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Polymer inclusion membranes (PIMs) with the ionic liquid (IL) Aliquat 336 as extractant: Effect of base polymer and IL concentration on their physical–chemical and elastic characteristics

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ABSTRACT

The effect of the base-polymer and carrier concentration on the physical–chemical characteristics of polymer inclusion membranes (PIMs) is investigated. Two typical polymers used to manufacture PIMs have been tested, i.e. poly(vinyl chloride) (PVC) and cellulose triacetate (CTA), and different amounts of the ionic liquid (IL) Aliquat 336, used as extractant, were the PIMs constituents. The resulting PIMs have been characterized using different techniques to provide information on both the surface and bulk material properties. XPS results do not practically show differences in the surfaces of CTA and PVC based membranes with similar Aliquat 336 content, and the total surface coverage for Aliquat 336 concentration higher than 40% (w/w) was obtained, which was also corroborated with the results of contact angle measurements. However, membrane elastic response seems to be strongly dependent on both base-polymer and Aliquat 336 concentration, which affect Young modulus and elongation at break. The IL concentration also increases dielectric constant and the conductivity of the PIMs from both polymers according to impedance spectroscopy results, providing a rather conductive character to both kind of samples for Aliquat 336 content higher than 40% (w/w) (average conductivity around 10^{-3} $(\Omega\ m)^{-1}$). CTA and PVC-based PIMs with Aliquat 336 content around 45% have been used in order to compare the influence of the polymer on the transport of As(V).

1. Introduction

Polymer inclusion membranes (PIMs) constitute a new class of membranes that has been developed for a variety of applications in separation science and chemical sensors. Since the late 1960s, PVC-based membranes containing a polymer, a plasticizer and an ionophore have been used in potentiometric sensors as well as in bulk optical sensors [1,2]. Moreover, PIM-based systems have been successfully designed for the separation of different species such as metal ions, small molecules and inorganic anions [3].

The basis of separation in PIMs is the same as in supported liquid membranes (SLMs). Both types of activated membranes contain a specific reagent (carrier) that can react in a more or less selective manner with the target species. The extraction mechanism is similar to that in conventional liquid–liquid extraction, but without the use of large amounts of organic diluents, and with the advantage that the extraction and stripping can be done continuously. It is notorious that PIMs exhibit better mechanical properties and chemical resistance than traditional SLMs since in the former the carrier is immobilized onto a polymer matrix [4,5]. For their inherent characteristics, simple preparation, and versatility, PIMs have a promising future both in analytical applications and in the water technology for the removal of pollutants.

The components of the PIM (base polymer, extractant and a plasticizer and/or modifier) play an important overall role in the separative efficiency of any PIM. Although the separation effectiveness depends significantly on the use of an appropriate carrier, it is also important to take into account the nature of the other components of the membrane since they can affect both the physical and chemical characteristics of the PIM [6,7]. The role of the base polymer is to provide the membrane with mechanical strength and, consequently, it might hardly affect its diffusive resistance. The polymer must also entrap the active component of the membrane (the carrier) and minimize any loss of the carrier on the surrounding solutions. The main polymers used for these purposes are poly(vinyl chloride) (PVC) and cellulose triacetate (CTA) [3,4,8–10]. Kozlowsky et al. [11] studied the effect of the polymer in PIMs with tri-*n*-octylamine as the carrier for the transport of Cr(VI), obtaining a higher rate of chromate ion transport through a CTA-based PIM than a PVC-based PIM. This

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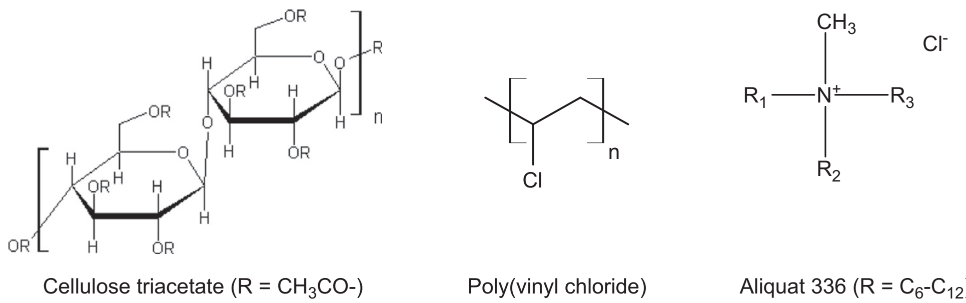

Fig. 1. Scheme of PIMs components formulae.

fact was attributed to the more hydrophilic character of CTA than PVC. Plasticizers are usually added into the PIMs casting solutions in order to make the polymers softer and more flexible, but they also enhance the chemical and mechanical stability of membranes since they can penetrate among the polymer molecules, increasing the distance among them and decreasing the polar groups of the polymers. Many works related to the effect of the plasticizer on metal ions transport through PIMs as well as structural modifications promoted by the nature of the plasticizer can be found in the literature [12–15].

It is worth pointing out that some carriers have also plasticizing abilities and they form flexible and stable membranes without the need of adding any other component, as it is the case of room-temperature ionic liquids (ILs). In such cases, the formulation of the membrane composition might contain only the polymer and the IL. ILs are a class of organic non-molecular solvents that are liquid at 20 °C; in general, they consist of an organic cation containing nitrogen or phosphorus and an organic or inorganic anion. Among the properties which make these compounds attractive for green chemistry are low volatility, in general high thermal stability (over 300 C), negligible vapor pressure, high viscosity and good wetting abilities. Particularly, the quaternary ammonium salt Aliquat 336 (tricaprylmethylammonium chloride) is a well-known IL and a versatile cation source for new hydrophobic ILs [16]. This IL has extensively been used as a carrier in PIMs made of both PVC [17–19] and CTA [5,8,20]. However, most of these works are devoted to the study of PIMs in specific transport systems, and thus, PIM performance might be affected not only by their components but also by the aqueous solution compositions, analyte to be transported or the characteristics of the experimental set-up among others.

In this work, we have focused on the characterization of PIMs material, depending on the polymer (CTA or PVC) and the IL Aliquat 336 content, in order to evaluate their effects on different physical–chemical characteristics of the resulting PIMs. For these reasons, different techniques that are able to give information on membranes surface and bulk material properties (XPS, contact angle, elasticity and impedance spectroscopy) have been used in order to have rather complete physical–chemical information of the studied PIMs. These results should be of valuable interest for the understanding of transport behavior when PIMs are used for separation purposes. In this context, a comparison of the effect of the base polymer on the transport of As(V) species through PIMs with an Aliquat 336 content around 45% (w/w) is also indicated.

2. Experimental

2.1. Reagents

Stock solution (100 mg L^{-1}) of As(V) was prepared from $Na_2HAsO_4 \cdot 7H_2O$ (Merck). Working solutions of As(V) were prepared by dilution of the corresponding stock solutions in deionized water (Milli-Q Plus system, Millipore) and the resulting pH was around 7 (pH meter GLP 22, Crison, Spain). Sodium chloride was used to prepare the stripping solution. Calibration standards of As were prepared using a Spectrascan standard As solution (1000 mg L^{-1}) for atomic absorption spectroscopy, AAS (Teknolab).

Table 1
PIMs identification and composition.

PIM composition (Aliquat 336 weight fraction, %)	Polymer (g)	Aliquat 336 (g)	mol Aliquat 336 cm^{-2} PIM ($\times 10^{-6}$)
PVC+9% Aliquat 336	0.400	0.041	1.6
PVC+26% Aliquat 336		0.141	5.5
PVC+45% Aliquat 336		0.327	12.5
PVC+60% Aliquat 336		0.600	27.5
CTA+9% Aliquat 336	0.200	0.020	0.8
CTA+26% Aliquat 336		0.071	2.7
CTA+48% Aliquat 336		0.182	7.1
CTA+60% Aliquat 336		0.300	11.6
CTA+70% Aliquat 336		0.467	18.2

The extractant Aliquat 336 (molecular weight, 404.16 g mol^{-1}) and the polymers PVC and CTA were purchased from Fluka Chemie. Fig. 1 shows the structures of the base polymer as well as the IL used in membrane manufacture. The organic solvents THF or $CHCl_3$ (Panreac) were used to dissolve the corresponding polymer.

2.2. Membrane preparation

PIMs were prepared by dissolving either CTA (200 mg) or PVC (400 mg) and the appropriated volume of a 0.5 M Aliquat 336 solution in chloroform or in THF, respectively. The solution was poured into a 9.0 cm diameter flat bottom glass Petri dish which was set horizontally and covered loosely. The solvent was allowed to evaporate over 24 h at room temperature, and the resulting film was then carefully peeled off from the bottom of the Petri dish and taken for further studies.

Different PIMs were prepared depending on the polymer and Aliquat 336 content. For CTA-based PIMs, Aliquat 336 concentration was varied from 9% to 70% (w/w); when PVC was used, Aliquat 336 concentration ranged from 9% to 60% (w/w). Table 1 shows PIMs identification and composition in both weight fraction (%) and Aliquat 336 mol cm^{-2} PIM.

Taking into account that PIMs made of PVC contain double amount of polymer that the CTA ones, equal Aliquat 336 concentration in weight fraction corresponds to different number of moles of carrier per cm^2 of membrane depending on the polymer. For that reason, discussion of PIMs results associated to surface techniques (XPS and contact angle) will be done in terms of the