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Highly Copper(II) Ion-Selective Transport Through Liquid Membrane Containing *N,N*-bis(salicylidene)-1,2-phenyldiamine

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Highly Copper(II) Ion-Selective Transport Through Liquid Membrane Containing *N*,*N*′-bis(salicylidene)-1,2-phenyldiamine

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Abstract: *N*,*N*′-bis(salicylidene)-1,2-phenyldiamine was synthesized for examining their ability to extract and transport Cu^{2+} through a liquid membrane. By using hydrazine sulfate and potassium thiocyanate as reducing agent and acceptor respectively in the receiving phase at the optimum pH of 1.5, the amount of copper transported across the liquid membrane after 3.5 hours was 96%. The selectivity and efficiency of copper transport from aqueous solution containing various metal ions were investigated.

Keywords: Bulk liquid membrane, salophen, copper transport

INTRODUCTION

The specific transport of metal ions through a membrane is widely known to play an essential role in biological process (1), medicine, water purification, and metallurgy (2–4). Liquid membrane transport in which the extraction and stripping operations are combined in a single process reduces the solvent inventory requirement, and allows the use of expensive and highly selective extractions, which other wise would be uneconomic in solvent extractions. For these reasons, liquid transport membrane has attracted worldwide attention and much work has been directed toward developing methods for its application to the separation of various metal ions (5–15). The Schiff bases derived from salicylaldehyd (salen) as polydentate ligands

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are well known to form very stable complexes with transition metal ions (16, 17). Schiff base complexes of transition metals have been frequently used as catalyst in such a diverse process as oxygen and atom transfer, enantioselective epoxidation and oziridination mediating organic redox reactions and as mediator in other oxidation processes (17–19). However, very little is known about their complex formation equilibria in solution (20) and also about the use of salens as carrier in ion transport (21–23). Therefore, the development of effective and specific systems for studying the transport of metal ions, particularly Cu^{2+}, is a remarkable task from both practical and theoretical viewpoints. *N*,*N*′-bis(salicylidene)-1,2-phenyldiamine (salophen) is a Schiff base (Fig. 1), which leads to form a complex with some metal ions. It is used for construction of ion selective electrode (24), optical sensor (25) etc. To the best of our knowledge, no work on the use of salophen as a carrier in transport systems has been reported previously. In this paper we report that salophen is an excellent carrier for the high selective and up-hill transport of Cu(II) ions through a liquid membrane.

EXPERIMENTAL SECTION

Reagents

Reagent-grade chloroform (99%) was used as a membrane organic solvent. Hydrogen chloride (37%), hydrazine sulfates (99%), and potassium thiocyanate (99.5%) were purchased from Merck and used as received. All other chemicals used in this study were of the highest purity available from either Merck or Fluka chemical companies and used without further purification. The salophen was synthesized according to the previous report (25) and recrystallized in methanol (96%). The pH of feed solution was adjusted with phosphate buffer (0.02 M). Doubly distilled deionized water was used throughout.

Apparatus

The atomic absorption spectrophotometer used for determination of metal ion concentrations was Shimadzu AA-670. pH measurements were made with a

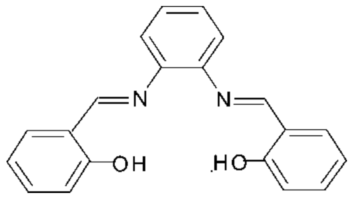

Figure 1. Salophen's structure.

HANA pH–meter (model 302) using a combined glass electrode. A bulk type liquid membrane cell (7) was used.

Procedure

All transport experiments were carried out at ambient temperature. A cylindrical glass cell (inside diameter of 4.6 cm) containing a glass tube (inside diameter 1.2 cm), thus separating the two aqueous phases, was used. The liquid membrane (25 ml of 8×10^{-3} M of salophen in $CHCl_3$) was located at the bottom of the glass beaker laying below two aqueous phases and bridging them. The outer aqueous phase (receiving phase) contained 0.4 M hydrazine sulfate and 0.6 M potassium thiocyanate (5 ml). 2 ml of aqueous solution containing 6.25×10^{-4} M copper nitrate, which was buffering with phosphate solution (pH = 6.5) used as inner aqueous phase (source phase). The organic layer was slowly stirred by a Teflon-coated magnetic bare (850 rpm). In the course of the transport experiment, samples of both aqueous phases were analyzed for metal content by atomic absorption spectroscopy. The reproducibility of copper transport of 2 ml of 6.25×10^{-4} mol l^{-1} of copper was investigated, and the percent of metal ion transported after 3.5 h from ten replicate measurements was found (96 ± 1.0)%.

RESULTS AND DISCUSSIONS

Salophen is a tetradentate ligand and characterized by its capacity to completely coordinate with metal ion and forming a chelate ring (26). This reagent is insoluble in water and soluble in organic solvents. To the best of our knowledge there is no report on the complexation of salophen with metal ions in the nonaqueous solvents. Prior to the study of the Cu^{2+}-salophen transport, the complexation of copper ions with salophen was studied in chloroform. In order to determine the stoichiometry and stability of resulting salophen complex with Cu^{2+}, the spectra of a series of solutions containing a constant concentration of ligand (5.0×10^{-5} mol l^{-1} in $CHCl_3$) at a fixed ionic strength of 0.01 mol l^{-1} of TEAP and varying amount of copper ion (1×10^{-2} mol l^{-1} in CH_3CN) was obtained at 25°C (Fig. 2a). As can be seen, the complexation was accompanied by a relatively strong shift of the absorption band of the salophen (365 nm) solution towards longer wavelength (440 nm) due to its complexation with copper ion. The absorbance vs. $[Cu^{2+}]/[\text{salophen}]$ mole ratio plot obtained at a wavelength 440 nm is shown in Fig. 2b. As it is seen (Fig. 2b) the absorbance mole ratio plot revealed a distinct inflection point at $[Cu^{2+}]/[\text{salophen}]$ molar ratio of 1 emphasizing the formation of 1:1 complex in solution. The formation constant of the resulting complex between Cu^{2+} and salophen was

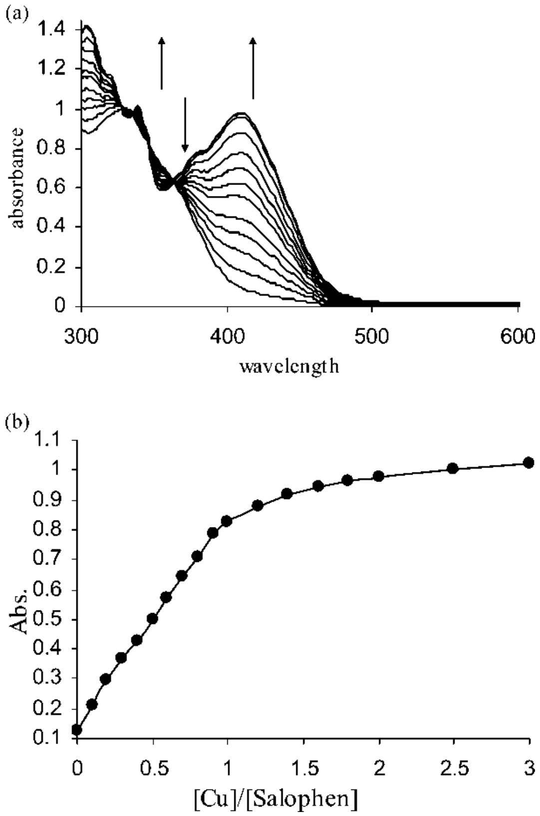

Figure 2. Absorption spectra of complexation of salophen ($5 \times 10^{-5}\,\mathrm{mol\,l^{-1}}$) in chloroform solution in the presence of varying concentrations of copper(II) ion ($1 \times 10^{-2}\,\mathrm{mol\,l^{-1}}$) in acetonitril.

evaluated by computer fitting of the corresponding mole ratio data to a derived equation for ML using a non-linear curve-fitting program, KINFIT (27) and was $\log K_f = 5.21 \pm 0.23$.

To investigate the suitability of the salophen as ion carrier, the transport of the copper was tested through a chloroform bulk liquid membrane. In preliminary experiments, the permeability of the membrane system for copper ion was found to be strongly depended on the nature of stripping agents used in the receiving phase. The transport of copper ion in the presence of different compounds in the receiving phase was studied and the results are shown in Table 1. As it is seen, in the absence of complexing ligand in the receiving phase, transport of Cu^{2+} to a acidic aqueous receiving phase is quiet low. This is probably because of the stability of complex in the membrane. Therefore, the influence of receiving phase composition on the transport of copper was studied.

Table 1. Effect of the composition of the receiving phase on the transport of copper(II)[a]

Receiving phase (mol l^{-1})	Time (h)	% Transport to receiving phase
H_2SO_4 (0.05)	5	0
Hystidine (2×10^{-2})	5	5
Trans-diaminocyclohexane tetraacetic acid (5×10^{-4})	5	12
HNO_3 (3×10^{-1})	5	0
H_3PO_4 (3×10^{-1})	5	5
HCl (1×10^{-1})	5	0
Theronine (3.8×10^{-2})	5	9
EDTA (1×10^{-1})	5	0
Hydrazine sulfate (0.1) + KSCN (0.2)	5	72

[a] Experimental conditions: source phase, 2 ml of 6.25×10^{-4} mol l^{-1} of copper at pH = 5.5; receiving phase, 5 ml of each of above stripping agents; liquid membrane, 25 ml of 5.0×10^{-3} mol l^{-1} salophen.

There was no improvement in the efficiency of transport of Cu^{2+} when the complexing agent was used individually. Thus, the mixture of the reducing agent and complexing ligand were selected for further studies. In the presence of reducing agents the Cu^{2+} turns to complex of Cu^{+} by which the back extraction of copper into the organic phase is avoided. The results (Table 1) revealed that with hydrazine sulfate as reducing agent and thiocynate as acceptor of Cu^{+} more than 70% of copper was transported in 5 h. In the next step, the experimental variables such as pH of source phase, concentrations of salophen in organic phase, thiocyanate, hydrazine sulfate in the receiving phase and its pH were optimized in order to achieve the highest efficiency in the transport of Cu^{2+} across the membrane system used.

Effect of pH of the Source Phase

The effect of pH of source phase on the efficiency of metal transport was studied (Table 2). The results revealed that the maximum copper transport occurs at pH range 6.5–7.0. At lower pH values there was a decrease in the percentage of Cu^{2+} transport due to the diminished complexing ability of the hydroxyl groups of the salophen at such pH values, and also indicates the proton/copper exchange mechanism at the interface of the source phase and organic phase. The hydrolysis of the metal ion decreases the transport of Cu^{2+} at higher pH values. pH = 6.5 was selected for further studied.

Table 2. Effect of pH of source phase on transport efficiency[a]

pH of source phase	% Transport to receiving phase	% Remaining in source phase
4.0	62.0	39.0
4.5	66.0	33.0
5.0	69.0	23.0
5.5	70.0	20.0
6.0	73.0	14.5
6.5	78.5	10.0
7.0	78.3	10.0
7.5	70.0	19.0
8.0	59.0	30.5

[a] Experimental conditions: source phase, 2 ml of 6.25×10^{-4} mol l^{-1} of copper at various pH; receiving phase, 5 ml of 0.1 mol l^{-1} hydrazine sulfate and 0.2 mol l^{-1} thiocyanate with pH 2.0; liquid membrane, 25 ml of 5.0×10^{-3} mol l^{-1} salophen; time of transport, 5 h.

Effect of pH of the Receiving Phase

The effect of pH of the receiving phase on the efficiency of Cu^{2+}transport was also studied. The results (Table 3) indicate that when the pH of receiving phase was varied from 1.5 to 3.5 a sharp decrease in the transport of copper is observed, that is due to remaining of high percentage of copper in

Table 3. Effect of pH of receiving phase on transport efficiency[a]

pH of receiving phase	% Transport to receiving phase	% Remaining in source phase
0.5	25.5	48.0
1.0	81.5	13.0
1.5	82.0	7.5
2.1	78.0	10.0
3.0	57.0	35.5
3.5	51.0	41.0

[a] Experimental conditions: source phase, 2 ml of 6.25×10^{-4} mol l^{-1} of copper at pH = 6.5; receiving phase, 5 ml of 0.1 mol l^{-1} hydrazine sulfate and 0.2 mol l^{-1} thiocyanate at various pH; liquid membrane, 25 ml of 5.0×10^{-3} mol l^{-1} salophen; time of transport, 5 h.

the membrane phase. However, from the results (Table 3) it is concluded that the elevation of the hydrogen concentration (up to 0.01 mol l^{-1}) of the receiving phase causes an increase in the rate of association of proton to carrier and releasing of Cu^{2+} ion into the receiving phase. As a result the concentration of free Cu^{2+} ion in receiving phase decreases (due to reducing Cu^{2+} ion to Cu^{+} ion and complex formation with thiocyanate) a process which makes the up-hill transport of Cu^{2+} possible. At pH range 1–1.5, the efficiency of transport did not change. Therefore, a solution containing 0.2 mol l^{-1} thiocyanate and 0.1 mol l^{-1} hydrazine sulfate with pH 1.5 was used for subsequent experiments.

Effect of Hydrazine Sulfate and Thiocyanate Concentrations

The effect of hydrazine sulfate and thiocyanate concentrations in the receiving phase on the Cu^{2+} transport was investigated. The data showed (Table 4) that, the maximum copper transport is achieved in the hydrazine sulfate concentration greater than 0.4 mol l^{-1} (at 0.2 mol l^{-1} thiocyanate) and in the thiocyanate concentration greater than 0.4 mol l^{-1} (at 0.4 mol l^{-1} hydrazine sulfate). For reducing the time of transport, the concentrations of 0.6 and 0.4 mol l^{-1} were selected as optimum concentrations for thiocyanate and hydrazine sulfate, respectively. Thus, the copper ions are transported from the source phase to the receiving phase through a chloroform membrane

Table 4. Effect of hydrazine sulfate and potassium thiocyanate concentrations on releasing of copper ion from membrane

Concentration of hydrazine (mol l^{-1})	Concentration of KSCN (mol l^{-1})	% Transport to receiving phase	% Remaining in source phase
0.1	0.2	81.8	12.0
0.2	0.2	83.0	11.2
0.3	0.2	85.5	9.4
0.4	0.2	86.0	9.4
0.5	0.2	85.5	9.3
0.4	0.3	86.0	9.1
0.4	0.4	88.0	8.0
0.4	0.6	87.5	8.7
0.4	0.8	88.0	8.1
0.4	1.0	88.0	7.6

[a] Experimental conditions: source phase, 2 ml of 6.25×10^{-4} mol l^{-1} of copper at pH = 6.5; receiving phase, 5 ml of various amount of hydrazine sulfate and thiocyanate with pH 1.5; liquid membrane, 25 ml of 5.0×10^{-3} mol l^{-1} salophen; time of transport, 5 h.

with simultaneous counter-transport of protons. The Cu^{2+} transport can be explained as follows:

1. at source phase/membrane interface, the carrier selectively complexes the copper ion from nitrogen and oxygen as the donor atoms, and hence, facilitates the extraction of cation into the membrane phase (by forming uncharged complex Cu(salophen)). As this stage, the carrier splits off protons into the source phase (the pH of unbuffered solution of source phase was about five, after transport of Cu^{2+} for 3.5 h);
2. the complex which formed diffuses across the membrane;
3. at the membrane/receiving phase interface, the release of the Cu^{2+} ion into the receiving phase occurs via the formation of complex. At this stage, the carrier associates with proton from the receiving phase and released Cu^{2+} ion is reduced to Cu^{+} by hydrazine sulfate for complex formation with thiocyanate ions;
4. the free carrier diffuses back across the membrane to the source phase/membrane interface, where the cycle starts again.

Permeability of the membrane system for Cu^{2+} ion depends largely on the mechanism of releasing of the cation in the receiving phase. The presence of hydrazine sulfate as reducing agent and thoicyanate as complexing agent in the receiving phase is believed to play an essential role in the metal ion releasing process via formation of Cu^{+}-thiocyanate complex. The formation of above-mentioned Cu^{+} complex reduces the concentration of free Cu^{2+} ion in the receiving phase and consequently increases the concentration gradient between two aqueous phases, which in turn results in a higher transport flux.

The copper ions in the receiving phase can be removed by its electrolysis as the metallic form, by electroplating at a suitable potential.

Effect of Salophen Concentration

Table 5 shows that, in the absence of ligand (salophen) in the membrane phase no transport of Cu(II) was taking place. With reference to the K_d values of different copper hydroxides (29) as $pK_1 = 7$ and $pK_2 = 6.68$, $pK_3 = 3.32$, $pK_4 = 1.5$ copper is mainly in the form of $CuOH^{+}$ and Cu^{2+} at pH values of 6.5 which is the pH of source phase. This explains why the transport of copper as molecular $Cu(OH)_2$ at $pH = 6.5$ through liquid membrane was not taking place. Therefore, the transport of Cu^{2+} in the presence of carrier is possible. As is seen from Table 5, the best results were obtained at $8.0 \times 10^{-3}\,mol\,l^{-1}$ of salophen. Thus, this concentration was selected for subsequent uses.

Effect of Time

Figure 3 shows that time dependence of Cu^{2+} transport through the liquid membrane containing salophen under the optimized experimental conditions.

Table 5. Effect of concentration carrier on the transport of copper ion[a]

Concentration of salophen $\times 10^{-2}$ (mol l^{-1})	percentage transport into receiving phase	percentage remaining in source phase
0.0	0.0	100.0
0.1	58.5	33.5
0.2	80.5	12.5
0.5	89.5	8.2
0.8	96.5	2.4
1.2	90.0	1.5
1.6	85.5	1.4
1.8	76.0	1.1

[a] Experimental conditions: source phase, 2 ml of 6.25×10^{-4} mol l^{-1} of copper at pH = 6.5; receiving phase, 5 ml of hydrazine sulfate (0.4 mol l^{-1}) and thiocyanate (0.6 mol l^{-1}) with pH 1.5; liquid membrane, 25 ml of various amount of salophen; time of transport, 5 h.

As it is seen, both the extraction of copper ions from the source phase into the membrane and the release of copper from the membrane into the receiving phase are nearly fast (and follow the same trend), so that some 96% copper transport occurs after 3.5 h. The reproducibility of copper transport of 2 ml of 6.25×10^{-4} mol l^{-1} of copper was investigated, and the percent of metal ion transported after 3.5 h from ten replicate measurements was found (96 ± 1.0)%.

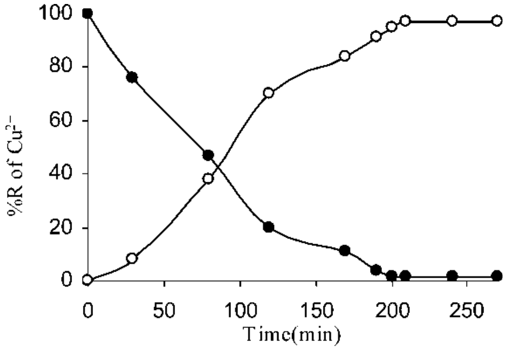

Figure 3. Time dependence of copper transport: (○) remaining; (●) transported. The conditions: source phase, 2 ml of 6.25×10^{-4} mol l^{-1} of copper at pH = 6.5; receiving phase, 5 ml of hydrazine sulfate (0.4 mol l^{-1}) and thiocyanate (0.6 mol l^{-1}) with pH 1.5; liquid membrane, 25 ml of 0.8×10^{-2} mol l^{-1} of salophen.

Selectivity of Bulk Membrane Technique

The selectivity of the membrane system proposed was studied under optimum conditions by undertaking competitive transport experiments equimolar and several times greater concentrations of interfering ion and the results obtained are summarized in Tables 6 & 7. The competitive extraction of copper ion and other metal ions in the mixtures, indicate that the ionophore exhibits selectivity towards Cu^{2+} when exist in the presence of other ions in mixtures. This behavior confirms the results obtained in the recent study of complexation of Cu^{2+}, Co^{2+} and Ni^{2+} with salophen in acetonitrile, dimethylsulphoxide, methanol, and binary mixtures of them that, are doing in my group. The results of the foregoing study show that, the stability constants of the resulting 1:1 complexes decrease in the order $Cu^{2+} > Co^{2+} > Ni^{2+}$ in all solvents used. Their stability constants were found to be in the range of 6.0 ± 1.0. In addition, the mechanism of releasing of metal ions from the membrane into the receiving phase plays a crucial role in the selectivity for Cu^{2+} and this is based on a combination of equilibrium constants and redox potentials. Whereas transport of the Cu^{2+} into the receiving phase does not occur, as a result of the relative equilibrium constants for carrier and thiocyanate complex formation, reduction of Cu^{2+} to Cu^{+} by hydrazine sulfate allows transport of the Cu^{+} because of a change in the relative equilibrium constants. For none of the other metal ions considered (including those formed in the presence of hydrazine sulfate) do the equilibrium constants allow transport to the receiving phase.

Table 6. Amount of cation transported from equimolar cation mixture through membrane ($6.25 \times 10^{-4}\,mol\,l^{-1}$ of each cation)

Cation	% Transport to receiving phase	% Remaining in source phase
Cu^{2+}	71.0	12.0
Ca^{2+}	0.0	99.0
Co^{2+}	9.0	84.0
Cr^{3+}	0.0	100.0
Fe^{3+}	0.0	100.0
Pb^{2+}	1.0	96.0
Li^{+}	0.0	100.0
Hg^{2+}	2.5	94.0
Na^{+}	0.0	100.0
Zn^{2+}	1.0	97.0
Al^{3+}	0.0	100.0
Ni^{2+}	6.0	91.0
Bi^{3+}	0.0	100.0

Table 7. Amount of cation transported from various cation mixtures through membrane $[Cu^{2+}] = 6.25 \times 10^{-4}\,mol\,l^{-1}$

$[M^{n+}]/[Cu^{2+}]$	Mixture	% Transport into receiving phase	% Remaining in source phase
1	Cu^{2+}, Ni^{2+}, Co^{2+}	89.0, 9.5, 11.5	6.5, 86.0, 81.0
	Cu^{2+}, Cd^{2+}, Ca^{2+}	93.5, 0.0, 1.0	2.0, 99.5, 99.7
	Cu^{2+}, Zn^{2+}, Pb^{2+}	91.0, 4.0, 6.0	3.5, 83.0, 87.0
	Cu^{2+}, Mg^{2+}, Fe^{2+}	86.0, 0.0, 3.0	8.5, 99.5, 84.0
10	Cu^{2+}, Ni^{2+}, Co^{2+}	83.0, 10.0, 13.0	9.6, 83.0, 81.0
	Cu^{2+}, Cd^{2+}, Ca^{2+}	91.0, 0.0, 2.0	4.3, 100, 98.5
	Cu^{2+}, Zn^{2+}, Pb^{2+}	85.0, 9.0, 8.0	7.5, 87.5, 88.0
	Cu^{2+}, Hg^{2+}, Fe^{2+}	79.5, 10.0, 4.0	14.0, 83.5, 91.5
40	Cu^{2+}, Ni^{2+}, Co^{2+}	73.0, 14.0, 19.5	14.0, 80.5, 75.0
	Cu^{2+}, Cd^{2+}, Ca^{2+}	89.5, 0.0, 1.5	5.0, 100, 97.5
	Cu^{2+}, Zn^{2+}, Pb^{2+}	81.0, 12.5, 9.5	7.5, 84.5, 83.0
	Cu^{2+}, Hg^{2+}, Fe^{2+}	73.5, 16.0, 7.0	15.0, 79.0, 87.0

CONCLUSIONS

The present study demonstrates that the salophen is an excellent carrier for selective and efficient transport of Cu^{2+}. The presence of hydrazine sulfate and thoicyanate in the receiving phase increases the efficiency of transport without affecting the selectivity. Up-hill transport of Cu(II) against its concentration gradient is easily performed with the above system. In addition, this study demonstrates the usefulness of the liquid membrane technique for making it possible to combine extraction and stripping operations in a single process and reducing the solvent inventory requirements. In conclusion, this system has the advantage of low solvent requirement, high precision, efficiency, selectivity, and simplicity.

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