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**POLYMERIC PROPERTIES AND METAL EXTRACTION
PERFORMANCE OF POLY (VINYL CHLORIDE)/ALIQUAT 336
POLYMER INCLUSION MEMBRANES AND ELECTROSPUN
FIBRES**

The thesis submitted in the fulfillment of the requirement for the award of the degree

Doctor of Philosophy

From

UNIVERSITY OF WOLLONGONG

By

Nurul Syazana Abdul Halim

School of Civil, Mining and Environmental Engineering

Faculty of Engineering and Information Science

March, 2015

Declaration

This is to certify that work reported in this thesis was done by the author, unless specified otherwise, and that no part of it has been submitted in a thesis to any other university or similar institution.

Nurul Syazana

March 2015

Dedicated to:

My lovely husband and our little caliph, Muhammad Solahuddin

ABSTRACT

This thesis aimed to investigate the polymeric properties and the metal extraction performance of polyvinyl chloride (PVC) and Aliquat 336 polymer inclusion membranes (PIMs) and electrospun fibres. The PIMs and the electrospun fibres were prepared using PVC and Aliquat 336 as the base polymer and extractant, respectively.

The results showed that PVC/Aliquat 336 PIMs were non-homogenous and phase separated at sub micrometre scale even though all PIMs were transparent and homogenous to the naked eye or upon microscopic examination by scanning electron microscopy. The surface morphology of PIMs showed smooth surface with no apparent pores for PIMs with less than 30 wt.% Aliquat 336. Above 30 wt.% Aliquat 336, the PIMs showed some wrinkles and it became obvious as the Aliquat 336 content reach 40 wt.% suggesting that it might contain two separate domains. The phase separation was confirmed by the DMA results where the glass transition (T_g) and the melting temperature (T_m) of separated PVC and Aliquat 336 rich phases was clearly identified. This two phases is assigned to the α transition and β transition respectively. But, the later transition was not detected by DSC due to small changes in heat capacity where it could only be used to determine the T_g of PIMs with low Aliquat 336 content. For the PIMs observed here, the T_g was independent of Aliquat 336. This result indicates that Aliquat 336 does not act as a plasticising reagent in PIMs even though it has successfully produced a transparent and flexible thin film.

The phase separation nature of PVC/Aliquat 336 PIMs has important implication towards the metal ion extraction performance in which the metal ions extraction could only occur when the proportion of Aliquat 336 exceeded 30 wt.%. This Aliquat 336 content of 30 wt.% also coincide with the appearance of Aliquat 336 rich phase observed by DMA. In addition, results from impedance study showed that PIMs with less than 30 wt.% Aliquat 336 were far out from the ideal plot and were not suitable to be used as a solid state polymer-electrolyte for metal ions extraction. This is due to the high resistance and low conductivity of the PIMs film. However, the metal extraction rate can also be improved by increasing the extraction temperature which increases the diffusivities in Aliquat 336 phase.

The impact of aging on PVC/Aliquat 336 PIMs was also investigated in this thesis work. The results showed that freshly prepared PIMs contain residual tetrahydrofuran (THF) which was used as solvent for membrane manufacture. Removal of some residual THF by membrane aging resulted in notable changes in the thermomechanical properties of the PIMs where the PIMs exhibited two thermal transitions over the same range temperature. Although there is a clear impact of aging on membrane properties, there is no significant impact on the extraction of Cd(II) by PVC/Aliquat 336 PIMs.

The preparation of electrospun fibres from PVC and Aliquat 336 was also demonstrated in this study. A detailed thermomechanical characterisation revealed that key characteristics and properties of PVC/Aliquat 336 PIMs and electrospun fibres differ significantly. The PVC/Aliquat 336 electrospun fibres were homogenous at sub micrometre scale. The homogeneity of PVC/Aliquat 336 electrospun fibres was confirmed by a single transition that is an α transition observed using DMA. Furthermore, the Aliquat 336 in electrospun fibres could function as a plasticizer. This was confirmed by the appearance of a single T_g that decreased with the increasing of Aliquat 336 content. In terms of metal ion extraction, the extraction of Cd(II) increased with the increasing of Aliquat 336 content. There was a significant extraction even at low Aliquat 336 content (i.e., 6 wt.%). In contrast, the extraction of Cd(II) in PIMs needs to exceed the percolation threshold of 30 wt.% Aliquat content. Besides, results from extraction capacity showed that electrospun fibres have higher absorption capacity compared to PIMs which clarify why they have better extraction. On the other hand, it appears that the applied voltage might influence the formation of beads and fibres diameters of PVC/Aliquat 336 electrospun mats but the level of significance may varies with the polymer concentration and tip distance or in this case Aliquat 336 concentration.

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THESIS RELATED PUBLICATIONS

Peer-reviewed Journal Paper:

1. **Abdul-Halim, N.-S.**, Whitten, P.G., and Nghiem, L.D., Characterising poly (vinyl chloride)/Aliquat 336 polymer inclusion membranes: Evidence of phase separation and its role in metal extraction. *Sep. Purif. Technol.*, **2013**. **119: p. 14-18.**
2. **Abdul Halim, N.S.**, Whitten, P.G., and Nghiem, L.D., The effect of aging on thermomechanical and metal extraction properties of poly (vinyl chloride)/Aliquat 336 polymer inclusion membranes. **Desalination Water Treatment**, **2014: p. 1-6.**

Conference Presentation:

1. **Abdul-Halim, N.-S.**, Whitten, P.G., and Nghiem, L.D., Characteristics and cadmium extraction performance of PVC/Aliquat 336 electrospun fibres in comparison with polymer inclusion membranes. Oral presentation at 4th IWA Regional conference on Membrane Technology 2014, 3-6 December 2014.

Chapter 1

Introduction

1.1 Background study

The use of heavy metals in many industrial applications has become a great concern especially when they are released into the environment. Notable examples of these heavy metals include cadmium and zinc which exist naturally in the earth crust and are used in many industrial activities such as metal plating, battery manufacturing, alloy production, metal coating [1, 2]. Without adequate treatment, the occurrence of heavy metals in wastewater from these industrial activities may cause severe adverse effects to human health and the environment. Unlike organic contaminants, heavy metals cannot biodegrade and tend to accumulate in living tissues, causing a range of both acute and chronic toxicity effects. Therefore, it is essential to develop cost-effective treatment options for the removal of heavy metals from industrial wastewater to their permitted levels before discharge into the environment.

Removals of metal ions have been performed by several methods such as chemical precipitations, adsorption, ion-exchange, electrochemical methods, solvent extraction and membrane separation [3]. Among these, solvent extraction is the most extensively used method for heavy metals removal especially in hydrometallurgy due to excellent process in extracting various metal ions which meets the standard environmental guideline. Besides, this process allows the recovery of the metal ions that can be recycled back in the industrial process and hence are more economical. To achieve this goal solvent extraction requires the use of organic solvents in liquid phase which can be a significant source of pollutants to the aquatic environment. Fire danger and explosion are amongst many other concerns associated with the use of a large amount of organic solvents which is hazardous, toxic and flammable [4].

Membrane technology has become an attractive alternative option for the treatment of industrial wastewater and water purification. In the last three decades, liquid membranes have been extensively studied due to significant advantages over solvent extraction method. Polymer inclusion membranes (PIMs) initially proposed by Suguira et al. [5] is a type of liquid membrane that has been developed for metal ions

extraction providing high selectivity and easy operation. PIM film consists of a polymer, an extractant and if necessary a plasticizer. Extractant is an essential component for the transport of metal ions that function as a guest host specific molecule to provide selective membrane permeability for target species [6, 7]. Among various kind of extractant, Aliquat 336 offers an efficient transport of numerous metal ions such as chromium, copper, cadmium, platinum and etc. A combination of Aliquat 336 and polyvinylchloride (PVC) as a base polymer has proven to be a good compatibility and no additional plasticizer is needed [8]. However, it is not yet clear whether the PVC/Aliquat 336 PIM is a solid homogenous solution or a two phase heterogeneous mixture.

On the other hand, electrospinning is a versatile method in producing polymer fibres with ultrathin diameters ranging from 50 to 500 nm. This technique has successfully produced polymer fibres with large surface area-to-volume ratio and high porosity which is favourable in various applications including tissue engineering, drug delivery, electronic and semi-conductive materials [9]. Numerous polymers have been used to electrospin the polymer fibres in different applications [10]. However, their applications in wastewater treatment especially for heavy metals removals are limited and scarcely reported. Besides, research on polymer fibres incorporating extractant for electrospun fibres is also new and barely reported.

Therefore, the aim of the present work is to develop and characterize the PIMs and electrospun fibres and to determine the miscibility of PVC and Aliquat 336 in both membranes. The potential of these membranes in removing metal ions is also investigated.

1.2 Research objectives

The overall objective of this research was to investigate the polymeric properties and metal extraction performance of PVC/Aliquat 336 polymer inclusion membranes and electrospun fibres in order to gain a better understanding on the relation of their polymeric properties to their metal extraction capacity.

This research aims to achieve the following objectives:

- 1) determine the miscibility of PVC/Aliquat 336 PIMs at various Aliquat 336 content produced and investigate the extraction of Cd(II) and Zn(II) in order to observe any correlation between solid structure, thermal analysis and membrane function.
- 2) examine impact of membrane aging on polymeric properties and subsequently the extraction of Cd(II) as a representative heavy metal by PVC/Aliquat 336 PIMs.
- 3) evaluate the influence of electrospinning condition including Aliquat 336 content, voltage and distance from tips to collector on the fabrication of electrospun fibres.
- 4) compare the physical properties and performance of PVC/Aliquat 336 PIMs and electrospun fibres with respect to Cd(II) and Zn(II) extraction.

1.3 Thesis structure

This thesis consists of six chapters as illustrated in Figure 1.1. Chapter 2 provides a comprehensive literature review on the occurrence of heavy metals and current technologies used for the treatment and recovery of the metals. The first part of the thesis research covers on the investigating PVC/Aliquat 336 PIMs. This work is covered in Chapter 3 and 4. In Chapter 3, the impact of Aliquat 336 concentration on the polymeric materials and metal extraction of PVC/Aliquat 336 PIMs is investigated. In Chapter 4, the effect of aging on the thermomechanical and metal extraction properties of PVC/Aliquat 336 PIMs is studied.

The second part of the thesis covers on the fabrication and development of PVC/Aliquat 336 electrospun fibres. In Chapter 5, the effect of electrospinning parameters including voltage, polymer concentration and distance from tips to collector are examined in order to find the suitable parameters for producing electrospun fibres. Chapter 5 also presents on the physical properties of electrospun fibres compared to PIMs. Lastly, a summary of this research is presented in Chapter 6 as well as future recommendation.

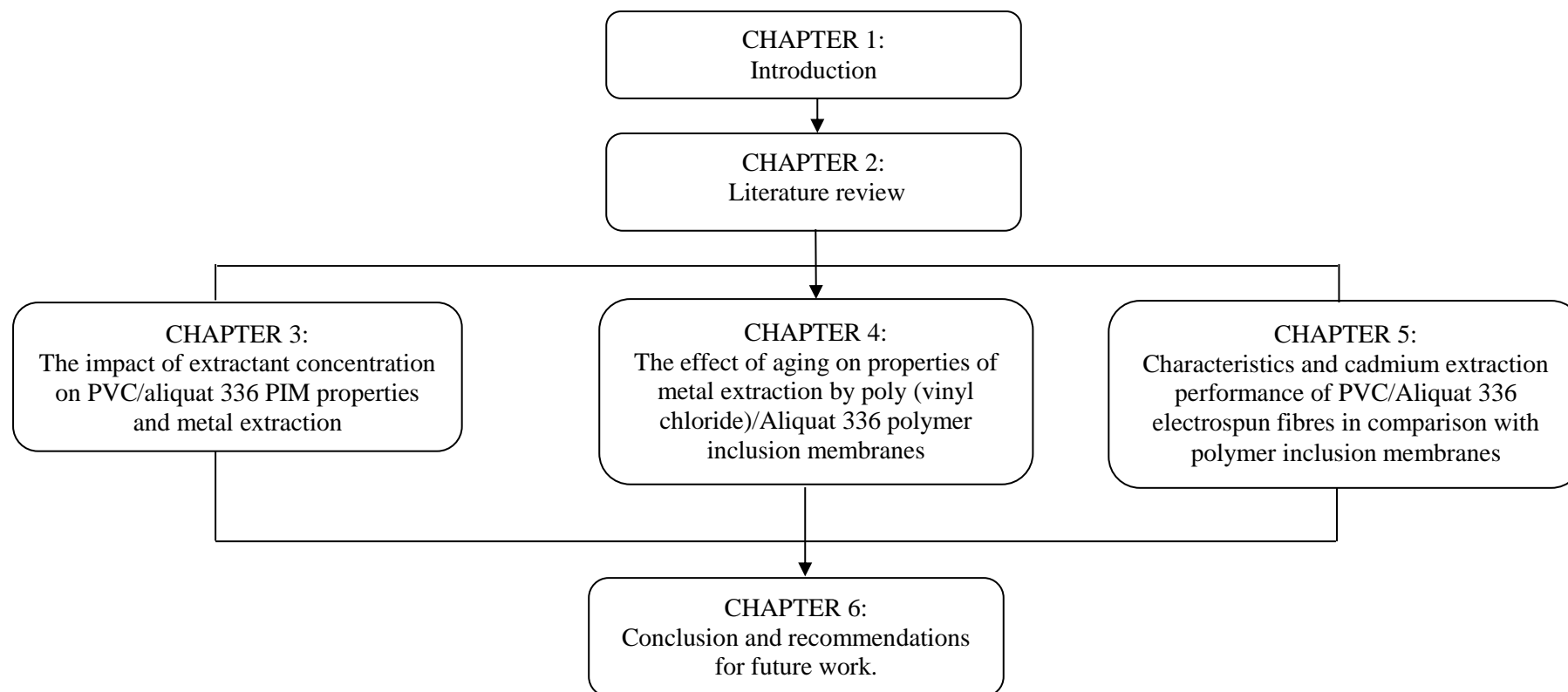


Figure 1.1: Thesis outline.

1.4 References

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Chapter 2

Literature Review

2.1 Cadmium and zinc: sources and effects

Heavy metals are metallic elements with atomic weights in the range from 63.5 to 200.6 g/mol and specific gravity greater than 5.0 [1]. Heavy metals can occur naturally in some rocks and thus they can be found at trace level concentration in soil and the aquatic environment, particularly after man made disturbances such as mining and other industrial activities. Heavy metals play a significant role in many industrial processes. For example, zinc, copper, nickel, and several other heavy metals are widely used in high strength alloy materials. Thus, there is a significant interest in the extraction of heavy metals through mining and mineral processing. In a very small quantity, some heavy metals can act as micronutrients, but most of them may cause acute or chronic poisoning.

A heavy metal of significant industrial and environmental interest is cadmium, which exists naturally in the crust of the earth. Cadmium is associated with many industrial activities. It is widely used in the fabrication of nickel–cadmium batteries, alloy production, industrial processes involving pigmenting, electroplating, leather tanning, and the manufacture of dye, paint, and paper [2, 3]. Unlike most organic contaminants which eventually degrade in the environment, heavy metals such as cadmium do not biodegradable. Indeed, they can bioaccumulate in sediments and can become a significant health hazard as a result of direct uptake from food or other means of exposure. As an example, cadmium poisoning has resulted in a devastating effect on the health of inhabitants of the Jinzu River basin in Japan. This is commonly known as *Itai-itai* disease caused by cadmium contamination from the effluent of a zinc mine located in the upper reaches of the river [4]. The disease has been reported to cause renal injuries (including tubular and glomerular dysfunctions), immune deficiencies, apathies, bone injuries (osteo malacia and osteoporosis), femoral pain, lumbago and skeleton deformations.

Zinc is another notable heavy metal of industrial and environmental interest. It also occurs naturally in the crust of the Earth. A very low concentration, zinc is an essential element to the gastrointestinal, immune, integumentary, reproductive, and central nervous systems [5]. Zinc deficiency may lead to loss of appetite, impaired sense of taste and smell, decreased immune function, slow wound healing and skin sores [6]. The average dietary daily intake endorsed by the international Recommended Dietary Allowance (RDA) is 11 mg for male and 8 mg for female age of 19 years and above [7]. On other hand, excessive zinc intake can cause disturbances such as stomach cramps, skin irritations, vomiting, nausea and anemia [8]. Elevated concentration of zinc in industrial waste has been found in processes involving the production of galvanized materials, zinc and brass metal works, zinc and brass plating, viscose rayon yarn and fibre production, ground wood pulp production and newsprint paper production [9] which is harmful to the aquatic organism if it is not well treated.

The presence of heavy metals such as cadmium and zinc can cause serious health and environmental effects when the tolerance levels are exceeded. Various regulatory bodies around the world have set the maximum contaminant limit (MCL) for these constituents in drinking water (Table 2) in order to protect human health and the ecosystem. Thus, appropriate methods for the removal of these metals are needed to ensure industrial wastes meet the prescribe standard and their discharges are safe to the environment.

Table 2.1: The maximum contaminant limit (MCL) of cadmium and zinc (mg/L) from several authorities.

Contaminant	Maximum Contaminant Level (MCL) or Treatment Technique (TT) (mg/L)		
	USEPA ¹	ADWG ²	WHO ³
Cadmium	0.005	0.002	0.003
Zinc	5.0	3.0	5.0

¹US EPA: United State Environmental Protection Agency [10]

²ADWG: Australian Drinking Water Guidelines [11]

³WHO: World Health Organization [12]

2.2 Technologies for the removal and recovery of heavy metals

Several methods can be used to remove and recover heavy metals from an aqueous solution including chemical precipitation, coagulation, ion exchange, solvent extraction and adsorption [13]. Among these, liquid-liquid solvent extraction is one of the most widely used technologies especially in hydrometallurgy processes [14, 15]. Solvent extraction has been used for the processing of copper, nickel, cobalt, zinc, uranium, molybdenum, tungsten, vanadium, rare earths, zirconium, hafnium, niobium, tantalum, indium, gallium, germanium, the platinum metal group, reprocessing nuclear fuels, purification of wet process phosphoric acid and nitric acid recovery [16]. Generally, this method separates compounds based on their relative solubilities in two different immiscible liquids, mainly water and organic solvent. However, this technology requires a large inventory of an organic solvent that is not only expensive but also presents major environmental and fire hazard due to the volatile, flammable, and toxic nature of these solvents [17]. Indeed, solvent extraction can potentially lead to the evaporation of solvent and consume a large amount of energy, thus imposing significant environmental and health hazards [14].

Membrane technology has become an alternative treatment especially in wastewater treatment and water purification. Due to the simple process and low energy consumption, it has become popular and more preferable technology to be applied in industrial application such as metal industries (metal recovery, pollution control, air enriching for combustion), food and biotechnology industries (separation, purification, sterilization and by-product recovery), leather and textile industry (chemicals recovery and pollution control), pulp and paper industries, chemical process industries (e.g.: gas separation, recovery, and recycle chemicals) and medical sector industries (e.g.: artificial organs and sterilization) [18]. There are many membrane processes including pressure driven membrane filtration, membrane distillation, liquid membrane and membrane bioreactor. These technologies are being expanded each day in various applications. For the last three decades, liquid membranes that integrate solvent extraction and membrane separation have been extensively studied. Studies reported to date in the literature demonstrate significant advantages over conventional solvent extraction techniques for heavy metal removal and recovery [19].

2.2.1 *Liquid membranes*

Liquid membranes consist of a liquid phase existing either in support or unsupported form, which act as a barrier between two aqueous solutions. They have been proposed as an effective method due to low cost and energy saving in comparison to conventional solvent extraction [20-22]. Liquid membranes can separate various species from dilute streams such as metal ions, weak acids and bases, hydrocarbons or biologically important compounds and gaseous mixtures [23]. The separation process combines the solvent extraction and stripping in a single step (unitary process) [24] and is less disturbed by interfacial emulsion formation and solvent evaporation which is known to decreased the effectiveness [25]. The extraction chemistry is similar to a liquid-liquid extraction process. However, the transport of target ions in liquid membranes is governed by the kinetics of the extraction process rather than equilibrium. In other words, the rate transport of liquid membranes is governed by a non-equilibrium mass transfer process [26].

In general, there are three basic types of liquid membranes namely bulk liquid membranes (BLM), emulsion liquid membranes (ELM), and supported liquid membranes (SLM). Among the above membranes, SLM is the most widely studied process. SLM consists of organic liquid which is embedded in small pores of a polymer support. This liquid contains an extractant which performs selectively separation as it binds with targeted components in feed solution and carries it to the other side of aqueous solution (stripping phase). Briefly, SLM involves three simultaneous processes that are extraction of the target species from feed phase to the SLM, diffusion through SLM and re-extraction of the target species to the stripping phase. The passage of the target ions from the source phase to stripping phase can be achieved by using different pH in both aqueous phases which will create different concentration gradient. This way, the targeted ions will be transported across the membrane against their concentration gradient and the process only uses chemical energy as a driving factor and does not need any transmembrane pressure or voltage. The transport of target species in SLM can occur in either the counter current or co-current modes depending on the type of the extractant used. In the counter current mode, two species (nominally denoted as A and C) are transported by the extractant molecule in opposite direction across the membranes as illustrated in Figure 2.1a. In contrast, in the co-current transport mode, two species (nominally denoted as A and

B) are coupled with an extractant molecule and transported from the source phase to the stripping phase (Figure 2.1b).

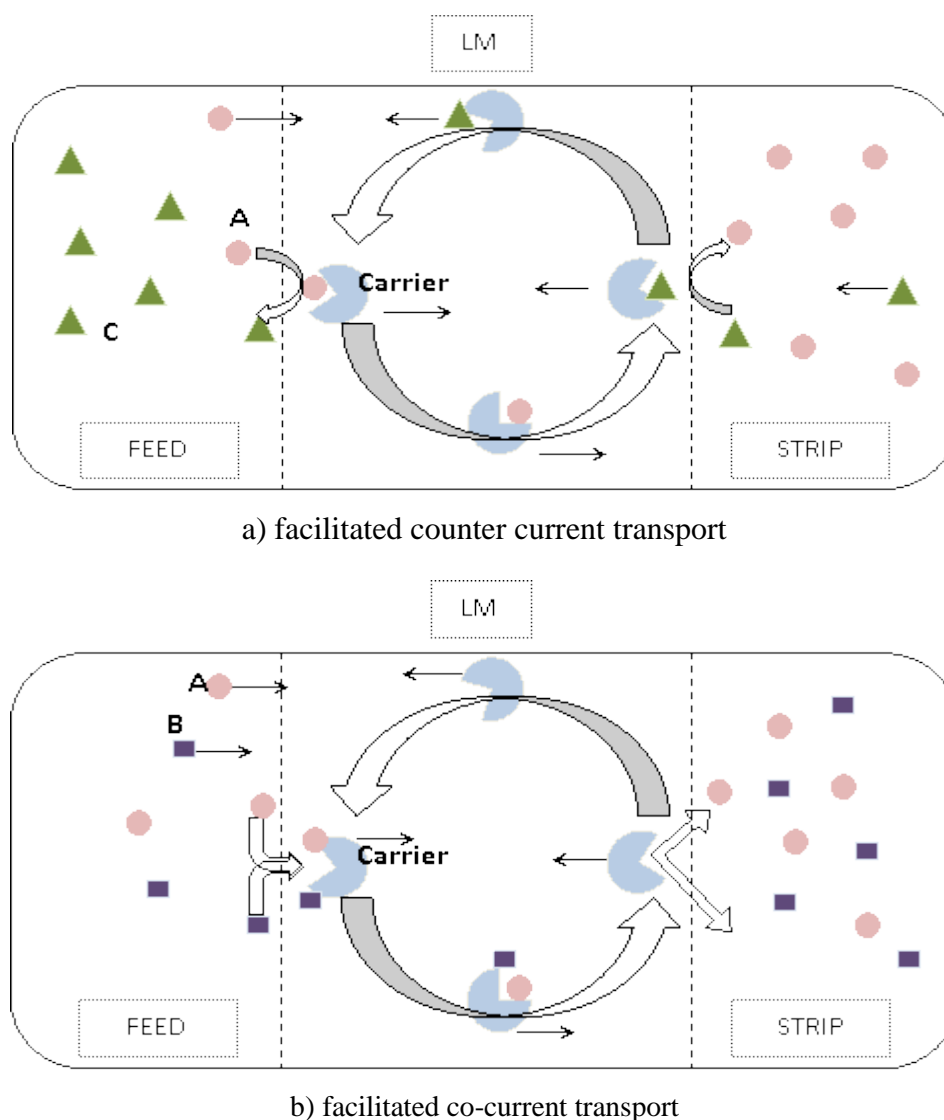


Figure 2.1: Facilitated couple transport of ions in liquid membrane.

SLM exhibited high efficiency for the cation separation due to the fast transport rate and only need a small amount of the organic extractant [27]. However, the practical applications of SLM in industrial areas are limited due to several weaknesses. As a major concern regarding the long term stability of SLM, the solvent and the organic extractant were found to be lost to the aqueous phase [28]. The loss of extractant and membrane solvent should be reduced in order to increase the membrane lifetime and to assure their practical application in the future.

To improve the stability of SLM, Neplenbroek et al. [29] applied a thin cross-linked polyvinylchloride (PVC) gel layers on the feed side of the SLM. Their technique was

effective for stabilizing the membranes for nitrate removal from water without any measurable influence on the flux. However, the reproducibility of their results was poor. This method is only suitable for flat sheet membranes. Several other attempts have been trialed with varied level of success [30-32] but none of them have led to real significant improvements. Hence, more studies on immobilization of extractant were carried out. An alternative technique suggested by Sugiura et al. [33] has achieved some initial success. This technique used the plasticized cellulose triacetate (CTA) membrane containing extractant where the liquid plasticizer acts as an organic solvent similar to that used in SLM. This new alternative approach which synthesizes membrane with extractant incorporated in a plasticizer thermoplastic polymer was called polymer inclusion membranes (PIMs) and has retained so much attention later on, due to its better stability in comparison to other forms of liquid membranes.

2.3 Polymer inclusion membranes (PIMs)

Similarly to SLM, PIMs is also used to separate the source and stripping (receiving) phase but does not contain any organic solvent [34]. Instead, the extractant that sustains the transport of the ionic species through PIM is immobilised within the polymer matrix. Thus, PIMs are much more chemically and mechanically stable than SLMs. PIM can be formed as a thin and flexible film from a solution containing a base polymer (normally CTA or PVC), an extractant and/or plasticizer, and a volatile solvent such as tetrahydrofuran (THF). After casting the solution over a flat surface, the solvent is allowed to evaporate to form an optically transparent membrane. Each of these components contributes to important features that affect the overall performance and physiochemical characteristics of the membranes.

The base polymer provides the mechanical strength to the membrane whilst the extractant and plasticizer provides elasticity and constitutes a quasi-liquid phase in which the extractant molecules can interact and facilitate the transport of the target ions [35]. The extractant is an essential component for metal extraction. Extractant molecules will act as a guest specific host which provides selective membrane permeability for target species [36] as they form an ion pair complexes between the metal ion and the extractant. This way, PIMs can effectively separate two aqueous phase without utilizing organic solvent to maintain phase separation [34]. This makes the membrane easy to handle and promotes membrane durability [37]. A

study showed that in the absence of extractant in CTA based-PIMs, no transport of cadmium was detected from the extraction phase to the stripping phase [19]. There are several classes of extractant namely as basic, acidic and chelating, neutral or solvating and macrocyclic and macromolecular that has been successfully used along with targeted metal ions as described in Table 2.2. It is noted that different types of extractant exhibit different transport efficiencies because of differences in their complexation mechanisms. Therefore, the selection of extractant is important in determining the effectiveness of PIMs for metal separation process.

Table 2.2: Examples of PIMs extractant reported in the literature and their typical target solutes modified from Nghiem et al. [38].

Type of extractant	Examples	Target solutes	Ref.
Basic	Aliquat 336	Au(III), Cd(II), Cr(VI), Cu(II), Pd(II), Pt(IV), Co(II), As(V)	[19, 39-52]
	TOA, other tri-alkyl amines	Cr(VI), Zn(II), Cd(II), Pb(II)	[53-56]
	TDPNO	Cr(VI), Zn(II), Cd(II)	[54, 57]
Acidic and Chelating	Kelex 100	Cd(II), Pb(II)	[14]
	Benzoylacetone, dibenzoylacetone,	Sc(III), Y(III), La(III), Pr(III), Sm(III), Tb(III),	[58]
	Benzoyl-trifluoroacetone	Er(III), Lu(III)	
	bis-(2-ethylhexyl) phosphate (D2EHPA), bis-2,2,4-trimethyl pentyl phosphinic acid (Cyanex 272) D2EHDTPA	Pb(II), Cd(II), Zn(II), Cu(II), Cr(III)	[49, 59-62]
Neutral or Solvating	DBBP	As(V)	[63]
Macrocyclic and Macromolecular	DC18C6, BuDC18C6	Cs ⁺ , Sr(II), Pb(II), Cu(II), Zn(II)	[27, 64-67]

Plasticizer is usually added to PIMs to improve the extraction characteristics of the membranes [68]. The addition of a plasticizer can enhance the flux and improve the compatibility between the membrane components and the membrane mechanical stability [69]. This is because plasticizer can neutralize the polar group of the

polymer with its own polar groups or/and to increase the distance between the polymer strands and reduce the strength of the intermolecular forces acting between them [70]. Polar groups are known as the strongest forces exist in the polymer that often result in rigid polymer structure [69] which is unfavourable for a diffusive flux of material within the polymer matrix. Thus, the addition of plasticizer can improve the metal species flux as well as increase the membrane softness and flexibility.

The two most common plasticizers in PIMs are 2-nitrophenyl octyl ether (2-NPOE) and 2-nitrophenyl pentyl ether (2-NPPE). Some extractants can also act as a plasticizer. Pereira et al. [69] has identified some of these extractants and their compatibilities with PVC and CTA based polymer as shown in Table 2.3. The existence of hydroxyl and acetyl groups in CTA are capable of forming highly oriented hydrogen bonding. Therefore, the most polar extractant that can disrupt the CTA hydrogen bonded structure and separate the polymer strands will act as successful plasticizer. On the other hand, PVC is less polar than CTA with carbon-chloride (C-Cl) functional group and the structure is dominated by non-specific dispersion forces. As a result, plasticizer with less polar and positively charged is expected to have good compatibility with PVC.

Table 2.3: Compatibility between PVC and CTA based polymer with the extractant studied (+ compatible; - not compatible) [69].

Extractant	Commercial name	Base polymer	
		PVC	CTA
Tri-octyl/decyl amine	Alamine 336	-	-
*Protonated tri-octyl/decyl amine	Protonated Alamine 336	+	+
Tri-alkylmethyl ammonium chloride	Aliquat 336	+	+
Bis(2,4,4-trimethylpentyl) phosphinic acid	Cyanex 272	+	+
Tri-alkyl phosphine oxide	Cyanex 923	-	+
Bis(2-ethylhexyl) phosphate	D2EPHA	+	-
2-hydroxy-5-nonyl benzaldehyde oxime	P50 Oxime	+	+
Tributyl-phosphate	TBP	+	+

* after being contacted with 0.1 mol/L HCl for 24 hours

PIMs does not only present most of the advantages of liquid membranes such as low cost, low energy consumption, high selectivity and comparable diffusion coefficient [71] but is also environmentally friendly since it does not require the use of any flammable solvents [38]. These factors certainly increase many researches on PIMs especially in carrier-mediated transport for selective separation and recovery of metal ions from aqueous solutions.

To date, PVC and CTA have been the only two polymers used as base polymer in PIMs. Both are thermoplastic polymers with linear polymer strands and no cross-links between them. Therefore are easily dissolved in an organic solvent. In this study, PVC has been chosen as the base polymer for all PIMs studied. This is because, PVC based PIMs are more durable than CTA based PIMs. PVC is also widely used because of its high compatibility with additives, easy process ability and recyclability [72]. Fontas et al. [73] showed that PVC based PIMs produced a homogenous metal ion distribution in the membrane than CTA based PIMs as observed by X-ray fluorescence analysis although both membranes revealed similar extraction efficiency for Cr(VI) removal. Moreover, results studied by Kebiche-

Senhadji et al. [48] on the effect of nature polymer of CTA and PVC with three different molecular weight showed that the base polymer only had weak influence on transport efficiency of Cr(VI). But, compared to CTA based PIMs, PVC based PIMs with the lowest molecular weight has the best extraction efficiencies.

2.3.1 PVC/*Aliquat 336* PIMs

Aliquat 336 is a mixture of tri-alkyl methyl ammonium chloride salts produced from the methylation of *Alamine 336*, with the substituent alkyl chain length containing between 6 and 12 carbon atoms (Figure 2.2). It is categorized as a basic carrier base on the presence of amine-based compounds. Numerous studies have shown successful extraction of metal ions from the aqueous phase using PVC/*Aliquat 336* PIMs [38].

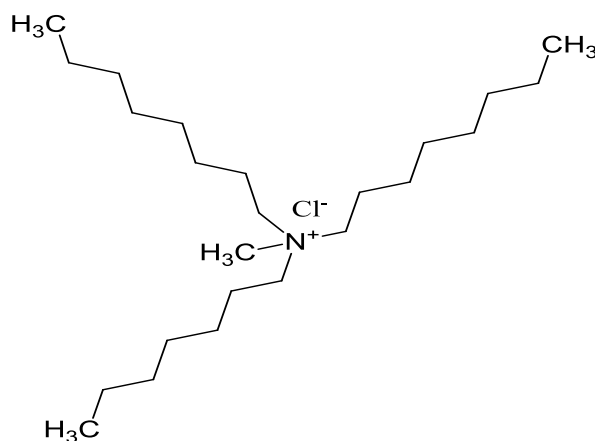


Figure 2.2: Structure of *Aliquat 336*.

Argiropoulos et al. [40] have successfully extracted gold(III) from hydrochloric (HCl) acid solution using *Aliquat 336*, immobilised in PVC. The membrane is also able to extract gold(III) in the presence of high concentration of copper(II) and thus has a potential to be applied in the treatment of electronic scrap with Aqua Regia. In a more recent study, the extraction of gold(III) from HCl was improved by adding an alcohol long chain as a modifier to the PVC/*Aliquat* PIMs [74]. Bonggotgetsakul et al. [74] reported that membrane containing 70% PVC, 20% *Aliquat 336* and 10% 1-dodecanol is mechanically and chemically stable with high initial gold(III) flux values between 100 and 50 folds higher than PIMs containing 20 to 40% *Aliquat 336*

without modifier. Moreover, the extraction rate was further increased by 200% and 300% by sonicating the aqueous phase without damaging the membrane.

PVC/Aliquat 336 PIMs have also been examined by Kolev et al. [42] for palladium(II) extraction from HCl solutions. They reported that PIMs can extract palladium rapidly and are suitable for analytical determination for trace level or recovery of palladium in industrial wastewater [42]. However, they also noted that the membrane surface became discoloured when the palladium concentration was higher than 100 mg/L [42]. Kolev et al. [42] applied a mathematical model by considering the interfacial complexation reaction between Aliquat 336, chloride, and palladium(II) and the diffusion of these complexes through the membranes. They [42] reported that all the extraction experiment data could be fitted with the corresponding model which demonstrated the validity of the model.

Blitz-Raith et al. [75] have studied the extraction of cobalt(II) using 40% Aliquat 336 as extractant in 60% PVC based PIMs. The extraction results showed a high selectivity of cobalt(II) from nickel(II) solution containing 7 M HCl. This is because nickel(II) maintain in its hexa-coordination while cobalt(II) has tendency to form to a tetrahedral anionic chlorocomplexes. The rapid extraction of cobalt(II) has reached equilibrium in less than 60 minutes. Besides by increasing the number of membrane used, the extraction was nearly completed. Blitz-Raith et al. [75] also showed that cadmium and iron were extracted by 99% using the same membrane suggesting that nickel(II) can also be separated from these metals. However, recent study by Kagaya et al. [46] who used the same PIMs composition has suggested that the extraction of cobalt(II) from nickel(II) is more effective by using a solution of both lithium ion and HCl than in a HCl solution alone. Approximately 2 mg/g of cobalt(II) was extracted after 3 hours from a solution containing 8 M LiCl and 1 M HCl. Moreover, lithium chloride solution is less corrosive than those of HCl.

Similar composition of PVC and Aliquat 336 was employed by Gherasim et al. [52] in the transport of Cr(VI) in stimulating industrial wastewater conditions. The performed experiments demonstrated more than 98% recovery for Cr(VI) solutions in the range of 53 to 160 mg/L. The process was achieved in less than 4 hours using an initial pH of 4 in the source solution and 0.05 M NaOH in the receiving solution. For Cr(VI), the distribution of the anionic species is pH dependent hence the initial

pH of the feed solution is a main concern. Kebiche-Senhadjji et al. [48] has investigated the effect of initial pH from 1.2 to 8 on the extraction efficiency of Cr(VI). At pH 1.2, an optimal extraction of HCrO_4^- was obtained in 8 hours using 36.4% PVC, 48.3% Aliquat and 15.3% NPOE where the chromate concentration was reduced from 10.2 mg/L to 0.2 mg/L. However at pH 2 the fraction of HCrO_4^- decreased due to pH increasing and thus decreased the extraction efficiency. The extraction increased back when the pH is increased from 4 to 8 which coincide with the change from HCrO_4^- to CrO_4^{2-} that is the predominant species in this pH range.

Extraction of cadmium, zinc and copper using HCl solutions has been studied by Wang et al. [39], Upitis et al. [45], Peterson and Nghiem [51] and Adelung et al. [50]. It was conclude that the extraction of metal ions increased as the Aliquat 336 content increased in PIMs. However, the Aliquat 336 concentration above 60% was mechanically weak [45]. This is because the mechanical properties of PIMs are strongly dependent on the PVC composition. In similar extraction condition of cadmium, zinc and copper conducted by Adelung et al. [50], cadmium(II) was more selective than zinc(II). More than 99% of cadmium was extracted but the extraction of copper(II) was quite negligible. Meanwhile, Wang et al. [39] demonstrated an appreciable amount of copper (II) transported through the membrane when using 3 M HCl solution in the feed phase. This is because at below 3 M HCl, there is no negatively copper chloride complexes exist in the chloride solution thus explained the poor transport ions [50]. This will be explained further in the next section.

2.3.2 Extraction and transport of target ions by PIMs

The extraction studies in PIMs have been carried out in batch experiments by immersing the PIMs in a solution containing target species as described in the literature [45, 51]. The samples were collected at specified time intervals for analysis. On the other hand, the transport experiments across the PIMs have been conducted using membrane cell consisted of two plexiglass compartments [34]. The two compartments which are the extraction and the stripping phases are separated by PIMs in the middle as illustrated in Figure 2.3. The transport dynamics can be studied by collecting sample from both compartments at preselected times for analysis.

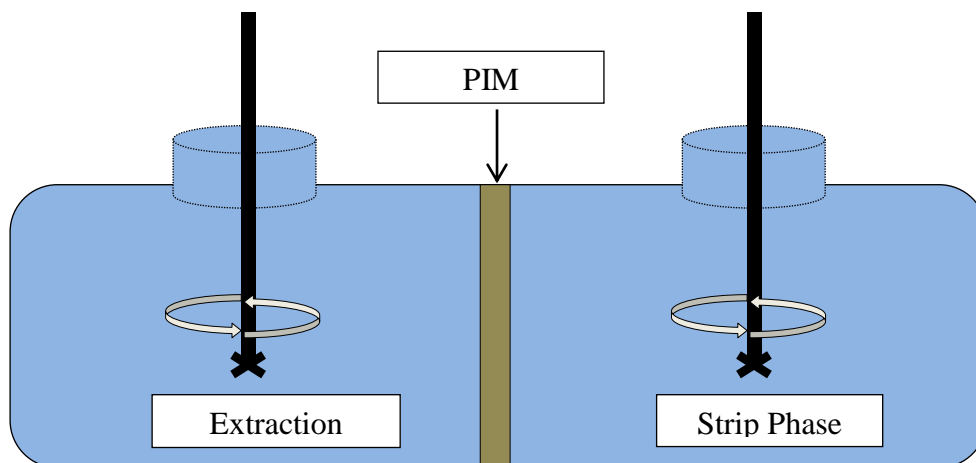
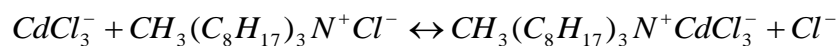


Figure 2.3: A schematic drawing of PIMs transport experiment.

The extraction process across PIMs involves ion exchange via extractant and metal ions complexes which can be achieved by using suitable ionic solution in the extraction phase. The reactions that take place between the metal ions and extractants vary depending on the type of the extractant used. For example, a hydrochloric acid solution can be used in the extraction phase for both cadmium(II) and zinc(II) because they can readily form chloride complexes.

In the case of PVC/Aliquat 336 PIMs, Aliquat 336 will form an ion pair with a metal anion complex from the aqueous solution [19]. Consequently in a chloride matrix, the availability of a metal chloride complex carrying one negative charge is crucial for the extraction of the metal ion to the membrane. Upitis et al. [45] demonstrated that trichloro metal complexes could be readily extracted by PVC/Aliquat 336 PIMs. This hypothesis was supported by Adelung et al. [50] who predicted the distribution of metallic ions in 0.05, 0.1 and 3 M of NaCl solution using the ChemEQL (version 3.1) thermodynamic modelling software. They found that at below 0.1 M of chloride solution, the trichloro zinc complex does not exist thus the extraction of zinc(II) to PVC/Aliquat 336 PIMs could not occur. As Adelung et al. [50] increased the chloride solution to 3 M, the trichloro zinc complex was formed and significant extraction of zinc(II) was observed. Both trichloro and tetrachloro cadmium complexes exist over the same chloride concentration (0.05, 1 and 3 M) and the molar fraction of the trichloro cadmium complex increased dramatically as the chloride concentration increased [50]. Therefore, the extraction of cadmium(II) to PVC/Aliquat 336 PIMs can be described as below:



The amount of extractant in PIMs composition can also influence the performance of metal ion extraction. Several researchers [44, 45] have reported that PVC PIMs with low Aliquat 336 content, resulted in lower extraction of Cd(II). They also showed that there exists a critical Aliquat 336 content in PIMs of 30 to 40 wt.% for the transport of Cd(II) to occur. However, it is noteworthy that PVC PIMs with Aliquat 336 content higher than 60 wt. % is mechanically weak and thus unsuitable for any extraction evaluation.

2.3.3 Morphological structure and properties of PVC/Aliquat 336 PIMs

The homogeneity of the PIMs has been a focus of several recent studies. This is because the homogeneity of PIMs determines the mechanism of facilitated transport inside PIMs. A heterogeneous PIMs, is corresponding to the mobile carrier model in which the extracted complex containing solutes is diffused through the membranes. On the other hand, the fixed site model is used to describe the transport of the solutes in homogenous structure. In this case, the solute is passed along the chain of the immobile extractant.

The homogeneity of PIMs has yet been verified in the literature. Generally, PIMs are assumed as chemically homogenous when they are visually homogenous, transparent and free of any extractant droplets. These assumptions may not always be appropriate. Even SLM looks transparent and homogenous although they are actually filled with organic liquids in their pores. Several techniques have been used to characterize the morphology and properties of PIMs in order to identify the homogeneity and to have better understanding on their extraction and transport mode. However, most of them are surface characterisation techniques and they can only offer limited insight toward the homogeneity of PIMs.

By using scanning electron microscopy (SEM), Xu et al. [44] suggested that PVC based PIMs with Aliquat 336 content below 30% appeared to be microscopically homogenous with no apparent pores. But as the Aliquat 336 content increased up to 40% and above, the structure becomes porous and somewhat rough. They postulated that the PIMs might contain micro channels filled with Aliquat 336. However, SEM images do not provide direct evidence of the existence of micro channel or micro

pores. In fact, the theory from Xu et al. [44] has been contradicted by St John et al. [76] who studied the homogeneity of PVC/Aliquat 336 PIMs using high resolution synchrotron-based fourier-transform infrared (FTIR) spectroscopy and proton-induced X-ray emission microspectrometry (μ -PIXE). μ -PIXE results reported by them showed that PVC based PIMs containing 10 to 40 wt.% Aliquat 336 are homogenous at the micro-scale which is comparable to the scale investigated by Xu et al. [44].

On the other hand, Wang et al. [77] used X-ray photoelectron spectroscopy (XPS) to demonstrate any changes in the chemical of PVC/Aliquat 336 PIMs. The XPS results suggested that no chemical composition change was detected in the PVC/Aliquat 336 PIMs after two weeks of exposure in 3 M HCl aqueous solution without metal ions. This finding is consistent with the result reported by Argiropoulos et al. [40] where no Aliquat 336 leakage from PIMs was detected after 10 days of contact with 2.5 M HCl solution. They also studied the PVC/Aliquat 336 PIMs before and after extracting of gold using transmission electron microscope (TEM) and no deterioration of the membrane morphology was observed. However, Wang and Shen [77] point out that the PVC/Aliquat 336 PIMs showed poor stability in the extraction of Cd(II) but excellent stability for Cu(II). The bleeding of Aliquat 336 after the extraction of Cd(II) was discovered using atomic force microscopy (AFM). They speculated that the membrane stability was likely dependent upon metal species extracted. However, they still incapable to fully clarify the cause of the poor stability in the Cd(II) extraction.

Apart from morphological and chemical studies, successful PIMs must also have an appropriate mechanical strength and thermal stability to resist any mechanical stress and high temperature operation without easily tears off or deteriorate. Tensile test has been used to investigate the mechanical properties of PVC/Aliquat 336 PIMs at different PVC composition [45]. The results showed that mechanical strength of PIMs were dependent on the base polymer composition. As the PVC composition increased from 40 to 70% the tensile strength increased however, PIMs with less than 50% of PVC content were mechanically incompatible for any physical test although the resultant membrane might have an excellent rate of metal ions rejection. Upitis et al. [45] also examined the membrane hydrophobicity using contact angle measurement and the results revealed that PVC/Aliquat 336 PIMs were quite

hydrophilic even though pure PVC is known as hydrophobic material. They hypothesized that Aliquat 336 has migrated and exposed its polar functional group to the PIMs surface making the membrane more hydrophilic. This hypothesis is accordance with the data reported by Wang and Shen [77] where a significantly higher atomic concentration of nitrogen at the surface than in the bulk of PVC/Aliquat 336 PIMs was detected.

Based on the methods mentioned above, study on the characterization of PVC/Aliquat 336 PIMs is still new and limited. So far, no study on the thermal analysis or electrochemical properties of the PIMs has been conducted. Thermal analysis is one of the useful methods to identify the glass transition (T_g) of a polymer system. The T_g describes the segmental motion of the polymer and can be used to identify the miscibility of the polymer system. For a miscible system, a single T_g will appeared but for an immiscible multiphase system, each phases will poses its own T_g . However, for a partly miscible system, the T_g are shifted to higher or lower temperature as a function of composition. Therefore, an observation of single T_g is used as an evidence of miscibility of the polymeric system [78] and also as an indicator for PIMs homogeneity. On the other hand, electrochemical properties are an important factor that related to conductivity and transport properties of the membranes which has been practiced on ion exchange membranes to identify their properties. By studying the electrochemical property, the rapidity of counter-ion migration occurs across a membrane can be determined. Although, this is just an initial presumption but this technique could be applied to PIMs since their transport mechanism also involve counter ion transport that is quite similar to ion exchange membranes.

2.4 Electrospinning

Electrospinning has recently gained popularity in producing ultrathin fibres. These fibres can be made by variety of materials such as polymers, ceramics and composites. Compare to conventional spinning method, this method has successfully produced much thinner fibres ranging from several nanometres to several micrometres in diameter. Due to higher surface area [79, 80], electrospun fibres have been effectively applied in various applications such as tissue engineering scaffold [81, 82], drug deliver carrier [82-84], biosensor/chemosensor [85, 86], protective

cloth [87, 88], electronic and semi-conductive materials [89, 90] and reinforced nanocomposite [91].

2.5 Electrospinning Process

Three main components are needed to complete the electrospinning process: a high voltage supplier, a capillary tube with a small diameter of needle (syringe) and metal screen as a collector [92] as shown in Figure 2.4. The process works when an electrically charged jet of polymer is produced to form an interconnected web of small solid fibres on the metal collector. The polymer solution which is encapsulated within a needle will form a hemispherical drop at the end of the capillary tube. When high voltage is applied it will overcome the surface tension of the droplet. Then a charged jet of polymer solution is ejected. The jet exhibits bending instabilities caused by repulsive forces between the charges carried with the jet. The jet extends through spiralling loops. As the loops increase in diameter, the jet grows longer and thinner until it solidifies or is collected on the target [93-96].

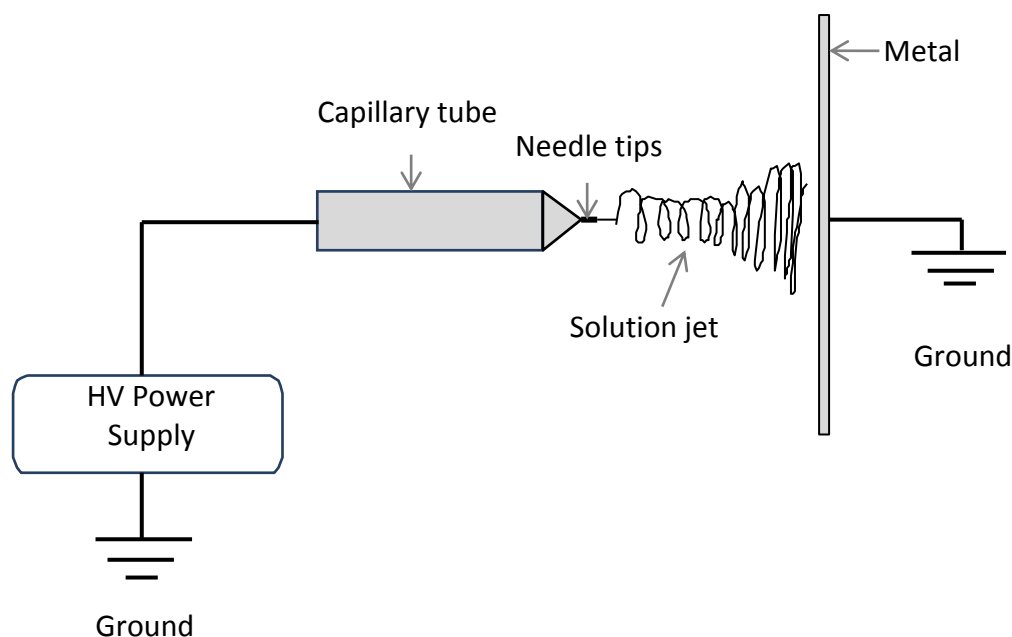


Figure 2.4: Schematic of a lab scale electrospinning apparatus.

2.6 Electrospinning Parameters

The transformation of polymer solutions into fibres via electrospinning is influenced by many parameters classified broadly into: (a) solution parameters such as

molecular weight, viscosity, conductivity and surface tension, (b) process parameters such as applied electric field, solution feed rate and spinning distance (distance between the tip and collecting screen) and (c) ambient parameters such as temperature, humidity and air velocity in the chamber [79, 92, 97, 98]. All of these parameters are known to significantly affect the morphology and diameter of electrospun fibres [98, 99].

Molecular weight of the polymer has a significant effect on rheological and electrical properties such as viscosity, surface tension, conductivity and dielectric strength [100]. Higher molecular weight polymer has been used in electrospinning process as it provides the desired viscosity for fibre generation. It has been observed that at lower molecular weight of polymer, a solution tends to form beads rather than fibres. Gupta et al. [93], showed that as the molecular weight of poly(methylmethacrylate) (PMMA) increased from 12.47 to 365.7 kDa, the number of beads and droplets decreased. Solution viscosity also influences the fibre size and morphology during the spinning process. It has been found that at very low viscosity there is no continuous fibre formation whereas higher viscosity favours the formation of fibres without beads. However, at a very high viscosity there is difficulty in ejection of jets from polymer solution. For instance, Fong et al. [101] found that viscosities of poly (ethylene oxide) (PEO) in the range of 1 to 20 P were suitable for fibre formation. But, as viscosities increased above 20 P, electrospinning was prohibited. While study by Liu and Hsieh [102] using cellulose acetate (CA) for electrospinning found that the applicable range of viscosities is between 1.2 and 10.2 P. Below 1.2 P, the fluid jet broke up to droplets. Therefore, finding the optimal viscosity is important and the viscosity range is different for a different polymer solution.

The formation of droplets, beads and fibres also depends on the surface tension of solution. By reducing the surface tension of polymer solution, fibres can be obtained without beads. However, high surface tension will inhibit the electrospinning process due to instability of the jets and the generation of droplets [103]. Surface tension is more likely to be a function of solvent composition of the solution and using different solvent will give different surface tension [104]. Furthermore, small diameter of electrospun fibres can be achieved by increasing the electrical conductivity [105, 106]. The solution conductivity is mainly determined by the type of polymer and solvent used. However, the addition of salt such as KH_2PO_4 , NaCl

and NaH_2PO_4 will increase the solution conductivity and thus produce uniform fibres with fewer beads. Fong et al. [95] has proven that the addition of NaCl in PEO solution has increased the net charge density carried by the moving jet and produced fibres with less beads. Moreover, Zhang et al. [107] demonstrated that increasing NaCl content from 0.05 to 0.2% in PVA solution has increased the conductivity of the solution and decreased the PVA fibre diameters from 214 ± 19 nm to 159 ± 21 nm. Therefore, the use of salts may reduce the fibre diameters and reduce beads generation.

The applied voltage is an important process parameter which affects the fibre diameter to a remarkable extent. In general, a higher applied voltage ejects more fluid in a jet thus, result in large fibre diameter [108]. However, Reneker and Chun [102], found that the applied voltage has no discernible effect on the diameter of electrospun polyethylene oxide fibres. This might be the result of more polymer ejection at high voltage which enables the larger diameter fibres [107, 108]. Yordem et al. [109] suggested that voltage may influence the fibre diameter but, the level of significant varies with the polymer solution concentration and spinning distance. Solution flow rate is another important parameter that influences the jet velocity and material transfer rate. By varying the flow rate, the morphology of nanofibres varies differently. Yuan et al. [110] reported that lower flow rate is more desirable because the solvent have enough time to evaporate. They observed ultrafine fibres at lower flow rate but beaded fibres morphology when the flow rate is increased. The formation of beads and fibre diameters can also be controlled by varying the spinning distance. Several research groups have found that a minimum distance between the tip and collecting screen is required to give the fibres sufficient time to dry before reaching the collector [111, 112]. If the distance of the tip is too close or too far from the collector, the beads will form. However, this parameter is not as important as other parameter because some fibre materials such as polysulfone produced smaller diameters at closer distance. Therefore, an optimum distance is needed in order to provide sufficient time for solvent evaporation.

Besides solution and processing parameters, ambient parameters have been found to affect the electrospinning process. For instance, when the temperature increased from 25 to 60 °C, Mit-Uppatham et al. [113] found that the diameter of polyamide-6

decreased. Demir et al. [108] electrospun polyurethane at a 70 °C and found that the fibres diameter were much more uniform than those conducted at room temperature. In addition, Casper et al. [114] reported that increasing humidity result in small circular pores on the surface of fibres. It was found that, at very low humidity, a volatile solvent may dry rapidly as the solvent evaporate faster. Sometimes, the evaporation rate is so fast than compared to the removal of solvent from the tip which results in needle clogged [115]. Li et al. [116] suggested that high humidity help the discharged of electrospun fibres.

2.7 Variety applications of electrospun fibres

Electrospinning is a flexible method of generating high performance fibres that can reform the world of structural materials. The process is versatile in term of there is a variety of polymer that can be spun. To date, more than 50 types of polymers have been electrospun in the past years for various applications and some of them are shown in Table 2.4. With outstanding properties such as large surface area to volume ratio, flexibility in surface functionalities and superior mechanical performance compare to general fibres, polymer electrospun fibres have been successfully applied in various fields such as wound dressing, drug delivery, protective clothing, and tissue scaffold.

Table 2.4: Several of electrospun polymers.

Polymer	Solvent	Applications	References
Poly(glycolic acid) (PGA)	1,1,1,3,3,3-hexafluoro-2-propanol Hexafluoro isopropanol (HFP)	Tissue engineering	[81]
Poly(lactic acid) (PLA)	chloroform, methylene chloride, and Hexafluoro isopropanol (HFP)	Tissue engineering	[81]
Polydioxanone (PDO)	Hexafluoro isopropanol (HFP)	Tissue engineering	[81]
Collagen	Hexafluoro-2-propanol	Tissue engineering (scaffold)	[117]
Collagen- polyethylene oxide (PEO)	Hydrochloric acid	Tissue engineering (wound healing)	[118]
poly(D,L-lactide- <i>co</i> - glycolide) (PLGA)	Tetrahydrofuran: dimethylformamide	Tissue engineering (scaffold)	[119]
Polyurethanes (PU)	Dimethyl formamide	Protective clothing	[120]
Nylon6,6, PA-6,6	Formic acid	Protective clothing	[120]
Polybenzimidazole, (PBI)	Dimethyl acetamide	Protective clothing (reinforced composite)	[120, 121]
Polyethylene- <i>co</i> -vinyl acetate (PEVA)	Dichloromethane	Drug delivery system	[122]
Poly(vinyl alcohol)	Water	Drug delivery	[123]
poly(lactide- <i>co</i> - glycolide) (PLGA) + poly(D,L-lactide)- poly(ethylene glycol) (PLA-PEG)	N,N-dimethyl formamide	Drug delivery	[124]
Polystyrene with nitrophenyl ending groups (PS-NPh)	Methyl ethyl ketone (MEK) and N,N-dimethylformamide (DMF)	Wound dressing	[125]
poly(ϵ -caprolactone) (PCL)/ Gelatine	Trifluoro ethylene (TFE)	Wound healing	[126]
Chitin	Hexafluoro isopropanol (HFP)	Wound healing	[127]
Collagen/ chitosan	Hexafluoro isopropanol (HFP)/ Trifluoro acetic acid (TFA)	Biomaterial scaffolds	[128]

Polymer fibres fabricated via electrospinning have been proposed as a treatment of wounds and burns of a human skin. With the aid of an electrical field, fine fibres of biodegradable polymers can be directly spun onto the injured location of skin to form a fibrous mat dressing [129]. Rho et al [130] who have investigated the wound healing properties of mats of electrospun type I collagen fibres on wound in mice found that the healing of the wounds was better with the nanofibres mat than with traditional treatment especially in the early stage of the healing process. On the other hand, nanofibrous scaffolds has been widely used in tissue engineering applications, as temporary templates for cell seeding, invasion, proliferation and differentiation prior to the regeneration of biologically functional tissue or natural extracellular

matrix (ECM) [104]. These nanofibrous scaffolds effectively mimic the structure and biological functions of the natural ECM and act as a substrate for cell growth [131]. Several researchers [84, 124, 132] have successfully encapsulated drugs within electrospun fibres by mixing the drugs in the polymer solution to be electrospun. Electrospun fibres have been applied as drug carriers in the drug delivery system because of their high functional characteristics and because the drug delivery system relies on the principle that dissolution rate of a particulate drug increases with increasing surface area of both the drug and the corresponding carrier [104]. Importantly, the large surface area associated with electrospun fibres allow for fast and efficient solvent evaporation which provides the incorporated drug limited time to recrystallize [133].

In protective clothing applications, electrospun fibres was preferable because of their light weight, large surface area, high porosity (breathable nature), great filtration efficiency, resistant to penetration of harmful chemical agents in aerosol form and their ability to neutralize the chemical agents without impedance of the air and water vapour permeability to the clothing [120, 134]. Due to their outstanding speciality, electrospun fibres have been applied for the protective clothing in military to help maximize the survivability, sustainability and combat effectiveness of the individual soldier system against extreme weather conditions, ballistics and nuclear, biological and chemical warfare.

Other possible application is in filtration process. It is known that polymeric membranes have been widely used in many types of extraction processes. For typical membrane filtration applications, smaller pores along with good mechanical and chemical stability are often required in order to remove particulates from air stream or liquid stream. Since electrospinning process can produce ultrafine fibres and have larger surface area, this technology is also capable to be used as filtration media. In fact, the ultrafine fibres prepared from eletrospinning can be developed into various nanotubes modules to further increase the ease of separation. For more than a decade, nanofibres technology have been applied in air filtration area [104]. A method for making a dust filter bag which constitutes a plurality of layers including a carrier material layer and a nanofiber nonwoven tissue layer has been disclosed in an US patent [135]. In addition, electrospun nonwoven mats have been successfully developed to remove airborne particles with diameters between 1 and 5 μm not only

by physical entrapment mechanism but also by the electrokinetic capture in the air filter [136].

In liquid filtration area, electrospun fibres mats have a huge potential as a pre-filter. This is because electrospinning process can produce ultrafine fibres and have larger surface area which is capable to remove macro particles in water treatment. Electrospun nylon-6 nanofibrous prepared by Aussawasathien et al. [137] has attained almost 90% separation of particles with nominal size of 0.5 μm . However, they experienced a low flux and pressure drop due to irreversible fouled cause by the presence of sub-micron particles in the separation process. Thus, the main challenge is to prepare the electrospun fibres that is not only higher in flux but also has low fouling rate. One way to overcome the fouling problem is by applying the nanofibrous support as a mid-layer to thin film composite membrane as a replacement for asymmetric porous membrane. This nanofibrous support is important as it offers selectivity and also prevents from surface fouling. For example, Yoon et al. [138] demonstrated that electrospun polyacrylonitrile (PAN) nanofibrous scaffolds as a mid-layer coupled with a chitosan coating layer and nonwoven polyester exhibited a flux rate that is an order magnitude higher than commercial NF membranes for 24 hours operation. In fact the rejection efficiency for oily wastewater filtration was more than 99%.

2.7.1 Electrospun fibres for metal ions removal

Even though there have been increasing amounts of literature on developing electrospun fibres for liquid filtration especially for micro particles removal, the application of electrospun fibres in small organics and metal ion removal is still new. Unlike macro particles, these ions have smaller ions size which can easily pass through the porous fibres. Therefore, the electrospun fibres have to be a functionalized membrane to allow the separation of molecules based on chemical or biological functions rather than molecular weight or size alone.

Recently, many researchers have adopted different kind of adsorbents to the fibres to produce nanofibres adsorbents for heavy metal ions removal. The electrospun polyvinyl alcohol (PVA)/zinc oxide (ZnO) was successfully prepared by Hallaji et al. [139] for the removal of uranium(VI), copper(II) and nickel(II). The FTIR analysis

showed that these metal ions were configured on the surface of PVA/ZnO. An optimum condition for absorption was reached by using 20 wt. % of ZnO, at operating temperature of 45 °C and 6 hours of contact time in the batch system. It is interesting to note that recovery process of the adsorbed metals is not impossible and can be done. However, it has to be carried out as independent recovery operation in a different plant by an entirely different process or a sequence of operations [139].

2.8 Electrospun fibres incorporated with extractant

Attempt to incorporate specific extractant to the electrospinning solution is a new way to functionalise electrospun fibres. The polymer fibres will have larger surface area containing extractant. Truong et al. [140] fabricated polyvinylidene fluoride (PVDF) electrospun fibres incorporated with Aliquat 336 to remove cadmium(II) from HCl solution. The PVDF/Aliquat was electrospun at 0.2 mL/h at 20 kV for 3 hours. A drum collector was used to collect the fibres at a constant speed of 1.0 m/s which was placed 20 cm away from the spinneret. The collected fibres were then cut into a 13 mm diameter and put in designated syringe holder (Sartorius) where a cadmium solution will pass through the membrane filter. Their results showed that about 93 % of cadmium(II) was removed from the HCl solution after 10 passes. They also reported that PVDF electrospun without Aliquat 336 has insignificant removal even after 10 passes. It is noteworthy that the extraction experiment was conducted in a small scale with initial cadmium(II) concentration of 3 mg/L.

To date, electrospun mats made with PVC and Aliquat 336 has been reported by Wong et al [141]. The PVC containing 40% Aliquat 336 solution in the ratio of 40:60 DMF/THF solvent was electrospun at 200 μ L/h at 25 kV for 8 hours at 10 cm distance from the needle tip to the aluminium collector. Wong et al. [141] also demonstrated that PVC electrospun incorporating with Aliquat 336 exhibit significant improvement in cadmium(II) extraction rate and capacity compared to PVC/Aliquat 336 PIMs. At the same Aliquat 336 concentration (40%) with an initial cadmium(II) concentration of 127 mg/L, PVC/Aliquat electrospun has extracted about 30% of cadmium(II) while PVC/Aliquat PIMs extracted about 9% within 40 hours. Besides, the sorption capacity was improved from 11.9 mg/g using PVC/Aliquat PIMs to 35.6 mg/g using PVC/Aliquat electrospun membranes. They speculated that increased in extraction rate was due to the increased in surface area as

a result of smaller diameter fibres and Aliquat 336 content. The preliminary study showed the potential of PVC/Aliquat 336 electrospun fibre for metal ions extraction. However, more research is needed in term of characterization in order to understand the extraction process.

2.9 Summary

The extraction of heavy metal using PIMs could potentially be a better method compared to solvent extraction and SLM in terms of chemical and physical stability and long term performance. This means that this technology may replace the conventional methods and been applied in industrial applications but more research are needed in order to produce superior stability of PIMs. In addition, the combination of PVC and Aliquat 336 has proven to be compatible and thus no added plasticizer is needed and hence simplifies the PIMs composition. Besides, PVC/Aliquat 336 PIMs has shown promising results in extracting metal ions and small organics molecules. However, studies on the characterization of PVC/Aliquat 336 PIMs are very limited and it is not yet clear whether the PVC/Aliquat 336 PIMs is a solid homogenous solution or a two phase heterogeneous mixture. Besides, no previous work has been conducted to study the process of membrane aging PIMs on the impact of membrane properties and extraction performance. Therefore, proper measurements on PIMs characterization are important as it helps to understand the transport properties and to ensure that PIMs can be practically applied in industries.

On the other hand, the electrospinning process has gained so much attention due to their flexibility method by which ultrafine polymer fibres can be produced using an electrostatically driven jet of polymer solution. However, the formation of fine electrospun fibres required a careful consideration of many solution parameters, process parameters and ambient parameters which could significantly affect the morphology and diameter of electrospun fibres. From a wide variety of polymers that can be electrospun, these fibres offer several advantages such as high surface to volume ratio, high porosity and excellent structural mechanical properties. Due to their outstanding characteristics this technology have been applied in many fields but their application in filtration areas especially in heavy metals removals are barely reported. Moreover electrospinning process normally used a melt polymer or a blend polymer solution in their fundamental procedure. But, study on the electrospun fibres

with the combination of polymer and extractant are scarcely reported. The integration of polymer and extractant are widely used to produce PIMs as describe in the previous sub topics and have shown promising result for heavy metals extraction. Since electrospinning method can successfully produce ultrafine fibres, it is expected that this method could improve the feasibility of PIMs for metal ions extraction. Thus, more studies are desirable to certify the competencies of this technology to produce ultrathin fibres that are capable for metal ions extraction.

3.0 References

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Chapter 3

The impact of extractant concentration on PVC/Aliquat 336 PIM properties and metal extraction

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3.1 Introduction

Over the last two decades, there has been a significant progress in the development of polymer inclusion membranes (PIMs) as a potential alternative to the conventional solvent-solvent extraction process for metal ion recovery [1, 2]. PIM is a thin film consisting of a polymer, an extractant and if necessary a plasticizer. The extractant is an essential component which functions as a guest host specific molecule that provides selective membrane permeability for target species [3]. PIMs consisting of poly-vinyl chloride (PVC) and Aliquat 336 were first applied by James et al. [4] for the construction of ion selective electrodes more than four decades ago. Since the early work by James et al. [4], PVC/Aliquat 336 PIMs have probably been the most studied system for the extraction of metallic ions from the aqueous phase. Previous studies have shown successful extraction of metal ions and small organic molecules using PVC based PIMs containing Aliquat 336 [5-10]. However, until now, it is still not clear whether the PVC/Aliquat 336 PIM is a solid homogenous solution or a two-phase heterogeneous mixture.

The mechanism of facilitated transport in PIMs is still open to speculation given the lack of understanding about the nature of their homogeneity. For a solid solution, the metal ion with the aid of an extractant is transported through a polymer matrix. For a heterogeneous solid, the metal ion with the aid of extractant is transported through

continuous channels within a polymer matrix. In some instances, a combination of these two extremes may occur.

In recent years, several studies have been conducted to investigate the homogeneity of PIMs. Through scanning electron microscopy analysis, Xu et al. [11] speculated that at above 30 wt.% Aliquat 336, the interior structure of PVC/Aliquat 336 PIMs contained micro channels filled with Aliquat 336. They also showed that there exists a critical Aliquat 336 content in PIMs of 30 to 40 wt.% for the transport of Cd (II) to occur. Although the critical Aliquat 336 content has been confirmed by several other studies [11, 12], their speculation about the existence of micro channel in PIMs has not been substantiated. In fact, their speculation has been recently contradicted by St John et al. [13] who employed high resolution synchrotron-based fourier-transform infrared (FTIR) spectroscopy and proton-induced X-ray emission microspectrometry (μ -PIXE) to study the homogeneity of PVC/Aliquat 336 PIMs. μ -PIXE results reported by them showed that PVC based PIMs containing 10 to 40 wt.% Aliquat 336 are homogenous at the micro-scale which is comparable to the scale investigated by Xu et al. [11].

In this chapter, PVC based PIMs were prepared with different Aliquat 336 concentrations. This work aims to determine whether the PIMs produced are a solid solution or mixture by application of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) techniques to characterise the thermal transitions. This approach clarifies the miscibility of PVC and Aliquat 336. Extraction of Cd (II) and Zn (II) were also investigated in order to observe any correlation between solid structure, thermal analysis and membrane function.

3.2 Materials and methods

3.2.1 Reagents

All reagents were obtained from Sigma Aldrich, Australia. High molecular weight poly (vinyl chloride) (PVC) and Aliquat 336 (tricaprylylmethylammonium chloride) were used as the base polymer and extractant respectively. The weight-average molecular weight of this PVC is 80,000 g/mol. Aliquat 336 is a mixture of tri-alkyl methyl ammonium chloride salts produced from the methylation of Alamine 336,

with the substituent alkyl chain length containing between 6 and 12 carbon atoms. HPLC grade tetrahydrofuran (THF) was used without any further purification. Cadmium (II) and zinc (II) solutions used in the membrane extraction experiments and for calibration purposes were prepared from $\text{Cd}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ (analytical grade). Milli-Q grade water (Milipore, Australia) was used for the preparation of all aqueous solutions.

3.2.2 Preparation of PVC/Aliquat 336 PIMs

PIMs at different Aliquat 336 concentrations were prepared by dissolving Aliquat 336 and PVC in THF. Each mixture contains a combined Aliquat 336 and PVC weight of 600 mg. The volume of THF used was between 5 to 10 mL depending on the weight fraction of PVC. The mixtures were stirred vigorously for 1 hour resulting in a clear solution. The solution was then poured into a Petri dish with a diameter of 70 mm and covered with filter paper (0.45 μm). The THF solvent was allowed to evaporate over about 48 hours forming a membrane. The membranes were peeled from the Petri dish and stored in the dry condition for further experiments. PVC films were prepared using the same protocol but without the addition of Aliquat 336.

3.2.3 Extraction protocol

Extraction experiments were conducted in batch mode [5, 6, 14]. Membranes were cut into small pieces of about 1 cm^2 in area. The membrane samples with a combined weight of approximately 0.55 g were placed in beakers containing 100 mL of extraction solution. The extraction solution contained 50 mg/L of either Cd (II) or Zn (II) in 1 M hydrochloric acid (HCl) and was placed in a temperature controlled water bath (Neslab RTE 7, Thermo Scientific Inc., Waltham, MA, USA). The solution was stirred continuously and 1 mL of aliquot was taken at a specific time intervals for metal ion analysis using Atomic Adsorption Spectrometry analysis (Varian SpectrAA 300 AAS, Australia). Calibration using standard Cd (II) and Zn (II) solutions was conducted prior to each batch of analysis. The linear regression coefficient for all calibration curves were greater than 0.98.

3.2.4 Differential scanning calorimetry (DSC) analysis

DSC analysis for PVC/Aliquat 336 PIMs was carried out using a DSC Q-100 (TA Instrument, USA). The experiment was conducted at a heating rate of 10 °C/min in the temperature range of –50 to 110 °C. Approximately 10 mg of PVC/Aliquat 336 PIM sample was used and encapsulated in standard aluminium pans while a hermetic pan was used for pure Aliquat 336 sample. Melting temperatures (T_m) were reported based on the onset value.

3.2.5 Dynamic mechanical analysis (DMA)

DMA Q 800 (TA Instrument, USA) was used to characterise the thermal transitions of PVC/Aliquat 336 PIMs. A film-clamp was used with a heating rate of 4 °C/min over the temperature range of –100 to 180 °C at a frequency of 1 Hz. The temperatures associated with transitions were identified by the peak in tan delta curve. For DMA, the thermal transitions were labelled in order from highest to lowest temperature.

3.2.6 Electrochemical Impedance Spectroscopy (EIS)

The PVC/Aliquat 336 PIMs were cut into a 2 cm² diameter circular discs and sandwiched it in a coin-cell system, thus assembled cells are connected to Biologic VMP3 electrochemical workstation machine. All measurements were taken at open circuit voltage (OCV) and frequency range between 100 kHz and 100 mHz.

3.2.7 Scanning Electron Microscopy (SEM)

The membrane morphology was characterized using a scanning electron microscope (SEM) (JEOL JCM 6000). For this purpose, the samples of the membranes were cut into small dimension and were mounted on an aluminium stub using conductive double sticky tape. Then the samples were gold coated using a DYNAVAC Mini Coater prior to SEM analysis.

3.2.8 Viscosity measurement

The viscosity of Aliquat 336 was measured using rheometer (Physica MCR 301, Anton Paar) with Rheoplus software. A small drop of Aliquat 336 liquid was loaded on the measuring cone (CD-50-1) and the viscosity was measured at constant shear rate (10 s⁻¹) from temperature 5 to 70 °C with a heating rate of 2 °C/min. Then, the

viscosity of Aliquat 336 was measured at different shear rate ranging from 1 to 100 s^{-1} at one specific temperature (10, 20, 35 or 50) $^{\circ}\text{C}$.

3.3 Results and discussion

3.3.1 Effect of Aliquat 336 content on surface morphology

All PVC/Aliquat 336 PIMs prepared in this study have relatively uniform thicknesses of approximately 85 μm . Besides, they looked transparent and homogenous to the naked eye. PVC PIMs without Aliquat 336 was rigid. However, they become more flexible when Aliquat 336 was added into the film. For a rigid polymer, the flexibility is improved by adding a plasticizer to the solution and thus lowering the glass transition (T_g). The T_g of the PVC/Aliquat 336 PIMs is further reported in the next section.

From SEM observation, PVC/Aliquat 336 PIMs at 0 to 20 wt.% Aliquat 336 content, had no apparent structure (Figure 3.1a-c). However at 30 wt.% Aliquat 336 content, some wrinkles could be observed (Figure 3.1d). The wrinkles were more obvious when Aliquat 336 content reached 40 wt.% and above suggesting that they might contain two separates domains (Figure 3.1e-g). It is possible that the wrinkles contain viscous liquid which was formed underneath of the skin. As THF solvent evaporates it took on smaller volumes of the viscous liquid which cause the surface to compress and buckle. Thus, the formation of the skin type layer could be related to the miscibility and Aliquat 336 concentration. This observation suggests that PVC Aliquat 336 PIMs were phase separated and this premise is further explained in the next section.

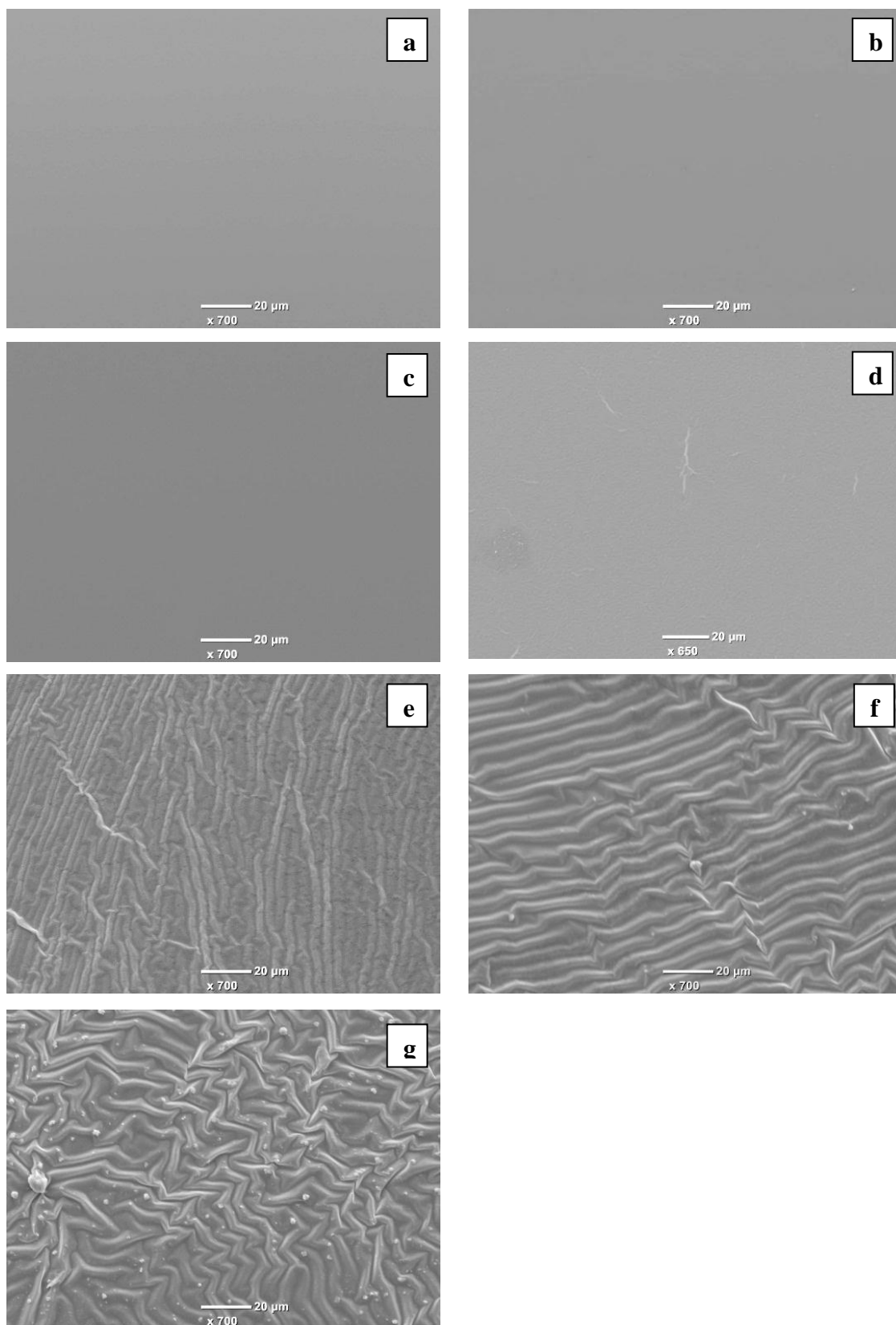


Figure 3.1: SEM images of PVC/Aliquat 336 PIMs at different Aliquat 336 content (w/w): (a) 0%, (b) 10%, (c) 20%, (d) 30%, (e) 40%, (f) 50% and (g) 60%.

3.3.2 *Effect of Aliquat 336 content on thermal analysis*

DSC analysis of the PVC as supplied showed a glass transition temperature (T_g) of 85 °C (Figure 3.2) which is consistent with literature values [15, 16]. In contrast, DSC analysis of the PVC cast from THF solution exhibited a T_g of 63 °C (Figure 3.2). PIMs containing 10 to 40 wt.% Aliquat 336 exhibited a T_g in the range of 55 to 63 °C (Figure 3.3). PIMs containing 50 to 70 wt.% Aliquat 336 exhibited a T_g that was too subtle for designation using the described experimental procedure (Figure 3.3). DSC analysis of the supplied neat Aliquat 336 did not exhibit a T_g but exhibited a T_m of -19 °C (Figure 3.2), which is also consistent with the report value of -20 °C [17].

The DMA is another thermal analysis technique that is frequently employed to characterise thermal transitions of polymers. The DMA isolates thermal transitions as substantial changes in the storage modulus and a corresponding peak in the dissipation of energy ($\tan \delta$). DMA results revealed that the PVC/Aliquat 336 PIMs contained one or two thermal transitions with the number dependent on the fraction of Aliquat 336 (Figures 3.4-3.5). An α transition was observed at 71 ± 8 °C for all Aliquat 336 concentrations studied here (Figure 3.3). A β transition was observed at -18 ± 1 °C for PIMs samples containing 40 to 70 wt.% Aliquat 336 (Figure 3.3). In addition, PIMs containing 10 wt.% Aliquat 336 or more started to undergo degradation at about 100 °C as evidenced in an increase in the storage modulus (Figure 3.4).

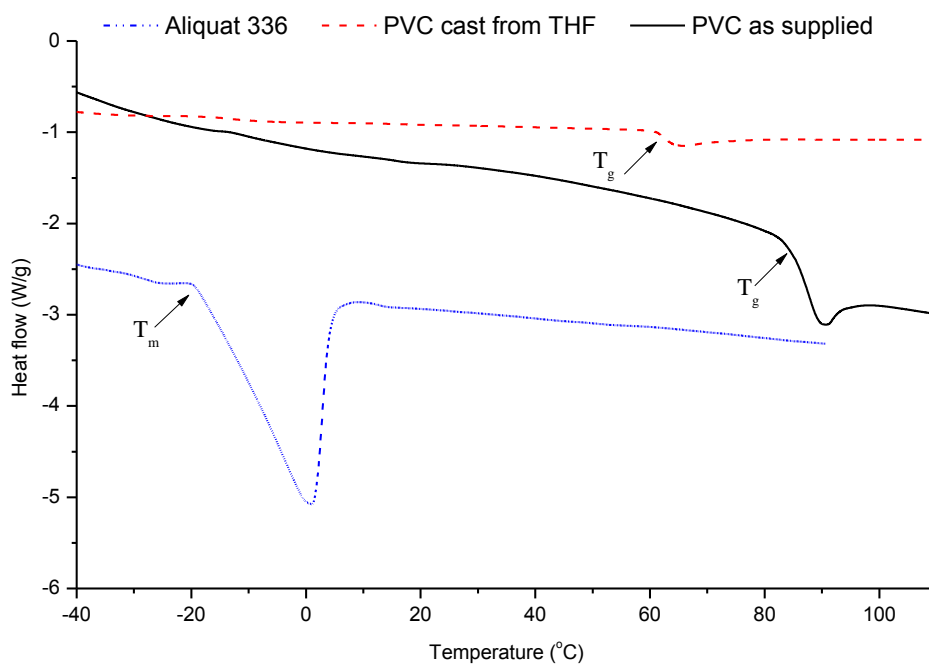


Figure 3.2: DSC thermographs of Aliquat 336, PVC cast from THF and PVC as supplied.

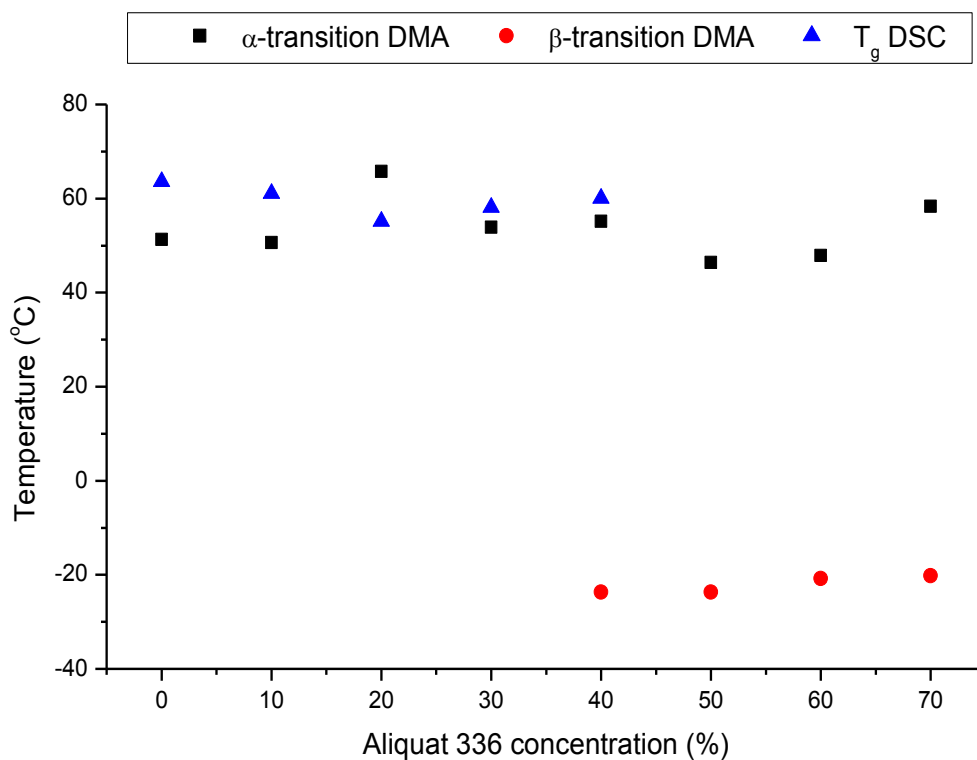


Figure 3.3: The thermal transition temperatures of PIMs with different Aliquat 336 content.

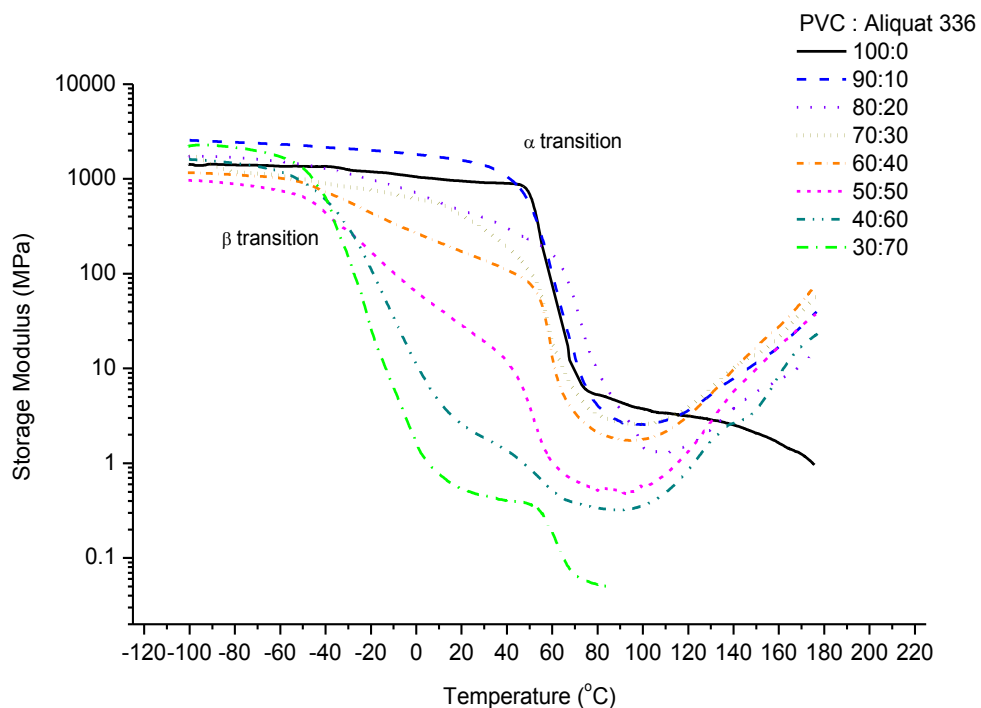


Figure 3.4: Storage modulus curves of PIMs with different Aliquat 336 content versus temperature.

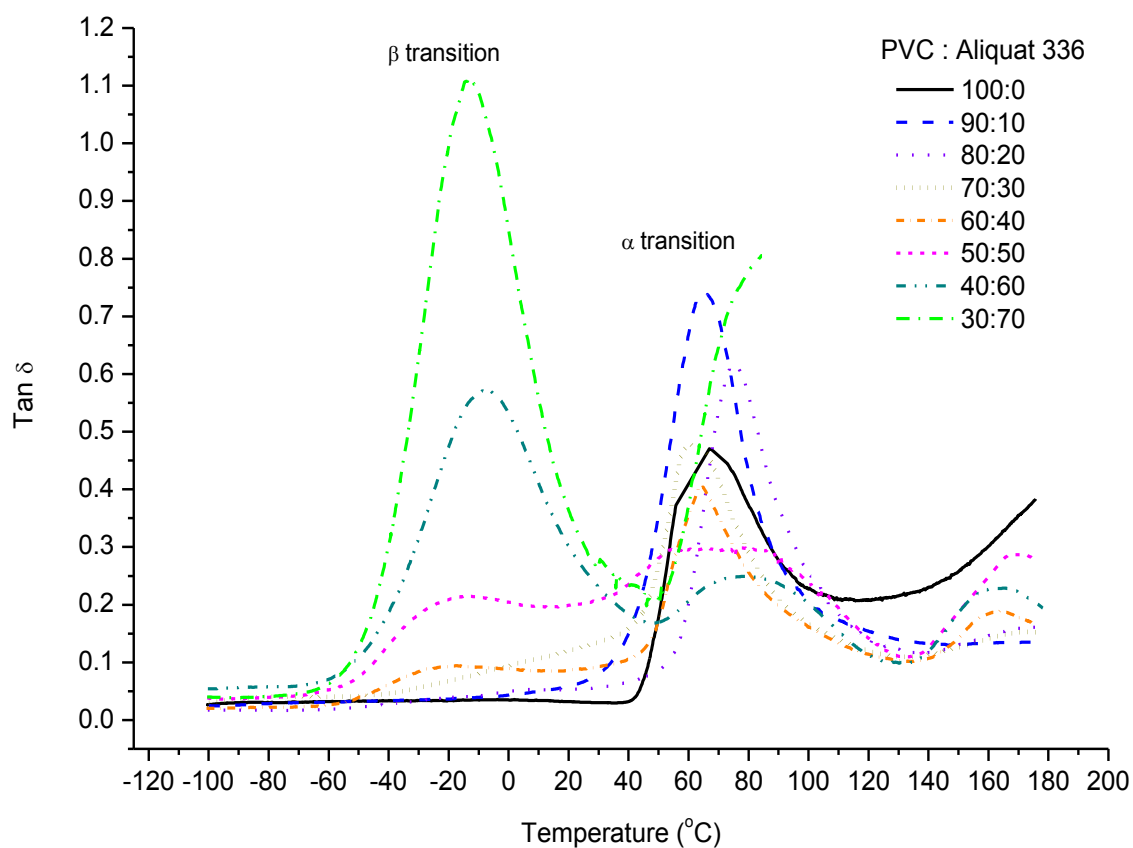


Figure 3.5: $\tan \delta$ of PIMs with various Aliquat 336 content versus temperature.

3.3.2.1 α transition

The α transition is assigned to the T_g of the PVC as it occurred in PVC cast from THF without Aliquat 336 and it was consistent with DSC T_g measurements (Figure 3.2). For the PIMs membranes, the T_g value coincides with the reduction in storage modulus from about 10^3 MPa to less than 10 MPa during heating (Figure 3.4). The PVC samples cast from THF without Aliquat 336 were semi-crystalline at temperatures higher than the α transition. The semi-crystalline nature of PVC the film (without any Aliquat 336) is evidenced by the observation of a storage modulus higher than 1 MPa at 100°C (Figure 3.4).

For many plasticised polymers, the T_g is typically a function of the plasticizer content predicted by the Fox equation [18]:

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}$$

where w_1 and w_2 are weight fractions of components 1 and 2. $T_{g,1}$ and $T_{g,2}$ are the T_g 's of components 1 and 2, and, T_g is the single T_g of the plasticized polymer.

This is because the plasticizer molecules form a solid solution with the polymer and enhance segmental mobility. For PVC based PIMs, Aliquat 336 has been widely reported to behave as a plasticizer [2, 10, 19]. For the PIMs observed here, the T_g was independent of the Aliquat 336 concentration over the range of 0 to 70 wt.%. In contrast, by using the Fox equation [18], the T_g for a PIMs containing 70 wt.% Aliquat 336 was predicted to be ≤ 4 °C by assuming that the T_g of the Aliquat 336 is about ≤ -20 °C [17], the T_g of PVC is about 85 °C and all of the Aliquat 336 is plasticizing the PVC. Hence, the Aliquat 336 is not solvating or depressing the T_g of a substantial fraction of the PVC, and, is likely to be present in a separate phase.

Aliquat 336 is classified as a plasticiser for PVC as its incorporation transforms brittle PVC into a plastic (a material capable of exhibiting substantial plastic deformation). Furthermore, the addition of Aliquat 336 also reduces the Young's modulus of PVC (also referred to as softening). The results presented here indicate that Aliquat 336 does not achieve the plasticization by forming a solid solution with

PVC and depressing its T_g . The mechanism of plasticization may be the formation of a sponge like structure of PVC containing Aliquat in the sponge pores.

The T_g of the PVC cast from THF as determined by DMA and DSC (68 °C and 63 °C respectively) was well below that observed for PVC in the supplied condition determined by DSC (85 °C). This difference occurred in the absence of Aliquat 336, but after dissolution and drying from THF. It is likely that the T_g depression observed after exposure to THF, results from a small amount of residual THF in the PVC. For example, 1 wt.% residual THF is sufficient to achieve a depression of 30 °C [20].

3.3.2.2 β transition

The β transition is assigned to the melting temperature (T_m) of the Aliquat 336 rich phase, as it corresponds to the T_m of neat Aliquat 336 observed by DSC (Figure 3.2). The correspondence was confirmed where a piece of cloth soaked in Aliquat 336 subjected to DMA exhibited a thermal transition over the same temperature range. The β transition was independent of Aliquat 336 concentration for concentrations of 40 to 70 wt.% as verified by a peak in the $\tan \delta$ indicating its composition is constant (Figures 3.3 and 3.5). The storage modulus also shows a decrease at about -22 °C for Aliquat 336 concentrations of 20 and 30 wt.% indicating that they also contain an Aliquat 336 rich phase (Figure 3.4). There is no indication of an Aliquat 336 rich phase for 10 wt.% Aliquat 336 by DMA. Although the temperature where the β transition occurred is independent of Aliquat 336 concentration, the storage modulus change associated with the β transition increases with Aliquat 336 concentration.

3.3.2.3 Membrane structure

The thermal analysis data demonstrate that the PIMs membranes containing 20 to 70 wt.% Aliquat 336 are a two phase structure containing a discrete Aliquat 336 rich phase, and a discrete PVC rich phase. However, thermal analysis provides no insights into whether the Aliquat 336 rich phase is continuous or in closed pores and it provides no insight into the spatial dimensions of the phases. As the membrane structure is heterogeneous, and previous reports have shown a threshold where heavy metals extraction begins, it is most likely that the extraction are dominated by transport via a continuous or semi-continuous Aliquat 336 rich phase.

As Aliquat 336 and PVC form a solution with an appropriate concentration of THF, phase separation may occur during the evaporation of THF when the membrane is formed. Consequently, the phase morphology is determined by both the composition and fabrication conditions of the PIMs. In other words, the shape, size and distribution of the second phase are a function of the solvent evaporation rate and PIM thickness. Therefore, the structure of the PIMs studied by St John et al. [13] and Xu et al. [11] may be different to that observed here.

3.3.3 Effect of Aliquat 336 content on electrochemical impedance profile

The electrochemical impedance spectroscopy (EIS) was conducted in order to study the influence of various Aliquat 336 content towards the improvement of conductivity profile. The corresponding Nyquist plots were shown in Figure 3.6. For an ideal case, the Nyquist plot should show a semicircle which represent a parallel combination of a capacitor, that is due to the immobile polymer chain and a resistor that is due to the mobile ions inside the polymer matrix.

Based on Figure 3.6, the Nyquist plot of the impedance of PVC/Aliquat 336 PIMs showed differences in membrane resistance at various Aliquat 336 content. For PVC/Aliquat 336 PIMs with Aliquat 336 content of 30 wt.% and below, the plots (Figure 3.6a-c) were completely different from the ideal plot where no semicircle were observed. Inadequate optimization of PVC and ionic liquid proportion in the PIM films to enable accurate measurement of the conductivity profiles could be a reason for this observation (Figure 3.6a-c). In addition, the rough or uneven surface of the PIM films are another possible cause. However, it is interesting to note that the impedance profile has changed towards the ideal impedance characteristics when the Aliquat 336 content increased to 40 wt.% and above (Figure 3.6d-f).

The direct measurement of diameter of semicircles in such impedance plots corresponds to the electronic conductivity profiles of the tested PIMs films. Hence, the diameter values for PVC PIMs at 40 wt.%, 50 wt.% and 60 wt.% of Aliquat 336 were 1875 k Ω , 470 k Ω and 48 k Ω respectively as shown in Figure 3.7. It is noteworthy that as Aliquat 336 content increased, the electrical conductivity has improved as the resistance decreased. This explain the importance of optimization between PVC and Aliquat 336 in PVC PIMs films for better conductivity profiles.

Hence, PIMs with 40 wt.% PVC and 60 wt.% Aliquat 336 could be a better candidate as solid-state polymer electrolyte for metal ions extraction.

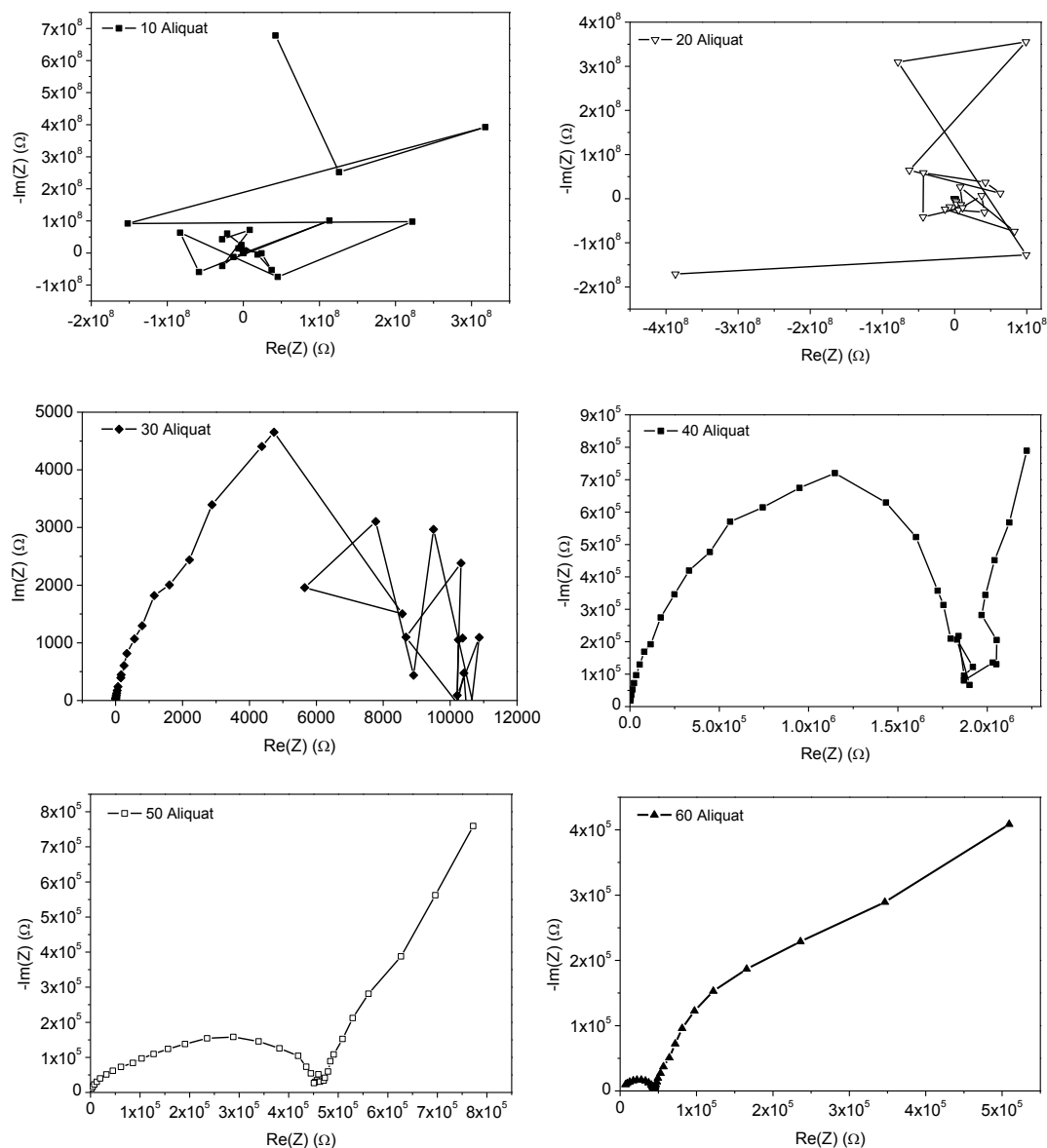


Figure 3.6: Nyquist plot of PVC/Alquat 336 PIMs at different Aliquat composition recorded at open circuit voltage between 100 kHz to 100 mHz.

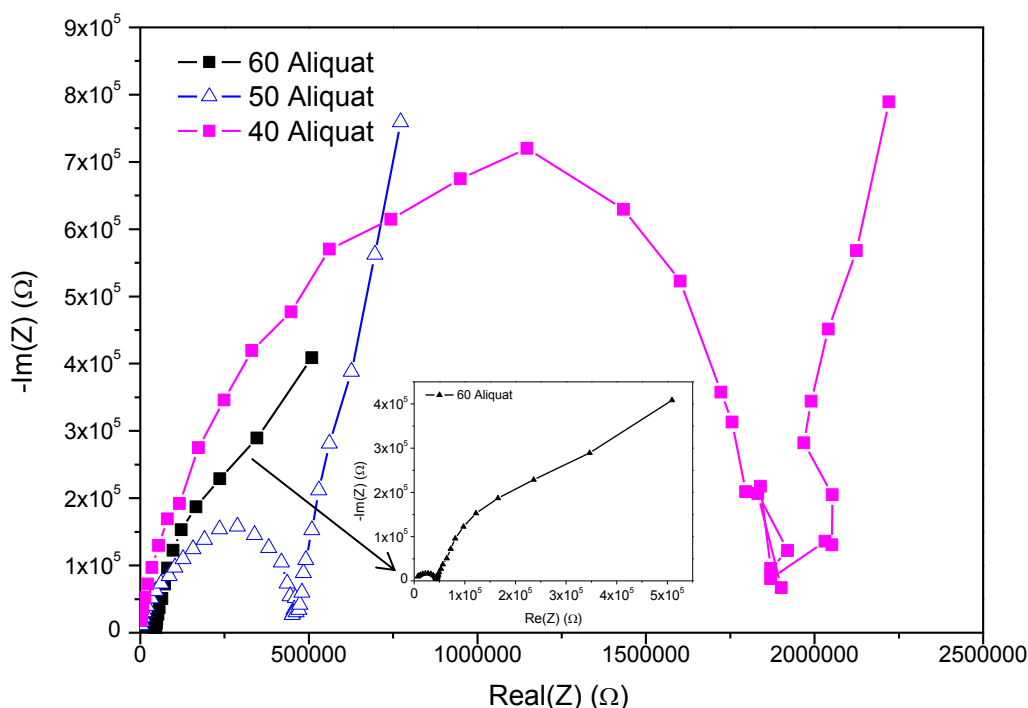


Figure 3.7: The Nyquis plot of PVC/Aliquat 336 PIMs at 40 wt.%, 50 wt.% and 60 wt.% of Aliquat 336 recorded at open circuit voltage between 100 kHz and 100 mHz.

3.3.4 Extraction experiments

3.3.4.1 Effect of Aliquat 336 content on metal ions extraction

The extractions of Cd (II) and Zn (II) into PVC/Aliquat 336 PIMs are shown in Figures 3.8 and 3.9, respectively. In general, the extraction rate increased as the Aliquat 336 content in PIMs increased. When the extraction experiment was performed using PVC film that had been cast from THF without Aliquat 336, the metal ions extraction was found to be negligible, suggesting that the transport of both Cd (II) and Zn (II) were fulfilled by the extractant. Previously, PVC/Aliquat 336 PIMs have separated into two individual phases with one phase being rich in PVC (α transition) and the other phase being rich in Aliquat 336 (β transition). For a heterogeneous PIM, the transport of ions across requires a continuous phase. Therefore, sufficient amount of extractant is essential to form continuous channels across the membrane for the extraction to occur. Assuming the stoichiometric binding ratio of extractant to heavy metal of 1:1, according to the experimental condition specified in section 3.2.3, the Aliquat 336 contents in PIMs for complete extraction of Cd (II) and Zn (II) are 6 and 3%, respectively.

The threshold of Aliquat 336 content was observed to be 30 wt.% where a major change was observed in both ion metals extractions (Figures 3.8 and 3.9). Below the percolation threshold, the extraction of PVC/Aliquat 336 PIMs was insignificant. Even though, the percolation threshold was attained at 30 wt.% of Aliquat 336, the extraction process was not completed even after 240 minutes. This result is in good agreement with the data reported by Xu et al. [11] that the extraction is not viable for PIMs containing less than 30 wt.% of Aliquat 336. However, as Aliquat 336 content reached 40 wt.%, the extraction of Cd (II) and Zn (II) were almost completed (Figures 3.8 and 3.9) after 240 minutes.

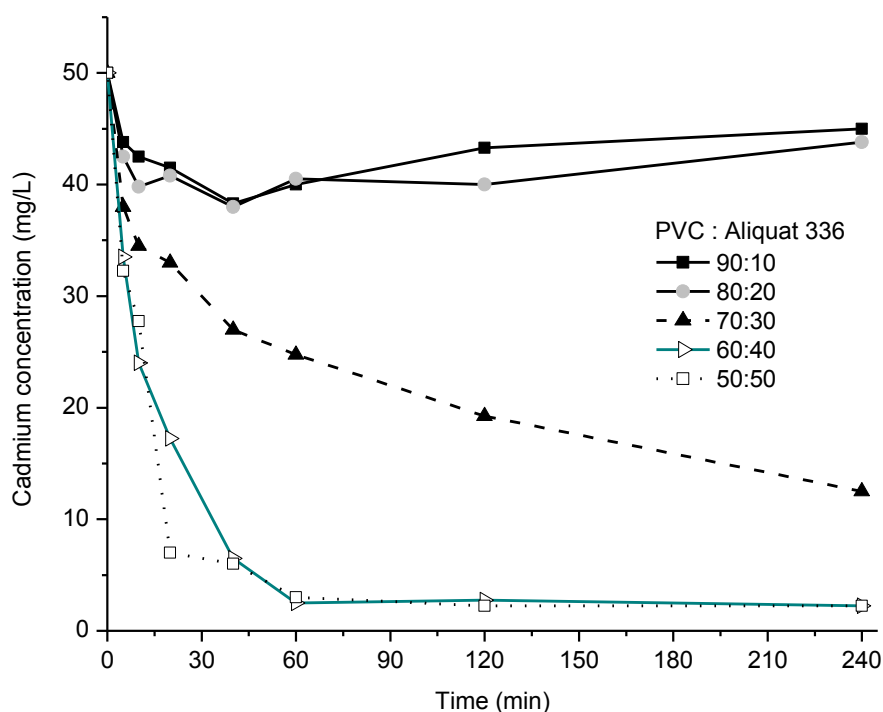


Figure 3.8 Extraction profile of Cd (II) into PIMs with different Aliquat 336 content. Experimental conditions: 100 mL of 50 mg/L Cd (II) in 1 M HCl solutions, 0.55 g PIM.

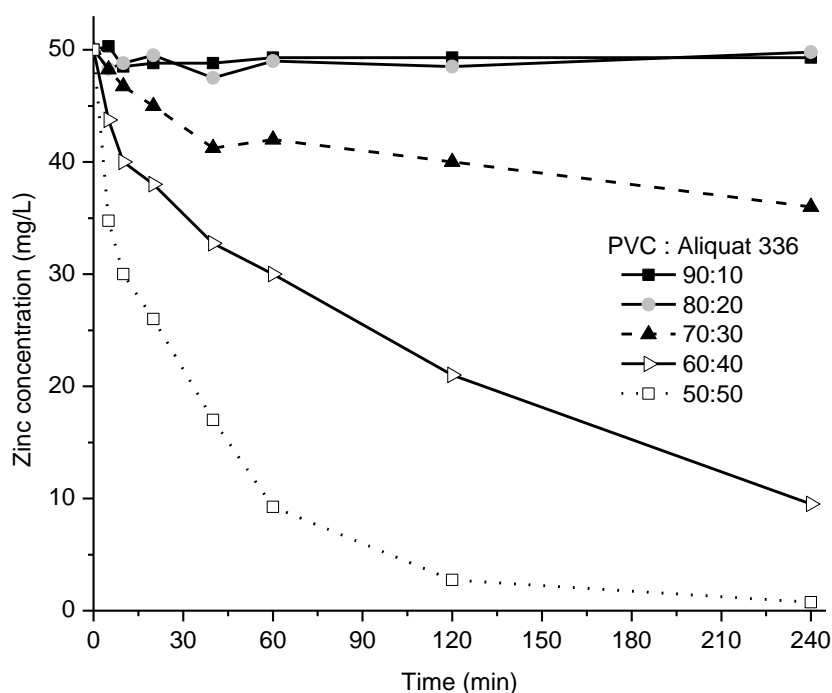


Figure 3.9: Extraction profile of Zn (II) into PIMs with different Aliquat 336 content. Experimental conditions: 100 mL of 50 mg/L Zn (II) in 1 M HCl solutions, 0.55 g PIM.

3.3.4.2 Effect of temperature on metal ions extraction

The influence of extraction temperature on the metal ions extraction was investigated for PIMs containing 30, 40 and 50 wt.% of Aliquat 336. The extraction temperature of Cd (II) and Zn (II) from hydrochloric solution was varied at 10, 20, 35 and 50 °C and the results are plotted in Figures 3.10 and 3.11, respectively. The results show that extraction temperature has a significant effect on the extraction rate. At higher temperature, the extraction of Cd (II) and Zn (II) was 95% completed, even though the Aliquat 336 content was only 30 wt.%. The transport of metal ions through PIMs requires the diffusion of the metallic species itself or the metal-extractant complex through the membrane. An increase in temperature can increase not only the diffusion rate of metal-Aliquat 336 complex and Aliquat 336 molecules but also the rate of ion-exchange reaction between metal-Aliquat complexes. In either case, an increase in temperature will enhance the transport of the target metal ions in PIMs.

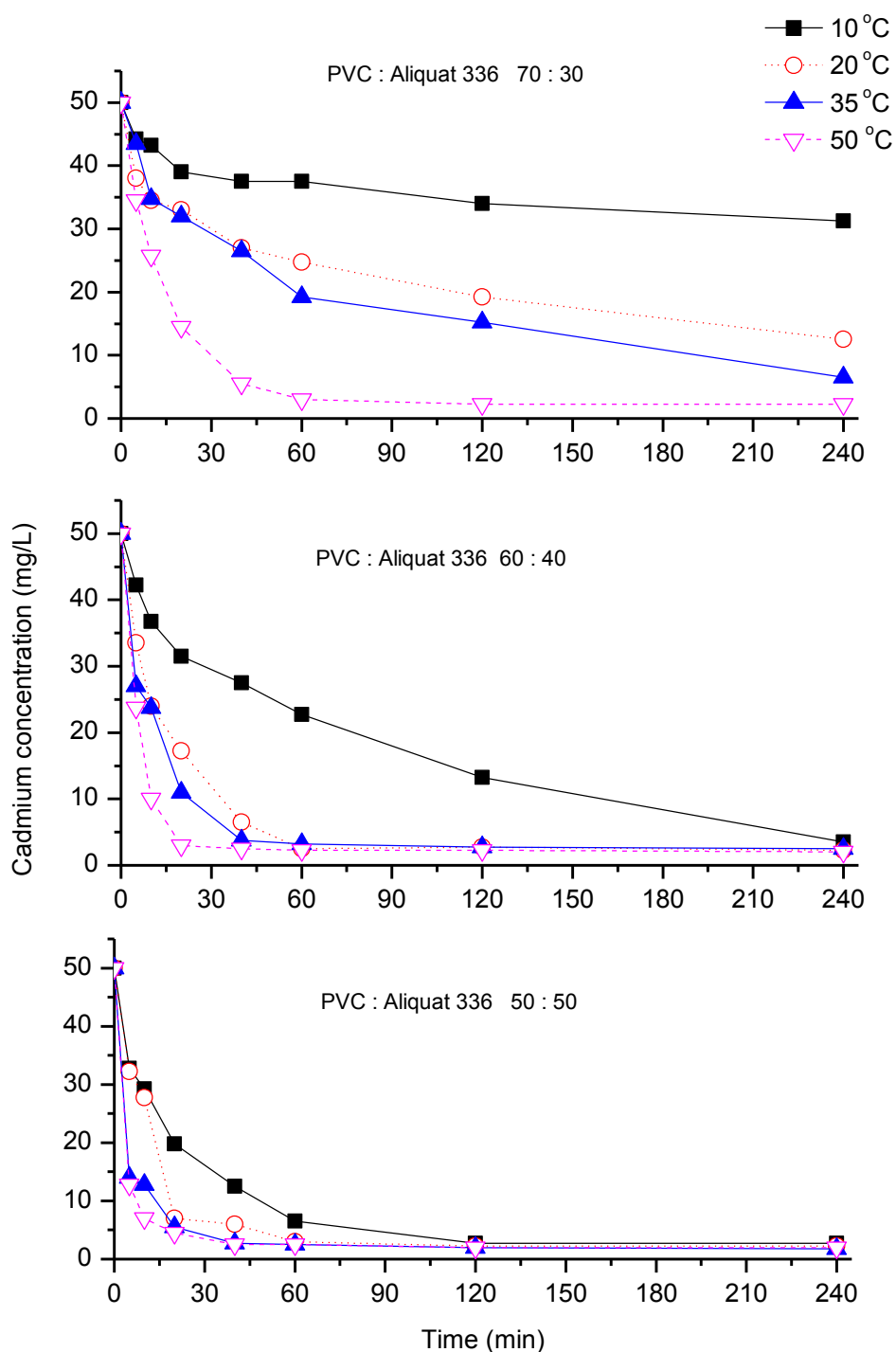


Figure 3.10: Extraction profile of Cd (II) into PIMs with different Aliquat 336 content and at different extraction temperatures. Experimental conditions: 100 mL of 50 mg/L Cd (II) in 1 M HCl solutions, 0.55 g PIM.

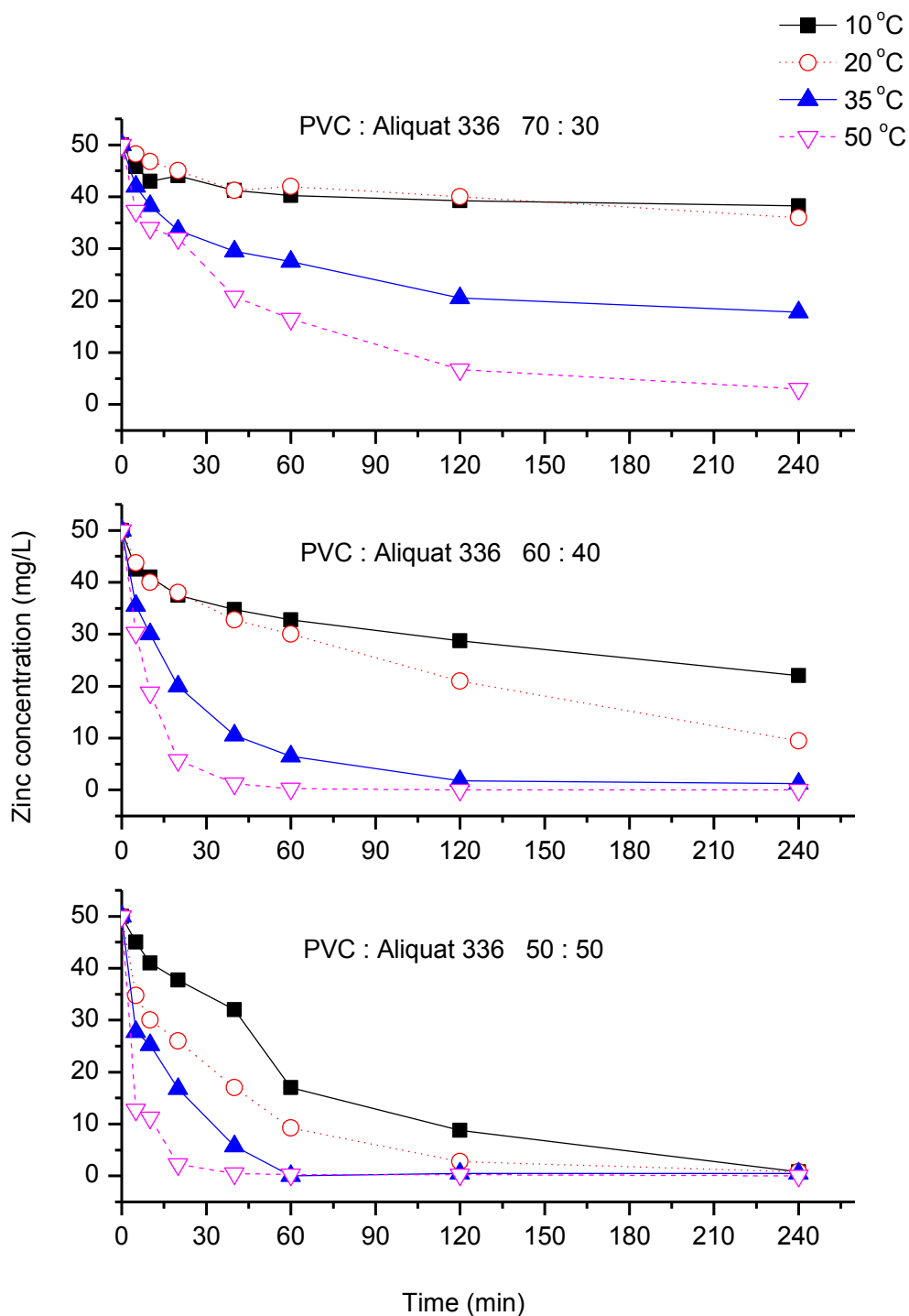


Figure 3.11: Extraction profile of Zn (II) into PIMs with different Aliquat 336 content and at different extraction temperatures. Experimental conditions: 100 mL of 50 mg/L Zn (II) in 1 M HCl solutions, 0.55 g PIM.

3.4 Conclusion

In this chapter, the morphology of PVC/Aliquat 336 PIMs at different Aliquat 336 content was investigated. All the PIMs produced in this study were transparent. The SEM images showed that the PVC/Aliquat 336 PIMs has smooth surface with no apparent pores. However as Aliquat 336 content increased from 40 wt. % to 60 wt. %, some wrinkles were formed and become more obvious at higher Aliquat 336 concentration.

The miscibility of the PVC/Aliquat 336 PIMs at various Aliquat 336 concentrations was examined by measuring the T_g . The DMA has provided a distinct result for T_g of PVC/Aliquat 336 PIMs and a T_m of Aliquat 336. Results reported here indicate that PVC/Aliquat 336 PIMs were phase separated with two distinctive phases observed by DMA, that is an α transition at 71 ± 8 °C and β transition at -18 ± 1 °C where the later was not detected by DSC. Besides, the DMA results also suggest that Aliquat 336 is not a plasticizer since the T_g did not decrease to below room temperature and is independent of Aliquat 336 content. However, an addition of Aliquat 336 has successfully produced transparent membranes with a flexible structure. It is noteworthy that, when more Aliquat 336 content was added, the PIMs become more flexible.

On the other hand, the impedance study from EIS revealed that PVC/Aliquat 336 PIMs at below 30 wt. % of Aliquat 336 were far out from the ideal plot and were not suitable to be used as a solid state polymer-electrolyte for metal ions extraction. However, the impedance profile has changed towards ideal characteristic when the PVC/Aliquat 336 PIMs contain 40 wt. % and/or more of Aliquat 336. At this stage, the conductivity of the PVC PIMs film had increased while the resistance decreased.

From the metal ions extraction experiments both cadmium and zinc extraction occurred when Aliquat 336 ≥ 30 wt.% which is not only coincided with the appearance of a defined β transition but also corresponded to the formation of ideal Nyquist plot. The β transition is assigned to the T_m of an Aliquat 336 rich phase. In order to form this phase, Aliquat 336 content needs to be more than 30 wt.%. Besides, the extraction rate also increases, as diffusivities in the Aliquat 336 phase increased which can be achieved by using higher extraction temperature.

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Chapter 4

The effect of aging on thermomechanical and metal extraction properties of poly (vinyl chloride)/Aliquat 336 polymer inclusion membranes

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4.1 Introduction

Polymer inclusion membranes (PIMs) have emerged as a promising material for extracting metal ions from aqueous and solvent solutions. Compared to all other forms of liquid membranes, PIMs have superior mechanical and chemical stability properties while their capacity for metal extraction is either slightly lower or similar [1]. PIMs can be formed from poly (vinyl chloride) (PVC) or cellulose triacetate (CTA) as a base polymer (which provides mechanical strength to the film), an extractant that acts as ion exchanger, and a plasticizer [1].

Aliquat 336 is a good extractant for selective and efficient transport of numerous metal ions [2-7]. Aliquat 336, a commercial name for tricaprylylmethylammonium chloride is a quaternary ammonium salt which is insoluble in water. It is composed of a large quaternary ammonium cation associated with a chloride anion. Aliquat 336 is not only an anion extractant but can also function as a plasticizer for PVC. Our previous study [8] showed that Aliquat 336 addition to PVC could substantially reduce the modulus relative to that of a neat PVC solid film with the product being transparent flexible membranes. However, it has also been established that Aliquat 336 does not plasticize PVC by an increase of its segmental mobility since the glass

transition (T_g) of PVC type PIMs membranes is independent of Aliquat 336 content [8].

The preparation of PVC/Aliquat 336 PIMs involves the use of tetrahydrofuran (THF) as the casting solvent. After dissolving both PVC and Aliquat 336 into THF and casting the solution over a glass plate, THF is allowed to evaporate over 24 to 48 hours forming flexible and transparent thin film PIMs. It is feasible that PIMs formed via this route contain some residual THF which can be reduced by membrane aging. However, it is unclear whether the presence of THF in PIMs affects their physical properties or metal extraction performance.

While the potential of PVC/Aliquat 336 PIMs have been widely demonstrated, no previous work has been conducted to study the process of membrane aging PIMs on the impact of membrane properties and extraction performance. This study aims to examine impact of membrane aging on polymeric properties and subsequently the extraction of Cd(II) as a representative heavy metal by PVC/Aliquat 336 PIMs. Changes in PIMs properties and chemical composition were also evaluated using dynamic mechanical analysis (DMA) and Fourier Transform Infrared Spectroscopy (FTIR).

4.2 Materials and Methods

4.2.1 Reagents

All reagents were obtained from Sigma Aldrich, Australia. High molar mass PVC (M_w 80,000 g/mol) and Aliquat 336 were used as the base polymer and extractant respectively. HPLC grade THF was used without further purification. Cadmium was used as a representative heavy metal. Cadmium is widely used in various applications such as nickel–cadmium batteries, metallurgy, pigmenting and other industries. In fact, the extraction of cadmium from other metallic elements is the focus for many recent studies [2, 3, 9]. Being a heavy metal, cadmium is highly toxic. Thus, cadmium removal from industrial wastewater is also important in many industries [10]. Cd(II) solution used in the membrane extraction experiments and for calibration purposes were prepared from analytical grade $Cd(NO_3)_2$. Milli-Q grade water (Milipore, Australia) was used for the preparation of all aqueous solutions.

4.2.2 Preparation of PVC/Aliquat 336 PIMs

PVC/Aliquat 336 PIMs were prepared by dissolving 360 mg Aliquat 336 and 240 mg PVC in 5 mL of THF [8]. The mixture was stirred in a beaker vigorously for 1 hour forming a clear solution. The solution was then poured into a 70 mm diameter glass Petri dish and covered with a filter paper (Advantec, Toyo, 0.45 μm). Petri dishes containing the solution are placed inside a fume extraction cupboard for 48 hours at room temperature ($\sim 25^\circ\text{C}$) where most of the THF evaporates and PIMs are formed. The membranes were peeled from the Petri dish and were immediately used for further experiments as freshly prepared PIMs. Membrane aging was simulated by placing freshly prepared PVC/Aliquat 336 PIMs in a closed oven at 40°C for one week. Note that aging at temperatures higher than $\sim 40^\circ\text{C}$ [11] is not feasible without PIMs composition modification due to oxidation of PVC as evidenced by discolouration [12].

4.2.3 Fourier Transform Infrared Spectroscopy (FTIR) analysis

FTIR analysis of freshly prepared and aged PVC/Aliquat 336 PIMs was conducted using an IRAffinity-1 (Shimadzu, Kyoto, Japan). The instrument was equipped with a diamond crystal. The measured spectrum was between 500 and 3500 cm^{-1} .

4.2.4 Dynamic mechanical analysis

A Q800 dynamic mechanical analyser (TA Instrument, USA) was used to characterise the thermal transitions of the PVC/Aliquat 336 PIMs. A film-clamp was used with a heating rate of $4^\circ\text{C}/\text{min}$ over the temperature range of -100 to 100°C at a frequency of 1 Hz. The temperatures associated with transitions were identified by local maximums in the tan delta response. The thermal transitions are labelled chronologically from the highest to lowest temperature at which they occur.

4.2.5 Mass loss during aging

An initial weight of PVC/Aliquat 336 PIMs was measured immediately following PIMs formation (i.e. after 48 hours of drying in a fume extraction cupboard) and a final weight of the membrane was measured after aging at 40°C for one week. Both samples were measured alone without the petri dish. THF reduction as a percentage

due to aging was determined by dividing the weight change due to aging into the initial weight.

4.2.6 Extraction protocol

Extraction experiments were conducted in batch mode at room temperature [5, 6]. Each membrane was cut into small pieces and was placed in beakers containing 100 mL of extraction solution. The extraction solution contained 35 mg/L of Cd(II). The solution was continuously stirred and 1 mL aliquots were taken at specific time intervals for analysis. Cd(II) concentrations were determined by atomic adsorption spectrometry analysis (Varian SpectrAA 300 AAS, Australia). Calibration using standard Cd(II) solutions was conducted prior to each batch of analysis. The linear regression coefficient for all calibration curves were greater than 0.98.

4.3 Results and discussion

4.3.1 Changes in membrane morphology and composition due to aging

Thin, flexible, and transparent PIMs were obtained from the casting method described in section 2.2. No discernible changes in the appearance and morphology of PIMs before and after aging could be visually identified. The FTIR spectra of freshly prepared and aged PIMs are shown in Figure 1. The peaks observed from the FTIR spectra of both freshly prepared and aged PIMs can be assigned to individual constituents of the membranes. No significant changes in peaks assigned to PVC or Aliquat 336 could be attributed to the aging process. Results reported in Figure 1 also show that no chemical interaction has occurred during the membrane preparation process and thus only weak interaction between constituents such as van der Waals and hydrogen bonds exist.

PVC shows strong absorption bands at 2924, 2855, 1772, 1717, 1458, 1425 and 1253 cm^{-1} [13-15] which can be attributed to the specific chemical groups such as carbon-hydrogen (C-H) bond, carbon-oxygen (C=O) bond or carbon-chlorine (C-Cl) bond (Table 1). The spectra of Aliquat 336 show strong bands at 2926, 2871 and 2855 cm^{-1} [13]. The spectra of the PVC also have absorption bands in this region but usually they are much less intense. FTIR of freshly prepared PIMs exhibited adsorption peaks in addition to those noted for PVC and Aliquat 336. Specifically,

substantial adsorption peaks at 903, 1036, 1066 and 1169 cm^{-1} which coincides with the THF coordinated bands [16]. The highest intensity adsorption bands of THF result from C-O-C stretching which generally appear as a strong bands at 1071 and 909 cm^{-1} [16] consistent with the peaks observed at 1066 and 903 cm^{-1} observed here. In this study, THF was used as a solvent for membrane preparation. Results shown in Figure 1 indicate that THF was still present in freshly prepared PVC/Aliquat 336 PIMs. Furthermore, the THF component was significantly reduced by aging for one week at 40 $^{\circ}\text{C}$ relative to that in freshly prepared PIMs.

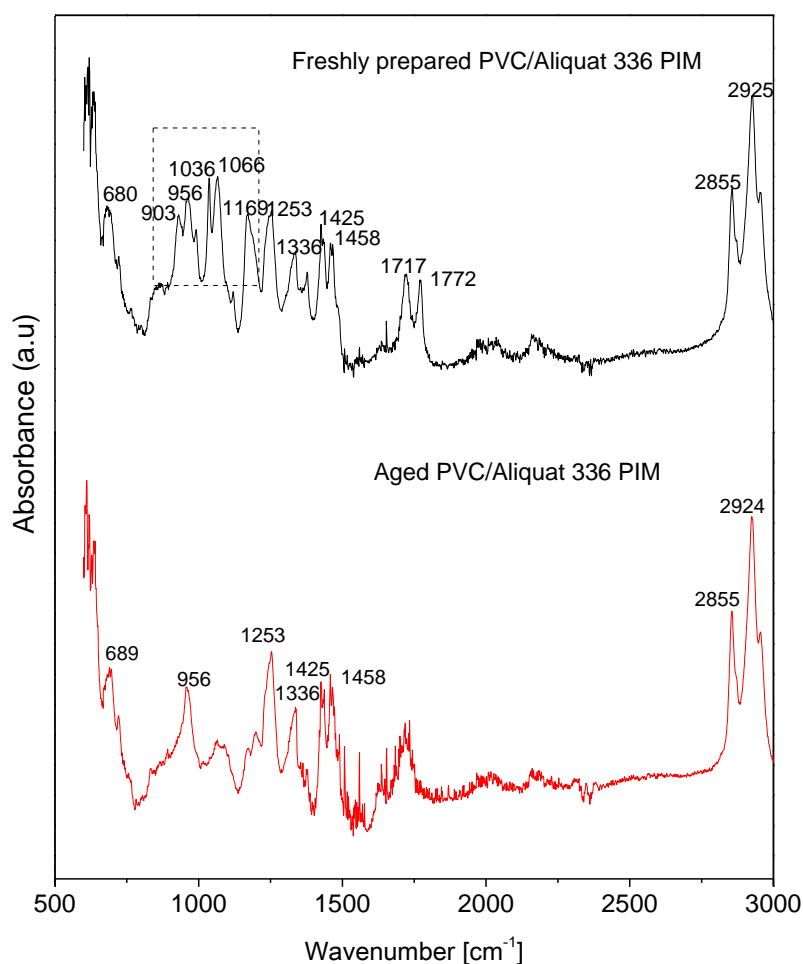


Figure 4.1: FTIR spectra of freshly prepared and aged PVC/Aliquat 336 (60/40) PIMs.

Table 4.1: Assignments of FTIR peaks.

Constituent	Wavenumber (cm ⁻¹)	Chemical group	Reference
PVC	2800-3000	C-H	[13]
	1717	C=O	[14]
	1426	CH ₂	[14]
	1339	CH ₂	[14]
	1250	C-H near Cl.	[15]
	956	CH	[14]
	669	C-Cl.	[15]
Aliquat 336	2926	C-H (CH ₂)	[13]
	2871	C-H (CH ₃)	[13]
	2856	C-H (CH ₂)	[13]
THF	1044, 1118, 1169, 1250, 1308 and 1348	C-O-C	[16]
	840, 846, 922, 956 and 993	C-O-C	[16]

4.3.2 Storage modulus and glass transition temperature

The storage modulus and the $\tan \delta$ of freshly prepared and aged PVC/Aliquat 336 PIMs as a function of temperature are shown in Figures 4.2 and 4.3 respectively. The freshly prepared PVC/Aliquat 336 PIMs has a broad α transition at 42 °C while the aged PVC/Aliquat 336 PIMs exhibits an α transition at 55 °C and a β transition at -19 °C. The α transitions are assigned to the glass transition (T_g) of PVC since they coincide with the reduction of storage modulus from greater than 100 MPa to less than 10 MPa. On the other hand, the β transition is assigned to the melting temperature (T_m) of Aliquat 336 [8, 17]. Note that the T_g of the freshly prepared PIMs was lower than the aged PIMs. In Chapter 3 [8], it has been reported that the T_g of PVC cast from THF without Aliquat 336 is also lower than the T_g of neat PVC. It is likely that the T_g depression relative to that for neat PVC of all PIMs membranes observed here results from a small amount of residual THF in the PVC. For example, 1 wt.% residual THF is sufficient to achieve a depression of 4 °C [18]. A T_g depressed below that for neat PVC is consistent for PVC cast from THF [19].

The increase in T_g value of PIMs due to aging is most likely attributed to a decrease in the residual THF that was identified by FTIR. All polymer solvents will function as a plasticizer for the same polymer when the concentration is sufficiently low. The T_g of THF was predicted to be in the range of -158 to -143 °C [20]. Application of the Fox equation predicts a reduction of THF in the PVC phase from 7 to 4 wt. % due to the aging process [21]. Similarly, interpolation of the experimental T_g

measurements presented by Adachi and Ishida [18] for PVC-THF systems estimates a reduction in THF from 9 to 6 wt. % by aging. Indeed, the experimentally observed mass loss of PVC/Aliquat PIMs after the aging process was 10 % (from an initial mass of 618 mg), which was slightly higher than that predicted by changes in the T_g .

The DMA results also indicate that aged PIMs exhibits a β transition, which can be assigned to the melting of Aliquat 336, whilst the freshly prepared PIMs does not. It is feasible that a residual amount of THF depresses the melting temperature of Aliquat 336 and hence, prevents its detection. Note that the T_g of the freshly prepared PIMs is much higher than what it would be expected for an Aliquat 336-PVC solid solution. Hence, it is likely that the Aliquat 336 is phase separated from the PVC in both the freshly prepared and aged PIMs.

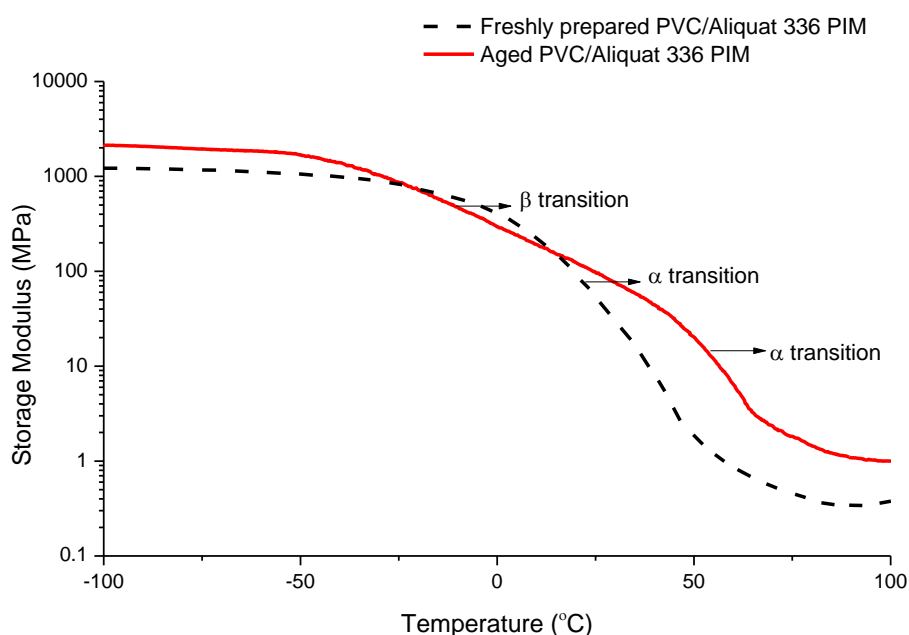


Figure 4.2: Storage modulus curves of freshly prepared and aged PVC/Aliquat 336 PIMs.

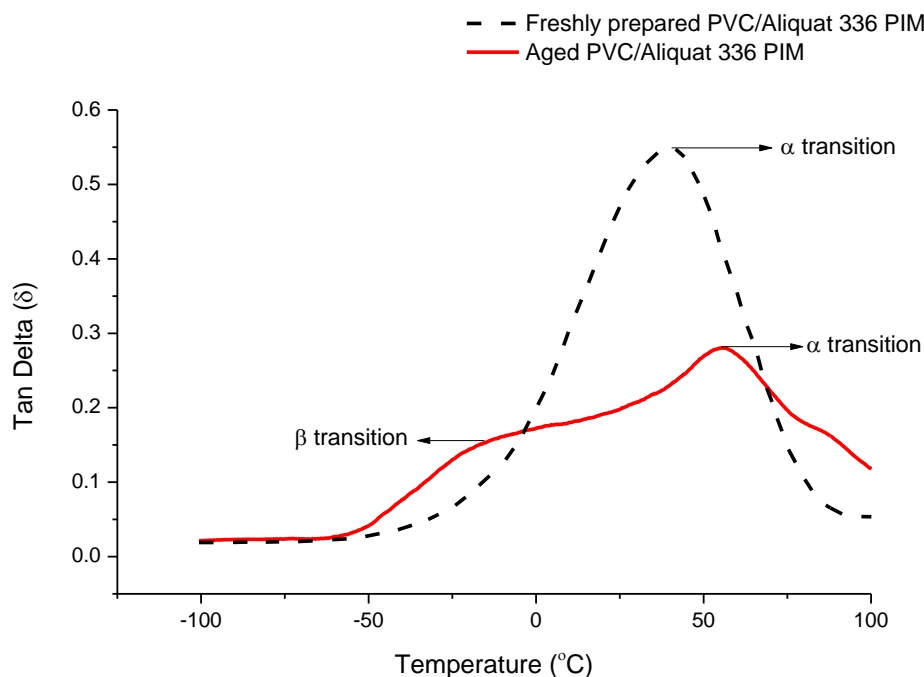


Figure 4.3: Tan δ of freshly prepared and aged PVC/Aliquat 336 PIMs versus temperature.

4.3.3 Extraction of cadmium

In general, the extraction of Cd(II) ions by Aliquat 336 is based on an ion exchange mechanism. Aliquat 336 reacts as an ion exchanger forming an ion pair with a metal anion complex from the aqueous solution. Consequently in a chloride matrix, the availability of a metal chloride complex carrying one negative charge is crucial for the extraction of the metal ion to the membrane. However, Uptis et al. [3] suggested that only trichloro metal complexes could be extracted by PVC/Aliquat 336 PIMs. This hypothesis was supported by Adelung et al. [2] who predicted the distribution of metallic ions in 0.05, 0.1 and 3 M of NaCl solution using the ChemEQL (version 3.1) thermodynamic modelling software. They found that at below 0.1 M of chloride solution, the trichloro zinc complex does not exist thus the extraction of Zn(II) to PVC/Aliquat 336 PIMs could not occur. But as they increased the chloride solution to 3 M, the trichloro zinc complex was formed and significant extraction of Zn(II) was observed. Meanwhile, both trichloro and tetrachloro cadmium complexes exist over the same chloride concentration (0.05, 1 and 3 M) and the molar fraction of the trichloro cadmium complex increased dramatically as the chloride concentration

increased [2]. Therefore, the extraction of Cd(II) to PVC/Aliquat 336 PIMs can be described as below:

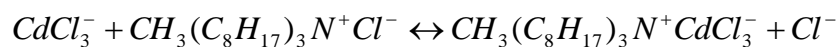


Figure 4 shows the extraction kinetics of Cd(II) from 1 M HCl solution into aged and freshly prepared PVC/Aliquat 336 PIMs. There is no difference on the extraction rate between both membranes. After 5 hours, more than 95% of Cd(II) was extracted by both PIMs indicating that aging process has not affected the membrane performance even though the membrane characteristics has somewhat changed.

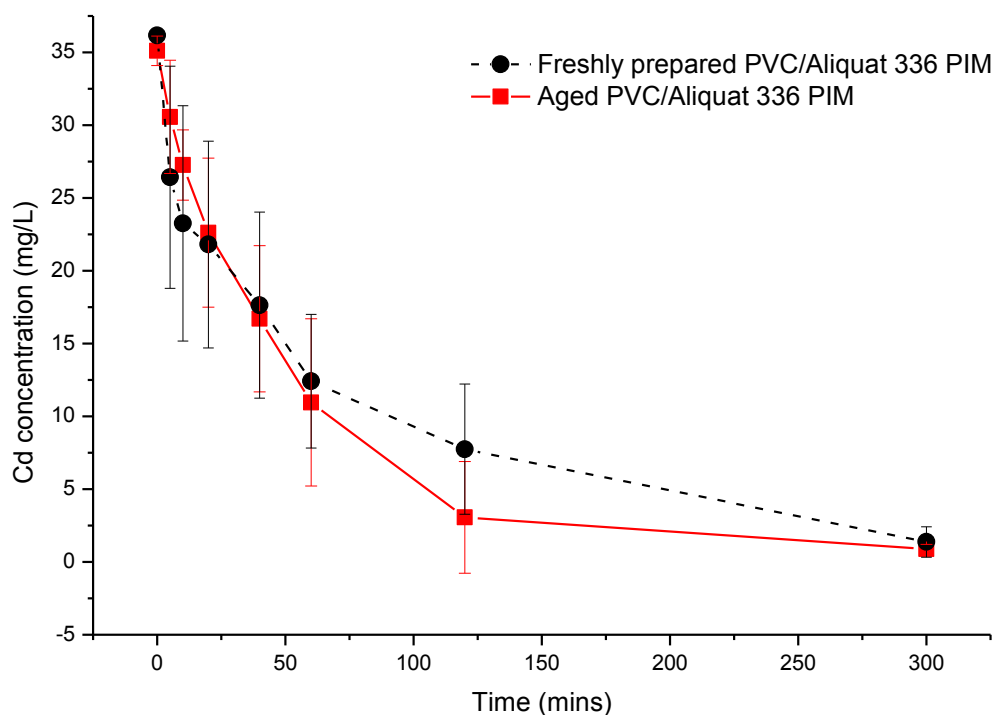


Figure 4.4: The extraction of Cd(II) in 1 M HCl solution into freshly prepared and aged PVC/Aliquat 336 (60/40) PIMs. Error bars show the standard deviation of three replicate experiments.

As described in our previous study [8], the presence of an Aliquat 336 melting transition in the aged PIMs is consistent with a phase separated membrane mesostructure. Similar Cd(II) extraction profiles were observed here for both the freshly prepared and aged PIMs. The Aliquat 336:PVC weight ratio used here was 3:2, which is well above the threshold ratio of 3:7 [8] where Aliquat 336 far from the

membrane surface starts to participate in the extraction process. The experimental design that Aliquat 336 far from the membrane surface participates in the extraction process is validated by the substantial extraction of Cd(II) ions observed. Furthermore, within experimental error, the same extraction profiles were observed for both aged and fresh PIMs. Hence, it is concluded that the access to the Aliquat 336 component is the same for each membrane which infers that the mesostructure of both the aged and fresh membranes is the same.

4.4 Conclusion

In this study, the aging effects on the polymeric and metal extraction properties PVC/Aliquat 336 PIMs were investigated. Freshly prepared PVC/Aliquat 336 PIMs exhibits a single thermal transition within the temperature range of – 100 to 100 °C formed. This transition was attributed to the glass transition of PVC with the melting transition of the Aliquat 336 masked by residual THF. However, after the aging process, THF residual has decreased and the PIMs exhibits two thermal transitions over the same temperature range. Although there is a clear impact of aging on membrane properties, there is no significant impact on the extraction of Cd(II) by PVC/Aliquat 336 PIMs.

4.5 References

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Chapter 5

Characteristics and cadmium extraction performance of PVC/Aliquat 336 electrospun fibres in comparison with polymer inclusion membranes

This chapter is under review for possible publication by Separation Science and Technology as:

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5.1 Introduction

The rapid development of modern industries such as electroplating, electronic production, solar photovoltaic and batteries has significantly heightened the interest in heavy metal extraction. In fact, heavy metals are essential for these industries. For example, cadmium is extensively employed for the production of batteries, pigmentation, electronic components, and nuclear power amongst many other industries [1, 2]. Cadmium is primarily produced from mineral ores and often a by-product during the refining zinc and lead. Thus, the extraction of heavy metals is of significant interest to the mineral processing industry. The disposal or accidental release of heavy metals to the environment is also of significant concern. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms. Many heavy metals are known to be toxic or carcinogenic. Toxic heavy metals of particular concern in treatment of industrial wastewaters include cadmium, zinc, copper, nickel, mercury, lead and chromium. Thus, the extraction of heavy metals from contaminated water is also of significant interest for environmental protection.

The extraction of most heavy metals including cadmium has been traditionally carried out by solvent-solvent extraction. However, this technique is energy intensive and uses a lot of organic diluents which are volatile, flammable and harmful to human health and the environment [3]. Polymer inclusion membranes (PIMs) present an alternative approach to recover heavy metals from an aqueous solution that potentially requires a smaller physical footprint and is significantly more environmentally friendly than solvent-solvent extraction. PIMs are a type of liquid membrane that relative to conventional liquid membranes exhibit longer process lifetimes, superior mechanical properties and higher chemical stability [4, 5]. In addition, PIMs allow for simultaneous extraction and stripping of the target ion and thus accelerate the separation process compared to conventional solvent extraction which can only be used in batch mode [4]. Generally, PIMs consist of polyvinyl chloride (PVC) or cellulose triacetate as a base polymer, an extractant, and a plasticizer. Numerous studies have shown effective metal ions extraction using PVC/Aliquat 336 PIMs [4, 6-10]. In addition, the use of PIMs for sample preparation [11] and low cost sensing [12] has recently been demonstrated.

Electrospinning is an innovative technique for the production of polymer fibres with diameter of less than a few micrometers, resulting in a large surface area-to-volume ratio and high porosity. These polymer fibres can potentially be used in numerous applications including tissue engineering, wound dressing, and drug delivery [13]. A few research groups [14, 15] have successfully developed polymer fibres using the electrospinning method for heavy metal extraction from aqueous solutions. Similar to the preparation of PIMs, a solution is first prepared by incorporating polymer and extractant using solvent. Then the solution is electrospun using electrospinning equipment at certain parameters to produce the mats consisting of electrospun fibres. Wong et al. [15] reported that the extraction of cadmium has improved using electrospun PVC/Aliquat 336 compared to film cast PVC/Aliquat 336 PIMs. However, in this pioneering work, Wong et al. [15] did not characterise the electrospun fibres and thus little is known about the influence of their thermomechanical properties on metal extraction.

In this study, electrospun fibrous mats and PIMs were fabricated from PVC at various Aliquat 336 concentrations. The effects of Aliquat 336 content on the

morphological structure as well as thermal properties of electrospun fibrous mats were investigated using scanning electron microscopy (SEM) and dynamic mechanical analysis (DMA). The physical properties of electrospun PVC/Aliquat 336 mats were then compared to those of PIMs to explain for the performance of these materials with respect to heavy metal extraction. The results provide insights for further development of electrospun PVC/Aliquat 336 fibres for heavy metal extraction.

5.2 Materials and methods

5.2.1 Reagents

High molecular weight PVC from Sigma Aldrich (Australia) was used as the base polymer. The weight-average molecular weight of this PVC is 80,000 g/mol. Aliquat 336 (tricaprylmethylammonium chloride) from Sigma Aldrich (Australia) was used as the extractant. Aliquat 336 is a mixture of tri-alkyl methyl ammonium chloride salts produced from the methylation of Alamine 336, with the substituent alkyl chain length containing between 6 and 12 carbon atoms. HPLC grade tetrahydrofuran (THF) and dimethylformamide (DMF) from BDH (Australia) were used without any further purification. Cd(II) was selected as a model heavy metal. Cd(II) solutions used in the extraction experiments were prepared from analytical grade $\text{Cd}(\text{NO}_3)_2$. Milli-Q grade water (Millipore, Australia) was used for the preparation of all aqueous solutions.

5.2.2 Preparation of PVC/Aliquat 336 fibres

Electrospun mats at different Aliquat 336 concentrations were prepared from PVC/Aliquat 336 solutions. The electrospinning apparatus consisted of a high voltage supply (Gamma Model ES30P-5W/DAM, Gamma High Voltage Research Inc.), a syringe pump (KDS 100, KD Scientific Inc.) and a 5 mL Terumo[®] syringe barrel with a 23 gauge needle tip (Figure 5.1). About 3 mL of the prepared solution was used to form an individual mat.

Several electrospinning conditions (in terms of flow rate, voltage, and distance to the collector) were evaluated to determine parameters that would result in consistent fibre formation. The optimised electrospinning conditions were then used in this

study. Briefly, the polymer solution was electrospun at 0.06 mL/h with an applied voltage of 17 kV, and distance between the syringe tip and the aluminium collector of 170 mm.

PVC/Aliquat 336 solutions were first prepared by dissolving Aliquat 336 (0-40 wt.%) and PVC (60-100 wt.%) in a 1:1 ratio solution of THF/DMF by volume. During the electrospinning process, due to the applied voltage, the charged polymer could overcome the surface tension of the solution. Thus, a charged polymer jet was ejected from the needle tip and deposited on the grounded aluminium collector as polymer fibres. The fibrous mats were collected after 5 hours of electrospinning.

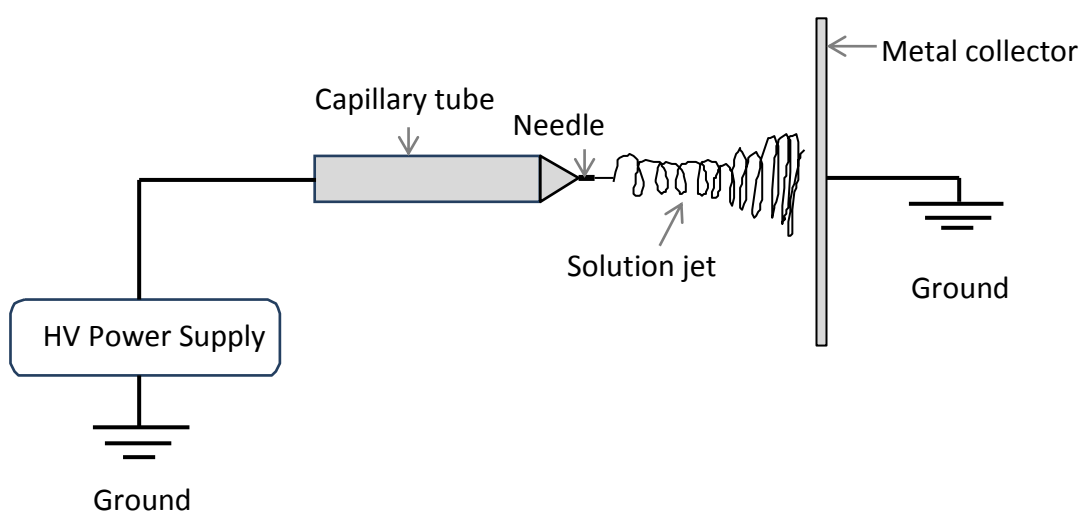


Figure 5.1: Schematic diagram of the experimental setup for electrospinning.

5.2.3 Preparation of PVC/Aliquat 336 PIMs

PIMs at different Aliquat 336 concentrations were prepared by dissolving Aliquat 336 and PVC in THF without DMF as described previously [16]. Each mixture contained a combined Aliquat 336 and PVC weight of 600 mg. The volume of THF used was between 5 to 10 mL depending on the weight fraction of PVC. The mixtures were stirred vigorously for 1 hour resulting in a clear solution. The solution was then transferred into a Petri dish with a diameter of 70 mm and covered with filter paper. The THF solvent was allowed to evaporate over about 48 hours to form PIMs. The membranes were peeled from the Petri dish and stored in the dry

condition for further experiments. PVC films were prepared using the same protocol but without the addition of Aliquat 336.

It has been established in Chapter 3 that a critical Aliquat 336 content of 30% in PIMs is required for heavy metal extraction. Thus, the Aliquat 336 content in PIMs include 30% and immediate value below (10% and 20%) and above 40%. On the other hand, the Aliquat 336 content in electrospun fibre was approximately doubled from 6% to cover a wide range of concentrations.

5.2.4 Scanning electron microscopy

Morphology of the electrospun fibrous mats and PIMs was characterized using a scanning electron microscope (SEM) (JEOL JCM 6000). Square sections of samples approximately 10 mm by 10 mm were mounted on aluminium stubs. The samples were then gold coated using a DYNAVAC Mini Coater prior to SEM analysis. For electrospun fibrous mats, fibre diameters were determined by Image J software. A minimum of six fibre diameter measurements were conducted for each condition.

5.2.5 Dynamic mechanical analysis

A DMA Q 800 (TA Instrument, USA) was used to characterise the thermal transitions of electrospun fibre mats and PVC/Aliquat 336 PIMs. A tensile film-clamp was used with a heating rate of 4 °C/min over the temperature range of -70 to 110 °C at a frequency of 1 Hz. For DMA, the approximate distance between clamps was 15 mm, and the oscillation displacement was 10 µm. The temperatures associated with transitions were identified by the maximum in the corresponding tan delta curve. Where defined, the thermal transitions are labelled in order from highest to lowest temperature.

5.2.6 Cadmium extraction protocol

Extraction experiments were conducted in batch mode using a protocol described in details elsewhere [16]. PIMs or electrospun fibrous mats with membrane mass of 0.57 ± 0.01 g and 0.03 ± 0.01 g respectively were placed in beakers containing 50 mL of extraction solution. For the electrospun mats, the extraction solution contained 3 mg/L of Cd(II) in 1 M hydrochloric acid (HCl) whereas for the PIMs, the extraction solution contained 50 mg/L of Cd(II) in 1 M hydrochloric acid (HCl).

These different extraction solution concentrations were used to obtain the same ratio of membrane mass to cadmium concentration. The extraction solution was stirred continuously with a 1 mL of aliquot was taken at specific time intervals for metal ion analysis using Atomic Adsorption Spectrometry analysis (Varian SpectrAA 300 AAS, Australia). Calibration using standard Cd(II) solutions was conducted prior to each batch of analysis. The linear regression coefficient for all calibration curves were greater than 0.98.

5.3 Results and discussion

5.3.1 *Fibrous mats preparation and thickness*

The electrospun PVC/Aliquat 336 fibrous mats obtained from this study were opaque regardless of the Aliquat 336 content which was from 0 to 40 wt.%. By contrast, the PVC/Aliquat 336 PIMs were transparent, homogenous, and flexible (Figure 5.2a). The opacity of the electrospun fibrous mat was expected and is due to light scattering from free fibre surfaces. It is noteworthy that the electrospun PVC/Aliquat 336 mat was thicker at the centre of the collector relative to the edge while the thickness of PVC/Aliquat 336 PIMs was relatively uniform over the entire area.

5.3.2 *Fibrous mats surface morphology*

A fibrous web like structure could be seen with all PVC/Aliquat 336 electrospun fibre mats obtained from this study (Figure 5.2b-f). Electrospun fibres obtained from only PVC were small, densely packed, and uniform (Figure 5.2b). As the Aliquat 336 content increased from 6 to 40 wt.%, the electrospun fibre diameter within the mat became less uniform (Figure 5.2b-f). In addition, the fibres diameter increased from about $1.5 \pm 0.2 \mu\text{m}$ (without any Aliquat 336) to $3.5 \pm 0.3 \mu\text{m}$ at 40 wt.% Aliquat 336. As the Aliquat 336 content increased beyond 12 wt.%, the formation of beads occurred. The number and size of these beads appear to increase monotonically with the Aliquat 336 content. Beads are common in electrospinning and are related to the instability of the polymer solution jet [17]. The formation of beads can be reduced by changing the polymer concentration, surface tension, flow rate, distance between tip and collector, and, voltage [18]. In this study, the same set of electrospinning parameters as explained in section 2.2 was used for all membrane compositions.

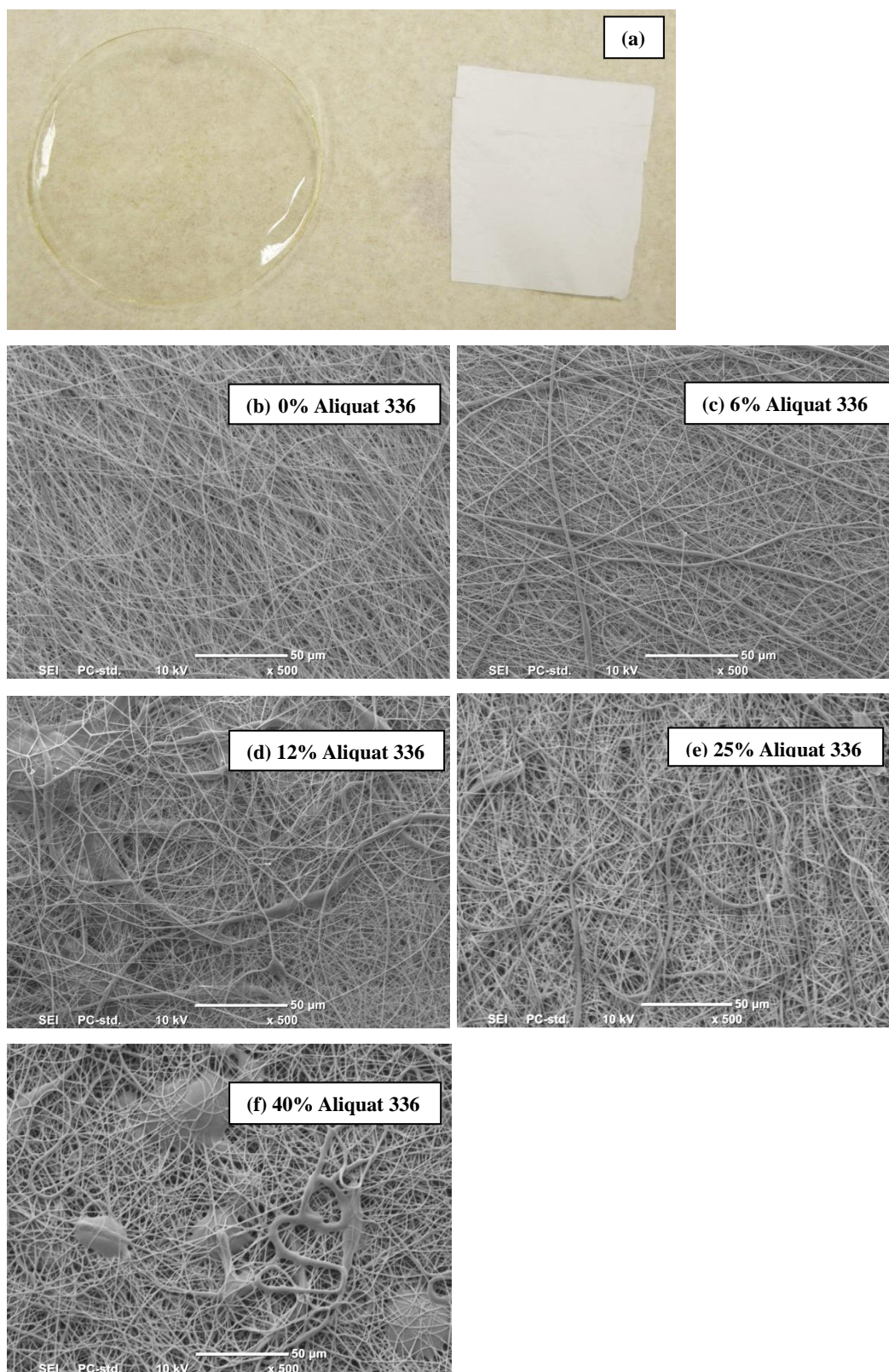


Figure 5.2: (a) Images of PVC/Aliquat 336 electrospun fibres (right) and PVC/Aliquat 336 PIMs (left) and (b-f) surface morphology of PVC fibres at different Aliquat 336 concentration.

Meanwhile, Figure 5.3 and 5.4 show the effect of applied voltage on PVC/Aliquat 336 at 25 wt.% and 40 wt.% of Aliquat 336 content respectively. Study on different applied voltage (13, 15, 17 and 19 kV) was conducted to observe any significant improvement on the morphology structure. For electrospun fibrous mats at 25 wt.% Aliquat 336 (Figure 5.3), changing in applied voltage from 13 to 19 kV has less significant on the formation of beads but the diameter of fibres become thicker as voltage increased. However for electrospun fibrous mats at 40 wt.% Aliquat 336 (Figure 5.4), the formation of beads also did not change much at 13 and 15 kV. But the sizes of the beads tend to reduce when the applied voltage is increased from 17 to 19 kV. In contrast with the electrospun fibrous mats at 25 wt.% Aliquat 336, the fibres diameter of electrospun fibrous mats at 40 wt.% Aliquat 336 has not changed with the applied voltage. In some cases, applied voltage might increase the fibres diameter whereas in some cases the increased in voltage decreased the diameter fibres. As for this study, it is concluded that the applied of voltage might influence the formation of beads and fibres diameters of PVC/Aliquat 336 electrospun mats but the level of significant may varies with the polymer concentration and tip distance or in this case Aliquat 336 concentration.

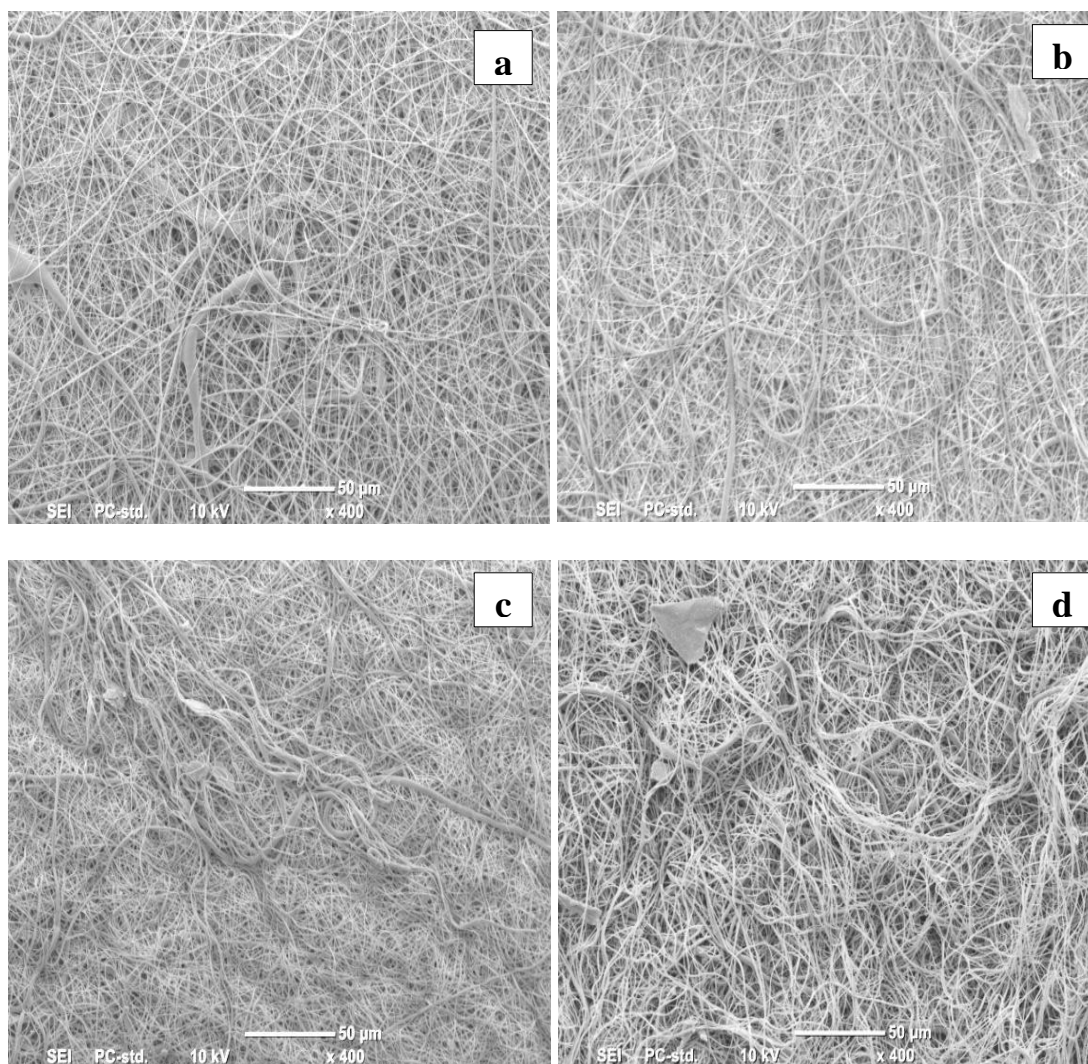


Figure 5.3: Images of PVC/Aliquat 336 electrospun fibres at 25 wt.% Aliquat 336 at different applied voltage: (a) 13, (b) 15, (c) 17 and (d) 19 kV.

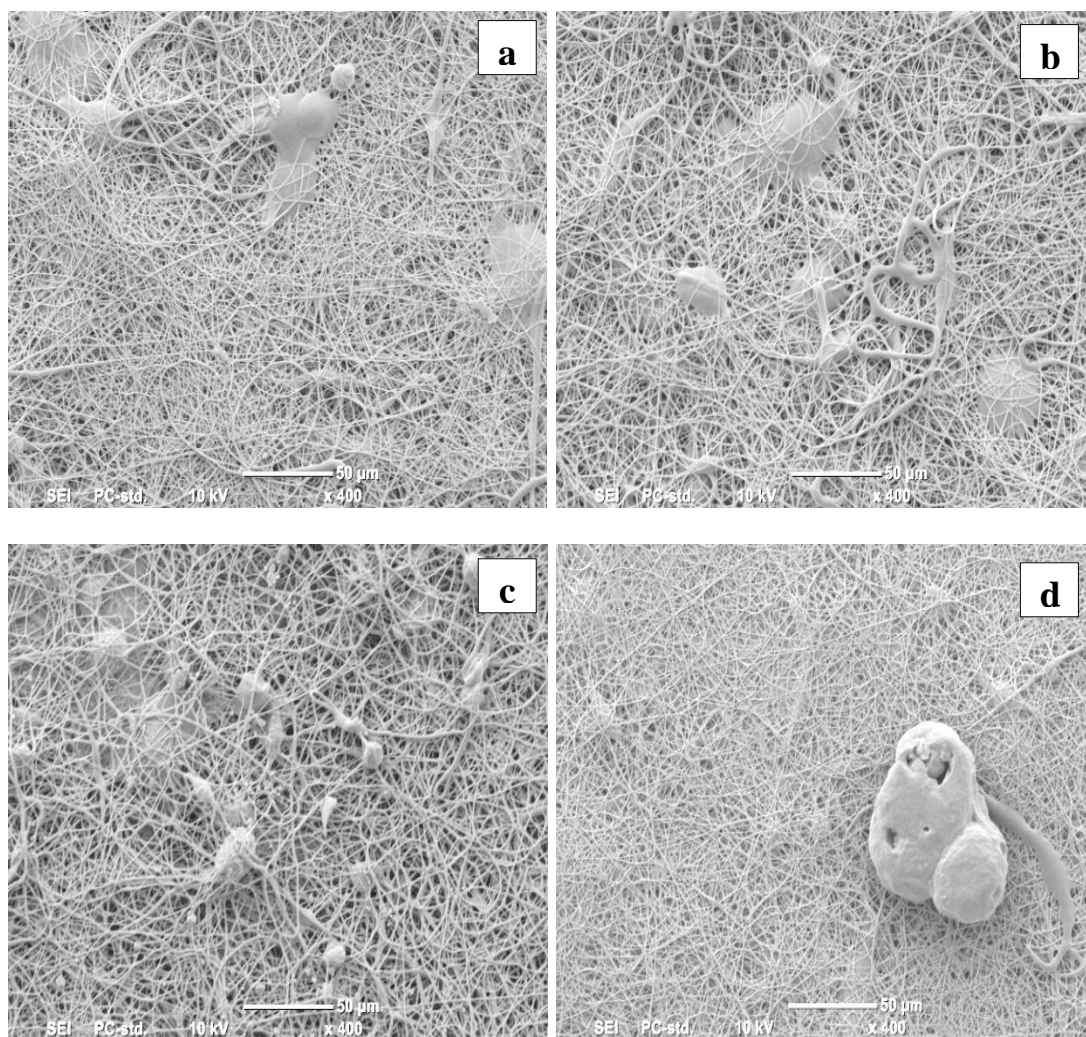


Figure 5.4: Images of PVC/Aliquat 336 electrospun fibres at 40 wt.% Aliquat 336 at different applied voltage: (a) 13, (b) 15, (c) 17 and (d) 19 kV.

Unlike the electrospun fibrous mats, all PVC/Aliquat 336 PIMs were transparent and have a non-porous surface (Figure 5.3). At 10 to 20 wt.% Aliquat 336, the PIM surface was featureless (Figure 5.3b-c). However at 30 wt.% Aliquat 336, some wrinkles could be observed (Figure 5.3d). The surface wrinkles are more regular at 40 wt.% Aliquat 336 (Figure 5.3e). The wrinkles are probably formed due to a THF concentration gradient during film formation. Typically, during the early stage of membrane formation the THF at the free surface will evaporate readily forming a membrane skin. Below this skin there is a relatively high THF concentration that over time diffuses through the skin with the formation of the membrane. Coinciding with the evaporation of THF is a reduction in volume, which places a compressive force on the membrane surface resulting in wrinkles. Also coinciding with a reduction in THF is the conversion of a solution to a mixture containing a PVC rich

phase and a Aliquat 336 rich phase [19]. The Aliquat 336 concentration dependence of wrinkle formation could be attributed to either a lower membrane elastic modulus or the Aliquat 336 rich phase. The former provides a lower buckling stress while the latter retains a large volume fraction of THF relative to the PVC rich phase in the preliminary stage of film formation.

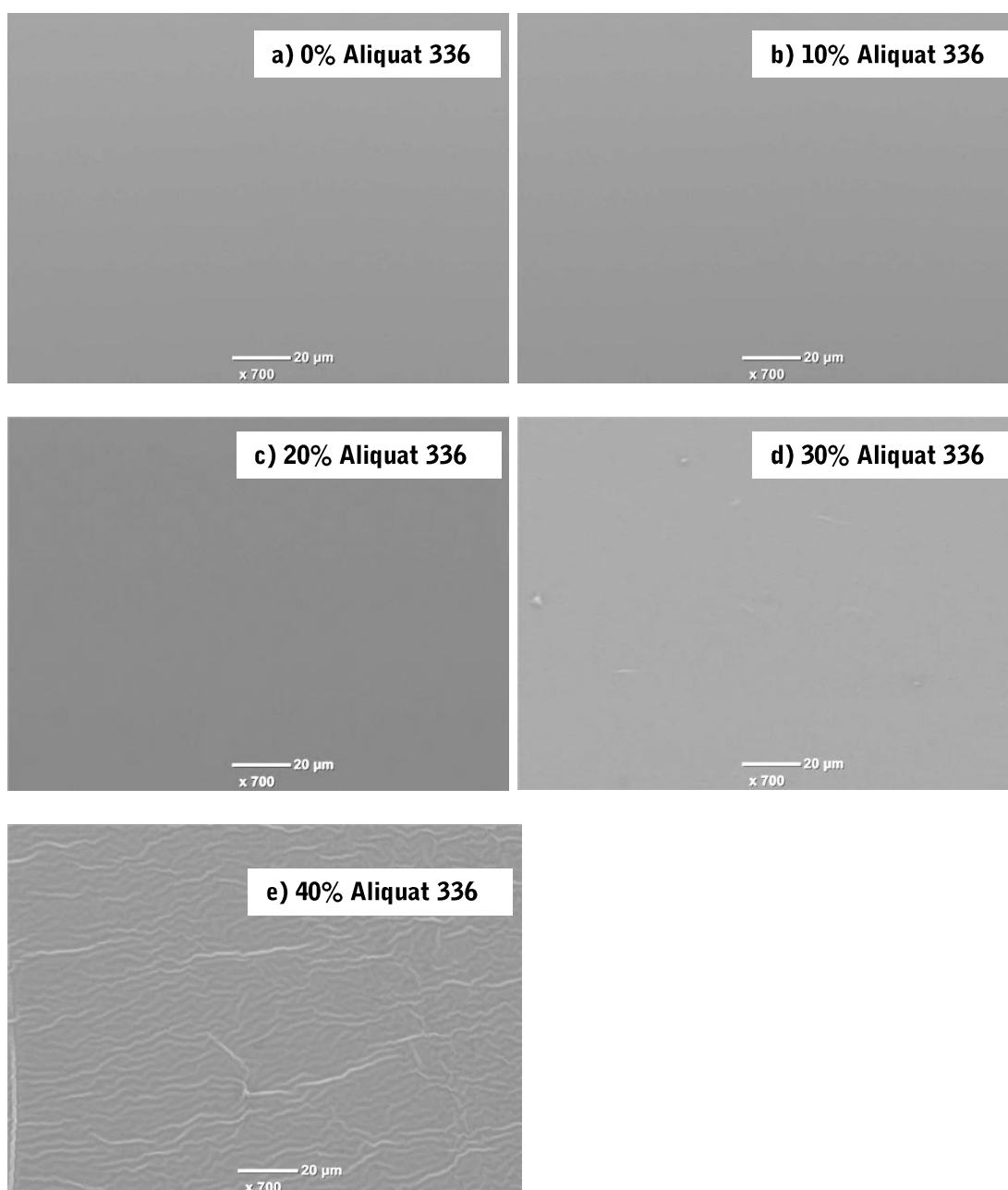


Figure 5.5: Surface morphology of PVC/Aliquat 336 polymer inclusion membranes at different Aliquat 336 concentration.

5.3.3 *Fibrous mats thermal analysis*

DMA is a complimentary method for assessing the thermo-mechanical properties of polymeric materials. Figures 5.6 and 5.7 show the storage modulus and $\tan \delta$ of electrospun PVC/Aliquat 336 and PVC/Aliquat 336 PIMs at different Aliquat 336 content.

DMA results revealed that electrospun PVC/Aliquat 336 and PVC/Aliquat PIMs exhibited α transitions which were determined to be the membranes T_g value. The T_g value of electrospun PVC without Aliquat 336 was 98 °C. This is consistent with the value reported for pure PVC in the literature [20]. However, the T_g of PVC PIMs without Aliquat 336 was 63 °C which is lower than that of pure PVC [16, 21, 22]. The depression of T_g observed is possibly due to the small amount of residual THF in the PVC/Aliquat 336 PIMs [19]. Hence, the THF/DMF solvent used for electrospun PVC/Aliquat 336 is likely to have completely evaporated during the electrospinning process.

The α transition of electrospun PVC/Aliquat 336 has shifted to a lower temperature as Aliquat 336 content increased from 0 to 40 wt. % (Figure 5.6a and 5.7a). This result indicates that Aliquat 336 maybe contributing to the PVC segmental mobility for electrospun mats, or, that the retained stress from electrospinning is relative to the Aliquat 336 concentration. In contrast, constant values of α transition were observed for PVC/Aliquat 336 PIMs containing 0 to 40 wt.% Aliquat 336 (Figure 5.6b and 5.7b).

The β transition was observed at -18 °C for PVC/Aliquat 336 PIM containing 40 wt.% Aliquat 336 (Figure 5.6b and 5.7b). The β transition is assigned to the melting temperature (T_m) of Aliquat 336 as it is consistent with the report value of -20 °C [23].

The addition of Aliquat 336 in PVC formed by electrospinning induced a decrease of T_g values (Figure 5.6a). In other words, Aliquat 336 has plasticized the electrospun fibres, or, THF that may be retained in the Aliquat which subsequently plasticizes the PVC phase of the fibres. By contrast, in the solvent cast PVC based PIM system, the T_g value was independent of Aliquat 336 concentration over the range of 0 to 40

wt.% indicating that PVC segmental mobility is not a function Aliquat 336 concentration [16].

A single transition observed with all PVC/Aliquat 336 electrospun fibres (Figure 5.6a and 5.7a) indicates that they are homogenous or that the PVC and Aliquat 336 are not phase separated. Alternatively, the elastic modulus of the electrospun mats is an order of magnitude lower than that of the PIMs. This substantially low elastic modulus is due to the high porosity and is function of fibre/fibre junction stiffness [24]. Hence, it is possible that the DMA used here is not sensitive to the beta transition in electrospun fibrous mats if it is present. On the other hand, PVC/Aliquat 336 PIMs containing 20 to 40 wt.% Aliquat 336 are phase separated with two discrete phases rich in PVC and Aliquat 336 (Figure 5.6b and 5.7b). Even though the PVC/Aliquat 336 PIMs at 20 and 30 wt.% Aliquat 336 did not exhibit any β transition (Figure 5.6b) but a decreased in storage modulus at about -22°C indicated that they also contain Aliquat 336 rich phase. However, there is no indication of an Aliquat 336 rich phase in PIMs containing 10 wt.% Aliquat 336 by DMA. Overall, the storage modulus of PVC/Aliquat 336 electrospun mats were much lower than PVC/Aliquat 336 PIMs but the values increased as the Aliquat 336 content increased (Figure 5.6a).

It is also noteworthy that the transparency of all the electrospun fibrous mats had changed during the DMA experiment. Specifically, the regions of the electrospun fibrous mat that were within and adjacent to the DMA clamps changed from opaque to transparent during a DMA heating sequence. Hence, the combination of temperature and pressure was sufficient to achieve viscous flow of the polymer with the electrospun fibres fusing to form a solid. The central section of the electrospun mat remained opaque, even after heating to 110°C .

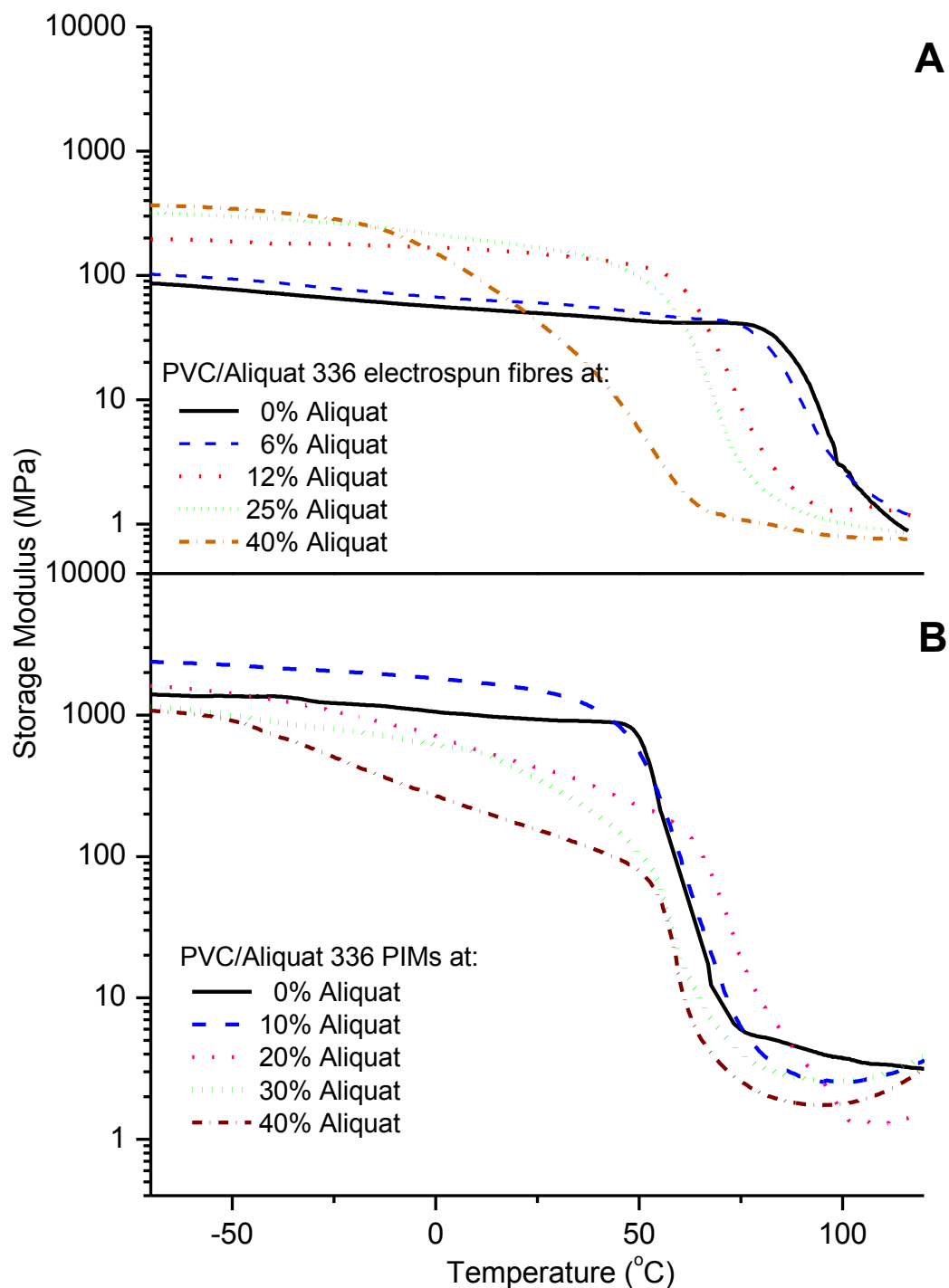


Figure 5.6: Storage modulus curves of (a) PVC/Aliquat 336 electrospun fibres and (b) PVC/Aliquat 336 PIMs at different Aliquat 336 composition.

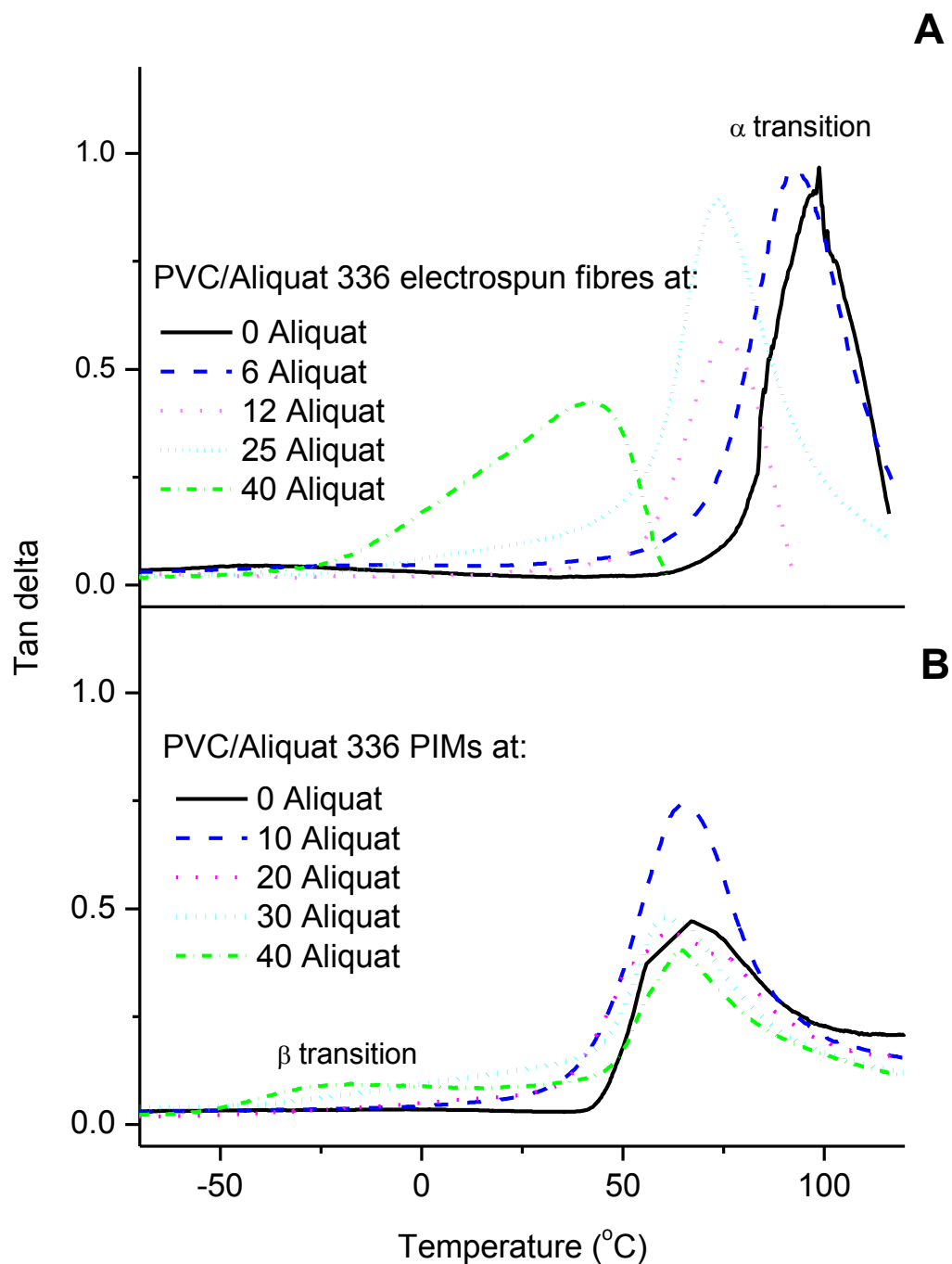


Figure 5.7: Tan δ versus temperature of (a) PVC/Aliquat 336 electrospun fibres and (b) PVC/Aliquat 336 PIMs.

5.3.4 Cadmium extraction performance

The extraction kinetics of Cd(II) to PVC/Aliquat 336 electrospun fibrous mats and PIMs are shown in Figure 5.8. As expected, in the absence of Aliquat 336 (which was used as the extractant), no extraction of Cd(II) to electrospun mats and PIMs could be observed. As can be seen from Figure 5.8a, the extraction rate of PVC/Aliquat 336 electrospun fibrous mats increased when Aliquat 336 content increased. There was a significant increase of Cd(II) removal for electrospun PVC/Aliquat 336 mats containing 12 to 40 wt.% Aliquat 336 (Figure 5.8a). Maximum extraction was reached at 25 and 40 wt. % Aliquat 336 with about 98% removal of Cd(II).

By comparison, the extraction of Cd(II) using PIMs was not significant at low Aliquat 336 content (Figure 5.8b). A significant extraction was observed in PIMs containing 30 wt.% Aliquat 336 where a major change in Cd(II) removal was witnessed. However the extraction was only 72% completed. This result is in good agreement with the data reported by Xu et al. [11] that the extraction is not viable for PIMs containing less than 30 wt.% of Aliquat 336. Maximum extraction was reached at 40 wt.% Aliquat 336 with 95% Cd(II) removal which coincides with the appearance of a defined β transition (Aliquat 336 rich phase).

The extraction capacity was also plotted against Aliquat 336 concentrations for both electrospun fibres and PIMs as shown in Figure 5.9. The extraction capacity can be calculated by using the equation as described below:

$$\text{Extraction capacity (mg/g)} = \frac{[C_i - C_f] \times C_s}{M}$$

where C_i and C_f are the initial and final concentration of Cd (mg/L) respectively. C_s is the starting of the feed volume (L) and M is the mass of the membrane (g).

Base on the result, the extraction capacity of the fibres and membranes was completed at 40 wt. % of Aliquat 336 content. However, in all other cases, electrospun fibrous mats has higher absorption capacity even at low Aliquat 336 content compared to PIMs which clarify why they have better extraction. The increasing of Cd(II) removal for electrospun fibrous mats maybe due to the

increasing of surface area containing Aliquat 336. Previously, electrospun mats revealed a homogenous web like structure. Therefore, electrospun fibrous mats have larger surface area containing Aliquat 336 than PIMs and hence improved the Cd(II) removal.

On the other hand, PVC/Aliquat 336 PIMs has distinctive PVC and Aliquat 336 rich phases. For heterogeneous membrane, the transport of metal ions requires continuous channels. Unlike electrospun fibres, sufficient amount of extractant is essential to form continuous channels across the PIMs for the extraction to occur. In this study the percolation threshold was observed to be at 30 wt.% Aliquat 336.

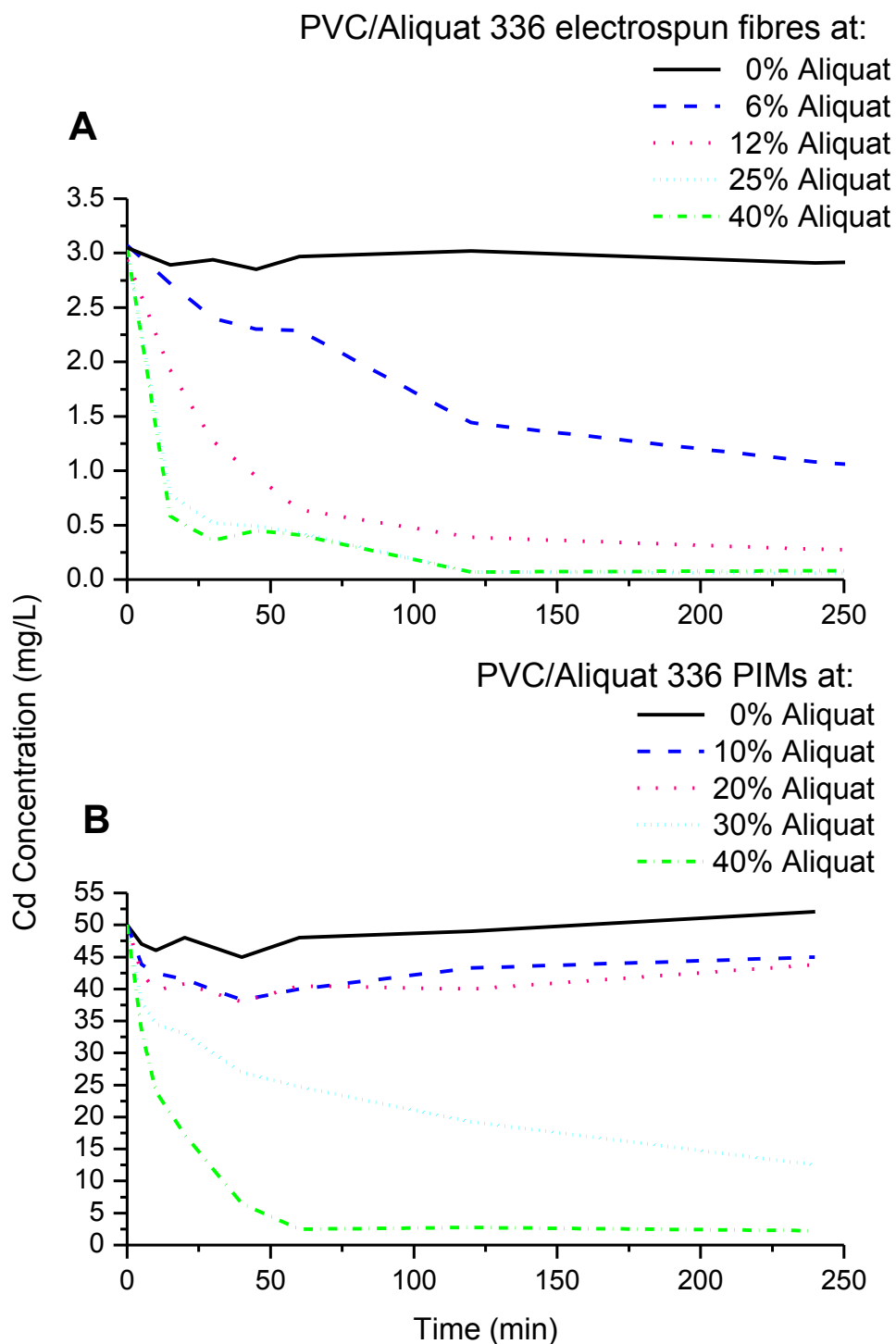


Figure 5.8: Extraction of Cd(II) using (a) PVC/Aliquat 336 electrospun fibres and (b) PVC/Aliquat 336 PIMs.

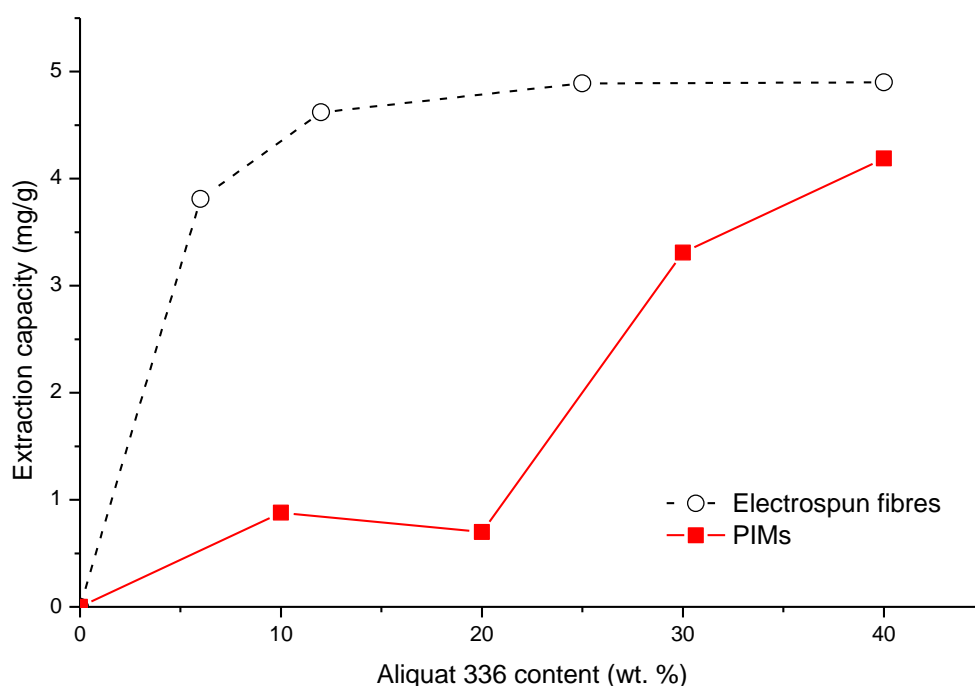


Figure 5.9: Extraction capacity against Aliquat 336 content for PVC/Aliquat 336 electrospun fibres and PIMs.

5.4 Conclusion

In this study, the properties and Cd extraction performance of PVC/Aliquat 336 fibrous mats and PIMs prepared by electrospinning and conventional casting, respectively, were evaluated and compared. The results showed that the role of Aliquat 336 in electrospun fibres differ from that in PIMs. The PVC/Aliquat 336 electrospun fibrous mats exhibited web like structures and were visually opaque. However, they were homogenous and have only a single phase that is α transition. The electrospuns were plasticized since the T_g observed by DMA decreased with the increasing of Aliquat 336 content. On the other hand, the PVC/Aliquat 336 PIMs were visually transparent but were phase separated with two distinct phases that is α transition and β transition observed by DMA. Besides, the Aliquat 336 did not plasticizing the PIMs since the T_g did not decreased. The extraction kinetics of Cd(II) to both PVC/Aliquat 336 electrospun fibre mats and PIMs increased when Aliquat 336 content increased. However, the extraction of PVC/Aliquat 336 PIMs was dependent on the appearance of the defined β transition. To facilitate cadmium extraction, the Aliquat 336 content in PIMs needs to exceed the percolation threshold

of 30 wt.%. By contrast, cadmium extraction to electrospun fibre mats could occur at a much lower Aliquat 336 content (i.e., 6 wt.%).

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Chapter 6

Conclusion and recommendations for future work

6.1 Conclusion

In Chapter 3, the miscibility of the base polymer poly (vinyl chloride) (PVC) and the extractant Aliquat 336 in polymer inclusion membranes (PIMs) was investigated by characterisation of thermal transitions using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The extractions of Cd (II) and Zn (II) using PVC/Aliquat 336 PIMs with different base polymer/extractant composition and different extraction temperature were also investigated. Changes in the PIM's heat capacity measured by DSC were too small for determining the glass transition temperature (T_g). On the other hand, DMA results clearly identify the (T_g) and melting temperature (T_m) of separate PVC and Aliquat 336 rich phases in the PIMs. Results reported here indicate that the PVC/Aliquat 336 PIMs are phase separated. This phase separation has important implications to the extraction of target metallic ions by PIMs. Extraction studies showed that the extraction of metallic ions occurred only when the proportion of Aliquat 336 in PIMs was about 30 wt.% or higher. At this stage, the impedance study revealed that the conductivity of PVC/Aliquat 336 PIMs has increased while the resistance decreased. Besides, the impedance profile has changed towards the ideal plot when Aliquat 336 content reached 30 wt.% and above.

Results in Chapter 4 demonstrated the impact of aging PVC/Aliquat 336 polymer inclusion membranes (PIMs) on their thermomechanical properties and heavy metal extraction performance. The results show that freshly prepared PIMs contains residual tetrahydrofuran (THF) which was used as the solvent for membrane manufacture. Removal of some residual THF by membrane aging resulted in notable changes in the thermomechanical properties of the PIMs. By aging the membrane for 1 week at 40 °C the glass transition increased from 42 to 55 °C. In addition, while the melting temperature (T_m) of the Aliquat 336 component could not be determined

for freshly prepared PIMs, the aged membrane showed a clear T_m value of $-19\text{ }^{\circ}\text{C}$. Metal extraction capacity was not affected by membrane aging.

The aim of Chapter 5 is to evaluate the effects of Aliquat 336 content on the thermomechanical properties and morphology of the electrospun fibres and PIMs using scanning electron microscopy (SEM) and dynamic mechanical analysis (DMA). The performance of these membranes in extracting cadmium from a hydrochloric solution was also investigated. Morphological and thermal analysis results showed that electrospun fibres have different properties compared to those of PIMs with similar PVC and Aliquat 336 composition. Electrospun PVC/Aliquat 336 fibrous mats have a porous web like structure while PVC/Aliquat 336 PIMs are a pore free solid. The thermal analysis results indicate that Aliquat 336 has a different plasticising effect on the electrospun fibres and PIMs. The plasticising effect of Aliquat 336 on the electrospun PVC/Aliquat 336 fibres was confirmed by a single glass transition temperature (T_g) shifted towards lower temperature. While PVC/Aliquat 336 PIMs were phase separated with two distinct phases that is a constant T_g and a melting temperature (T_m). Both PVC/Aliquat 336 fibres and PIMs could be used for cadmium extraction. However, cadmium extraction to electrospun fibres could occur at any Aliquat 336 concentration and was higher than that to PIMs. By contrast, there appears to be a percolation threshold of Aliquat 336 in PIMs of 30 wt.% where cadmium extraction could be observed.

6.2 Recommendations for future works

It would be beneficial to develop PIMs in a larger scale or as a membrane module and apply it in a proper system using actual wastewater sample. This way it will enhance the membrane surface area, so that the application of PIMs in a real industry will become reality. On the other hand, PVC and CTA has been the only polymer used for PIMs. It's about time to explore other type of thermoplastic polymer including polyethylene, polypropylene, polystyrene, polytetrafluoroethylene (PTFE, commonly known as Teflon), acrylonitrile butadiene styrene (ABS plastic), and polyamide (commonly known as nylon) that might have better potential as base polymer for PIMs. Moreover the use of PIMs can be extended to different application and industries such as in removing trace organic contaminants which hardly ever investigated in literature.

The results reported in Chapter 4 indicate that membrane aging did not affect the performance of metal extraction but changed the thermomechanical properties of PIMs. A further research on the effect of annealing PVC/Aliquat 336 PIMs with stabilizer would be interesting. Basically by adding a stabilizer to PVC one will be able to age it at higher temperatures which will lead to a coarsening of the phases. This process might decrease the number of Aliquat 336 rich phases but at the same time increased the diameter. Therefore, the effect of metal extraction capacity after the annealing process will be a great advantage in the future studies.

The potential of electrospinning technique to produce homogenous PVC/Aliquat 336 polymer inclusion fibres has shown great promise as demonstrated in Chapter 5. Despite their significant improvement in cadmium extraction capacity, it is essential to address the reproducibility and robustness of these fibres using different extraction solutions. If homogeneity can improve the stability of this membrane, then it is also important to investigate whether there is Aliquat 336 leakage from the PVC/Aliquat 336 fibres during the extraction process. From the DMA results, the storage modulus of the electrospun fibrous was lower than PIMs, which means that they have lower elasticity. Elasticity can increased the strength of the polymer inclusion fibres. Therefore, it is recommended that in the future, the PVC/Aliquat 336 is electrospun on a support layer so that they will have better mechanical property and can be recycled in the system. The electrospun fibre specific surface area should also be quantified and correlated to metal extraction capacity. Last but not least, it is necessary to assess if different combination of polymer and extractant can be used to examine their potential using different heavy metal samples.