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Selective transport of Cu(II) ions from a mixture of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) cations through a bulk liquid membrane using benzyl bis (thiosemicarbazone) as carrier

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ABSTRACT

A dichloromethane membrane system incorporated with benzyl bis(thiosemicarbazone) **(LH_2)** as carrier is introduced for the selective transport of Cu(II) ion from an aqueous source solution containing Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) metal cations to a receiving aqueous phase. The optimum transport conditions were established by studding the composition of receiving phase, time of transport, stirring rate, pH of source phase, presence of fatty acid in the membrane as a phase modifier, type and concentration of surfactant, and concentration of mineral acid in the receiving phase, carrier concentration, and temperature. A kinetic model was also used to describe the Cu(II) ion transport behavior, assuming that it obeys the kinetic laws of two consecutive irreversible first-order processes. Under the optimal conditions, 43% of the initial concentration of Cu(II) ion from the aqueous source phase was extracted into the receiving phase through the bulk liquid membrane.

Keywords: Bulk liquid membrane; Ion transport; Benzyl bis(thiosemicarbazone); AAS; Cation

1. Introduction

The discharge of organic and metal pollutants into the environment without prior treatment is a serious problem of concern [1]. Because heavy metals are not biodegradable in natural conditions, they tend to accumulate in living organisms causing various diseases and disorders [2]. Furthermore, the presence of heavy metal ions in wastewater inhibits biodegradation of organic pollutants, which might be present in the wastewater [3]. Therefore, it is necessary to treat metal contaminated wastewater prior to its discharge to the environment. A variety of chemical techniques have been employed for metal cation separations, including chemical precipitation, ion exchange, and liquid–liquid extraction. Among these methods, liquid–liquid extraction has been the most widely commercially used method for the recovery and purification of metal ions [4]. One serious limitation in traditional solvent extraction processes is the consumption of high purity solvents and carriers, especially in dilute solutions [5]. The membrane extraction, an improved version of solvent extraction, has found application in the environmental sciences,

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in water pollution control, and hydrometallurgical separation [6,7]. The extraction chemistry is basically the same as that found in liquid–liquid extraction, but the transport is governed by kinetic rather than equilibrium parameters, that is, it is governed by a non-equilibrium mass transfer [8]. The attractive features of transport through membranes are their high selectivity and the simultaneous separation and preconcentration of elements, their simplicity, low operational costs, low-energy consumption, and the fact that they can be used for a broad spectrum of elements by carefully selecting the carrier [9]. Liquid membranes may be broadly classified into three types: bulk, emulsion, and supported liquid membranes. Bulk liquid membranes (BLMs) usually consist of an aqueous source and receiving phase, separated by a water-immiscible liquid membrane phase. BLMs are often used to study the transport properties of novel carriers [10].

Copper(II) ion is an environmental contamination, which has been tested and assessed over the past few years from both the toxicological and human health viewpoints [11]. It has been well reported that the accumulation of copper in human body causes brain, skin, pancreas, and heart diseases [12]. In the recent years, the bulk liquid membrane has widely been used to study of copper(II) ions transport [13–18].

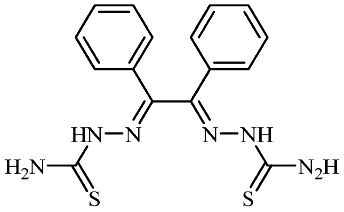

Fig. 1. Chemical structure of LH_2.

In this work, we have described a selective and proton-driven BLM system using LH_2 (Fig. 1) in membrane phase and nitric acid in receiving phase to competitive transport of Cu(II) ions.

2. Experimental

2.1. Reagent

The carrier LH_2 was synthesized according to reports of Matesanz et al. [19]. Dichloromethane (Merck) was used as membrane solvent. Cobalt(II) nitrate (Merck), zinc(II) nitrate (Merck), nickel(II) nitrate (Merck), lead(II) nitrate (Merck), manganese(II) nitrate (Fluka), and copper(II) nitrate (Scharlau) were used with the highest purity.

All the other chemicals used in this study were of the highest purity available without further purification. All aqueous solutions were prepared using deionized double-distilled water.

2.2. Instrumentation

A GBC Sens AA atomic absorption spectrometer (AAS) was used for measurement of metal ions concentration. The pH measurements were made with a Metrohm-827 pH meter using a combined glass electrode. An Ayat 90 circulator (Mashhad/Iran) was used to controlling the temperature of BLM transport cells.

2.3. Procedure

The transport experiments were done on standardized concentric cells (Fig. 2) in which the aqueous source ($5\,cm^3$) and receiving phases ($12\,cm^3$) were separated by an organic phase ($20\,cm^3$). The cells were enclosed by a water jacket.

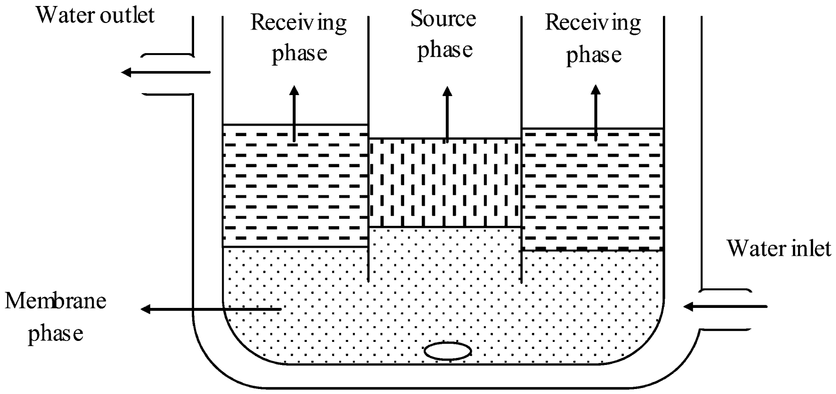

Fig. 2. The standardized concentric cell employed for transport experiments.

The aqueous source phase consisted of buffer solution at pH 5 (acetic acid/sodium hydroxide) containing an equimolar mixture of the metal ions, each at concentration of 1.0×10^{-3} M. LH_2 was dissolved in minimum required volume of dimethylformamide and the resulted solution was expanded to desirable volume by adding dichloromethane to it and the solution was used as organic phase. The receiving phase contained a suitable stripping agent. The organic layer was stirred by a Teflon-coated magnetic bar. Under the applied conditions, not only the mixing processes were perfect, but the two aqueous phases remained flat. Determination of the metal ions concentration in both aqueous phases was carried out by AAS.

3. Results and discussion

The preliminary experiments revealed that LH_2 was not an effective carrier for the transport of any metal cations through the liquid membrane. On the other hand, this carrier displayed a remarkable capacity to extract the Cu(II) ions from the source phase to the organic phase. Therefore, the effective parameters on the transport of Cu(II) ions were investigated.

3.1. Effect of receiving phase composition

In the first step, the influence of receiving phase composition was studied. The results are shown in Table 1.

It was found that the studied acids could afford the transport of Cu(II) ion into the receiving phase. These observations are reasonable because according to proton-driven mechanism [20–22]. The hydrogen ion concentration in the receiving phase could be an influencing factor on the transport process. Thus, the effect of the presence of 0.1 M of some different mineral acids in the receiving phase was examined on the transport of Cu(II) ion. As it is seen (Table 1), all the studied could affect Cu(II) ion transport into the receiving phase, but 0.1 M HNO_3 solution was chosen for our further studies. The reason for choosing nitric acid was not only based on results of preliminary experiments (Table 1) but also according to the literature [23], nitrate ion has been reported to be a more acceptable matrix for both flame and electrothermal AAS experiments than chloride and sulfate ions.

3.2. Kinetic modeling and time effect

A kinetic model was used to describe the Cu(II) ion transport behavior [24,25]. The behavior can be described according to following kinetic Scheme [26]:

$$\mathrm{Cu_{SP}} \xrightarrow{k_e} \mathrm{Cu_{MP}} \xrightarrow{k_s} \mathrm{Cu_{RP}}$$

where Cu_{SP} and Cu_{RP} represent the Cu(II) ions in the source and receiving phases, respectively, while Cu_{MP} is the Cu(II)-L complex in the liquid membrane phase. k_e and k_s are the first-order apparent rate constants of the extraction and the stripping processes, respectively.

The transport rate of Cu(II) ion can be described by the following rate equations:

$$\frac{dR_{sp}}{dt} = -k_e R_{sp} \tag{1}$$

Table 1
Effect of composition of receiving phase on the transport of Cu(II) ion

Receiving phase	% Transport into receiving phase
Cysteine (0.01 M)	0
Histidine (0.01 M)	0
Methionine (0.01 M)	0
Ethylenediamine (0.01 M)	0
Ethylenediaminetetraacetic acid (0.01 M)	0
KSCN (0.01 M)	0
NH_3 (0.01 M)	0
H_2SO_4 (0.1 M)	3.48
HNO_3 (0.1 M)	5.37
$HClO_4$ (0.1 M)	2.87
HCl (0.1 M)	2.28

Notes: Conditions: source phase, 5 ml of 1.0×10^{-3} M mixture of six metal cations; membrane phase, 20 ml of 1×10^{-4} M LH_2 in dichloromethane; receiving phase, 12 ml solution of each proposed releasing agent on separate experiment; stirring rate, 100 rpm; time of transport, 24 h; and temperature, 25˚C.

$$\frac{\mathrm{d}R_{\mathrm{MP}}}{\mathrm{d}t} = \varepsilon k_{\mathrm{e}} R_{\mathrm{sp}} - \lambda k_{\mathrm{s}} R_{\mathrm{MP}} \tag{2}$$

$$\frac{\mathrm{d}R_{\mathrm{RP}}}{\mathrm{d}t} = k_{\mathrm{s}} R_{\mathrm{RP}} \tag{3}$$

where ε and λ are the volume ratio of the source phase to the liquid membrane phase and the receiving phase to the liquid membrane phase, respectively ($\varepsilon = 0.2$ and $\lambda = 0.6$ in this study).

R_{SP}, R_{MP}, and R_{RP} are the dimensionless concentrations of Cu(II) ion in source, liquid membrane, and receiving phases, respectively. They are defined as

$$R_{\mathrm{SP}} = \frac{C_{\mathrm{SP}}}{C_{\mathrm{SP,in}}} \tag{4}$$

$$R_{\mathrm{MP}} = \frac{C_{\mathrm{MP}}}{C_{\mathrm{SP,in}}} \tag{5}$$

$$R_{\mathrm{RP}} = \frac{C_{\mathrm{RP}}}{C_{\mathrm{SP,in}}} \tag{6}$$

in which $C_{\mathrm{SP,in}}$ is the initial concentration of Cu(II) ion in the source phase.

Combining Eqs. (1)–(3), and integration of these differential equations yields

$$R_{\mathrm{SP}} = \exp(-k_{\mathrm{e}} t) \tag{7}$$

$$R_{\mathrm{MP}} = \frac{0.2 k_{\mathrm{e}}}{0.6 k_{\mathrm{s}} - k_{\mathrm{e}}} \left(k_{\mathrm{s}} \exp(-k_{\mathrm{e}} t) - \exp(-0.6 k_{\mathrm{s}} t) \right) \tag{8}$$

$$\begin{aligned} R_{\mathrm{RP}} = \frac{1}{3} - \frac{1}{3(0.6k_{\mathrm{s}} - k_{\mathrm{e}})} & (0.6 k_{\mathrm{s}} \exp(-k_{\mathrm{e}} t) \\ & - k_{\mathrm{e}} \exp(-0.6 k_{\mathrm{s}} t)) \end{aligned} \tag{9}$$

These equations can be used to describe the kinetic behavior of bulk liquid membrane, which show that the time dependence of R_{SP} is monoexponential, while the time variation of both R_{MP} and R_{RP} is bi-exponential behavior. According to Eq. (8), R_{MP} has a maximum value at $\frac{\mathrm{d}R_{\mathrm{MP}}}{\mathrm{d}t} = 0$, with a maximum time $t_{\max}$:

$$t_{\max} = \frac{\mathrm{Ln}\left(\frac{k_{\mathrm{s}}}{k_{\mathrm{e}}}\right)}{0.6 k_{\mathrm{s}} - k_{\mathrm{e}}} \tag{10}$$

The maximum value of R_{MP} is

$$R_{\mathrm{MP,max}} = 0.2 \left(\frac{k_{\mathrm{e}}}{0.6 k_{\mathrm{s}}} \right)^{\frac{0.6 k_{\mathrm{s}}}{(0.6 k_{\mathrm{s}} - k_{\mathrm{e}})}} \tag{11}$$

By considering the first-order time differentiation of Eqs. (7)–(9) at $t = t_{\max}$, Eqs. (12)–(14) could be resulted:

$$\left.\frac{\mathrm{d}R_{\mathrm{SP}}}{\mathrm{d}t}\right|_{\max} = -k_{\mathrm{e}} \left(\frac{0.6 k_{\mathrm{s}}}{k_{\mathrm{e}}} \right)^{\frac{-k_{\mathrm{e}}}{(0.6 k_{\mathrm{s}} - k_{\mathrm{e}})}} \equiv j_{\mathrm{SP}}^{\max} \tag{12}$$

$$\left.\frac{\mathrm{d}R_{\mathrm{MP}}}{\mathrm{d}t}\right|_{\max} = 0 \tag{13}$$

$$\left.\frac{\mathrm{d}R_{\mathrm{RP}}}{\mathrm{d}t}\right|_{\max} = 0.2 k_{\mathrm{s}} \left(\frac{0.6 k_{\mathrm{s}}}{k_{\mathrm{e}}} \right)^{\frac{-0.6 k_{\mathrm{s}}}{(0.6 k_{\mathrm{s}} - k_{\mathrm{e}})}} \equiv j_{\mathrm{RP}}^{\max} \tag{14}$$

where $j_{\mathrm{SP}}^{\max}$ and $j_{\mathrm{RP}}^{\max}$ are maximum entrance and exit fluxes, respectively. The extraction rate constant, k_{e}, was obtained from Eq. (7) using donor phase data, while the re-extraction rate constant, k_{s}, could determined from the acceptor phase data using Eq. (9) or indirectly from the membrane phase data calculated (k_{s}) on the basis of Eq. (8). The variation of Cu(II) ion concentration in the source, receiving, and liquid membrane phase as a function of time is shown in Fig. 3.

It was found that maximum transport of Cu(II) ion could achieved about 24 h. The variations of R_{SP}, R_{MP}, and R_{RP} with time through liquid membrane are shown in Fig. 4. As seen, there is a satisfactory agreement between the theoretical curves and the experimental points. The parameters obtained from the kinetic model are listed in Table 2.

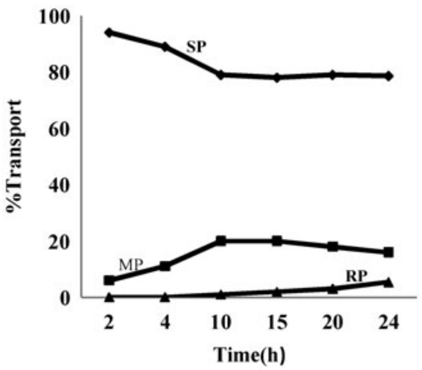

Fig. 3. The effect of time on the competitive transport efficiency of six metal cations. Conditions: source phase, 5 ml of 1.0×10^{-3} M mixture of six metal cations at pH 5; membrane phase, 20 ml of 1×10^{-4} M $\mathrm{LH_2}$ in dichloromethane; receiving phase, 12 ml solution of 0.1 M $\mathrm{HNO_3}$; stirring rate, 250 rpm; and temperature, 25℃.

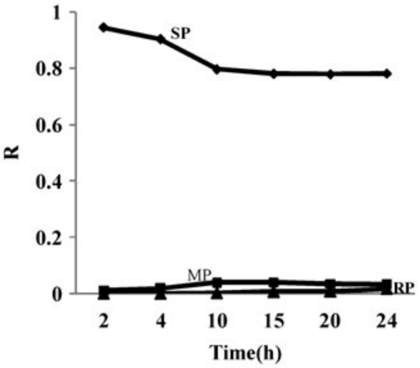

Fig. 4. Time dependence of R_{SP}, R_{MP}, and R_{RP} for transport of Cu(II). Theoretical curves calculated from Eqs. (7)–(9). Conditions: similar to those mentioned in Fig. 3.

3.3. *Effect of the stirring rate*

The influence of stirring rate on Cu(II) ions transport was studied in order to optimize uniform mixing of the solution and to minimize thickness of aqueous boundary layers. In the present investigation, the stirring of membrane phase was carried out at four different rates, 100, 200, 250, and 300 rpm. The results indicate that the stirring rate has no serious effect on the transport efficiency of Cu(II) ions at this range (data were not shown). To prevent the mixing of aqueous phases, 250 rpm as normal stirring rate was chosen for further experiments.

3.4. *Effect of source phase pH*

pH is an important factor affecting the separation of metal ions using chelating agents [27,28]. It would determine the values of conditional stability constants of the metal complexes that affect the transport efficiency [29]. In order to investigate the effect of pH, the competitive transport experiments of mixture of six metal cations were carried out as a function of pH of the source phase. The results are shown in Table 3.

Table 2
The results of the kinetic model at different times

Time (h)	k_e (h^{-1})	k_s (h^{-1})	t_{max} (h)	$R_{MP,max}$	j_{SP}^{max} (h^{-1})	j_{RP}^{max} (h^{-1})	% transport
2	0.0282	0.0440	36.6220	0.0760	−0.0100	0.0033	0.23
4	0.0252	0.0265	49.4860	0.0909	−0.0072	0.0024	0.35
10	0.0227	0.0113	75.9990	0.1196	−0.0040	0.0013	1.00
15	0.0164	0.0196	71.7110	0.0859	−0.0050	0.0016	2.00
20	0.0112	0.0177	91.8580	0.0753	−0.0040	0.0013	3.00
24	0.0102	0.0167	98.8210	0.0742	−0.0040	0.0012	5.37

Note: Conditions: similar to those mentioned in Fig. 3.

Table 3
The effect of source phase pH on the competitive transport efficiency of the six metal cations

pH	Cu(II)	Co(II)	Mn(II)	Ni(II)	Zn(II)	Pb(II)
4						
%(transport)	5.46	0	0	0	0	0
4.5						
%(transport)	5.36	0	0	0	0	0
5						
%(transport)	5.37	0	0	0	0	0
5.5						
%(transport)	5.09	0	0	0	0	0
6						
%(transport)	4.29	0	0	0	0	0.78
6.5						
%(transport)	1.81	0	0	0	0	3.52

Notes: Conditions: source phase, 5 ml of 1.0×10^{-3} M mixture of six metal cations at various pH values; membrane phase, 20 ml of 1×10^{-4} M LH_2 in dichloromethane; receiving phase, 12 ml solution of 0.1 M HNO_3; stirring rate, 250 rpm; time of transport, 24 h; and temperature, 25℃.

Table 4
The kinetic model results at different pH values

pH	k_e (h^{-1})	k_s (h^{-1})	t_{max} (h)	$R_{MP,max}$	j_{SP}^{max} (h^{-1})	j_{RP}^{max} (h^{-1})	% transport
4	0.0098	0.0169	100.1360	0.0722	−0.0040	0.0012	5.46
4.5	0.0084	0.0143	117.6700	0.0727	−0.0030	0.0010	5.36
5	0.0102	0.0167	98.8210	0.0742	−0.0040	0.0012	5.37
5.5	0.0138	0.0233	71.6862	0.0732	−0.0050	0.0017	5.09
6	0.0156	0.0198	72.9999	0.0837	−0.0050	0.0017	4.29
6.5	0.0230	0.0055	98.0131	0.1442	−0.0020	0.0008	1.81

Note: Conditions: similar to those mentioned in Table 3.

As is obvious (Table 3), except two cases the only transported cation is Cu(II) and the maximum transport efficiency for this cation was obtained at pH 4–5. As is shown on Table 3, increasing pH of source phase to 5 and more amount decrease the transport efficiency of Cu(II) ion. Moreover, at higher pH, the transport of Pb(II) ion was observed. The diminished efficiency of Cu(II) ion transport at higher pH is probably due to the formation of stronger complex between Cu(II) ion and LH_2, which do not let to Cu(II) ion release into the receiving phase and causes to remaining of high percentage of Cu(II) ion in the membrane phase. So, pH of source phase was adjusted at 5 for all further experiments. The obtained kinetic parameters for Cu (II) ion transport at various pH values are shown in Table 4.

3.5. Effect of fatty acids

It has been found that a major role of the fatty acids is to aid the transport process by providing a lipophilic counter ion in the organic phase on proton loss to the aqueous source phase, giving rise to charge neutralization of the metal cation being transported through ion pairing or adduct formation [30]. The influence of palmitic acid, oleic acid, and stearic acid as a phase modifier in the membrane was investigated. The results are summarized in Table 5.

According to the obtained results, the efficiency of Cu(II) ion transport increases in the presence of these fatty acids, but transport of Pb(II) ion also occurs and reduces the selectivity of carrier. Based on this fact, in the next steps no fatty acids were used. The kinetic parameters for transport of Cu(II) ions are presented in Table 6.

Table 5
The effect of fatty acids on the competitive transport efficiency of the six metal cations

Fatty acid	Cu(II)	Co(II)	Mn(II)	Ni(II)	Zn(II)	Pb(II)
Palmitic acid						
%(transport)	7.38	0	0	0	0	6.32
Oleic acid						
%(transport)	7.62	0	0	0	0	11.98
Stearic acid						
%(transport)	7.62	0	0	0	0	3.40

Notes: Conditions: source phase, 5 ml of 1.0×10^{-3} M mixture of six metal cations at pH 5; membrane phase, 20 ml of 1×10^{-4} M LH_2 and 10^{-2} M various fatty acids in dichloromethane; receiving phase, 12 ml solution of 0.1 M HNO_3; stirring rate, 250 rpm; time of transport, 24 h; and temperature, 25˚C.

Table 6
The kinetic model results for different fatty acids

Fatty acid type	k_e (h^{-1})	k_s (h^{-1})	t_{max} (h)	$R_{MP,max}$	j_{SP}^{max} (h^{-1})	j_{RP}^{max} (h^{-1})	% transport
Palmitic acid	0.0509	0.0241	34.55	0.1214	−0.009	0.0029	7.38
Oleic acid	0.0249	0.0245	51.683	0.0936	−0.007	0.0023	7.62
Stearic acid	0.017	0.0274	59.883	0.074	−0.006	0.002	7.62

Note: Conditions: similar to those mentioned in Table 5.

Table 7
The effect of nitric acid concentration on the competitive transport of the six metal cations

Acid concentration	Cu(II)	Co(II)	Mn(II)	Ni(II)	Zn(II)	Pb(II)
0.1 M						
%(transport)	5.37	0	0	0	0	0
0.3 M						
%(transport)	8.16	0	0	0	0	0
0.6 M						
%(transport)	6.67	0	0	0	0	0
1 M						
%(transport)	5.76	0	0	0	0	0

Notes: Conditions: source phase, 5 ml of 1.0×10^{-3} M mixture of six metal cations at pH 5; membrane phase, 20 ml of 1×10^{-4} M LH_2 in dichloromethane; receiving phase, 12 ml solution of HNO_3 at different concentrations; stirring rate, 250 rpm; time of transport, 24 h; and temperature, 25℃.

3.6. Effect of nitric acid concentration

The concentration effect of nitric acid in receiving phase on the efficiency of Cu(II) ion transport was studied. The results are shown in Table 7. As shown in Table 7, an increase in Cu(II) ion concentration in the receiving phase was observed by increasing nitric acid concentration up to about 0.3 M (Table 7).

The transport effecting was decreased by increasing HNO_3 concentration. The increasing HNO_3 concentration in receiving phase may be produces higher strength of solution which results in a lower activity coefficient for hydrogen ions and reduces less active H^+ to decompose the complex [31]. Thus, a solution of 0.3 M nitric acid was used as a suitable amount for the acid in receiving phase. The kinetic parameters for this step of optimization process are shown in Table 8.

3.7. Effect of carrier concentration in the organic phase

The competitive metal ion transport experiments were carried out at different LH_2 concentrations and the results are shown in Table 9.

As it is seen, the transport efficiency of Cu(II) ion increases with an increase in LH_2 concentration in the organic phase because the interface between the source and the membrane phase is not saturated by the carrier in lower concentrations, while in higher concentrations, this interface is saturated [32] and hence there are more effective conditions to complex metal ions by carrier. A maximum transport was occurred at a concentration of about 4×10^{-4} M LH_2. Further increase in carrier concentration nearly does not change transport efficiency of Cu(II) ion. Moreover, at higher concentration (more than 4×10^{-4} M) of carrier, transport of Pb(II) ion occurs. According to the results, the carrier concentration of 4×10^{-4} M was selected as optimal level. The obtained parameters from the kinetic model are listed in Table 10.

3.8. Effect of type and concentration of surfactant

The surfactants are usually organic compounds that are amphipathic, meaning they contain both hydrophobic and hydrophilic groups. Therefore, they are typically sparingly soluble in both organic solvents and water. The hydrophobic non-polar end attaches to organic solvents, while the hydrophilic end attaches to water. In fact, they serve as a bridge between two immiscible solvents in liquid–liquid interface through which the transport and exchange of molecules and ions take place easily. Thus, the influence of surfactant

Table 8
The kinetic model results at different acid concentrations

Acid concentration (M)	k_e (h^{-1})	k_s (h^{-1})	t_{max} (h)	$R_{MP,max}$	j_{SP}^{max} (h^{-1})	j_{RP}^{max} (h^{-1})	% transport
0.1	0.0102	0.0167	98.8210	0.0742	−0.0040	0.0012	5.37
0.3	0.0173	0.0281	58.4860	0.0745	−0.0063	0.0020	8.16
0.6	0.0181	0.0262	59.1860	0.0788	−0.0062	0.0020	6.67
1	0.0161	0.0241	65.4570	0.0775	−0.0056	0.0018	5.76

Note: Conditions: similar to those mentioned in Table 7.

Table 9
The effect of carrier concentration on the competitive transport of the six metal cations

Carrier concentration	Cu(II)	Co(II)	Mn(II)	Ni(II)	Zn(II)	Pb(II)
10^{-4}						
%(transport)	8.16	0	0	0	0	0
2×10^{-4}						
%(transport)	12.85	0	0	0	0	0
4×10^{-4}						
%(transport)	20.50	0	0	0	0	2.50
6×10^{-4}						
%(transport)	21.55	0	0	0	0	4.62
8×10^{-4}						
%(transport)	22.03	0	0	0	0	16.90

Notes: Conditions: source phase, 5 ml of 1.0×10^{-3} M mixture of six metal cations at pH 5; membrane phase, 20 ml of LH_2 at various concentrations in dichloromethane; receiving phase, 12 ml solution of 0.3 M HNO_3; stirring rate, 250 rpm; time of transport, 24 h; and temperature, 25℃.

Table 10
The kinetic model results at different carrier concentrations.

Carrier concentration (M)	k_e (h^{-1})	k_s (h^{-1})	t_{max} (h)	$R_{MP,max}$	j_{SP}^{max} (h^{-1})	j_{RP}^{max} (h^{-1})	% transport
0.0001	0.0173	0.0281	58.4860	0.0745	−0.0063	0.0020	8.16
0.0002	0.0148	0.0246	67.627	0.0737	−0.0050	0.0018	12.85
0.0004	0.0252	0.0420	39.702	0.0736	−0.0090	0.0031	20.50
0.0006	0.0323	0.0534	31.063	0.0739	−0.0120	0.0039	21.55
0.0008	0.0374	0.0589	27.508	0.0756	−0.0130	0.0045	22.03

Note: Conditions: similar to those mentioned in Table 9.

type on Cu(II) ion transport was studied by adding three different surfactants into the receiving phase. In the experiments, Triton X-100 as a non-ionic surfactant, sodium dodecyl sulfate (SDS) as an anionic surfactant and hexadecyl trimethyl ammonium bromide (HDTMAB) as a cationic surfactant were used. As it is seen from Table 11, the efficiency of Cu(II) ion transport increases in the presence of SDS and Triton X-100 in the receiving phase.

This observation probably highlights the idea that the interaction between the positive ions and the negative charge of anionic surfactant head is necessary. If the surfactant is to be effective perfectly [33], non-ionic surfactants show larger depression than anionic surfactants [34], which causes Triton X-100 to be effective in the Cu(II) ion transport, too. Using SDS lead to transport of other cations and reduced the selectivity of the carrier. According to the results, Triton X-100

Table 11
The effect of surfactant type on the competitive transport efficiency of the six metal cations

Surfactant type	Cu(II)	Co(II)	Mn(II)	Ni(II)	Zn(II)	Pb(II)
SDS						
%(transport)	25.84	0	5.44	0	9.31	24.14
HDTMAB						
%(transport)	18.60	0	0	0	0	0.88
Triton X-100						
%(transport)	23.00	0	0	0	0	2.54

Notes: Conditions: source phase, 5 ml of 1.0×10^{-3} M mixture of six metal cations at pH 5; membrane phase, 20 ml of 4×10^{-4} M LH_2 in dichloromethane; receiving phase, 12 ml solution of 0.3 M HNO_3 and 0.001 M surfactant; stirring rate, 250 rpm; time of transport, 24 h; and temperature, 25℃.

Table 12
The results of the kinetic model for different surfactants

Surfactant type	k_e (h^{-1})	k_s (h^{-1})	t_{max} (h)	$R_{MP,max}$	j_{SP}^{max} (h^{-1})	j_{RP}^{max} (h^{-1})	% transport
SDS	0.0483	0.0684	22.441	0.0796	−0.016	0.0054	25.84
HDTMAB	0.0197	0.0327	50.903	0.0736	−0.0070	0.0024	18.60
Triton X-100	0.0340	0.0562	29.517	0.0738	−0.0124	0.0041	23.00

Note: Conditions: similar to those mentioned in Table 11.

was selected as a suitable surfactant. Then, the effect of this surfactant concentration on the transport efficiency was investigated and the concentration of 1×10^{-3} M was selected as the optimal amount. The kinetic parameters are presented in Table 12.

3.9. Effect of temperature

Temperature has an effect on the complexation reaction of metal ion by the extractant carrier at the source/membrane interface, decomplexation of the metal at the membrane/receiving phase, and membrane viscosity [35]. So the effect of temperature on the competitive transport of Cu(II) ion was examined at 15, 20, 25, 30, and 35˚C. The experimental results are shown in Table 13.

It is quite obvious that transport increases with an increase in temperature, so 35˚C was selected as the best temperature. At higher temperature, evaporation of liquid membrane phase could be occurs. The effect of temperature on kinetic parameters is shown in Table 14.

3.10. Suggested mechanism

From the obtained results, the following mechanism (Fig. 5) is suggested for the transport of Cu(II) ion through a liquid membrane containing LH_2.

In source phase and the membrane interface, the copper ions are absorbed into the membrane due to L-Cu(II) adduct formation (Fig. 6) [36].

At this stage, the carrier splits off protons into the source phase as a result of complex formation with copper(II) ion. The formed complex diffuses down its concentration gradient. In the interface between the membrane and the receiving phase, the copper(II)

Table 13
The effect of temperature on the competitive transport of the six metal cations

Temperature	Cu(II)	Co(II)	Mn(II)	Ni(II)	Zn(II)	Pb(II)
15	21.14	0	0	0	0	2.91
20	20.14	0	0	0	0	2.42
25	23.00	0	0	0	0	2.54
30	27.25	0	0	0	0	2.55
35	43.00	0	0	0	0	2.33

Notes: Conditions: source phase, 5 ml of 1.0×10^{-3} M mixture of six metal cations at pH 5; membrane phase, 20 ml of 4×10^{-4} M LH_2 in dichloromethane; receiving phase, 12 ml solution of 0.3 M HNO_3; stirring rate, 250 rpm; and time of transport, 24 h.

Table 14
The kinetic model results at different temperatures.

Temperature (˚C)	k_e (h^{-1})	k_s (h^{-1})	t_{max} (h)	$R_{MP,max}$	j_{SP}^{max} (h^{-1})	j_{RP}^{max} (h^{-1})	% transport
15	0.0450	0.0479	27.567	0.0905	−0.0130	0.0043	21.14
20	0.0389	0.0548	27.919	0.0798	−0.0131	0.0043	20.14
25	0.0340	0.0562	29.517	0.0738	−0.0124	0.0041	23.00
30	0.0422	0.0683	24.053	0.0746	−0.0153	0.0051	27.25
35	0.0508	0.0846	19.686	0.0736	−0.0186	0.0062	43.00

Note: Conditions: similar to those mentioned in Table 13.

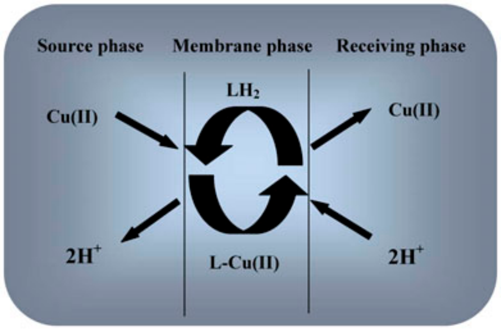

Fig. 5. The suggested liquid membrane system for transport of Cu(II) ion using LH_2 as carrier.

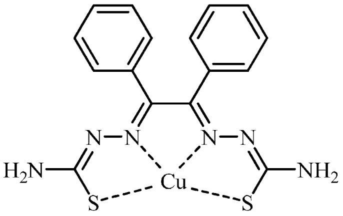

Fig. 6. Chemical structure of LH_2 Cu(II) ion complex.

complex of LH_2 because of the presence of high concentration of hydrogen ions should be broken and release copper(II) ion into the receiving phase. The free protonated carrier diffuses back across the membrane to the interface of the source phase and the cycle will be repeated.

4. Conclusion

The liquid membrane transport experiments of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) metal cations using LH_2 as an ion carrier in dichloromethane membrane showed that it is possible to separate selectively Cu(II) ions from the other metal ions by this ligand. Based on the literatures [13,14], most of the ligands containing N and S donor atoms, especially Schiff–base compounds have a high tendency to complex formation with Cu(II) ions in comparing to the some transition and post-transition metal cations. In this research, LH_2 selectively transported Cu(II) ions from the mixture of six metal cations solution. The efficiency of the method depends on various parameters, such as receiving phase composition, pH of the source phase, carrier concentration, temperature, and transport time. It was found that the efficiency of Cu (II) ion transport increases in the presence of fatty acids in the membrane, but in this condition, transport of Pb(II) ion also occurs and the selectivity of system reduces. The transport occurs via a counter flow of protons from the receiving phase to the source phase. The simplicity, cost-effectiveness, and selectivity of Cu(II) ion transport by the studied liquid membrane system demonstrates its potential applicability for selective removal of the Cu(II) ion from a mixture of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Pb(II) metal cations.

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