# Mobile Carrier Properties of $N_2O_2$- and $N_3O_2$-Type Schiff Base Molecules Towards Copper(II) Ions

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**ABSTRACT:** *Mobile carrier properties of two schiff base ligands, named bis(2-hydroxypropiophenone)-1,2-propanediimine ($N_2O_2$) and bis(1'-hydroxy-2'-acetonaphthone)-2,2'-diiminodiethylamine ($N_3O_2$), dissolved in dichloromethane for the extraction of copper(II) ions from an ammonium buffer feed phase into a nitric acid solution (receiving phase) were investigated and compared. The parameters influencing the transport efficiency such as pH of the feed phase, chemical composition of the receiving phase, carrier concentration in the membrane and time dependency of the process were studied and discussed. Addition of sodium dodecysulfate (SDS), an anionic surfactant, to the receiving phase enhances significantly the process efficiency. This reveals that the transport is controlled by the kinetics of decomplexation at the stripping interface. The transported amount of copper ions from ammonium buffer (pH 7) into the receiving phase including $HNO_3$ and SDS across a dichloromethane layer containing $N_2O_2$ and $N_3O_2$, at 20 ºC, was found to be 90.6 (±0.7) % and 97.4 (±0.4) % after 4 h, respectively. The selectivity of the processes towards copper ions were tested by performing the competitive transport experiments on the mixture containing $Pb^{2+}$, $Ni^{2+}$, $Cd^{2+}$, $Zn^{2+}$ and $Co^{2+}$ ions. Although $N_3O_2$ possess higher transport efficiency with respect to that of $N_2O_2$, both ligands present adequate selectivity for separation of Cu(II) ions.*


**KEY WORDS:** *$N_xO_y$-type schiff base ligands, Extractant-carrier properties, Bulk liquid membrane, Copper(II) ions, Separation.*

## INTRODUCTION

Owing to their coordinating ability with a variety of metal ions, schiff base ligands have been involved in various analytical investigations for many years. As instance, they are a category of important sensory molecules for fabricating cation- [1] and anion- [2] selective electrodes. Octadecyl disks modified by schiff base ligands have been used for enrichment and separation of trace amount of metal ions [3]. *Shemirani et al.* [4]

studied the application of bis(2-methoxybenzaldehyde) ethylenediimine as a complexing agent for Cr(III) ions and a subsequent entrapment of these complexes in surfactant micelles for pre-concentration and separation of chromium ions. In addition, a variety of schiff base ligands of types $N_4$ [5] and $N_2O_2$ [6] were used as extractant in liquid-liquid extraction studies. Surprisingly, the mobile carrier properties of this type of ionophores

have been rarely studied. *Rouhollahi et al.* reported recently [7] the uphill transport of copper ions using a schiff base, named N,N-bis(salicylidene)-naphthylene-1,8-diamine.

Following to our recent studies on the complexing abilities, extractive properties and analytical applications of $N_xO_y$-type schiff base ligands [8-10], we now report a comparative investigation of copper ion transport through bulk liquid membranes containing bis(2-hydroxypropiophenone)-1,2-propanediimine ($N_2O_2$) and bis (1'- hydroxy -2'- acetonaphtone) -2,2'- diimino-diethylamine ($N_3O_2$) (Fig. 1) as extractant- carriers. The parameters affecting the transport efficiency were examined, compared and discussed. The influence of sodium dodecylsulfate in receiving phase is also evaluated. The selectivity of the process is determined by the competitive transport of copper ions from its mixtures with other normally associated metal ions.

**EXPERIMENTAL**

*Materials*

Bis (2-hydroxypropiophenone)-1,2-propanediimine ($N_2O_2$) and bis(1'-hydroxy-2'-acetonaphtone)-2,2'-diiminodiethylamine ($N_3O_2$) were synthesized according to the procedures reported previously [8,9]. Stock solutions (0.01 M) of copper, nickel, cobalt, cadmium lead and zinc were prepared by dissolving appropriate amount of corresponding nitrate salts (Fluka) in distilled water. Dichloromethane (Merck) was washed three times with distilled water before being used for the experiments. Sodium hydroxide, glycine, acetic acid, di-sodium salt EDTA, potassium iodide, ammonia solution, sulfuric, hydrochloric and nitric acid solutions were analytical reagent grade and were purchased from Merck or Fluka chemical companies.

*Transport experiments and analysis*

The experimental set-up [11, 12] was a double jacket cylindrical glass cell (4.5 cm diameter) holding a glass tube (2.25 cm diameter) for separating the two aqueous phases. Temperature of the solution was kept constant using theromstated water circulating through the jacket of the cell. The source phase (10 mL) contained copper ions ($1\times10^{-4}$ M) and ammonia solution (0.05 M at adjusted pH by adding HCl). The receiving phase (10 mL) included nitric acid solution (0.1 M) and sodium dodecylsulfate
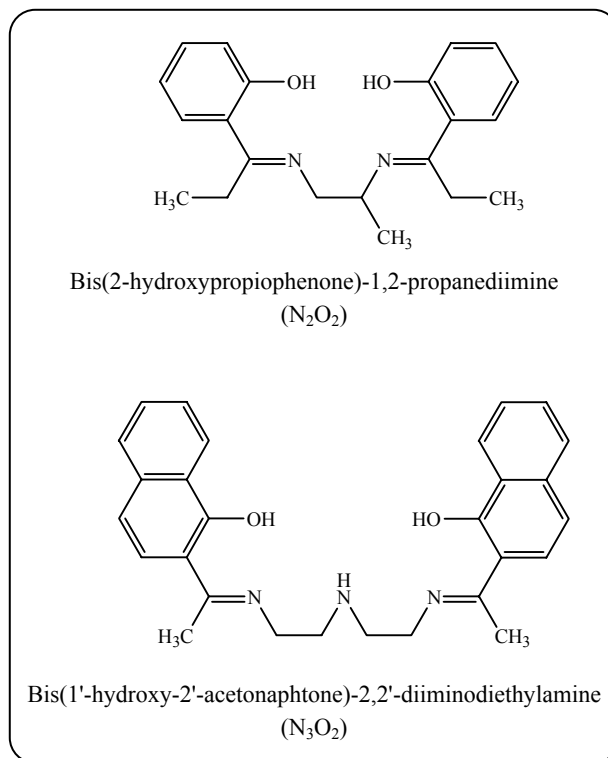


Bis(2-hydroxypropiophenone)-1,2-propanediimine
($N_2O_2$)

Bis(1'-hydroxy-2'-acetonaphtone)-2,2'-diiminodiethylamine
($N_3O_2$)

***Fig. 1: Chemical structure of the studied carriers.***

($1\times10^{-3}$ M). The aqueous phases were bridged by a dichloromethane solution (20 mL) of the investigated schiff bases ($N_2O_2$ and $N_3O_2$), which is placed below them. The experiment was started by stirring the organic phase (100 rpm) and the concentration of the metals in the aqueous phases was determined by atomic absorption spectrometry (AAS: Varian 220 AA).

**RESULTS AND DISCUSSION**

*Effect of feed phase pH*

The results of transfer of copper ions (initial concentration $1\times10^{-4}$ M) from feed phase (10 mL, 0.05 M ammonia solution) across a stirred (100 rpm) bulk liquid membrane (20 mL) containing $N_2O_2$ or $N_3O_2$ ($2\times10^{-3}$ M in dichloromethane) into a hydrochloric acid solution (0.1 M, 10 mL, receiving phase) as a function of feed phase pH, after 4 h at 20 ºC are shown in Fig. 2.

It is seen that for both carriers the transport efficiency increases with pH of the feed phase. This reveals a proton exchange mechanism for the extraction process at the first interface. However at higher pH values, a decrease in transported value of copper ions may be attributed to the depletion of the membrane from ionized carrier, although the formation of copper hydroxide cannot be ignored.
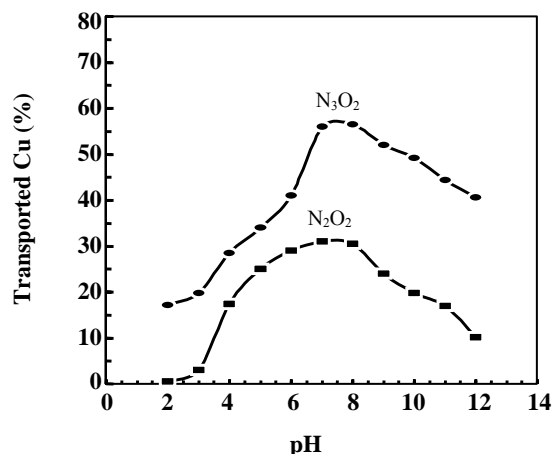
Fig. 2: Percentage of the transported copper ions from feed phase into the receiving phase through the bulk liquid membranes containing $N_2O_2$ or $N_3O_2$ ligands as a function of feed phase pH. Feed phase: 10 mL, initial copper concentration $1\times10^{-4}$ M, 0.05 M ammonia at various pH; Membrane: 20 mL, carrier concentration $2\times10^{-3}$ M in dichloromethane; Receiving phase: 10 mL, hydrochloric acid (0.1 M); Stirring rate: 100 rpm; Time: 4 h; Temperature: 20 °C.
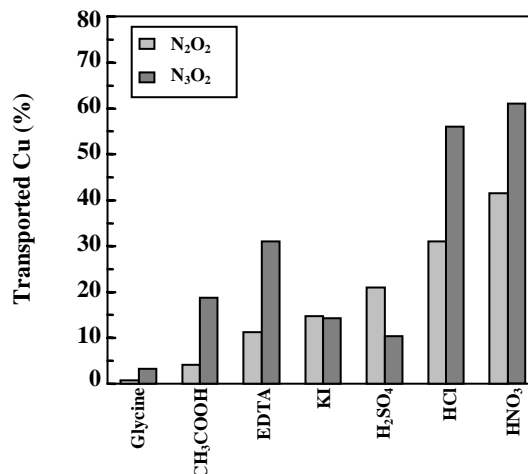


Fig. 3: Percentage of the transported copper ions from feed phase (0.05 M ammonia at pH = 7) into the receiving phase through the bulk liquid membranes containing $N_2O_2$ or $N_3O_2$ ligands as a function of the chemical composition (all at 0.1 M) of the receiving phase. EDTA solution was buffered at pH 5 by acetic acid/sodium acetate buffe. rother experimental conditions are given in Fig. 2.

Thus, pH 7 was selected for following experiments. At this pH, the amount of transported copper ions was found to be 31 and 56 percent with $N_2O_2$ and $N_3O_2$, respectively. The higher efficiency of the latter can be described by its more complexing ability, due to the presence of more donating atoms in its structure, on the one hand, and the more flexible structure of $N_3O_2$, that makes possible a better interaction between the donor atoms of the ligand and the cation, on the other hand.

## Influence of chemical composition of the receiving phase

Fig. 3 demonstrates the percentage of transported copper ions (initial concentration $1\times10^{-4}$ M) from feed phase (0.05 M ammonia, pH 7) across the organic layer containing $N_2O_2$ and $N_3O_2$ ($2\times10^{-3}$ M) into various receiving phase. Solutions containing 0.1 M glycine, acetic acid, EDTA (pH = 5, adjusted by acetic acid/ sodium acetate buffer), potassium iodide, hydrochloric acid and nitric acid were checked as receiving phase. The results reveal that nitric acid acts as the most efficient stripping reagent in comparison with other studied solutions.

## Effect of nitric acid concentration in the receiving phase

In order to evaluate the effect of nitric acid

on the process efficiency, the transport of copper ions through bulk liquid membranes containing studied schiff base ligands as a function of the acid concentration in the receiving phase was studied (Fig. 4). The initial increase in the percentage of transported copper ion with nitric acid concentration confirms the proton exchange mechanism of the copper complexation by the studied carriers. The observed decrease beyond 0.1 M of acid can be attributed to a probable extraction of copper ions by solvation mechanism in the presence of nitrate counter ion.

## Influence of carrier concentration

In the facilitated transport processes the extractant-carrier acts as a phase transfer catalyst. It complexes the metal ion and forms a lipohilic species diffusing in the organic membrane and then release the analyte into the stripping phase. Fig. 5 shows the results of the transport of copper ions through dichloromethane solutions containing different amounts of $N_2O_2$ and $N_3O_2$, under experimental conditions given in the caption of the figure. For both systems the transport efficiency is independent to the carrier concentration beyond about $5\times10^{-3}$ M. Therefore, a concentration of $7.5\times10^{-3}$ M was chosen as an optimum carrier concentration for following the experiments.
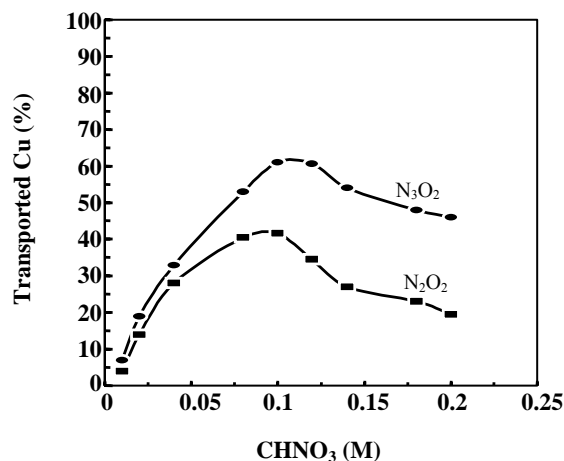
*Fig. 4: Percentage of the transported copper ions from feed phase into the receiving phase through the bulk liquid membranes containing $N_2O_2$ and $N_3O_2$ ligands as a function of the nitric acid concentration in the receiving phase. Other experimental conditions are given in Fig. 3.*



*Fig. 5: Percentage of the transported copper ions from feed phase into the receiving phase (HNO$_3$ 0.1 M) through the bulk liquid membranes containing $N_2O_2$ or $N_3O_2$ ligands as a function of the carrier concentration in the membrane. Other experimental conditions are given in Fig. 3.*

### Effect of SDS in the receiving phase

The decomplexation process of the diffused copper complexes at the stripping interface may influence the transport efficiency. This controls the transport if it is being kinetically or thermodynamically unfavorable. Under optimum experimental conditions (i.e. feed phase 0.05 M ammonia solution at pH 7; membrane $7.5 \times 10^{-3}$ M carrier in dichloromethane; receiving phase 0.1 M nitric acid), the amount of copper in the receiving phase achieves nearly to 45 and 63 percent using $N_2O_2$ and $N_3O_2$, respectively, regardless to the time of transport (tested for 4-6 h). In contrast, a decrease in copper concentration was observed in the feed phase as a function of time. It means that the decomplexation step at the membrane/receiving phase interface controls the transport process, probably due to a saturation of the copper-schiff base complexes at this interface. Recent report on the transport of copper ions by a $N_2O_2$-type schiff base [7] consists with the enhancement of the transport efficiency by the presence of anionic surfactant sodium dodecylsulfate (SDS) in the receiving phase.

In order to assess the effect of SDS, we examined the transport of copper ions in the optimum conditions, as a function of SDS concentration in the receiving phase (Fig. 6). The presence of SDS results a significant increase on the amount of transported copper ions. The presence of such surfactant may change the mechanism and thus favors the decomplexation kinetics.
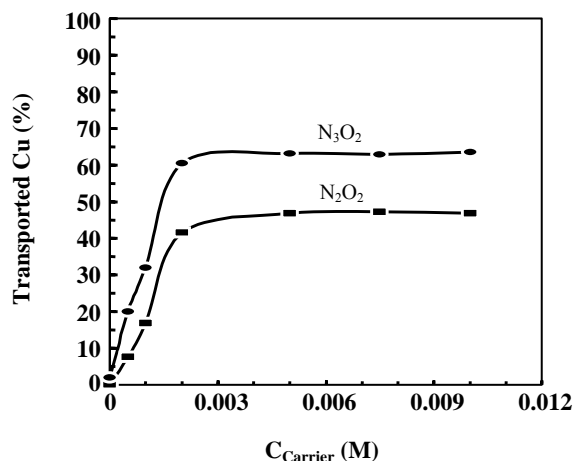
The copper transport by $N_3O_2$ is maximized when the concentration of SDS is $5 \times 10^{-4}$ to $1.3 \times 10^{-3}$ M. This condition is achieved at the concentrations of SDS higher than $1 \times 10^{-3}$ M by using $N_2O_2$. Thus, a concentration of $1 \times 10^{-3}$ M sodium dodecylsulfate was selected for modifying the receiving phase composition.

### Influence of time

To this point of study 4 hours was taken as time of transport. For checking the effect of this parameter the transport experiments as a function of time were performed (Fig. 7). The stripping phase was a solution of nitric acid (0.1 M) and SDS ($1 \times 10^{-3}$ M). The results reveal that the transport of copper ions does not vary beyond 2 and 3 hours by $N_2O_2$ and $N_3O_2$, respectively.

### Repeatability of the transport process

Based on the results obtained in the described experiments the following conditions were selected: feed phase, 10 mL, $Cu^{2+}$ ($1 \times 10^{-4}$ M), ammonia solutions (0.05 M) at pH=7; membrane, 20 mL, schiff base ($N_2O_2$ or $N_3O_2$) $7.5 \times 10^{-3}$ M in dichloromethane; receiving phase, 10 mL, HNO$_3$ (0.1 M), SDS ($1 \times 10^{-3}$ M); time, 4 h; stirring rate, 100 rpm; temperature, 20 °C.

Under optimum conditions, the results of three replicate experiments show a value of 90.6 ($\pm$0.7) % and 97.4 ($\pm$0.4) % of the initial amount of copper ions is extracted into receiving phase by $N_2O_2$ and $N_3O_2$, respectively.
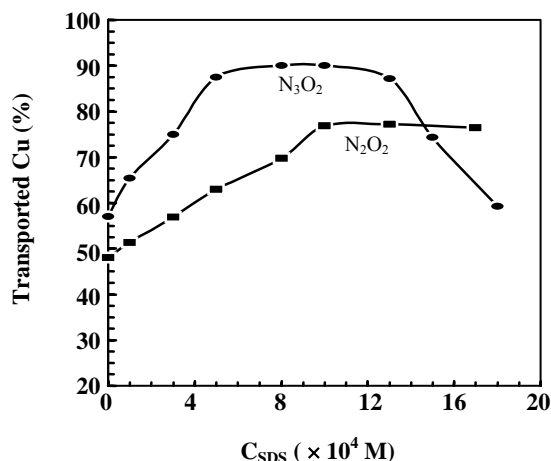
*Fig. 6: Percentage of the transported copper ions from feed phase into the receiving phase ($HNO_3$ 0.1 M and SDS) through the bulk liquid membranes containing $N_2O_2$ or $N_3O_2$ ($7.5 \times 10^{-3}$ M) ligands as a function of SDS concentration in the receiving phase. Other experimental conditions are given in Fig. 5.*



*Fig. 7: Percentage of the transported copper ions from feed phase into the receiving phase ($HNO_3$ 0.1 M and SDS $1 \times 10^{-3}$ M) through the bulk liquid membranes containing $N_2O_2$ or $N_3O_2$ ($7.5 \times 10^{-3}$ M) ligands as a function of time. Other experimental conditions are given in Fig. 5.*

### Selectivity of the processes

Selectivity of the transport experiments using $N_2O_2$ and $N_3O_2$ carriers under similar experimental conditions towards copper ions over lead, nickel, cobalt, cadmium and zinc ions from binary mixtures and a mixture containing all of the mentioned ions was evaluated (table 1). The results present the suitable selectivity of the studied carriers towards copper ions over the examined ions.

It is noteworthy that, the presence of other metal ions in the mixture decreases the percentage of copper transported in comparison with those in the single species experiments. This probably being due to a multi-ion competition or crowding effect [13-15].

### CONCLUSIONS

$N_xO_y$-Type schiff base ligands are known as effective complexing agents for Cu(II) ions. The influence of the number of donating atoms and the chemical structure of this type of ligands has been verified by using a $N_2O_2$- and $N_3O_2$-type schiff bases as extractant-carrier for transporting copper ions through dichloromethane bulk liquid membrane into a nitric acid receiving phase.

The schiff base bis(1'-hydroxy-2'-acetonaphtone)-2,2'-diiminodiethylamine ($N_3O_2$) shows to be a more effective carrier agent with respect to the studied $N_2O_2$-type schiff base bis(2-hydroxypropiophenone)-1,2-propanediimine ($N_2O_2$).
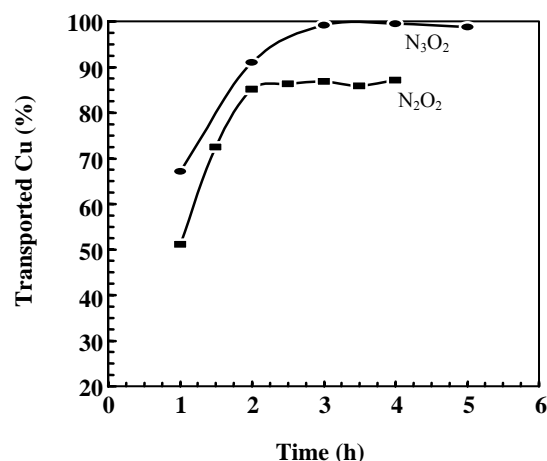
*Table 1: Percentage of the transported copper, zinc, cobalt, cadmium, nickel and lead ions from its mixtures by $N_2O_2$ and $N_3O_2$.[a]*

| Mixture | $M^{2+}$ | Transported value (%) | |
|---|---|---|---|
| | | $N_2O_2$ | $N_3O_2$ |
| Mix. 1 | $Cu^{2+}$ | 83.2 | 96.7 |
| | $Zn^{2+}$ | 6.2 | 4.3 |
| Mix. 2 | $Cu^{2+}$ | 82.7 | 95.6 |
| | $Co^{2+}$ | 14.6 | 4.7 |
| Mix. 3 | $Cu^{2+}$ | 89.6 | 97.8 |
| | $Cd^{2+}$ | 1.3 | 12.6 |
| Mix. 4 | $Cu^{2+}$ | 80.1 | 98.0 |
| | $Ni^{2+}$ | 6.8 | 16.8 |
| Mix. 5 | $Cu^{2+}$ | 88.0 | 97.2 |
| | $Pb^{2+}$ | 2.1 | 18.1 |
| Mix. 6 | $Cu^{2+}$ | 79.6 | 94.3 |
| | $Zn^{2+}$ | 3.6 | 1.5 |
| | $Co^{2+}$ | 12.3 | 1.4 |
| | $Cd^{2+}$ | <1 | 4.1 |
| | $Ni^{2+}$ | 3.5 | 5.2 |
| | $Pb^{2+}$ | 1.7 | 6.7 |

It is resulted that the kinetics of copper ion transport by schiff bases control by decomplexation of the diffused species through bulk liquid membrane at the stripping interface. This process is modified by the presence of an anionic surfactant, i.e., sodium dodecylsulfate.

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