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Metallic ion extraction using polymer inclusion membranes (PIMs): Optimising physical strength and extraction rate

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ABSTRACT

This study investigated both extraction performance and physical properties of a novel type of facilitated transport membrane known as polymer inclusion membrane (PIM). Five different types of poly(vinyl chloride) representing a wide range of viscosity and average molecular weights were used as the base polymer and Aliquat 336 was used as the carrier. Physical properties including membrane hydrophobicity and tensile strength were measured and systematically correlated against the fraction of PVC and Aliquat 336 in the PIMs. Selective extraction between Cd(II) and Cu(II) of the membranes from aqueous solution was then investigated. Results reported in this study indicate that tensile testing can be excellent tool to tune the membrane composition for an optimised mechanical strength. Membranes synthesized in this study showed excellent extraction selectivity between Cd(II) and Cu(II). This could be explained by examining the extraction mechanisms of metal cations involving Aliquat 336 and the speciation of such metals in a chloride matrix which was used in the extraction experiments. Results reported here indicate that physical properties of PIMs are primarily governed by types and composition of the base polymer. In addition, the optimum composition for physical strength does not necessarily result in the best extraction capability. There is a significant scope to fine tune both the extraction rate and physical properties for an optimum PIM performance.

Keywords: Polymer inclusion membranes (PIMs); Metal extraction; Base polymer; PVC; Aliquat 336

1. Introduction

Concern about environmental sustainability under current industrial practices has drawn considerable attention to the need of improving the conventional extraction methods used in metal recovery. Current techniques of metal ion recovery use solvent extraction separations, consuming large amounts of energy and reactants which impose both environmental and health hazards [1]. However, the recent development of a novel type of liquid membrane, commonly called polymer inclusion membranes (PIMs), can be seen as an environmentally conservative alternative [1,2] which could potentially revolutionise current methods of extraction [3]. While traditional solvent extraction systems are unlikely to be replaced in the near future [4], PIMs are expected to infiltrate into a diverse range of large-scale industrial separation processes [3,5].

To date, liquid membranes have had little practical industrial usage despite the high demand for metal ion

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Table 1
Physicochemical properties of the five types of PVC base polymer.

Base polymer	Monomer structure	Density (g/cm^3)	Weight-average MW (g/mol)	Number-average MW (g/mol)	Intrinsic viscosity (dL/g)
PVCs 1	C_2H_3Cl	1.385	43,000	22,000	0.51
PVCs 2			62,000	35,000	0.68
PVCs 3			80,000	47,000	0.80
PVCs 4			97,000	55,000	0.92
PVCs 5			233,000	99,000	1.40

recovery in hydrometallurgy, extraction of small organic compounds in biotechnology and in the treatment of industrial wastewater [4]. Due to a variety of undesirable characteristics, including low interfacial surface areas and mass transfer rates, emulsion breakage, and in particularly poor stability, liquid membranes have remained unsuitable for large-scale use [4]. PIMs however, overcome many of these problems and have demonstrated potential for future use relative to other liquid membranes [4,6]. For this reason, PIMs are speculated to play a significant role in the future of extraction technology [3].

PIMs designed for facilitated transport of cations consist of the three main components; a polymer, a plasticizer and an extractant. These three components each contribute essential characteristics to the overall performance and physiochemical characteristics of the membranes. A delicate balance exists between the components of PIMs that govern the performance of the membrane during its use in extracting metallic ions and small organic compounds. Although there have been numerous dedicated investigations examining the interplay amongst these components, more research is required to elucidate the intricate relationships between this composition and the membrane characteristics [4]. This paper aims to examine the extraction of Cu(II) and Cd(II) by Aliquat 336/PVC PIMs. Variations in the composition of the base polymer PVC and the extractant Aliquat 336 were related to the physical and extraction properties of membranes. The obtained data were then used to delineate the role of each constituent of the membranes.

2. Materials and methods

2.1. Reagents

Aliquat 336 (tricaprylylmethylammonium chloride) was purchased from Sigma-Aldrich (Australia) and was used without any further purification. Five high molecular mass PVCs (Sigma-Aldrich, Australia) were used in the preparation of the solid-phase absorbent membranes. These PVC's have the same density but differ markedly from one another in the weight-average molecular weight, number-average molecular weight, and thus the intrinsic viscosity (Table 1). HPLC grade tetrahydrofuran (THF) was purchased from BDH (Australia). All other chemicals used in this study were of analytical grade from Sigma-Aldrich (Australia). Copper(II) and cadmium(II) solutions, used in the membrane extraction experiments and for calibration purposes, were prepared from $CuCl_2$ and $Cd(NO_3)_2$. Laboratory grade MilliQ water (Millipore, Australia) was used for the preparation of all solutions.

2.2. Preparation of Aliquat/PVC PIMs

Different combination of Aliquat 336 chloride and PVC with a total mass of 600 mg were dissolved in approximately 10 ml of THF by vigorously stirring the mixture for about 1 h until the solution became clear. The solution was then poured into a petri glass dish. The petri dish was covered with filter paper (0.45 μm) to allow the THF to slowly evaporate. After the THF has evaporated, the membranes were then peeled from the petri dish and stored in dry condition for further experiments.

2.3. Extraction protocol

Membrane extraction was conducted with a series of beakers and a multiple place stirring plate. Extraction solution contained either 140 mg/L of Cu(II) or 73 mg/L of Cd(II) in 2 M of HCl. The solutions were stirred continuously at a constant speed and 1 mL of aliquot was taken at a specific interval for Atomic Adsorption Spectrometry analysis (Varian Carrier, AAS 300). Calibration curves using the standard Cu(II) and Cd(II) solutions were obtained with typical R^2 values of at least 0.98 in all analysis.

2.4. Contact angle measurement

The contact angle of all membrane samples was measured by placing a cut sample of the membranes onto a slide. A micro-droplet of HPLC grade water was

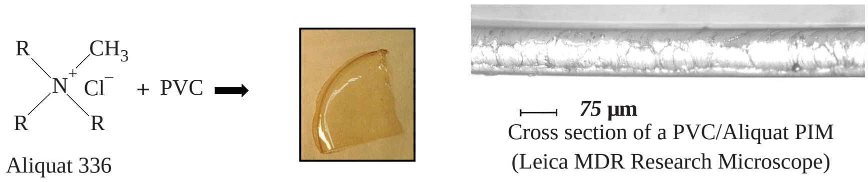

Fig. 1. Aliquat/PVC polymer inclusion membranes.

placed on the membrane surface and a goniometer (Rame-Hart, NJ, USA) was then used in conjunction with specialised computer software, to accurately measure the angle of contact between the water droplet and membrane surface. Each measurement was repeated four times.

2.5. Tensile testing protocol

Mechanical properties of the samples were evaluated using an INSTRON testing machine (Model 5566 with a 100 N load cell) and analyzed in accordance with ASTM D882-91 standard test protocol for thin film tensile tests. Specimens were approximately 60 mm long and 20 mm wide. A thin film grip was used to hold the membrane specimens. All tests were conducted at a crosshead speed of 10 mm/min under room temperature at 23°C. The grip distance was set at 40 mm. The engineering stress (σ is defined as the ratio of the load (L) to the area (A), ($\sigma = L/A$, $A = w \times t$, where w is the specimen width (20 mm) and t is the thickness (85 µm)). The percentage strain (λ) is $[(l - l_o)/l_o] \times 100\%$, where l is the total extension measured from the grip displacement and l_o is the gage length (40 mm). The initial Young's modulus (E) was calculated from the initial slope of stress–strain curve obtained.

3. Results and discussion

3.1. Membrane preparation

In order to gain a general understanding of the relationship between membrane composition and the physical quality of the membranes, a wide spectrum of membrane compositions were initially prepared. The membranes were initially prepared with Aliquat/PVC compositions of 30%, 40%, 50%, 60% and 70% (w/w). However, membranes with Aliquat/PVC ratio of 70/30 were deemed unsuitable for further use. Membranes consisting of 70% Aliquat and 30% PVC were sticky and mechanically too weak for any subsequent tests. This observation was consistent for all five PVCs used in the study. Consequently, only PIMs with 40–70% of PVC were used for further study. These PIMs are transparent and quite flexible (Fig. 1). These Aliquat/PVC membranes had a uniform thickness of approximately 85 µm (Fig. 1).

The difference in physicochemical properties of the five PVC types (see Table 1) had an obvious influence on the resulting membranes. These differences first became apparent during the process of mixing PVC, Aliquat 336 and THF as the casting solution. The solution containing PVC 5 was very viscous and more difficult to dissolve than the solutions containing the other four types of PVC. Since PVC 5 was by far the highest molecular weight PVC, it can be expected that its solubility in THF would be lower than that of the other four PVCs. Due to the viscous nature of PVC 5 and its tendency to form a sticky and non-uniform solution, the process of creating a uniform membrane thickness proved more difficult than the membranes prepared from lower molecular weight PVC.

All membranes had at least a minor loss of mass when comparing the initial mass of ingredients to the mass of the formed membrane. These mass differences were mainly due to solution losses when transferring from the beaker to the petri dish. Most significant losses of up to 25.7% were recorded for membranes prepared with PVC 5 while losses of less than 5% were typical for membranes made with lower molecular weight PVC. It is probably because of the poor solubility of PVC 5 and the high intrinsic viscosity of this polymer. Noting these loses and slight variation in mass of PVC and Aliquat 336 used for the membranes, there will be a small discrepancy in the actual membrane composition. However, for simplicity in further discussion, these membranes will still be referred to by their nominal composition.

3.2. Selective extraction of cadmium

Extraction experiments were conducted with aqueous solutions containing 140 mg/L Cu(II) or 73 mg/L Cd(II) in 1 M HCl. Both Cu(II) and Cd(II) are known to favourably form chloride complexes. It is surprising that the copper extraction was quite small and copper concentration reduced only slight over 21 h of extraction. In contrast, significant extraction of Cd(II) to the membranes was clearly observed. Extraction kinetics of copper and cadmium to a PIM consisting of 50%

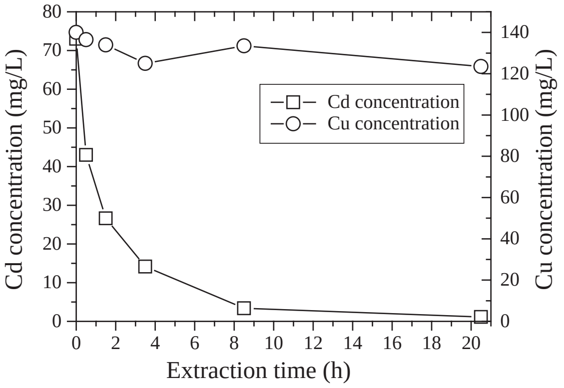

Fig. 2. Extraction kinetics of cadmium and copper to a PIM (50% Aliquat and 50% PVC 1). Initial solution contained 73 mg/L Cd or 140 mg/L Cu in 2.0 M HCl solution.

Aliquat and 50% PVC 1 were shown in Fig. 2 as an example. This superior extraction selectivity for Cd(II) over Cu(II) by Aliquat 336/PVC membranes can be explained by examining the distribution of cadmium and cupric chloride complexes. According to Nghiem et al. extraction of metallic species by basic extractants such as Aliquat 336 is governed by the formation of an ion pair between the extractant and a metal anion complex [4]. Consequently, in a chloride matrix, the availability of a metal chloride complex carrying one negative charge is crucial for the extraction of the metal to the membranes. Speciation simulation conducted using the MineQL modeling software revealed that only 0.1% of copper exists in the form of $[CuCl_3]^-$ in a background electrolyte of 1 M Cl^- (Table 2). In contrast, $[CdCl_3]^-$ exist as the second most available species, with a relative distribution of 36.6% (Table 2). Results reported here suggest that solution chemistry can be fine tuned to achieve desirable selectivity amongst certain metallic species.

3.3. Role of extractant and base polymer

3.3.1. Effects of Aliquat content on Cd(II) extraction

Influence of the membrane make-up composition on the extraction rate of Cd(II) was investigated using membrane samples containing between 30% and 60% of Aliquat 336. As can be seen in Fig. 3, a lower Aliquat 336 content (or higher PVC content) in the membrane resulted in a lower extraction rate of Cd(II). This trend was consistently observed with membranes cast from all five types of PVC. While the effect of Aliquat 336 content on extraction rate was quite significant, it should be noted that the total extraction capacity remained unaffected and extraction was close to complete in approximately 21 h regardless of the Aliquat content in PIMs. Assuming that formation of an ion pair between Aliquat and a trichloro cadmium complex was the only extraction mechanism, even with 30% Aliquat 336, the amount of extractant exceeded the initial amount of Cd(II) by 3.5 times. In fact, for membranes with 50% and 60% of Aliquat 336, extraction was almost completed (more than 99%) within only 4 h. The extraction rate of membranes with 30% of Aliquat was significantly lower, continuous extraction beyond 20 h was clearly observed.

Table 2
Calculated distribution of cupric and cadmium chloride complexes in an aqueous matrix containing ≥1 M HCl using MineQL+ (www.MineQL.com).

	M^{2+} (%)	MCl^+ (%)	MCl_2 (%)	MCl_3^- (%)	Total (%)
Copper	19.5	52.3	28.1	0.1	100
Cadmium	0.2	12.8	53.4	33.6	100

M represents either copper or cadmium.

3.3.2. Hydrophobicity of Aliquat/PVC PIMs

The membrane surface hydrophobicity was evaluated by contact angle measurement. The results reported in Fig. 4 reveal that all membranes were quite hydrophilic. This is somewhat surprising as pure PVC is known to be a hydrophobic material. A clear trend of increasing hydrophilicity (or decreasing contact angle value) was also observed in this study as the composition of PVC increased from 40% to 70%. However, it is quite remarkable that these Aliquat/PVC PIMs were quite hydrophilic. The hydrophilic nature of the membranes reported here clearly indicates that Aliquat 336 can act as not only an extractant but also an excellent plasticizer. Results reported here are consistent with previous study by Määttä et al. who investigated the effects of several plasticizers on the hydrophobicity of PVC [7]. Määttä et al. [7] reported that contact angle values of plasticized PVC thin films containing approximately 20–30% of a plasticizer were in the range of 76.2–90.9° and that contact angle decreased slightly as plasticizer composition in the film increased. It is hypothesized that Aliquat 336 can migrate and expose its polar functional group to the surface, thus rendering the membrane very hydrophilic. This hypothesis is also consistent with the data reported in a previous study in which Wang and Shen reported a significantly higher atomic concentration of nitrogen at the surface than in the bulk of Aliquat 336/PVC membranes [8].

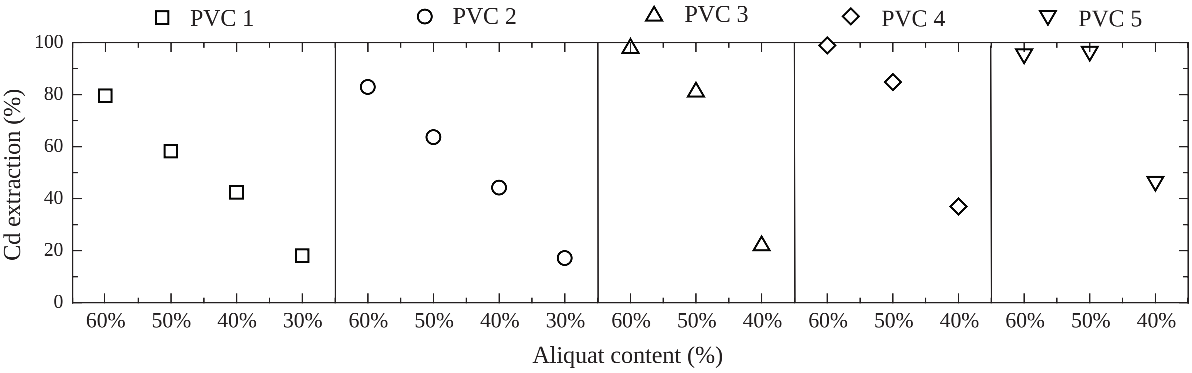

Fig. 3. Percentage of cadmium being extracted to the membranes after 1.5 h with different Aliquat content. Initial solution contained 73 mg/L Cd in 2.0 M HCl solution.

3.3.3. *Effects of base polymer PVC on Cd(II) extraction*

All five PVC polymers used in this study consist of linear polymer strands and because there are no cross-links between these strands, they can be effectively dissolved in the THF solvent, where the polymer strands become separated. The mechanical strength of a thermoplastic PVC thin film membrane is a combination of intermolecular forces and the process of entanglement [9]. It is noteworthy that the molecular weight (MW) of all five polymers used in this study (see Table 1) was considerably larger than the critical entanglement molecular weight (MW_c) of PVC, which was reported to be 12.7 kDa [10]. Above the MW_c value, variation in the base polymer MW has been speculated to exert a negligible influence on the membrane physical properties and extraction performance [11]. This hypothesis is in fact supported by data reported here. Fig. 5 shows no discernible effects of PVC molecular weight or intrinsic viscosity on the rate of Cd(II) extraction. It is noted that molecular weight and intrinsic viscosity of these five PVC were marked different as previously described in Table 1.

3.3.4. *Mechanical strengths of Aliquat/PVC PIMs*

Mechanical properties of PIMs were strongly dependent on the composition of the base polymer PVC as can be seen in Fig. 6. The tensile strengths of the membranes, defined as stress at the ultimate breakage, increased dramatically as the percentage of PVC increased. The reported results confirm that the primary role of the base polymer is to provide mechanical strength to the membranes. It is noteworthy that at 30% PVC, the resultant membranes were mechanically too weak for any physical tests while the tensile strength of PIMs containing 40% PVC was very small (Fig. 6).

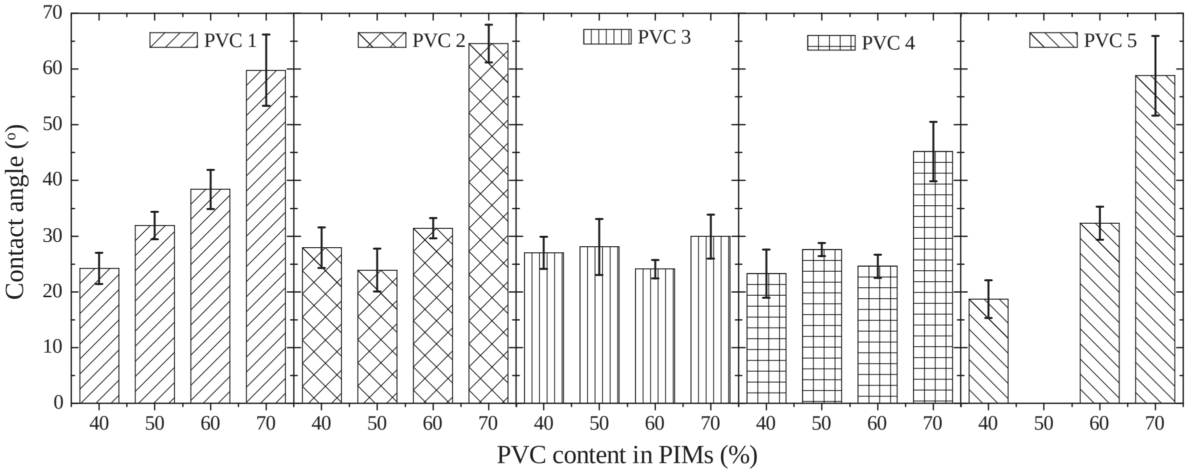

Fig. 4. Contact angle of the membranes as a function of Aliquat content (w/w percentage) and types of PVC. Error bars shows standard deviation of repeated contact angle measurements at four different locations.

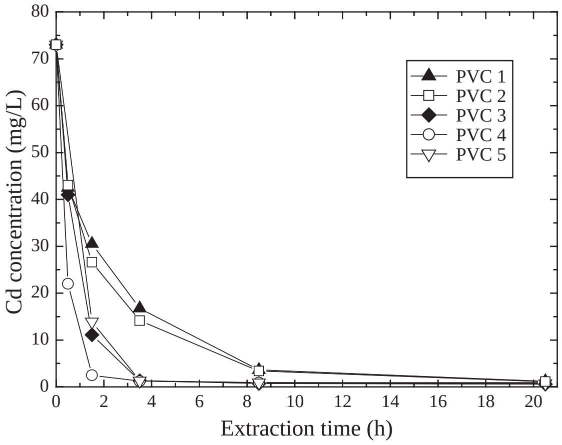

Fig. 5. Effects of base polymer on the kinetics of cadmium to PIMs made of five different PVCs (50% Aliquat and 50% PVC 1). Initial solution contained 73 mg/L Cd in 2.0 M HCl solution.

Fig. 7 shows the Young's modulus (*E*) values of PIMs prepared from the five selected PVCs with different PVC and Aliquat composition. Once again, it is apparent that the amount of the base polymer PVC in PIMs was a predominant factor governing the Young's modulus value of the membranes. For all five PVCs used in this study, Young's modulus increased as the percentage of PVC in PIMs increased. Surprisingly, while the Young's modulus values varied considerably amongst the five PVCs used here there was no obvious correlation between the intrinsic viscosity or molecular weight (see Table 1) of the base polymer PVC and the membrane Young's modulus. Results reported in this study clearly suggest that it is essential to optimise the composition of PIMs for both extraction rate and mechanical properties. While the rate of extraction increases as the composition of the extractant increases, the same correlation can also be seen between the composition of the base polymer and mechanical properties of the membranes. Although there are no minimum thresholds for tensile strength and Young's modulus of a membrane, it is commonly accepted that the tensile strength and Young's modulus of a durable and engineerable thin film or fiber membrane should be in the order of tens of MPa [12]. As a result, PIMs with less than 50% PVC can be deemed mechanically unsuitable even thought they may exhibit an excellent rate of extraction.

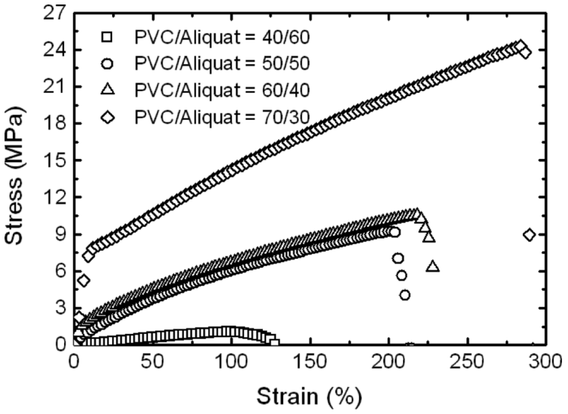

Fig. 6. Typical stress–strain curve of Aliquat/PVC PIMs with different composition of the base polymer PVC.

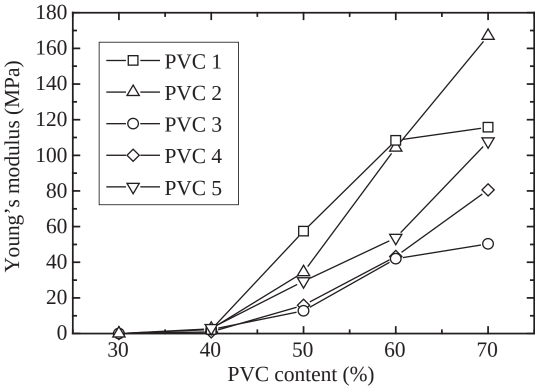

Fig. 7. Young modulus of the membranes prepared from five different types of PVC as a function of PVC content.

4. Conclusion

Membranes synthesized in this study showed excellent extraction selectivity between Cd(II) and Cu(II). While Cd(II) was almost completely extracted within approximately 8 h by all membranes containing 50% Aliquat 336, extraction of Cu(II) to the same PIM was quite negligible. It was found that a higher Aliquat 336 content of the membranes could considerably increase the extraction rate of Cd(II). Aliquat 336 could also act as a good plasticizer rendering the membranes quite hydrophilic. It is however important to note that Aliquat 336 content above 60% could significantly weaken the membrane physical properties. Results reported here also confirm that above the critical entanglement molecular weight, variation molecular weight of the base polymer PVC did not exert any discernible influence on the extraction performance of the membranes. A primary role of the base polymer was to provide mechanical strength to the membranes. It was suggested that both extraction rate and physical properties can be fine tuned for an optimum PIM performance.

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