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# Influence of the composition of polymer inclusion membranes on their homogeneity and flexibility

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**Abstract**

This study involves the preparation of a number of polymer inclusion membranes (PIMs) using a variety of commercial solvent extraction reagents immobilized in cellulose triacetate (CTA), cellulose acetate, poly(vinyl chloride) (PVC), PVC co-polymerized with vinyl alcohol and vinyl acetate, and carboxylated PVC. The influence of the molecular structure and physicochemical properties of the extractants studied on their ability to form homogeneous, flexible and mechanical strong PIMs are discussed. The physicochemical properties found to be of most importance in this respect are the extractant's lipophilicity, hydrogen bonding capacity, ability to participate in dipole–dipole interactions and its liquid aggregate state at room temperature.

*Keywords:* Polymer inclusion membranes; PIMs; Membrane extraction

## 1. Introduction

Polymer Inclusion Membranes (PIMs) offer an attractive alternative to conventional solvent extraction by mimicking this important industrial separation process but without the use of a large inventory of diluents which are often expensive, highly volatile and flammable liquids [1]. Unlike solvent extraction based separation where back-extraction takes place after the end of the extraction step, PIMs allow both extraction and back-extraction to proceed simultaneously at the opposite sides of the membrane. This arrangement can improve substantially the overall rate of separation and its selectivity and

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can reduce the complexity of industrial separation processes. A PIM in some cases can incorporate only a base polymer and a suitable extractant while in other cases a plasticizer may also need to be added for obtaining a homogeneous and flexible membrane. Combinations of polymers and extractants have been found to be capable of extracting inorganic cations and anions, neutral and charged metal complexes, and organic anions [2]. There are, however, no systematic studies on the influence of the composition of PIMs on their homogeneity, flexibility and mechanical strength, all of which are characteristics of a successful PIM.

This paper reports on a screening of a number of PIM compositions in order to compile a library of compatible combinations of frequently used and commercially available base polymers and extractants.

## 2. Experimental section

### 2.1. Reagents

#### 2.1.1. Polymers

The following polymers were used as received: poly(vinyl chloride) (PVC) (High molecular weight, Fluka, Italy), cellulose acetate (CA) (average molecular weight of 30,000 Da, Aldrich, USA), cellulose triacetate (CTA) (Selectophore®, Fluka, Switzerland), carboxylated PVC (1.8% carboxyl content, Selectophore®, Fluka, USA) and a copolymer of 91% vinyl chloride, 3% vinyl acetate and 6% vinyl alcohol (Selectophore®, Fluka, Switzerland).

#### 2.1.2. Extractants

Aliquat 336® (Aldrich, USA), Cyanex 272® and Cyanex 923® (Cytec, USA), di-(2-ethylhexyl) phosphoric acid (D2EHPA) (97%, Aldrich, USA), P50 Oxime (Cytec, USA), tri-*n*-butyl phosphate (TBP) (Unilab, LR, Australia), tri-iso-octylamine (TiOA) (TG, Aldrich, USA), tris-(2-ethylhexyl) amine (TEHA) (purum, Fluka, Switzerland), tri-*n*-octyl phosphine oxide (TOPO) (97%, Fluka, Switzerland) were all used as received. Alamine 336® (Cognis, USA) was used both as received and after being contacted with 0.1 mol $L^{-1}$ HCl for 24 h (''protonated Alamine'').

#### 2.1.3. Solvents

Tetrahydrofuran (THF) (99.9%, Merck, Germany) and dichloromethane (DCM) (AR, Merck, Australia) were used as received.

### 2.2. Membrane preparation

A large range of combinations involving a base polymer and an extractant were tested to evaluate which would afford homogenous, flexible and stable membranes. A base polymer and an extractant with a total mass of 800 ± 10 mg and in varying proportions were weighed into a 30 mL Pyrex beaker and 10–15 mL of an appropriate solvent (THF for PVC and its derivatives, DCM for CA and CTA) were added. The mixture was mechanically stirred until all components had dissolved. This solution was then poured into a glass ring (internal diameter 76 mm) placed on a glass plate (10 × 10 cm). If removing the membrane from the glass plate was difficult, the latter was covered with a Teflon sheet (10 cm × 10 cm × 0.08 mm) prior to casting the membrane. The solvent was allowed to gradually evaporate overnight. The glass ring was covered with a filter paper to slow the evaporation rate and to prevent dust particles from falling onto the membrane mixture. Once all the solvent had evaporated, the membrane was removed from the glass ring and plate. The range of membrane compositions studied is listed in Table 1.