

Chemical and morphological stability of Aliquat 336/PVC membranes in membrane extraction: A preliminary study

Lijuan Wang^a, Wei Shen^{b,*}

^a Department of Chemistry, La Trobe University, Bundoora, Vic. 3083, Australia

^b Department of Chemical Engineering, Monash University, Wellington Road, Clayton, Vic. 3800, Australia

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Abstract

Aliquat 336/PVC-based polymer liquid membranes were used to extract Cd(II) and Cu(II) from aqueous solutions. The membranes demonstrated different extraction rate, capacity and chemical and morphological stabilities in the extraction of Cd(II) and Cu(II). Although the membrane showed good extraction rate and capacity to Cd(II), its chemical and morphological properties deteriorated badly after extraction. On the other hand, although the membrane showed a somewhat lower extraction capacity to Cu(II), it showed a much higher chemical and morphological stability. In this study, X-ray photoelectron microscopy (XPS) and lateral force atomic force microscopy (AFM) were used to characterize the chemical and morphological changes of the membrane before and after the extraction. The data in this work show that, XPS and AFM are good tools for membrane surface characterization. The sources of bleeding of the extractant (Aliquat 336) on membrane surface can be clearly identified. Although that actual cause of the membrane deterioration is not yet clear, the results from this work suggest that it could be related to the redistribution of the Aliquat 336 from the membrane bulk to the membrane surface. Information from this study is therefore useful to the future work on improving the membrane stability.

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1. Introduction

The extraction of heavy metal ions from aqueous solutions using PVC-based polymer liquid membrane containing Aliquat 336 as a carrier species has been reported by several authors [1–9]. This type of membrane film has been shown to be quite effective in removing trace amount of heavy metal ions from aqueous solutions [3,4]. A shortcoming of this type of membrane is that the extraction rate is much lower than that of solvent extraction [3,4]. Since Aliquat 336 acts as a plasticizer in the PVC, it was believed that the extractant molecules in the polymer matrix “entangle” with the polymer chains [5]. Argiropoulos et al. suggested that this type of the polymer liquid membrane was different from the supported liquid membrane (SLM) in that the extractant molecules in the former is more tightly held in the membrane through the

molecular entanglement and would be much less prone to bleeding than SLMs [5]. Following such a picture, the activity and mobility of Aliquat 336 molecules in the membrane are expected to be greatly reduced. This is consistent with the extraction results reported previously which showed that extraction rates of PVC-based polymer liquid membranes lightly loaded with Aliquat 336 were very low [3–5].

More recently, Xu et al. [2] showed that the state of distribution of Aliquat 336 in the PVC-based polymer liquid membrane is dependent upon the loading level of the extractant in the membrane. Beyond a certain loading level, Aliquat 336 starts to form aggregates in the membrane bulk and, as a result, not all Aliquat 336 molecules are in the entangled state with the PVC polymer chains. Xu et al. [2] showed that this loading level was between 30% and 40% (Aliquat 336/PVC, m/m). These authors also noticed that, corresponding to this loading level, the extraction rate increases rapidly as the Aliquat 336 loading level in PVC membrane exceeded 30% (m/m).

* Corresponding author. Tel.: +61 3 99053447; fax: +61 3 99053413.
E-mail address: wei.shen@eng.monash.edu.au (W. Shen).

The extraction mechanism of Aliquat 336/PVC-based polymer liquid membrane was investigated experimentally by Argiropoulos et al. [5] for extracting Au(III) from HCl solutions and by Wang [4] and Wang et al. [3] for extracting Cd(II) and Cu(II) from HCl solutions. The extraction reactions at the solution/membrane interface proposed by these authors can be summarized as follow [3–5]:



where ACl is Aliquat 336 chloride and $\text{A}^+[\text{AuCl}_4]^-$ and $\text{A}^+[\text{CdCl}_3]^-$ are the extractant complexes (ion pairs). The subscripts m and a refer to the membrane and aqueous phase, respectively.

A major potential advantage of membrane extraction over solvent extraction is that the former has a smaller impact to the environment than the later. For this to be true, the membrane must have a high stability chemically and morphologically so that the extractant loss from the membrane can be minimized and the membrane should be reusable. The stability of the Aliquat 336/PVC-based polymer liquid membrane has but only received a limited research attention to date. Argiropoulos et al. studied the loss of Aliquat 336 from the membrane after a period of 10 days of contact with distilled water and a 2.5 M HCl solution [5]. They reported that the membrane lost approximately a quarter to a third of its Aliquat 336 content in distilled water, but only 2–3% in 2.5 M HCl solution [5]. Xu et al. [1] also investigated the loss of Aliquat 336 from membrane to an aqueous solution and found that the concentration of the extractant being leached into the solution from the membrane was lower than the solubility of Aliquat 336 in water. Wang [4] noticed that Aliquat 336/PVC-based polymer liquid membranes showed some macroscopic morphological deterioration after the extraction of Cd(II), but the same type of membrane demonstrated high morphological stability in the extraction of Cu(II). The results in this work suggest that the morphological deterioration may be related to the redistribution of the extractant in the membrane. It is also likely that such deterioration is dependent upon the rate of the extraction reaction, although at this stage this is still only an unproven hypothesis. Further discussion will be given in a later section. Since any form of membrane deterioration could seriously reduce the reusability of the membrane, we think both chemical and morphological stabilities of the membrane warrant a thorough investigation.

In this preliminary work, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) were used to demonstrate changes in chemical and morphological properties of Aliquat 336/PVC-based polymer liquid membranes in the extraction of Cd(II) and Cu(II). Membrane extraction (and also solvent extraction) data were presented to facilitate comparisons of the behaviour of the two metal complexes in the membrane. This work provides a detailed picture of the form of the deterioration that has not been reported before. This work will also provide useful informa-

tion to future research in the reusability of the membrane. Another motivation of this work is to demonstrate the effectiveness of the lateral force AFM in the membrane surface characterization. It is a good tool for mapping the viscous materials on membrane surface.

2. Experimental

2.1. Reagents

Aliquat 336 (tricaprylylmethylammonium chloride) and high molecular weight PVC powder (average $M_w = 180,000$) were obtained from Fluka. They were used as received. Hydrochloric acid, cadmium chloride and cupric chloride were analytical reagents from BDH. Tetrahydrofuran (THF) was HPLC grade from BDH and was treated to remove the stabilizer and peroxides by passing through an activated alumina column.

Cadmium(II) and copper(II) standard solutions for atomic absorption spectroscopy were obtained from BDH. The concentration of both standards was 1000 mg/L. Milli-Q water was used for all dilutions.

Shellsol AB was obtained from Shell Chemical (Australia) Pty. Ltd., and was used as the solvent for solvent extraction studies. It was a clear and colourless liquid and contains approximate 99% aromatics, according to the supplier's specification. The solvent was used without further purification.

2.2. Aqueous sample preparations

Cd(II) and Cu(II) solutions were prepared from CdCl_2 and CuCl_2 salts. Accurately weighed CdCl_2 and CuCl_2 salts were transferred into volumetric flasks and diluted to volume with 2 M and 3 M hydrochloric acid solutions, respectively.

2.3. Solvent extraction study

Aqueous solutions of Cd(II) and Cu(II) of 200 mg/L and 140 mg/L, respectively, were prepared in 2 M and 3 M HCl solutions, respectively. An organic phase was prepared by diluting 0.04 M Aliquat 336 with Shellsol AB. Solvent extraction was performed by mixing equal volumes of Cd(II) or Cu(II) solution and the organic phase in an indented round bottomed flask and then vigorously shaking in a thermostated water bath (25 °C) for a preset period of time. Immediately after the two phases were separated, an aliquot of the aqueous phase was taken out of the system for metal analysis using atomic absorption spectroscopy (AAS). More descriptions of AAS analysis are given below and a detailed procedure of AAS measurement can be found elsewhere [4].

2.4. Preparation of membranes

The membranes were prepared by dissolving known weights of Aliquat 336 and PVC in 5–10 ml of THF. The

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