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# Competitive Bulk Liquid Membrane Transport and Extraction of Cu(II), Ni(II), Zn(II) and Mn(II) Cations Using 5-Methyle-4[thiophen-2-yl-methylen-amino]-3-thio-oxo-1, 2, 4-triazol-5-one and phthalic dicarboxaldehyde

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**Abstract:** The competitive metal ion extraction and transport of Cu(II), Ni(II), Zn(II) and Mn(II) with a S-N donor, *i.e.* 5-methyle-4[thiophen-2-yl-methylen-amino]-3-thio-oxo-1,2,4-triazol-5-one(ATTT) and oxygen donor, phthalic dicarboxaldehyde(PHDC) compounds was examined and compared each other. Although the extraction and transport behavior of Cu(II) and Zn(II) with both ATTT and PHDC ligands is fundamentally similar, but the transport efficiency for Cu(II) is much better than Zn(II) ion. The transport and extraction results closely parallel for the cations using the present ligands. The experiments were buffered (acetic acid/sodiumacetate and formic acid/sodiumformate ) at pH 3-7. The concentrations in the all transport and extraction experiments for the cations and ligands were 0.01M and  $1.0 \times 10^{-3}$ M respectively

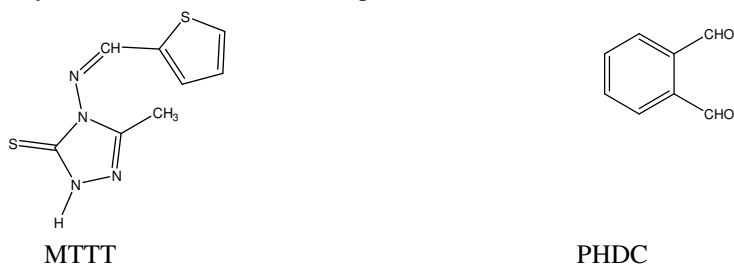
**Keywords:** Transport, Extraction, pH, ATTT, PHDC

## Introduction

Among the separation techniques, ion transport is a selective, efficient and simple method. In the recent years, the liquid membrane has widely been used to study ion transport with a concentration gradient<sup>1-5</sup>. Ion transport through the liquid membrane plays an important role

in simulating biological membrane functions and separation technologies because of the high transport efficiency, excellent selectivity and economic advantages of the liquid membrane. Selective transport of transition metal ions through liquid membranes has become increasingly noteworthy. A number of carriers for heavy metal ions, particular Cu(II), which is both vital and toxic to many biological systems, have been reported<sup>6-8</sup>. A series of oxygen- nitrogen and sulfur donor macrocycles were employed as extractants/ionophores in competitive experiments<sup>9-10</sup>. Ion transport is inherently a reaction based method, and its advantages are due to controllability of the carrier reaction conditions<sup>11</sup>. An efficient separation process combines a high transport rate with a high Selectivity<sup>12</sup>.

Solvent extraction process based on simple organic complexing extractants are often used commercially for the recovery and purification of metal ions. Metal ion extraction depends up on number of parameters. Some of these include ligand structure, pH of solutions, solvent, temperature and time of extraction<sup>13</sup>. In this research, we describe the liquid membrane transport and extraction system containing 3-thiophen-1, 2, 4-triazole and phthalic dicarboxaldehyd for the selective transport of copper (II) ion. 5-methyle-4[thiophen-2-eyl-methylen-amino]-3-thio-oxo-1, 2, 4-triazol-5-one (MTTT) and phthalic dicarboxaldehyde (PHDC) are the carrier as presented in scheme I.



Scheme 1. The structures of ligand.

## Experimental

### *Materials and solutions*

All of the chemicals used were of analytical reagent grade of Merck. All aqueous solutions were prepared with double distilled deionized water. The standard stock solution of copper (II), Mn (II), Zn (II), and Ni (II) was prepared by dissolving nitrate salts of them. MTTT ligand was synthesized as described before<sup>14</sup>. A  $1 \times 10^{-3}$  M stock solution of MTTT and PHDC was prepared in chloroform.

### *Instrumental*

Concentrations of cations were obtained using a Philips PU9100X atomic absorption spectrometer. The extraction samples were shaken on a IKA-WERKE shaker.

### *Extraction Experiments*

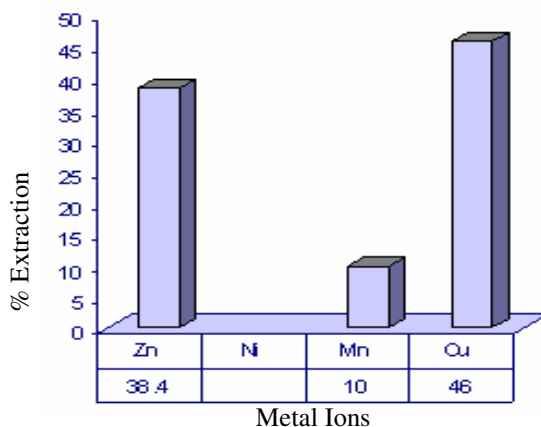
The competitive metal ion extraction from an aqueous phase in to a chloroform phase was employed. The aqueous phase was buffered at pH 3.5, 4.5, 5.5, 6 and 7.0 with sodium acetate/acetic acid and sodium formate/formic acid. The metal ions present at a concentration of 0.01 M were Cu(II), Mn(II), Zn (II), and Ni (II) as their nitrate salts. The extraction was carried out in small sealed flasks (25mL). The flasks were shaken for 24 hours on a mechanical shaker (at 25°C). The metal ion concentrations after each extraction experiment, was determined using atomic absorption spectrophotometer. Each experiment was performed in triplicate runs and values are the average of them.

### Membrane Transport

The transport experiments employed in a "concentric cell" in which the aqueous source phase (10cm<sup>3</sup>) and receiving phase (50cm<sup>3</sup>) were separated by chloroform phase (70 cm<sup>3</sup>). Details of the cell design have been reported elsewhere<sup>15-16</sup>. For each experiment both aqueous phases and the chloroform phase were stirred at 8 rpm; the cell was enclosed by a water jacket and thermo stated at 25 °C. The aqueous source phase was buffered (acetic acid/sodium acetate) at pH 5.0 and 6.0, contained the required ligand (1.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>). The receiving phase was buffered (formic acid/sodium format) at pH 3.0. All transport runs were terminated after 24h and were performed in triplicate. In a separate experiments the transport of cations through the cell (no using of the ligand) were checked. In this case there was no evidence of metal ion transport from source phase to the membrane or receiving phases. Atomic absorption spectrometry was used to determine the amount of ion transported. Transports rates represent mean values from duplicate runs measured over 24h.

### Results and Discussion

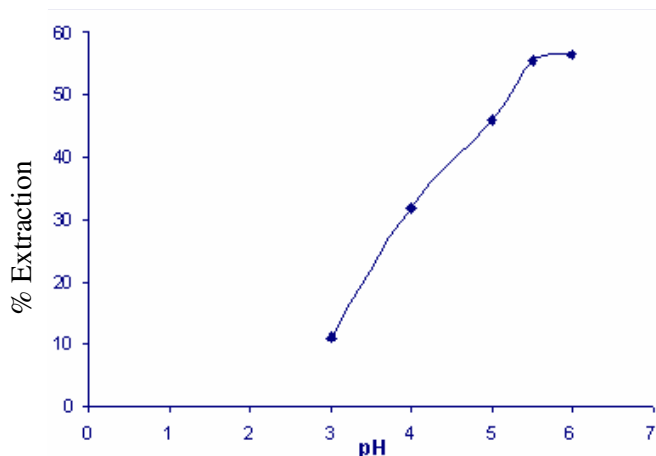
The competitive metal ion solvent extraction experiments (water/chloroform) have been carried out using each of the MTTT and PHDC as extractants. In individual experiments MTTT and PHDC were employed as the ionophore in the respective chloroform phases. Ionophore concentrations 1.0 X 10<sup>-3</sup> mol dm<sup>-3</sup> for each ligand was employed. The results of competitive metal ion extractions using MTTT at pH 5.0 are presented in Figure 1.



**Figure 1.** The competitive metal ion extraction using MTTT as a ligand.

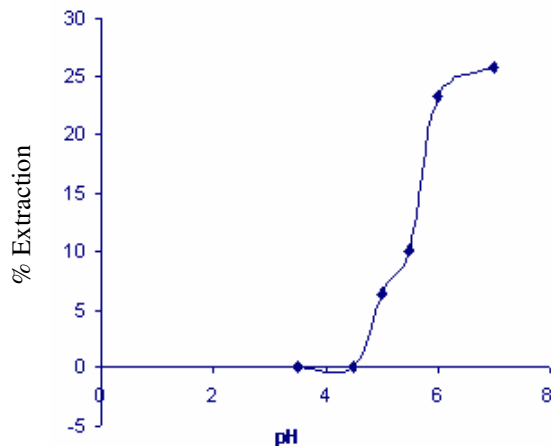
*(The aqueous phase was buffered at pH 5.0 with sodium acetate/acetic acid. The metal ions Cu (II), Mn (II), Zn (II), and Ni (II) were 0.01M as their nitrate salts. The extraction was carried out in small sealed flasks (25mL). The flasks were shaken for 24 h on a mechanical shaker (at 25 °C). Each experiment was performed in triplicate runs and values are the average of them)*

In the conditions employed for extraction experiments, MTTT by N, S-donor is a more effective and showed sole selectivity for copper (II) ion in confirmation of the expected affinity of this ion for an S-N-donor set<sup>17</sup>. The extraction of copper (II) with MTTT and PHDC was studied under the optimum conditions of the pH. Figures 2 and 3 show the extraction dependence to pH of the source phase solutions for the employed cations.



**Figure 2.** The effect of pH on the extraction of MTTT-copper complex.

*(The competitive metal ion extraction from an aqueous phase in to a chloroform phase was employed. The aqueous phase was buffered at pH 3-7 with sodium acetate/acetic acid and sodium formate/formic acid. The metal ions present at a concentration of 0.01 M were Cu (II), Mn (II), Zn (II), and Ni (II) as their nitrate salts. The extraction was carried out in small sealed flasks (25mL). The flasks were shaken for 24 hours on a mechanical shaker (at 25°). Each experiment was performed in triplicate runs and values are the average of them)*

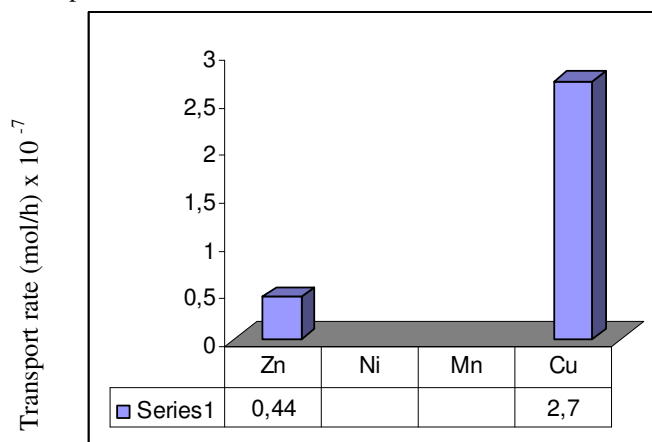


**Figure 3.** The effect of pH on the extraction of PHDC-copper complex.

*(The competitive metal ion extraction from an aqueous phase in to a chloroform phase was employed. The aqueous phase was buffered at pH 3-7 with sodium acetate/acetic acid and sodium formate/formic acid. The metal ions present at a concentration of 0.01 M were Cu(II), Mn(II), Zn (II), and Ni (II) as their nitrate salts. The extraction was carried out in small sealed flasks (25mL). The flasks were shaken for 24 hours on a mechanical shaker (at 25°). Each experiment was performed in triplicate runs and values are the average of them)*

The study involved competitive metal ion transport from an aqueous source phase Containing copper(II), Nickel (II), Zinc (II) and Manganese (II) across a bulk chloroform membrane incorporating an ionophore chosen from MTTT and PHDC. Transport was maintained with buffering the source and receiving phases. The results of the transport experiments at pH 5.0 are shown in Figure.4. Like as the extraction experiments MTTT triazol

ligand (N, S-donor) are more efficient ionophore than PHDC ( $O_2$ -donor). Clearly, the transport and extraction results closely parallel each other for the present ligands. Table 1, compares the results of competitive metal ion extraction and transport for the cations. As it is shown on the Figs. 1,4 and Table 1, both MTTT and PHDC ligands have more selectivity for Cu (II) ion respect to the other cations.



**Figure 4.** The competitive transport rates for the MTTT.

(The aqueous source phase ( $10\text{cm}^3$ ) and receiving phase ( $50\text{cm}^3$ ) were separated by a chloroform phase ( $70\text{cm}^3$ ). For each experiment both aqueous phases and the chloroform phase were stirred at 8 rpm; the cell was enclosed by a water jacket and thermo stated at  $25^\circ$ . The aqueous source phase was buffered (acetic acid/sodium acetate) at pH 5.0 contained the ligand ( $1.0 \times 10^{-3}\text{ mol dm}^{-3}$ ). The receiving phase was buffered (formic acid/sodium format) at pH 3.0. All transport runs were terminated after 24h. Transports rates represent mean values from duplicate runs measured over 24h)

**Table 1.** The results of competitive metal ion extraction and transport experiments using MTTT and PHDC as carriers at  $25^\circ\text{C}$ . The results are mean of triplicate (extraction) and duplicates (transport) runs.

Metal ion	MTTT (at pH 5.0)		PHDC (at pH 6.0)	
	Extraction %	Transport rate $10^{-7}$	Extraction %	Transport rate $10^{-7}$
Mn (II)	10	0	0	0
Ni (II)	0	0	0	0
Zn (II)	38.4	0.44	6	0.05
Cu (II)	46	2.7	23.23	0.13

### Acknowledgments

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