Selective transport of Cadmium by PVC/Aliquat 336 polymer inclusion membranes (PIMs): the role of membrane composition and solution chemistry

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Abstract.　　This study investigated the extraction and stripping performance of PIMs consisting of PVC and Aliquat 336. Extraction and stripping of three representative heavy metals - namely Cd^{2+}, Cu^{2+}, and Zn^{2+} - by the synthesized membranes were evaluated as a function of sodium chloride concentration and under different stripping solutions (0.01 M HNO_3, Milli-Q water, 0.01 M HCl and 0.01 M NaOH), respectively. Results reported here indicate that the formation of negatively charged metal chloride complex species was responsible for the extraction of the target metal to PIMs. Experimental results and thermodynamic modeling of the speciation of chloro metal complexes further confirm that the extraction selectivity between Cd^{2+}, Cu^{2+} and Zn^{2+} can be controlled by regulating the chloride concentration of the feed solution. An acidic solution without any chloride was the most effective stripping solution, followed by Milli-Q water, and a diluted hydrochloric acid solution. On the other hand, the stripping of metals from PIMs did not occur when a basic stripping solution was used.

Keywords:　 polymer inclusion membranes (PIMs); metal extraction; base polymer; PVC; Aliquat 336

1. Introduction

　　Polymer inclusion membranes (PIMs) present an exciting and novel approach for the separation of metallic and small organic ions from aqueous solutions (St John *et al*. 2011, O'Rourke *et al*. 2011, Nghiem *et al*. 2006). Potential applications of PIMs include metal recovery in mineral processing and the fabrication of passive sampling devices (Nghiem *et al*. 2006). In fact, it has been suggested that PIMs may complement current liquid-liquid extraction techniques, which are commonly referred to as solvent extraction (SX) techniques. Although current state of the art SX processes are very efficient and cost effective (Ritcey 2006), the operation of SX facilities presents considerable occupational and environmental hazards. This is because SX techniques require large quantities of flammable and toxic organic solvents (known as diluents) to dissolve extraction reagents (or extractants). These chemicals are usually corrosive, toxic, and highly volatile (O'Rourke *et al*. 2009, Marinova and Yankov 2009). PIMs minimize the risk of releasing these chemicals into the environment by encapsulating the extractant in a polymer matrix (Nghiem *et al*. 2006). In fact, the stability of PIMs has been recently confirmed by Cho *et al*. (2011) who showed no leaching of the extractant or any significant loss of

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performance of a PVC/Aliquat 336 PIM after repetitive cycles of extraction and de-extraction of thiocyanate. This removes the in-situ need for large inventories of solvents and reduces the environmental exposure to extractants in their mobile form (Nghiem *et al*. 2006). Another unique and potential application of PIMs is the fabrication of passive sampling devices for trace levels of metal ions and small organic molecules. Indeed, PIMs have been used in chemical sensing for more than 30 years in the form of polymer membrane ion-selective electrodes (ISEs) (Cattrall 1997). In 1970, it was demonstrated that calcium complexing reagents could be immobilized into PVC to produce a polymer film for the fabrication of ISEs for the detection of calcium (Moody 1970). Since then, numerous PVC-based membranes have been developed for the potentiometric sensing of various cations and anions. Such membranes for use in potentiometry have also been termed "gelled liquid membranes" and "entangled liquid membranes" (Cattrall 1997). Also in the 1970s, Bloch *et al*. (1967) demonstrated that PVC-based membranes could also be used for metal ion separation although the requirements for the membrane characteristics were somewhat different for the two applications.

PIMs designed for facilitated transport of metals consist of the three main components; a polymer, a plasticizer and an extractant. These three components each contribute to the overall performance and physiochemical characteristics of the membrane. A delicate balance exists between the components of PIMs and this balance governs the performance of the membrane during its use in extracting metallic ions and small organic molecules (Nghiem *et al*. 2006). Although there have been numerous dedicated investigations examining the interplay amongst these components, more research is required to elucidate the extraction mechanisms of metallic ions and small organic molecules by PIMs (Nghiem *et al*. 2006). Liquid-liquid extraction of various base metals from solution containing high concentration of chloride using quaternary ammonium salts including Aliquat 336 has been widely studied by numerous researchers (see for examples: Juang *et al*. 2004, Sato *et al*. 1984, Grudpan and Taylor 1984). The extraction mechanism has been shown to involve negatively charge chloro metal complexes (Juang *et al*. 2004). The extraction mechanism of base metals such as cadmium to PVC/Aliquat PIMs is thought to be similar to that in a liquid-liquid extraction process, however to date, this premise has not been verified. Pont *et al*. (2008) studied the extraction of Cd to PIMs made of cellulose triacetate, Aliquat 336 and o-nitrophenyl octyl ether and reported that extraction could only occur in a chloride matrix of 0.1 M or higher. They hypothesized that $CdCl_3^-$ was responsible for the extraction of Cd to PIMs in a similar fashion to that of SX using Aliquat 336 as the extractant. However, they did not explain why the rate of extraction did not significantly vary with chloride concentration in the range from 0.1 to 2 M although the percentage of the $CdCl_3^-$ species changed dramatically from almost zero at 0.1 M of Cl^- to close to 40% at 2 M of Cl^-. This paper aims to examine the extraction and stripping of three base metals namely cadmium, copper, and zinc to and from PVC/Aliquat 336 PIMs. Variations in the composition of the base polymer PVC and the extractant Aliquat 336 as well as the solution chemistry were related to the extraction and de-extraction (stripping) properties of PIMs. The obtained data were then used to delineate the extraction of base metals to PVC/Aliquat PIMs.

2. Materials and methods

2.1 Reagents

Technical grade Aliquat 336 (tricaprylylmethylammonium chloride) was purchased from Sigma-

Aldrich (Australia) and was used without any further purification. A high molecular weight (MW) PVC (Sigma-Aldrich, Australia) was used as the base polymer. The weight average MW and number average MW of this PVC were 233 and 99 kDa, respectively. HPLC grade tetrahydrofuran (THF) was purchased from BDH (Australia). All other chemicals used in this study were of analytical grade from Sigma-Aldrich (Australia). Cadmium (II), copper (II), and zinc (II) solutions, used in the membrane extraction experiments and for calibration purposes, were prepared from their corresponding nitrate salts. Laboratory grade Milli-Q water (Millipore, Australia) was used for the preparation of all solutions.

2.2 Preparation of PVC/Aliquat 336 membranes

The membranes were prepared by dissolving the base polymer PVC and the extractant Aliquat 336 chloride in approximately 10 mL THF solvent as previously described elsewhere (Upitis *et al*. 2009). The total mass of PVC and Aliquat 336 was 600 mg. The PVC, Aliquat, and THF mixture was vigorously mixed using a stirring bar for approximately 1 hour until the solution became clear. The solution was then poured into a petri glass dish. The petri dish was covered with 0.45 µm filter paper to control the evaporation rate of THF. After the THF has evaporated, the membrane was then peeled from the petri dish and stored in dry condition for further experiments.

2.3 Extraction and stripping protocol

Extraction was conducted in bath mode. The membrane was cut into small pieces of approximately 1 cm^2 each and placed in a beaker containing 250 mL of an appropriate extraction solution. The extraction solution contained either Cd(II), Cu(II) or Zn(II) and a specified concentration of NaCl. 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 Cd(II), Cu(II) and Zn(II) solutions were obtained with typical R^2 values of more than 0.99 in all analysis. All samples were analysed in triplicate and the standard deviation of 3 replicate measurements was always less than 3%. At the end of the extraction experiment, the membrane samples were removed from the extraction solution using a pair of tweezers. After removing all excessive liquid, the membrane samples were then placed into a beaker containing 250 mL of a stripping solution, containing either 0.01 M HNO$_3$, Milli-Q water, 0.01 M HCl or 0.01 M NaOH. The solutions were also stirred continuously at a constant speed and 1 mL of aliquot was taken at a specific interval for analysis. During the extraction and stripping experiments, the test solution was covered with paraffin film to avoid any evaporation.

2.4 Scanning electron microscope

The PVC/Aliquat 336 membranes were visually characterised with a JSM-6490LA (JEOL Japan) scanning electron microscope (SEM). To prepare for SEM analysis, the membrane sample was frozen instantaneously by dipped into liquid nitrogen. The membrane was then snapped using a pair of tweezers to reveal the cross section. Prior to SEM analysis, the membrane samples were coated with a thin layer of gold using a gold sputter.
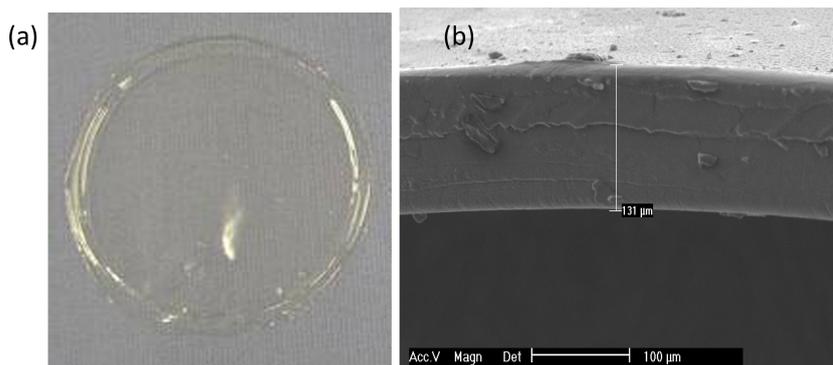
Fig. 1 Aliquat/PVC polymer inclusion membranes: (a) a real scale image of the membrane and (b) an SEM micrograph of the membrane cross section

3. Results and discussion

3.1 Membrane preparation

The combination of 40-70% PVC with the balance of Aliquat 336 resulted in a thin, transparent, and flexible film (Fig. 1(a)). The weight of each membrane was measured and was consistently within 5% of the initial weight (600 mg) of the combined PVC and Aliquat mixture. The small deviation between the final weight of the membrane and that of the initial ingredient can be attributed to solution losses during the fabrication procedure of PIMs particularly when transferring the PVC/ Aliquat/THF solution from the beaker to the petri dish. SEM analysis revealed that the obtained membrane has a homogeneous internal structure. A typical SEM image of the membrane is shown in Fig. 1(b). No correlation between the actual PVC/Aliquat composition and the membrane thickness could be observed. These PVC/Aliquat membranes had a uniform thickness of approximately 130 µm.

3.2 Effects of Aliquat content on Cd(II) extraction

Extraction experiments were conducted with aqueous solutions containing Cd(II), Cu(II), or Zn(II) in 0.05 M of NaCl. These base metals are known to readily complex with chloride. Results reported in Fig. 2 show that Cd(II) was favourably extracted by PVC/Aliquat PIMs. Since Aliquat 336 is the extractant and the base polymer PVC only provides mechanical support to the membranes, not surprisingly, the rate of extraction increased as the Aliquat content in PIMs increased (Fig. 2(a)). Correspondingly, the rate of de-extraction using Milli-Q water as the stripping solution also increased as the Aliquat content in PIMs increased (Fig. 2(b)). In contrast, no extraction of both Cu(II) and Zn(II) could be observed when the extraction solution contained 0.05 M of NaCl (data not shown). The rate of Cd(II) extraction to PVC/Aliquat PIMs in a 2 M HCl solution previously observed by Upitis *et al*. (2009) was significantly higher than that reported in Fig. 2(a) where the feed solution contained 0.05 M NaCl. Chloride is abundant in seawater and some groundwater. Results reported here demonstrate the potential of PVC/Aliquat PIMs for the fabrication of passive sampling devices for heavy metals contamination such as cadmium in seawater and brackish water in addition to their applications in mineral processing. In good agreement with the current study, Upitis *et al*. (2009)
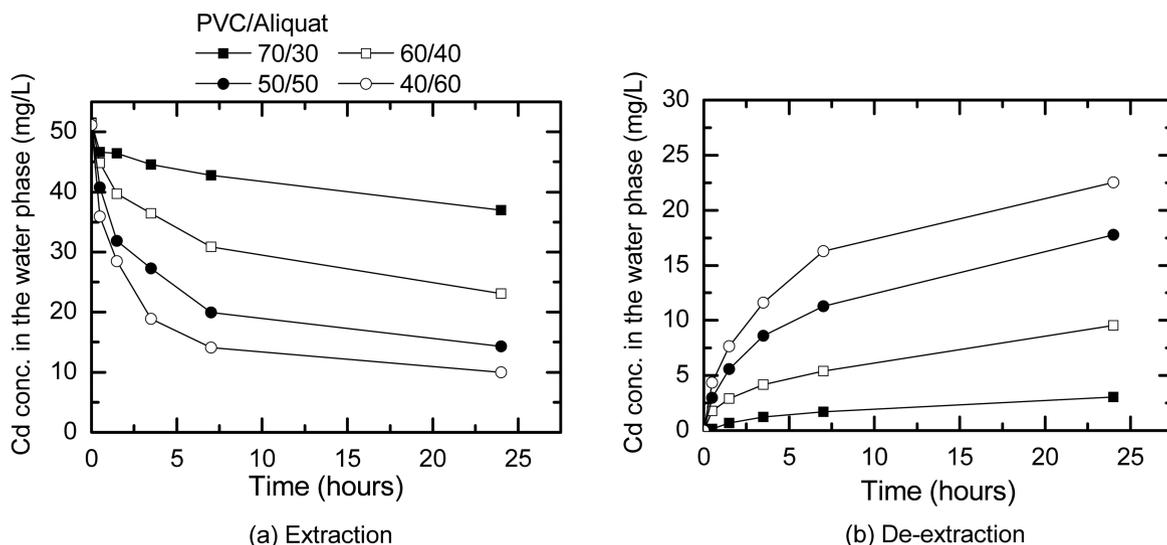
Fig. 2 (a) Extraction and (b) de-extraction (stripping) kinentics of cadmium to PIMs with different PVC and Aliquat 336 contents. Extraction solution contained 50 mg/L Cd in 0.05 M NaCl solution. Milli-Q water was used as the stripping solution

also reported negligible extraction of Cu(II) into PVC/Aliquat PIMs in a 2 M HCl solution. Upitis *et al*. (2009) speculated that the extraction selectivity of Cd(II) over Cu(II) could be attributed to the occurrence of different metal chloride complex species and that only trichloro metal complex could be extracted by PVC/Aliquat PIMs. To substantiate this hypothesis, extraction experiments were conducted with aqueous solutions containing Cd(II), Cu(II), or Zn(II) in 0.05, 0.1 and 3 M of NaCl and the results are presented in Figs. 3(a)-3(c), respectively. The distribution of different metallic ions in a chloride matrix was also modeled using the ChemEQL (version 3.1) thermodynamic modeling software developed by EAWAG (Figs. 3(d)-3(f)).

The extraction of the three base metals investigated here correlates very well to their speciation in the chloride matrix (Fig. 3). Significant extraction of Cd(II) PVC/Aliquat PIMs can be observed when the extraction solution contain NaCl in the range from 0.05 to 3 M. In good agreement with the above discussion, Cu(II) was not extracted to the PVC/Aliquat PIMs regardless of the concentration of chloride in the extraction matrix (Fig. 3(b)) and this observation can be attributed to the absence of any negatively charged copper chloride complex species within the chloride concentration range from 0.05 to 3 M (Fig. 3(e)). Interestingly, while the extraction of Zn(II) did not occur when the extraction solution contained less than 0.1 M of NaCl, significant Zn(II) extraction could be observed at high NaCl concentration (3 M). Once again, the speciation of zinc chloride complex can be used to explain this observation. At below 0.1 M of NaCl, the trichloro zinc complex does not exist (Fig. 3(f)) thus the extraction of Zn(II) to PVC/Aliquat PIMs could not occur at diluted chloride concentration (less than 0.1 M). At higher chloride concentration, the trichloro zinc complex could be formed and thus the extraction of Zn(II) to PVC/Aliquat PIMs could only occur at high chloride concentration (Fig. 3(c)).

It is noteworthy that the rate of Cd(II) extraction to PVC/Aliquat PIMs only marginally increased as the concentration of NaCl in the extraction solution increased from 0.05 to 0.1 M. No discernible
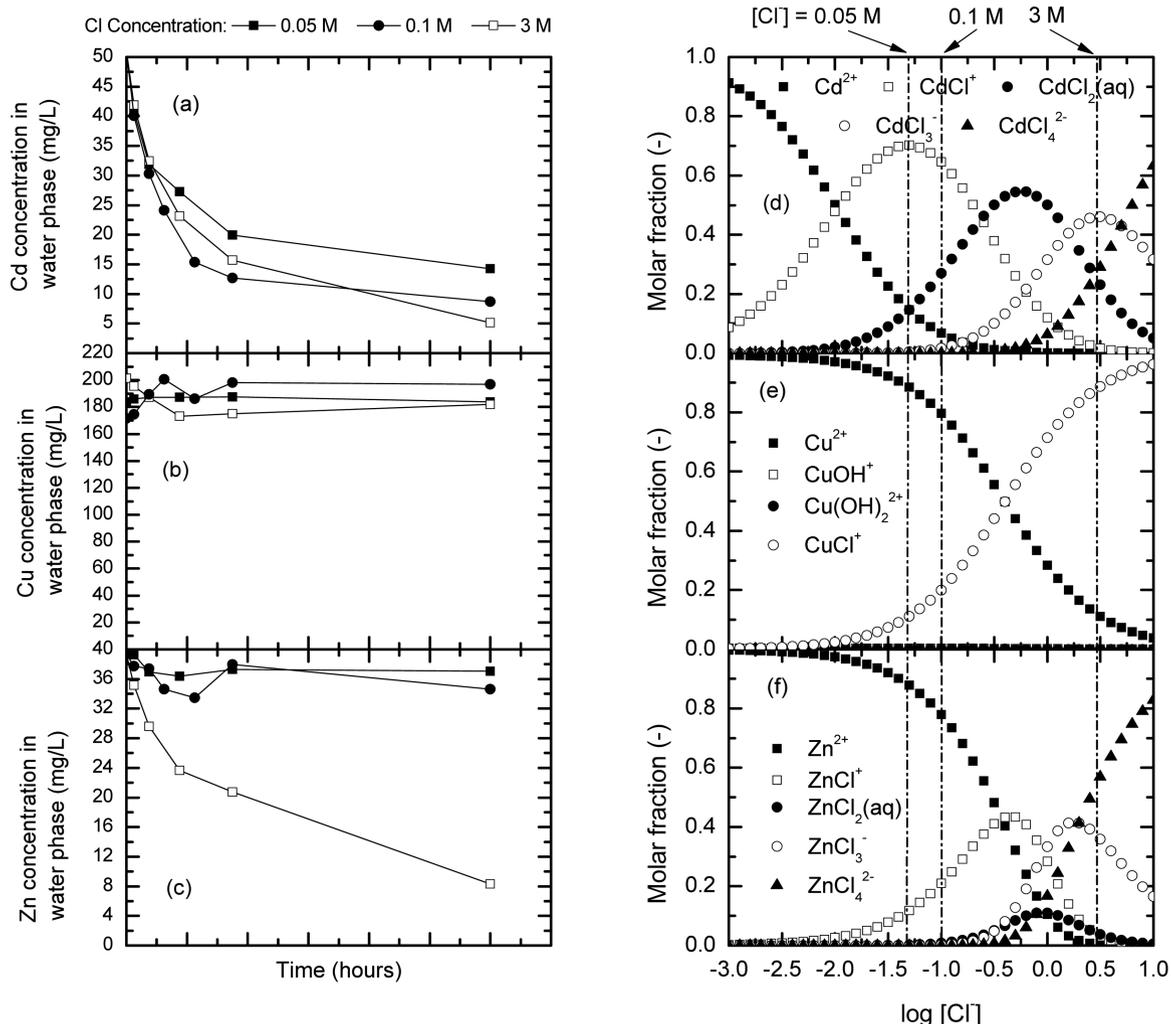
Fig. 3 Extraction of (a) Cd(II), (b) Cu(II), and (c) Zn(II) into PVC/Aliquat PIMs (wt/wt = 50%/50%) from solutions containing different NaCl concentration. The speciation of (d) cadmium, (e) cupper, and (f) zinc chloro complex as a function of NaCl concentration (solution chemistry is the same as the extraction experiments)

increase in the extraction rate of Cd(II) to PVC/Aliquat PIMs could be observed as the NaCl concentration increased from 0.1 to 3 M. On the other hand, over the same NaCl concentration range, the molar fraction of the trichloro and tetrachloro cadmium complex species increased dramatically. Results reported here suggest that the kinetic of the formation of base metal chloride complex is much faster than the rate of PIM extraction and that only a minute amount of extractable species is enough for the extraction process to occur. The reported results also highlight the potential of regulating the concentration of chloride to manipulate the extraction selectivity between certain base metals. Data reported in Fig. 3 does not provide sufficient evidence to ascertain the role of tetrachloro metal complex in the extraction process. Nevertheless, assuming that trichloro metal complex is the

only species involved in the extraction process, the extraction of base metal to PVC/Aliquat PIMs (taking cadmium as an example) can be described as

$$CdCl_3^- + CH_3(C_8H_{17})_3N^+Cl^- \Leftrightarrow \overline{CH_3(C_8H_{17})_3N^+CdCl_3^-} + Cl^- \tag{1}$$

Eq. (1) suggests that for each trichloro cadmium complex molecule extracted to the membrane, one chloride molecule will be released into the aqueous phase. Eq. (1) is also consistent with the extraction mechanism of cobalt to PVC/Aliquat PIMs recently proposed by Kagaya *et al*. (2011). However, the stripping (or de-extraction) of cadmium from PVC/Aliquat PIMs cannot be taken in the reverse order. Further discussion of the stripping process is available in the next section.

3.3 Stripping of cadmium from PVC/Aliquat PIMs

Four different stripping solutions namely Milli-Q water, 0.01 M of NaOH, 0.01 M of HCl and 0.01 M of HNO$_3$ were used to evaluate the de-extraction of cadmium from PVC/Aliquat PIMs. The extraction of cadmium to PVC/Aliquat (wt/wt = 50%/50%) PIM was first conducted and the results were highly reproducible (Fig. 4(a)). Cadmium could not be stripped from the membrane when 0.01 M NaOH was used as the stripping solution. This is possibly because of the low solubility of cadmium in a basic condition. The stripping of cadmium from the membrane could be observed with 0.01 M HCl. However, it is notable that the stripping efficiency was lower than that with Milli-Q water. In fact, the stripping of cadmium from the membrane was most effective with a 0.01 M HNO$_3$ solution. Results presented in Fig. 4 indicate that the stripping of cadmium can only occur in acidic or neutral condition. In addition, the presence of chloride is actually unfavourable for the stripping process. The stripping of cadmium from PVC/Aliquat PIMs is hypothesized as below

$$\overline{CH_3(C_8H_{17})_3N^+CdCl_3^-} \Leftrightarrow CH_3(C_8H_{17})_3N^+Cl^- + CdCl^+ + Cl^- \tag{2}$$

$$\overline{CH_3(C_8H_{17})_3N^+CdCl_3^-} \Leftrightarrow CH_3(C_8H_{17})_3N^+Cl^- + Cd^{2+} + 2Cl^- \tag{3}$$
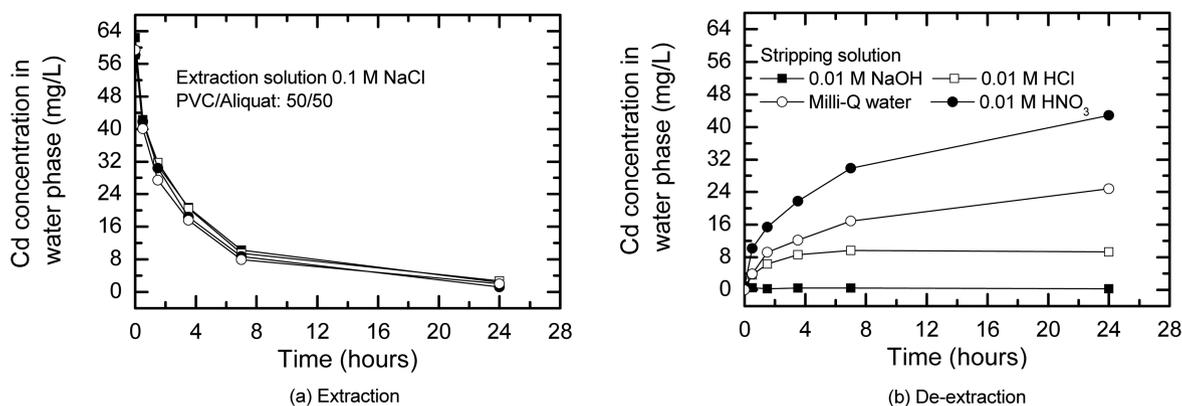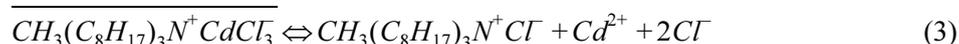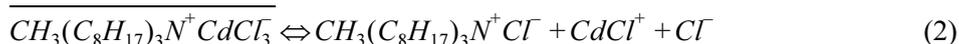

Fig. 4 (a) Extraction and (b) de-extraction (stripping) kinentics of cadmium to PVC/Aliquat PIMs (wt/wt = 50%/50%)

As can be seen in Eqs. (2) and (3), the stripping of cadmium generates chloride, and thus in good agreement with the discussion above, the presence of chloride in the stripping solution is unfavourable. Based on the extraction and stripping mechanisms proposed in Eqs. (1)-(3), it appears that facilitative transport of cadmium through PVC/Aliquat PIMs can be achieved with a chloride concentration gradient across the membrane in a co-current transport mode. Facilitated transport of base metals through PVC/Aliquat PIMs is beyond the scope of this current investigation but will be reported in a future study.

4. Conclusions

This study demonstrated the fabrication of PVC/Aliquat PIMs for selective extraction of Cd(II) over other base metals. The rate of Cd(II) extraction from a chloride matrix increased as the Aliquat content in PIMs increased. Results reported here showed that the trichloro and possible tetrachloro complex species were responsible for the extraction of base metals into PVC/Aliquat PIMs. Therefore, the selectivity of Cd(II) over Cu(II) and Zn(II) can be controlled by regulating the chloride concentration in the extraction solution. The de-extraction of Cd(II) was most effective when the stripping solution was acidic and in the absence of any chloride.

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