



Ionic liquids as a carrier for chloride reduction from brackish water using hollow fiber renewal liquid membrane



Agustin Fortuny*, Maria Teresa Coll, Ana Maria Sastre

EPSEVG, Universitat Politècnica de Catalunya, Chemical Engineering Dep, Av. Victor Balaguer, 1, 08800 Vilanova i la Geltru, Spain

HIGHLIGHTS

- Different ILs were successfully used as ion-exchange extractants to reduce the chloride in water.
- Equilibrium constants have been obtained.
- The reversibility of the $\text{Cl}^-/\text{HCO}_3^-$ interchange process has been verified.
- The ILs show a promising behavior with SLM.
- This technique could be applied to exchange any other anion present in aqueous solutions.

ARTICLE INFO

Article history:

Received 25 July 2013

Received in revised form 21 October 2013

Accepted 24 October 2013

Available online 22 November 2013

Keywords:

Chloride reduction

Ammonium and phosphonium ionic liquid

Supported liquid membrane

Hollow fiber renewal liquid membrane

ABSTRACT

High concentration of chloride ions in continental water is a great problem for the exploitation of these natural resources. In industry, the use of this water involves additional conditioning steps. For drinking water and irrigation uses, the Cl^- must be reduced by conventional water treatment processes, like ion exchange or reverse osmosis, but for large scale production these techniques could be very expensive due to resin regeneration or energy costs. The possibility of using supported liquid membranes (SLM) with ionic liquids (IL), Aliquat 336, Cyphos IL 101 and Cyphos IL 167, as carriers to exchange Cl^- for HCO_3^- anion has been shown to work. The reversibility of this anion exchange was corroborated by solvent extraction experiments and implemented in flat sheet supported liquid membrane (FSSLM) and hollow fiber renewal liquid membrane technologies (HFRLM). About double transport values have been obtained in HFRLM compared to SLM and 1 h is the time enough to reduce the chloride concentration up to 250 mg/L using HFRLM at the best experimental condition. The results obtained allow us to be optimistic about the implementation of this technology on a large scale to chloride reduction in drinking water when the source is inadequate for direct use.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Because water is the main solvent in nature, the presence of different species in ground water is very variable and its quality is dependent on the climate and geological factors. Salinity in continental waters is one of the most serious problems in many places on the planet, making it unsuitable for irrigation or as a source for potabilization treatment plants.

In the conventional processes to produce drinking water chloride is not eliminated. For this reason, when brackish water is used, it is necessary to apply other additional processes to achieve the limit (250 mg/L) established by the 98/83/EC Directive.

Reverse osmosis, electrodialysis and membrane distillation are the most generalized processes to reduce salts from seawater (about 35,000 mg/L) and from brackish (500–30,000 mg/L) water. All these

processes use energy to produce adequate water and the associated energetic cost is considerable. Of course more efficient membrane designs [1], inclusion of the energy saving steps [2], utilization of renewable energies [3–5], emerging adsorption methods [6,7], etc. have been applied to improve the profitability of plant operations.

When the concentration of salts in the water is lower than in the above cases, like some river water with chloride concentration less than 1000 mg/L, processes based on chemical separation may be able to reduce the chloride content. The advantage of these technologies is their low energetic requirements [8]. Ion exchange membranes [9] and other membrane processes like those shown in this work are examples of this tendency.

Liquid membrane technologies are an attractive alternative for chloride reduction in salty water; it allows simultaneous extraction and stripping processes in the same stage, non-equilibrium mass transfer, high selectivity and low solvent consumption.

In this study, we have worked with extraction using supported liquid membranes (SLM) to reduce the chloride concentration in water

* Corresponding author. Tel.: +34 938967754; fax: +34 938967700.
E-mail address: agustin.fortuny@upc.edu (A. Fortuny).

up to the specification for drinking water chloride contents. To achieve this goal, ammonium and phosphonium based ionic liquids have been used as a carrier.

Ionic liquids (ILs) are compounds with an organic cation and either organic or inorganic anions. They are very interesting because they remain liquid over a wide temperature range including room temperature. The greatest advantage of the ILs is their practically zero vapor pressure compared with the commonly used volatile organic solvents. Actually the ILs can be designed for specific proposals, and their applications are extended to different fields: media for green synthesis [10–12], CO₂ capture [13–18], removal of fermentation products [19,20] and pharmaceuticals [21], and as solvents or extractants for liquid–liquid extraction [21–25] and hence, for supported liquid membrane processes [26].

This work proposes an alternative solution to chloride ion reduction from brackish water. The aim of this paper is to investigate the ability of hollow fiber renewal liquid membrane technique use to desalt ground and superficial brackish water for drinking and irrigation purposes.

2. Experimental

2.1. Reactants

Quaternary ammonium salt, Aliquat 336 (methyl trioctyl/decyl amine) and two other phosphonium ionic liquids, Cyphos IL 101 (triethyl(tetradecyl)phosphonium chloride) and Cyphos IL 167 (tributyl(tetradecyl)phosphonium chloride), supplied by Cytec Industries Inc., were mixed with 10% decanol/kerosene (v/v) and used as extractants in liquid extraction or as a carrier in the liquid membrane experiments. A mixture of 10% decanol/kerosene (v/v) was the diluent used to prepare the organic phase.

Water with 1 g NaCl/L has been used in the experiments because it is one of the most commonly found concentrations.

Stock solution was prepared dissolving the adequate amount of NaCl in distilled water. The stripping solution used was NaHCO₃. All the used reagents were analytical reagent grade.

2.2. Determination of the chloride concentration

The concentration of Cl[−] in the samples was determined by titration with AgNO₃ using the potentiometric method. The potential has been measured using a Ag Ag/AgCl Crison 5260 electrode.

The AgNO₃ standard solution 0.02 M was previously standardized with a solution of 0.028 M NaCl (1000 mg/L Cl[−]). The experimental error did not exceed 2%.

2.3. Liquid–liquid extraction

The anion exchange mechanism by liquid–liquid extraction between the Cl[−] in the water and the HCO₃[−] in the ionic liquid molecules (E⁺HCO₃[−]) allows us to determine the viability of this operation.

The liquid–liquid extraction by anion exchange was carried out in typical glass separatory funnels. Equal volume of the aqueous phase containing 1000 mg/L of Cl[−] was mechanically shaken with the corresponding liquid ionic (R₄N⁺HCO₃[−]) phase in an SBS horizontal shaker at 140 rpm for 20 min at room temperature (21 ± 1 °C). After separation of the phases, an aliquot of the aqueous phase was taken for chloride concentration analysis and the loaded organic phase was stripped with 0.9 M of NaHCO₃ solution.

Measuring the Cl[−] concentration before and after the contact made it possible to determine the extraction extension. The concentration of Cl[−] in the stripping samples allows us to balance the mass and in this way corroborate the results.

2.4. R₄NHCO₃ and R₄PHCO₃ preparation

Preliminary conditioning of Aliquat 336, Cyphos IL 101 and Cyphos IL 167 (ECl) by contact with a NaHCO₃ solution allows us to generate the EHCO₃ molecule. A generalized chemical reaction associated with this exchange could be:



where E is the cationic part of each ionic liquid: (R₄N⁺ or R₄P⁺) and the bar denotes the compound present in the organic phase.

These new species provide us with the possibility to carry out the anion exchange between Cl[−] and HCO₃[−]. In this sense, successive contacts between the ILs, at different concentrations, and fresh solutions of NaHCO₃ 0.9 M have been done. The aqueous phase was completely replaced after each step and the concentration of chloride anion was measured to know the remaining Cl[−] in the organic phase. High concentration of HCO₃[−] compared to IL concentration was used to assure maximum exchange in each step.

2.5. FSSLM transport

The flat sheet supported liquid membrane (FSSLM) is the simplest form of the liquid membrane. The support in FSSLM, as is well-known, must be on a porous and hydrophobic material, with good thermal stability and high chemical resistance to the organics used. The experimental setup consists of two acrylic cylindrical compartments, feed cell and receiving cell, with the hydrophobic support placed in between. Both aqueous solutions were mixed by mechanical stirrers. The support membrane was previously impregnated with the ionic liquid to be used as a carrier. Table 1 gives the characteristics of the polymeric support provided by Millipore.

The feed cell was filled with 210 mL of the solution of sodium chloride and the stripping cell with 210 mL of sodium bicarbonate solution. Chloride ions from the feed phase are exchanged with the HCO₃[−] of the membrane; this process takes place in the feed–membrane interphase. After that, the ionic liquid loaded with Cl[−] anions crosses the membrane by a diffusional process. Finally, on the membrane–stripping interphase the reverse exchange Cl[−]/HCO₃[−] occurs. In this way, chloride anions are continuously removed from the feed.

Samples from feed and receiving phases were withdrawn at regular time intervals, and the evolution of the Cl[−] concentrations was quantified.

2.6. HFRLM transport

Hollow fiber modules give a better ratio area transfer/volume. However, not all hollow fiber membrane technologies are appropriate for this implementation, because membrane stability is one of the most important problems with this kind of membrane.

The stability of the supported liquid membrane has been improved by using renewal liquid membrane technique, where the diluted ionic liquid used as a carrier is mixed with the stripping solution. While the feed flows along the shell side of the module, the mixture of stripping phase and carrier flows along the lumen side, preventing any loss of organic solution from the membrane pores.

Table 1
Characteristics of the polymeric support Durapore GVHP04700.

Material	PVDF
Pore diameter	45 μm
Porosity	75%
Thickness	125 μm
Effective area	11.4 cm ²

Download English Version:

<https://daneshyari.com/en/article/623544>

Download Persian Version:

<https://daneshyari.com/article/623544>

[Daneshyari.com](https://daneshyari.com)