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# Facilitated kinetic transport of Cu(II) through a supported liquid membrane with calix[4]arene as a carrrier

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ABSTRACT

In the present investigation, *p*-morpholinomethylcalix[4]arene (**1**) has been examined as a carrier in supported liquid membrane (SLM) for Cu(II) transport. The influence of different parameters, such as solvent, membrane dipping time, support membrane, co-anions, donor and acceptor pH, and carrier concentration on Cu(II) transport, was checked. The permeability values were calculated by using Danesi mass transfer model. Higher Cu(II) permeability was observed in diphenyl ether, with 1 h dipping time, Celgard 2500 and $Cl^-$ as co-anion. The optimum pH for donor phase was 2 and that for acceptor phase was neutral at $10^{-3}$ M carrier concentration. Diffusion coefficients were calculated using Reinhoudt's model, lag time measurements as well as by Wilke–Chang relation and compared. The transport was found to be diffusion-controlled in the membrane phase and the diffusion coefficient was calculated to be $1.54 \times 10^{-10}$ m/s whereas the extraction constant was calculated to be $1.19 \times 10^{-5}$ m/s.

## 1. Introduction

Toxic heavy metal discharge is infecting the atmosphere day by day. Finding out ways to minimize their harmful effect is a challenging task for scientists. Copper is a heavy metal widely present in nature. It is a soft transition metal and constituent of alloys, pharmaceutical products and found in almost all body tissues [1]. The suggested safe limit by WHO in drinking water for copper is 2 ppm [2]. Its excess has a deleterious effect on living organisms. Copper toxicity is based on its oxidation state: Cu(I) and Cu(II) [3]. It can pollute the environment through various means. Different industries, such as mining, paper, refining, petrochemical, metallurgy and fertilizer dispose copper in their effluents [4]. Therefore, the workers of these industries are more exposed to copper toxicity [5]. Corrosion of water supply pipes also releases it into aqueous streams [3]. Prolonged copper exposure is associated with a number of health problems, including jaundice, liver dysfunction, headache, nausea, diarrhea, stomach and intestinal problems, depression, learning disorders, fatigue, kidney and brain damage [6,7]. Wilson's disease is a hereditary disorder in which the body is unable to metabolize copper. Thus, patients suffering from this disease accumulate copper both by food and environmental sources. Hence, they are affected badly by copper toxicity [7]. Marine life also reveals severe effect of copper contamination. It distorts the normal functioning of gills, liver, kidneys, smell organs and the nervous system in them [8]. Furthermore, in waste water, it hinders the biodegradation of organic pollutants and hence, aid in increasing pollution. Therefore, it is of prime importance to search for methods which effectively remove copper from industrial discharge prior to its dumping [9].

Among the numerous techniques applied to eliminate copper from the atmosphere are biosorption [10], adsorption [11], ion exchange [12], electrochemical treatment [13], chemical precipitation [14] and solvent extraction

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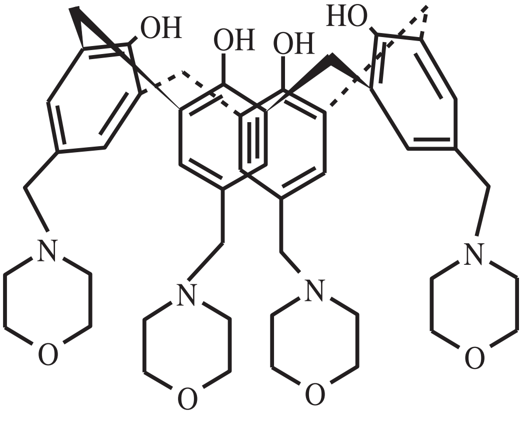
[15]. In this connection, liquid membrane (LM) is emerged as a truly green technology. The most prominent features of LM are cost effectiveness, less laboriousness, easy handling, specificity, and use of fewer amounts of expensive carrier as well as organic liquids. It has low carrier to metal solution ratio [16–19].

Supported liquid membrane (SLM) is a type of LM mostly used in industries. An organic liquid with carrier supported on the membrane is sandwiched between the two aqueous phases. Carrier solution is impregnated on support membrane due to capillary forces. Despite the proper choice of solvent and membrane, carrier leaching during the passage of time is still a challenging difficulty [20–23]. Therefore, new technological advancements are carried out in SLM to overcome membrane instability and for its wider application in separation fields. Typical applications of SLM are recovery and separation of precious metals [24], radioactive metals [25], rare earth metals [26], toxic metals [20,22], heavy metals [6], sugar [27], dyes [28], and drugs [29].

Carrier plays a key role in specific membrane separation. Recently, macrocyclic carriers have been explored and found efficient as well as selective towards ionic and neutral guests. Calixarenes are popular vase-like macromolecules capable of forming inclusion complexes with ions and neutral species. Their derivatives can be easily synthesized by adding the desired functionality [30–34]. In LM transport, many calixarene derivatives have been employed successfully [16–21,35–38]. Herein, we report the SLM study of *p*-morpholinomethylcalix[4]arene (**1**), as shown in Fig. 1 for Cu(II), whose selectivity has been previously evaluated by our group [33]. Celgard 2400 and 2500 membranes have been used as the solid support in SLM. The effect of the fundamental parameters influencing the transport process, e.g. carrier concentration, type of solvent used in the membrane, pH of donor and acceptor phases, anion types and dipping time for membrane preparation has been investigated. Danesi mass transfer model was used to calculate the permeability coefficients for each parameter studied. The diffusion coefficient was obtained experimentally using the Reinhoudt's model, lag time method and by Wilke–Chang relation and compared.



**1**

**Fig. 1.** *p*-Morpholinomethylcalix[4]arene (**1**).

## 2. Experimental methods

### 2.1. Materials

Analytical grade reagent chemicals were used to make aqueous solutions. Ultra pure deionized water for the solution preparation was taken from a Milli-Q system (ELGA Model CLASSIC UVF, UK). The **1** was synthesized following the method reported in [33]. The solid polymeric membranes, Celgard 2500 (thickness: 25 μm, porosity: 45%) and Celgard 2400 (thickness: 25 μm, porosity: 38%) were provided by Selcuk University, Department of Chemistry, Konya, Turkey and AMTech, Islamabad, Pakistan.

### 2.2. Apparatus

The cell used in the present study for SLM was made from Perspex material as presented in Fig. 2. It consisted of two cylindrical portions of equal size with volume capacity of 106 mL each. The support membrane was clamped between the two portions with flanges. Both portions were equipped with electrical stirrers at a speed greater than 1000 rpm. The inlet and outlet openings were given to fill and drain donor and acceptor solutions, respectively. The effective membrane exposing area was 12.56 $cm^2$. The membrane impregnated with **1** is used here. $Cu(NO_3)_2$ solution and deionized water were used as donor phase and acceptor phase, respectively. Temperature was kept constant for all experiments, i.e. 25 °C. Conductivity change was analyzed periodically with the help of a conductivity electrode placed in the acceptor phase. The experiments were repeated twice for each parameter and the experimental error was calculated.

### 2.3. Analytical instruments

The conductivity of the solutions was checked with Inolab Cond 720 conductivity meter. Scanning electron microscope (SEM) images were obtained by Model JSM-6490 A (Jeol Japan). The solutions pH was maintained with 781-pH/ion meter (Metrohm Switzerland). Stirring was accomplished by using a mechanical shaker (Gallenkamp) with temperature controller. Perkin Elmer Lambda 35 UV/Vis spectrophotometer was used to measure the solution absorbance.

### 2.4. Membrane preparation

The solution of **1** ($1 \times 10^{-3}$ M), in diphenyl ether, was prepared to soak Celgard membrane for 60 min. Membrane pores were filled through capillary action by this solution. The impregnation of **1** onto the membrane results in an increase in its weight, which confirms the loading of **1**. Soft tissue paper was used to absorb extra solution from the membrane surface and kept in open atmosphere for few minutes so that it could dry well. Afterwards, the membrane was clamped in the SLM apparatus.