

Active transport of metal ions by using Schiff bases

Wail Al Zoubi*, Frouk Kandil and Khaled Chebani

Laboratory of Organic Chemistry, Department of Chemistry, Faculty of Science, University of Damascus, Syria.

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ABSTRACT

Schiff bases are aldehyde- or ketone-like compounds in which the carbonyl group is replaced by an imine or azomethine group. In this paper, the transport of metal ions from an aqueous solution into an aqueous receiving solution through a bulk liquid membrane containing Schiff bases as a carrier was described. Therefore, synthetic methods for the preparation of Schiff bases are also reviewed.

Keywords: Schiff bases, active transport, liquid membrane, liquid-liquid extraction.

*Corresponding author. E-mail: wailalzoubi@yahoo.com, wailzoubi@yahoo.com.

INTRODUCTION

Schiff bases, named after Hugo Schiff (Schiff, 1864), are formed when any primary amine reacts with an aldehyde or a ketone under specific conditions. Structurally, a Schiff base (also known as imine or azomethine) (Figure 1) is a nitrogen analogue an aldehyde ketone in which the carbonyl group (C=O) has been replaced by an imine or azomethine group.

Schiff bases are some of the most widely used organic compounds. They are used as pigments and dyes, catalysts, intermediates in organic synthesis, as polymer stabilisers, and separation of trace amount of metal ions (Dhar and Taploo, 1982). Schiff bases have also been shown to exhibit a broad range of biological activities. Imine groups are present in various natural, natural-derived, and non-natural compounds (Figure 2) (Bringmann et al., 2004; de Souza et al., 2007; Guo et al., 2007).

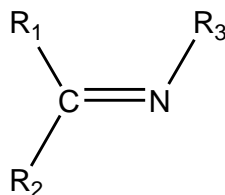
SYNTHESIS OF SCHIFF BASES

The first preparation of imines was reported in the 19th century by Schiff (1864). Since then a variety of methods for the synthesis of imines have been described (Zheng et al., 2009). The classical synthesis reported by Schiff involves the condensation of a carbonyl compound with an amine under azeotropic distillation (Moffett, 1963). Molecular sieve are then used to completely remove water formed in the system (Taguchi and Westheimer, 1971). In the 1990s, *in situ* method for water elimination

was developed, using dehydrating solvents such as tetramethyl orthosilicate or trimethyl orthoformate (Love and Ren, 1993; Look et al., 1995).

Chakraborti et al. (2004) demonstrated that the efficiency of these methods is dependent on the use of highly electrophilic carbonyl compounds and strongly nucleophilic amines. They proposed as an alternative the use of substances that function as Bronsted-Lowry or Lewis acids to activate the carbonyl group of aldehydes, catalyze the nucleophilic attack by amines, and dehydrate the system, eliminating water as the final step. Examples of Bronsted-Lowry or Lewis acids used for the synthesis of Schiff bases include $ZnCl_2$, $TiCl_4$, $MgSO_4$ -PPTS, $Ti(OR)_4$, alumina, H_2SO_4 , $NaHCO_3$, $MgSO_4$, $Mg(ClO_4)_2$, H_3CCOOH , $Er(OTf)_3$, P_2O_5/Al_2O_3 , HCl (Chakraborti et al., 2004; Billman and Tai, 1958; White and Weingarten, 1967; Branchaud, 1983; Armstrong et al., 1997; Liu et al., 1999; Roman and Andrei, 2001; Samec and Backvall, 2002; Baricordi et al., 2004; Panneerselvam et al., 2005; Dalpozzo et al., 2006; Naeimi et al., 2006; Kulkarni et al., 2009).

In the past 12 years, a number of innovations and new techniques have been reported, including solvent-free/clay/microwave irradiation, solid-state synthesis, K-10/microwave, water suspension medium, [bmim]BF₄/molecular sieves, infrared irradiation/no solvent, $NaHSO_4 \cdot SiO_2$ /microwave/solvent free, solvent-free/CaO/microwave, and silica/ultrasound irradiation [Varma et al., 1997; Schmeyers et al., 1998; Vass et al., 1999; Tanaka and Shiraiishi, 2000; Andrade et al., 2004;



R₁, R₂ and / or R₃=alkyl or aryl

Figure 1. General structure of a Schiff base.

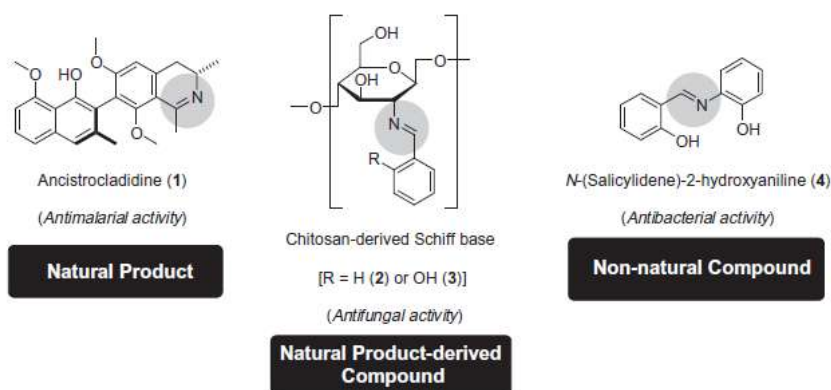


Figure 2. Examples of bioactive Schiff bases. The imine or azomethine group present in each molecular structure is shaded.

Vázquez et al., 2004; Gopalakrishnan et al., 2005; Gopalakrishnan et al., 2007; Guzen et al., 2007). Among these innovations, microwave irradiation has been extensively used due to its operational simplicity, enhanced reaction rates, and great selectivity (Gedye et al., 1986). The use of microwave irradiation commenced with the independent studies of Rousell and Majetich groups (Gedye et al., 1986; Giguere et al., 1986). Microwave irradiation is less environmentally problematic than other methods because it abolishes the excessive use of aromatic solvents and the Dean-Stark apparatus for azeotropic removal of water. Another feature of this technique is that the reactions achieve high efficiency in a shorter period of time.

LIQUID MEMBRANES

A liquid membrane consists of a water immiscible organic phase containing organic extractants or carriers in a hydrophobic microporous support to facilitate selective transport. A lot of work has been done in the development of artificial membranes for the recovery or removal of a wide variety of ionic and molecular species.

If one component of a mixture moves through the membrane faster than another mixture component, these

get separated. Liquids immiscible with the source and receiving phase can be used as membrane materials. As the diffusion coefficients in liquids are higher than that in polymers, a larger flux can be obtained with liquid membranes. The extraction chemistry involved in liquid membrane process is essentially the same as that in solvent extraction, but the overall process is governed by kinetic rather than equilibrium parameters (Nobel and Way, 1987).

Liquid membranes have gained wide interest since their discovery. These have been shown to have great potential for water treatment (Halwachs and Schugerl, 1980), separation of hydrocarbons (Kato and Kawasaki, 1987), hydrometallurgy (Naim et al., 1997), biotechnological and biomedical applications (Asher et al., 1980).

Liquid membrane may be broadly classified into three type: bulk, emulsion and supported liquid membranes (SLM). Bulk liquid membranes usually consist of an aqueous feed and stripping phase, separated by a water-immiscible liquid membrane phase in a U-tube. BLMs are often used to study the transport properties of novel carriers and a small membrane surface area of BLMs makes them technologically not very attractive. Emulsion liquid membranes suggested by Li (1968) have a very high surface area per unit of volume and low thickness

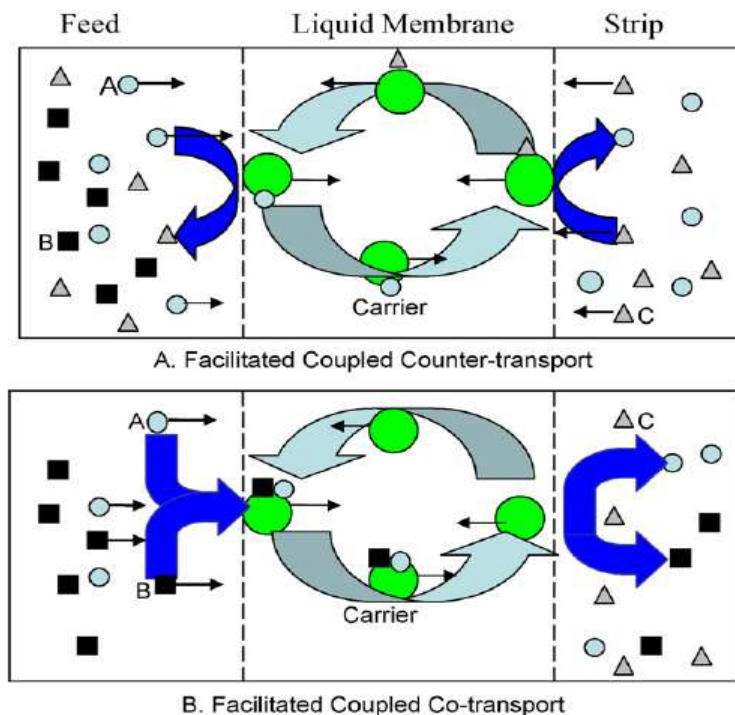


Figure 3. Facilitated coupled transport of ions through liquid membrane.

and it means the separation process and accumulation inside the emulsion vehicle is fast. The problem is that the vehicles have to be produced before the process; they have to be stable enough so that leakage is reduced to minimum, but still not stable so that they could be destroyed after the separation, thus allowing the removal of the transported species. As the result the process has to use several unit operations and becomes technologically not very attractive (Kocherginsky et al., 2007).

Figure 3A shows the mechanism of SLM based separation of ions. In this case, charged species A from the feed solution are selectively extracted by the carrier through organic membrane/feed interface. The carrier picks up A, moves across the membrane as a complex and finally exchanges A with the charged species C on the other side of membrane. In this case, C has the same charge as A. To preserve electrical neutrality the carrier acts as a shuttle carrying A and C in the opposite directions. That is why the process is called facilitated coupled counter-transport. The most typical example of this process is metal cation exchange with H^+ ions, facilitated by acidic carriers. Basic carriers, like amines, can be used to carry H^+ ions together with negatively charged ions, such as Cl^- in the same direction. This process is called facilitated coupled co-transport (Figure 3B) (Kocherginsky et al., 2007).

It is easy to make the feed and strip solutions with different pH, so that ion exchange processes on the two membrane surfaces will be shifted in opposite directions.

This creates a concentration gradient of different forms of the carrier (with and without ions) in the membrane, and results in the directed ion flux through the membrane. Evidently the process leads to the transport of targeted ionic species across the membrane against their concentration gradient. Thus type of so-called "uphill" or active transport will continue until one driving factor (difference of chemical potentials of H^+ ions) is balanced by difference of chemical potentials of another transported ion. If the carrier selectively extracts A in the presence of B, and then purified and concentrated in the strip solution, it is important that the process is using only chemical energy as a driving factor, and does not need transmembrane pressure or voltage (Kocherginsky et al., 2007).

The liquid membrane extraction was introduced as an alternative separation technique to the solvent extraction and to the separation by means of solid polymeric membranes (Li, 1971). Several types of liquid membrane configuration are reported (Boyadzchiev and Lazarova, 1994) differing mainly in performance of the membrane. Figure 4 shows the most common configurations: (a) the bulk liquid membrane (BLM), (b) the supported liquid membrane (SLM) and (c) the emulsion liquid membrane (ELMS). All other types of LM can be related to these ones. The BLM technique requires a simple design of the cell for the membrane process to work (Figure 4a). The membrane liquid is placed above the feed and stripping solutions, separated with a solid barrier, thus being in contact with both of these solutions. In the SLM (Figure 4b),

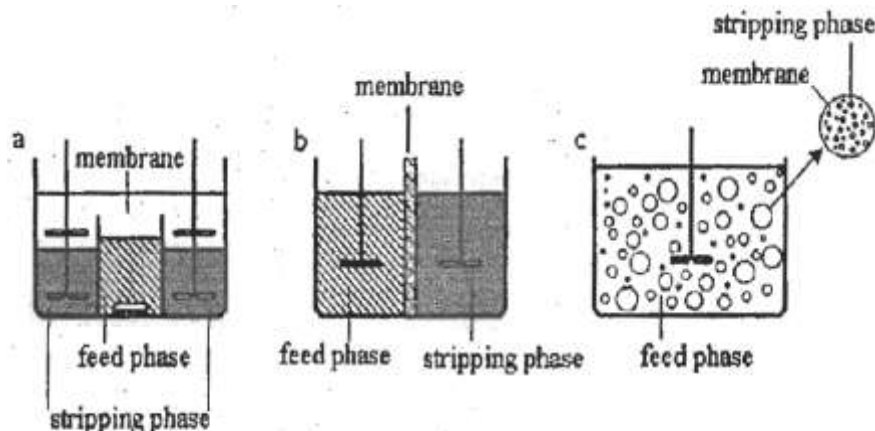


Figure 4. Liquid membrane types (a) bulk membrane, (b) supported liquid membrane, (c) emulsion liquid membrane.

a porous, solid barrier, is in contact with both of these solutions. In the SLM (Figure 4b), a porous, solid and inert, support is required to hold liquid within the membrane phase and fixed between the two aqueous, feed and stripping, solutions. ELMS are based on emulsion of the aqueous/organic/aqueous type. To obtain this, a fine emulsion of the stripping phase in the membrane phase is produced and stabilized by a surfactant. The resulting water-in-oil emulsion is then dispersed by stirring in the feed solution to create a double emulsion (Figure 4c).

Thus, a large interface area between the feed solution and the emulsion globules, and even a larger surface area of the encapsulated stripping solution, accelerates the transport of selected species (Bukhart, 2007).

This setup has a very thin membranes and a large surface area to volume ratio, which enhances the transport rate of the membrane. Concentrations in the receiving phase volume, which occurs whenever the organic phase emulsion is added to an even larger quantity of source phase (Bukhart, 2007).

In bioanalysis, membrane techniques have been applied to the determination of drugs and also to other compounds in biological fluids such as blood plasma and urine (Bukhart, 2007).

PREVIOUS STUDIES ON METAL ION SEPARATION BY LM

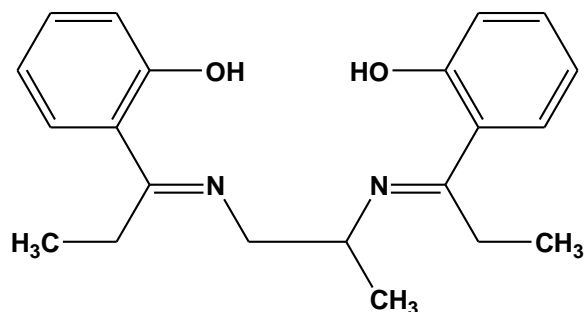
During the last three decades, an increased interest has been shown in trace elements in water. Considerable success has been achieved in the development of artificial membranes for the recovery or removal of a wide variety of ionic and molecular species, so that LMs have found their major application in separation technology (Bachiri et al., 1996).

Notably, they offer the advantage to perform the extraction and the stripping in one single step. The

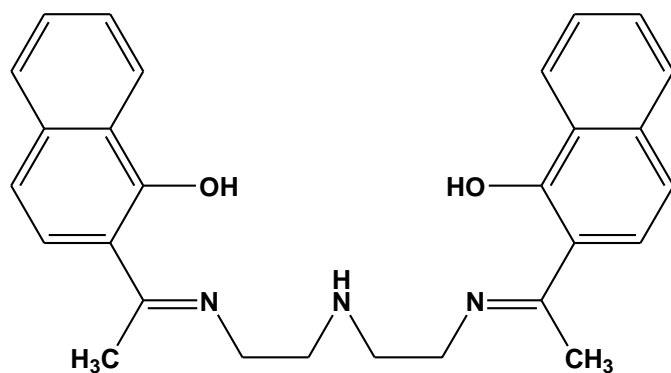
literature about the liquid membrane has been mainly devoted to their use in the field of chemical separation (Cleiji et al., 1997; Saito, 1998; Li et al., 1998; Guyon et al., 1999; Breembroek et al., 1998; Shirai et al., 1995). More fundamental studies were devoted to a better understanding of the nature of ion transfer processes taking place at the membrane interface.

Selective separation of a given metal ion from a complex mixture of other ionic species is of increasing importance in industrial and analytical chemistry and separation sciences. In most cases, various interfering species must be removed and/or the species of interest must be enriched before detection. Carrier mediated transport through liquid membrane is well known as one of the most powerful tools for such concentration, separation and recovery processes (Shirai et al., 1995). An important advantage for the use of this procedure is that in the liquid membrane technology, the extraction, stripping and regeneration operations are combined in one single step.

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 (Mashhadizadeh et al., 2007; Gupta et al., 2006; Ardakani et al., 2005) and anion (Sadeghi et al., 2006; Shamsipur et al., 2001) selective electrodes. Octadecyl disks modified by Schiff base ligands have been used for enrichment and separation of trace amount of metal ions (Shamsipur et al., 2000; Shamsipur et al., 2003). Shemirani et al. (2003) 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 Type N_4 (Oshima et al., 2001; Oshima et al., 2002; Oshima et al., 2003) and N_2O_2 (Hirayama et al., 1997; Kara and Alkan, 2002) were used as extractant in



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



Bis(1-hydroxy-2-acetonaphthone)-2,2'-diiminodiethylamine
(N_3O_2)

Figure 5. Chemical structure of the studied carriers.

liquid-liquid extractions studies. Surprisingly, the mobile carrier properties of this type of ionophores have been rarely studied. Rouhollahi et al. (2007) reported recently the uphill transport of copper ions using a Schiff base, named N,N'-bis(salicylidene)-naphthylene-1,8-diamine.

Mobile carrier properties of two Schiff base ligands (Figure 5), 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 dodecylsulfate (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

Table 1. Percentage of the transport copper, zinc, cobalt, cadmium, nickel and lead ions from mixtures by N_2O_2 and N_3O_2 .

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	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

N_3O_2 , at 20°C, 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 (Massoumeh and Reza, 2009).

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 is probably due to a multi-ion competition or crowding effect (Alguacil et al., 2004; De Gyves and Rodriguez de San, 1999; Parinejad and Yafian, 2007).

So far as for transition and heavy metal ions, a number of carriers for Cu (II) that is both vital and toxic for many biological system have been reported (Kubo et al., 1998; Safavi and Rastegarzadeh, 1995; Maruyama et al., 1981;

Kishii et al., 1985; Hiratani et al., 1990). These methods for the specific transport of Cu (II) ions across a liquid membrane have the drawbacks of a slow rate of transport or a lack of high selectivity and efficiency. For example, it has been reported (Safavi and Rastegarzadeh, 1995) that the urea-containing octameric oligomer $[-CH_2CH_2N(CONHph)-]_8$ provide the selective passive transport of copper ion through a liquid membrane. However, the flux of transport was small; after 24 h only 37% of total copper ion was transported. The reported carriers such as 6-amino-6-dodecylamino-2,2-bipyridine (Maruyama et al., 1981) and N,N-bis(8-quinolyl) glutaramide (Kishii et al., 1985) showed that after 20 and 48 h only 50 and 63% of copper (II) were transported to the receiving phase, respectively. Therefore, the development of effective and specific systems for studying of transport of metal ions, and in particular Cu(II), is still a challenging task form both the practical and theoretical viewpoints.

The transport of Cu(II) through a chloroform bulk liquid membrane containing a new tetradentates Schiff base; N,N-bis(salicylidene)-naphthylene-1,8-diamine (NBSND) (Figure 6) as an excellent synthetic carrier was studied. Although in the case of acidic receiving phase without any surfactant, only a few percent of copper had been transported into the receiving phase after several hours, the addition of sub millimolar of an anionic surfactant such as sodium dodecyl sulfate (SDS) into the receiving phase increases the percent of copper transported to more than 97%. This transport is very selective to copper over alkali, alkaline earth and several transition and heavy metal ions (Rouhollahi et al., 2007).

The selectivity of the membrane system proposed was studied under optimum conditions by undertaking competitive transport experiments with equimolar concentrations of different alkali, alkaline earth, transition and heavy metal ions. The results obtained are summarized in Table 2. As can be seen, among a wide variety of cations tested, only Ni²⁺ and Mn²⁺ ions shows some interfering effect on the transport of Cu²⁺ ions (mixture number 4) and the system is very selective to Cu²⁺ ion over other cations (Rouhollahi et al., 2007).

Conditions, source phase, 5 ml of 1.0×10^{-4} M of each cation and 0.1 M ammonia at pH; liquid membrane phase, 20 ml of 8.0×10^{-4} M NBSND in chloroform; receiving phase, 10 ml solution of 5.0×10^{-4} M SDS and 0.1 M nitric acid

The ability of pyrazole (Figure 7) and its derivatives to act as ligands with sp² hybrid nitrogen donors is evident from the large number of articles, several of them being reviews as the synthesis of a new tetrapyrazolic macrocyclic structure with a functionalised arm was described. The complexing properties of this new compound towards alkali metal ions (K⁺, Na⁺, Li⁺) were studied by liquid-liquid extraction and liquid membrane transport processes (Radi et al., 2006).

The competitive metal ion extraction and transport of

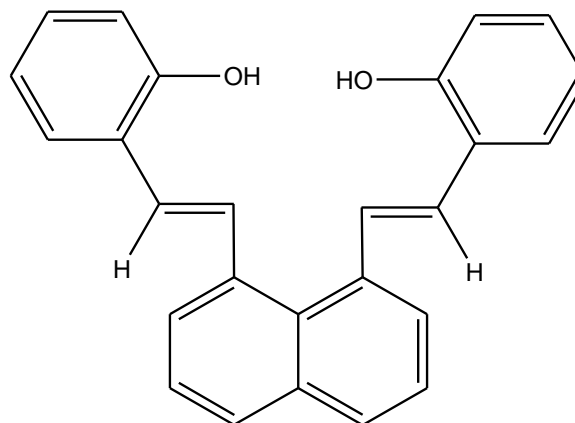


Figure 6. Structure of NBSND.

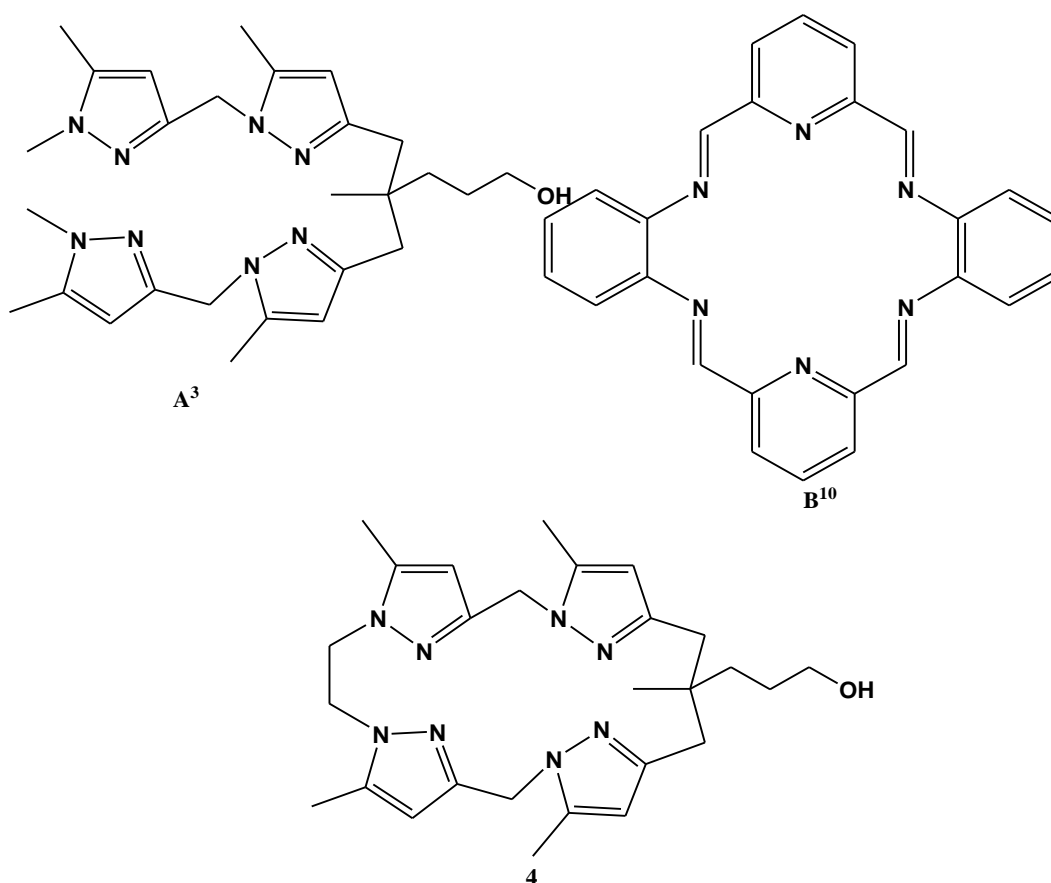
Cu(II), Ni(II), Zn(II) and Mn(II) with a S-N donor, that is, 5-methyle-4[thiophen-2-ylmethylene-amino]-3-thio-oxo-1,2,4-triazol-5-one (ATTT) and oxygen donor, phthalic dicarboxaldehyde (PHDC) compounds was examined and compared each other. Although the extraction and transport behavior of Cu(II) and 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 to 7. The concentrations in the all transport and extraction experiments for the cations and ligands were 0.01 M and 1.0×10^{-3} M, respectively (Nezhadali et al., 2008).

5,6,14,15-Dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene (DBDA15C4) (Figure 8) as a mobile carrier and histidine as a stripping agent were used for the selective uphill and proton driven transport of Zn²⁺ ions through a bulk liquid membrane. A study of different parameters on zinc transport has been carried out. This includes the pH of the feed phase, amount of DBDA15C4 in the liquid membrane, type and concentration of acid and amino acid in the strip phase and transport. In the optimum procedure conditions, the maximum transport of Zn²⁺ ions at 3 h was observed ($96.2 \pm 1.2\%$). With this system, Zn²⁺ as Zn-histidine complex could be separated from Cu²⁺, Cd²⁺, Pb²⁺, Mn²⁺, Cr³⁺, Al³⁺, Co²⁺, Ni²⁺, Ca²⁺, Mg²⁺ and Fe³⁺. The transport mechanism of this system has been described (Fakhari et al., 2006).

The selectivity of the membrane system was studied at optimum conditions for the transport of Zn²⁺ ion over other cations, which were initially present with Zn²⁺ in equimolar concentrations. Table 3 shows the percentage of cations transported into strip phase and remained in feed phase in the presence and absence of histidine. As it is seen, the presence of histidine in the strip phase could largely increase the selectivity of Zn²⁺ transport.

Table 2. Amount of cation transported from various cation mixtures through the membrane.

Cation	Percentage transported into receiving phase	Percentage remaining in source phase
Mixture 1		
Cu ²⁺	99	0
K ⁺	0	100
Ca ²⁺	1	98
Mg ²⁺	0	99
Mixture 2		
Cu ²⁺	97	2
Mn ²⁺	12	84
Cd ²⁺	1.2	96
Mixture 3		
Cu ²⁺	95	4
Ni ²⁺	15	82
Co ²⁺	3	94
Mixture 4		
Cu ²⁺	98	0
Pb ²⁺	0	98
Zn ²⁺	1	97
Hg ²⁺	0	99

**Figure 7.** New tetrapyrrolic macrocycle 4 and literature compounds A and B.

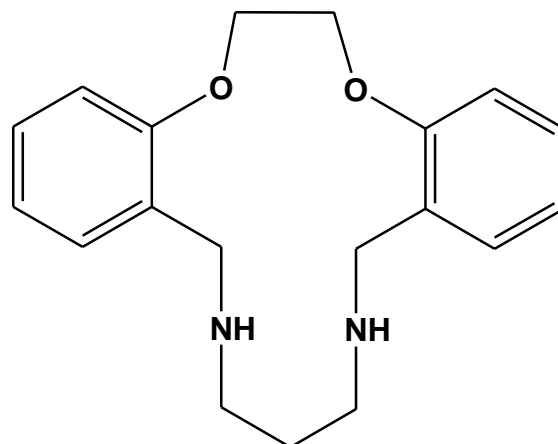


Figure 8. The structure of DBDA15C4.

Table 3. Percentage transported and remained of cations from a cation mixture in the presence and absence of histidine.

Cation	In the presence of histidine ^b		In the absence of histidine ^c	
	Transported (%)	Remained (%)	Transported (%)	Remained (%)
Zn ²⁺	96	2	14	83
Cu ²⁺	5	90	9	89
Cd ²⁺	3	93	3	94
Pb ²⁺	0	99	3	94
Mn ²⁺	0	97	6	90
Cr ³⁺	0	99	5	93
Al ³⁺	0	94	3	92
Co ²⁺	0	97	1	97
Ni ²⁺	0	99	0	98
Ca ²⁺	0	96	0	99
Mg ²⁺	0	99	5	93
Fe ³⁺	0	92	14	83

^a Strip phase: 1×10^{-3} M histidine and 0.1 M HNO₃. Feed phase: 1×10^{-4} M Zn²⁺ and 1×10^{-4} M Mn²⁺ at pH 7.2. Membrane phase: 5×10^{-3} M DBDA15C4.

Stirring speed: 200 min⁻¹. Temperature: 25°C.

^b Time of transport: 3h.

^c Time of transport: 8h.

This high affinity of histidine for Zn²⁺ ion over other cations have been reported (Tanaka and Shiraishi, 2000; Andrade et al., 2004). This observable fact is based on the specific interaction of imidazole group of histidine with the Zn²⁺ ion (Table 3) (Lipscomb and Sträter, 1996; Brown et al., 1983).

New Schiff base (N₂O₂) (Figure 9) containing nitrogen-oxygen atoms was designed and synthesized by the reaction of 5-amino-2-methoxy phenol with terephthalaldehyde. Transportation of copper ion across bulk chloroform containing (N₂O₂) as carrier has been studied. The selectivity of the processes toward copper ions were tested by performing the competitive transport experiments on the mixture containing Pb²⁺,

Ni²⁺, Cd²⁺, Zn²⁺ and Co²⁺ ions. The amount of copper transport through the liquid membrane after 90 min 99% at 25°C was studied (Zoubi et al., 2011).

Selectivity of the transport experiments using N₂O₂ carrier under similar experimental conditions toward copper ions over lead, nickel, cobalt, cadmium and zinc ions from binary mixtures was evaluated (Table 4). It is noteworthy that the presence of other metal ions in the mixture decreases the percentage of copper transported in comparison with in single species experiments. This is probably due to a multi-ion competition or crowding (Alguacil et al., 2004; De Gyves and Rodriguez de, 1999; Parinejad and Yafian, 2007).

New Schiff base (H₂L) containing nitrogen-sulfur-

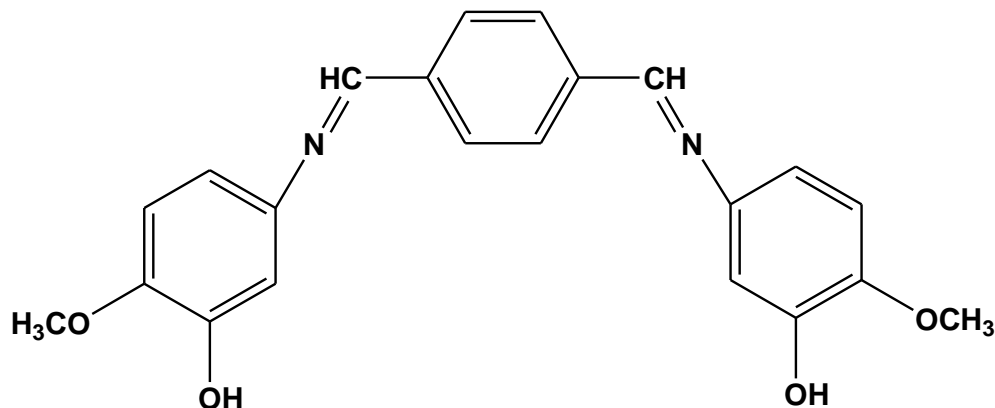


Figure 9. Structure of Schiff base.

Table 4. Percentage of transported copper, zinc, cobalt, cadmium, nickel, and lead ions from its mixtures by N_2O_2 .

Mixture	M^{2+}	Transported value (%)
Mix. 1	Cu^{2+}	88.2
	Zn^{2+}	9
Mix. 2	Cu^{2+}	81.7
	Co^{2+}	13.6
Mix. 3	Cu^{2+}	88.2
	Pb^{2+}	22
Mix. 4	Cu^{2+}	80.1
	Ni^{2+}	5.5
Mix.5	Cu^{2+}	89.6
	Cd^{2+}	2

oxygen atoms was synthesized by reaction of α,α' -bis(5-bromo-2-carboxyaldehyde phenoxy)-1,4-xylene with aminothiophenol (Figure 10). Transport of copper ion across a bulk chloroform membrane containing Schiff base ligand (H_2L) as carrier has been studied. The parameters influencing the transport efficiency such as composition of receiving phase, pH of the feed phase, carrier concentration in the membrane, EDTA concentration in the receiving phase, effect of temperature and time dependency of the process were studied and discussed (Zoubi et al., 2012).

MECHANISM OF METAL IONS TRANSFER IN LIQUID MEMBRANE

The copper ions are transported from source phase to the receiving phase through chloroform with simultaneous counter-transport of protons. The Cu^{2+}

transport can be explained as follows: at source phase/membrane interface, the carrier complex of copper ion forms uncharged complex CuL . At this stage, the carrier splits off protons into the source phase.

The formed complex diffuses across the membrane and at the membrane/receiving phase interface, the release of the Cu^{2+} ion into the receiving phase occurs via the decomposition of the complex. At this stage, the carrier associates with proton from the receiving phase releasing Cu^{2+} ion into the receiving phase. The free carrier diffuses back across the membrane to the source phase/membrane interface, where the cycle starts again.

Conclusions

The transport of alkali metal cations through bilayers presents a challenge that nature has met through millions of years of evolution.

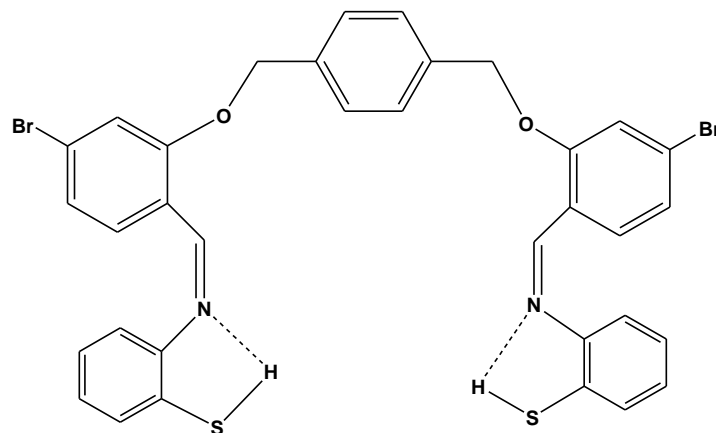


Figure 10. Structure of [N,N'-bis(2-aminothiophenol)- α,α' -bis(5-bromocarboxylidene phenoxy) xylene [H₂L].

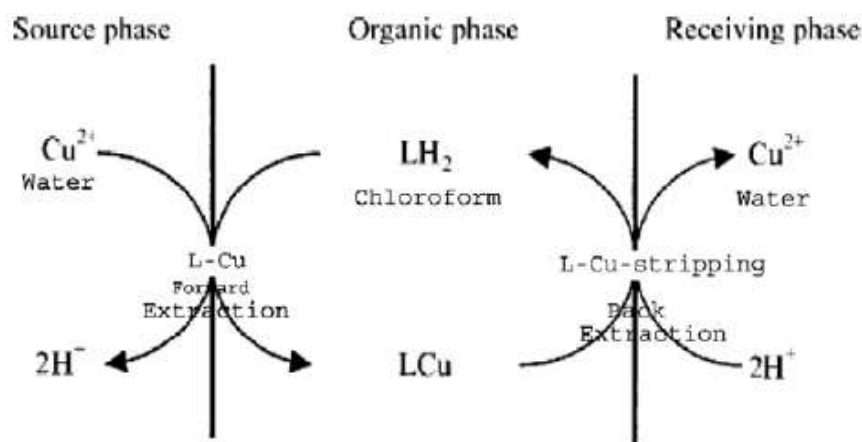


Figure 11. Liquid membrane system for transport of Cu(II) ion.

Uphill transport of Cu(II) against its concentration gradient is easily performed with the illustrated system (Figure 11). Also, 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 advantages of high precision, efficiency, simplicity and speed.

In conclusion, we have reviewed prepared Schiff bases, which have an unusual aptitude for formation of complexes with metal ions. It has been demonstrated that these Schiff bases transport metal ions. Also the present study demonstrates that the Schiff bases are an excellent carrier for selective and efficient transport of metal ions.

Uphill transport of M^{n+} against its concentration gradient is easily performed with the above system. Also, 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.

REFERENCES

- Alguacil F, Lpez-Delgado A, Alonso M, Sastre AM, 2004. The phosphine oxides Cyanex 921 and Cyanex 923 as carriers for facilitated transport of chromium (VI)-chloride aqueous solutions. *Chemosphere*, 57:813-819.
- Andrade CKZ, Takada SCS, Alves LM, Rodrigues JP, Suarez PAZ, Brandaõ RF, 2004. Molecular Sieves in Ionic Liquids as an Efficient and Recyclable Medium for the Synthesis of Imines. *Synlett*, 12:2135-2138.
- Ardakani M., Kashani MK, Niasari MS, Ensafi AA, 2005. Lead ion-selective electrode prepared by sol-gel and PVC membrane techniques. *Sens. Actuators B Chem*, 107:438-445.
- Armstrong JD, Wolfe CN, Keller JL, Lynch J, Bhupathy M, Volante RP, 1997. A novel synthesis of disubstituted ureas using titanium(IV) isopropoxide and sodium borohydride. *Tetrahedron Lett*, 38(9):1531-1532.
- Asher WJ, Bovee KC, Vogler TC, Hamilton RW, Holtzapple PG, 1980. Secretion modified release of urease from liquid membrane capsules (LMC). *Trans Am Soc Artif Intern Organs*, 26:120.
- Bachiri AEI, Hagage A, Borgard AM, 1996. Recovery of silver nitrate by transport across a liquid membrane containing dicyclohexano 18

- crown 6 as a carrier. *J Membr Sci*, 121:159.
- Baricordi N, Benetti S, Biondini G, de Risi C, Pollini GP, 2004. A new 'one-pot' synthesis of 2-substituted 3-nitro pyrrolidines through a multicomponent domino reaction. *Tetrahedron Lett*, 45(7):1373–1375.
- Billman JH, Tai KM, 1958. *J Org Chem*, 23(4):535–539.
- Boydazchiev L, Lazarova Z, 1994. Liquid membranes (Liquid pertraction). In: R.D. Noble and S. A. Stern (Eds): *Membrane Separation Technology, Principles and Applications*, Elsevier Sci. B. V.; Amsterdam, p283.
- Branchaud BP, 1983. Studies on the preparation and reactions of tritylsulfenimines. *J Org Chem*, 48(20) 3531–3538.
- Breembroek GRM, Van Straalan A, Witkamp GJ, Van Rosmalen GMJ, 1998. Design Extraction of cadmium and copper using hollow fiber supported liquid membranes. *J Membrane Sci*, 146(2):185-195.
- Bringmann G, Dreyer M, Faber JH, Dalsgaard PW, Staerk D, Jaroszewski JW, 2004. Ancistrotananzine C and related 5,1'- and 7,3'-coupled naphthylisoquinoline alkaloids from *Ancistrocladus tanzaniensis*. *J Nat Prod*, 67(5) 743–748.
- Brown RS, Huguet J, Curtis NJ, 1983. *Metal Ions in Biological Systems*, Marcel Dekker, New York.
- Bukhart N, 2007. Study of Metal ions Separation by using coupled transport liquid membrane systems. Department of Chemistry Quaid-I-Azam University Islamabad.
- Chakraborti AK, Bhagat S, Rudrawar S, 2004. Magnesium perchlorate as an efficient catalyst for the synthesis of imines and phenylhydrazones. *Tetrahedron Lett*, 45(41):7641–7644.
- Cleiji MC, Scrimin P, Tecilla P, Tonellato U, 1997. *J Org Chem*, 62, 5592.
- Dalpozzo R, de Nino A, Nardi M, Russo B, Procopio A, 2006. Erbium(III) Triflate: A valuable catalyst for the synthesis of aldimine. *Synthesis*, 7:1127–32.
- De Gyves J, Rodriguez de San ME, 1999. *Ind Eng Chem Res*, 38, 2182.
- de Souza AO, Galetti FCS, Silva CL, Bicalho B, Parma MM, Fonseca SF, 2007. Antimycobacterial and cytotoxicity activity of synthetic and natural compounds. *Quim Nova*, 30(7):1563-1556.
- Dhar DN, Taploo CL, 1982. Schiff bases and their applications. *J Sci Ind Res*, 41(8):501-506.
- Fakhari AR, Khorrami AR, Shamsipur M, 2006. Selective uphill Zn²⁺ transport via a bulk liquid membrane using an azacrown ether carrier. *Sep Purif Technol*, 50:77-81.
- Gedye R, Smith F, Westaway K, Ali H, Baldisera L, Laberge L, 1986. The use of microwave ovens for rapid organic synthesis *Tetrahedron Lett*, 27(3):279-282.
- Giguere RJ, Bray TL, Duncan SM, Majetich G, 1986. Application of commercial microwave ovens to organic synthesis. *Tetrahedron Lett*, 27(41):4945-4948.
- Gopalakrishnan M, Sureshkumar P, Kanagarajan V, Thanusu J, 2007. New environmentally-friendly solvent-free synthesis of imines using calcium oxide under microwave irradiation. *Res Chem Intermed*, 33(6):541-548.
- Gopalakrishnan M, Sureshkumar P, Kanagarajan V, Thanusu J, Govindaraju R, 2005. Silica gel supported sodium hydrogen sulfate as an efficient and reusable heterogeneous catalyst for the synthesis of imines in solvent-free conditions under microwave irradiation. *J Chem Res*, 5:299–303.
- Guo Z, Xing R, Liu S, Zhong Z, Ji X, Wang L, 2007. Antifungal properties of Schiff bases of chitosan, N-substituted chitosan and quaternized chitosan. *Carbohydr Res*, 342(10):1329–1332.
- Gupta VK, Singh AK, Gupta B, 2006. A cerium(III) selective polyvinyl chloride membrane sensor based on a Schiff base complex of N,N'-bis[2-(salicylideneamino)ethyl]ethane-1,2-diamine. *Anal Chim Acta*, 575, 198-204.
- Guyon F, Parthassrnanthy N, Buffle J, 1999. Mechanism and kinetics of copper(II) transport through diaza-crown ether fatty acid-supported liquid membrane. *Analyt chem*, 71(4), 819-826.
- Guzen KP, Guarezemini AS, Orfa'o ATG, Cella R, Pereira CMP, Stefani HA, 2007. Eco-friendly synthesis of imines by ultrasound irradiation. *Tetrahedron Lett*, 48(10):1845-1848.
- Halwachs W, Schugerl K, 1980. The liquid membrane technique — a promising extraction process, *Inter Chem Eng*, 20(4); 519 - 528.
- Hiratani K, Hirose T, Fujiwara K, Saito K, 1990. N,N'-Bis(8-quinolyl)glutaramide as a highly selective and effective Cu(II) carrier for the uphill transport through liquid membranes. *Chem Lett*, 19: 725-728.
- Hirayama N, Takeuchi I, Honjo T, Kubono K, Kokusen H, 1997. Ion-pair extraction system for the mutual separation of lanthanides using divalent quadridentate schiff bases. *Anal. Chem.*, 69, 4814-4818.
- Kara D, Alkan M, 2002. Preconcentration and separation of copper (II) with solvent extraction using N,N'-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane. *Microchem J*, 71:29-39.
- Kato S, Kawasaki J, 1987. Enhancement of hydrocarbon permeation by polar additives in liquid emulsion membranes. *J Chem Eng Japan*, 20(6):585-590.
- Kishii N, Araki A, Shiraishi S, 1985. The extraction and transport of metal ions by 6,6'-diamino-2,2'-bipyridine derivatives. *J Chem Soc Dalton Trans*. pp: 373-378.
- Kocherginsky NM, Yang Q, Seelam L, 2007. Recent advances in supported liquid membrane technology. *Sep Purif Tech*, 53:171-177.
- Kubo K, Kubo J, Kaminaga C, Sakurai T, 1998. Transport of Cu(II) with hydroxamic acid through a liquid membrane. *Talanta*, 45(5):963-968.
- Kulkarni A, Patil SA, Badami PS, 2009. Synthesis, characterization, DNA cleavage and *in vitro* antimicrobial studies of La(III), Th(IV) and VO(IV) complexes with Schiff bases of coumarin derivatives. *Eur J Med Chem*, 44(7):2904–2912.
- Li NN, 1968. US Patent No. 3,410 794.
- Li QM, Liu Q, Zhang QV, Wei XJ, Guo JZ, 1998. Separation Study of Cadmium through an Emulsion Liquid Membrane Using Triisooctylamine as Mobile Carrier. *Talanta*, 46, 927-932.
- Li, N.N. A.I.Ch.E.J, 17(1971) 459.
- Lipscomb WN, Strater N, 1996. Recent advances in zinc enzymology. *Chem Rev*, 96:2375-2433.
- Liu G, Cogan DA, Owens TD, Tang TP, Ellman JA, 1999. Synthesis of enantiomerically Pure N-tert-butanesulfinyl imines (tert-butanesulfinimines) by the direct condensation of tert-butanesulfinamide with aldehydes and ketones. *J Org Chem*, 64(4):1278–1284.
- Look GC, Murphy MM, Campbell DA, Gallop MA, 1995. Trimethylorthoformate: A mild and effective dehydrating reagent for solution and solid phase imine formation. *Tetrahedron Lett*, 36(17):2937–2940.
- Love BE, Ren J, 1993. Synthesis of sterically hindered imines. *J Org Chem*, 58(20):5556–7.
- Maruyama K, Tsukube H, Araki T, 1981. Highly selective membrane transport of copper(II) ion by synthetic linear oligomer carriers. *J Chem Soc Dalton Trans*, pp: 1486-1491.
- Mashhadizadeh MH, Pour Taheri E, Sheikhshoaei I, 2007. A Novel Mn²⁺ PVC Membrane Electrode Based on a Recently Synthesized Schiff Base. *Talanta*, 72, 1088.
- Massoumeh P, Reza MY, 2009. *Iran J Chem Chem Eng*, 28, 2.
- Moffett RB, 1963. *Organic Syntheses*. In: Rabjohn N, Ed. New York (USA): John Wiley & Sons, Inc. p. 605–608.
- Naeimi H, Salimi F, Rabiei K, 2006. Mild and convenient one pot synthesis of Schiff bases in the presence of P₂O₅/Al₂O₃ as new catalyst under solvent-free conditions. *J Mol Catal A Chem*, 260(1–2):100–104.
- Naim MM, Mahdy MA, Fouad EA, 1997. Concentration of uranium from hydrochloric acid solutions by emulsion liquid membranes containing tri-cetyl-phosphine oxide, in: American Engineering Foundation Conference Proc. American Engineering Foundation Conference, Cairo, Egypt, Nov., P16-21.
- Nezhadali A, Hakimi M, Heydari M, 2008. 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. *J Chem*, 5(1):52-57.
- Nobel RD, Way JD, 1987. *Liquid membranes: theory and applications*. American Chemical Society, Washington, ACS Symposium, 347.
- Oshima S, Hirayama N, Kubono K, Kokusen H, Honjo T, 2001. Speciation analysis of arsenic in environmental solids Reference Materials by high-performance liquid chromatography–hydride generation–atomic fluorescence spectrometry following orthophosphoric acid extraction. *Anal Chim Acta*, 441:257-268.
- Oshima S, Hirayama N, Kubono K, Kokusen H, Honjo T, 2002.

- Structural control of Schiff base ligands for selective extraction of copper(II). *Anal Sci*, 18:1351-1355.
- Oshima S, Hirayama N, Kubono K, Kokusen H, Honjo T, 2003. Ion-pair extraction behavior of divalent metal cations using neutral di-Schiff base ligands derived from 1,2-cyclohexanediamine and o-phenylenediamine. *Talanta*, 59, 867-874.
- Parinejad M, Yaftian MR, 2007. *Iran J Chem Chem Eng*, 26, 19–27.
- Panneerselvam P, Nair RR, Vijayalakshmi G, Subramanian EH, Sridhar SK, 2005. Synthesis of Schiff bases of 4-(4-aminophenyl)-morpholine as potential antimicrobial agents. *Eur J Med Chem*, 40(2):225–229.
- Radi S, Yahyi A, Ramdani A, Zidana I, Hacht B, 2006. A new tetrapyrrolic macrocycle. Synthesis and its use in extraction and transport of K^+ , Na^+ and Li^+ . *Tetrahedron*, 62:9153-9155.
- Roman G, Andrei M, 2001. Application of characteristic vector analysis for calculations of constants of dissociation for some indoles. *Bull Chem Technol Macedonia*, 20(2):131–136.
- Rouhollahi A, Zofonoun E, Salavati-Niasari M, 2007. Effect of anionic surfactant on transport of copper(II) through liquid membrane containing a new synthesis Schiff base. *Sep Purif Technol*, 54:28-33.
- Rouhollahi A, Zofonoun E, Salavati Niasari MS, 2007. Effect of anionic surfactant on transport of copper(II) through liquid membrane containing a new synthesis Schiff base. *Sep Purif Technol*, 54:28-33.
- Sadeghi S, Fathi F, Esmaeili AA, Naeimi H, 2006. A zinc-selective electrode based on N,N'-bis(acetylaceton)ethylenediamine. *Sens Actuators B*, 114:812-818.
- Safavi A, Rastegarzadeh S, 1995. Selective and efficient uphill transport of Cu(II) through liquid membrane. *Talanta*, 42:2039-2042.
- Saito T, 1998. Transport of silver(I) ion through a supported liquid membrane using bathocuproine as a carrier. *Sep. Sci Technol*, 33, 855.
- Samec JSM, Backvall JE, 2002. Ruthenium-catalyzed transfer hydrogenation of imines by propan-2-ol in benzene. *Chem Eur J*, 8(13):2955–2961.
- Schiff H, 1864. Mitteilungen aus dem universitatlaboratorium in Pisa: Eineneue reihe organischer basen. (in German). *Justus Liebigs Ann Chem*, 131(1); 118–119.
- Schmeyers J, Toda F, Boy J, Kaupp G, 1998. Quantitative solid–solid synthesis of azomethines. *J Chem Soc Perkin Trans*, 2, 2989–994.
- Shamsipur M, Ghiasvand AR, Sharghi H, Naeimi H, 2000. Solid phase extraction of ultra trace copper(II) using octadecyl silica membrane disks modified by a naphthol-derivative Schiff's base. *Anal. Chim. Acta*, 408, 271-277.
- Shamsipur M, Soleimanpour A, Akhond M, Sadeghi H, Naseri MA, 2001. Iodide-selective carbon paste electrodes based on recently synthesized Schiff base complexes of Fe(III). *Anal Chim Acta*, 450: 37-44.
- Shamsipur T, Mashhadizadeh MH, Sheikhshoaei I, 2003. Flame atomic absorption spectrometric determination of silver ion after preconcentration on octadecyl silica membrane disk modified with bis[5-((4-nitrophenyl)azosalicylaldehyde)] as a new Schiff base ligand. *J Anal At Spectrom*, 18, 1407-1410.
- Shemirani F, Abkenar SD, Mirroshandel AA, Niasari SM, Kozania RR, 2003. Preconcentration and speciation of chromium in water samples by atomic absorption spectrometry after cloud-point extraction. *Anal Sci*, 19, 1453-1456.
- Shirai O, Kihara S, Yoshida Y, Matsui M, 1995. Ion transfer through a liquid membrane or a bilayer lipid membrane in the presence of sufficient electrolytes. *J Electroanal Chem*, Vol. 389, (): p. 61.
- Taguchi K, Westheimer FH, 1971. Catalysis by molecular sieves in the preparation of ketimines and enamines. *J Org Chem*, 36(11):1570–1572.
- Tanaka K, Shiraishi R, 2000. Clean and efficient condensation reactions of aldehydes and amines in a water suspension medium. *Green Chem*, 2(6):272–273.
- Va'zquez MA, Landa M, Reyes L, Miranda R, Tamariz J, Delgado F, 2004. Infrared irradiation: Effective promoter in the formation of N-benzylideneanilines in the absence of solvent. *Synth Commun*, 34(15):2705–2718.
- Varma RS, Dahiya R, Kumar S, 1997. Clay catalyzed synthesis of imines and enamines under solvent-free conditions using microwave irradiation. *Tetrahedron Lett*, 38(12):2039–2042.
- Vass A, Duda J, Varma RS, 1999. Solvent-free synthesis of N-sulfonylimines using microwave irradiation. *Tetrahedron Lett*, 40(27):4951–4954.
- White WA, Weingarten H, 1967. A versatile new enamine synthesis. *J Org Chem*, 32(1):213–214.
- Zheng Y, Ma K, Li H, Li J, He J, Sun X, 2009. One pot synthesis of imines from aromatic nitro compounds with a novel Ni/SiO₂ magnetic catalyst. *Catal Lett*, 128(3-4):465–474.
- Zoubi WA, Kandil F, Chebani MK, 2011. The synthesis of N₂O₂-Schiff base ligand and bulk liquid membrane transport of Cu²⁺. *Arabian Journal of Chemistry*. In Press.
- Zoubi WA, Kandil F, Chebani MK, 2012. Synthesis of New N,N'-bis(2-aminothiophenol)- α,α' -bis(5-bromocarboxylidene phenoxy)xylene and their Liquid Membrane Transport of Copper Cations. *J Separ Sci Technol*, 48(3):501-507.