Journal of Physical Science, Vol. 24(2), 63–81, 2013

Transfer and Separation of Zn(II)/Co(II) by Supported Liquid Membrane Containing CYANEX 925 in Kerosene as Carrier

Mona S. Gasser, Naglaa E. El-Hefny*, Soad E. Rizk and Jacqueline A. Daoud

Hot Laboratories Centre, Atomic Energy Authority, 13759, Cairo, Egypt

*Corresponding author: neelhefny@hotmail.com

Abstract: *Transfer of Zn(II) ions from a mixed sulphate and thiocyanate solution through a supported liquid membrane (SLM) containing CYANEX 925 in kerosene as carrier has been studied as a function of stirring rate, $[H^+]$, [CYANEX 925], $[SCN^-]$, $[H_2SO_4]$ and ammonia solution concentrations. The experimental results show that the transfer of Zn(II) ions increases with the increase in stirring rate, thiocyanate concentration in the feed and concentration of NH_4OH used as the stripping solution. The transfer experiments of Zn(II) from its admixture with Co(II) indicated that Zn(II) could be extracted more than Co(II) by CYANEX 925; the transfer rate increased with time. The investigated SLM system could be used for removal of Zn(II) from an aqueous mixed thiocyanate/sulphate medium of $[H^+] = 0.01$. In addition, the present system is selective for Zn-Co separation from aqueous mixed thiocyanate/sulphate medium. This selectivity was found to decrease with time and a maximum value of 25 is reached after 60 min. Repeated transfer of Zn(II) individually and from its admixture with Co(II) through the same membrane film with reasonable efficiency indicate that the used SLM is stable and durable.*

Keywords: Separation of Zn (II), supported liquid membrane, separation of Co(II), sulphate/thiocyanate medium, hydrometallurgical processing

1. INTRODUCTION

Liquid membrane is one of the most important separation processes which is explored for the hydrometallurgical processing of heavy metals, rare earths, purification of wet process phosphoric acid, nitric acid recovery, etc. In the purification-separation of these metal ions, liquid membranes play a vital role. Liquid membranes first invented by Li[1] remove the equilibrium limitations of solvent extraction by combining extraction and stripping in a single operation. In the past years, the use of liquid membranes has gained a general interest in the treatment of effluents where solute concentrations are low and large volumes of solutions could be processed.[2,3] There are two basic forms of liquid membrane processes: emulsion liquid membranes (ELMs) and supported liquid membranes (SLMs).

Zinc, which is one of the elements studied in this work, is used in galvanising iron in making alloys and metallic coating to improve corrosion resistance of various types of steel. It is also used in rubber industry, ceramics and pharmaceuticals. The transport through liquid membranes has been experimentally successful in the hydrometallurgical field for the recovery and separation of Zn(II) ions in wastewater.[4–12] Significant advances in zinc recovery by liquid membranes has gained a general interest in plant scale by Draxler and Marr in the application of ELMs,[13] but disadvantages have been discovered in the processes of operations with liquid membranes. One disadvantage of ELMs is that the emulsion swells upon prolonged contact with the feed stream, causing a reduction of the stripping reagent concentration in the aqueous droplets, which reduces stripping efficiency. A second disadvantage is membrane rupture, resulting in leakage of the contents of the aqueous droplets into the feed stream and a concomitant reduction of separation efficiency. In the case of SLMs, among its advantages are high selectivity of the process, modest capital and operating costs, low energy consumption, and the possibility of using expensive extractants.

Organophosphorus extractants are a good choice for metal extraction due to their solvation properties related to the basic properties of the oxygen atom, as well as their chemical stability and low solubility in water. These extractants have been widely used for the separation and recovery of Zn(II) from HCl medium.[14,15] Regel et al.[16] used CYANEX 921, a mixture of 4 trialkylphosphine oxide (CYANEX 923), bis(2,4,4-trimethyl pentyl) monothio phosphinic acid (CYANEX 302), Alamine 336, tri-n-octyl phosphine oxide (TOPO) and tri-n-butyl phosphate (TBP) for the recovery of zinc and concluded that TBP is relatively the best extractant for the recovery process. Liquid–liquid extraction of Co(II) and Zn(II) from NH_4SCN/H_2SO_4 media by methylisobutyl ketone (MIBK) has been studied systematically.[17]

The influence of sulphuric acid concentration on the percentage of extraction of Co(II) and Zn(II) has been discussed and the separation of Zn(II) from Co(II) was found to be possible when [NH_4SCN] is 0.5 mol and [H_2SO_4] is about 2 mol l^{-1}; under these conditions the separation factor ($S_{Zn/Co}$) is around 580. The extraction of Zn(II), Fe(II), Fe(III) and Cd(II) with tributylphosphate (TBP) and commercial trioctylphosphine oxide (CYANEX 921) in kerosene from chloride medium has been studied.[18] Based on the obtained results, undiluted TBP was selected as a suitable extractant for the recovery of zinc from pickling solution resulting from hot dipping galvanising bath.

As sulphate is a common aqueous medium in many industrial applications, the extraction of zinc from sulfuric media has experienced a renewed interest because of the use of this process on a commercial scale for treating wastewater streams and secondary materials.[19] On the other hand, the presence of the thiocyanate ion in the aqueous medium can increase the extraction of metal ions from other media. In this context, the present work is directed to study the transfer of Zn(II) and Co(II) from mixed sulphate and thiocyanate solutions through a supported liquid membrane (SLM) impregnated with CYANEX 925 in kerosene.

The effects of the different parameters affecting the transfer rate and permeability coefficient of the used SLM for Zn(II) and Co(II) were separately investigated. Therefore, the individual transfer of Zn(II) was studied as a function of stirring rate, $[H^+]$, [CYANEX 925], $[SCN^-]$, $[H_2SO_4]$ and ammonia solution concentrations. In addition, the transfer of Zn (II) from its admixture with Co (II) was investigated. The results are elaborated to assess the optimum conditions for maximum recovery of Zn(II) and Co(II) from aqueous sulphate solutions using SLM. The selectivity and durability of the used membrane for Zn(II)/Co(II) separation is also discussed.

2. EXPERIMENTAL

2.1 Chemicals and Reagents

Most of the chemicals, materials and reagents used in this work are of analytical reagent (AR) grade. Double distilled water is used for preparation of all aqueous solutions and final washing of glassware. The commercial extractant CYANEX 925 (a mixture of branched chain alkylated phosphine oxides), was kindly offered by Cytec Inc. and used as received. Odourless kerosene was supplied from Misr Petroleum Company, Egypt.

2.2 Procedure

2.2.1 Preparation of solutions

The aqueous phase of 0.005 M Zn(II) and 0.005 M Co(II) stock solutions were prepared by dissolving a known weight of zinc sulphate and cobalt sulphate in a mixed solution of 0.1 M NH_4SCN and 0.1 M H_2SO_4. All the extraction and stripping experiments were carried out at ambient temperature 25 ± 1°C.

2.2.2 Determination of Zn(II) and Co(II)

Based on the formed soluble complex between Xylenol Orange and Zn(II) at pH 6,[20] the concentration of Zn(II) in the aqueous thiocyanate solution was spectrophotometrically[21] determined by measuring its maximum absorbance at 570 nm using a Shimadzu double beam recording spectrophotometer model 160 A.

The concentration of cobalt in aqueous solution was spectrophotometrically determined based on the colour of the water soluble complex formed between PAR and cobalt (II) at pH 8.2.[22] The spectrum of Co(II) shows the maximum absorption peak at 510 nm.

2.2.3 Mass transfer investigations through SLM cell

In the mass transfer reactions through the SLM, the support membrane film (cellulose nitrate or mixed cellulose ester, MFS, USA) was soaked in the CYANEX 925/kerosene solution for 24 h, washed with distilled water to remove excess extractant then dried between two filter papers. The membrane was fixed between the two half-cells (Figure 1). One compartment was filled with the feed solution and the other with the strip solution (70 ml each). The two solutions were independently stirred with mechanical stirrers and in all experiments both feed and stripping solutions were stirred at the same speed. The experiments were performed at 25 ± 1°C. The experiment began by starting the stirring motors in the two compartments of the cell. Equal aliquots were withdrawn from the two compartments at different time intervals, and the concentration of the metal in these aliquots was analysed as mentioned before.

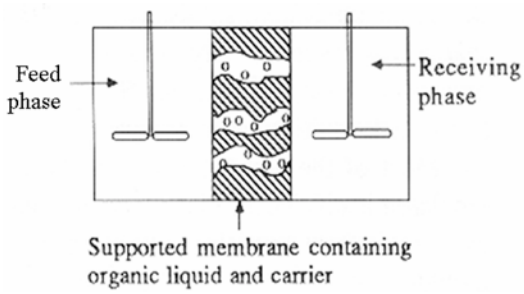

Figure 1: Thin sheet supported liquid membrane.

3. RESULTS AND DISCUSSION

According to the previous results obtained from the liquid-liquid extraction of Zn(II) and Co(II) from aqueous medium,[23] the optimum conditions for Zn(II) extraction and stripping were used for the transfer of both Zn(II) and Co(II) through the flat sheet supported liquid membrane presented in this work.

In this respect, two sets of kinetic experiments through the cell were carried out. In the first set of experiments the effects of stirring rate, $[H^+]$, [CYANEX 925], $[SCN^-]$, $[H_2SO_4]$, and ammonia solution concentrations on the individual transfer of Zn through the SLM were separately studied. In the second set of experiments the optimum conditions derived from the individual transfer experiments of Zn were used to study its transfer from its admixture with Co(II).

The apparent rate constant (k) of metal ion transfer was obtained from the slope of ln C/C_o vs. t plot according to the relation:

$$\ln C / C_o = -kt$$

or

$$\log C / C_o = -kt.\,2.303 \quad (1)$$

where C_o is the initial concentration of metal ion in the feed and C its concentration at time t.

Based on the value of k, which was obtained from the slope of the plot of C/C_0 against t on semi- log graph, the permeability coefficient (P) of the membrane was calculated according to the following equation:[24]

$$P = kV / A\varepsilon \quad (2)$$

where V is the volume of the feed solution, A is the area of the membrane film and ε is its porosity.

The values of P under different conditions are calculated and given in Table 1.

Table 1: Effect of stirring rate, sulfuric acid, hydrogen ion, CYANEX 925, ammonium thiocyanate and ammonia solution concentrations on the permeation rate and permeability coefficient of Zn(II) transfer through SLM impregnated with CYANEX 925 in kerosene.

Investigated parameter		Permeation rate constant (*k*) $s^{-1} \times 10^5$	Permeability coefficient (P) $cm\ s^{-1} \times 10^6$
Stirring rate, rpm	150	2.363	2.9
	250	3.866	4.8
	300	3.758	4.7
[CYANEX 925], M	0.075	2.506	3.1
	0.015	3.866	4.8
	0.025	5.88	7.3
	0.04	6.063	7.5

(*continued on next page*)

Table 1: (*continued*)

Investigated parameter		Permeation rate constant (k) $s^{-1} \times 10^5$	Permeability coefficient (P) cm $s^{-1} \times 10^6$
$[H_2SO_4]$, M	0.005	3.303	4.1
	0.1	1.581	2.0
	0.5	0.475	0.6
	1.5	0.312	0.4
$[H^+]$, M	0.005	3.284	4.1
	0.01	3.866	4.8
	0.1	1.306	1.6
	0.4	0.462	0.6
$[NH_4SCN]$, M	0.01	1.4	1.7
	0.05	3.305	4.1
	0.1	3.866	4.8
	0.2	4.03	5.0
	0.5	4.165	5.2
$[NH_4OH]$, M	0.1	0.1173	0.15
	1	3.866	4.8
	3	4.96	6.2
	5	4.414	5.5

3.1 Transfer of Zn(II) through SLM Impregnated with CYANEX 925 in Kerosene

In supported liquid membranes, the metal permeation process starts by diffusion of the metal from the feed solution to the external membrane layer followed by chemical reaction of the metal with the extractant at the external membrane interface.

3.1.1 Effect of the nature of the supporting film

To evaluate the effect of the nature of the supporting film on the permeability and the selectivity of the SLM, two membrane films, namely, cellulose nitrate and mixed cellulose ester, with different chemical composition, pore size, thickness (d_m) and porosity (ε) were tested under the same experimental conditions of aqueous feed solution, stripping solution and carrier concentrations and the results obtained are shown in Table 2.

Table 2: Influence of the nature of the support used in the membrane phase on the Zn(II) transfer through SLM impregnated with CYANEX 925 in kerosene.

Solid support	dm (mm)	Pore size (μm)	P ($\mu m\ s^{-1}$) $\times 10^6$
Mixed Cellulose ester	47	0.45	3.34
Cellulose Nitrate	47	0.2	4.81

Experimental conditions: Feed solution: 0.005 M Zn(II) in 0.1 M NH_4SCN/SO_4^{2-}; $[H^+]$ = 0.01; stripping solution: 1 M NH_3 solution; stirring rate = 250 rpm; temperature: 25 ± 1°C.

The tabulated data show that the permeability of Zn(II) changes with the change in the membrane material and cellulose nitrate was found to give higher permeability of Zn(II) compared with mixed cellulose ester under similar experimental conditions. Therefore, cellulose nitrate was used as support in all the SLM experiments carried out in this work.

3.1.2 Effect of stirring speed

As the stirring speed is a hydrodynamic parameter, its effect on the diffusion process is more pronounced, i.e., as the stirring speed increases the diffusion process increases gradually until a region is reached where the diffusion remains constant with any further increase in the speed. Accordingly, the effect of stirring speed was studied by equally varying the stirring rate of the feed and strip solutions in the range 150–300 rpm range while fixing the other parameters.

The plot of C/C_o as a relation versus t (on a semi-log graph of Figure 2), indicates that the increase in the stirring speed increases the diffusion process until a constant value is reached after 5.4×10^3 seconds at 250 rpm or more (Figure 2). In this region the diffusion contribution of the metal ions from the feed to the external layer of the membrane and through the aqueous film of the membrane surface to the strip solution is constant. Therefore, a stirring speed of 250 rpm was chosen for the investigations carried out on the effect of the other parameters on the permeation process.

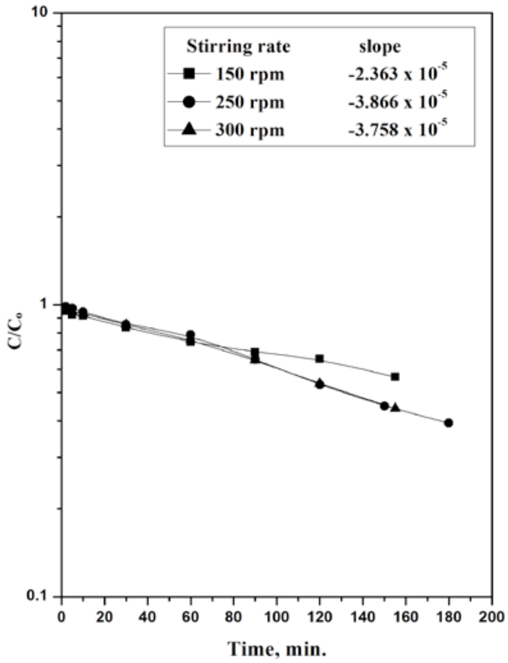

Figure 2: Effect of stirring rate on the transfer of Zn(II) through SLM in the aqueous mixed sulphate and thiocyanate solutions ([Zn (II)] = 0.005 M, [NH_4SCN] = 0.1 M, [H_2SO_4] = 0.01 M, [H^+] = 0.01, [Na_2SO_4] = 0.49 M, [NH_3] Soln. = 1 M, [CYANEX 925] = 0.015 M).

3.1.3 Effect of carrier concentration

The effect of CYANEX 925 concentration on the permeation of 0.005 M Zn(II) dissolved in mixed sulphate/thiocyanate solution was studied in the range of (7.5×10^{-3} M)–(4×10^{-2} M). It was observed that the rate of transfer (Figure 3) and permeability coefficient of the SLM for Zn(II) increases by increasing the carrier concentration till 0.025 M (Table 2).

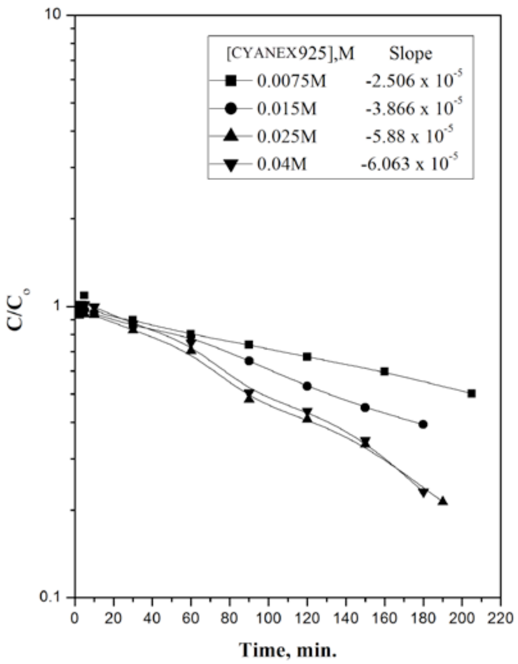

Figure 3: Effect of CYANEX 925 concentration on the transfer of Zn(II) through SLM from the aqueous mixed sulphate and thiocyanate solutions ([Zn (II)] = 0.005 M, [NH_4SCN] = 0.1 M, [H_2SO_4] = 0.01 M, [H^+] = 0.01, [Na_2SO_4] = 0.49 M, [NH_3] Soln. = 1 M).

3.1.4. Effect of hydrogen ion concentration in the feed solution

The effect of hydrogen ion concentration, when keeping the concentration of NH_4SCN constant at 0.1 M, on the transfer rate of 0.005 M Zn(II) through the SLM impregnated with 0.015 M CYANEX 925/kerosene solution was investigated in the initial [H^+] range 0.005–0.4 M, while keeping constant the [SO_4^{2-}] at 0.5 M by using sodium sulphate salt. The increase in hydrogen ion concentration in the investigated range was found to decrease the transfer rate (Figure 4) and the permeability coefficient of the SLM for Zn(II), as in Table 2.

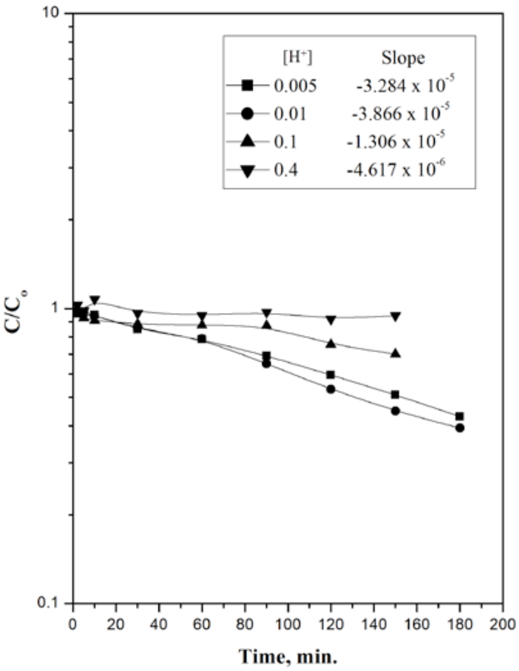

Figure 4: Effect of hydrogen ion concentration on the transfer of Zn(II) through SLM impregnated with CYANEX 925 in kerosene from the aqueous mixed sulphate and thiocyanate solutions ([Zn (II)] = 0.005 M, [NH_4SCN] = 0.1 M, [CYANEX 925] = 0.015 M, [NH_3] Soln. = 1 M).

3.1.5 Effect of sulphuric acid concentration in the feed solution

The effect of sulphuric acid concentration in the feed solution on the transfer rate of metal ions was investigated in the range of 0.005–1.5 M, while keeping all other experimental conditions fixed as mentioned in the experimental section. The results of C/C_o versus t as a semi-log relation are shown in Figure 5, indicating that the rate of Zn(II) transport decreases as the sulphuric acid concentration increases and also the permeability coefficient of the SLM for Zn(II) decreases.

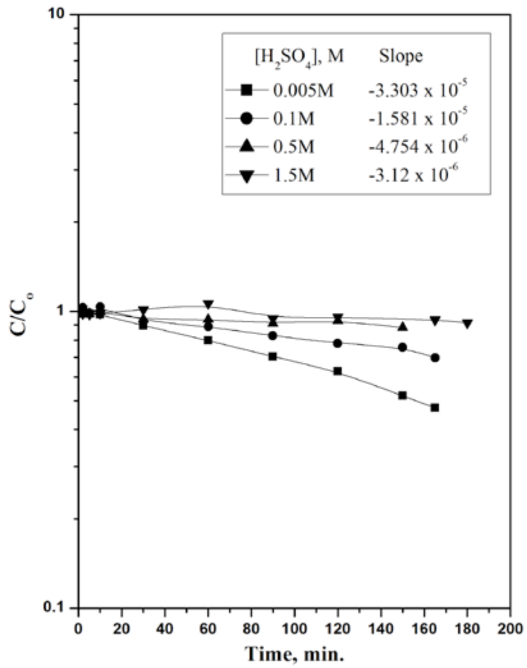

Figure 5: Effect of H_2SO_4 concentration on the transfer of Zn(II) through SLM impregnated with CYANEX 925 in kerosene from the aqueous mixed sulphate and thiocyanate solutions ([Zn (II)] = 0.005 M, [NH_4SCN] = 0.1 M, [CYANEX 925] = 0.015M, [NH_3] Soln. = 1M).

3.1.6 Effect of thiocyanate ion concentration in the feed solution

The effect of increasing the thiocyanate concentration in the feed solution on the transfer rate of Zn(II) was studied in the range 0.01–0.5 M. The results of C/C_o versus t relation shown in Figure 6 indicate that the increase in the thiocyanate concentration in the investigated range increases the transfer rate and the permeability coefficient of SLM for Zn(II) in the system (Table 2).

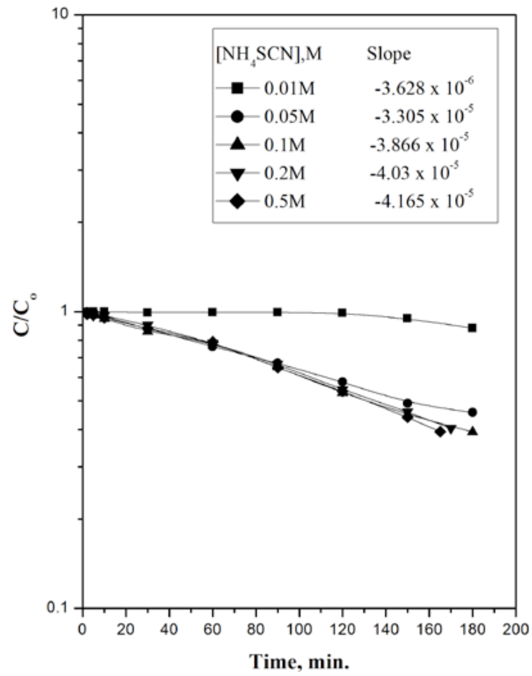

Figure 6: Effect of NH_4SCN on the transfer of Zn(II) through SLM impregnated with CYANEX 925 in kerosene from the aqueous mixed sulphate and thiocyanate solutions ([Zn(II)] = 0.005 M, [CYANEX 925] = 0.015M, [H_2SO_4] = 0.01 M, [H^+] = 0.01, [Na_2SO_4] = 0.49M [NH_3] Soln. = 1M).

3.1.7 Effect of concentration of the stripping solution

Since the extraction and stripping processes in SLM system are carried out simultaneously, it is significant to explore the effect of strippant concentration in the stripping phase in order to enhance the metal ion transfer by making efficient stripping process at the interface of the membrane and receiving solutions. As found by solvent extraction experiments,[24] NH_4OH solution is an efficient stripper for Zn(II) ions from loaded CYANEX 925/kerosene solution. Therefore, the study will be mainly directed to ammonia solution. The effect of NH_4OH solution concentration in the stripping side on the transport rate of the metal ion investigated in the range 0.1–5 M showed that that the transfer rate of Zn(II) increases as the NH_4OH concentration increases from 0.1 to 3 M, then decreases with further increase in NH_4OH concentration (Figure 7).

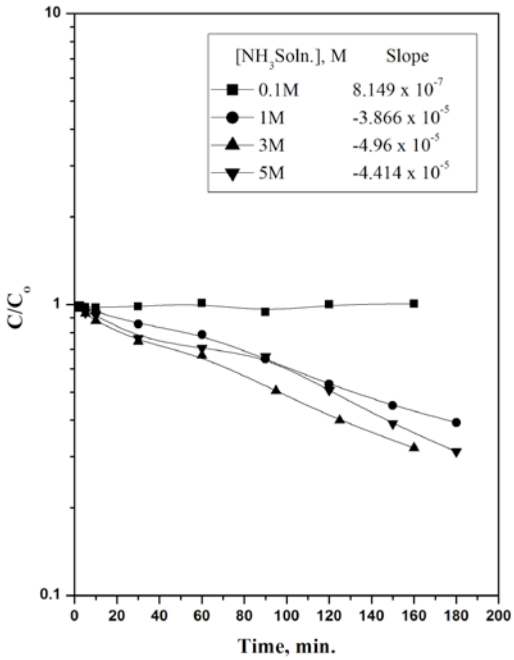

Figure 7: Effect of ammonia solution concentration on the transfer of Zn(II) through SLM impregnated with CYANEX 925 in kerosene from the aqueous mixed sulphate and thiocyanate solutions ([Zn (II)] = 0.005 M, [NH_4SCN] = 0.1 M, [H_2SO_4] = 0.01 M, [H^+] = 0.01, [Na_2SO_4] = 0.49 M, [CYANEX 925] = 0.015 M).

3.2 Transfer of Co(II) and Zn(II) from their Admixture

In this set of experiments the transfer rate of Co(II) and Zn(II) from a feed solution containing a mixture of 5×10^{-3} M Co and 5×10^{-3} M Zn was also studied when using 0.025 M CYANEX 925 in kerosene as carrier. The results of the relative transfer of Co from this mixture, represented as the C/C_o vs. time t as a semi-log relation, shown that the transfer rate of Co(II) is nearly not affected by the increase in contact time (Figure 8). On the other hand, the transfer rate of Zn(II) in presence of Co(II) increased gradually with the increase in contact time.

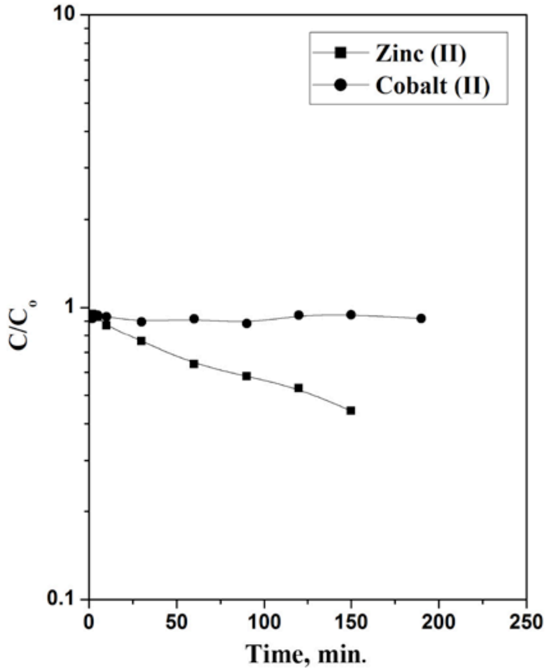

Figure 8: Effect of time on the transfer of metal ions through SLM impregnated with CYANEX 925 in kerosene from its admixture under the optimum conditions of Zn(II) transfer ([Zn (II)] = 0.005 M, [NH_4SCN] = 0.1 M, [H_2SO_4] = 0.01 M, [H^+] = 0.01).

3.3 Selectivity of the SLM System

The difference in the kinetic behaviour of Zn(II) and Co(II) in the investigated system could be used to favour the selectivity of the investigated system for the removal of Zn in the presence of Co. The selectivity of one ion over the other is defined as the ratio of their respective enrichment factors,[25] is given as:

$$S = Y_{Zn} / Y_{Co} \tag{3}$$

where S is the selectivity and Y is the enrichment factor.

The enrichment factor of zinc or cobalt is given by the following relation:

$$Y = [C_s] / [C_f] \tag{4}$$

where, [C_s] and [C_f] represent the concentration of the species in the stripping and feed solutions at time t, respectively, [25] under similar experimental conditions.

The selectivity of the used SLM for Zn-Co separation was calculated at different time intervals from the ratio of their maximum enrichment factors show that a maximum selectivity of 25 is reached after 60 min (Tables 3 and 4).

Table 3: Enrichment factor (Y) of Zn(II) and Co(II) from their mixture in the investigated SLM at the optimum conditions* of the transfer of zinc through the SLM system at different time intervals.

Time (min)	$Y = Zn_s/Zn_f$	$Y = Co_s/Co_f$
2	0.0136	–
5	0.0226	–
10	0.0498	–
30	0.118	–
60	0.226	0.009
90	0.348	0.0137
120	0.498	0.024
150	0.561	0.028

Experimental conditions: [Zn (II)] = [Co(II)] = 0.005 M, [NH $_4$SCN] = 0.1 M, [H_2SO_4] = 0.01 M [H^+] = 0.01, [Na_2SO_4] = 0.49 M, [NH_3] Soln. = 1M, [CYANEX 925] = 0.025 M.

Table 4: Selectivity (S) of Zn(II) / Co(II) separation in the used SLM at different time intervals.

Time (min)	$S = Y_{Zn}/Y_{Co}$
60	25.1
90	25.4
120	20.75
150	20.04

3.4 Membrane Stability and Durability

The performance of the SLM depends not only on the permeation and the selectivity of the membrane but also on its stability. Although, the present system (CYANEX 925 dissolved in kerosene and supported on cellulose nitrate film) is stable enough to transfer almost Zn(II) in the feed solution to the strip solution, it is of interest to investigate its stability for long term operation. The stability of the SLM was tested by carrying out the transport experiments repeatedly using the same membrane impregnated with 0.025 M CYANEX 925 in kerosene under the optimum conditions for maximum Zn-Co separation.

Five consecutive runs, each of 150 min were performed using fresh solutions in both compartments for each run. The results of the relative transfer of Zn(II) with and without Co(II), represented as the C/C_o vs. time t on a semi-log relation, show a gradual increase in the transfer rate of Zn(II) with the increase in contact time but a gradual decrease in the rate transfer of Zn(II) is observed with the increase in the number of runs (Figure 9).

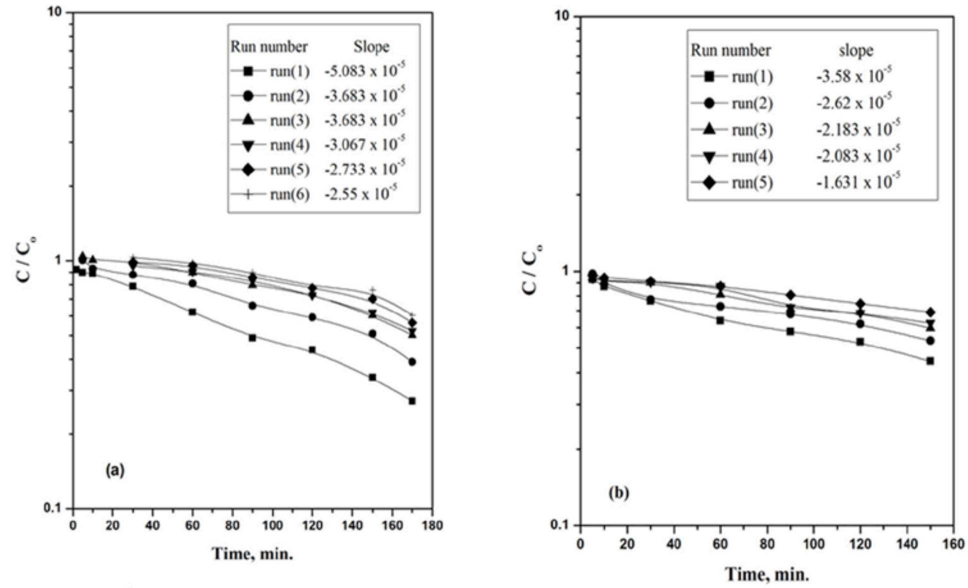

Figure 9: Effect of time on the transfer of Zn(II) through SLM impregnated with CYANEX 925 in kerosene under the optimum conditions of Zn(II) transfer for five runs: (a) without Co(II), (b) with Co(II). ([Zn(II)] = 0.005 M, [NH_4SCN] = 0.1 M, [H_2SO_4)] = 0.01 M, [Co(II))] = 0.005 M, [Na_2SO_4] = 0.49M, [NH_3]Soln. = 3M, [CYANEX 925] = 0.025 M, [H^+] = 0.01).

The percent extraction at the different investigated runs is shown in Figure 10. It is clear from the results obtained that the SLM formed by cellulose nitrate membrane supporting 0.025 M CYANEX 925 dissolved in kerosene as carrier is quite stable, where the extraction percent Zn(II) with and without Co(II) gradually decreases. The extraction percent of Zn(II) without Co(II) is higher than with Co(II). It is found that the extraction percentage of Zn(II) without Co(II) decreases from 73% to 45% while the percent with Co(II) decreases from 55.7% to 36.9% after five runs.

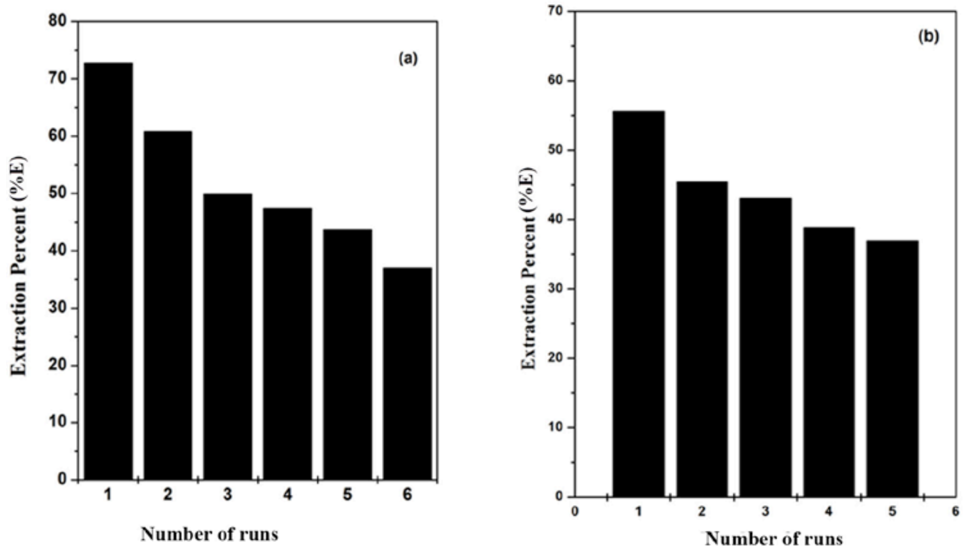

Figure 10: Effect of number of runs on the transfer of Zn(II) through SLM impregnated with CYANEX 925 in kerosene under the optimum conditions of Zn(II) transfer for five runs: (a) without Co(II), (b) with Co(II). Conditions: [Zn(II)] = 0.005 M, [NH_4SCN] = 0.1 M, [H_2SO_4)] = 0.01 M, [Co(II))] = 0.005 M, [Na_2SO_4] = 0.49M, [NH_3] Soln. = 3M, [CYANEX 925] = 0.025 M [H^+] = 0.01.

4. CONCLUSION

From the aforementioned results and discussions, the following are concluded:

- The individual transfer experiments of Zn(II) through a cellulose nitrate membrane impregnated with CYANEX 925 in kerosene increased with the increase in stirring rate, thiocyanate concentration in the feed, and molarity of NH_4OH used as the stripping solution.
- The transfer experiments of Zn(II) from its admixture with Co(II) showed that Zn(II) could be extracted more than Co(II) by CYANEX 925; the transfer rate increased with time.
- The investigated SLM system could be used for removal of Zn(II) from an aqueous mixed thiocyanate/sulphate medium of [H^+] = 0.01. In addition, the present system is selective for Zn-Co separation from aqueous mixed thiocyanate/sulphate medium, and this selectivity decreases with time and a maximum value of 25 is reached after 60 min.
- The SLM system is economic and efficient where the same membrane film can be used for more than one run.

5. REFERENCES

1. Li, N. N. (1968). Separating hydrocarbons with liquid membranes. U.S. Patent No. 3,410,794.
2. Ho, W. S. & Poddar, T. K. (2001). New membrane technology for removal and recovery of chromium from waste waters, *Environ. Prog.*, 20(1), 44–52.
3. Sastre, A. M. et al. (1998). Improved techniques in liquid membrane separation: An overview. *Sep. Purif. Methods*, (27), 213–298.
4. Juang, R. S., Kao, H. C. & Wu, W. H. (2004). Analysis of liquid membrane extraction of binary Zn(II) and Cd(II) from chloride media with Aliquat 336 based on thermodynamic equilibrium models. *J. Membr. Sci*., 228, 169–177.
5. Miesiac, I. & Szymanowski, J. (2004). Separation of zinc(II) from hydrochloric acid solutions in a double Lewis cell. *Solvent Extr. Ion Exch*., 22(2), 243–265.
6. Dimitrov, K. et al. (2002). The recovery of zinc from chloride media by batch pertraction in a rotating film contactor. *J. Membr. Sci*., 207, 119–127.
7. He, D. et al. (2000) Kinetic analysis of Zn(II) extraction by liquid membrane containing di (2-ethythexyl) phosphoric acid in kerosene. *Chin. J. Appl. Chem*., 17, 47–50.
8. Kunungo, S. B. & Mohapatra, R. (1995). Coupled transport of Zn(II) through a supported liquid membrane containing bis (2,2,4-trimethylpentyl) phos-phinic acid in kerosene II. Experimental evaluation of model equations for rate process under different limiting conditions. *J. Membr. Sci*., 105, 227–235.
9. Saito, T. (1994). Selective transport of copper (I, II), cadmium (II), and zinc (II) ions through a supported liquid membrane containing bathocuproine, neocuproine, or bathophe-nanthroline. *Sep. Sci. Technol*., 29, 1335–1346.
10. Fernandez, L., Apricio, J. & Muhammed, M. (1986). Coupled zinc transport through a bis (2-ethylhexyl) phosphoric acid solid-supported liquid membrane from aqueous perchlorate media. *J. Membr. Sci*., 27, 77–91.
11. Luo, F., Li, D. & Wu, Y. (2004). Extraction and separation of cadmium (II), iron (II), zinc (II), and europium (III) by CYANEX 302 solutions using hollow fiber membrane modules. *Solvent Extr. Ion Exch*., 22, 105–120.
12. He, D. et al. (2006). Study of transport and separation of Zn(II) by a combined supported liquid membrane/strip dispersion process containing D2EHPA in kerosene as the carrier. *Desalin.*, 194, 40–51.

13. Protsch, M. & Marr, R. (1983). Development of a continuous process for metal ion recovery by liquid membrane permeation. Proceedings of International Solvent Extraction Conference, Denver, Colorado, 66–67.
14. Schurgerl, K., Larm, A. & Guodorf, M. (1996). Proc. ISEC 96, vol. 2, Melbourne, Australia, 1543.
15. Tait, B. K. (1992). The extraction of some base metal ions by CYANEX 301, CYANEX 302 and their binary extractant mixtures with Aliquat 336. *Solv. Extr. Ion Exch*., 10, 799–809.
16. Regel, M., Sastre, A. M. & Szymanawski, J. (2001). Recovery of zinc from HCl spent pickling solutions by solvent extraction. *Environ. Sci. Technol*., 35, 630–635.
17. Avila Rodríguez, M. et al. (1998). Sulphuric acid influence on liquid–liquid extraction of Co(II) and Zn(II) by MIBK from NH4SCN medium. *Talanta*, 45(5), 875–882.
18. El Dessouky, S. I. et al. (2008). Solvent extraction separation of Zn(II), Fe(II), Fe(III) and Cd(II) using tributylphosphate and CYANEX 921 in kerosene from chloride medium. *Chem. Eng. Process.*, 47, 177–183.
19. Sainz-Diaz, C. I. et al. (1996). New approach in the modelling of the extraction equilibrium of zinc with bis-(2-ethylhexyl) phosphoric acid. *Hydrometal*., 42(1), 1–11.
20. Studlar, K. & Janousek, I. (1961). The photometric determination of zinc with xylenol orange. *Talanta*, 8, 203–208.
21. Marczenko, Z. (1976). *Spectrophotometric determination of elements*. Chichester: Ellis Harwood.
22. Bobrowska-Grzesik, E. & Grossman, A. M. (1996). Derivative spectrophotometry in the determination of metal ions with 4-(pyridyl-2-azo) resorcinol (PAR). *Anal. Bioanal. Chem.*, 354(4), 498–502.
23. El-Hefny, N. E. et al. (2010). Separation and recovery of Zinc(II) and Cobalt(II) from a mixed sulfate/Thiocyanate solution using some commercial organophosphorus extractants. *Solv. Extr. Ion. Exch*., 28, 244–266.
24. Danesi, P. R. & Cianetti, C. (1984). Permeation of metal ions through a series of two complementary supported liquid membranes. *J. Membr. Sci.*, 20(2), 201–213.
25. Rickelton, W. A. (1992). Novel uses for thiophosphinic acids in solvent extraction. *J. Metals*, 44(5), 52–54.