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The Influence of the Interior Structure of Aliquat 336/PVC Membranes to their Extraction Behavior

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ABSTRACT

In this study, new results of the cross-sectional structures of Aliquat 336/PVC-based composite membranes were obtained using Scanning Electron Microscopy (SEM). The SEM images show that micro channels exist when the Aliquat 336 content reaches a certain level. Our data suggests that this level is between 30–40% (m/m) Aliquat 336/PVC. The extraction of Cd(II) using these membranes clearly shows that the

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micro channels in the membrane facilitated the transportation of the free Aliquat 336 molecules and the Aliquat 336-$CdCl_3$ ion pairs within the membrane and as such enhances the extraction rate. Results of this study provide valuable information for future work in modeling of the extraction mechanism.

Key Words: Membrane extraction; Aliquat 336; PVC composite membrane; Cadmium(II); Membrane structure; Semi-Liquid membrane.

INTRODUCTION

Several researches have reported the extraction of heavy metal ions [Cd(II), Cu(II), and Au(III)] from aqueous solutions using PVC-based polymer composite membrane film containing Aliquat 336.[1–7] This type of membrane film has been shown to be quite effective in removing trace amount of heavy metal ions from aqueous solutions.[4–6] More recently, Xu et al. have demonstrated that various extraction assemblies could be made using those membrane films to suit different extraction conditions and requirements.[1–3] Since, comparing with solvent extraction, the use of composite membranes in extraction has the advantage of significantly reducing the use of solvents, it is regarded as a potential cleaner approach to the separation technology. For this reason, it is expected that research in membrane extraction technology will continue.

A serious shortcoming of the membrane extraction systems is that the extraction capacity is much lower than that of the solvent extraction systems.[1,3,4]. Several authors have shown that extraction rates of PVC membranes containing the Aliquat 336 were very slow and with low extraction capacity.[3–6] It was believed that the Aliquat 336 extractant molecules in the polymer matrix are entangled with the PVC polymer chains. As a consequence, the activity and the diffusivity of Aliquat 336 are expected to be greatly reduced. This is consistent with the extraction results reported by several authors, which showed that extraction rates of PVC membranes lightly loaded with Aliquat 336 were very low.[3–6] Result reported by Xu et al.[2] has also shown that after a prolonged exposure of a PVC-based membrane lightly loaded with Aliquat 336 to an aqueous solution, the amount of Aliquat 336 being leached into the aqueous solution could not saturate the solution.[2] This too suggests that the activity (and diffusivity) of Aliquat 336 molecules in the membrane is quite low.

In a study of the extraction of Cd(II) using Aliquat 336/PVC membrane extraction system, Wang[5] showed that the extraction rate and capacity of an Aliquat 336/PVC membrane is dependent upon the loading level of the

Aliquat 336 extractant. In this study, it was proposed that the extraction reaction at the membrane-solution interface results in the formation of an Aliquat 336-trichlorocadmium(II) complex, as shown in Eq. (1):

$$(A^{+}Cl^{-})_{m} + ([CdCl_{3}]^{-})_{a} = (A^{+}[CdCl_{3}]^{-})_{m} + (Cl^{-})_{a} \qquad (1)$$

where $A^{+}Cl^{-}$ is Aliquat 336 chloride, $[CdCl_{3}]^{-}$ is the trichlorocadmium(II) ion and $A^{+}[CdCl_{3}]^{-}$ is the extracted complex (an ion-pair). The subscripts m and a represent the membrane and the aqueous phases, respectively.

The mechanism involved in this study was proposed by Wang et al.[4] which made use of the computer mathematical model developed by Kolev et al.[7] In this model, the mechanism proposed involves the extraction reaction at the membrane–aqueous solution interface and diffusion of the Aliquat 336-anionic metal complex within the membrane. The Aliquat 336-anionic metal complex molecules migrate from the membrane–solution interface into the membrane-bulk, while the free Aliquat 336 molecules migrate at an equal rate from the bulk to the interface, replacing the reacted Aliquat 336 molecules.[4,5] Under this assumption where only one mode of diffusion was considered, the modeling suggested that as the Aliquat 336 content in the membrane increased from 30% (m/m) to 40% (m/m) and further to 50% (m/m), the (apparent) diffusion coefficient (D_A) of $(A^{+}Cl^{-})_{m}$ [and thus $(A^{+}[CdCl_{3}]^{-})_{m}$] increased from $3.85 \times 10^{-14}\,m^2/s$ to $13.1 \times 10^{-14}\,m^2/s$ and further to $24.0 \times 10^{-14}\,m^2/s$, respectively.[4]

In an earlier study of the membrane extraction of Au(III), Kolev et al.[7] mathematically modeled the extraction kinetics of Au(III) using Aliquat 336/PVC membrane films. The model considered the following reaction:

$$(A^{+}Cl^{-})_{m} + ([AuCl_{4}]^{-})_{a} = (A^{+}[AuCl_{4}]^{-})_{m} + (Cl^{-})_{a} \qquad (2)$$

where $[AuCl_{4}]^{-}$ is tetrachloroaurate(III) species, $A^{+}[AuCl_{4}]^{-}$ is the Aliquat 336- tetrachloroaurate(III) ion-pair, m and a are membrane and aqueous phase, respectively. These authors found that the equilibrium coefficient of the extraction reaction, which is defined as the ratio of the forward and backward rate constants of reaction (2), remained almost unchanged as the Aliquat 336 content in the membrane increased from 22 to 40% (m/m), but increased sharply by 12.5 folds as the Aliquat 336 content increased to 50% (m/m). Kolev et al.[7] proposed that such a significant increase in the equilibrium coefficient was due to the change in the properties of the membrane. However, no evidence of this change was offered.

Xu et al. also observed a large increase in the extraction rate and the extraction capacity of the membrane as the Aliquat 336 content in the membrane film was increased.[1,3] We believe that the significant change in membrane kinetics observed by Kolev et al.,[7] Wang,[5] Wang et al.[4] and

Xu et al.[1,3] was due to a similar cause. It is most likely that such a change in the kinetics of membrane extraction is associated with changes in the activity of Aliquat 336 molecules, and the mode of diffusion of Aliquat 336 molecules and the extracted complex in the membrane. This change in the kinetics may be related to the structural alteration in the membrane caused by the increase in Aliquat 336 content.

Understanding the membrane microstructure that affects the diffusion rates of the extractant and the extracted complex is of critical importance. It assists in the designing of a more efficient extraction system, and developing mathematical models that can offer a possible mechanism of extraction of the membranes of specific structures. In this work SEM was used to study the morphology of the cross sectional area of Aliquat 336-PVC membrane films in order to determine any possible microstructures that exist in the membrane which are responsible for the changes in diffusion coefficients reported previously.

EXPERIMENTAL

Reagents

Aliquat 336 was obtained from Fluka. It was a mixture of quaternary ammonium chlorides and was used as received. High molecular weight poly(vinyl chloride) (Mw $>$ 90,000) was also obtained from Fluka. It was used as received for the membrane preparation. Tetrahydrofuran (THF) was HPLC grade received from BDH. It was purified by passing through an activated alumina column to remove any stabilisers and peroxides before use. Hydrochloric acid and cadmium(II) chloride were of analytical grade from BDH. A series of Cd(II) standard solutions for atomic absorption spectroscopic measurements was prepared by diluting a Cd(II) stock solution of 1000 mg/L (BDH Spectrosol) with a 2.0 M HCl solution.

Preparation of Aliquat 336/PVC-based Membrane Film

The membrane films used in this study were prepared by dissolving a mixture of Aliquat 336 and PVC in about 50 mL of THF. The homogeneous solution obtained was then poured into a glass ring on a flat glass plate. The THF was allowed to evaporate slowly over 12 h to yield a colourless, flexible, transparent and mechanically strong membrane films. The membrane was then removed from the glass plate and used for the membrane extraction study. In this study, membrane films containing 20–50% (m/m) Aliquat 336/PVC were prepared.

Preparation of Membrane Assembly, and Membrane Extraction Experiments

The preparation of the membrane assembly can be found elsewhere.[1,2] It involves transferring a known mass of undiluted Aliquat 336 into a bag made using two Aliquat 336/PVC membrane films. The bag was then heat-sealed. Membrane extraction studies were carried out at room temperature in a two-compartment cell, i.e., compartment A and compartment B. Each compartment has a volume capacity of 220 mL. The membrane assembly was inserted between the two compartments as shown in Fig. 1. Each compartment was stirred at a constant rate throughout the extraction process by a magnetic stirrer. An aqueous solution of the same composition was placed

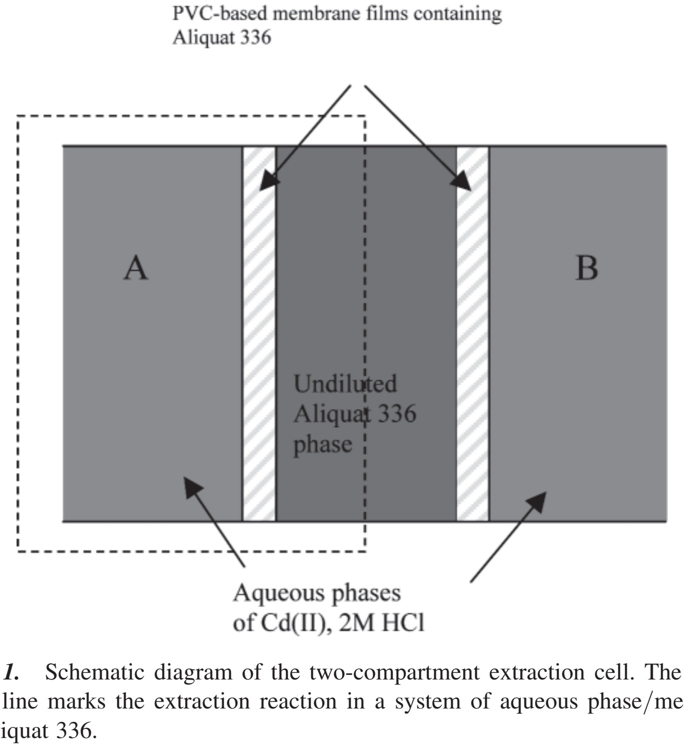

Figure 1. Schematic diagram of the two-compartment extraction cell. The box of broken line marks the extraction reaction in a system of aqueous phase/membrane film/Aliquat 336.

in both compartments. The box shown as the broken lines in Fig. 1 marks the extraction reaction in a system of aqueous phase/membrane film/Aliquat 336. The decrease in Cd(II) concentration in the compartments was plotted against extraction time and was used to express the rate of extraction.

Morphology of the Aliquat 336/PVC Membranes

The cross sectional morphology of Aliquat 336/PVC membranes was studied by scanning electron microscopy (SEM) using a LEO 1530 scanning electron microscope. The cross section of membrane was created using the freeze-fracture technique.[8] The membrane was immersed in liquid nitrogen and was then fractured using a pair of forceps. The fractured samples were mounted on the sample studs by means of clips with the fractured surface facing upward for examination. The samples were lightly sputter-coated with gold. The SEM measurements were performed at an accelerating voltage of 5 kV. The magnification of all SEM images was 5000×.

RESULTS AND DISCUSSION

Cross-Sectional Morphology of the Aliquat 336/PVC-Based Membrane Film

Figures 2–5 are SEM images of the cross-sections of Aliquat 336/PVC membranes containing 20, 30, 40, 50% (m/m) of Aliquat 336. These images provide a clear view of the interior structures of the Aliquat 336/PVC membrane films. As are shown by Figs. 2 and 3, there is no apparent pore structure in the membrane films containing 20 and 30% (m/m) Aliquat 336. Microscopically, the polymer phase appears to be homogeneous. However, as the Aliquat 336 content reaches 40%, the interior of the membrane film becomes evidently porous (Fig. 4). When Aliquat 336 content reaches 50% (Fig. 5), micro pores in the membrane appear to be slightly different in shape. They are less circular in cross section and appear to be somewhat "scaly."

The observed morphology of the membrane films of high Aliquat 336 content offers a qualitative explanation of the weakened mechanical strength of these membranes, which was reported previously.[1,4–6] At a low Aliquat 336 content (i.e., below 30%) where no micro pores are evident, the extractant molecules may well be "entangled" with the polymer chains. In this state the extractant molecules behave like a plasticiser to the polymer film, but would have low activity and mobility through the polymer matrix. At high Aliquat

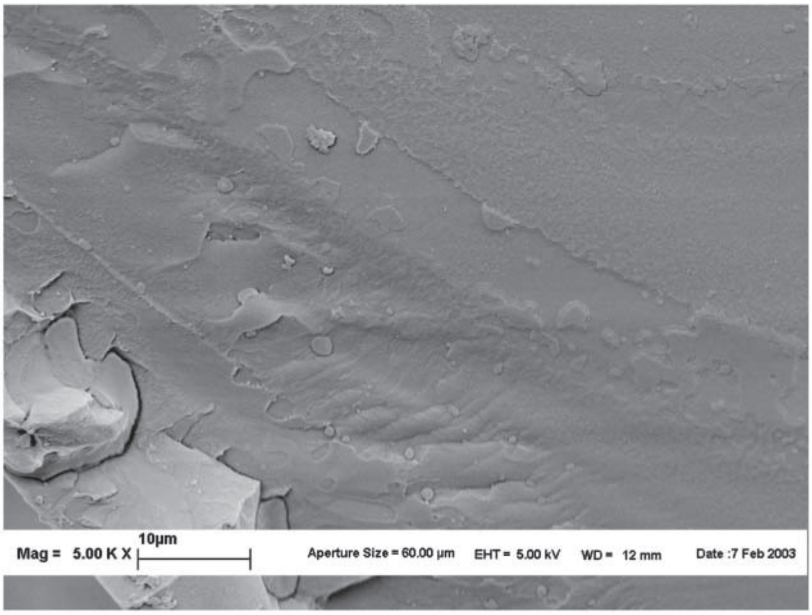

Figure 2. A cross-sectional SEM image of a 20% (m/m) Aliquat 336/PVC membrane film (5000×).

336 content (i.e., above 40%), the excess amount of Aliquat 336 might form micro aggregates, which prevent the PVC polymer chains to form a complete polymer matrix. Wang et al.[4,5] showed in an earlier study that the pore structure in Figs. 4 and 5 were not observed from the surfaces of the membrane films.

It is interesting to note that the SEM results do not clearly show signs of Aliquat 336 in the micro pores. However, there is little doubt that the presence of excess amount of Aliquat 336 disrupted the bonding between PVC chains. One of the functions of a plasticizer is to act as a lubricant to allow the molecules to slide over one another freely, or to act as a partial solvent for the polymer. In the second case, however, the plasticizer molecules break some of the secondary polymer-to-polymer bonds (which are mainly the molecular interactions of van der Waals and hydrogen bonding nature) and replace them with polymer-to-plasticizer bonds.[9]

It is also possible that although Aliquat 336 and PVC form a solution when Aliquat 336 content was low, phase separation could occur when Aliquat 336 content becomes high (e.g., $>30\%$). THF may serve as a common solvent to both Aliquat 336 and PVC. However, as THF evaporates

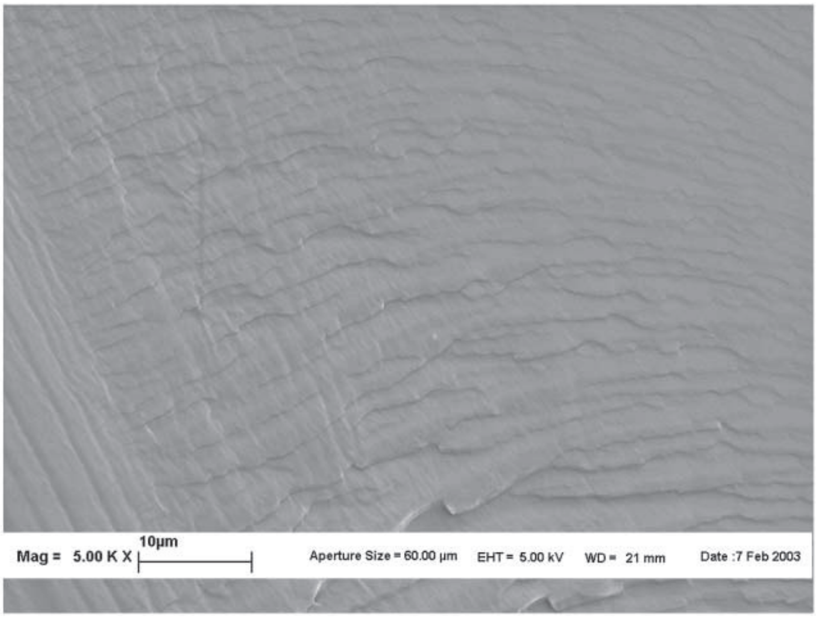

Figure 3. A cross-sectional SEM image of a 30% (m/m) Aliquat 336/PVC membrane film (5000×).

away from the system, de-mixing of Aliquat 336 and PVC could have occurred. Since the microscopic aggregates appear to be reasonably uniform, such a de-mixing process might have occurred at the time when the three-dimensional polymer matrix was almost formed (or the membrane was almost set). This possible phase separation will be investigated in our future study. The feasibility of using an alternative solvent to form the membrane film to avoid the phase separation will also be investigated in future.

A study carried out by Wang[5] using X-ray Photoelectron Spectroscopy (XPS) on the Aliquat 336/PVC membrane film has shown that Aliquat 336 has a tendency to migrate to the polymer-air interface. This may be related to the surface-active nature of Aliquat 336. The surface concentration of Aliquat 336 was found to be higher than that of the membrane bulk. It is quite possible that the surface concentration on the wall of the microstructures is also much higher than that of the membrane bulk. Thus, it is likely that the activity of Aliquat 336 in these microstructures, and the diffusivities of both the free Aliquat 336 and $(A^{+}[CdCl_3]^{-})_m$ ion-pairs in those microstructures are much higher than those of the Aliquat 336 molecules which are 'entangled' within the polymer matrix.

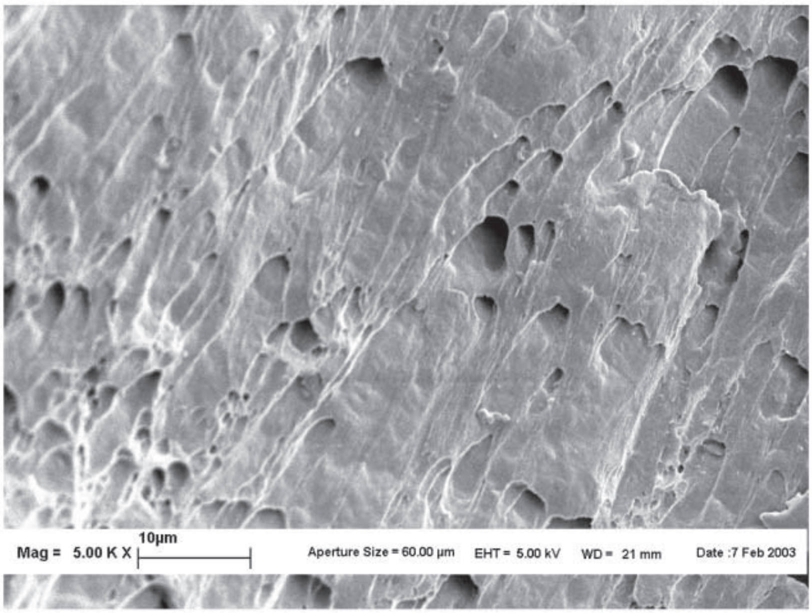

Figure 4. A cross-sectional SEM image of a 40% (m/m) Aliquat 336/PVC membrane film (5000×).

SEM results do not, however, provide direct evidence as to whether the microstructures in membranes of high Aliquat 336 content are micro pores or micro channels. The extraction behaviour of the membrane suggests that these microstructures could well be somehow connected, forming channels which provide a passageway for Aliquat 336 and $(A^{+}[CdCl_3]^{-})_m$ ion-pairs to diffuse across the membrane film. Such a hypothesis is in good agreement with the trend observed by Wang,[4,5] Kolev et al.[7] and Xu et al.[1,3] in that the apparent diffusion coefficients increased significantly as the content of Aliquat 336 reaches certain level.

Membrane Extraction Studies

To support this hypothesis, experiments were designed using the membrane assembly to extract Cd(II) from an aqueous hydrochloric acid solution. As shown in Fig. 1, one surface of the membrane film faces the aqueous solution containing Cd(II) and the other faces the undiluted Aliquat 336. Such an arrangement offers a situation that the chemical potential difference

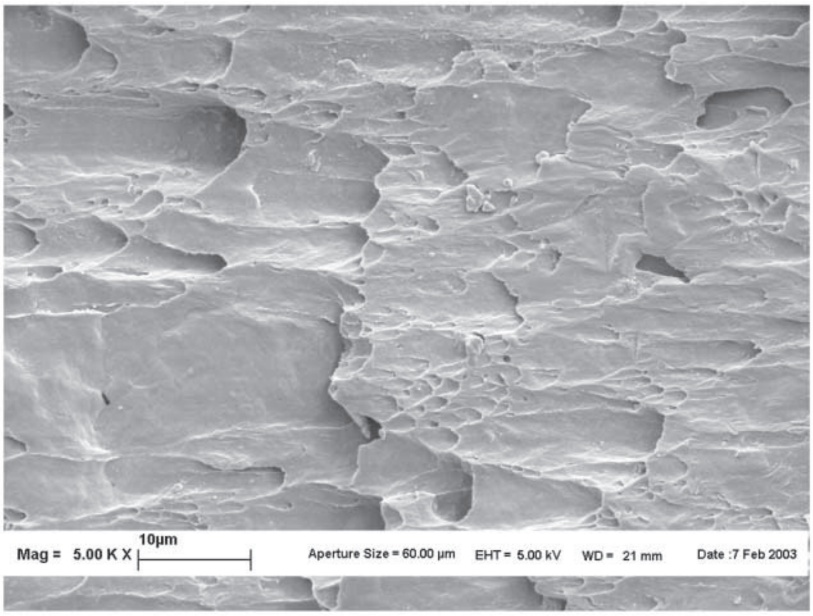

Figure 5. A cross-sectional SEM image of a 50% (m/m) Aliquat 336/PVC membrane film (5000×).

of the free metal ion across the membrane film is so great that a complete removal of metal ions from the aqueous phase is possible.

Figure 6 shows the extraction rates of Cd(II) using PVC membrane films containing 20% (m/m), 30% (m/m) and 40% (m/m) of Aliquat 336. Extraction rate was low for assemblies made using membrane films containing 20% (m/m) (diamond legend) and 30% (m/m) (square legend) Aliquat 336. In the former case, the aqueous concentration of Cd(II) was reduced from 72 to 50 mg/L in 340 h. Although the initial extraction rate of the 30% membrane film was faster than that of the 20% one, it slowed down after 100 h. The Cd(II) concentration in the aqueous phase dropped from 72 to around 45 mg/L, only marginally better than in the case of the 20% (m/m) Aliquat336/PVC membrane film. These results are in good agreement with data reported by Xu et al.[3] that the Cd(II) concentration in the aqueous phase could never be completely extracted using membrane films containing less than 30% Aliquat 336. The slow extraction rates in the above cases clearly indicate the slow migration/diffusion of the $(A^+[CdCl_3]^-)_m$ ion-pairs (and thus also Aliquat 336 molecules) within the polymer matrix.

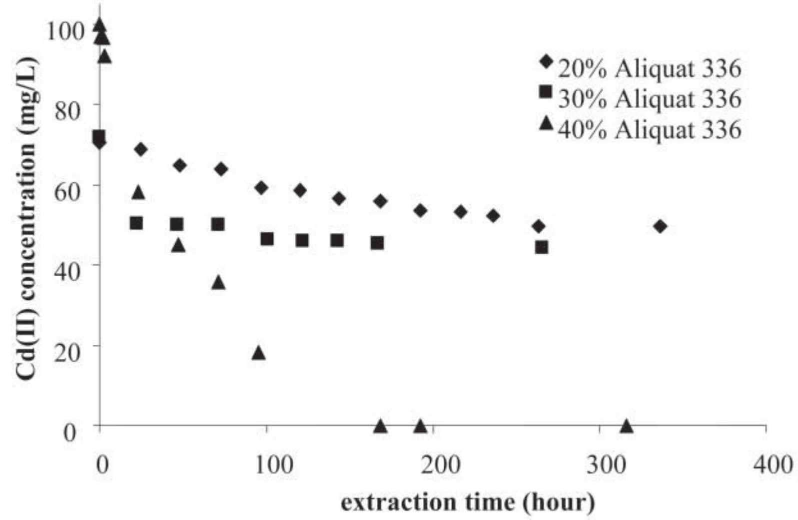

Figure 6. Extraction results using the membrane assemblies shown in Fig. 1. The Aliquat 336 contents in the membrane films for making the assemblies were different and are indicated by different legends. Cd(II) concentration data were collected from compartment A in all cases.

The triangle legend in Fig. 6 shows the extraction results of a membrane assembly using membrane films containing 40% (m/m) Aliquat 336/PVC. It can be seen that the extraction rate is greatly increased and the concentration of Cd(II) ions was reduced to zero within 200 h. This result supports the hypothesis that the microstructures formed in the membrane film are most likely to be micro channels. Some Aliquat 336 molecules in these channels are not entangles with the polymer chains and have higher activity and diffusivity. These channels provide pathways through which the extractant and the extractant-metal complex ion-pairs diffuse faster than through polymer matrix where such micro channels are not available.

Another important point that can be gathered from the SEM study of this membrane system is that the formation of micro channels occurs only when the content of the Aliquat 336 in the PVC membrane film exceeds 30% (m/m). Previous mathematical modeling work assumed that Aliquat 336 molecules in the membrane film are in an entangled state, and that the initial Aliquat 336 concentration in the membrane film was homogeneous.[7] Results from this study, however, show that this assumption is not valid if membrane film used contains more than 30% (m/m) Aliquat 336. Thus, for membrane films containing greater than 30% of Aliquat 336, it is necessary to consider possible new mechanism(s), or another mode of diffusion, such as one that can occur in the micro channels.

CONCLUSION

This study shows, through SEM analyses, that the interior structure of the membrane film varies with the extractant content in the film. At low extractant content (below 30%), the interior structure of the membrane film appears to be homogeneous. This is in agreement with the view that the extractant molecules are entangled with the polymer chains and act as a plasticiser. As the extractant content is increased to 40%, microstructures in the membrane bulk start to form. The results of the extraction experiments demonstrated that the extraction rates significantly increase when the Aliquat 336 content is increased from 30 to 40%. Thus, from the results of the SEM and the extraction studies, it can be concluded that a critical Aliquat 336 content lies in the range of 30 to 40% (m/m), beyond which the extractant molecules in the membrane film can no longer be described as entangled. At this point, some of the Aliquat 336 starts to aggregate (possibly due to the de-mixing of Aliquat 336 and PVC) and interfere with the formation of PVC polymer matrix. As a result, microstructures become apparent in the bulk of membrane film under SEM. It is proposed that the significant increase in the extraction rate is linked to the formation of the microstructures in the membrane film and these are likely to be micro channels. The activity and diffusion coefficient of the extractant molecules and the metal-extractant ion-pairs are higher in those micro channels than in the polymer matrix where those channels are absent. These results provide valuable information for future mathematical modeling study. It may be necessary to assume that there are two modes of diffusion and at a high extractant content [>30% (m/m)], the diffusion through micro channels dominates the transport mechanism in the membrane.

REFERENCES

1. Xu, J.; Paimin, R.; Shen, W.; Wang, X. A novel polymer membrane for extraction applications. Fibers and Polymers **2002**, *3* (2), 68–72.
2. Xu, J.; Paimin, R.; Shen, W.; Wang, X. An investigation of solubility of aliquat 336 in different extracted solutions. Fibers and Polymers **2003**, *4* (1), 27–31.
3. Xu, J.; Paimin, R.; Shen, W.; Wang, X. Improved membrane for the extraction of heavy metals. Fibres and Polymers **2004**, *5* (1), 68–74.

4. Wang, L.; Paimin, R.; Cattrall, R.W.; Shen, W.; Kolev, S.D. The extraction of cadmium(II) and copper(II) from hydrochloric acid solutions using Aliquat 336/PVC membrane. Membr. Sci. **2000**, *176*, 105–111.
5. Wang, L. Extraction study of cadmium(II) and copper (II) using Aliquat 336. Victoria University of Technology: Australia, 1999; MSc Thesis.
6. Argiropoulos, G.; Cattrall, R.W.; Hamilton, I.C.; Kolev, S.D.; Paimin, R. The study of a membrane for extracting gold(III) from hydrochloric Acid Solutions. Membr. Sci. **1998**, *138*, 279–285.
7. Kolev, S.D.; Argiropoulos, G.; Cattrall, R.W.; Hamilton, I.C.; Paimin, R. Mathematical modelling of membrane extraction of gold(III) from hydrochloric acid solutions. Membr. Sci. **1997**, *137*, 261–269.
8. Bridge, M.J.; Broadhead, K.W.; Hlady, V.; Tresco, P.A. Ethanol treatment alters the ultrastructure and permeability of PAN-PVC hollow fibre cell encapsulation membranes. Membr. Sci. **2002**, *195*, 51–64.
9. Hanlon, J.F. *Handbook of Package Engineering*, 2nd Ed.; Technomic Publishing AG: PA; 1992; 8–44.

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