text{g mL}^{-1}$ )	
		Spectrophotometry	FAAS
$\text{Ca}^{+2} \dots \text{CaCl}_2$	60	2.98	3.00
$\text{Ag}^{+} \dots \text{AgNO}_3$	80	2.97	2.99
$\text{Co}^{+2} \dots \text{CoCl}_2$	70	2.99	2.98
$\text{Ba}^{+2} \dots \text{BaCl}_2$	95	3.00	2.98
$\text{Zn}^{+2} \dots \text{ZnCl}_2$	70	2.96	2.99
$\text{Mn}^{+2} \dots \text{MnCl}_2$	90	2.98	3.01
$\text{Pb}^{+2} \dots \text{Pb}(\text{NO}_3)_2$	92	2.97	3.00
$\text{Ni}^{+2} \dots \text{NiCl}_2$	80	2.96	2.98
$\text{Hg}^{+2} \dots \text{HgCl}_2$	95	3.00	2.99
$\text{Cd}^{+2} \dots \text{CdSO}_4$	96	3.00	3.00
$\text{UO}_2^{+2} \dots \text{UO}_2(\text{NO}_3)_2$	70	2.97	2.99
$\text{Ga}^{+3} \dots \text{GaCl}_3$	93	2.98	3.00
$\text{La}^{+3} \dots \text{La}(\text{NO}_3)_3$	89	2.99	3.00
$\text{Fe}^{+3} \dots \text{FeCl}_3$	95	2.98	3.00
$\text{Th}^{+4} \dots \text{Th}(\text{NO}_3)_4$	80	3.00	2.98
$\text{Sr}^{+2} \dots \text{Sr}(\text{NO}_3)_2$	95	2.98	2.99
$\text{Ce}^{+4} \dots (\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$	80	2.98	3.00

<sup>a</sup> Extraction conditions: Cu(II): 10 mL,  $3 \mu\text{g mL}^{-1}$ ; Reagent : 0.015 % o-APCRCPD; Solvent: *iso*-amyl alcohol; pH: 5;  $\lambda_{\text{max}}$ : 540nm.

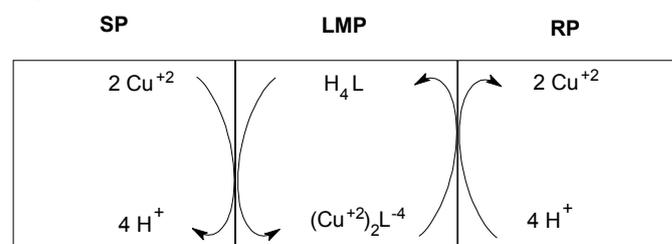
### 3.2. Liquid Membrane Transport Studies

A liquid membrane is a liquid phase, which separates two other liquid phases with which it is immiscible. These liquid membranes are of interest for both, possible technological application and fundamental studies of the transport process. The transport of Cu (II) through the membrane containing  $1.167 \times 10^{-4} \text{ M}$ , o-APCRCPD from source phase containing  $0.58 \times 10^{-4} \text{ M}$ , Cu (II) to the receiving phase of 1.0 M HCl was carried out. As evident from the Figure 6 the concentration of Cu(II) in the source phase started to decrease continuously and it took about 28 min to transport half of the Cu(II) from source phase to receiving phase (*curve A*). On the other hand, concentration of Cu (II) in the receiving phase starts increasing as shown in the *curve B*.



**Figure 6.** Transport profile of Cu(II) through the liquid membrane containing o-APCRCPD at 30°C

Therefore, it is clear that Cu (II) moved from the source to receiving phase through the liquid membrane. Based on these facts and knowledge obtained by the extraction equilibria, the proposed mechanism of transport of copper through the liquid membrane of o-APCRCPD is as shown in Figure 7.



**Figure 7.** Proposed mechanism for transport of Cu(II) through a liquid membrane containing o-APCRCPD

(SP: Source Phase; LMP: Liquid membrane Phase; RP: Receiving Phase)

The carrier in the membrane reacts with Cu(II) in the source phase at the interface of these phases and forms a complex  $[(\text{Cu}^{+2})_2\text{L}^{-4}]$  while releasing 4 moles of proton into the source phase. On the other hand, interface of the membrane and the receiving phase the complex reacts with 4 moles of protons while releasing 2 moles of Cu(II) in the receiving phase.

**Table 4.** Determination of Cu (II) in natural water samples by spectrophotometry<sup>a</sup> and ICP-AES

Types of water	Cu(II) added ( $\mu\text{g mL}^{-1}$ )	Spectro-photometry	ICP-AES	Cu(II) found ( $\mu\text{g L}^{-1}$ )
Distilled water	- 1.0	ND 1.00	ND 1.000	0
Ground water University area, Ahmedabad	- 1.0	ND 1.01	ND 1.009	9
Sabarmati River Near thermal power station, Ahmedabad	1.0	1.0 4	1.042	42
Ground water Vatva industriazone, Ahmedabad	1.0	1.06	1.056	56

ND = not detected

<sup>a</sup> Extraction conditions: 0.015% o-APCRCPD; pH: 5; Solvent: *iso*-amyl alcohol,  $\lambda_{\text{max}}$ : 540nm.

### 3.3. Preconcentration of Cu(II)

The concentration of Cu(II) in natural water is too low for its direct determination. Therefore, preconcentration or enrichment step is necessary to bring the sample to the detectable limits of existing instrumental methods. The method was studied for the preconcentration of copper in terms of its preconcentration factors.

PF=Concentration of metal in organic solution/Initial concentration of metal in aqueous solution.

The preconcentration study was carried out by extracting 40  $\mu\text{g}$  of Cu (II) in 1000 mL aqueous phase with 6 mL of 0.015% o-APCRCPD in *iso*-amyl alcohol. To evaluate the efficiency of preconcentration, expressed as recovery, the concentration of Cu (II) in organic phase and the aqueous phase was determined by spectrophotometry/ FAAS/ICP-AES respectively. Quantitative determination was possible with recovery up to 97% with a concentration factor of 120.

### 3.4. Analytical Applications

To investigate the applicability of the recommended procedure to natural water samples (taken from different locations of Ahmedabad city, Gujarat, India), the recoveries of known amounts of Cu (II) added to these samples were examined. The results obtained are given in Table 4. Spectrophotometric determination of Cu (II) gave satisfactory results when compared to those obtained by ICP-AES.

## 4. Conclusions

Out of eight azocalix[4]pyrrole dyes, prodigious resorcinarene-calix[4]pyrrole 2b was found to be an effective reagent for the liquid-liquid extraction, preconcentration and transport of Cu(II) across a liquid membrane in *iso*-amyl alcohol. This reagent bearing a calixpyrrole ring, which are known anion sensors, holds great potential for their use as ditopic receptors[24] and the work is under progress in our lab. The described method is simple, sensitive and specific for the determination of copper ion in presence of large quantities of associated metal ions. The results obtained from the analysis of natural water samples establish the reliability, simplicity and robustness of the method.

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