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Development and characterization of hybrid membranes based on an organic matrix modified with silanes for metal separation

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Abstract

New hybrid membranes for metal ion transport were synthesized with the aim of improving mechanical and chemical stabilities, mean lifetime and loss of carrier. Hybrid organic–inorganic materials present several advantages with respect to organic and inorganic materials considered independently. Organic–matrix membranes usually have limitations related to chemical and thermal stabilities while organosilicone materials may present serious difficulties for film formation. The new membranes proposed here are based on a mixture of organic (cellulose triacetate, CTA) and organosilicone materials (dichlorodimethylsilane and tetraethoxysilane, DDMS and TEOS, respectively) as membrane support. Membrane preparation was optimized varying the amount of metal carrier (bis(2-ethyl hexyl phosphoric acid), D2EHPA) and plasticizer (2-nitrophenyloctyl ether, NPOE and/or tris(2-butoxyethyl)phosphate), TBEP). Total Reflection Infrared Spectroscopy, Scanning Electron Microscopy, Thermogravimetric Analysis, ^{29}Si Nuclear Magnetic Resonance and X-Ray Diffraction were used to characterize the hybrid membranes and to correlate structural properties with permeability values for zinc metal ions.

Keywords: Hybrid membranes; D2EHPA; Plasticizer; Cellulose triacetate; Silanes

1. Introduction

Up to now, numerous types of membranes have been developed for selective metal separation processes from aqueous solutions [1] such as liquid membranes used in facilitated transport separations [2]. In this sense, selective metal ions transport has been thoroughly studied with supported liquid membranes (SLMs), which consist in a polymeric porous support that retains by capillary forces an organic solvent and, usually, an extracting agent [3,4]. Their high selectivity, high diffusion rates and the possibility of ion recovery and concentration make them interesting for environmental applications or for the selective recovery of added value substances [5]. Nevertheless, they are not frequently used for practical separation processes because of their low stability due to the loss of solvent and carrier to the water phases. In order to prevent this degradation, several strategies have been performed to increase their stability [6–8]. As an alternative to SLMs, polymer inclusion membranes (PIMs) [9] and hybrid materials [10,11] have been developed. In PIMs, the carrier is efficiently entrapped in an organic polymeric matrix consisting of a support (cellulose triacetate, CTA or polyvinyl chloride, PVC) and a plasticizer (or a mixture of them) what results in a membrane with improved elasticity and reduced fragility [9,12]. As for, organic–inorganic hybrid materials they have been developed lately as an alternative to overcome those limitations that organic and inorganic materials present independently and their application areas have considerably expanded with current generation of materials used in optoelectronic, ion-conduction, biology, catalysis and membranes [10,13,14]. In this respect, hybrid materials have been used to tailor new materials [15,16] and to prepare a new kind of ion-exchange membranes with great potential [10,17] because they show a positive synergistic effect when compared to the single materials used separately. Organic materials have important limitations associated with mechanical, chemical and thermal stability; however, the flexibility and low cost of polymers make them highly interesting for many applications. On the contrary, although inorganic materials normally do not form films

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properly, some other desirable membrane properties, such as mechanical or thermal resistances are ensured by the inorganic network formed throughout the material. Additionally, they can correctly work in very corrosive environments [1].

Many hybrid materials synthetic procedures are based on hydrolysis and condensation reactions of silanes by the sol–gel route [18,19]. The organically modified silicates present different physical characteristics depending on their chemical composition and the synthetic conditions [20]. According to Judeinstein and Sanchez the sol–gel process could be defined as the formation of inorganic materials mixed in a solvent through the growth of cross-linked metal-oxo-polymers and this growth can be varied by addition of modifiers [21]. Moreover, Brinker and Scherer expand the definition of ceramics to include organically modified materials [18].

In the present work, continuing our research on membrane preparation and their application in the separation of metal ions, a new family of hybrid membranes has been prepared. These membranes maintain the same polymeric matrix structure of PIMs while an organic–inorganic material is entrapped inside the membrane together with the carrier. We study the effects on membrane performance when varying the amounts of carrier, support and plasticizer (nature and concentration). Several analytical techniques (Attenuated Total Reflection Infrared Spectroscopy, Scanning Electron Microscopy, Thermogravimetric Analysis, ^{29}Si Nuclear Magnetic Resonance and X-Ray Diffraction) were applied in order to obtain information about the structural properties. Permeability values of zinc metal ions using D2EHPA as carrier and membranes with one (NPOE) or two (NPOE + TBEP) plasticizers were determined.

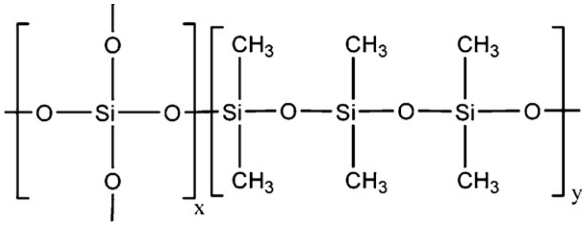
2. Experimental

2.1. Chemicals

Tetraethyl orthosilicate (TEOS) >98% (Merck) and dichlorodimethylsilane (DCDMS) >98% (Merck) were used to obtain the silanes mixture. The plasticizers tested were 2-nitrophenyl octyl ether (NPOE) (Fluka) and tris(2-butoxyethyl)phosphate (TBEP) 94% (Aldrich). Di(2-ethylhexyl) phosphoric acid (D2EHPA) 97% (Aldrich) was used as carrier and cellulose triacetate (CTA) (Aldrich) as organic support.

2.2. Silanes mixture preparation

Silanes fraction was prepared by a multistage synthetic procedure developed in our laboratory [22]. This process involves an accurate control of the hydrolysis–condensation conditions in order to obtain reproducible materials because the species are kinetically unstable [18]. Dichlorodimethylsilane (4 mL) was dissolved in diethyl ether (10 mL); then 1.5 mL of water were added in aliquots of 0.5 mL every 20 min while mixing carefully at 3.33 Hz (200 rpm) in a IKA Yellowline TTS2 vortex during 1 h. At the end, an aqueous phase was distinguishable. Due to the exothermic reaction between DCDMS and water it was necessary to maintain the mixture cold (in an iced water bath) to avoid any undesired reaction that could lead to the production of silica or cyclic tetramer species [18]. Later, both immiscible phases were separated and the leftover water in the organic part was eliminated with Na_2SO_4. In order to obtain a cross-linked network, 1 mL of TEOS was added to the extracted phase. Finally, the obtained homogeneous sol was kept in a water bath during five days at 50 °C. Accordingly to the synthetic procedure here described, the general obtained structure should be that which is presented in Scheme 1.



Scheme 1.

2.3. Hybrid membranes preparation

For membrane samples preparation, different amounts of CTA, plasticizer or plasticizers and carrier were dissolved in chloroform. The carrier contained in the membrane (D2EHPA) is an organophosphorous derivative with plasticizing properties that shows a high compatibility with cellulose triacetate and good transport properties for zinc ions in both liquid–liquid and membrane extractive procedures [23,24]. After complete dissolution of the components, the silanes mixture prepared as described above was added to obtain the hybrid membrane casting solution. For each membrane sample, the whole mixture was vigorously stirred to merge the components homogeneously and the mixture was poured into a Petri dish to carry out the evaporation at room temperature using a method previously reported for PIM fabrication [25]. Finally, the prepared membranes were cured in an oven at 80 °C during 20 h. The side of the membrane exposed to the air during the evaporation was the one used to face the feed solution containing the metal ion in the transport experiences.

2.4. Hybrid membranes characterization

Membrane thickness was measured with an electronic digital micrometer and corroborated with the Scanning Electron Microscopy images obtained with a Jeol JSM-840 instrument. For this technique, the samples were coated at room temperature with graphite by sputtering and fixed to the microscope metal stubs with colloidal silver. A complementary technique (Energy Dispersion Spectroscopy, EDS) was used to identify different elements present in the membrane.

Attenuated Total Reflection spectra were recorded by means of a Bruker Tensor 27 and with a Perkin-Elmer Spectrum GX FTIR spectrometer. Both were used for the acquisition of FTIR spectra using the manufacturer's software together with an ATR accessory (DuraSampl IR II from SensIR Technologies). Measures were taken in a wave number range from 600 to 4000 cm^{-1} and analyzed using commercial software.