Experimental and Computational Studies of Membrane Extraction of Cu(II)

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DOI 10.1002/aic.10947

A comparative study of membrane extraction of copper using LIX54- or LIX84-impregnated supported liquid membrane (SLM) systems was carried out in this work to remove copper from ammoniacal wastewater. Experimental and computational characterizations of LIX54/Cu(II) and LIX84/Cu(II) complexes were performed and the results agreed well in the reaction mechanisms, complex geometries, and copper extraction strengths of these two carriers. Copper transmembrane fluxes at different conditions were compared and LIX54 was found to have slightly higher copper transmembrane flux in ammoniacal solution but much poorer copper loading in acidic media. Much higher selective separation performances of Cu(II) over Zn(II) and Cd(II) and no ammonia carryover provide LIX54 significant advantages over LIX84 for the treatment of ammoniacal copper solutions. In this work, an impedance spectroscopy technique and initial flux measurement were used to study the long-term stabilities of both LIX54- and LIX84-impregnated vertical flat membrane systems. The results reveal that the membrane stability of both LIX54- and LIX84-impregnated SLM in ammoniacal copper solutions is promising for practical industrial applications. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3266–3277, 2006

Keywords: supported liquid membrane (SLM), carrier, selectivity, stability, quantum chemical computation

Introduction

Recovery of copper from ammoniacal etching solutions generated by printed circuit board (PCB) manufacturing in the microelectronic industry has become an important process and a large number of studies have been reported toward this end.[1-7] Usually, two kinds of copper-containing ammoniacal solutions were generated by PCB-producing companies: (1) ammoniacal wastewater with low copper and ammonia content as rinse water after the etching process, and (2) spent etchant solution with high copper and ammonia content as the effluent from the PCB etching system. Both solutions have trace amounts of other metal impurities taken from the etching process. Generally, copper concentration in ammoniacal wastewater is around several hundred parts per million (ppm). It has to be reduced to <5 ppm before the solution can be reused or discharged safely. In this work, ammoniacal wastewater was used as the model solution for membrane flux, selectivity, and stability studies.

Supported liquid membrane (SLM) based separation/concentration of copper has received considerable attention over the past few past decades[8-13] because of its low operation and capital cost, ease of operation, low energy consumption, and high selectivity advantages. Unlike traditional membranes, liquid membrane extraction targets and removes the solute from bulk solutions based on chemical potential rather than by size difference. SLM technology is somewhat similar to the solvent extraction process but with extraction and back-extraction performed in just one technological step. Liquid membranes provide relatively higher flux than that of solid polymeric membranes because of their higher diffusivity and smaller thickness. In addition, transport through the liquid membrane can be facilitated with an appropriate carrier. The carrier usu-

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Table 1. Typical Compositions of Copper-Containing Ammoniacal Solutions

	Ammoniacal Waste Solution	Spent Ammoniacal Etchant Solution
Cu(II)	5.6 mM	2.5 M
Total NH_3	400 mM	11 M
Cl^-	500 mM	5 M
Zn(II)	5.5 mM	1.7×10^{-3}M
Ni(II)	0.37 mM	0.34×10^{-3}M
Cd(II)	1.8×10^{-3}mM	1.8×10^{-6}M
pH	~7.25	~10

ally presents in the membrane pores and binds selectively with targeted species in the feed phase and transports the species into the strip phase.

Since the Cognis Corporation (formerly Henkel KGaA) developed extractants for solvent extraction processes, a few of its materials have found broad applications in metals recovery and purification. The LIX® reagents have been used by numerous metal-recovery operations around the world. Among them, LIX54 and LIX84 are well-established copper extractants.[14,15] It is commonly accepted that a weak β-diketone extractant LIX54 should be used for copper recovery from ammoniacal solutions, whereas a strong hydroxyoxime extractant LIX84 is used for copper recovery from acidic sulfate solutions.[2,10,16-21] However, to the best of our knowledge, no reasonably theoretical explanations for the above empirical statement have been proposed in the extant literature. In this work, efforts were made to illustrate the different copper extraction capabilities by these two extractants, both experimentally and computationally. The results can be used to screen other potential carriers in SLM systems for Cu(II) extraction from different aqueous acidic or alkaline media. In addition, the scarce information regarding the selectivity of copper over other cation contaminants, as well as ammonia in SLM systems, also fueled our intentions to conduct investigations in this area from a molecular level. Furthermore, in this work the stabilities of immobilized SLMs with LIX54 and LIX84 were monitored with impedance spectroscopy together with the flux observations over extended periods of time and the mechanisms of instabilities of SLMs were proposed.

Experimental

Reagents

LIX54 and LIX84 were supplied by the Cognis Corporation (Tucson, AZ) and were diluted in kerosene (Aldrich, Singapore) as the carrier in the liquid membrane phase. Reagent-grade sulfuric acid (Merck, Singapore) was diluted with deionized water and used as the strip solution. All chemicals were used as received without any further purification.

Two kinds of copper-containing ammoniacal solutions were kindly supplied by a PCB-producing company in Singapore: (1) ammoniacal wastewater and (2) spent etchant solution. Generally the Cu(II) concentration in the ammoniacal wastewater generated in this company was in the range of 100–1400 ppm (1.5×10^{-3}–0.021 M), together with other trace amounts of impurities. Table 1 gives the typical compositions of these two copper-containing ammoniacal solutions.

Analytical methods

Metal concentrations in the aqueous solutions were measured by an inductively coupled plasma–atomic emission spectroscopy (ICP-AES, Perkin Elmer, Norwalk, CT). In some cases solutions in the feed and strip were diluted to coincide with the measuring range. Values of pH were measured with a digital pH meter (Horiba F-23, Hiroshima, Japan) and combined pH glass electrode.

The β-diketone LIX54 and hydroxyoxime LIX84 extractants and their complexes formed after reaction with spent etchant solution (typical composition shown in Table 1) were analyzed by an FT-IR spectrometer (Bio-Rad, Hercules, CA) to study the reaction mechanisms of the extractants with $Cu(NH_3)_4^{2+}$.

Electron paramagnetic resonance (EPR) spectra of two types extractant–Cu complexes were also investigated at low temperature of 77 K with an Elexsys Series E500 CWEPR X-band spectrometer (Bruker BioSpin GmbH, Rheinstetten/Karlsruhe, Germany). The Spin Hamiltonian parameters were obtained from the simulation results using WINEPR Simfonia software (Bruker Biospin GmbH) to fit experimental EPR spectra.

Experimental setup

Flat-Sheet Supported Liquid Membrane. Two kinds of flat membrane systems—that is, horizontal and vertical setups—were used (Figure 1). Effective membrane surface area in the horizontal flat membrane system was 10 cm². Volumes of the strip solution and feed solution were 20 and 100 mL, respectively. Both aqueous phases were mechanically stirred with magnetic stirrers at 250 rpm. The smaller strip volume compared to that of the feed can provide a faster accumulation of targeted species in the strip (acceptor) solution. Sometimes it is even possible to reach saturation of the strip solutions and finally precipitation of the product. The stirring of both aqueous solutions was aimed at reducing the mass transfer resistances in the aqueous nonstirring layers and also at providing homogeneous environments in both feed and strip solutions when sampling. The polymer porous support used for the horizontal flat membrane system was a fluoropore [polytetrafluoroethylene (PTFE)] membrane filter (Millipore, Bedford, MA) with an average thickness of 50 μm, 70% porosity, and average pore size of 0.2 μm. The horizontal flat membrane system was used to study the effects of feed pH and membrane carrier concentration on Cu transmembrane flux to determine the optimal conditions for the SLM-based copper recovery process using LIX54 and LIX84 as carriers.

In the vertical flat membrane system, effective membrane

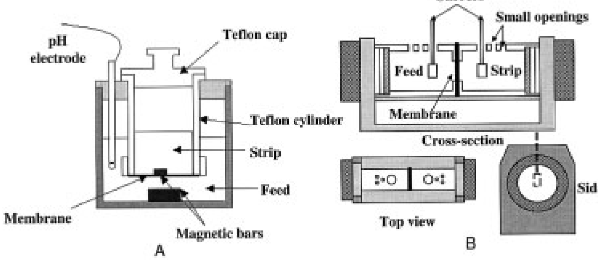

Figure 1. (A) Horizontal flat membrane system. (B) Vertical flat membrane system.

Table 2. Specifications of Liqui-Cel® Extra-Flow 2.5 in. × 8 in. Membrane Contactor

Fiber type	Polypropylene
Number of fibers	9950
Fiber internal radius	120 μm
Fiber outer radius	150 μm
Effective module outer diameter	4.67 cm
Effective module inner diameter	2.2 cm
Effective pore size	0.03 μm
Porosity	40%
Tortuosity	2.5
Effective fiber length	15 cm
Effective surface area	1.4 m^2

surface area was 4.9 cm^2. It had two Teflon® chambers holding the feed and strip solutions with volumes of 37 mL each. Both aqueous phases were mechanically stirred with Teflon® impellers in connection with an overhead mixer (CAT R18, M. Zipperer GmbH, Staufen, Germany) at 200 rpm. A PTFE membrane filter (WhatmanBiosystems Ltd., Maidstone, UK) was used as a membrane support. It has a diameter of 4.7 cm and a thickness of 150 μm with roughly 80% porosity and an average pore size of 0.2 μm. At the top of each Teflon® chamber there were opening holes in which electrodes could be inserted. The electrodes connected to analytical equipment were specifically designed for real-time monitoring of physicochemical conditions of the impregnated membrane filter.

In this work, two flat membrane setups were used. The horizontal setup is used when a continuous pH control is required. For long-term stability studies and real-time monitoring of the physicochemical properties of impregnated membranes, the vertical membrane setup is used.

To prepare a supported liquid membrane, the membrane filter was immersed into the organic solution (that is, LIX54 in kerosene under a predetermined volume ratio). After being fully wetted by the organic solution, the membrane filter was then removed and blotted by tissue paper to remove extra oil on the membrane surface. Then the impregnated filter was fixed in the membrane module. If weight gain in the membrane after impregnation was close to what could be expected, based on the known porosity and the density of carrier, the membrane pores were considered to be fully impregnated by the organic carrier.

Hollow-Fiber Supported Liquid Membrane. A laboratory-scale microporous polypropylene hollow-fiber module (Liqui-Cel® Extra-Flow 2.5 in. × 8 in. membrane contactor; Hoechst Celanese, Chatham, NJ) was used to prepare the hollow-fiber supported liquid membrane. Detailed specifications of the hollow-fiber membrane module are listed in Table 2.[22] The liquid membrane phase (33 vol/vol % LIX54 in kerosene in this case) was impregnated in the fiber wall by pumping the organic membrane phase through the contactor using a peristaltic pump (Cole-Parmer, Vernon Hills, IL) in a recycling mode for about 1 h. The extra oil was washed out with deionized water.

A comparative study of Cu(II) transmembrane flux in a horizontal flat membrane setup with LIX54 and LIX84 as carriers

The effects of feed pH and membrane carrier concentration on Cu(II) flux were studied using the horizontal flat membrane setup. In the study of the effect of feed pH on Cu(II) flux, the feed pH was adjusted by the addition of HCl and aqueous $NH_3{\cdot}H_2O$ solutions while the feed Cu(II) concentration was kept 0.021 M. The transmembrane flux J is determined according to the expression

$$J = \frac{dC}{dt}\frac{V}{S_m} \tag{1}$$

where dC is the change in concentration in the strip over time interval dt, V is the strip solution volume, and S_m is the effective membrane surface area.

In this work we also tried to determine the optimal carrier concentrations for SLM-based ammoniacal or acidic copper solution treatment using LIX54 or LIX84, respectively. Cu(II) concentrations in both ammoniacal and acidic solutions were the same (0.021 M) but pH values were adjusted continuously at pH 3 for the acidic solution and pH 7.25 for the ammoniacal solution.

Selective separation of copper over other cations in ammoniacal waste solutions using hollow-fiber SLM system

Although it is useful for the fundamental mechanism studies, the flat-sheet SLM system is not suitable for practical application of SLM technology because of its small membrane surface area. On the other hand, hollow-fiber SLM represents a very attractive solution to the need of applying SLM with very high throughputs. In addition, the hollow-fiber SLM system has attractive advantages such as high membrane surface area per unit volume and favorable hydrodynamics, which minimizes aqueous concentration polarization and membrane-fouling problems.

Therefore, the treatment of industrial ammoniacal wastewater with typical compositions shown in Table 1 by LIX54 or LIX84 as the carrier was conducted in the hollow-fiber SLM system. After liquid membrane preparation, the ammoniacal wastewater was pumped through the lumen side of hollow-fiber membrane contactor once through, whereas the strip solution was cocurrently fed in the shell side in a recirculation mode. The feed and strip solutions were pumped at the same volumetric flow rates. The cocurrent flow mode and the same volumetric flow rates were adopted to provide a stable SLM system and prevent the Kelvin–Helmholtz instability caused by the hydrodynamic velocity difference between tube and shell sides of the hollow-fiber membrane contactor.

Both inlet and outlet concentrations of targeted metal species [Cu(II), Zn(II), Ni(II), Cd(II)] in aqueous solutions were measured to obtain the corresponding overall mass transfer coefficient P according to

$$P = \frac{Q}{S_m}\ln\frac{C_{in}}{C_{out}} \tag{2}$$

where C_{in} and C_{out} are the inlet and outlet concentrations of metal ions in the lumen side, respectively; Q is the volumetric flow rate in the tube side; and S_m is the inner membrane surface area.

The separation factor (SF) of copper over other cation contaminants (M) is defined as

$$SF = \frac{P_{Cu}}{P_M} \tag{3}$$

The effect of feed and strip volumetric flow rates on copper selectivity performances was also studied. Before the experiment was carried out with a different volumetric flow rate, the lumen and shell side of the hollow-fiber membrane contactor were thoroughly cleaned with deionized water and any remaining solutions in the module were pumped out.

A comparative study of long-term stability of vertical flat membrane system to treat ammoniacal waste solutions using LIX54 and LIX84 as carriers

The liquid membrane stability was investigated by monitoring copper transmembrane flux using 33 vol/vol % LIX54 or LIX84 as the carrier in the vertical flat membrane systems. The strip solutions were pumped through a quartz flow cell (Hellma GmbH, Müllheim, Germany) with optical window of 1 × 0.1 cm (height × width), where the copper concentration in the strip side was monitored in real time using a UV–Vis scanning spectrophotometer (Libra S32, Hamburg, Germany) at a wavelength of 780 nm. A calibration of the system was performed by diluting a standardized $CuSO_4$ solution with 2 M H_2SO_4, and then the optical absorbances of the diluted Cu^{2+} solutions at 780 nm were plotted as a function of concentrations. A 37 mL feed ammoniacal solution containing 2.5×10^{-3} M Cu(II) and 42 mL 2 M H_2SO_4 as strip solutions (additional volumes of 5 mL were used to fill up the tubing and quartz cell) were homogeneously stirred at 200 rpm in the two Teflon® chambers of the vertical flat membrane setup. After preset time intervals (one day) the feed and strip solutions were replaced by fresh ones with the same compositions to prevent the variation of flux arising from composition differences. The plot of optical absorbance vs. time was always a straight line over a long period of time in each run.

Membrane stability of the vertical flat membrane setup was also monitored by measuring the electrical resistance and capacitance of the Whatman® PTFE membrane impregnated by 33 vol/vol % LIX54 or LIX84. The electrical characteristics of the liquid membrane were measured by impedance spectroscopy (Autolab, PGSTAT20, Eco Chemie BV, Utrecht, The Netherlands) with a four-electrode (two platinum and two Ag/AgCl) electrochemical system. When the impedance measurement was carried out, the aqueous solutions were not stirred to prevent the interference caused by mechanical stirring.

Computational Methodology

With recent advances in computer resources and the development of sophisticated algorithms, quantum chemical computations are playing an increasingly important role in chemical science and engineering. The objective of computational chemistry is to mathematically reveal molecular structure–property relations. In the current work, the reaction processes of LIX carriers with $Cu(NH_3)_4^{2+}$ were analyzed from the first-principles density functional theory (DFT) calculations. It is well recognized that DFT generally performs well for the organometallic compounds.[23] Geometries of the related reactants and products in $Cu(NH_3)_4^{2+}$/LIXs reaction processes were fully optimized with Becke's three-parameter hybrid functional coupled with the Lee–Yang–Parr correlation functional (B3LYP) level of theory at 6-31g basis set. One of the most important properties of a molecule is its orbitals, which can be approximated by additive basis sets. The split-valence basis set 6-31g used here means that the inner shell orbitals are represented by six Gaussians, and the valence orbitals by three Gaussians for the first Slater type orbital (STO) and by one Gaussian for the second STO.

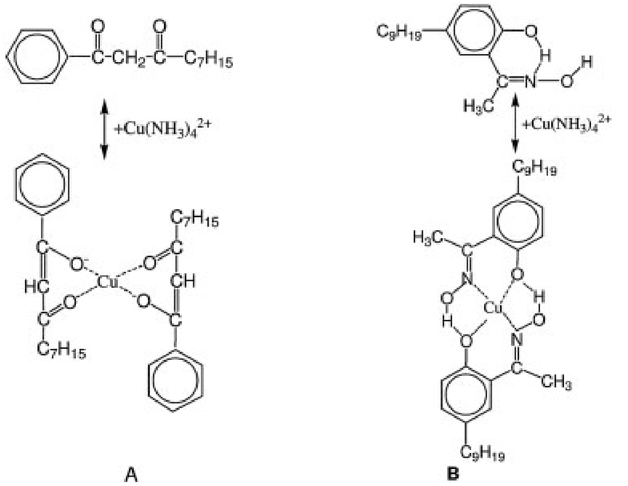

Figure 2. Proposed reaction mechanisms involving (A) $Cu(NH_3)_4^{2+}$/LIX54 and (B) $Cu(NH_3)_4^{2+}$/LIX84.

To provide good starting coordinates for DFT optimization, the geometries of the carriers and copper–carrier complexes were mechanically minimized using AMBER 8 with the general Amber force field.[24] There were 5000 steps in the minimization, in which the first 1000 steps used the steepest descent method, whereas the second 4000 steps used the conjugate gradient method. The single point energies of the fully optimized geometries were calculated using B3LYP at the 6-31+g(d) basis set. Here the "+" sign means the 6-31g basis set is supplemented by a diffuse function. Normally a basis set is centered in the inner shell. However, the incorporation of a diffusion function can account for electrons at large distances from nuclei. The "d" means a single polarization function is added to the 6-31g basis set, which results in the addition of one d function to the first and second row atoms and one f function to the first transition row atoms.[25] All the first-principles DFT calculations were performed using the GAUSSIAN 03 program suite.[26] The energy changes in complex formation processes were estimated by $\Delta E = \sum E_{\text{Products}} - \sum E_{\text{Reactants}}$.

Results and Discussion

Formation of copper complexes with LIX54 and LIX84

The active ingredients of LIX54 and LIX84 are 1-phenyl-1,3-decanedione and 2-hydroxy-5-nonylacetophenone oxime, respectively. For LIX54, it exists as an equilibrium mixture of the enol and keto forms. The mixture of keto and enol is involved in valence and coordination bonding with copper.[14,27] The general reaction mechanisms involving $Cu(NH_3)_4^{2+}$/LIX54 and $Cu(NH_3)_4^{2+}$/LIX84 are described in Figure 2 and both the reactions can be described as

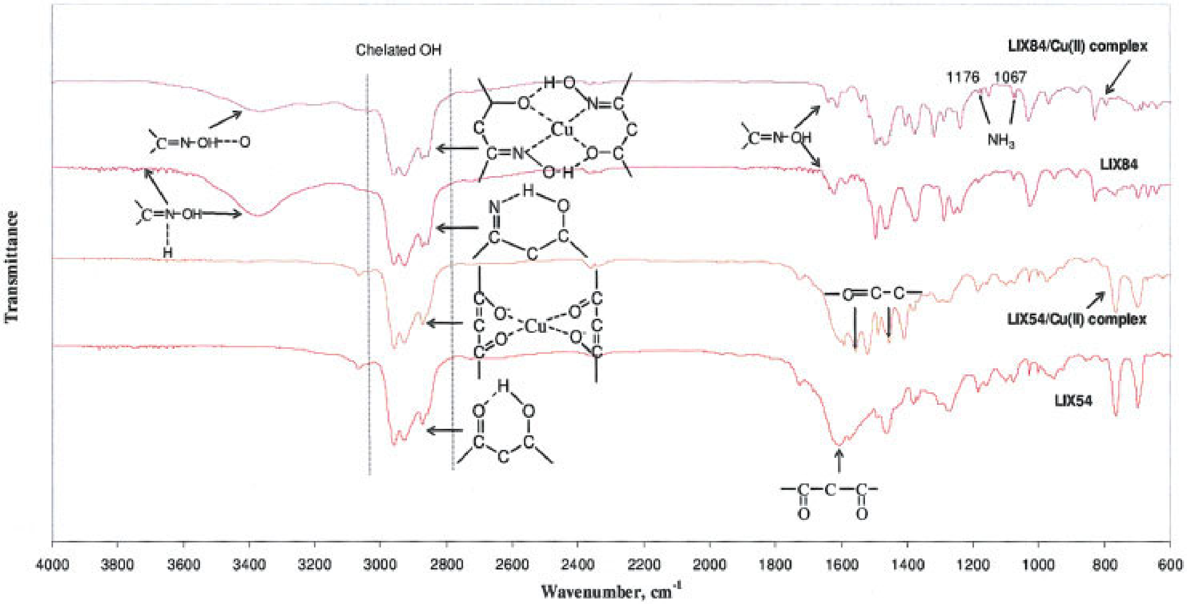

Figure 3. FTIR spectra of extractants and their complexes with spent etching solutions.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

$$Cu(NH_3)_4^{2+} + 2HR \Leftrightarrow CuR_2 + 2NH_3 + 2NH_4^+ \quad (4)$$

where HR represents the carrier LIX54 or LIX84 and CuR_2 represents the copper–carrier complexes.

It is well known that Cu^{2+} in aqueous solutions with ammonia forms octahedral complexes from $Cu(NH_3)(H_2O)_5^{2-}$ to $Cu(NH_3)_4(H_2O)_2^{2-}$, and the fifth and sixth ammonia do not bind strongly with Cu^{2+} because of the Jahn–Teller effect.[28,29] It was recently demonstrated that Cu complexes with four NH_3 is the predominant form in ammoniacal solutions containing an excess of NH_3 in comparison to Cu.[18] The complex is characterized by a high value of stability constant $K_s = 10^{12.46}$ M^{-4} of the copper–tetra ammonia complex.[30] Evidently, $Cu(NH_3)_4^{2+}$ is the dominant species in the ammoniacal wastewater and spent ammoniacal etchant solution used in our experiments.

Figure 3 shows the IR spectra of extractants and their complexes after extraction with spent etching solutions. All the spectra have strong peaks around 3200–2500 cm^{-1}, which are the characteristic peaks of chelated O—H groups.[31,32] The IR spectrum of LIX54 shows a strong band in the region around 1610 cm^{-1}, which represents the existence of the β-diketone fragment. However, the vibration bands between 1520 and 1400 cm^{-1} of the LIX54 complex with copper indicate C═C stretching vibrations. This proves the chelation reaction between the carbonyl groups of LIX54 with $Cu(NH_3)_4^{2+}$ (Figure 2A). For the aromatic oxime, the $R_2C{=}N{-}OH$ stretching band occurring in the region 1670–1620 cm^{-1} appears in the spectra of both LIX84 and its complex with Cu(II). The oxime with the intramolecular hydrogen bond has characteristic stretching vibrations in the region 3400–3200 cm^{-1}, which appear in the spectra of both LIX84 (O—H · N) and LIX84/Cu(II) complex (O—H · O). The N—H stretching vibrations in the high-wavenumber area occurring in the LIX84 spectra confirm its intramolecular hydrogen bond (O—H · N), whereas this is not the case for LIX84 complex with copper.

Notice should be taken that there are small peaks at 1067 and 1176 cm^{-1} in the LIX84/Cu(II) complex spectrum. The presence of NH_3 in the extracted organic solution will result in peaks at these ranges.[33] It was also mentioned that nonylphenol used in the synthesis of hydroxyoxime was found to extract ammonia quite strongly at high pH.[14,34] The appreciable ammonia carryover from the feed to the strip by the organic carrier over long periods is deleterious to the subsequent performance of the electrowinning step. It has been discovered that the use of diketone having very high steric hindrance will provide a further improved process in which the strip kinetics remains rapid and substantially reduced coextraction of ammonia occurs during loading with copper.[35] This is also confirmed in our IR spectrum of LIX54/Cu(II) complex. The low or no extraction of ammonia provides a significant advantage for LIX54 over other copper extractants in ammoniacal copper solution treatment.[14,15]

Figure 4 displays the EPR spectra of LIX54/Cu(II) and LIX84/Cu(II) at 77 K. Typical spectra with axial symmetry consist of an intense (perpendicular) absorption in the high-field range and a weaker (parallel) signal in the low-field side, which usually splits into four equally spaced hyperfine lines and shows the shifts depending on the nature of the copper complex.[36] The spectrum of LIX54/Cu(II) complex demonstrates the Cu^{2+} as a magnetic nuclear center surrounded by a symmetric square planar arrangement of four ligating ligands, such as 4O, which corresponds to the super-hyperfine splitting structure in the high-field range. When two ligands are of one type and the other two of another type, such as 2N and 2O in the LIX84/Cu(II) complex, the symmetry will be orthorhombic for a square planar transconfiguration.[37] The greater number of super-hyperfine splitting lines in the high-field range illustrates that the Cu^{2+} nuclear center is surrounded by both O and N ligands in the LIX84/Cu(II) complex. Given that the naturally abundant O^{16} has no nuclear spin, the naturally scarce O^{17} with

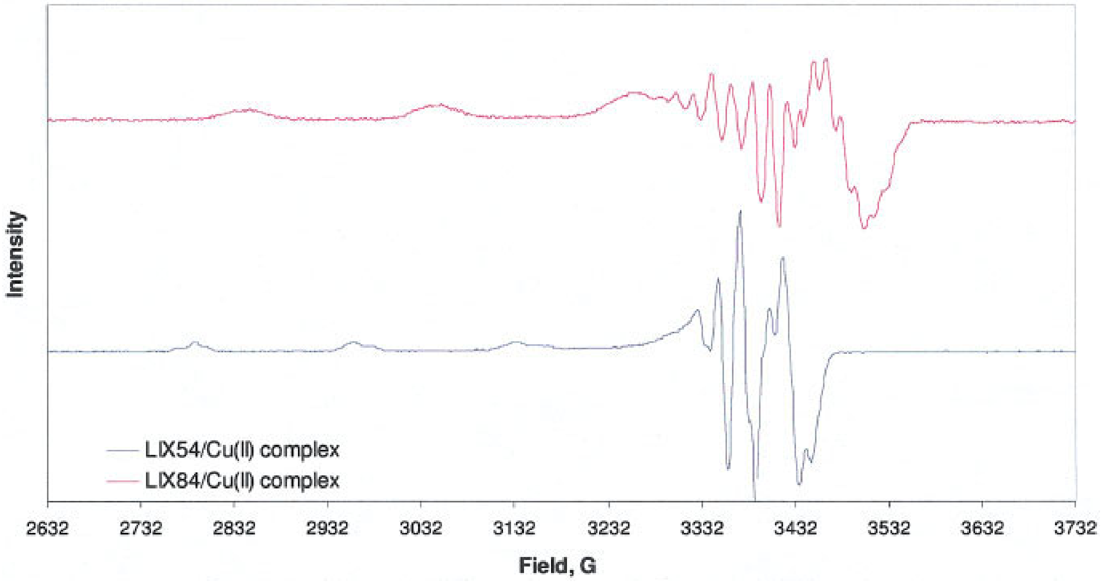

Figure 4. EPR spectra of LIX54/Cu(II) and LIX84/Cu(II) complexes at 77 K.

Spin Hamilton parameters are: $g_\perp = 2.053$, $g_\parallel = 2.277$, ${}^{Cu}A_\perp = 22$, ${}^{Cu}A_\parallel = 170$ for LIX54/Cu(II) complex and $g_\perp = 2.053$, $g_\parallel = 2.196$, ${}^{Cu}A_\perp = 18.7$, ${}^{Cu}A_\parallel = 207$, ${}^{N}A_\perp = 23$, ${}^{N}A_\parallel = 10$ for LIX84/Cu(II) complex. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

nuclear spin 5/2 has little contribution to either LIX54/Cu(II) or LIX84/Cu(II) EPR spectra, whereas for N^{14} with nuclear spin 1 and natural abundance of 99.63%, its contribution to the EPR spectrum of LIX84/Cu(II) complex has to be taken into consideration.

It was suggested that the most reliable information from the observed Cu(II) complex EPR spectra was derived from the $g_\perp$ and $A_\perp$ values.[37] The A value further provides a very good indication of the extent to which electrons have migrated from the central Cu to the surrounding ligands.[38] For the LIX84/Cu(II) complex, the hyperfine splitting constant ${}^{Cu}A_\perp$ of the Cu nucleus surrounded by 2N and 2O is 18.7, which is smaller than ${}^{Cu}A_\perp = 22$ in the LIX54/Cu(II) complex. According to Shriver and Atkins,[38] the higher value of the hyperfine splitting constant indicates that the orbital occupied by the unpaired electron in the LIX54/Cu(II) complex becomes more ligand-like and interacts more weakly with the Cu(II) nucleus.

Furthermore, the quantum chemical calculation results agree well in the experimental characterization results and support the proposed reaction mechanisms. From the optimized LIXs/Cu(II) geometries (Figures 5 and 6), Cu^{2+} as a center is surrounded by a square planar arrangement of four oxygen ligands in the LIX54/Cu(II) complex, whereas in the LIX84/Cu(II) complex it is surrounded by an orthorhombic arrangement of two oxygen ligands and two nitrogen ligands. This is confirmed by all the same distances between copper and four oxygen atoms in the LIX54/Cu(II) complex and different distances between Cu—O and Cu—N in the LIX84/Cu(II) complex. In addition, there are intramolecular hydrogen bonds between $O^1 \cdot H^2$ and $O^2 \cdot H^1$ with a bond length of 1.65 Å in the optimized LIX84/Cu(II) complex geometry, which evidently support the reaction mechanism proposed in Figure 2. The single point energy calculation using the B3LYP/6-31+g(d) shows that formation of the LIX84/Cu(II) complex is more favorable than that of the LIX54/Cu(II) complex, with a greater negative energy change in the complex formation process (Table 3). The computational results also show that LIX84 is a stronger extractant for copper than LIX54, which is in accordance with Kyuchoukov et al.[14] and our EPR results.

Effect of the feed pH on copper transmembrane flux with LIX54 or LIX84 as the carrier

Figure 7 shows LIX54 has a very low copper transport rate through SLM at pH values < 3. At pH values > 3 copper is transported fairly well through SLM and the rate increases gradually with increasing pH, reaching a plateau at pH ≈ 6. The results are qualitatively similar to the findings by Alguacil and Alonso,[16] who conducted detailed liquid–liquid copper extraction experiments at various pH values using LIX54. There is a slight decrease of flux in more alkaline solution (1.46×10^{-8} mol $cm^{-2} \cdot s^{-1}$ at pH 8.66 vs. 1.48×10^{-8} mol $cm^{-2} \cdot s^{-1}$ at pH 7), which arises from higher NH_3 content at higher feed pH solutions. This makes it more difficult for the extractant to compete with NH_3 for copper. The effect is especially strong at low copper concentrations when a significant excess of ammonia is present in the feed solution.[14]

We recently developed a "Big Carrousel" model to describe Cu(II)-facilitated transportation through a flat membrane by the carrier LIX54, where the carrier is assumed to move slightly out from the membrane into an aqueous reaction layer, then transfers from the aqueous reaction layer to another aqueous phase (the interface between the aqueous reaction layer and the aqueous stagnant layer) through the membrane, and finally moves back.[39] The flux expression derived by the "Big Carrousel" model is actually determined by the resistance in the aqueous stagnant (nonstirring) layer, the resistance in the aqueous reaction layer, the resistance in the membrane phase, and also the equilibrium distributions of copper–carrier complex and free carrier between the aqueous and organic phases. It is well known that the equilibrium

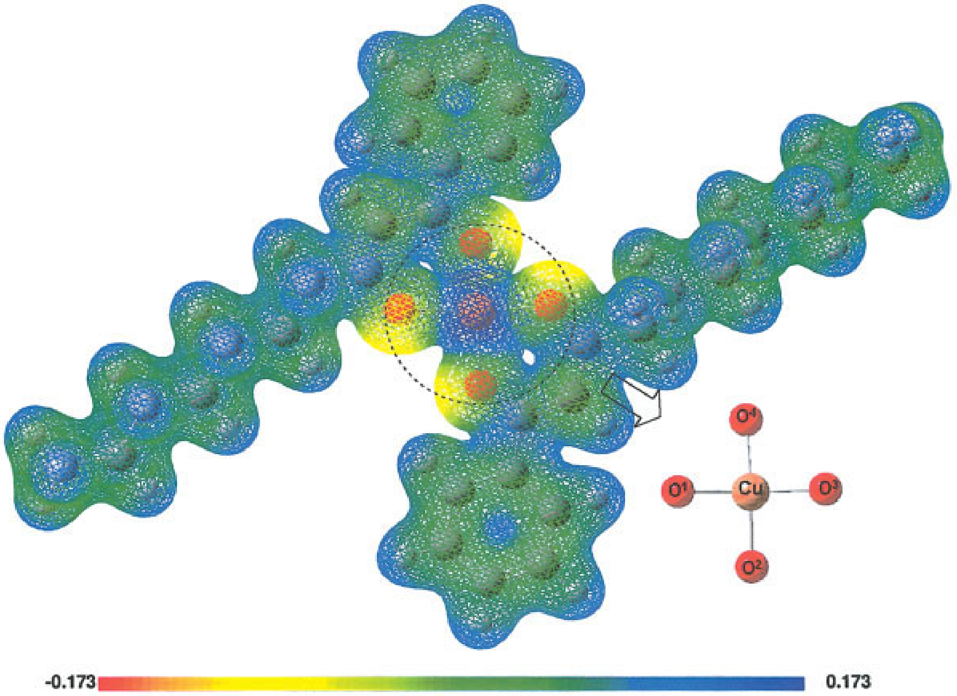

Figure 5. Molecular model of the optimized geometry of LIX54/Cu(II) complex with mapped electrostatic potential (ESP) using B3LYP/6-31g level of theory.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

distribution of copper between the aqueous and organic phases depends on pH of the feed solution.[2,14,27] This is also true for the carrier LIX54.[40]Furthermore, we found the thickness of the aqueous reaction layer is also changed with the feed pH. Taking account of these factors, we can give a satisfactory quantitative description of Cu(II) transmembrane flux dependency on feed pH

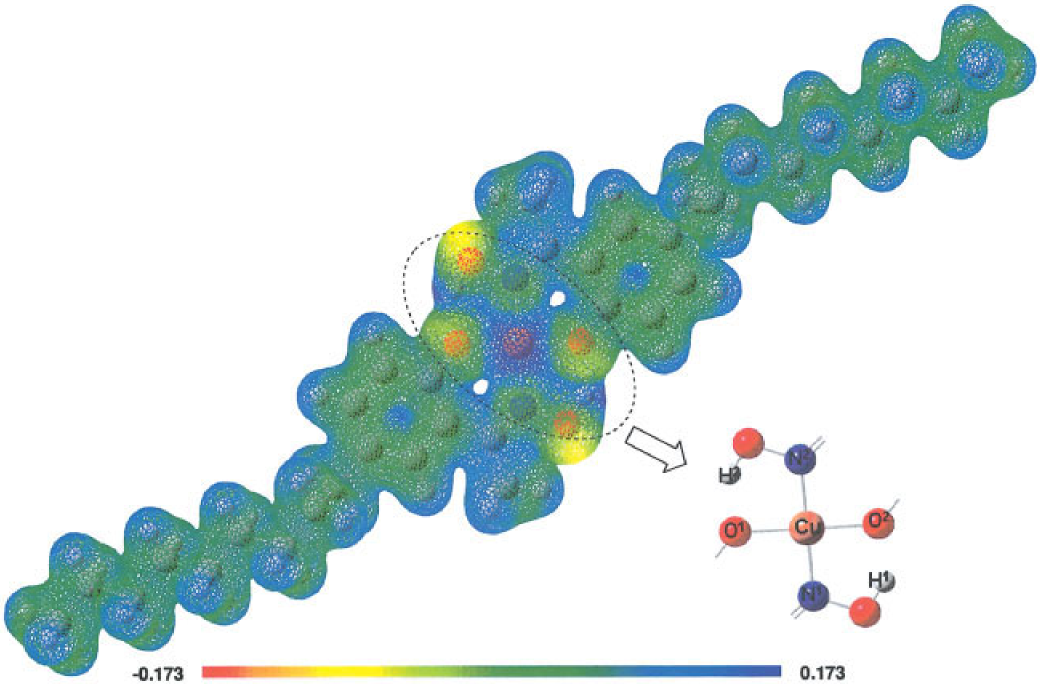

Figure 6. Molecular model of the optimized geometry of LIX84/Cu(II) complex with mapped electrostatic potential (ESP) using B3LYP/6-31g level of theory.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

Table 3. Quantum Chemical Computation Results of LIXs/Cu(II) Complexes

	LIX54/Cu(II) Complex				LIX84/Cu(II) Complex			
	Cu—O^1	Cu—O^2	Cu—O^3	Cu—O^4	Cu—O^1	Cu—O^2	Cu—N^1	Cu—N^2
Bond distance (Å)	1.91	1.91	1.91	1.91	1.89	1.89	1.95	1.95
ΔE (kJ/mol)	−99.33				−114.61			

as shown in Figure 7 using the "Big Carrousel" model, whereas the simple mechanism where the carrier stays in the membrane and two ion-exchange reactions take place on the water/membrane interfaces gives the constant flux at different feed pH.

In comparison, LIX84 can transfer copper fairly well through SLM even at pH values < 1. The maximum copper transmembrane fluxes are reached at pH ≈ 2 and then the fluxes are almost constant at pH values > 2. This is attributed to possible saturation of LIX84 by Cu at the feed/membrane interface, which was observed to be very rapid.[20] The high copper loading capacity in acidic copper solution provides LIX84 as a good candidate for copper recovery from acidic media. However, the compromise between higher copper loading and slower strip kinetics in ammoniacal copper solutions treatment makes copper transmembrane fluxes in an SLM system with LIX84 as the carrier slightly lower than that of LIX54: At pH ≈ 7, the flux of an SLM system with LIX54 as the carrier is 1.48×10^{-8} mol cm^{-2}·s^{-1} and is 1.35×10^{-8} mol cm^{-2}·s^{-1} for LIX84. The lower flux together with its significant ammonia carryover in extended periods of process time render LIX84 incompetent to treat ammoniacal copper solutions.

Effect of carrier LIX54 or LIX84 concentration on copper transmembrane flux

Figure 8 shows that an increase in the carrier concentration results in an increase in the copper transmembrane flux for both the LIX54 and LIX84 systems and flux reaches the maximum at a carrier concentration of roughly 33 vol/vol %. Further increase of the copper removal rate is hindered probably by the reduced copper–carrier diffusion coefficient in the membrane phase. A decreasing copper–carrier diffusion coefficient at higher carrier concentrations is attributed either to the increasing membrane phase viscosity[41-43] for both carriers or to the dimerization of the extractant LIX84 in more concentrated extractants.[34,42] In subsequent experiments, 33 vol/vol % carriers in kerosene were used as the organic membrane phase.

Selective separation of copper over other cations contaminants by once-through transport in hollow-fiber SLM using LIX54 or LIX84 as the carrier

Table 4 shows the comparative results of selective separation of Cu(II) over Zn(II), Ni(II), and Cd(II) with LIX54- and LIX84-impregnated hollow-fiber SLM. Obviously, LIX54 enjoys much higher selective separations of Cu(II) over Zn(II) and Cd(II) than LIX84. However, selective separation of Cu(II) over Ni(II) is almost the same for both LIX54 and LIX84. The same results are obtained in solvent extraction experiments: LIX54 can extract both Cu(II) and Ni(II) very well at pH $\approx$ 7.25, but it has low Zn(II) loading capacity[44,45]; LIX84 can coextract Cu(II) and Ni(II) from alkaline conditions[46] and it was further found at equilibrium pH $\approx$ 7.25, all Cu(II), Zn(II), and Ni(II) were well extracted by LIX84.[47] It is entirely practical in solvent extraction that the recovery and separation of specific cation from the mixtures after coextraction can be achieved by a selective stripping process.[46,48] Similarly to the solvent extraction method, the SLM-based membrane extraction technology performs extraction and back-extraction in one technological step. The coextraction of cations by carrier can be separated and purified in strip solutions with different strip concentrations or even in different strip solutions. Nevertheless, this operation makes SLM-based membrane extraction not economically and practically attractive because more membrane contactors are needed in the selective stripping process and also the operation becomes more complicated. The high selectivity of Cu(II) over Zn(II) and Cd(II) provides another significant advantage for LIX54 over other copper extractants such as LIX84 to treat copper-containing ammoniacal solutions using hollow-fiber SLM.

It is worth noting that the light blue ammoniacal waste

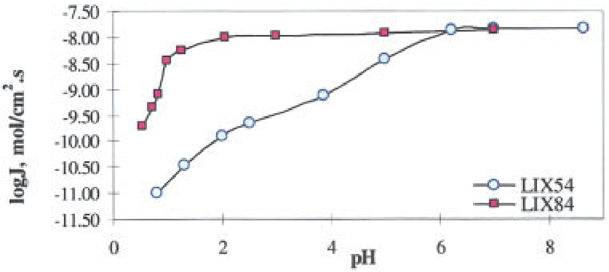

Figure 7. Cu(II) flux as a function of pH in the feed solution.

Feed: ammoniacal copper solutions with 0.021 M Cu(NH$_3$)$_4$$^{2+}$ at different pH; strip: 2M H$_2$SO$_4$; horizontal flat membrane with 33 vol/vol% LIX54 or LIX84 in kerosene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

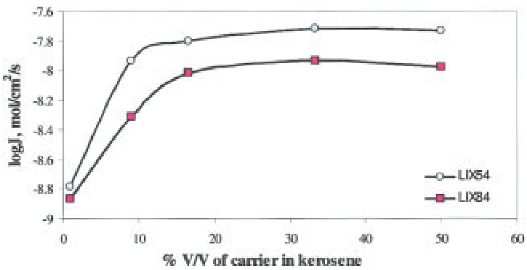

Figure 8. Cu(II) flux as a function of carrier concentrations in SLM.

Feed: 0.021 M Cu(II) solution at pH 7.25 for LIX54 and pH 3 for LIX84; strip: 2M H$_2$SO$_4$; horizontal flat membrane with different volume ratios of LIX54 or LIX84 in kerosene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

Table 4. Once-through Selective Separation of Copper over Other Cation Contaminants by Hollow-Fiber SLM Using LIX54 or LIX84 as the Carrier

	Flow Rate											
	55 mL/min			140 mL/min			210 mL/min			390 mL/min		
Separation factor	Cu/Zn	Cu/Ni	Cu/Cd	Cu/Zn	Cu/Ni	Cu/Cd	Cu/Zn	Cu/Ni	Cu/Cd	Cu/Zn	Cu/Ni	Cu/Cd
LIX54	17.05	3.77	103.26	21.25	1.65	35.16	11.73	0.73	11.51	11.19	0.37	5.53
LIX84	1.08	1.51	0.49	1.21	1.73	0.47	0.89	1.82	0.54	0.64	1.08	0.42

solution with 5.6 mM Cu(II) became colorless [outlet Cu(II) concentration measured was <5 ppm] when it was pumped through the LIX54- or LIX84-impregnated hollow-fiber SLM once through at low volumetric flow rate of 55 mL/min. This means the ammoniacal copper solutions after the hollow-fiber SLM single pass-through treatment can be reused as the rinse water or be discharged directly in compliance with environmental regulations. The ammoniacal wastewater treatment capacity of one Liqui-Cel® Extra-Flow 2.5 in. × 8 in. membrane contactor with 1.4 m^2 membrane area is around 3.5 L/h. In addition, Table 4 shows that selective separation of copper with LIX54 as the carrier will be somehow decreased with increasing flow rate, which may be a result of the decreasing "residence time" of cations contacted with this highly selective extractant of copper over other cation contaminants. However, the selective separation of copper over other cations using LIX84-impregnated hollow-fiber SLM did not change significantly at various flow rates. This is mostly attributed to the coextraction of copper with other cations at pH 7.25 of the ammoniacal solutions by LIX84.

Long-term stability of vertical flat membrane system to treat ammoniacal wastewater using LIX54 or LIX84 as the carrier

Although SLMs have been widely studied for the separation and concentration of a variety of compounds and present many potential advantages over other separation methods, there have been very few large-scale applications of SLMs because of insufficient membrane stability. Various mechanisms have been proposed for SLM instability: loss of the organic phase (carrier and/or solvent) from the membrane phase by dissolution, progressive wetting of the support pores, pressure difference or osmotic pressure gradient over the membrane,[49-52] and emulsion formation[52] or attrition of the organic film[53] arising from lateral shear forces. The time period of instability observed varies from a few hours to several months[54-56] depending on the system.

Different approaches were used to determine SLM (in)stability: measuring membrane liquid loss by weighing methods[51,57,58]; determining water content within the decayed SLM[59]; and measuring physicochemical properties of the organic phase (interfacial tensions, viscosities, contact angles, and water solubilities).[60] All the above-mentioned techniques are membrane-destructive methods, that is, the experiments have to be terminated and the membrane cannot be used again after analysis.

Membrane stability measurement using impedance spectroscopy, first proposed by Zha et al.,[61] is based on the idea that the effective area and thickness of an SLM would change as the membrane liquid is lost to the adjacent aqueous solutions and subsequently the empty parts of SLM would be occupied by the aqueous solutions. The sufficiently different dielectric and conductance properties of the individual substructural layers within the SLM would result in a significant difference in the capacitance and resistance of the decayed membrane (Figure 9B) from that of the original and intact SLM (Figure 9A). Therefore, based on measurements of the changes of the capacitance or the resistance of the SLM with time, it should be possible to characterize the process of the membrane liquid loss.

In this work for liquid membrane stability studies, noninvasive impedance spectroscopy technique and initial flux measurement over extended periods of time were used to compare SLM stabilities using LIX54 and LIX84 as the carrier. Figure 10 shows that the resistances of both LIX54- and LIX84-impregnated SLM in the first 2 days dropped considerably. For LIX54-impregnated SLM, the resistance decreased from 5 MΩ on the first day to 2 MΩ on the second day, whereas for LIX84, the resistance decreased from 1.88 to 0.78 MΩ. This resistance decrease is probably a result of the partial dissolution of membrane solvent kerosene into the adjacent aqueous phases. It can be confirmed by the same transmembrane flux on the first 2 days (Figure 11), which indicates the effective carrier in the membrane phase did not change to an appreciable degree. The resistances and capacitances of the LIX54-impregnated membrane then were kept almost the same for next 280 h, whereas for LIX84-impregnated membrane the period was about 230 h. After that the resistances of both membranes strongly de-

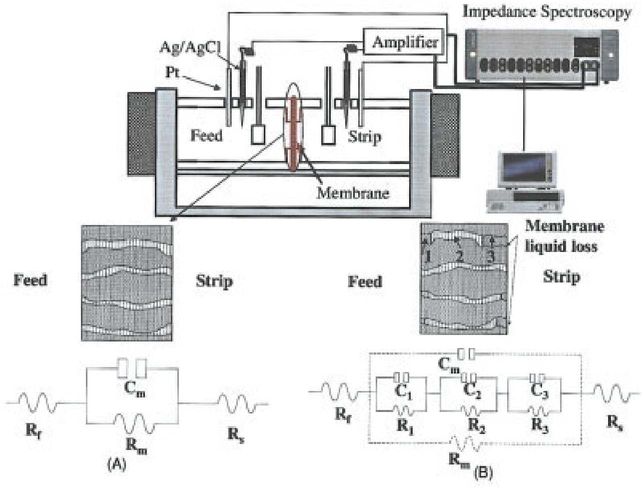

Figure 9. Descriptions and representative equivalent circuits of (A) intact SLM and (B) partially degraded SLM.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com] creased and the capacitances increased. The significant decrease of membrane resistances from several megaohms to several kilohms indicates that the liquid membranes are under degradation and micropores of the membrane support are gradually occupied by the adjacent aqueous solutions. Degraded SLM has the equivalent circuit as shown in Figure 9B, which is a combination of two aqueous layers in feed and strip sides in series with one organic membrane layer. As long as the effective surface area of the capacitance double plates during the experiment is constant, a change in the capacitance is probably a result of changes of SLM thickness as the membrane liquid is lost with time. The dielectric constant (or permittivity) of water is much greater than that of organic carrier and solvent, which results in the much larger membrane capacitance of the degraded membrane than that of the original or intact one. This conclusion is based on the following equation:

$$\frac{1}{C'_m}=\frac{1}{C_1}+\frac{1}{C_2}+\frac{1}{C_3}=\frac{\delta_1}{\varepsilon_0 A\varepsilon_1}+\frac{\delta_2}{\varepsilon_0 A\varepsilon_2}+\frac{\delta_3}{\varepsilon_0 A\varepsilon_3}$$

$$=\frac{1}{\varepsilon_0 A}\left(\frac{\delta_1}{\varepsilon_1}+\frac{\delta_2}{\varepsilon_2}+\frac{\delta_3}{\varepsilon_3}\right)<\frac{1}{\varepsilon_0 A}\frac{\delta_m}{\varepsilon_m}=\frac{1}{C_{m0}} \qquad (5)$$

where C is the capacitance; δ is the thickness; A is the surface area of capacitance double plates; ε_0 is the permittivity of vacuum space; ε is the dielectric constant (or permittivity); subscripts m' and m represent the degraded SLM and the intact or original one, respectively; and subscripts 1, 2, and 3 represent the feed aqueous solution into the microporous support, remaining liquid membrane, and strip aqueous solution into the microporous support, respectively. The effective membrane capacitance of the degraded SLM is just the combination of these three capacitances in series.

The initial flux measurement over extended periods of time (Figure 11) also shows a similar time dependency of membrane stabilities as that of the impedance spectroscopy technique. SLM with LIX54 as carrier has a slightly higher transmembrane flux than that of LIX84, which is consistent with the previous results. Furthermore, LIX54-impregnated SLM also has a slightly higher stability than that of LIX84. After 15 days of treatment, the copper transmembrane flux through LIX54-impregnated SLM decreases by 28.9%, from 1.24×10^{-9} to 8.82×10^{-10} mol cm^{-2}·s^{-1}, whereas for LIX84-impregnated SLM, its transmembrane flux is decreased by half from 1.07×10^{-9} to 5.28×10^{-10} mol cm^{-2}·s^{-1} after 13 days of treatment. For LIX84, its active substance losses during metal extraction from ammoniacal solutions likely occurred as the result of enhanced hydrophilicity of the carrier arising from its phenolic group dissociation.[34] Nevertheless, the carrier is not fully leaking from membrane support and one can still observe active/facilitated transport. The control experiment with only kerosene-impregnated membrane shows no copper transport at all over a long time span. Stability of supported liquid membrane in ammoniacal copper solutions treatment is promising for practical industrial applications.

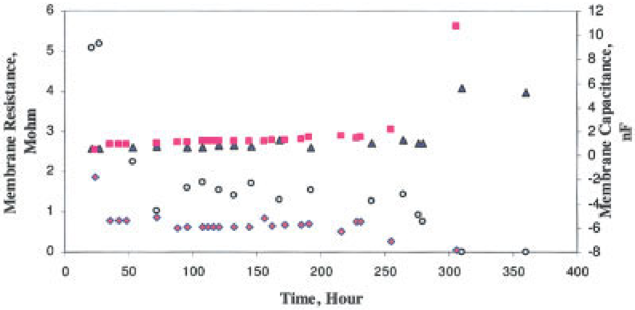

Figure 10. Electrical capacitance and resistance changes of the vertical flat membranes impregnated by 33 vol/vol % LIX54 or LIX84 with time.

Circle-resistance of membrane impregnated with LIX54; triangle-capacitance of membrane impregnated with LIX54; diamond-resistance of membrane impregnated with LIX84; square-capacitance of membrane impregnated with LIX84. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

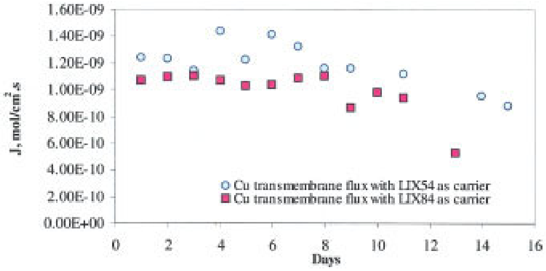

Figure 11. Initial copper transmembrane flux measurement of SLMs immobilized with LIX54 or LIX84 over extended periods of time.

Feed: 37 mL ammoniacal solutions with 2.5 mM $Cu(NH_3)_4^{2+}$; strip: 42 mL 2M H_2SO_4; vertical flat membrane impregnated with 33 vol/vol% LIX54 or LIX84 in kerosene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Conclusions

In this work, two well-established copper extractants—LIX54 and LIX84, commonly used in solvent extraction process—were chosen as the carrier candidates in supported liquid membrane system to remove copper from ammoniacal wastewater. Comparative studies in the membrane flux, selectivity, and stability by these two carriers were carried out. The geometries of LIXs/Cu(II) complexes and the energy changes in the formation processes of these complexes were studied for the first time by use of sophisticated quantum chemical computations to confirm the experimental results. The following conclusions can be drawn:

(1) Experimental characterization results, based on LIX54/Cu(II) and LIX84/Cu(II) complex geometries and reaction mechanisms, are in accordance with the quantum chemical computations results. The EPR results together with the computational results show that LIX84 is a stronger extractant than LIX54 for Cu(II). However, the compromise between higher copper loading and slower strip kinetics in treatment of ammoniacal copper solutions makes copper transmembrane fluxes in an SLM system with LIX84 as the carrier slightly lower than those of LIX54.

(2) The high selectivity of copper over other cation contaminants and low or no ammonia carryover provide significant

advantages for LIX54 as a better candidate over LIX84 for SLM-based treatment of ammoniacal copper solutions. As a modern strong extractant, LIX84 can be used for copper recovery from acidic solutions.

(3) The hydrophilic nonylphenol group makes LIX84-impregnated SLM stability slightly shorter than that of the LIX54-impregnated one. However, the stability of both LIX54- and LIX84-impregnated SLM in the treatment process of ammoniacal copper solutions is promising for practical industrial applications.

Acknowledgments

Financial supports from Agency for Science, Technology and Research, Singapore (Grant No. R-279-000-164-305) and National University of Singapore (Grant No. R-279-000-184-112, R-279-000-198-122/133) are gratefully acknowledged. The authors thank Dr. Y. Y. Kostetski for help with EPR measurements. Cognis Corporation (Tucson, AZ) kindly supplied the LIX54 and LIX84, which is also greatly appreciated.

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Manuscript received Mar. 31, 2006, and revision received Jun. 13, 2006.