

Solvent extraction of Cu(II) by LIX 54-100 and its application to a solid supported liquid membrane system[†]

Juan Carlos Bermejo^a, Manuel Alonso^a, Ana María Sastre^b and Francisco José Alguacil^{a*}

^aCentro Nacional de Investigaciones Metalúrgicas (CSIC), Avda. Gregorio del Amo 8, Ciudad Universitaria, 28040 Madrid, Spain

^bDepartament d'Enginyeria Química, E.T.S.E.I.B., UPC, Diagonal 647, 08028 Barcelona, Spain

The extraction of Cu(II) by LIX 54-100 (β -diketone) in Iberfluid (kerosene type diluent) from ammoniacal/ammonium sulphate solutions has been investigated. The analysis of metal distribution data suggested the formation of CuR_2 species in the organic phase with formation constant $\log K_{\text{ext}} = -6.15$. The results obtained on Cu(II) distribution have been implemented in a solid supported liquid membrane system, using H_2SO_4 solutions (e.g. 0.9 mol/l) to strip the metal from the organic solution.

Introduction

Extraction of copper from aqueous solutions into an organic phase has been widely used for both the separation and concentration of the metal. Although β -diketones cannot compete with oximes for the extraction of copper from acidic media, they do have advantages for the extraction from ammoniacal solutions because, unlike oximes, they do not transfer ammonia.¹

One of these β -diketones, LIX 54, produced by Henkel Corp. is used in several installations to recover copper from ammoniacal solutions obtained from printed circuit board manufacture.^{2,3} LIX 54 was used to recover copper in a number of industrial processes.^{4,5} In addition, it has also been used in the extraction of zinc and nickel.^{6,7}

These extraction systems can also be implemented in solid supported liquid membranes (SLMs) where the performance of the separation operation is enhanced by combination of the extraction and stripping process in one step.⁸ The application of this technology in the treatment of copper-bearing solutions had been described in the literature.^{9–12} However, to the best of our knowledge, there is no information available on the applications of LIX 54-100 to Cu(II) extraction and of LIX 54-100-Cu(II) extraction system to membrane transport of the metal from ammoniacal solutions.

The present investigation was undertaken to characterise quantitatively the extraction reactions between aqueous Cu(II) and the new LIX 54-100 extractant in Iberfluid. Furthermore, a liquid membrane system has been designed using the extraction process mentioned above, and parameters affecting the liquid membrane have been studied.

Experimental

The characteristics and composition of the commercially available β -diketone LIX 54-100 (Henkel Corp.) have been described elsewhere.¹³ Concentrations were measured by the copper ultimate loading.¹⁴ The desired extractant concentration was prepared by diluting the as-received extractant with the as-received corresponding diluent: Iberfluid (mainly aliphatic), Varsol 30 (22% aromatics) or Solvesso 100 (mainly aromatic). Iberfluid is a product of CS, Spain, Varsol 30 and Solvesso 100 are from ExxonMobil Chem. Iberia, Spain. Stock solutions of copper were prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (AR grade) in distilled water. All other chemicals were also of AR grade. Extraction experiments were carried out in thermostatically controlled separatory funnels by shaking (700/min) together equal volumes of the corresponding aqueous and organic phases at 20°C and for the time required. The concentration of copper in the aqueous solution was measured by AAS using a Perkin Elmer 1100B spectrophotometer. The concentration of the metal in the organic solution was calculated

from the mass balance. From these data, the distribution coefficient D_{Cu} was calculated as the ratio

$$D_{\text{Cu}} = \frac{[\text{Cu}]_{\text{org}}}{[\text{Cu}]_{\text{aq}}} \quad (1)$$

where $[\text{Cu}]_{\text{org}}$ and $[\text{Cu}]_{\text{aq}}$ are the total copper concentration in the organic and aqueous phases, respectively. Permeation experiments were carried out with a two compartment permeation cell which consisted of a source phase (200 ml) separated from a receiving phase chamber (200 ml) by a liquid membrane having an effective membrane area of 11.33 cm². The support for the liquid membrane was a polyvinylidenedifluoride film (Millipore Durapore GVHP) with a thickness of 125 μm , porosity 75% and average pore size 0.22 μm . The liquid membrane was prepared by impregnating the laminar microporous film with the corresponding LIX 54-100 solution for 24 hours, then leaving it to drip for a few seconds before being placed in the permeation cell. In each experiment, stirring rate in both the source and receiving solution was kept constant at 1500/min. Membrane permeabilities were determined by monitoring Cu(II) concentrations by AAS, using the same apparatus as described above, in the source phase as a function of time. Permeability coefficient, P_{Cu} , was calculated as

$$P_{\text{Cu}} = \frac{-d[\text{Cu(II)}]}{dt} \frac{V}{A} \frac{1}{[\text{Cu(II)}]} \quad (2)$$

where $[\text{Cu(II)}]$ is the metal concentration in the source phase at time t , A is the effective membrane area and V is the volume of source solution. Integration of equation (2) gives

$$\ln \frac{[\text{Cu(II)}]_t}{[\text{Cu(II)}]_0} = -\frac{A}{V} P_{\text{Cu}} t \quad (3)$$

Thus, permeability values were obtained from the slope of $\ln [\text{Cu(II)}]_t / [\text{Cu(II)}]_0$ versus time plots.

Results and discussion

Extraction: Preliminary experiments were carried out in order to determine the time needed to achieve equilibrium. From the results plotted in Fig. 1, at 2 g/l Cu(II), ammonium sulphate 0.15 mol/l, $\text{pH}_{\text{eq}} 8.5 \pm 0.02$ and LIX 54-100 10% v/v in the organic solution, equilibrium is observed to be reached after 1 minute of mixing. Nevertheless, the contact time was fixed at 5 min. The extraction of copper (0.25 g/l) at $\text{pH}_{\text{eq}} 8.5 \pm 0.02$ by 1% v/v LIX 54-100 in Iberfluid was studied over the range 10–50°C. Under these conditions, increasing temperature gave an increase in copper extraction, and a plot of $\log D_{\text{Cu}}$ versus $1/T$ was linear ($\log D_{\text{Cu}} = 2.65 - 360/T$ with $r^2 = 0.980$), thus, indicating that only a single species is involved in metal extraction.¹⁵ From this plot, the value of ΔH° was calculated as 6.9 kJ/mol.

* To receive any correspondence. E-mail: fjalgu@cenim.csic.es

[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

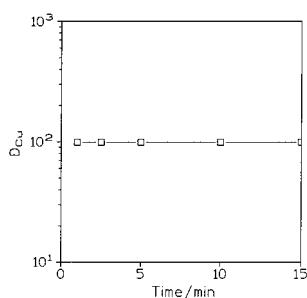


Fig. 1 Copper distribution coefficient as a function of equilibration time in the extraction of copper from ammoniacal/ammonium sulphate solutions by LIX 54–100 in Iberfluid.

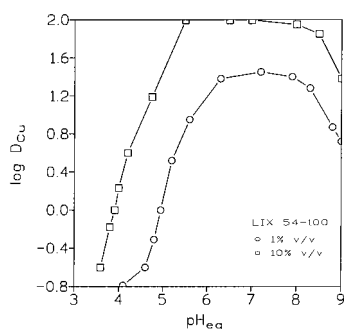


Fig. 2 Extraction of copper by LIX 54–100 in Iberfluid from 0.15 mol/l aqueous ammonium sulphate medium at different pH values. Aqueous solutions: 0.5 g/l Cu (LIX 54–100 1% v/v), 1 g/l Cu (LIX 54–100 10% v/v).

The variation of pH from 3 to 8.5 for the aqueous medium containing 0.5–1 g/l copper showed a gradual increase in the extraction of the metal for both 1% and 10% v/v LIX 54–100 in Iberfluid, but the extraction tended to decrease at higher pH values (Fig.2), this behaviour being shown in a number of solvent extraction systems.^{6,7,16}

The metal distribution ratio, D_{Cu} , at ammonium sulphate concentration of 0.15 mol/l and pH_{eq} 8.5 ± 0.02 , was determined for various LIX 54–100 concentrations (1–10% v/v) in Iberfluid at different Cu(II) concentrations (0.01–0.1 g/l). The results show that D_{Cu} does not depend on the copper concentration, this behaviour indicates that no polynuclear complexes are formed in the organic phase. The extraction reaction can be expressed as:



where HR represents the active form of the extractant and org and aq the organic and aqueous phases, respectively. For equation (4), the equilibrium constant can be expressed by:

$$K_{ext} = \frac{[CuR_{2,org}][H_{aq}^{+}]^2}{[HR]_{org}^2[Cu_{aq}^{2+}]} \frac{\gamma_{CuR_2} \gamma_{H^+}^2}{\gamma_{HR}^2 \gamma_{Cu^{2+}}} \quad (5)$$

If the activity coefficients of both the aqueous and organic phases are considered as constant and equal to the unity and taking into account the definition of D_{Cu} , the following expression is obtained:

$$\log D_{Cu} = \log K_{ext} + 2pH + 2 \log [HR]_{org} \quad (6)$$

Thus, a plot of $\log D_{Cu}$ against $\log [HR]_{org}$ should give a straight line with an intercept equal to $(\log K_{ext} + 2pH)$ and a slope of 2. Since copper concentration is very low, the concentration of

LIX 54–100 bound in the complexes can be neglected compared to total initial extractant concentration. As expected from equation (6), a straight line of slope near 2 is obtained when $\log D_{Cu}$ is plotted against $\log [LIX\ 54-100]_{TOT}$ ($\log D_{Cu} = 4.98 + 2.0 \log [LIX\ 54-100]_{TOT}$, $r^2 = 0.998$). Therefore, the experimental data could be explained assuming the extraction of the species CuR_2 . To determine the compositions of the extracted species and their extraction equilibrium constants, extraction data were also numerically treated by using the LETAGROP-DISTR program,¹⁷ which is based on the minimisation of the error-square sum

$$U = \sum (\log D_{cal} - \log D_{exp})^2 \quad (7)$$

where D_{exp} is the experimental value of the distribution coefficient and D_{cal} is the value calculated by the program solving the mass balance equation for copper(II) and the extractant, assuming a particular set of species and constants. The program fits the existence of the CuR_2 species in the organic phase and the value of $\log K_{ext}$ was calculated to be -6.15 [$\sigma(\log K_{ext}) = 0.05$] with $U = 0.62$ ($\sigma = 0.185$).

For the present extraction system the values of ΔG° and ΔS° were calculated as 34.3 kJ/mol and -93 kJ/mol/K, respectively. The positive value of ΔG° reflects the relatively high pH value necessary to allow copper extraction to proceed, whereas the negative entropy change indicates that copper is being transferred from a highly disordered state to one of a greater order.⁷

Membrane transport: The extraction system of copper(II)-LIX 54–100 has been implemented in a supported liquid membrane, where the transport of copper species across the liquid membrane depends not only on the equilibrium distribution ratios but also on the kinetics of the extraction and stripping processes. However, previous tests had shown that in the present system copper is easily strippable from loaded organic solutions using 0.9 mol sulphuric acid, thus, this variable was not investigated in the present study.

The transport of Cu(II) through the liquid membrane has been studied by varying the chemical conditions of the two phases, namely the aqueous source solution and the membrane phase. The influence of the membrane composition was first studied, Figure 3 shows permeability values for the transport of copper through a SLM impregnated with solution 1–20% v/v LIX 54–100 in Iberfluid. As expected, the permeability value increases with LIX 54–100 concentration, this may be due to an increase in extractability into the liquid membrane. However, P is independent of carrier concentration for extractant concentration above 1.7×10^{-1} M, this is attributable to an aqueous diffusion film controlled permeation process such that:

$$P = D_a / d_a \quad (8)$$

where D_a is the aqueous diffusion coefficient of the metal and d_a is the thickness of the aqueous diffusion film. Assuming a typical value of 1×10^{-5} cm²/s for D_a and P equal to 7.2×10^{-3} cm/s, the value of d_a is 1.4×10^{-3} cm. This value is the minimum thickness of the stagnant aqueous diffusion layer in the present experimental conditions.

The effect of carrier diluent on the permeability of copper(II) was also studied. The membrane diluent chosen as a water-resistant barrier in any liquid membrane process exerts a major influence on membrane performance. It was concluded that the polarity of the diluent is the most decisive factor in determining effectiveness as a membrane medium; on the other hand, the membrane stability versus rapid transport is the major choice to be made in choosing a membrane diluent.¹⁸ The diluent employed as a membrane should retain the carrier to the maximum extent and yet at the same time retain a relatively high

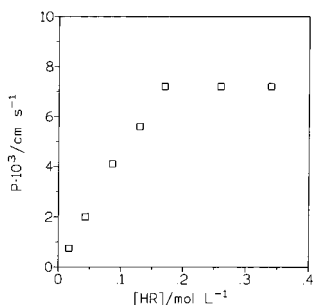


Fig. 3 Copper permeability vs. carrier concentration. Source phase: 0.025 g/l Cu(II) in 0.15 mol/l ammonium sulphate (pH 8.5±0.01). Receiving phase: 0.9 mol/l sulphuric acid.

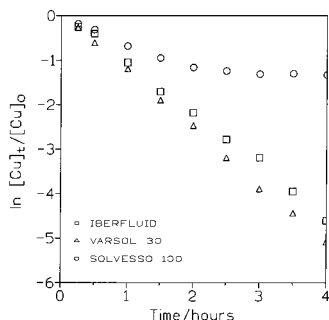


Fig. 4 Effect of various diluents on permeability of copper. Source phase: 0.05 g/l Cu(II) in 0.15 mol/l ammonium sulphate at pH 8.5±0.01. Receiving phase: 0.9 mol/l sulphuric acid. Extractant concentration: 10% v/v LIX 54-100.

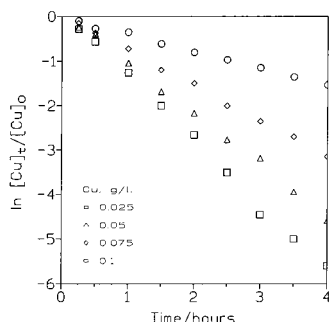


Fig. 5 Influence of metal concentration on copper transport. Source phase: 0.15 mol/l ammonium sulphate at pH 8.5±0.01. Receiving phase: 0.9 mol/l sulphuric acid.

concentration of water to aid in the transfer of hydrated species without loss of carrier to the aqueous solution. SLM performance is primarily dependent on intrinsic membrane diluent properties such as viscosity, volatility, surface tension, etc. In the present study, the copper permeation decreases as a fully aromatic diluent is used to dissolve LIX 54–100 reagent. The obtained permeation coefficient of Cu(II) in Iberfluid, Varsol 30 and Solvesso 100 is 5.6×10^{-3} , 6.3×10^{-3} and 2.8×10^{-3} cm s⁻¹, respectively. Excellent copper(II) permeation was achieved using both Iberfluid and Varsol 30 as diluents for LIX 54–100. The transport behaviour of copper using various diluents is presented in Fig. 4.

Table 1 Influence of pH on copper permeabilities values

pH	P (cm/s)
8.5	5.65×10^{-3}
9.5	4.16×10^{-3}
10.5	2.10×10^{-3}

The influence of the initial Cu(II) concentration in the source side on transport across the SLM containing 10% v/v LIX 54–100 in Iberfluid is shown in Fig. 5. It can be seen that copper transport through the SLM is increased as the initial copper concentration decreases.

The single ion transport through the SLM of 0.05 g/l Cu(II) from an aqueous source phase adjusted to varying pH (8.5 to 10.5) was studied using 0.9 mol/l sulphuric acid as receiving phase. Table 1 shows that as the pH value of the source phase increases, the permeability of copper decreases.

Conclusions

The results of the present study indicate that the extraction of copper from ammoniacal/ammonium sulphate medium by LIX 54–100, dissolved in Iberfluid, expressed in terms of the copper distribution coefficient, increases with the increase in extractant concentration. Slope analysis of the effect of LIX 54–100 concentration on D_{Cu} gave a slope of near two, indicating that the extracted species contains two molecules of the extractant. Numerical treatment of the experimental data agrees with the stoichiometric formula CuR_2 (R represents the extractant) for the extracted species, the value of $\log K_{ext}$ being of -6.15 . In carrier-facilitated membrane transport of Cu(II) across a supported liquid membrane using LIX 54-100 as carrier, the permeability of copper(II) increases with the increase of LIX 54–100 concentration and the decrease of the initial copper concentration in the source phase. Copper transport also depends upon the pH value of the source phase and the change of the diluent of the organic solution.

We thank the CICYT (Spain) for Project MAT98-1345-CE.

Received 16 May 2000; accepted 29 September 2000
Paper 00/315/320

References

- M. Cox, in: *Principles and Practices of Solvent Extraction*, J. Rydberg, C. Musikas and G. R. Choppin (eds), Marcel Dekker, NY, 1992.
- S.O.S. Andersson and H. Reinhardt, H., in: *Handbook of Solvent Extraction*, T.C. Lo, M.H.I. Baird and C. Hanson (eds), Jh Wiley & Sons, NY, 1983.
- J. Szymanowski, *Hydroxyoximes and Copper Hydrometallurgy*, CRC Press, Boca Raton, FL, 1993.
- W. Hopkin, W.H. Hunter, K. Nakade, A. Asano and Kobasyashi, S., in: *Hydrometallurgy: Research, Development and Plant Practice*, K. Osseo-Asare and J.D. Miller (eds), The Metallurgical Society of AIME, Warrendale, PA, 1983.
- W.P.C. Duyvestein and B.J. Sabacki, in: *The Paul E. Queneau International Symposium. Extractive Metallurgy of Copper, Nickel and Cobalt*. Volume I: *Fundamental Aspects*, R.G. Reddy and R.N. Weizenbach (eds), TMMMS, Warrendale, PA, 1993.
- F.J. Alguacil and A. Cobo, *J. Chem. Technol. Biotechnol.*, 1998, **71**, 162.
- F.J. Alguacil and A. Cobo, *Hydrometallurgy*, 1998, **48**, 291.
- A.M. Sastre, A. Kumar, J.P. Shukla and R.K. Singh, *Separat. Purificat. Meth.*, 1998, **27**, 213.
- T.-C. Huang and R.-S. Juang, *J. Chem. Technol. Biotechnol.*, 1988, **42**, 3.
- L. Boyadzhiev and S. Alexandrova, *Hydrometallurgy*, 1994, **35**, 109.
- M. Szpakowska, *J. Membr. Sci.*, 1996, **109**, 77.
- F.Z. El Aamrani, A. Kumar and A.M. Sastre, *New J. Chem.*, 1999, **23**, 517.
- E. Dziwinski and J. Szymanowski, *Solvent Extr. Ion Exch.*, 1996, **14**, 219.
- M. Amores, A.G. Coedo and F.J. Alguacil, *Hydrometallurgy*, 1997, **47**, 99.
- L.E. Orgel and R.S. Mulliken, *J. Am. Chem. Soc.*, 1957, **29**, 4839.
- N.M. Rice, M. Nedved and G.M. Ritcey, *Hydrometallurgy*, 1978, **3**, 35.
- D.H. Liem, *Acta Chem. Scand.*, 1971, **25**, 1521.
- F.Z. El Aamrani, A. Kumar, L. Beyer, J.L. Cortina and A.M. Sastre, *Hydrometallurgy*, 1998, **50**, 315.