Article

The pseudo-protic ionic liquids $TOAH^+Cl^-$ and $TODAH^+Cl^-$ as carriers for facilitated transport of In(III) from HCl solutions

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Abstract: The behaviour of the pseudo-protic ionic liquids $TOAH^+Cl^-$ and $TODAH^+Cl^-$ in the facilitated transport of indium(III) from HCl solutions is described. Metal transport is investigated as a function of different variables: hydrodynamic conditions, HCl concentration in the feed phase and indium and carrier concentrations. The experimental data are used to model both transport systems and to estimate diffusional parameters associated to them.

Keywords: facilitated transport; $TOAH^+Cl^-$; $TODAH^+Cl^-$; pseudo-protic ionic liquids; indium; hydrochloric acid.

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1. Introduction

At the time in which this manuscript is being written (November 2022), there is in industrialized countries a general concern about the regular supply of metals to fulfil the various industrial necessities. Among these metals, and according with the use of smart technologies in communications, computers, batteries, electronics, etc., the doubtful supply of strategic metals, such as lithium, niobium, tantalum, rare earths, indium, etc., makes that the academia, government and private research institutions, and private companies and entrepreneurs try to check for new sources in which these strategic metals can be found. This is because from a time ago, the concept of urban mining and the recycle of its wastes are becoming more popular.

Particularly, indium appeared in several urban devices in the form of ITO (Indium Tin Oxide). This oxides mixture, when deposited as a thin film on glass or clear plastic, is used in several display technologies, such as LCD, OLED, plasma, electroluminescent, and electrochromatic displays, as well as in several touch screen technologies.

In the treatment of these wastes, Hydrometallurgy emerged as a real solution to solve the problem of the treatment of these residues and the recovery of the valuables metals encountered in them. Generally speaking and after the pre-treatment of the waste, including i) dismantling, ii) shedding and iii) comminution, a leaching step dissolved, totally or partially, the metallic component of the waste, and from the leachate, very often containing more than one metal species, different separation technologies are used to separate (sometimes also concentrate) one metal from another, and prior to the final recovery of the valuable metal or metallic compound.

The more extended separations technologies used in the recovery of metals, and indium is not an exception, are liquid-liquid extraction, ion exchange and adsorption. Liquid membranes processes have been of increasing interest, though, and against the above technologies, not a single process has known industrial application. Main liquid membranes operations included: supported and unsupported liquid membranes, and while the latter is currently of a minor interest, the former consisting of a thin microporous and hydrophobic polymer support in which the carrier phase (organic phase containing the extractant) is immobilized; this support separates the feed and receiving or stripping solutions. First batch investigations in the form of flat-sheet configuration can be scaled-up to a continuous form by the use of hollow fibers modules. From an engineering and practical point of views, supported liquid membranes are of particular interest due to their stability (if corrected operated) and simplicity because they combine in a single operation the extraction and stripping stages.

In the particular case of indium, recent data about the use of the above separation technologies included:

i) liquid-liquid extraction: D2EHPA (di-2-ethylhexyl phosphoric acid) is used to extract indium(III) [1], however, difficulties found in the stripping stage recommended the use of certain additives to facilitate this operation; among the additives used, 2-ethylhexanol presented the best characteristics for its practical use. Spent copper indium gallium selenide (CIGS) materials are found to be a source for the recovery of indium and galium [2]. After some previous steps, the leaching solution was extracted with P204 (di-2-ethylhexyl phosphoric acid) extractant for the sequential removal of indium and gallium, both metals are recovered from the respective organic phase using HCl as strippant. Differing in the number and size of coordination sites, calix[4]arene, alkenyltrimethylol, and trihydroxytriphenylmethane frameworks are prepared to extract indium(III) [3].The calix[4]arene and trihydroxytriphenylmethane derivatives demonstrated the extraction of In3+ with an unexpected stoichiometry of 1:2. In the treatment of spent liquid crystal displays (LCDs) of monitors, a process which includes microwave pyrolysis, leaching and solvent extraction is investigated [4]; as extraction agent D2EHPA is again used, whereas the stripping stage is carried out with 6 M HCl as strippant solution. In another investigation using also real solutions from the treatment of spent LCDs [5], Cyanex 923 (industrial phosphine oxides mixture) is used to extract iron(III) and indium(III) from the leachate. Separation of both elements is performed varying the V_{aq}/V_{org} phases relationship, firstly, iron is extracted using a high relationship, and after, indium(III) is extracted at a low ratio, i.e. 1. A real sulphate solution obtained by leaching of dross is subjected to solvent extraction operation to separate germanium and indium [6]. After the extraction of germanium with a trioctyl amine and tributyl phosphate mixture, indium is extracted with D2EHPA and stripped in a hydrochloric acid medium. 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), and thia-benzo-15-crown-5 (TB15C5) extractants are investigated for selective indium recovery from end-of-life liquid crystal displays (LCDs) leaching solution [7]. In this case, the theoretical and experimental extraction order are 15C5 > B15C5 > TB15C5. Various hydrometallurgical processes involving pressure acid leaching and solvent extraction are investigated for the recovery of indium from zinc slag, which is produced in the imperial smelting process [8]. Pressure leaching with sulfuric acid is the preferred method to recover indium from the slag, and again, indium is extracted with D2EHPA and stripped in HCl medium.

ii) adsorption: Metal-organic frameworks (MOFs) of UiO-66 is used in the adsorption of indium at acidic pH values [9]. Results show that the adsorbent structure is stable even at these acidic pH values, and that together an adsorption process, cation exchange mechanism is involved in indium uptake onto the adsorbent.

iii) ion exchange: After the leaching of indium from waste liquid crystal displays with HCL solutions, the metal is recovered from the corresponding leachate with an anion exchange resin [10]. This resin is a strongly basic (with quaternary ammonium functional groups on polystyrene-DVB matrix) gel type resin (Varion AD) in chloride form. Spent LCD screens are leached with sulfuric acid in order to recover indium [11]. The leachate is then treated with ion exchangers to separate indium from other metallic impurities. Best results are obtained with Lewatit VP OC 1026, a D2EHPA impregnated resin, and the corresponding metal elution is carried out with HCl solutions. Lewatit TP 208 was impregnated with different extractants to enhance its properties in the removal of indium from diluted solutions [12]. The impregnation of the resin with D2EHPA and Cyanex 272 (organic alkyl fosfinic acid derivative), not only improves the selective indium recovery but also the resin capacity was increased approximately two times. The resin impregnated with Cyanex 272 presented the best results with respect indium uptake onto the resin and elution.

iv) membranes: A bipolar membrane electrodialysis (BPED) using ethylenediaminetetraacetic acid (EDTA) as a chelating agent is used to separate indium(III) from aluminium(III) [13]. I.n the above medium, indium forms the anionic complex InY^- (Y represents the chelating agent), whereas aluminium is present as Al^{3+}.

With respect to ionic liquids, much has been written about this compounds and uses, Just remember that the term of ionic liquids included those chemicals, composed only by ions (anion and cation), which are liquids at temperatures below 100º C. A special case of these compounds was the pseudo-protic ionic liquids (PPILS) formed from tertiary amines [14,15]. Due to their properties, ionic liquids are considered as *green solvents,* however, some authors questioned against some of these properties, i.e. stability [16].

The aim of the present work is to estimate parameters to optimize performance of a flat-sheet supported liquid membrane, impregnated with $TOAH^+Cl^-$ and $TODAH^+Cl^-$ PPILs, in the active transport of indium(III) from HCl solutions. Different experimental variables are evaluated in the transport of indium(III) by these carriers, and from the experimental data, diffusional parameters are calculated for both systems: In(III)-HCl-$TOAH^+Cl^-$ and In(III)-HCl-$TODAH^+Cl^-$.

2. Materials and methods

2.1. Materials

The precursors for the generation of the PPILs was the tertiary amines Hostarex A324 and Hostarex A327 (Sanofi), Hostarex A324 was formed by tri-octyl amine (TOA), whereas Hostarex A327 was composed by a 50% mixture of tri-octyl and tri-decyl amines (TODA). The reagents was diluted in Solvesso 100 (aromatic diluent, Exxon Iberia)) in order to adequate the range of amine concentrations, and thus, of the ionic liquid to the indium transport experiments. The corresponding PPILs $TOAH^+Cl^-$ and $TODAH^+Cl^-$ were formed by contacting the organic phase (amine and diluent) with the adequate HCl solutions. After equilibrium, the ionic liquids were formed, in the organic phase, accordingly to the next equilibrium [17,18]:

$$R_3N_{org} + H^+_{aq} + Cl^-_{aq} \Leftrightarrow R_3NH^+Cl^-_{org} \tag{1}$$

where the subscripts org and aq represented to the respective organic and aqueous phases. For both amines the percentage of conversion to the pseudo-protic ionic liquid exceeded 99%. The use of an organic diluent, as Solvesso 100, was recommended due that it allowed i) to adequate the range of carrier concentrations to the investigation, and ii) to decrease the viscosity of the ionic liquid and thus, to reduce the resistance to transport due to the organic phase.

A 1 g/L indium(III) stock solution was prepared by dissolving an indium salt (Fluka) with distilled water. All the chemicals used in the experimentation, except the amines and Solvesso 100, were of A.R. grade. The solid support used in the present work was Millipore Durapore GVHP4700 (polyvinylidene fluoride) of 75% porosity, 1.67 tortuosity and 12.5×10^{-3} cm thickness.

2.2. Methods

Transport experiments were performed in a two compartment cell, consisting of a feed phase (200 cm^3) separated from the receiving phase (200 cm^3) by the membrane support. The effective membrane area for the transport experiments was of 11.3 cm^2. Both feed and receiving phases were mechanically stirred by four blades glass impellers (2.5 cm diameter), at 20º C, to avoid concentration polarization conditions at the support interfaces and in the bulk of both phases.

The supported liquid membrane was prepared by impregnation of the solid support, with the corresponding organic phase, by immersion for 24 h and then left to drip for 20 seconds before placed it in the membrane cell. Previous tests demonstrated that extended immersion times did not influence indium transport.

doi:10.20944/preprints202211.0337.v1

The percentage of indium transported, from the feed phase to the membrane phase, was determined by monitoring the metal concentration in the feed phase at elapsed times by atomic absorption spectrometry (Perkin Elmer 1100B spectrophotometer), and using the next relationship:

$$\%T = \frac{[In]_{f,0} - [In]_{f,t}}{[In]_{f,0}} x100 \qquad (2)$$

where $[In]_{f,0}$and $[In]_{f,t}$ were the indium concentrations in the feed phase at time zero and at elapsed time, respectively.

In the cases in which the permeation coefficient (P) value was needed, it was calculated by the next equation::

$$\ln \frac{[In]_{f,t}}{[In]_{f,0}} = -\frac{A}{V} Pt \qquad (3)$$

where A was the membrane area, V was the volume of the feed phase, and t represented the elapsed time.

3. Results and discussion

The transport of indium(III) across the membrane containing the ionic liquid phase can be described by applying Fick´s first diffusion law to the diffusion layer at the feed phase side, to the membrane phase, and to the receiving phase, however, this last contribution is often negligible compared with that at the feed phase side since the distribution coefficient of indium(III) between the membrane and the receiving phases uses to be much lower than the value between the feed and the membrane phases. Figure 1 shows the concentration profiles of indium(III) and the pseudo-protic ionic liquidsdiss olved in Solvesso 100, across the supported liquid membrane. Accordingly, in the transport of indium(III) the driving force was the difference in acidity between the feed and receiving phases.

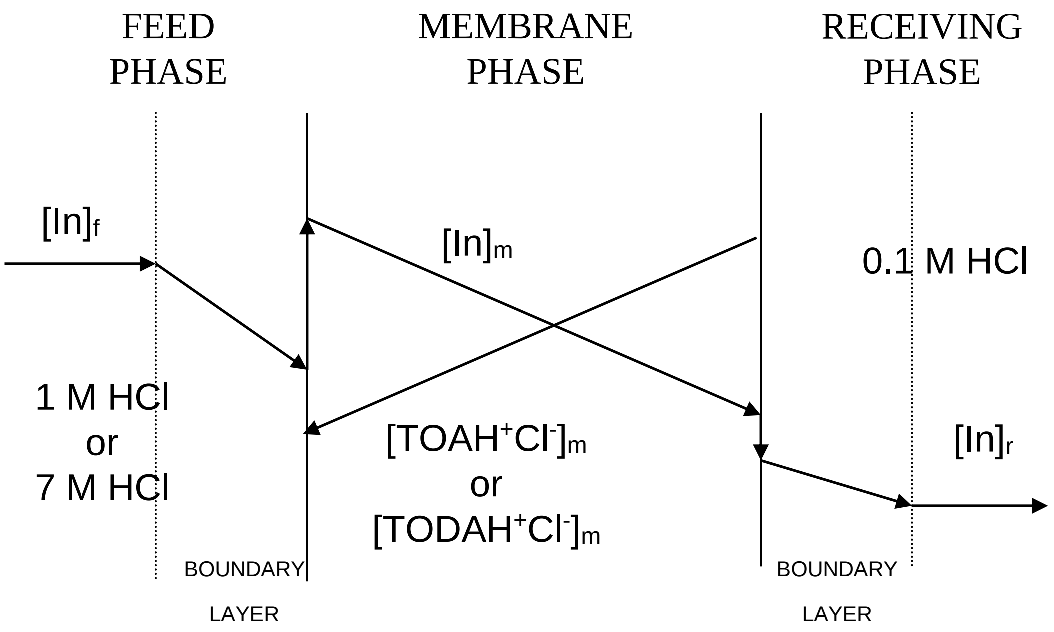

Figure 1. Concentration profiles of indium and PPILs species across the supported liquid membrane.

3.1. The system In(III)-TOAH⁺Cl⁻

3.1.1. Influence of stirring speeds in the feed and receiving phases

A series of experiments were carried out to establish adequate hydrodynamic conditions both in the feed and the receiving phases. The transport of indium(III) across the supported liquid membrane was dominated by diffusional resistances which were of two types: i) the resistance associated to the feed phase boundary layer, and ii) the resistance associated to the membrane support. It was not rare that the magnitude of the first competed with the value of the support resistance [19]. Experimental conditions and results obtained were shown in Table 1.

Table 1. Influence of the stirring speed in the feed phase on indium transport.

Stirring speed (min^{-1})	**Percent transport (%)**
375	64
500	73
750	83
1000	63
1500	47

Feed phase: 0.01 g/L In(III) in 1 M HCl. Membrane phase: 10% v/v $TOAH^+Cl^-$ in Solvesso 100 supported on GVHP4700. Receiving phase: 0.1 M HCl. Stirring speed: 500 min^{-1}. Temperature: 20º C. Time: 3 hours

Maximum metal transport was obtained at 750 min^{-1} and then decreased. At this 750 min^{-1}, the thickness of the feed phase diffusion layer and the aqueous resistance to mass transfer were minimized, and the diffusion contribution of the aqueous species to the mass transfer phenomena was considered constant. At stirring speeds above 750 min^{-1} the percentage of indium transport decreased, being this situation attributable to an increment in the turbulence caused by the stirring speed which also resulted in a probable displacement of the carrier phase from the support. The value of the maximum percentage of indium transport (83%) corresponded to a limiting permeability (P_{lim}) value defined as:

$$P_{lim} = \frac{D_{aq}}{d_f} \tag{4}$$

where D_{aq} represented the value of the aqueous diffusion coefficient with an estimate value of 10^{-5} cm^2/s, and d_f was considered the minimum thickness of the feed aqueous layer. According with eq. (3), P_{lim} was calculated as $3.0 \cdot 10^{-3}$ cm/s, and thus, d_f value was estimated as $3.3 \cdot 10^{-3}$ cm.

The variation of the stirring speed in the receiving phase (500 to 750 min^{-1}) had a negligible influence on the variation of the percentage of metal transport. In the case of the receiving phase, and if the stirrer in the half-cell was very close to the membrane support, the thickness of the boundary layer was considered to be minimized and the resistance in this side can be neglected [20]. Thus, stirring speeds of 750 and 500 min^{-1} were used in the feed and the receiving phases, respectively.

3.1.2 .Influence of HCl concentration in the feed phase

Experiments were performed using organic phases of the ionic liquid dissolved in Solvesso 100 and feed phases of 0.01 g/L In(III), which also contained different HCl concentrations and Table 2 showed the results obtained. It can be seen that the presence of HCl in the feed phase tended to increase the percentage of indium transport up to 1-2 M HCl concentrations in this phase, and then decreased for higher HCl concentrations. At a first instance, this decrease can be attributed to the increase of the ionic strength in the aqueous medium.

3.1.3 Influence of carrier concentration in the membrane phase

The variation in the percentage of indium transport at various carrier concentrations was shown in Figure 1. The experiments were carried out with organic phases of 2.5% v/v-40% v/v ionic liquid in Solvesso 100, and feed phases of 0.01 g/L In(JJJ) and 1 M HCl.

Table 2. Influence of the HCl concentration on indium transport

HCl (M)	**Percent transport (%)**
0.5	25
0.75	50
1	83
2	83
4	68
6	60

Membrane phase: 10% v/v $TOAH^+Cl^-$ in Solvesso 100 supported on GVHP4700. Receiving phase: 0.1 M HCl. Temperature: 20º C. Time 3 hours

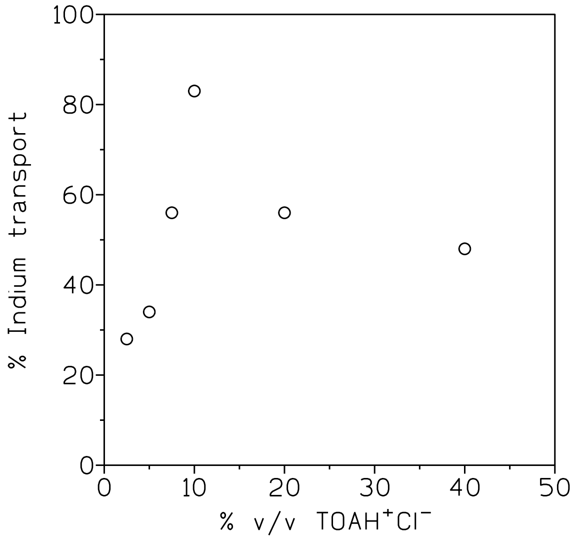

Figure 2. Influence of $TOAH^+Cl^-$ concentration on the transport of indium. Membrane support: GVHP4700. Receiving phase: 0.1 M HCl. Temperature: 20º C. Time: 3 hours

The results obtained showed that increasing the carrier concentration, from 2.5% v/v to 10% v/v, in the membrane phase increased the percentage of indium transport, however from 10% v/v this percentage decreased, this probably being attributable to the increase of the viscosity of the organic phase, and as a consequence, an increase of the membrane resistance to indium transport.

3.1.4. Influence of the initial indium concentration in the feed phase

Figure 3 showed the variation in the percentage of indium transport versus the initial concentration of indium, ranging from 0.01 to 0.1 g/L, in the feed phase side. It can be observed that within the present experimental conditions, the percentage of metal transport decreased with the increase of the initial indium concentration in the feed phase. This behaviour was attributable to the grown population effect due to the increase of the metal concentration in the solution [21]. Also, the increase of indium concentration in the feed phase resulted in the saturation of the membrane and thus, to a lower effective membrane area, and to the retention of the metal-ionic liquid species on the entry side of the feed-membrane sites. All together caused a decrease in indium transport

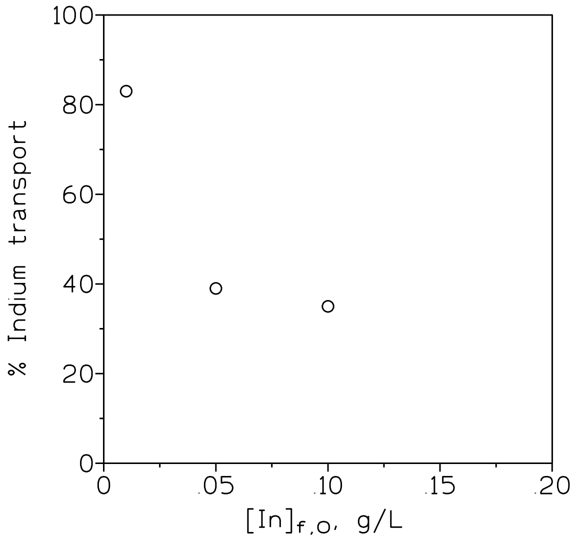

Figure 3. Influence of initial indium concentration on metal transport. Feed phase: indium and 1 M HCl. Membrane phase: 10% v/v $TOAH^+Cl^-$ in Solvesso 100 supported on GHVP4700. Receiving phase; 0.1 M HCl. Temperature: 20º C. Time: 3 hours

3.2. The system In(III)-$TODAH^+Cl^-$

Previous liquid-liquid extraction experiments demonstrated that, with this ionic liquid, maximum indium(III) extraction was obtained at 6-8 M HCl concentrations in the aqueous solution. Thus, indium transport experiments were carried out using 7 M HCl concentration in the feed solution.

3.2.1 .Influence of stirring speed in the feed and receiving phases

Firstly, it was investigated the variation of the stirring speed in the feed phase maintaining that of the receiving phase constant at 500 min^{-1}. Results from these series of experiments were shown in Table 3.

It can be seen that the percentage of indium(III) transport increased up to 800-1000 min^{-1}, indicating that at these stirring speeds the thickness of the feed boundary layer reached a minimum and metal transport maximized. At higher stirring speeds, i.e. 1200 min^{-1}, the percentage of transport decreased, being this decrease attributable to the same effect than that described in subsection 3.1.1.

Taking into consideration eq.(4), and being in the present case P_{lim} calculated as $2.3\cdot10^{-3}$ cm/s, the minimum thickness of the feed layer was calculated as $4.3\cdot10^{-3}$ cm for the system In(III)-$TODAH^+Cl^-$.

Using the same experimental conditions of Table 3, and a stirring speed of 850 min^{-1} in the feed phase, while the stirring speed applied on the receiving phase was varied in the 500-750 min^{-1} range, the results showed that this variation had a minor effect on the percentage of indium transport across the supported liquid membrane. Thus, stirring speeds of 850 min^{-1} and 500 min^{-1} were used throughout the experimentation in the feed abd receiving phases, respectively.

Table 3. Influence of the stirring speed on indium transport

Stirring speed (min^{-1})	**Percent transport (%)**
600	55
800	77
1000	77
1200	66
1500	60

Feed phase: 0.01 g/L In(III) and 7 M HCl. Membrane phase: 10% v/v TODAH$^+$Cl$^-$ in Solvesso 100 supported on GHVP4700. Receiving phase: 0.1 M HCl. Temperature: 20º C. Time: 3 hours

3.2.2. Influence of carrier concentration on indium transport

Figure 4 represented the results obtained in this investigation about the effect of TODAH$^+$Cl$^-$ concentration on indium transport. The feed phase contained 0.01 g/L In(III) and 7 M HCl, whereas the corresponding organic phases were of 2.5% v/v-20% v/v ionic liquid in Solvesso 100.

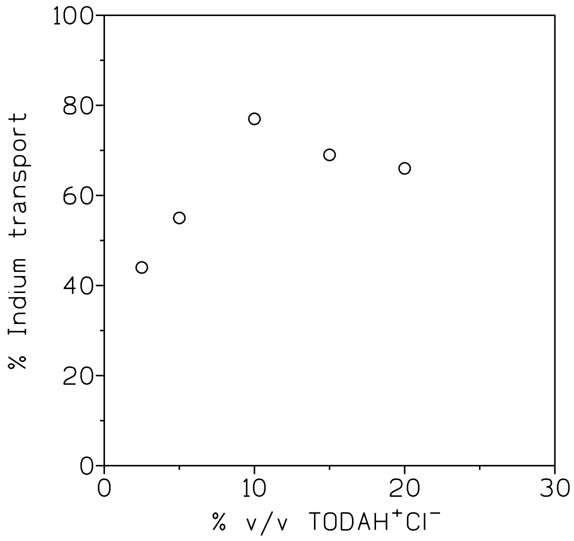

Figure 4. Influence of TODAH$^+$Cl$^-$ concentration on the transport of indium across the supported liquid membrane. Membrane support: GVHP4700. Receiving phase: 0.1 M HCl. Temperature: 20º C. Time. 3 hours

From these results, it was shown that the percentage of indium transport increased with the increase of the carrier concentration, up to 10% v/v, in the organic phase immobilized on the GVHP4700 support. At carrier concentrations higher than 10% v/v, a slight decrease in metal transport was observed, this probably due to an increase in the viscosity of the organic phase, that as it was mentioned before, resulted in an increase of membrane resistance to transport.

3.2.3 .Effect of initial indium concentration in the feed phase on metal transport

The influence of the initial indium concentration on the percentage of indium transport by TODAH$^+$Cl$^-$ was investigated. This study was performed using feed phases that contained various indium concentrations in 7 M HCl and organic phases of 10% v/v carrier in Solvesso 100.

Table 4. Influence of initial metal concentration on indium transport

Initial indium(III) concentration (g/L)	Percent transport (%)
0.01	77
0.05	69
0.1	58
0.2	50

Membrane support: GVHP4700. Receiving phase: 0.1 M HCl. Temperature: 20º C. Time: 3 hours

The results were resumed in Table 4, in which it was shown that the maximum percentage of metal transport was obtained with the feed phase containing the lowest initial indium concentration, being this percentage continuously decreasing as the initial metal concentration in this feed phase increased. These results can be explained due to the same effects than that described in subsection 3.1.4.

3.3. Modeling of metal transport: estimation of the diffusional parameters

3.3.1. The system In(III)-TOAH$^+$Cl$^-$

It was described [22], that at 1 M HCl the predominant indium(III) species in aqueous solution was InCl$_3$, thus, the extraction (transport) of this metal can be expressed by the reaction:

$$\mathrm{TOAH^+Cl^-_{org}} + \mathrm{InCl_{3_{aq}}} \Leftrightarrow \mathrm{TOAH^+InCl^-_{4_{org}}} \quad (5)$$

being representative of an ion-pair extraction (transport) mechanism. The extraction constant relative to the above equilibrium can be expressed as:

$$\mathrm{K} = \frac{\left[\mathrm{TOAH^+InCl_4^-}\right]_{\mathrm{org}}}{\left[\mathrm{TOAH^+Cl^-}\right]_{\mathrm{org}}\left[\mathrm{InCl_3}\right]_{\mathrm{aq}}} \quad (6)$$

being the subscripts org and aq representatives of the organic phase (membrane phase) and aqueous phase (feed phase), respectively.

If the same assumptions than those described in the literature [23] were followed, an expression such as:

$$\mathrm{P} = \frac{\mathrm{K}\left[\mathrm{TOAH^+Cl^-}\right]_{\mathrm{m}}}{\Delta_{\mathrm{m}} + \Delta_{\mathrm{f}}\left(\mathrm{K}\left[\mathrm{TOAH^+Cl^-}\right]_{\mathrm{m}}\right)} \quad (7)$$

this expression combining both the equilibrium and diffusion parameters involved in the transport of In(III) from 1 M HCl solution across a membrane support containing this ionic liquid dissolved in Solvesso 100. In this eq. (7), m represented the membrane (organic phase) and f to the feed (aqueous phase).

Rearranging the above expression, the next relationship resulted:

$$\frac{1}{\mathrm{P}} = \Delta_{\mathrm{f}} + \Delta_{\mathrm{m}}\frac{1}{\mathrm{K}\left[\mathrm{TOAH^+Cl^-}\right]_{\mathrm{m}}} = \Delta_{\mathrm{f}} + \Delta_{\mathrm{m}}\frac{1}{\mathrm{Z}} \quad (8)$$

where Δ_f and Δ_m were the mass transfer resistances due to the feed and the membrane phase, respectively. At various concentrations of the ionic liquid, a plot of 1/P versus 1/Z may result in a straight line with ordinate to calculate Δ_f and slope of Δ_m. These values were of 177 s/cm and 1.1 s/cm for Δ_f and Δ_m, respectively.

The membrane diffusion coefficient (D_m) can be calculated accordingly to the next expression::

$$D_m = \frac{d_m}{\Delta_m} \tag{9}$$

was estimated as $1.1 \cdot 10^{-2}$ cm²/s, considering Δ_m= 1.1 s/cm and the thickness of the membrane support, d_m, as $12.5 \cdot 10^{-3}$ cm.

The diffusion coefficient of the indium(III)-ionic liquid species in the bulk organic phase is estimated using the next relationship [24]:

$$D_{b,m} = D_m \frac{\tau^2}{\varepsilon} \tag{10}$$

where τ is the membrane tortuosity (1.67) and ε is the support porosity (75%), thus, $D_{b,m}$ is estimated as $4.1 \cdot 10^{-2}$ cm²/s.

The diffusion coefficient in the bulk organic phase presented a greater value than the diffusion coefficient being this attributable to the diffusional resistance caused by the support thickness separating the feed and receiving solutions.

Considering that the ionic liquid concentration in the membrane support is constant, the apparent diffusion coefficient for gold (III) can be calculated as:

$$D_m^a = \frac{J d_m}{\left[R_3NH^+Cl^-\right]} \tag{11}$$

using a 10% v/v (0.23 M) ionic liquid concentration and being d_m $12.5 \cdot 10^{-3}$ cm, this apparent diffusion coefficient has the value of $1.4 \cdot 10^{-8}$ cm²/s.

Finally, the mass transfer coefficient in the feed phase (Δ_f^{-1}) can be calculated as $5.6 \cdot 10^{-3}$ cm/s.

3.3.2. The system In(III)-TODAH$^+$Cl$^-$

In a 7 M HCL medium the predominant indium(III) species was $InCl_4^-$ [22], thus, the transport of the metal can be represented by the next reaction:

$$TODAH^+Cl^-_m + InCl^-_{4_f} \Leftrightarrow TODAH^+InCl^-_{4_m} + Cl^-_f \tag{12}$$

being in this case, representative of an anion exchange mechanism, and the corresponding extraction constant as:

$$K = \frac{\left[TODAH^+InCl_4^-\right]_m \left[Cl^-\right]_f}{\left[TODAH^+Cl^-\right]_m \left[InCl_4^-\right]_f} \tag{13}$$

Similarly to was described in subsection 3.3.1., an expression which combined both diffusional and equilibrium parameters involved in indium(III) transport can be written as:

$$P = \frac{K\left[TODAH^{+}Cl^{-}\right]_{m}\left[Cl^{-}\right]_{f}^{-1}}{\Delta_{m} + \Delta_{f}\left(K\left[TODAH^{+}Cl^{-}\right]_{m}\left[Cl^{-}\right]_{f}^{-1}\right)} \tag{14}$$

and:

$$\frac{1}{P} = \Delta_{f} + \Delta_{m}\frac{1}{K\left[TODAH^{+}Cl^{-}\right]_{m}\left[Cl^{-}\right]_{m}^{-1}} = \Delta_{f} + \Delta_{m}\frac{1}{Z} \tag{15}$$

being Δ_f and Δ_m calculated from the corresponding plot of 1/P and 1/Z. In the present system, the values were 420 s/cm and 10200 s/cm for the resistances due to the feed phase (Δ_f) and the membrane (Δ_m), respectively.

Following the same series of equations than in subsection 3.3.1., the values of the various diffusional parameters involved in the transport of indium(III) by $TODAH^{+}Cl^{-}$ pseudo-potric ionic liquid were resumed in Table 5.

Similarly to that described in subsection 3.3.1., the value of the diffusion coefficient in the bulk membrane phase was greater than the value of the membrane diffusion coefficient.

Table 5. Diffusional parameters in the In(III)-$TODAH^{+}Cl^{-}$ system

Parameter	Value
Membrane diffusion coefficient (D_m)	$1{,}2\cdot10^{-6}$ cm²/s
Diffusion coefficient in the bulk membrane ($D_{b,m}$)	$4.5\cdot10^{-6}$ cm²/s
Apparent diffusion coefficient in the membrane (D_m^a)	$1.2\cdot10^{-8}$ cm²/s
Mass transfer coefficient in the feed phase (Δ_f^{-1})	$2.3\cdot10^{-3}$ cm/s

Values at the maximum indium transport at 7 M HCl in the feed phase

4. Conclusions

From the experimental data obtained from this work, it is shown that the pseudo-protic ionic liquids $TOAH^{+}Cl^{-}$ and $TODAH^{+}Cl^{-}$ can be used as carriers for indium(III) membrane transport from hydrochloric acid solutions.

For both carriers, the transport of indium is influenced by a number of variables, such as the stirring speed applied on the feed phase, and metal and carrier concentrations. In the case of $TOAH^{+}Cl^{-}$ the variation of the HCl concentration in the feed phase also influenced the transport of this strategic metal. Also for both carriers, at carrier concentrations of 10% v/v in Solvesso 100, a maximum in indium(III) transport is obtained, under this condition the transport process is controlled by diffusion in the feed phase boundary layer; at carriers concentrations lower than 10% v/v membrane diffusion controlled the overall indium(III) transport.

Though with both ionic liquids, the driving force for indium transport is the difference in the acidities between the feed and receiving phases, based in the HCl concentration in the feed phase, the facilitated transport mechanism for indium differs from one ionic liquid to the other. At 1 M HCl concentration in the feed phase, metal is transported by an ion pair mechanism, and formation of $TOAH^{+}InCl_4^{-}$ complex in the membrane phase. At 7 M HCl and using $TODAH^{+}Cl^{-}$ as carrier, the complex formed in the membrane phase has the same stoichiometry, but the transport mechanism corresponded to an anionic exchange between $InCl_4^{-}$ of the feed phase and the chloride ions of the carrier, thus these chloride ions are released to the feed phase.

Various diffusional parameters are calculated for both In(III)-$TOAH^{+}Cl^{-}$ and In(III)-$TODAH^{+}Cl^{-}$ systems.

Author Contributions: Conceptualization, F.J.A.; Methodology, F.J.A.;F.A.L.; Investigation, F.J.A., F.A.L.; Writing-Original Draft Preparation, F.J.A.; Writing-Review & Editing, F.J.A., F.A.L.; Supervision, F.A.L.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: Authors are grateful to Interdisciplinary Platform for Sustainable Plastics towards a Circular Economy (PTI-SUSPLAST,CSIC).

Conflicts of Interest: The authors declare no conflict of interest

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