

Applicability of liquid membranes in chromium(VI) transport with amines as ion carriers

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Abstract

Chromium(VI) transport across supported liquid membranes (SLMs) and polymer inclusion membranes (PIMs) with tertiary amines and quaternary ammonium salt (Aliquat 336) from chloride acidic aqueous solution to 0.1 M NaOH has been studied. The initial flux of Cr(VI) decreases linearly with logarithm of *n*-octanol/water partition coefficient increase for R₃N amines (R = *n*-C₆H₁₃–*n*-C₁₂H₂₅). The chromate ions are transported across polymer inclusion membranes with lower rate using polyvinyl chloride (PVC) instead of cellulose triacetate (CTA) support. The decreasing of Cr(VI) initial fluxes in following order of plasticizers: *o*-nitrophenyl pentyl ether > bis(2-ethylhexyl) adipate > dibutyl phthalate was observed. The comparative Cr(VI) transport studies of bulk, supported and polymer inclusion membranes were done. The highest permeability coefficient values for Cr(VI) was found for SLM, while the lower values were observed for BLM. The repeated transport experiments of SLM and PIM were shown and the stability of PIM was described using the Danesi's thermodynamic model. The long-term integrity of PIM was found. Non-contact atomic force microscope was applied to obtain images of pores in polymer inclusion membranes.

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1. Introduction

Liquid membranes are slowly but continuously becoming a very important and promising alternative to the current processing practices normally employed for wastewater treatment, and metals recovery from residual aqueous solutions generated by galvanic plants and mine waters. Chromium(VI) is one of major toxic elements present in environmental samples [1]. For this reason, the applicability of liquid membranes for Cr(VI) removal from aqueous solutions is evaluated.

In recent years, a remarkable increase of the applications of liquid membranes in separation processes is observed. These membranes include bulk liquid membranes (BLMs), emulsion liquid membranes (ELMs), and supported liquid

membranes (SLMs). Two papers [2,3] deal with applications of BLMs for Cr(VI) removal using dicyclohexane-18-crown-6 as the ion carrier. Several results of the concentration and separation of chromium(VI) with ELM process have been also reported. Tertiary amines, such as tri-*n*-dodecylamine [4], and Alamine 336 [5] were used as the ion carriers. Quaternary ammonium salt, i.e., Aliquat 336 was also applied as an ion carrier in ELMs [6–8]. The applications of SLMs for chromium(VI) concentration and separation with tertiary amines and quaternary ammonium salts as the most widely used ionic carriers have been shown in a few papers [9–11]. Recently, Alguacil et al. reported the use of the commercially available phosphine oxide, i.e., Cyanex 923 [12]. A common problem for SLMs is the loss of membrane solvent and/or carrier to the both aqueous phases, and as the result the SLM-based processes have not been exploited industrially due to their poor durability. Recently were published papers,

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which deal with chromium(VI) transport across ELMs [13] and SLMs [14,15].

In 1987, Sugiura et al. reported the use of polymer inclusion membranes (PIMs) for carrier-mediated transport of metal ions from an aqueous feed phase into an aqueous receiving phase [16]. The PIMs are formed by casting using as a support cellulose triacetate (CTA) or polyvinyl chloride (PVC) from an organic solution to form a thin, stable film. This casting solution also contains an ion carrier and a membrane plasticizer (mostly *o*-nitrophenyl alkyl ethers). The resulting membrane is used to separate feed and receiving phases.

Recently, we have been involved in the design and preparation of polymer inclusion membrane systems containing amines, crown ethers, and phosphine oxide for selective and efficient transport of a metal ions variety, such as Cr(VI) and Cr(III) [17], Cr(VI) [18], Cs(I), Sr(II) and Co(II) [19], and alkali metal cations [20]. The chromium(VI) extraction and transport with 4-(1'-*n*-tridecyl)pyridine *N*-oxide across the CTA-based polymer inclusion membrane system were found to be strongly dependent upon the concentration of sulphuric acid in the source aqueous phase [21].

The present work deals with the transport of chromium(VI) from chloride aqueous solutions by polymer inclusion membranes with tertiary amines and quaternary ammonium chloride as ion carriers. The effect of different tertiary amines on chromium(VI) transport across PIMs is presented together with the investigation of PIMs and SLMs stability and the effect of plasticizer.

2. Experimental

2.1. Chemicals

Organic compounds, such as tri-*n*-butylamine (TBA), tri-*n*-hexylamine (THA), tri-*n*-octylamine (TOA), tri-*n*-dodecylamine (TDA), tri-*n*-dodecylamine (TDDA), Aliquat 336, *o*-nitrophenyl pentyl ether (ONPPE), dibutyl phthalate, bis(2-ethylhexyl) adipate, CTA ($M_n = 72,000\text{--}74,000$), PVC (M_n ca. 60,000, M_w ca. 106,000), dichloromethane, toluene, and tetrahydrofuran were purchased from Fluka and used without further purification.

Inorganic compounds, such as potassium dichromate, sodium hydroxide and hydrochloric acid solutions were prepared from analytical grade reagents (POCh, Gliwice, Poland). The gamma radioactive isotope, Cr-51, was used as $K_2Cr_2O_7$ in HCl aqueous solution. This isotope was of a sufficiently high specific activity to neglect the effect of carrier concentration (4.5 GBq/g), and was obtained from the Atomic Energy Institute (Swierk, Poland).

2.2. Polymer inclusion membrane preparation

A solution of support (cellulose triacetate), the ion carrier (amine or quaternary ammonium salt), and the plasti-

cizer (*o*-nitrophenyl pentyl ether, dibutyl phthalate, bis(2-ethylhexyl) adipate) in dichloromethane was prepared. A portion of this solution was poured into a membrane mold comprised of a 9.0 cm glass ring attached to a glass plate with CTA–dichloromethane glue. The organic solvent was allowed to evaporate overnight and the resulting membrane was separated from the glass plate by immersion in cold water. The membrane was soaked in aqueous solution of HCl for 12 h and stored in distilled water. Membrane with PVC support was prepared using tetrahydrofuran as the solvent, *o*-nitrophenyl pentyl ether as a plasticizer, and TOA as an ion carrier.

2.3. Supported liquid membrane preparation

Microporous polypropylene membrane Celgard® 2500 (Hoechst Celanese Co.) was used as the solid support. The membrane possessed a porosity of 0.45, a thickness of 0.025 mm, and 0.04 μm effective pore size. The membrane was soaked for 12 h in 1.0 M TOA in toluene solution.

2.4. Atomic force and scanning electron microscopy

A surface characterization study of TOA/ONPPE/CTA membrane was carried out using atomic force microscopy (AFM) (Topometrix Explorer TMX 2000, Topometrix, CA, USA). Surfaces of TOA/ONPPE/PVC membrane samples were examined using a Philips SEM 535M after gold coating. The coating thickness was about 20–25 nm.

2.5. Membrane transport experiments

The transport experiments through SLMs and PIMs were carried out in a permeation cell in which the membrane film was tightly clamped between two cell compartments. The average CTA and PVC membranes thickness was 28 and 27 μm , respectively (measured by digital ultra-meter of A2002M type from Inco-Veritas with 0.1 μm standard deviation over four readings). The effective surface area of membrane was 6.0 cm^2 . Both, the source and receiving aqueous phases (45 ml each) were stirred at 10 Hz (600 rpm) with synchronous motors.

The transport experiments across bulk liquid membranes were carried out in the apparatus previously shown [22]. The aqueous feed solutions (40.0 ml) contained of chromium(VI) ions and hydrochloric acid. The aqueous feed solution was in the outer part of the vessel and stirred at 10 Hz (600 rpm). The aqueous receiving solution was 0.10 M NaOH (20 ml) and was located in the inner part of the vessel. The liquid membrane phase (20 ml) containing 0.10 M TOA dissolved in toluene was added on the top of the water phases and stirred at 10 Hz (600 rpm). The interface surfaces were as follows: 9.0 cm^2 for feed phase/liquid membrane, and 7.0 cm^2 for liquid membrane/receiving phase.

Samples of the aqueous feed phase were removed periodically via a sampling port with a syringe and analyzed to

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