

The Transport of Iron (III) Through Bulk Liquid Membrane Using Aliquat 336 As Carrier

CRISTINA MONICA MIREA, IOANA DIACONU*, ECATERINA ANCA SERBAN, ELENA RUSE*, GHEORGHE NECHIFOR

University Politehnica of Bucharest, Department of Analytical Chemistry and Environmental Engineering, 1-3 Gh. Polizu Str., 011061, Bucharest, Romania,

This paper presents experimental data on the transport of Fe (III) cation through the bulk liquid membrane in the presence of Aliquat 336 (N-Methyl-N,N,N-trioctyloctan-1-ammonium chloride) as a carrier. The transport experiments were carried out in a wall in wall type of cell in the presence of a chloroform membrane in which the carrier Aliquat 336 is dissolved at a concentration of 10^{-2} mol/L. Transport parameters such as: the concentration of Fe (III) in the feed phase, the concentration of HCl in the feed phase and stripping phase, the time of transport were investigated. In optimal transport conditions there were obtained transportation efficiencies higher than 90%. The transport mechanism was assessed.

Keywords: bulk liquid membrane, iron, transport through membrane, Aliquat 336

The iron salts are widely used in water treatment both the ferrous (Fe (II)) as well as the ferric (Fe (III)) for odor removal, but also to remove various contaminants such as: phosphorus, antimony or arsenic [1, 2 3]. These iron salts may remain at high levels after the water treatment process and can affect the aquatic environment if not treated or removed properly [4]. The same study [4] specifies a highly toxicity for the iron salts (III) due to rapid oxidation to insoluble forms. Other fields of pollution with iron salts are the anthropogenic ones or the solutions resulting from hydrometallurgical processes for the recovery of ions such as: nickel (II), cobalt (II) or copper (II) [5].

Most of the techniques used for the removal of iron salts (III) involve the use of precipitation [6] because recovery from aqueous solutions of iron (III) is very difficult [5]. But, there are numerous studies [6] that present the removal of iron (III) from aqueous solutions using solvent extraction or membrane techniques. A particular attention presents membrane techniques due to their versatility.

The separation or removal of the iron salts was carried out using the supported liquid membranes, polymeric inclusion membranes, membrane contactors, membrane bioreactors and polyurethane ether-type membranes [5, 7-16].

The separation of iron salts of titanium ones from the acidic solutions was possible using the supported liquid membranes and trioctylamine (TOA) as carrier [7]. Thus, using a feed phase of HCl 5M, a supported liquid membrane impregnated with a TOA solution in kerosene and a stripping phase of HClO₄ at a temperature of 80°C, the iron is transported 99.9% in 6.4 h. The authors [7] claim that in this case the process seems to be controlled by diffusion of the organic phase through the membrane because the temperature increase rate increased the transport rate of iron.

The supported liquid membranes have been successfully used for the transport of iron (III) and copper (II) ions [8]. In this case di-2-ethylhexyl phosphoric acid (D2EHPA) has been used as carrier dissolved in *n*-decanol and then impregnated in the polymeric support. The feed phase was composed of the studied ions dissolved in sulphuric acid

and stripping phase of the phosphoric acid. The transport of the both metal species is influenced by the carrier concentration, while the acid concentration from the feed phase influences the transport of iron ions, while the stripping phase influences the transport of copper ions. It has also been proposed a non-steady state model for the transport of iron(III) across *n*-decanol supported liquid membrane facilitated by D2EHPA [9].

As it has been seen previously the carrier has an important role in the transport process of iron salts from supported liquid membranes. Among the most used carriers we can list: 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPA) [10], trioctylphosphine oxide (Cyanex 921) [11], phosphine oxides mixture (Cyanex 923) [12] sau 2-hydroxy-5-nonylacetophenone oxime (LIX84I) [13].

Special types of the supported liquid membranes are the polymeric inclusion membranes. Thus was achieved using the polymeric inclusion membranes a selective transport of iron salts (III) using tributyl phosphate (TBP) [6] and D2EHPA [5]. The selective separation of iron (III) is influenced by the composition of the membrane that influences the stability of membrane and the extractant concentration.

Polyurethane ether-type membranes [14] have also been used for the transport of iron halides. The membrane contactor is presents as a new technique for the separation of iron ions from ilmenite (FeTiO₃) [15], achieving even a speciation of the iron in the membrane bioreactor [16].

The bulk liquid membranes are also recommended for the transport of metals due to multiple advantages such as: high selectivity transport, low cost of the transport process with low energy consumption and high efficiency transport or the simplicity of operation [17-25].

Thus, the bulk liquid membranes have been used in the transport and separation of iron (III) and nickel (II) [3]. Using trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL101), as carrier, dissolved in chloroform there was carry out the separation of iron (III) with an efficiency of 99.9% from a feed phase that contains in addition to the metal ion HCl 6 mol/L into a stripping phase formed from HCl at a 0.5 M concentration. The study demonstrated that the

* email: diaconuioana12@yahoo.com; e_ruse@chim.upb.ro

extractant and concentration of HCl influences the transport process.

In this paper was carried out a study of the Fe (III) cations transport in HCl medium in the presence of Aliquat 336 (methyl trioctyl ammonium chloride) as a carrier.

Experimental part

Reagents

All the reagents used were analytically grade and were used without further purification. These (chloroform, hydrochloric acid, ferric chloride solution, Aliquat 336) were purchased from Merck. Aliquat 336 and chloroform were used to prepare the organic phase (membrane). Ferric chloride solution and hydrochloric acid were used to prepare the feed phase and stripping phase. The distilled water used to prepare the aqueous phases was previously saturated with chloroform and the chloroform used to prepare the organic membrane phase was previously saturated with distilled water.

Apparatus

The analytical control was realized using a LAMDA UV-VIS-NIR (Perkin Elmer Life and Analytical Sciences) spectrophotometer at 460 nm wavelength for the determination of concentration of Fe (III) in feed phase and stripping phase. The content of iron (III) in the membrane was determined from mass balance.

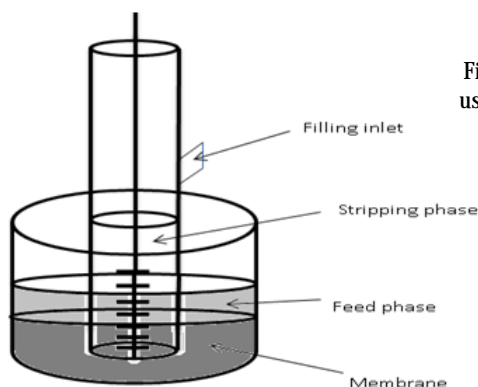


Fig.1. The device used for transport experiments

The experimental device used for the transport experiments was a wall in wall type of cell, shown in the figure 1:

Procedure

The membrane system is composed from:

-feed phase (FP) - formed from a ferric chloride solution of concentration $10^{-4} - 5 \cdot 10^{-4}$ mol/L in the presence of HCl 1 mol/L; 2 mol/L and 2.5 mol/L. The volume of feed phase was 20 cm^3 .

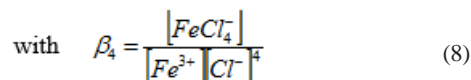
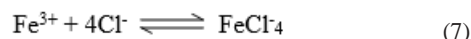
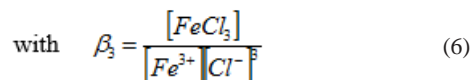
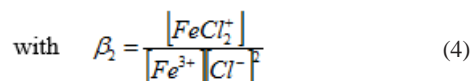
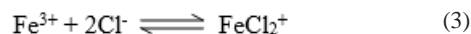
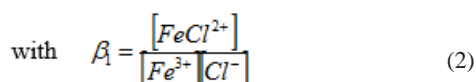
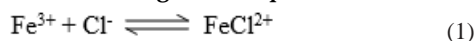
-membrane (M) - formed from a 10^{-2} mol/L Aliquat 336 solution in chloroform. The volume of membrane was 50 cm^3 .

-stripping phase (RP) - formed from a HCl of concentration 10^{-3} mol/L. The volume of stripping phase was 7 cm^3 .

The experiments were realized using the following conditions: room temperature, a stirring speed of 180 rot/min and a transport time of 18 h.

Results and discussions

As shown in the literature study [3] in HCl medium Fe (III) cations form different chemical species of the type FeCl_x^{3-x} , ($x = 1-4$) according to the equilibriums (1,3,5,7):

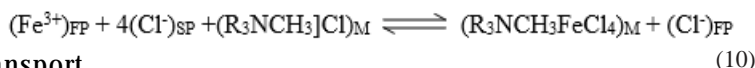


These equilibriums are characterized by $\beta_1 - \beta_4$ stability constants (2,4,6,8). The formation rate of these chemical species (α) depends on the stability constants and hydrochloric acid concentration and it can be assessed by relationship (9):

$$\alpha_i = \frac{\beta_i [\text{Cl}^-]^i}{1 + \sum_{i=1}^4 \beta_i [\text{Cl}^-]^i} \quad (9)$$

The equation was obtained assuming that $C_{\text{Fe}^{3+}} \ll C_{\text{Cl}^-}$. Based on the value of stability constants [26] there were calculated the complex formation degree for the Fe -Cl complexes in the possible HCl concentration range (0-12M). The results obtained are shown in table 1.

From the data presented in the table 1 it can be observed that the cationic species are predominant. Since Aliquat 336 is known as a carrier for anionic species, the literature [27] indicates as possible equilibrium at the interface feed phase %organic membrane:



where:

FP = feed phase

M = membrane

In this hypothesis we can consider that the transport of Fe (III) cations in HCl medium take place following assisted transport accompanied by a counter-transport or anions Cl^- in an equivalent flux in the same way.

The transport mechanism is shown in figure 2.

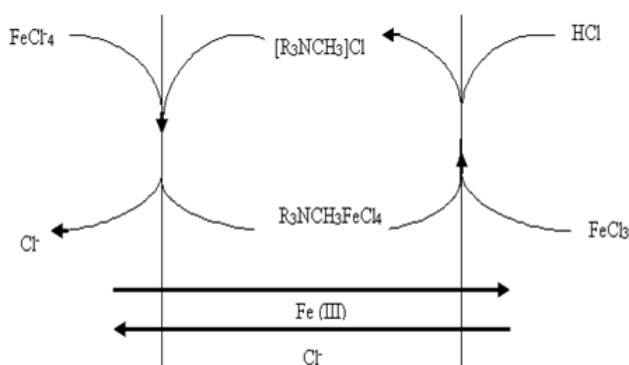


Fig 2. The transport mechanism of Fe (III) in the presence of Aliquat 336 as carrier

[Cl ⁻][mol/L]	α_1	α_2	α_3	α_4
0	0	0	0	0
1	0.154	0.721	0.117	0.000
2	0.074	0.696	0.226	0.001
3	0.046	0.640	0.311	0.003
4	0.031	0.584	0.379	0.005
5	0.023	0.536	0.434	0.007
6	0.018	0.493	0.480	0.009
7	0.014	0.456	0.518	0.011
8	0.011	0.424	0.550	0.014
9	0.009	0.396	0.578	0.016
10	0.008	0.371	0.602	0.019
11	0.007	0.349	0.623	0.022

In the present paper the study aimed the transport Fe (III) cation as a function of the aqueous phases characteristic parameters such as: the HCl and Fe (III) concentration from the feed phase and the HCl concentration from the stripping phase.

The quantification of the transport process was realized by assessing the molar percentage composition for each of the membrane system phases. For the aqueous phases equation (11) was used:

$$\% \text{ mol} = \frac{C_{F_{aq}} \times V_{F_{aq}}}{C_{F_{S_0}} \times V_{F_{S_0}}} \times 100 \quad (11)$$

where:

% mol = molar percentage of aqueous phase of the membrane system

$C_{F_{aq}}$ = aqueous phase concentration (feed and stripping) at the end process transport, mol/L

$V_{F_{aq}}$ = aqueous phase volume, L

$C_{F_{S_0}}$ = initial feed phase concentration, mol/L

$V_{F_{S_0}}$ = initial feed phase volume, L

The molar percentage content in the membrane phase was determined by the mass balance of membrane system phases.

Influence of HCl concentration in the feed phase

The concentration of HCl from the feed phase is the most important parameter for the transport process of Fe (III) in the presence of Aliquat 336.

The influence of HCl concentration in the feed phase in the range 1-2.5 mol/L at a Fe (III) concentration between 10^{-4} - 10^{-3} mol/L was studied. The transport time was 18 hours. The experimental results are shown in figure 3.

It was found that the transport efficiency of the Fe (III) cation in the presence of Aliquat 336 increases with increasing HCl concentration in the feed phase. The extraction process of Fe(III) through bulk liquid membrane is nearly quantitative at HCl concentrations of at least 2.5 mol/L and a time transport of 18 h.

Influence of Fe (III) concentration in the feed phase

The concentration of Fe (III) from the feed phase in the range 10^{-4} - 10^{-3} mol/L was investigated. The obtained experimental results are shown in figure 4.

Table 1
THE DEPENDENCE OF FORMATION RATE OF THE CHEMICAL SPECIES OF THE TYPE $FeCl_x^{3-x}$ ON THE STABILITY CONSTANTS AND HYDROCHLORIC ACID CONCENTRATION

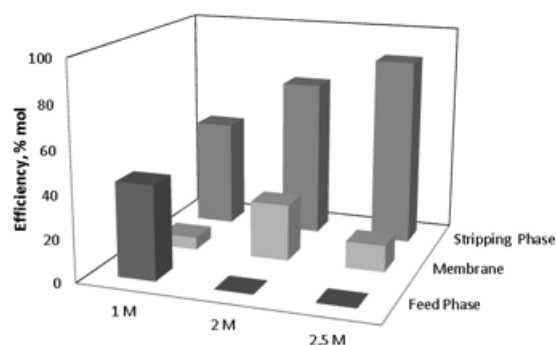


Fig. 3 Influence of HCl concentration in the feed phase on the efficiency of transport process. Working conditions: Feed phase - 5×10^{-4} mol/L Fe (III) solution, 1 - 2.5 mol/L HCl, Membrane: 10^{-2} mol/L Aliquat 336 in chloroform, Stripping phase: 10^{-3} mol/L HCl solution

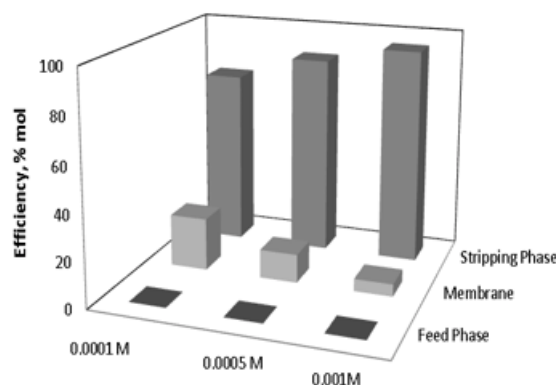


Fig. 4 Influence of Fe (III) concentration in the feed phase. Working conditions: Feed phase - 10^{-4} - 10^{-3} mol/L Fe (III) solution, 2.5 mol/L HCl, Membrane: 10^{-2} mol/L Aliquat 336 in chloroform, Stripping phase: 10^{-3} mol/L HCl solution

The obtained experimental data indicate an increase of the efficiency of the transport process with the increase of Fe (III) concentration in the feed phase from 77% at a concentration of 10^{-4} mol/L Fe (III) to 94.6% at a concentration of 10^{-3} mol/L Fe (III).

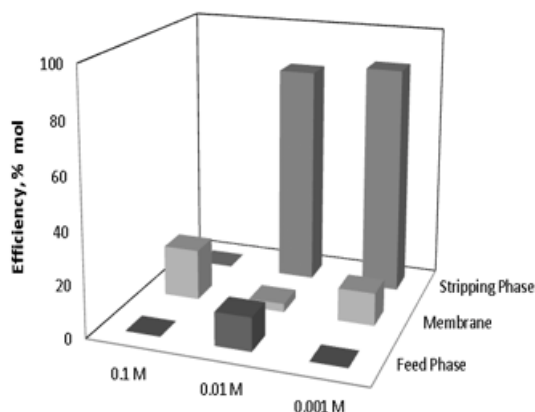


Fig. 5. Influence of HCl concentration in the stripping phase. Working conditions: Feed phase – 5×10^{-4} mol/L Fe (III) solution, 2.5 mol/L HCl, Membrane: 10^{-2} mol/L Aliquat 336 solution in chloroform, Stripping phase: 10^{-1} – 10^{-3} mol/L HCl solution

Influence of HCl concentration in the stripping phase

To facilitate the breaking of the complex at the interface membrane | stripping phase diluted HCl solutions were used. As stripping phase HCl solutions in the concentration range of 10^{-1} – 10^{-3} mol/L were used. The experimental results obtained are shown in figure 5

It can be concluded that the process efficiency is greater in the stripping phase if it has a lower concentration of HCl. But too low concentrations of HCl in the stripping phase does not ensure the necessary stability conditions for complex ($R_3NCH_3FeCl_4$). Thus at the interface membrane | stripping phase the equilibrium (12) occurs:



However these low concentrations of HCl are not indicated because they are in favor for the precipitation of the Fe (III) ions. This phenomenon is not a characteristic for a separation process through liquid membrane.

Conclusions

The study carried out in this paper demonstrated the possibility of the transport of Fe (III) cations with Aliquat 336 from hydrochloride medium using the bulk liquid membrane technique. The influence of the operating parameters such as: the concentration of HCl in the feed and stripping phase and the concentration of Fe (III) in the feed phase were determined. In optimal transport conditions the process is almost quantitative, which opens the prospect of analytical applications of this process.

Acknowledgement: The study has been funded by the Sectoral Operational Programme Human Refeeds Development 2007 – 2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/134398.

References

1. WU, Z., HE, M., GUO, X., & ZHOU, R. Sep.Purif. Technol., **76**, no. 2, 2010, p. 184
2. CUI, J., JING, C., CHE, D., ZHANG, J., DUAN, S., J. ENVIRON. Sci., **32**, 2015, p. 42
3. WU, H., IKEDA-OHNO, A., WANG, Y., WAITE, T. D. Water Res., **76**, 2015, p. 213
4. SOTERO-SANTOS, R. B., ROCHA, O., POVINELLI, J., Chemosphere, **68**, no. 4, 2007, p. 628
5. POCEPIECH, B., WALKOWIAK, W., Physicochem. Probl. Mi. **44**, 2010, p. 195
6. POCEPIECH, B., WALKOWIAK, W., WOŃNIAK, M. J., Physicochem. Probl. Mi., **39**, 2005, p. 89
7. MAHMOUD, M. H. H., Sep.Purif.Technol., **84**, 2012, p. 63
8. ZHANG, B., GOZZELINO, G, Colloid Surface A, **215**, no. 1, 2003, p. 67
9. ZHANG, B., GOZZELINO, G., DAI, Y., J.Membr. Sci., **210**, no. 1, 2002, p. 103
10. AKIBA, K., ITO, M., NAKAMURA, S., J.Membr. Sci., **129**, no. 1, 1997, p. 9
11. ALGUACIL, F. J., ALONSO, M., Hydrometallurgy, **58**, no. 1, 2000, p. 81
12. ALGUACIL, F. J., MARTINEZ, S., J.Membr. Sci., **176**, no. 2 (2000): 249-255.
13. ADEBAYO, A. O., SARANGI, K., Sep.Purif.Technol., **63**, no. 2, 2008, p. 392
14. OLESCHUK, R. D., CHOW, A., Talanta, **42**, no. 7, 1995, p. 957
15. ABDEL-AAL, E. A., MAHMOUD, M. H. H., SANAD, M. M. S., CRISCUOLI, A., FIGOLI, A., DRIOLI, E., Int. J. Miner. Process., **96**, no. 1 (2010): 62-69.
16. WU, H., IKEDA-OHNO, A., WANG, Y., & WAITE, T. D. Water research, **76**, 2015 p.213
17. DIACONU, I., GIRDEA, R., CRISTEA, C., NECHIFOR, G., RUSE, E., TOTU, E.E., Rom. Biotech. Lett., **15**, no. 6, 2010, p. 5702
18. DIACONU, I., ZAHARIA, I., RUSE, E., RADU, D. A., Rev. Chim. (Bucharest), **63**, no. 2, 2012, p. 153
19. ZAHARIA, I., ABOUL-ENEIN, H.Y., DIACONU, I., RUSE, E., BUNACIU, A.A., NECHIFOR, G., J. Iran. Chem. Soc., **10**, no. 6, 2013, p. 1129
20. ZAHARIA, I., DIACONU, I., RUSE, E., NECHIFOR, G., Dig. J. Nanomater. Bios., **7**, no. 3, 2012, p. 1303
21. ZAHARIA, I., DIACONU, I., RUSE, E., NECHIFOR, G., Rev. Chim. (Bucharest), **65**, no. 11, 2014, p.1256
22. DIACONU, I., MIREA, C.M., RUSE, E., NECHIFOR, G., Environmental Engineering and Management Journal, **14**, nr. 3, 2015, p.625
23. ZAHARIA, I., DIACONU, I., RUSE, E., NECHIFOR, G. Rev. Chim. (Bucharest), **66**, no.2, 2015, p.169
24. DIACONU, I., ABOUL-ENEIN, H.Y., AL-OMAR, M.A., NECHIFOR, G., RUSE, E., BUNACIU, A.A., EFTIMIE, TOTU, E., Arabian Journal of Chemistry **4** (1), 2011, p.99
25. DIACONU, I., NECHIFOR, G., NECHIFOR, A.C., EFTIMIE TOTU, E., RUSE, E., Rev. Chim. (Bucharest), **60**, no. 12, 2012, p. 1243
26. SILLEN, L.G., MARTEL, A.E., BJERRUM, J., Stability Constants of Metal-Ion Complexes, London, Chemical Society, 1964
27. MISHRA, R.K., ROUT, P.C., SARANGI K., NATHSARMA, K.C., Hydrometallurgy **108** (2011) p.93

Manuscript received: 16.07.2015