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Selective Extraction and Bulk Liquid Membrane Transport of Cu(II) from Aqueous Nitrate Solution in the Presence of Zn(II), Ni(II) and Mn(II) Cations Using Benzoyl Acetone

A. NEZHADALI, H. VAHEDI*, M. ROIGAR and A.SADEGHI

Department of Chemistry, Payame Noor University (PNU), Mashhad, Iran.
hooshangvahedi@yahoo.co.uk

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Abstract: The competitive metal ion extraction and transport of Cu(II), Ni(II), Zn(II) and Mn(II) with benzoyl acetone and EDTA was studied. In the experiments the ligand was dissolved in chloroform and the pH and time of extraction or transport were varied. Also the rate of shaking and ligand concentration on the efficiency of extraction and transport was studied. The results revealed that the ligands exclusively extract Cu(II) from the mixture of the above cations.

Keywords: Extraction, Transport, Benzoyl acetone, Chloroform, pH.

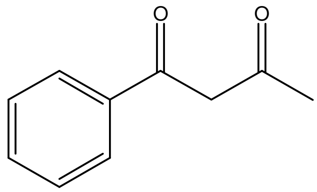
Introduction

The design of highly selective reagents for binding of metal ions is of vital importance to broad areas of analytical chemistry and separation science. In recent years, the liquid membrane has widely been used to study ion transport with a concentration gradient[1-5].

There has been a growing interest in the transport of metal ions mediated by receptor molecules where the carrier operates selective across artificial or biological membranes. Selective transport of transition metal ions through liquid membrane has become increasingly noteworthy[6]. A number of carriers for heavy metal ions, particular Cu(II), which is both vital and toxic too many biological systems have been reported[7-8]. A series of oxygen-nitrogen and sulfur donor macrocyles have been well known for selective recognition of specific metal ions or molecules[9-10]. Ion transport advantages are due to controllability of the carrier reaction condition[11] which combines a high transport rate with a high selectively[12].

Solvent extraction processes based on simple organic complexing extractants are often used commercially for the recovery and purification of metal ions[13]. Metal ion extraction depends to ligand structure, pH of solution, type of solvent, temperature and time of Extraction[13]. The coupled transport of Cu(II) and Ni(II) ions through a bulk liquid membrane (BLM) containing pyridine-2-acetaldehyde benzoylhydrazone (2-APBH) as carrier dissolved in toluene has been reported[14]. Gholivand *et al.* investigated the selectivity and efficiency of copper transport from aqueous solution containing various metal ions using *N*, *N*'-bis(salicylidene)-1,2-phenyldiamine[15]. Also selective transport of metal ions has been studied and reported using N/O/S-donor macrocycle thioethers[16-21]. However, the synthesis of these ligands requires carrying out the low yield multi-step reactions.

In this research, we describe competitive liquid membrane transport and extraction system using benzoyl acetone (Scheme 1) which is cheap and commercially available compound for the selective transport of Cu(II) ion.



Scheme 1. Chemical structure of benzoyl acetone.

Experimental

All of the chemicals used were Merck analytical reagent grade. The standard stock solution of Cu(II), Mn(II), Zn(II) and Ni(II) were prepared by dissolving the corresponding nitrate salts. A 10 mM stock solution of benzoyl acetone was prepared in chloroform.

Instrumentation

The concentration of cations was determined by using a Philips PU9100X atomic absorption spectrometer. The extraction of samples was undertaken using an IKA-WERKE shaker. The pH measurements were carried out using 741 Metrohm pH meter.

Extraction experiments

The competitive metal ion extraction from an aqueous phase into a chloroform phase was employed. The aqueous phase was buffered at pH 3.0 - 7.0 using sodium acetate/acetic acid and sodium formate/formic acid. The metal ions present were Cu(II), Mn(II), Zn(II) and Ni(II) as their nitrate salts at a concentration of 10 mM. The extractions were carried out in sealed flasks (25 mL). The flasks were shaken for 24 h on a mechanical shaker (at 25 ^{o}C). The metal ion concentrations were determined after each extraction experiment, using atomic absorption spectrophotometer. Each experiment was performed in triplicate runs and the reported value is the average of them.

The optimal value for pH was used to optimize the ligand concentration. Alternatively, the obtained values were used in the optimizations of time and finally, all these values were used to optimize the rate of shaking on the extraction and transport experiments.

Results and Discussion

Extraction with benzoyl acetone pH effect

Most chelating ligands are conjugate bases of weak acid groups and, accordingly, have a very strong affinity for hydrogen ions. The pH, therefore, will be a very important factor in the separation of metal ions by chelating, because it will determine the values of the conditional stability constants of the metal complexes on the surface of the sorbent. Thus, the effect of pH on the extraction of copper ions was studied.

The extraction experiments of Cu(II), Mn(II), Zn(II) and Ni(II) has been carried out by benzoyl acetone at different pH values. The ligand is completely selective in pH= 6-7 for Cu(II) and the results are presented in Table 1. At lower pH values, there is a decrease in the percentage transport of copper, due to the diminished complexing ability of the ligand at such pH values.

Table 1. Effect of the pH on competitive extraction of Cu(II), Mn(II), Zn(II) and Ni(II).

pH of aqueous phase	% Extraction			
	Cu(II)	Zn(II)	Mn(II)	Ni(II)
3.0	0	0	0	0
3.5	0	0	0	0
4.0	0	0	0	0
4.5	0	0	0	0
5.0	0	0	0	0
5.5	0	0	0	0
6.0	9.8 (± 0.03)	0	0	0
6.5	9.8 (± 0.03)	0	0	0
7.0	9.8(± 0.03)	0	0	0

Conditions: Initial concentration of [Cu(II), Mn(II), Zn(II) and Ni(II)] 10 mM, shaking time: 24 h, rate of shaking: 300 rpm, benzoyl acetone 1 mM.

The Irving-Williams series of stability of metal complexes with dipositive metal ions increases in the series Ba-Cu, decreases with Zn[22]. The trend is essentially independent of the ligand. The position of Cu(II) is considered out-of-line with predictions based on crystal field theory and is probably a consequence of the fact that Cu(II) often forms distorted octahedral complexes[23].

The effect of ligand concentration

The effect of ligand concentration for extracting Cu(II) was studied and the results revealed that the highest extraction percentage was at the concentration of 0.005 mol/L of the ligand (Figure 1). We did not continue the experiment using further amount of the ligand concentration since the selectivity of competitive extraction decreases.

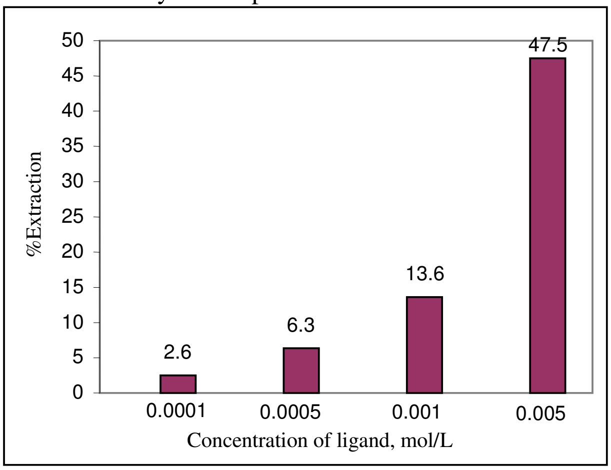


Figure 1. Effect of the ligand on the competitive extraction of Cu(II).

Conditions: Initial concentration of [Cu(II), Mn(II), Zn(II) and Ni(II)] 5 mM, time: 24 h, pH: 6.5, shaking rate:300 rpm.

Time effect

Figure 2, shows the time dependence of Cu(II) extraction through the liquid extraction designed under optimal experimental conditions using benzoyl acetone. It is obvious that the extraction of Cu(II) from the aqueous feed phase into the organic phase occurs very rapidly, so that the extraction seems to be about half complete after approximately 4 h. However, the release of Cu(II) ions into the aqueous strip phase remains constant (45%) after 4 h, under optimal conditions.

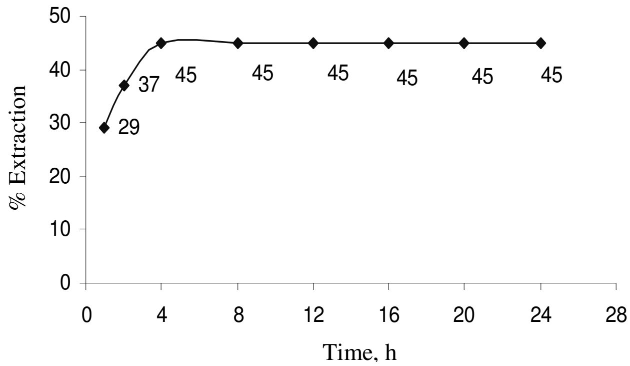


Figure 2. Effect of time on the competitive extraction of Cu(II).
Conditions: Initial concentration of [Cu(II), Mn(II), Zn(II) and Ni(II)] 10 mM, pH: 6.5, benzoyl acetone 5 mM, shaking, rate: 300 rpm.

Rate of shaking

In order to explore the effect of stirring speed, the extraction experiments were performed at five different speeds, 0, 100, 150, 300, 500 and 700 rpm. The results in Figure 3, indicate that the stirring speed affects the extraction efficiency of Cu(II) ions through the organic extraction. The effect of the stirring speed on the diffusion of species through organic extraction is an important factor in order to minimize the diffusion layer at the interfaces. However, it was found that the extraction efficiency increases although it comes to a constant amount after 100 rpm.

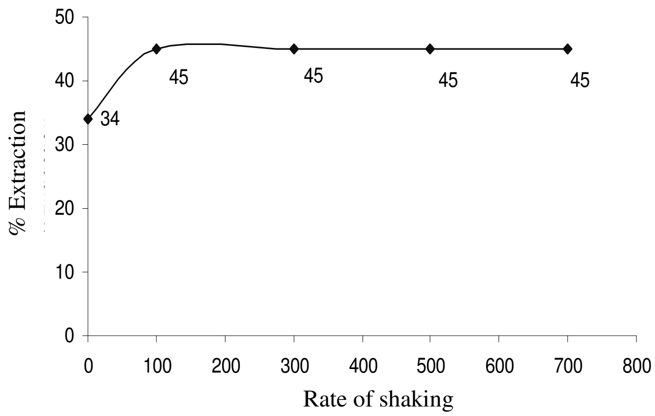


Figure 3. Effect of the rate of shaking on the competitive extraction of Cu(II).
Conditions: Initial concentration of [Cu(II), Mn(II), Zn(II) and Ni(II)] 10 mM, benzoyl acetone: 5 mM, time: 4 h, pH: 6.5.

Membrane transport

The transport experiments were employed in a "concentric cell" in which the aqueous source phase (10 mL) and receiving phase (30 mL) were separated by chloroform phase (70 mL). Details of the cell design have been reported elsewhere[24]. For each experiment both aqueous phases and chloroform phases were stirred at 8 rpm. The cell was enclosed by a water jacket and thermostated at 25 ^{o}C. The aqueous source phase was buffered by acetic acid/sodium acetate.

The receiving phase was buffered by formic acid/sodium format. All transport runs were terminated after 24 h and were performed in triplicate. In a separate experiments the transport of cations through the cell (in the absence of ligand) were checked. In this case there was no evidence of metal ion transport from source phase to the membrane or receiving phases. Transports rates represent mean values from triplicate runs measured over 24 h.

Transport with benzoyl acetone pH effect

The transport experiments of the mixture of Cu(II), Mn(II), Zn(II) and Ni(II) by benzoyl acetone at different pH was carried out and the results are given in the Table 2. The results shows that the ligand is completely selective in pH=3.5-6.0 for Cu(II) while slightly selective for Mn(II), Zn(II) and Ni(II) only at the pH = 6.5-7.0. However, by increasing the pH, the rate of transport of Cu(II) by benzoyl acetone decreases (Table 2). In membrane transport the aqueous receiving phase should be acidic to accompany the ligand so can return to interface between source and membrane phase.

Table 2. Effect of the pH on the competitive transport of Cu(II), Mn(II), Zn(II) and Ni(II).

pH of aqueous phase	Rate of transport, mol/h, × 10^{-7}			
	Cu (II)	Zn(II)	Mn(II)	Ni(II)
3.5	3.7	0	0	0
4.0	3.8	0	0	0
4.5	3.9	0	0	0
5.0	3.5	0	0	0
5.5	3.3	0	0	0
6.0	2.5	0	0	0
6.5	2.2	1.7	1.2	0.8
7.0	1.1	0.7	0	0.8

Conditions: Initial concentration of [Cu(II), Mn(II), Zn(II) and Ni(II)] 10 mM, Time: 24 h, Benzoyl acetone: 1 mM, Stirring rate: 8 rpm, Temperature25 ^{0}C.

It has been suggested that the mechanism is proton driven[6]. That is, the transport phenomenon is based on a protonation-deprotonation cycle of benzoyl acetone in the membrane interfaces of the source and the receiving phase, respectively. The ions form a complex with a deprotonated ionophore to be extracted from the receiving phase into the membrane phase. In the interface between the membrane and the receiving phase, the Cu(II) complex of benzoyl acetone because of the presence of high concentration of hydrogen ions should be broken and release Cu(II) into the source phase. The protonated ionophore would be transferred through the membrane phase to the interface of the feed phase.

Table 2, shows the effect of pH of the receiving phase on the efficiency of Cu(II) transport. It is quite clear that the transport of Cu(II) ions is influenced by the pH of receiving phase. The results revealed that the maximum Cu(II) transport occurs at pH 3.5-5.5. At higher pH values there was a decrease in the percentage of transport of Cu(II) probably due to the incomplete protonation of benzoyl acetone in the membrane interfaces of the receiving phase to accompany the ligand so can return to the donor aqueous phase. Since the most ions transport was happened at pH = 4, therefore it was used as an optimal value for the next experiments.

Time effect

The transport experiments of Cu(II) with benzoyl acetone in pH = 4.5 at different times has been studied. The results showed that rate of transport by increasing the time is decrease (Figure 4).

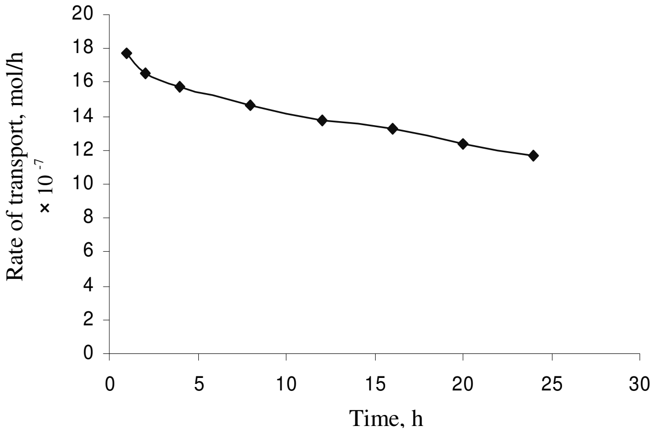


Figure 4. The effect of time on the rate of competitive transport of Cu(II).

Conditions: Initial concentration of [Cu(II), Mn(II), Zn(II) and Ni(II)] 10 mM, pH: 4.5, Benzoyl acetone: 1 mM, Stirring rate: 8 rpm, Temperature: 25 ^{0}C.

The ligand concentration effect

Figure 5 shows, rate of competitive transport for Cu(II) at pH = 4.5 for different concentration of ligand. However, it was found that the transport efficiency increases although it comes to a constant amount after 0.006 M/L of the ligand concentration. The amount 10 mM for the ligand concentration was used to optimize the EDTA concentration.

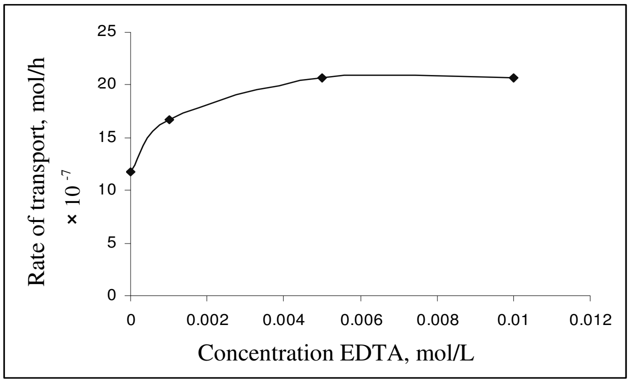


Figure 5. Effect of the ligand concentration on the rate of transport of Cu(II).

Conditions: Initial concentration of [Cu(II), Mn(II), Zn(II) and Ni(II)] 10 mM, Time: 5 h, pH 4.5, Stirring rate: 8 rpm, Temperature: 25 ^{0}C.

The effect of EDTA addition in acceptor phase

Figure 6, shows rate of transport for Cu(II) in pH = 4.5 for different concentrations of EDTA(1.0- 10 mM). Results showed that by increasing the amount of EDTA the rate of transport increases.

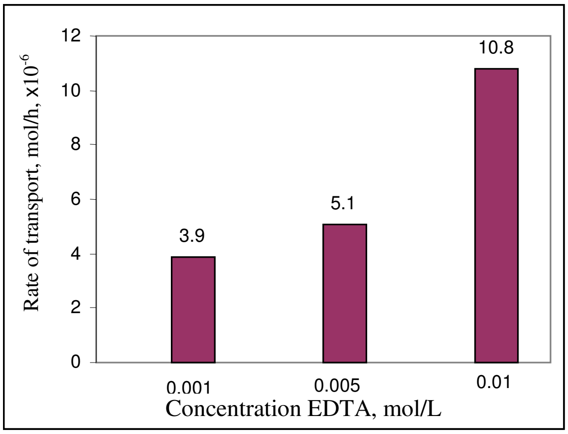


Figure 6. Effect of the EDTA addition in acceptor phase on the transport efficiency of Cu(II).

Conditions: Initial concentration of [Cu(II), Mn(II), Zn(II) and Ni(II)] 10 mM, Benzoyl acetone 10 mM, Time: 5 h, pH: 4.5, Stirring rate: 8 rpm, Temperature: 25 ^{0}C.

The EDTA plays an essential role in the metal ion releasing process in the receiving phase *via* the formation of a ternary amino acid-metal ion-complex. This co-operation probably assists the selective releasing of Cu(II) metal ion to the receiving phase, which can be seen from the growing in the percentage of transported Cu(II).

Conclusion

Results show benzoyl acetone is a selective ligand for Cu(II) from aqueous nitrate solution in the presence of Zn(II), Ni(II) and Mn(II) cations. Optimum conditions of competitive extraction experiment were found to be 6.5, 4 h, 5 mM, 100 rpm for pH, time, concentration of ligand and rate of shaking, respectively. In the competitive transport experiment the results are 4.5, 10 mM, 5 mM for pH, concentration of ligand and concentration of EDTA in acceptor phase, respectively. However, both extraction and transport have significant effect on the selective transfer of Cu(II), albeit not with the same efficiency which is due to different mechanism procedure during ion extraction and transport.

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