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Structural effects on metal ion migration across polymer inclusion membranes: Dependence of transport profiles on nature of active plasticizer

Eduardo Rodríguez de San Miguel*, Julio César Aguilar, Josefina de Gyves

Departamento de Química Analítica, Facultad de Química, UNAM, Ciudad Universitaria, 04510 México, D.F., Mexico

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Abstract

Structural modifications promoted by the nature of the plasticizer that affect metal ion migration in polymer inclusion membranes (PIMs) were evaluated using transport data, transmission infrared mapping microspectroscopy (TIMM) and electrochemical impedance spectroscopy (EIS). An analysis of the effects of different plasticizers on indium(III) transport across cellulose triacetate membranes with bis(2,4,4-trimethylpentyl)phosphinic acid (CYANEX 272) as carrier revealed differences in transport profiles that can be explained on the basis of the nature of plasticizer used. While a transport profile of the type carrier-diffusion was observed for tris(2-ethylhexyl)phosphate (TEHP), a transport profile of the type chained-carrier with reduced mobility was suggested by the presence of a percolation threshold for PIMs with tris(2-butoxyethyl)phosphate (TBEP), 2-nitrophenyloctylether (NPOE) and without plasticizer under the experimental conditions used in this work. Accordingly, diffusional equations and percolation theory were used to model permeation and to gain insight into the transport processes occurring in these systems. A correlation between the structural conformation of the PIMs and the transport profiles was successfully achieved using the aforementioned characterization techniques and theoretical frames. Values of the percolation parameters were rationalized considering the distribution of the membrane components observed by TIMM and PIM resistances evaluated by EIS. Membrane behavior for metal extraction was characterized by the determination of the equilibrium constants via solid–liquid extraction experiments. EIS measurements allowed correlating the equilibrium constants with membrane resistances as well.

Keywords: PIM; Plasticizer; Membrane characterization; Transport mechanism; Percolation

1. Introduction

The implementation of solvent extraction (SX) separation methods in membrane-based technologies can be easily performed by the immobilization of an organic extracting phase in a polymeric support [1–3]. Such implementation allows to overcome the use of high inventories of organic solvents, control the interfacial area making easier the scale-up operation, perform extraction and back-extraction simultaneously and reduce energy utilization in industrial processes [3,4]. Supported liquid membranes (SLMs) and polymer inclusion membranes (PIMs) represent two alternatives to immobilize extractants for metal ions using a reduced amount of extracting phase. In the former case, the capillary action of a porous support allows the impregnation of the extractant and the solvent, while in the latter the extractant is contained within the polymeric network of a non-porous support (generally CTA or PVC) in the presence of a plasticizer. Although SLMs using commercial carriers have been extensively studied during the last years [1–3,5], surprisingly, PIMs have not, in spite that they are usually addressed as membranes with long life-time [6] showing extraction capabilities better or at least comparable to those of SLMs [7,8]. Recently, the potential of these PIMs in the separation of small molecules and metal ions has been highlighted [9], and commercial applications of these membranes in the near future are expected, especially if more fundamental research in this area is performed.

Concerning PIM performance optimization, the influence of plasticizer type and viscosity on flux has called the attention of several research groups [10–13]. Other authors have focused on transport mechanisms and several transport mechanisms have

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* Corresponding author. Tel.: +52 55 56223792; fax: +52 55 56223723.
E-mail address: erdsmg@servidor.unam.mx (E. Rodríguez de San Miguel).

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been observed in PIMs: jumping [14], carrier-diffusion [15] and mobile-site jumping [16]. In this concern, recently the hypothesis of coalescence of liquid-phase micro-domains inside PIMs was formulated to clarify the permeation mechanisms of Cd and Pt with two particular carriers, Lasalocid A and Aliquat 336, respectively [17]; however, to the best of our knowledge, no study of the variables that affect transport mechanisms in PIMs has been reported. Furthermore, although backscattering spectrometry, AFM [18], FTIR, X-ray, SEM, DSC, TGA [19–21], TIMM [22], Far-IR, Raman and Fluorescence correlation spectroscopy (FCS) [17] are some of the analytical techniques that have been applied for PIM characterization, the limited number of studies concerning correlations between characterization techniques and theoretical schemes from which it could be possible to explain the interactions between supporting polymer, plasticizer and carrier do not allow a systematic understanding of the role that the different PIM components play in membrane transport in order to facilitate the design of membrane systems for particular applications. With the aim to contribute in membrane performance optimization, in this work, we continue our studies on the characterization of metal ion transport across PIMs [21–23] through the evaluation of the dependence of indium(III) permeability with the nature of membrane plasticizer, using the commercial carrier CYANEX 272, and CTA as support. This system was selected due to the potential use of indium in electronic devices that has increased attention in SX-based methods for its recovery [24]. The influence of membrane composition in metal ion permeability was studied applying diffusional equations and percolation theory, as well as through the evaluation of the extraction equilibrium constants by solid–liquid extraction experiments, and using TIMM and EIS for membrane characterization. The proposed transport models were correlated with the information obtained from the characterization techniques to contribute in the understanding of metal ion transport across PIM systems.

2. Experimental

2.1. Reagents

In_2O_3 A.R. was used to prepare a 1000 mg dm^{-3} stock solution from which the working solutions were prepared by dilution with deionized water. HNO_3 (Fisher A.R.) was used for pH adjustment. CYANEX 272, used mainly as received, has the active component bis(2,4,4-trimethylpentyl)phosphinic acid (87–88%) and was kindly supplied by CYTEC Industries. Cellulose triacetate (CTA, Aldrich), 2-nitrophenyloctylether (NPOE, Aldrich), tris(2-ethylhexyl)phosphate (TEHP, Aldrich), tris(2-butoxyethyl)phosphate (TBEP, Aldrich) and chloroform (Merck) were employed in PIM preparation. Concentrated HCl, HNO_3 and deionized water (MilliQ, 18 MΩ cm) were used to prepare the solutions for transport and EIS experiments.

2.2. Equipments

Metal ion concentrations were determined using F-AAS (3100 Perkin-Elmer spectrophotometer) under the conditions recommended by the manufacturer. The pH of the feed solution was measured using a Metrohm model 620 pH-meter with a combined glass electrode Cole-Palmer 62014. A Perkin-Elmer Spectrum GX FTIR spectrometer coupled with an Autoimage FTIR microscope was used for acquisition of FTIR maps using the manufacturer's software (Autoimage 5.0). A Burrel 75 mechanical shaker was employed for solid–liquid extraction experiments. PIM thicknesses were measured with a Fowler IP54 electronic micrometer. The impedance measurements were carried out under potentiostatic control, at open circuit potentials with a Solartron 1260 frequency analyzer coupled to a Solartron 1287 electrochemical interface. The analysis of impedance data was done using the ZView software from Scribner Associates.

2.3. Procedure

2.3.1. Membrane preparation

PIMs were prepared according to the procedure reported by Hayashita [25], i.e., a weighted amount of CTA was dissolved in 10 cm^3 of chloroform and specific quantities of plasticizer and CYANEX 272 were mixed. The mixture was poured into a glass culture dish (9 cm diameter). After one day at room temperature, cold water was added and the membrane was peeled away from the dish. Membranes prepared in this form were transparent films with average thickness of $4.5 \pm 1.1 \times 10^{-5}$ m. Since it was observed that PIM thickness is controlled by the amount of CTA, independently of the amounts of the other components within the concentration range studied, the mass of the support was maintained constant at 0.1 g for transport and EIS experiments.

The volume fraction of the extractant in the membrane was evaluated as the ratio between the volume of CYANEX 272 added during membrane preparation and the membrane volume (determined by displacement of water using a 25 cm^3 pycnometer).

2.3.2. Solid–liquid extraction experiments

Solid–liquid extraction experiments were carried out by distributing 0.1 mmol dm^{-3} In(III) aqueous solutions (10 cm^3) at pH 1.75–2.1 with membrane phases (19.6 cm^2) of variable composition as reported elsewhere [23]. As for the CYANEX 272, total concentration in the membrane (mmol g^{-1}), the weighted quantity of extractant corrected for purity, was considered to be completely dissolved within the membrane phase. Duplicate experiments were performed at 25 ± 2 °C. The deviation observed was within 5%.

2.3.3. Transport experiments

0.1 mmol dm^{-3} solution of In(III) in HNO_3 (pH 2) and 1 mol dm^{-3} HCl solution were used as the feed and stripping phases, respectively. No metal ion transfer was observed when no extracting reagent was present in the membrane phase. The extraction cell employed [20] shows a plateau region as a function of the stirring speed at rate values higher than 43.982316 rad/s (420 rpm), so that feed and strip solutions stirring rates were adjusted at 68.06787 rad/s (650 rpm) and 62.83188 rad/s (600 rpm), respectively, with the aid of an optical tachometer. The aqueous volume of the compartments was