EXTRACTION STUDY OF CADMIUM(II) AND COPPER(II) USING ALIQUAT 336

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DECLARATION

Except where reference is made in the text of the thesis, this thesis contains no material published elsewhere or extracted in whole or in part from the thesis presented by me for another degree or diploma.

No other person's work has been used without due acknowledgment in the main text of the thesis.

This thesis has not been submitted for the award of any other degree or diploma in any other tertiary institution.

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SUMMARY

The research work described in this dissertation focuses on the investigation of the extraction of Cd(II) and Cu(II) from hydrochloric acid solutions using Aliquat 336 in Shellsol AB solvent and Aliquat 336/PVC membranes.

In the solvent extraction study, factors that affect the extraction rate, such as the extractant concentration in the organic phase, the chloride ion concentration in the aqueous phase and extraction time were investigated. Two phase titration method was used to investigate the distribution of the metal complexes, stoichiometry of the extracted complexes and the equilibrium constants of extraction reactions.

In the membrane extraction study, extraction rates and capacities of the membrane were studied as functions of major variables such as the concentration of Aliquat 336 in the membrane and the thickness of the membrane. Mathematical modeling was used to calculate the extraction kinetic rate constants and the diffusion coefficients of the metal complexes in the membrane. The possibility of using the Aliquat 336/PVC membrane to concentrate Cd(II) from a feed solution into a receiver solution was explored for the first time in this work.

The surface of the Aliquat 336/PVC membrane was analyzed for the first time using X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM) to reveal the surface chemical composition and topographic structure of the membrane and to study the stability of the membrane at a microscopic level.

It was found in this work that in the solvent extraction study using Shellsol AB as the solvent, Aliquat 336 extracted Cd(II) more efficiently than Cu(II). The extracted Cd(II) and Cu(II) complexes had a metal-to-extractant ratio of 1:1.

The Aliquat 336/PVC membrane was able to extract both Cd(II) and Cu(II) from hydrochloric acid solution. The extraction capacity of membrane, however, was inferior compared to that of the solvent extraction. It was possible to concentrate Cd(II) from one solution into another using the membrane, provided that the chemical potential of Cd(II) in the receiver solution could be lowered relative to that of the feed solution. The surface analysis using both the AFM and XPS techniques clearly indicated that the surface of the membrane was covered entirely by the monolayer of Aliquat 336. The stability of the membrane in the extraction was dependent upon the actual metal species being extracted.

CHAPTER ONE

INTRODUCTION

1.1 GENERAL INTRODUCTION

Separation and purification of chemicals from a mixture are fundamental technologies in chemistry and chemical engineering. One of the traditional methods for chemical separation and purification is solvent extraction. The basic concept of solvent extraction is to remove one or more chemical components from a mixture by the use of a solvent with which the liquid is immiscible or nearly so [1]. Solvent extraction technique has grown over the last century to be one of the most powerful separation and purification techniques and it has been widely used in many fields such as hydrometallurgy [2-4], nuclear industry [5-8], petrochemical industry [9, 10], biotechnology [11-13], environmental science and technology [14-17] and industrial wastes treatment [18-20]. There has also been a tremendous research effort directed to the understanding of the fundamental mechanism of solvent extraction systems [21-24] and developing new and more effective extractants [25-27]. Those studies have greatly enriched our knowledge of the science of solvent extraction.

Solvent extraction technique, however, is not without its associated problems. Problems such as solvent loss, difficulties in solvent disposal and in some cases, poor separation of the analytes, are well recognized. As our society becomes more environmentally conscious, there is a real demand for the development of new and more environmentally friendly separation technologies. One of these is the membrane separation technology because it minimizes the use of organic solvents.

The research and application of membrane technology to separation and extraction have a shorter history compare to the conventional solvent extraction. Its simplicity and its potential have made this technology grow steadily during the last two decades. Today, membrane separation technology is used in a wide range of applications, such as water treatment [28, 29], biotechnology [30, 31], pharmaceutical industry [32], food processing [33, 34] and waste water treatment [35-37], and the number of such applications is still growing.

In the present work, the extraction behaviours of cadmium(II) and copper(II) by high molecular weight quaternary ammonium salts such as tricaprylmethylammonium chloride (Aliquat 336) have been investigated using both conventional solvent extraction and membrane extraction techniques.

1.2 SOLVENT EXTRACTION OF Cd(II) AND Cu(II) FROM HYDROCHLORIC ACID SOLUTIONS BY ALIQUAT 336

1.2.1 The Basic Principle of Solvent Extraction

When a metal-containing aqueous phase and an extractant-containing organic phase are in contact and mixed by shaking, the metal will be distributed between the two phases. The distribution may be controlled by a chemical or a physical process or both, depending on the system. Chemical distribution processes involve chemical reactions between the metal species present in the aqueous phase and one or more components in the organic phase. Normally, a metal ion exists in an aqueous phase as a hydrated ion, with little or no tendency to be transferred to an organic phase in the absence of the extractant. Thus, the metal ion needs to be modified in order to be extracted. Various ways of modifying metal ions to form an extractable species are [38]:

(a) Compound formation — complexing the metal ion with ion(s) of the opposite charge to form a neutral species which, at the same time, replaces some or all of the water of hydration of the metal ion.

(b) Ion-association — formation of metal ion-association complexes which can form neutral species with an extractant.

(c) Solvation — replacing the water of hydration around the metal ion with solvent molecules.

The overall process is then one of converting a hydrophilic metal species into a hydrophobic species. The nature of the extractable metal species is therefore of fundamental importance in metal extraction systems.

1.2.2 The Metal Extraction Systems

1.2.2.1 Compound formation extraction systems

These systems include extraction with chelating extractants and extraction with acidic extractants [38].

In the chelating extraction systems, the metal ion reacts with an organic chelating extractant to form a neutral chelate complex. The simplest equation that can be written to illustrate the extraction of a metal ion by a chelating extractant in these systems is,

$$M^{n+}{}_{aq} + nHA_{org} \rightleftharpoons MA_{n,\,org} + nH^{+}{}_{aq} \qquad (1.1)$$

Where *aq* and *org* are aqueous and organic phase respectively, M^{n+} is a metal ion and HA is a chelating extractant.

Equation (1.1) indicates that the extraction of a metal ion in these systems strongly depends on the equilibrium $[H^+]$ (hydrogen ion concentration) of the aqueous phase. Thus, as the $[H^+]$ is increased, metal extraction will decrease since the equilibrium is towards the left. Conversely, as the $[H^+]$ is decreased, metal extraction will increase. The extraction is also dependent on the stability of the extractable metal complex formed, the distribution of the extractable metal complex between the two phases and the solubility of the extractant in the aqueous phase.

Another type of extractant, which is included in these systems is the acidic extractant. These extractants, unlike chelating extractants, interact with metal ions mainly through electrostatic forces and have great tendency to polymerize through hydrogen bonds in the organic phase. The extraction process of the metals with this extractant is more complicated than with the chelating extractant. Acidic extractants usually form dimers or polymers in non-polar organic solvents as a result of hydrogen bonding. In the case where dimerization or polymerization of the extractant occurs, the equilibrium or mass action equation must be modified. As an example of the extraction of a metal ion M^{n+} with a dialkylphosphoric acid into nonpolar organic solvents, the reaction is represented as;

$$M^{n+}{}_{aq} + n(HA)_{2,\,org} \rightleftharpoons M(HA_2)_{n,\,org} + nH^{+}{}_{aq} \qquad (1.2)$$

where $(HA)_2$ represents the dimeric form of the extractant.

It may be seen from equation (1.2) that factors affecting the extraction of metals by acidic extractants are not only the $[H^+]$, the metal ion concentration, the stability of the extractable metal complex, the distribution of the extractable metal complex between the two phases and the solubility of the extractant in the aqueous phase, but also the polymerization of the extractant in the organic phase [38].

1.2.2.2 Ion-association extraction systems

These systems include the extraction of metals with basic extractants such as high molecular weight primary (RNH_2), secondary (R_1R_2NH), and tertiary amines ($R_1R_2R_3N$), or quaternary ammonium salts ($R_1R_2R_3R_4N^+X^-$). These extractants are used for solvent extraction of anionic species. The interaction of these extractants with the anionic species is due mainly to the electrostatic forces. The general extraction reaction for the extraction of metal anionic species in these systems can be expressed as;

$$M^-_{aq} + B^+_{org} \rightleftharpoons (B^+M^-)_{org} \tag{1.3}$$

where M^- is an anionic metal complex species in the aqueous phase, B^+ is an amine or a quaternary ammonium salt extractant in the organic phase and (B^+M^-) is the metal-extractant complex formed in the organic phase.

The solvent extraction work described in this thesis involves an ion-association extraction system because the extractant used is a high molecular weight quaternary ammonium salt and the extractable species are anionic metal complexes.

1.2.2.3 Solvation extraction systems

These systems are based on the power of oxygen-containing organic extractants to solvate inorganic molecules or complexes. By such solvation, the solubility of the inorganic species in the organic phase is greatly increased.

There are two main groups of extractants in these systems: (a) extractants containing oxygen bonded to carbon such as alcohols (C-OH), ketones (C=O), ethers (C-O-C) and esters (-COOR); (b) extractants containing oxygen bonded to phosphorus such as alkyl-phosphate esters (≡P=O). One distinguishing feature of these extractants involves the role played by water. The strongly polar organophosphorus compounds compete favourably with water and can replace water molecules in the first hydration sphere of a metal atom. With ethers and ketones, water is a necessary part of the complex, probably forming bridge between the organic and metal components of the complex through hydrogen bonding. These extractants can, by virtue of solvation, extract both acids and metal complexes.

1.2.3 High Molecular Weight Amines and Quaternary Ammonium Salts

There are three types of amines, namely, primary RNH_2, secondary R_1R_2NH, and tertiary $R_1R_2R_3N$ amines, in addition to quaternary ammonium salts $R_1R_2R_3R_4N^+X^-$ (some or all of the R_1, R_2, R_3 and R_4 may be the same). All these organic derivatives of ammonia can be used for solvent extraction of metal ions and other anions. These amines in the aqueous phase are weak bases. They can accept one further proton and form amine salts. However, when the four hydrogen atoms of ammonium ion are substituted with hydrocarbons, the quaternary ammonium ion is formed which cannot accept a further proton. These quaternary ammonium salts are strong electrolytes and can extract anions and anionic metal complexes from acidic, neutral and basic solutions, whereas, amines can only be used in acidic or neutral conditions.

The extraction behaviour of many amines and ammonium salts has been extensively studied [39-43], and various types of amines and quaternary ammonium salts have been used for the extraction of metal complexes. Rao and Sastri [44] reviewed the extraction of metals using high molecular weight amines and quaternary ammonium compounds, and concluded that the extraction efficiency of the amines generally increases with increased basicity of the amines. Seeley and Crouse [45] investigated the extraction coefficients for 63 metals and found a similar correlation between the extraction efficiency and the basicity of amines. Quaternary ammonium salts were found to be better extractants than amines [44, 45].

The structural effect of the quaternary ammonium salts on their extraction efficiency was also investigated. It was reported that, under the same conditions, symmetrical quaternary ammonium cations are more efficient extractants than the unsymmetrical cations and the carbon chain length also contributes to the extraction efficiency of alkylammonium salts [46-48].

Amongst the various high molecular weight amines used in extraction studies, the quaternary ammonium salts exhibit considerable advantages. Since many quaternary ammonium compounds, such as quaternary ammonium chloride or nitrate, may be considered to be salts formed from strong acid and base and they do not strongly hydrolyze. Therefore, by using the quaternary ammonium salts as extractants, the extraction can be carried out under acidic, neutral or basic conditions [38]. Aliquat 336 (tricaprylylmethyl ammonium chloride) is one such compound and the interest in its use for the extraction of metal complexes is reflected by the continuous research into its applications over the last three decades. Aliquat 336 has been used in a wide range of metal extraction studies [27, 49, 50], in various analytical methods [51], chromatographic studies [52] and ion-selective electrode work [53, 54].

Aliquat 336 is represented by the formula $R_3MeN^+Cl^-$ where R_3 represents alkyl-groups which contain a mixture of C_8 and C_{10} straight chains with C_8 predominating [55] and Me is the methyl group ($-CH_3$). It is available commercially in the chloride form. The average molar mass of Aliquat 336 reported by the manufacturer is 404.17 [55]. Lee *et al.* have developed a chromatographic method for quantitative analysis of various components of Aliquat 336 [56]. In their approach, they used an internal standard and a pure component of quaternary ammonium chloride. Their approach eliminates any assumptions concerning the thermal decomposition products formed from quaternary ammonium chlorides and therefore offered a more reliable estimate of the quaternary components present in Aliquat 336. Paimin [57] used this method to analyze the composition of Aliquat 336 and compared the results with those published by Lee *et al.*. Both Lee *et al.* and Paimin have found that Aliquat 336 contains four major components of quaternary ammonium salts (with C_8 and C_{10} side chains), with the methyldioctyldecylammonium chloride being the most abundant component [56, 57]. Small amounts of n-octanol, n-decanol and water were also found to be present in the Aliquat 336. It is, therefore, expected that since Aliquat 336 is mixture of many components, there may be a slight variation in its composition in different synthetic batches.

Recently, Argiropoulos *et al.* have used electrospray mass spectrometry (EMS) method to analyze the composition of Aliquat 336 [58]. In this technique, the intact ions are produced in vacuo through an ionization technique that makes use of high electric fields to desorb ions from solution which are analyzed by the mass spectrometer. Individual quaternary ammonium cations were thus identified from their mass/charge ratios. It was reported that the results from the internal standard method using electrospray mass spectrometry compared well with the results using gas chromatography [58]. The results reported by the above-mentioned authors were very close to that reported by the manufacture.

1.2.4 Extraction Study of Cd(II) and Cu(II) by Aliquat 336

The extraction of Cd(II) and Cu(II) from various solutions using a number of extractants have been extensively studied [15, 27, 59-66]. These studies covered many aspects of the solvent extraction of these metals including the effect of extractant concentration on the extraction efficiency, selectivity, reversibility, extraction thermodynamics and mathematical modellings of the extraction mechanism. Other work focused on the selection of the extractants and diluents for the extraction of certain metal ions, since extractants and diluents are major factors affecting extraction efficiency [67]. Some information is available in the extraction of Cd(II) and Cu(II) by high molecular weight Aliquat 336. Hayati *et al.* [60] investigated the extraction equilibrium for the extraction of Cd(II) and Cu(II) from hydrochloric acid solutions by Aliquat 336 in chloroform. Their results showed that Aliquat 336 has a higher extraction efficiency to Cd(II) than Cu(II). Another investigation on the extraction of Cd(II) and Cu(II) using Aliquat 336 was carried out by Sato *et al.* [66]. They systematically studied the extraction efficiency of Cd(II) and Cu(II) using Aliquat 336 in benzene under different conditions and found that the order of the extraction efficiency is Cd(II) » Cu(II).

In present work, Aliquat 336 in Shellsol AB solvent was used in the investigation of the extraction of Cd(II) and Cu(II) from hydrochloric acid solutions. This work involves the use of one of the most commonly available commercial solvents, Shellsol AB, as the diluent to extract Cd(II) and Cu(II). Although the major part of this work is to study the use of Aliquat 336/PVC membrane in the extraction of Cd(II) and Cu(II) from hydrochloric acid solutions, the study of the conventional solvent extraction system using Aliquat 336 is an important preliminary step, a necessary and an integral part of this work, that can provide the necessary information for the study of the membrane extraction of Cd(II) and Cu(II).

1.3 EXTRACTION OF Cd(II) AND Cu(II) FROM HYDROCHLORIC ACID SOLUTIONS BY ALIQUAT 336/PVC MEMBRANES

An alternative and more recent separation technique is the membrane extraction. It is a promising method for separating and concentrating metals which can extract valuable and/or toxic substances down to residual concentrations. This method may be particularly valuable in the analysis of materials from environment, for purifying effluents, and for developing waste-free technology.

Some work has been reported on the study of membrane extraction of cadmium and copper. These studies include the membrane extraction of cadmium with dithizone in multiple emulsion [67], the extraction of cadmium from dilute aqueous solution using hollow-fibre membrane [68], the extraction of cadmium from aqueous solution using a liquid membrane [69], the extraction of copper using liquid surfactant membrane [70], membrane extraction of copper with macrocyclic compounds [71] and copper removal and recovery by contained liquid membrane permeator [72]. Recently, the use of polyvinylchloride (PVC) [73-76], polyurethane foam [77] and filter paper [78, 79], instead of an organic solvent as the extracting medium, has been investigated for the extraction of metal ions. Extraction processes aided by ion-exchange membranes and supported liquid membranes have also been studied [36, 80-82].

Quite recently Argiropoulos *et al.* [83] used Aliquat 336/PVC membrane to investigate the extraction of Au(III) from hydrochloric acid solutions. Their results showed that membranes containing 20% to 40% of Aliquat 336 exhibited quite high extraction rate to Au(III). The Aliquat 336/PVC membranes have also shown a reasonable selectivity to Au(III) against Cu(II) [83], although the extraction efficiency of the membranes to Au(III) was slightly affected when Cu(II) was present in the aqueous phase. Their results also showed that the Aliquat 336/PVC membrane had considerable stability and that the loss of reagent to the aqueous phase was reasonably low in strong acid solutions.

Based on the above studies, Aliquat 336/PVC membrane is studied in this work for the extraction of Cd(II) and Cu(II). The focus of this study is on the extraction rate and capacity of Aliquat 336/PVC membrane, the possibility of performing the extraction from the feed phase to the receiver phase using Aliquat 336/PVC membrane and the stability of Aliquat 336/PVC membrane in the extraction of Cd(II) and Cu(II).

1.3.1 Basic Principles of The Membrane Extraction

A membrane may be defined as a permselective barrier between two phases. It can be homogeneous or heterogeneous in chemical composition. It may be solid or liquid and it may be either electrically neutral, or carry positive or negative charge(s), or both. The thickness of a membrane may vary between less than 100 μm to more than a centimetre. Mass transport through a membrane can be driven by diffusion of individual molecules or by convection induced by gradients in electrical potential, concentration, pressure or temperature.

In the present membrane extraction system, the membrane used (Aliquat 336/PVC membrane) is a homogeneous membrane. The solution containing metal species is transported through this membrane under the driving force of the chemical potential of the metal complex. Since the pressure and temperature were held constant during extraction experiments, the chemical potential of a metal complex is determined by the concentration of the metal ion and the concentration of the ligand. This will be further discussed in Chapter 3. The extraction of various components in a solution is directly related to their transport rate within the membrane phase, which is determined by their diffusivity and concentration in the membrane matrix.

The membrane extraction process may be described by the following simplified expression:

$$pM_{aq} + qB_{mem} \rightleftharpoons (B_qM_p)_{mem} \qquad (1.4)$$

where, M_{aq} is the metal species, such as Cd(II) and Cu(II), in the aqueous phase, B_{mem} is the free extractant held in the membrane and B_qM_p is complex moiety in the membrane.

The performance of the membrane in the extraction is defined in terms of two factors: the flux and the selectivity. Flux is the net mass or molar transport rate of the compound to be extracted from the feed into the membrane or through the membrane to the receiver per unit membrane area per unit time. Selectivity is a measure of the relative fluxes of different components to the membrane or through the membrane [84]. A high performance membrane should therefore have a high flux and a high selectivity to the compound of interest. However, in membrane extraction system, diffusion coefficient of species is usually used to describe the performance of the membrane instead of the flux. The relationship between the diffusion coefficient and the flux is given by Fick's law (or the law of diffusion):

$$J_i = -D_i \, dc_i/dx \qquad (1.5)$$

Here, J_i is the flux of species i, D_i is the diffusion coefficient and dc_i/dx is the gradient of concentration.

1.3.2 Aliquat 336/PVC Membranes

The membrane used for the present study is PVC membrane and the extractant held within the membrane is Aliquat 336. This type of membrane has been widely used in ion-selective electrodes [85]. It has been found that Aliquat 336 acts as a plasticizer for PVC and produces a membrane which has high stability [85]. However, this type of membrane differs from other supported liquid membranes in that no diluent is required in the membrane and the reagent is trapped within the polymer structure in liquid channels rather than occupying pores. This type of membrane may therefore be called, more accurately, as the "entangled" membrane. PVC membranes of this type with appropriate complexing agents show considerable promise in the removal of Au(III) from hydrochloric acid solutions [83].

A similar type of PVC membrane was used by Neplenbroek *et al.* [86] to study the stability and transport rate of the supported liquid membrane. In this membrane a homogeneous gel network containing PVC and an extractant was applied in the pores of the support. In doing so both the mechanical stability and the long term permeability increase substantially. Bromberg *et al.* [87] later studied the transport rate of metals through such gelled supported liquid membranes and found high flux through these membranes.

1.3.3 Extraction of Cd(II) and Cu(II) From Both Sides of Aliquat 336/PVC Membranes

Extraction experiments were first carried out to study the extraction ability of Aliquat 336/PVC membrane in extracting Cd(II) and Cu(II) from hydrochloric acid solutions. It has been postulated that the extraction mechanism at the interface of the feed and the membrane is similar to that occurring at the interface of aqueous and organic phases in solvent extraction [88]. The latter has been proposed to be a very fast ion-exchange reactions between the mono- and/or divalent anionic complexes to form extractable ion-pair which then diffused into the bulk organic phase and is replaced at the interface by fresh Aliquat 336 [57].

In this work, the experimental data of the membrane extraction of Cd(II) and Cu(II) were tested using the diffusion-kinetic model [88]. In this model, the extraction rate of metal ions was assumed to be governed by both the rate of the chemical reactions occurring at the interface and by diffusion of the extracted complex species within the membrane [88]. It was also suggested that diffusion was the dominant transport mechanism of the extracted complex within the membrane.

In the present study, the conditions in which the extraction rate and the diffusion coefficient of the extracting complex could be increased have been investigated. The investigation included studying the extraction rates using membranes containing different composition of Aliquat 336 and PVC.

1.3.4 Extraction of Cd(II) and Cu(II) From The Feed Phase Through the Aliquat 336/PVC Membrane Into The Receiver Phase

The ultimate goal in any membrane extraction study is to transfer and concentrate the compound of interest from the 'feed' phase to the 'receiver' phase. It must be noted that, although the back-extraction of an extracted compound from a membrane that is saturated with this compound into a receiver solution is possible, a continuous operation which combines both the extraction (from the 'feed') and the back-extraction (into the 'receiver') has so far not been successfully performed for this system [83].

In continuous membrane extraction system, an aqueous phase that contains the metal complex, or the 'feed', is made to contact with an Aliquat 336/PVC membrane. On the other side of the membrane, there is a second aqueous phase, or the 'receiver', which initially is devoid of the metal complex. The metal complex transfers from the 'feed' phase to the Aliquat 336/PVC membrane and forms the complex with the Aliquat 336 held within the membrane. Then, driven by chemical potential, the complex moves across the membrane and into the 'receiver' phase. Information obtained from the investigation of the diffusion behaviour of the extracted metal complex within the membrane in the extraction of Cd(II) and Cu(II) from both sides of the Aliquat 336/PVC membrane was used for the study of the continuous extraction system.

1.4 SURFACE CHARACTERIZATION OF ALIQUAT 336 /PVC MEMBRANES

One of the major differences between the membrane and solvent extraction is that in the former, the metal is transported through the interface of the aqueous phase and a polymer matrix, which has certain characteristics of solid polymeric materials. The chemical and physical properties of the membrane may affect its extraction behaviour. In order for the extracted complexes to be concentrated in the Aliquat 336/PVC membrane, the extracted complex must first undergo an ion-exchange with Aliquat 336 at the liquid-membrane interface. Therefore, characterization of the membrane surface is very important in its own right.

The techniques which have been most widely used for the study of surface structure and the chemical compositions of the surface are Atomic Force Microscopy (AFM) and X-Ray Photoelectron Spectroscopy (XPS) [89, 90]. AFM provides topographic images by scanning a sharp tip over a surface and has been used to produce atomic resolution images of both insulators and conductors [91] including biological materials [92]. It has also been used to investigate the membrane surface structure of microfiltration and ultrafiltration membrane [93-97] and to characterize the forces between various surfaces under many different conditions in colloid and surface science [98-100]. All these studies have clearly shown the possibility of applying surface imaging, surface force measurements and micromechanical measurements to the Aliquat 336/PVC membrane using the AFM techniques. XPS, also known by another name - ESCA (Electron Spectroscopy for Chemical Analysis), is an excellent technique for elemental identification, and gives information about the chemical environment of the observed atoms [101]. It has been extensively and successfully used in polymer studies [101-103] and has become one of the main tool, for the surface characterization of polymers [101-105]. In this study, AFM was used to investigate the surface structure of the Aliquat 336/PVC membrane and XPS was used to examine the surface chemical compositions of the Aliquat 336/PVC membrane. The effects of Aliquat 336 concentration and extraction on the physical properties of the Aliquat 336/PVC membrane were also studied.

1.5 AIMS OF THIS STUDY

The general aim of this research is to study the extraction behaviour of Cd(II) and Cu(II) from hydrochloric acid solutions using Aliquat 336 in solvent and membrane extraction systems.

The specific aims of this project are:

(a) to determine the nature of the extracted complex,

(b) to determine extraction equilibrium constants in solvent extraction,

(c) to determine extraction rates of Cd(II) and Cu(II) in membrane extraction,

(d) to elucidate the mechanism of the membrane extraction,

(e) to determine the conditions for the continuous operation of the extraction of Cd(II) and Cu(II) by the membrane,

(f) to investigate the microscopic structure of the membrane and the chemical composition of the membrane surfaces, and

(g) to further understand the fundamental chemistry which is involved in both extraction systems.

CHAPTER TWO

SOLVENT EXTRACTION OF Cd(II) AND Cu(II) FROM HYDROCHLORIC ACID SOLUTIONS BY ALIQUAT 336 IN SHELLSOL AB

2.1 INTRODUCTION

High molecular weight quaternary ammonium salts have been used widely in solvent extraction studies [21, 23, 27, 51, 60, 61, 66, 106-112]. These studies included the extraction of Au(III) [51, 66], Co(II) [66, 107-109], Zn(II) [23, 60, 61, 66, 110, 111], Cd(II) [27, 60, 61, 66, 111] and Cu(II) [60, 66, 111] using high molecular weight quaternary ammonium salts in various diluents. Most of these studies have focused on the equilibrium distribution of the metal ions between the aqueous and organic phases and the control parameters that affect such distribution [21, 51, 60, 61, 66, 108, 109, 111, 112]. Some authors also investigated the effects of diluents on the extraction of metal ions using high molecular weight quaternary ammonium salts [108, 110, 113].

It is known that the extraction mechanism for the extraction of metal ion complexes from an aqueous phase using quaternary ammonium salts is via ion-exchange process [21, 23, 51, 60, 61, 66, 106-112]. The ligand concentration in the aqueous phase and the diluent used for forming the organic phase have been identified to be important factors that can substantially affect the equilibrium distribution of the metal ion complexes [60, 61, 66, 108, 110, 111, 113]. In this chapter, solvent extraction of Cd(II) and Cu(II) was studied using Aliquat 336 in Shellsol AB. The purpose of this study is to establish the extraction conditions, to determine the nature of the extracted complexes formed in the organic phase and to elucidate the mechanism processes involved during extraction. As part of the study, the effect of diluents on the extraction was also investigated. A more detailed review on the extraction mechanisms and the experimental methods used in this study is given below.

2.1.1 Equilibrium Studies of The Extraction of Cd(II) and Cu(II) Using Aliquat 336

An equilibrium extraction study is essential in solvent extraction work and one of the purpose of this study is to determine the exact nature of the metal complexes which are being extracted into the organic phase. Accordingly, identification of these complexes is important in postulating the reaction mechanism occurring in an extraction system.

In amine extraction system, metal extraction is carried out from acidic media, so that the amine in the organic phase is first converted to its salt [114]. This limitation on the aqueous condition, however, does not apply to quaternary ammonium salts, which can be employed in neutral, slightly alkaline or acidic solutions.

In the case of the extraction of metal ions by amine salts, the extraction reaction can be described by the following simplified equations [114]:

$$(RNH_3^+X^-)_{org} + M^-_{aq} \rightleftharpoons (RNH_3^+M^-)_{org} + X^-_{aq} \qquad (2.1)$$

$$(R_2NH_2^+X^-)_{org} + M^-_{aq} \rightleftharpoons (R_2NH_2^+M^-)_{org} + X^-_{aq} \qquad (2.2)$$

$$(R_3NH^+X^-)_{org} + M^-_{aq} \rightleftharpoons (R_3NH^+M^-)_{org} + X^-_{aq} \qquad (2.3)$$

Where subscripts *org* and *aq* represent the organic and aqueous phases respectively, and RNH_2, R_2NH and R_3N, primary, secondary and tertiary amines respectively. M^-_{aq} represents the metal anionic species in the aqueous phase.

The overall reaction is described as anion-exchange, which implies that an anionic species is transported across the aqueous-organic interface into the organic phase. Equations (2.1) to (2.3) suggest that in the case of metal ion extraction, it is essential that the metal ion is in an appropriately complexed anionic form in the aqueous phase in order for its transfer to the organic phase to occur.

In the case of the extraction of metal ions by quaternary ammonium salts ($R_4N^+X^-$), ion-exchange is again thought to be the mechanism involved and the extraction reaction can be written as:

$$(R_4N^+X^-)_{org} + M^-_{aq} \rightleftharpoons (R_4N^+M^-)_{org} + X^-_{aq} \qquad (2.4)$$

An alternative mechanism has also been proposed by Coleman *et al.* [115] in the study of the extraction of uranium(VI) from sulfate solutions. He suggested that extraction of uranium(VI) occurs via adduct formation (i.e. direct complexation). This mechanism does not require the anionic form of the metal species to be present in the aqueous phase and it implies that a neutral metal containing species is transferred across the interface. This mechanism can be represented as,

$$UO_2{}^{2+}{}_{aq} + SO_4{}^{2-}{}_{aq} \rightleftharpoons UO_2SO_{4aq} \qquad (2.5)$$

followed by,

$$\{(R_3NH)_2SO_4\}_{org} + UO_2SO_{4aq} \rightleftharpoons \{(R_3NH)_2UO_2(SO_4)_2\}_{org} \qquad (2.6)$$

Coleman [116] later suggested that it is possible for the two mechanisms to operate simultaneously in the extraction of uranium(VI). One mechanism is described as in equation (2.6) and the other, via anion-exchange, may be written as:

$$UO_2{}^{2+}{}_{aq} + 2SO_4{}^{2-}{}_{aq} \rightleftharpoons \{UO_2(SO_4)_2{}^{2-}\}_{aq} \qquad (2.7)$$

$$\{(R_3NH)_2SO_4\}_{org} + \{UO_2(SO_4)_2{}^{2-}\}_{aq} \rightleftharpoons \{(R_3NH)_2UO_2(SO_4)_2\}_{org} + SO_4{}^{2-}{}_{aq} \qquad (2.8)$$

Since both mechanisms result in the formation of the same stoichiometric species in the organic phase, they are, according to Coleman [116], thermodynamically equivalent and the description for the equilibrium processes is considered arbitrary. However, in making this suggestion, he overlooked a very important distinction between the two reactions. As was pointed out by Cattrall [117], extraction can occur even in the absence of anionic metal containing species in the aqueous phase, as long as the metal in the form of the neutral species is not fully coordinated with ligand other than water in the aqueous phase.

It is now generally accepted that anion-exchange and adduct-formation mechanisms can occur in the extraction processes. The mechanism which predominates depends mainly on the composition of the aqueous phase and possibly on the type of extractants [118].

Daud and Cattrall [60] studied the extraction of Cd(II) and Cu(II) using Aliquat 336 in chloroform. They have identified that for both Cd(II) and Cu(II) (under the specified HCl concentrations), the singly and doubly charged metal complexes were extracted into the organic phase. They concluded that the mechanism involved in the extraction of Cd(II) and Cu(II) using Aliquat 336 in chloroform was the ion-exchange process.

2.1.2 The Extraction Mechanism

The extraction mechanism in an extraction system can be classified into two major categories [108], depending on the locality of the extraction processes. These are the homogeneous and the heterogeneous mechanisms. The homogeneous mechanism involves the distribution of the reagent between the organic and the aqueous phases, complexation (the term that is used to describe adduct-formation, ion-exchange and chelation) within the aqueous phase followed by the distribution of the complex formed into the organic phase. Heterogeneous mechanism, on the other hand, consists of the processes which occur at the interface. These processes include diffusion of the reagent to the interface, complexation at the interface and finally diffusion of the complex formed away from the interface.

For the extraction of anionic metal complexes by high molecular weight quaternary ammonium salts, the complexation reactions at the aqueous-organic interface seem to provide the most plausible mechanism, since the quaternary ammonium salts are surface active reagents [119, 120]. In the extraction of iron (III) from chloride solutions by the high molecular weight quaternary ammonium chloride, $R_4N^+Cl^-$, the reaction mechanism can be represented as [108],

$$(\mathrm{FeCl_3})_{aq} + \mathrm{Cl^-}_{aq} \rightleftharpoons (\mathrm{FeCl_4^-})_{aq} \tag{2.9}$$

$$(\mathrm{FeCl_4^-})_{aq} + (\mathrm{R_4N^+Cl^-})_i \rightleftharpoons (\mathrm{R_4N^+FeCl_4^-})_i + \mathrm{Cl^-}_{aq} \tag{2.10}$$

$$(R_4N^+FeCl_4^-)_i \rightleftharpoons (R_4N^+FeCl_4^-)_{org} \tag{2.11}$$

where *i* represents the interface.

Extraction via ion-exchange of an anionic metal complex from the aqueous phase has been described in several studies [21, 23, 27, 51, 60, 61, 66, 106-113, 121]. However, it should not be overlooked that an adduct-formation reaction (extraction of a neutral species), such as described by McDowell and Coleman [118], may still be possible in many cases. The adduct-formation reaction, for the extraction of iron(III) above, can be described as,

$$(FeCl_3)_{aq} + (R_4N^+Cl^-)_{org} \rightleftharpoons (R_4N^+FeCl_4^-)_{org} \tag{2.12}$$

It is obvious that many factors, such as the nature of the extractant, the metal complexes present in the aqueous phase, the nature of the extracted metal species and the composition of the extracted complex can affect the mechanism for the extraction of metals. Thus, in this chapter, the nature of the Cd(II) or Cu(II) species which was extracted into organic phase by Aliquat 336 was investigated and the extraction mechanism for the extraction of Cd(II) or Cu(II) with Aliquat 336 was also evaluated.

2.1.3 Methods for Identification of The Extracted Complex and Evaluation of The Extraction Equilibrium Constant

Several approaches have been employed for identification of the extracted complex. These approaches include various spectroscopic methods (e.g., infra-red, ultra-violet and visible spectroscopy) and other physical and chemical techniques [122]. Despite the straightforward approach of spectroscopic methods, the traditional distribution experiments have been found to be by far the most useful method for studying the extracted complexes as well as the mechanistic processes involved in the extraction [108]. The experimental data obtained from distribution experiments, in most cases, is analyzed using the loading ratio, the slope analysis and the elemental analysis methods.

Another method which has been used for the data treatment was based on the integration procedure by Sillén [123]. In this method no assumptions regarding the stoichiometry of the extracted complex are made. A full mathematical and graphical procedures of this method are given in references [108] and [123]. This method has been found to be highly suitable for the treatment of the data obtained from the two-phase titration experiments [15, 51, 108-110, 124], which was developed independently by Dyrssen [125] and Högfeldt [126]. The experimental details will be presented in section 2.2.2.2.

Recently, Argiropoulos *et al.* used a modified but simpler method for calculating the extraction equilibrium constants [51]. However, in this method, knowledge of the stoichiometry of the extracted complex is required. This method is outlined in Section 2.3.3.3.

In the present study, the integration method [108, 123, 127] and the method proposed by Argiropoulos *et al.* [51] were used in the calculation of the stoichiometric coefficients and the extraction equilibrium constants of the extraction of Cd(II) and Cu(II) using Aliquat 336.

2.1.4 The Distribution Ratio and The Efficiency of Extraction

The distribution of a metal ion species between the organic and aqueous phases is governed by the Nernst partition or distribution law which states that at equilibrium, a given solute will distribute itself between two essentially immiscible liquids in a specific ratio [128]. Thus, distribution ratio (D) of a metal ion species (M) between the organic phase (org) and the aqueous phase (aq) is given by the equation,

$$D = \frac{[M]_{org}}{[M]_{aq}} \tag{2.13}$$

The efficiency of an extraction is described as the amount of a metal species being extracted into the organic phase versus the total amount of the metal species in the system [128]. Therefore, the calculation of the efficiency of an extraction must take into account the magnitude of D as well as the relative volumes of the two phases. Extraction efficiency is defined as the percentage of extraction given by the following equation,

$$\%E = \frac{100 \times D}{D + (\frac{V_{aq}}{V_{org}})} \tag{2.14}$$

where V_{aq} and V_{org} are the volumes of the aqueous and organic phases, respectively. In the case where V_{aq} and V_{org} are equal, equation (2.14) can be rewritten as,

$$\%E = \frac{100 \times D}{D + 1} \tag{2.15}$$

2.1.5 The Effect of Diluents on The Extraction of Metal Ions by Aliquat 336

The effect of diluents on the extraction of metal ions by high molecular weight amines and quaternary ammonium compounds has been investigated by several authors [129-132]. Sato *et al.* [133] studied the effect of diluents on the extraction efficiency of Aliquat 336 for zirconium (IV) chloride. They found that the extraction efficiency of Aliquat 336 chloride for zirconium was strongly influenced by the diluent used but no simple relationship holds between the extraction efficiency and physical parameters of the organic solvents. Horwitz *et al.* [131] investigated the effect of some selected diluents on the distribution coefficient of americium (III) using Alamine 336 nitrate and Aliquat 336 nitrate. They found that the most suitable solvent was diisopropylbenzene for Alamine 336 nitrate and xylene for Aliquat 336 nitrate. According to Diamond [130], the solvent employed in the extraction was not 'inert' but interacted with the extractant through its functional groups. It is therefore evident that solvents play an important role in the extraction of metals using high molecular weight ammonium compounds. Various attempts to explain the influence of diluents on the extraction efficiency has been based on purely qualitative considerations. Many authors have assumed that the influence of diluents on the extraction efficiency is attributed to a variety of interaction between the extractant and the diluent [129, 130]. They have assumed that two types of solvation may occur:

(a) An electrostatic solvation which is directly related to the dielectric constant of the solvent.

(b) A chemical solvation which is directly related to short range specific (Lewis acid-base) interactions between the extractant and the solvent.

Diamond [130] proposed that the extraction efficiency of an extractant for the metal complex is reduced if the extractant is more strongly solvated relative to the metal complex. However, Shmidt *et al.* [134] suggested that the extraction efficiency is dependent upon the type of functional groups (either basic or acidic) presented in the extractant that is involved in the solvation, or extractant-diluent interaction. Thus, in both types of solvation, if the extractant is mainly basic and the diluent is acidic, the solvation of the coordination site would reduce the extraction. If the diluent is basic and the extractant is mainly acidic, the solvation would not reduce the extractant but would enhance it.

One conflicting view was observed, however, when aromatic diluents were used for trilaurylamine hydrochloride extraction system. Shmidt *et al.* [134] proposed that benzene interacts as an acidic solvent with the anion of the salt, whereas Diamond *et al.* [130] proposed that it interacts as a basic solvent with the hydrogen of the ammonium cation.

In the investigation of the influence of diluents on the extraction of Zn(II) [111], it has been found that different Zn(II) species are preferentially extracted into different diluents. The preferential extraction of certain metal species can be explained in terms of various interactions involved in the aqueous and the organic phases.

In this work, study was conducted on the extraction of Cd(II) using Aliquat 336 in different diluents. The effect of diluents on the extraction efficiency and the nature of metal species being extracted are discussed.

2.2 EXPERIMENTAL

2.2.1 Materials

2.2.1.1 Reagents

Aliquat 336 (tricaprylylmethylammonium chloride with the formula of $R_3MeN^+Cl^-$) was obtained from Fluka. The compound is a viscous and straw colored liquid. It was used as received.

Hydrochloric acid (HCl), cadmium chloride ($CdCl_2{\bullet}H_2O$) and cupric chloride ($CuCl_2{\bullet}2H_2O$) were analytical reagents from BDH.

Shellsol AB was obtained from Shell Chemical (Australia) Pty. Ltd. It is a clear and colourless liquid and contains approximate 99% aromatics [135]. Analytical reagent grade chloroform ($CHCl_3$) was obtained from BDH. The solvents were used without any further purification.

Cd(II) and Cu(II) standard solutions for Atomic Absorption Spectroscopy measurements were obtained from BDH. The concentration of both standards was 1000 mg/L.

Milli-Q water was used for all dilutions.

2.2.1.2 Preparation of cadmium(II) chloride solutions

A series of Cd(II) chloride solutions were prepared in a concentration range of 0.0006M to 0.02M with 2M hydrochloric acid solution. All the aqueous solutions were presaturated with the organic solvents (Shellsol AB or Chloroform) prior to the solvent extraction.

2.2.1.3 Preparation of copper(II) chloride solutions

A series of Cu(II) chloride solutions were prepared in a concentration range of 0.003M to 0.25M with 3M hydrochloric acid solution. All the aqueous solutions were presaturated with the organic diluents (Shellsol AB/chloroform) prior to the solvent extraction.

2.2.1.4 Preparation of Aliquat 336 solutions

Aliquat 336 concentrations prepared were 0.04M, 0.06M, 0.08M and 0.12M in Shellsol AB and 0.04M and 0.08M in Chloroform. Shellsol AB and Chloroform were presaturated with 2M HCl or 3M HCl solutions prior to solvent extraction.

2.2.1.5 Preparation of cadmium(II) and copper(II) working standards

Cd(II) and Cu(II) standards were prepared from 1000mg/L stock solution prior to each analysis. Concentration range for Cd(II) was 0.005-1.0 mg/L and for Cu(II) was 0.5-3.0 mg/L.

2.2.2 Solvent extraction procedure

2.2.2.1 Batch extraction

Batch extraction technique was used to determine the equilibrium time of the extraction and to study the effect of concentration of chloride ion (Cl^-) on the extraction. Experiments were carried out by mixing equal volumes of the Cd(II) or Cu(II) solution and the organic phases containing Aliquat 336 in Shellsol AB or chloroform in an indented round bottomed flask and then vigorously shaking in a themostated water bath (25°C) for a preset period of time. Immediately after the two phases were separated, an aliquot of the aqueous phase was taken out of the system for metal analysis using Atomic Absorption Spectroscopy (AAS).

2.2.2.2 Two-phase titration technique

The extraction equilibrium studies were carried out using the two-phase titration technique. The main advantage of this technique compared to the batch-wise extraction method, is that it allows collection of a large number of data points in a short period of time. 100ml of an Aliquat 336/Shellsol AB solution was added to an indented round bottomed flask secured in a thermostated water bath (25°C) (Figure 2.1). An accurate 100ml of the lowest concentration metal solution was then added into the same flask and the phases were rapidly stirred for the pre-determined equilibration time. After equilibration, 10ml of the aqueous phase was removed for metal analysis. 10ml of the same fresh metal solution was then added and the process repeated. This was then repeated once before proceeding to the next higher metal concentration. At each step the concentration of metal in the organic phase was obtained by difference.

2.2.2.3 Metal analysis

The Cd(II) and Cu(II) concentrations in aqueous phase were analyzed by an Atomic Absorption Spectrophotometer (GBC 902) using the standard method. The operating parameters were carefully optimized. Instrumental parameters used in this investigation are listed in Table 2.1.

Table 2.1. Instrumental parameters used in this investigation for the analysis of metals by AAS

Parameters	Cd(II)	Cu(II)
Lamp current (mA)	3.0	3.0
Wavelength (nm)	228.8	324.7
Slit width (nm)	0.5	0.5
Flame composition	a	a

a = Air-acetylene, oxidizing

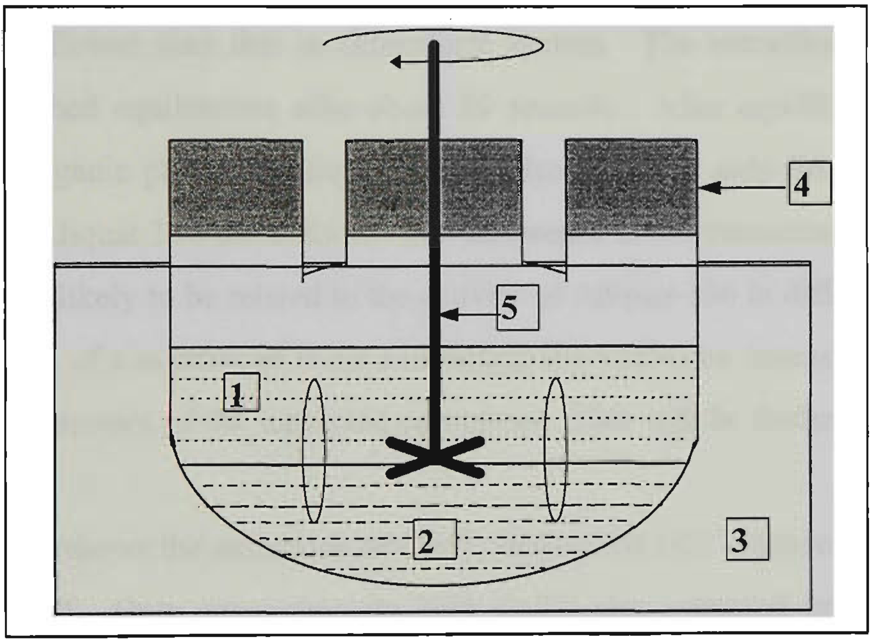


Figure 2.1. Schematic diagram of the two-phase titration apparatus. (1) Organic phase, (2) Aqueous phase, (3) Thermostated water bath, (4) Three-neck round bottomed flask with indentations to facilitate mixing and (5) Stirrer

A calibration curve was established prior to each analysis using a series of metal standard solutions. In each of these solutions, dilution of the standards was done using 2M hydrochloric acid solution for cadmium(II) and 3M hydrochloric acid solution for copper(II), since samples being analyzed were also diluted with 2M and 3M hydrochloric acid solutions, respectively.

2.3 RESULTS AND DISCUSSION

2.3.1 Effect of Organic-Aqueous Phase Contact Time on The Extraction of Cd(II) and Cu(II)

Using batch extraction method, the extraction of Cd(II) and Cu(II) from HCl solutions by Aliquat 336 was studied as a function of extraction time. Shellsol AB was used as the diluent for the organic phase. Since extraction of Cd(II) and Cu(II) by Aliquat 336 using chloroform as the diluent has been reported previously [60], in the present work, only the extraction of Cd(II) by Aliquat 336 in chloroform was re-investigated for the purpose of comparison. Figure 2.2 shows the time dependence of these extraction systems expressed in terms of %E.

It is clear from Figure 2.2 that the extraction of Cd(II) by Aliquat 336 in Shellsol AB system is more efficient than that in chloroform system. The extraction of Cd(II) in both systems reached equilibrium after about 30 seconds. After equilibrium, 99.98% Cd(II) is in the organic phase of Aliquat 336/Shellsol AB, but only 86.89% is in the organic phase of Aliquat 336/chloroform. The difference in the extraction efficiency of the two diluents is likely to be related to the activity of Aliquat 336 in different diluents, which is as a result of a number of factors including the molecular interactions between the diluent and extractant of the extracted complexes. This will be further discussed in Section 2.3.4.

Figure 2.2 also shows the extraction of Cu(II) from a 3M HCl solution using Aliquat 336 in Shellsol AB. Only approximately 16% Cu(II) was extracted into the organic phase at equilibrium. This result shows that the extraction of Cu(II) by Aliquat 336 in Shellsol AB is less efficient than that of Cd(II). The substantially poorer extraction of Cu(II) by Aliquat 336 compared with Cd(II) was also reported previously by Daud *et al.* in chloroform system [60], in which Cu(II) was extracted from an aqueous solution which was acidified with various concentrations of HCl (from 3 to 8 M). In both Shellsol AB and chloroform systems, distribution of Cu(II) was two to three orders of magnitude lower than that of Cd(II). The most likely cause of the difference in the extraction efficiencies between Cd(II) and Cu(II) may be due to the different degree of complexation of Cd(II) and Cu(II) with Aliquat 336. A further discussion of this point will be given in a later section (Section 2.3.3.3). The difference in the extraction efficiency between Cd(II) and Cu(II) by Aliquat 336 indicates that these metals can be separated from aqueous chloride solutions.

In the two-phase titration study of Cd(II) and Cu(II), 5 and 10 minutes of phase-mixing were used to allow the equilibrium to be established, respectively. These equilibrium times were considered sufficient, since the extraction of Cd(II) and Cu(II) by Aliquat 336 reaches equilibrium after 30 seconds of phase-mixing, and prolonged phase-mixing was found to have no further effect on the extraction equilibrium.

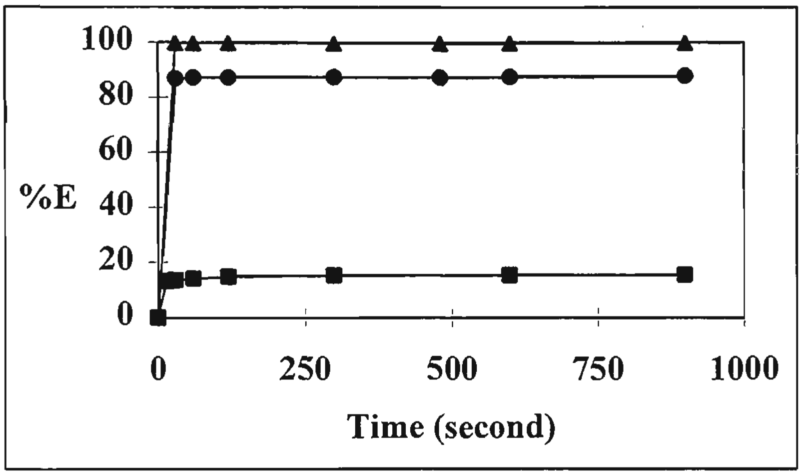


Figure 2.2 Effect of organic-aqueous phase contact time on the extraction of Cd(II) and Cu(II) from 3M hydrochloric acid solutions by Aliquat 336. (▲ Cd(II)/Shellsol AB, ● Cd(II)/Chloroform, ■ Cu(II)/Shellsol AB. The initial aqueous phase Cd(II) and Cu(II) concentration were 200 mg/L and 140mg/L, respectively. The Aliquat 336 concentration in the organic phase was 0.04M.)

2.3.2 Effect of Hydrochloric Acid Concentrations on The Extraction of Cd(II) and Cu(II)

The effect of hydrochloric acid concentrations on the extraction of Cd(II) and Cu(II) was examined. The results are presented in Figure 2.3.

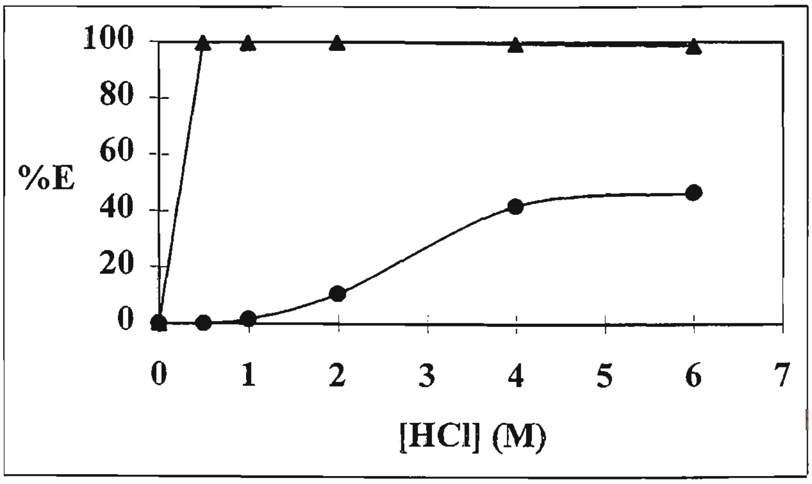


Figure 2.3. Effect of HCl concentrations on the extraction of Cd(II) and Cu(II) from hydrochloric acid solution by Aliquat 336 in Shellsol AB (▲ Cd(II) and ● Cu(II). The initial aqueous phase Cd(II) and Cu(II) concentration were 200 mg/L and 140 mg/L, respectively. The initial Aliquat 336 concentration of the organic phase was 0.04M.)

Figure 2.3 shows the extraction efficiency of Cd(II) and Cu(II) as a function of hydrochloric acid concentrations. For Cd(II) an extraction percentage ≥99.98% was reached for all HCl concentrations ≥ 0.5M. However, for Cu(II), the extraction percentage was found increased as the HCl concentration was increased up to 4M and reached a plateau (≈ 42% extraction) for HCl concentration > 4M.

Extraction of Cd(II) and Cu(II) from an aqueous phase containing no HCl and 0.1M HCl concentrations was also studied, but stable emulsions formed in both phases which made the phase separation and the metal concentration analysis impossible. The result indicates that HCl is needed for the phases to separate and to avoid the formation of emulsion.

From the above results and results of previous studies [60], HCl concentrations chosen to be used in the extraction systems were 2M for Cd(II) and 3M for Cu(II).

2.3.3 Equilibrium Studies of The Extraction of Cd(II) and Cu(II) From Hydrochloric Acid Solutions by Aliquat 336 in Shellsol AB

There have been many reports of the extraction of Cd(II) using various extractants [15, 27, 59, 66, 136-139]. However, most of these studies used the batch-wise extraction technique and the distribution data were treated by slope analysis and loading ratio calculation in predicting the nature of the extracted species. Only a few studies have been reported in the past using Aliquat 336 as the extractant [60, 61] to extract Cd(II) and Cu(II) by means of two-phase titration technique. In this section, two-phase titration technique was employed to study the extraction of Cd(II) and Cu(II) from HCl solutions using Aliquat 336 dissolved in Shellsol AB. The stoichiometry of the extracted complex and the equilibrium constant of the extraction reaction were evaluated.

2.3.3.1 The equilibrium data for the extraction of Cd(II) and Cu(II)

The experimental data for the extraction of Cd(II) and Cu(II) from hydrochloric acid solutions using organic phase of Aliquat 336 in Shellsol AB are presented in the form of plots of Z versus the logarithm of the concentration of the neutral metal species MCl_2 in the aqueous phase at equilibrium (Figures 2.4 and 2.5). Z is defined as the ratio of the total metal concentration in the organic phase to the total Aliquat 336 concentration in the organic phase [60]. The concentration of the neutral metal species, in each case, was calculated from the total metal concentration using the values for the formation constants of the various metal complexes [140] and is shown below.

The distribution of the various metal species in solution was determined by considering the metal complex equilibria described below [140]. The generalized metal complex formation equilibria between a metal (M) and an anionic ligand (X) in aqueous solution, neglecting the coordinated water and charges for convenience, are,

$$M + X \overset{k_1}{\rightleftharpoons} MX \qquad k_1 = \frac{[MX]}{[M][X]} \tag{2.16}$$

$$MX + X \overset{k_2}{\rightleftharpoons} MX_2 \qquad k_2 = \frac{[MX_2]}{[MX][X]} \tag{2.17}$$

In general,

$$MX_{n-1} + X \overset{k_n}{\rightleftharpoons} Mx_n \qquad k_n = \frac{[MX_n]}{[MX_{n-1}][X]} \tag{2.18}$$

where k_1, k_2, ... k_n are the stepwise formation constants. The overall formation constant β_n, which is the product of the stepwise formation constants, may be expressed as follow,

$$M + nX \xrightleftharpoons{\beta_n} Mx_n \qquad \beta_n = \frac{[MX_n]}{[M][X]^n} \tag{2.19}$$

The total concentration of metal ion in the aqueous phase, $[M]_T$, assuming that there are no hydrolysis or side reactions, is,

$$[M]_T = [M] + [MX] + [MX_2] + ... + [Mx_n] \tag{2.20}$$

Substitution of the appropriate stepwise formation constants into equation (2.20) gives,

$$[M]_T = [M] + \beta_1[M][X] + \beta_2[M][X]^2 + ... + \beta_n[M][X]^n \tag{2.21}$$

$$\frac{[M]_T}{[M]} = 1 + \beta_1[X] + \beta_2[X]^2 + ... + \beta_n[X]^n \tag{2.22}$$

If the total metal ion concentration is small in comparison to the total concentration of the anionic ligand, the free anion concentration may be assumed to be that of the total concentration, as the amount of anion complexed with metal ions is negligible. Thus, if the concentration of free anion and the stepwise formation constants are known, and if the total concentration of metal ion in the aqueous phase can be experimentally determined, the free metal ion concentration [M] in the aqueous phase can be calculated from equation (2.22). Hence the concentrations of the other species present in the aquesous phase can be calculated by incorporating the appropriate stepwise formation constants to the equation:

$$\frac{[MX]}{[M]_T} = \frac{\beta_1[X]}{1 + \beta_1[X] + \beta_2[X]^2 + ... + \beta_n[X]^n} \tag{2.23}$$

$$\frac{[MX_2]}{[M]_T} = \frac{\beta_2[X]^2}{1 + \beta_1[X] + \beta_2[X]^2 + \ldots + \beta_n[X]^n} \qquad (2.24)$$

Therefore the concentration of the neutral metal species, $CdCl_2$ and $CuCl_2$, can be calculated as below,

$$[CdCl_2] = \frac{[Cd(II)]_T\beta_2[Cl^-]^2}{1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2 + \beta_3[Cl^-]^3 + \beta_4[Cl^-]^4} \qquad (2.25)$$

$$[CuCl_2] = \frac{[Cu(II)]_T\beta_2[Cl^-]^2}{1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2 + \beta_3[Cl^-]^3 + \beta_4[Cl^-]^4} \qquad (2.26)$$

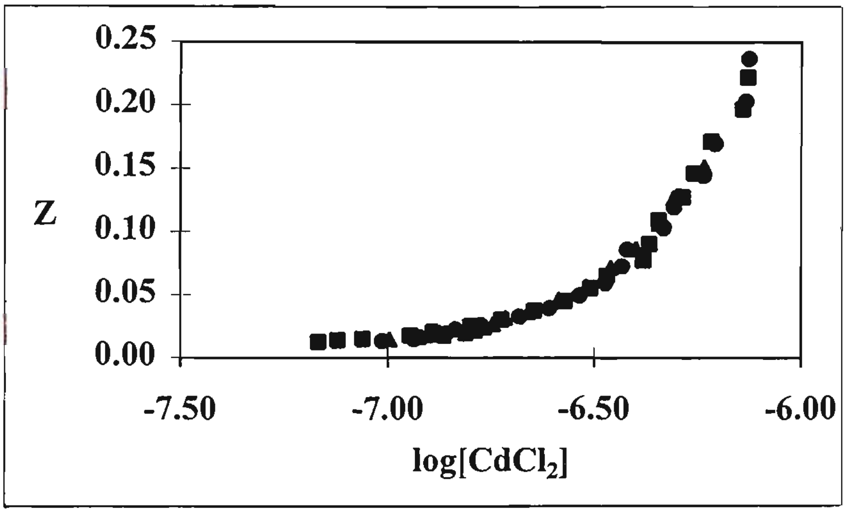


Figure 2.4 Equilibrium data for the extraction of Cd(II) from 2M hydrochloric acid solution using Aliquat 336 in Shellsol AB solvent (▲ 0.04M Aliquat 336; ● 0.06M Aliquat 336; ■ 0.08M Aliquat 336. The aqueous phase Cd(II) concentration range was 0.0006 to 0.02M)

Figure 2.4 and 2.5 represent the equilibrium data (Z vs $\log[CdCl_2]$ or $\log[CuCl_2]$) for the extraction of Cd(II) and Cu(II), respectively, from hydrochloric acid solutions by various concentrations of Aliquat 336 in Shellsol AB. Results for both metal ions clearly demonstrate that the data points for the various concentrations of Aliquat 336 all lie close to a common curve. Such a distribution is strongly indicative of only one complex is being extracted into the organic phase. Daud and Cattrall [60] have reported the extraction of Cu(II) from HCl solutions using Aliquat 336 in chloroform. In their work, they investigated the extraction of Cu(II) from relatively low HCl concentrations. The data points obtained for this system lie close to a common curve, thus, they concluded that there was only one metal complex being extracted into the organic phase [60]. They further concluded that the extracted metal complex was the singly charged anionic species, $CuCl_3^-$, as this species was the dominant species within the HCl concentration range studied [60].

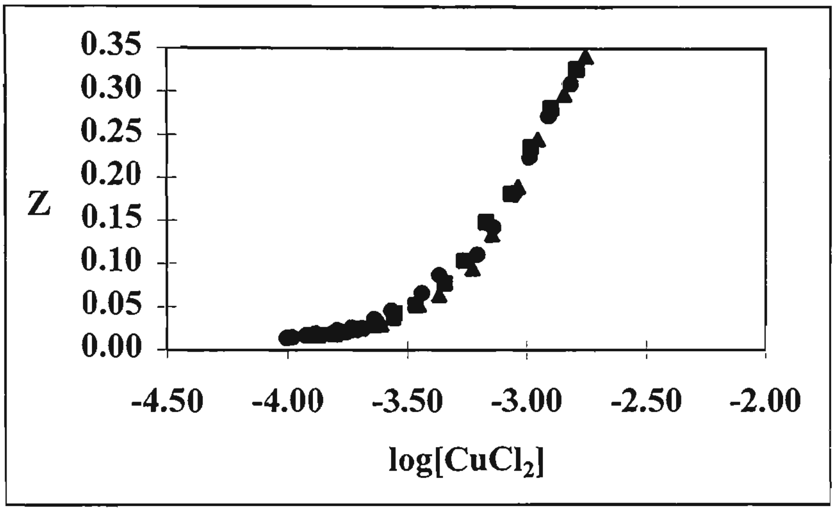


Figure 2.5. Equilibrium data for the extraction of Cu(II) from 3M hydrochloric acid solution using Aliquat 336 in Shellsol AB (▲ 0.04M Aliquat 336; ● 0.08M Aliquat 336; ■ 0.12M Aliquat 336. The aqueous phase Cu(II) concentration range was 0.003-0.25M)

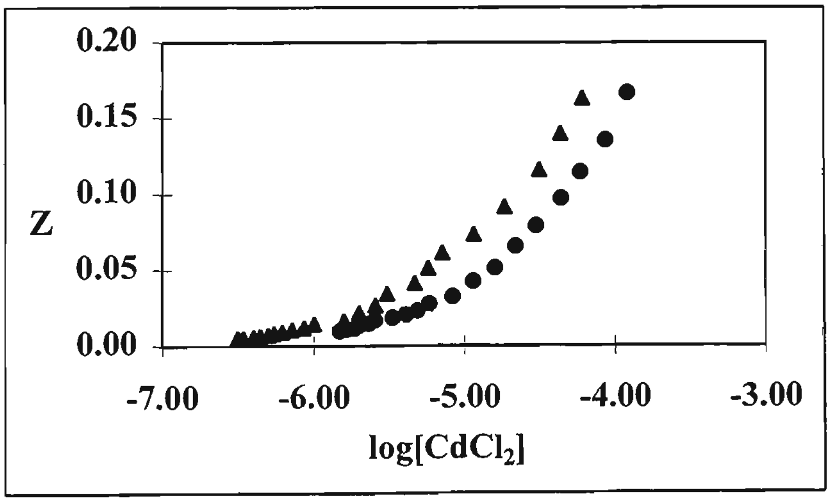


Figure 2.6 Equilibrium data for the extraction of Cd(II) from 2M hydrochloric acid solution using Aliquat 336 in chloroform (▲ 0.04M Aliquat 336; ● 0.06M Aliquat 336). The aqueous phase Cd(II) concentration range was 0.0006 to 0.02M)

In the present study, the extracted metal complex is also most likely to be the singly charged anionic species, $CdCl_3^-$ or $CuCl_3^-$. Further discussion on the average composition of the extracted complex will be given in the following section.

The extraction of Cd(II) using Aliquat 336 in chloroform reported previously by Daud and Cattrall showed, however, that more than one species were extracted into the organic phase and these species were identified as $CdCl_3^-$ and $CdCl_4^{2-}$ [60]. This was shown by the plots of Z against $\log[CdCl_2]$ at different Aliquat 336 concentrations obtained for this system which did not fall on the same curve. To re-enforce this point, the extraction of Cd(II) using Aliquat 336 in chloroform was re-investigated at two different Aliquat 336 concentrations (Figure 2.8). The results clearly show that the points on the Z against $\log[CdCl_2]$ plots did not fall on the same curve. It is therefore re-confirmed experimentally that if the Z against $\log[MCl_2]$ plots at different Aliquat 336 concentrations fall on a common curve, there may only be one species being extracted into the organic phase.

2.3.3.2 Average composition of the extracted complex

To validate the above assumption that only one metal species is being extraction into the organic phase for the extraction of Cd(II) and Cu(II), the stoichiometry of the species formed in the organic phase is evaluated. This is done by using the integration method of Sillén [123] as described below.

A general expression can be written to describe the equilibrium reaction for Cd(II) and Cu(II) extraction system [60]. This expression makes no assumptions concerning the stoichiometry of the extracted complex, and for the sake of simplicity involves the reaction of Aliquat 336 with the species MCl_2 ($CdCl_2$ or $CuCl_2$) from the aqueous phase.

$$qR_3MeN^+Cl^-_{org} + pMCl_{2aq} \rightleftharpoons (R_3MeN^+Cl^-)_q(MCl_2)_{p\ org} \qquad (2.27)$$

For the extraction of Cd(II) or Cu(II) from hydrochloric acid solutions by Aliquat 336 in Shellsol AB system, it is expected that the extraction involves the monovalent and divalent anionic complexes $CdCl_3^-$ and $CdCl_4^{2-}$ or $CuCl_3^-$ and $CuCl_4^{2-}$. These monovalent and divalent anionic species were found to be the extracted metal species for the extraction of Cd(II) or Cu(II) in chloroform system [60].

The stoichiometry of the species formed in the organic phase of the present system can be evaluated using the integration method proposed Sillén [123] which was later described in detail by Högfelt and Fredlund [141]. In this method the average $\bar{p}$ and $\bar{q}$, which are the average numbers of MCl_2 and $R_3MeN^+Cl^-$ moieties per complex molecules respectively, are evaluated from the Z versus $\log[MCl_2]_{aq}$ experimental data plot, assuming that the law of mass action is valid [141].

According to previous studies [108, 123, 141], the average $\bar{p}$ and $\bar{q}$ can be evaluated from the following equations [108]:

$$\bar{q} = \frac{\bar{p}}{Z}\left[1 - 10^{\left[(-\int DdZ - \int Zd\ln[MCl_2])/2.303\right]}\right] \qquad (2.28)$$

$$\bar{p} = \frac{-Z}{\left[\int DdZ + 10^{\left[(-\int DdZ - \int Zd\ln[MCl_2])/2.303\right]} - 1\right]} \qquad (2.29)$$

When employing the above approach, the following treatments are required to obtained the values of $\bar{p}$ and $\bar{q}$.

From the data given in the plot of Z against log $[MCl_2]_{aq}$, a plot of $\log[MCl_2]_{aq}$ against $\log[\text{Aliquat } 336]_{Total}$, for constant Z, can be obtained. The latter plot is then used to evaluate the D value by the taking partial derivative of $\text{Log}[MCl_2]_{aq}$ (or $\ln[MCl_2]_{aq}$) against $\log[\text{Aliquat } 336]_{Total}$ (or $\ln[\text{Aliquat } 336]_{Total}$):

$$\left[\frac{\partial\, ln[MCl_2]}{\partial\, ln[\text{Aliquat } 336]}\right]_Z = -D \qquad (2.30)$$

where D is obtained from the slope of the plot.

For the extraction of Cd(II) or Cu(II) from hydrochloric acid solutions by Aliquat 336 in Shellsol AB, as are presented in Figure 2.4 and 2.5, the experimental points for various concentrations of Aliquat 336 all lie close to the same curve. Thus, the -D value various concentrations of Aliquat 336 all lie close to the same curve. Thus, the -D value (equation (2.30)) is zero as the slope of the plot $\log[MCl_2]_{aq}$ against $\log[\text{Aliquat 336}]_T$ is zero. Therefore, the value of the integral, $\int D\,dZ$, in equations (2.28) and (2.29) equals to zero. These equations then become

$$\bar{q} = \frac{\bar{p}}{Z}\left[1 - 10^{\left[-\int Z d\ln[MCl_2]/2.303\right]}\right] \qquad (2.31)$$

$$\bar{p} = \frac{-Z}{10^{(-\int Z d\ln[MCl_2]/2.303)} - 1} \qquad (2.32)$$

Substituting equation (2.32) into equation (2.31), $\bar{q}$ can then be calculated as:

$$\bar{q} = \frac{-Z}{\left[10^{(-\int Z d\ln[MCl_2]/2.303)} - 1\right]} \times \frac{\left[1 - 10^{(-\int Z d\ln[MCl_2]/2.303)}\right]}{Z} \qquad (2.33)$$

$$\bar{q} = \frac{-Z}{-\left[1 - 10^{(-\int Z d\ln[MCl_2]/2.303)}\right]} \times \frac{\left[1 - 10^{(-\int Z d\ln[MCl_2]/2.303)}\right]}{Z} = 1 \qquad (2.34)$$

From the general expression of the equilibrium reaction (equation (2.27)) it is clear that if $\bar{q}$ equals to 1, then $\bar{p}$ must equal to 1. Thus, it can be concluded that Cd(II) or Cu(II) complexes extracted into Aliquat 336/Shellsol AB system has the formulation of $R_3MeN^+CdCl_3^-$ or $R_3MeN^+CuCl_3^-$. In other words, the metal ion/extractant ratio in the extracted complexes is 1:1. On the other hand, the metal ion/extractant ratios of the complexes extracted into the Aliquat 336/chloroform system must include both 1:1 and 1:2, since the points on the Z against $\log[MX_2]$ plots for the extraction of Cd(II) or Cu(II) from the Aliquat 336/chloroform system did not lie on the same curve.

For the extraction of Cd(II) and Cu(II) from hydrochloric acid solutions in the Aliquat 336/Shellsol AB system, the extraction reactions can be written as,

$$(R_3MeN^+Cl^-)_{org} + CdCl_3^-{}_{aq} \overset{k_{11}}{\rightleftharpoons} (R_3MeN^+CdCl_3^-)_{org} + Cl^-_{aq} \qquad (2.35)$$

$$(R_3MeN^+Cl^-)_{org} + CuCl_3^-{}_{aq} \overset{k_{11}}{\rightleftharpoons} (R_3MeN^+CuCl_3^-)_{org} + Cl^-_{aq} \qquad (2.36)$$

Here, *org* and *aq* represent the organic and the aqueous phases respectively. k_{11} is the extraction equilibrium constant for the monovalent metal ion/Aliquat 336 complex.

Equations (2.35) and equation (2.36) are written with the assumption that anion-exchange reactions are occurring. These equations also suggest that reactions can occur either in the bulk phases or at the aqueous-organic interface. For quaternary ammonium salts, which are highly surface active, it is reasonable to assume that the anion-exchange reactions are occurring at the interface. This assumption is supported by the interfacial tension studies previously reported [117].

The extraction equilibrium constants for the extraction of species MCl_3^- ($CdCl_3^-$ or $CuCl_3^-$) from the aqueous phase can be written as,

$$k_{11} = \frac{[R_3MeN^+MCl_3^-]_{org}[Cl^-]_{aq}}{[R_3MeN^+Cl^-]_{org}[MCl_3^-]_{aq}} \qquad (2.37)$$

The above equation is written with the assumption that the activity coefficients of species in the organic phase are unity, or at least constants, and those in the aqueous phase are also constants. This assumption is not unreasonable since Sekine and Hasegawa [142] pointed out that when the ionic composition of a medium is kept as constant as possible, by using a large excess of an 'inert' electrolyte, the activity coefficients of the chemical species in the solution are practically constant. Paimin and Cattrall [143] have also shown that the activity coefficients of high molecular weight quaternary ammonium salt are approximately equal to unity at concentrations below 0.001M and nearly constant at concentrations above 0.05M. Hence, it is assumed in this study that the activity coefficients of Aliquat 336 in the concentration range of 0.04-0.12M are constant.

As previously discussed, the equilibrium study results are plotted in the form of Z versus the concentration of species MCl_2 at equilibrium phase. For the convenience of the following discussion, equation (2.37) is rewritten in the following form.

$$\frac{[R_3MeNCl]_{org}}{[R_3MeNMCl_3]_{org}} = \frac{[Cl^-]_{aq}}{k_{11}[MCl_3^-]_{aq}} \tag{2.38}$$

The total concentration of Aliquat 336 in the organic phase, $[R_3MeNCl]_{T,org}$, is,

$$[R_3MeNCl]_{T,org} = [R_3MeNCl]_{org} + [R_3MeNMCl_3]_{org} \tag{2.39}$$

Substituting equation (2.39) into equation (2.38) leads to:

$$\frac{[R_3MeNCl]_{T,org} - [R_3MeNMCl_3]_{org}}{[R_3MeNMCl_3]_{org}} = \frac{[Cl^-]_{aq}}{k_{11}[MCl_3^-]_{aq}} \tag{2.40}$$

Since Z is defined as the ratio of the total metal concentration in the organic phase to the total Aliquat 336 concentration in the organic phase, then equation (2.40) can be written as,

$$\frac{1}{Z} - 1 = \frac{[Cl^-]_{aq}}{k_{11}[MCl_3^-]_{aq}} \tag{2.41}$$

Take logarithms for equation (2.41) leads to:

$$\log(1/Z - 1) = -\log[MCl_3^-]_{aq} - \log k_{11} + \log[Cl^-]_{aq} \tag{2.42}$$

This equation describes a linear relationship between log(1/Z-1) and $\log[MCl_3^-]_{aq}$ with a slope of -1. This relationship is plotted in Figure 2.7 for Cd(II) and Figure 2.8 for

Cu(II). Equilibrium concentrations of the species [MCl_3^-] were again calculated from the appropriate formation constants.

Good linearity is seen in both Figures 2.7 and 2.8 with a slope of -1.42 and an R^2 of 0.98 for Cd(II) and -1.35 and 0.99 for Cu(II). In an ideal case, the plot of the equation (2.42) should result in a slope of -1. In cases of Cd(II) and Cu(II) presented here, the slopes are smaller than -1. Similar situation was also encountered in the study by Argiropoulos *et al.* [51]. The linearity of both plots offers further support to the proposed formation of a single complex in the organic phase with a 1:1 metal ion/Aliquat 336 complex stoichiometry. The extraction equilibrium constants for these metals can be calculated from equation (2.42) and from the intercepts of Figure 2.7 and Figure 2.8. The values of $\log k_{11}$ for the extraction of Cd(II) and Cu(II) are 7.81 and 3.39 respectively (Table 2.2).

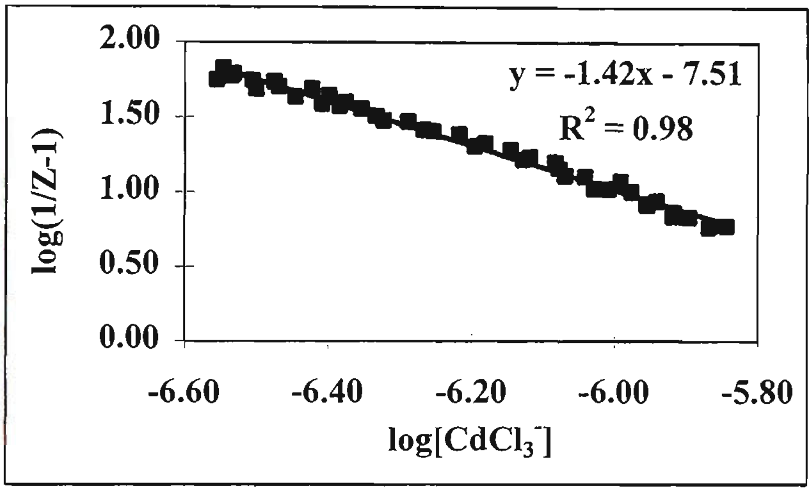


Figure 2.7 Relationship between log(1/Z-1) and log[$CdCl_3^-$]$_{aq}$

Table 2.2 The extraction equilibrium constants for Cd(II) and Cu(II)

Metals	Shellsol AB	chloroform[60]	
	$\log k_{11}$	$\log k_{11}$	$\log k_{12}$
Cd(II)	7.81	3.19	5.67
Cu(II)	3.39	2.61	

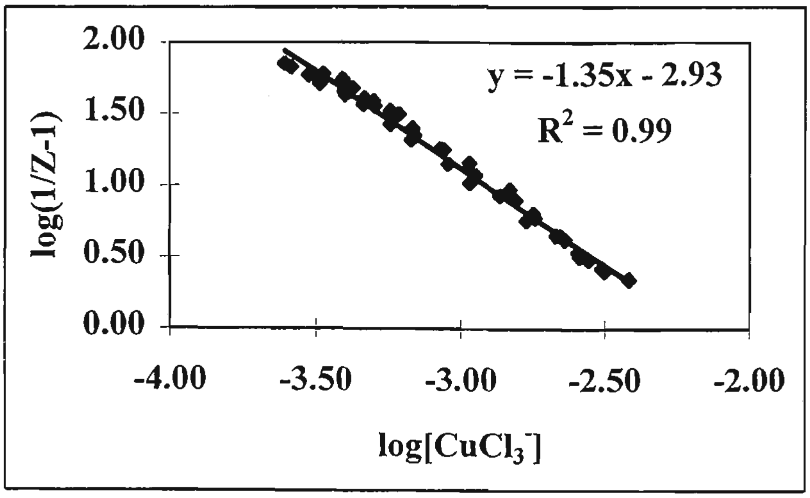


Figure 2.8 Relationship between log(1/Z-1) and log$[CuCl_3^-]_{aq}$

The high value for the extraction constant of Cd(II) demonstrates a much stronger affinity of the Aliquat 336 cation to the anionic cadmium species compares to the anionic copper species. This suggests that the Aliquat 336/Shellsol AB system is more suitable for the recovery of cadmium from chloride solutions.

In previous studies involving extraction with Aliquat 336, the mechanism for the Aliquat 336 extraction proposed was the interfacial mechanism [107]. In their study, considerable evidence was obtained for a reaction mechanism which consisted of fast ion-exchange at the interface followed by a rate determining step which involved the replacement of the metal containing complex at the interface by reagent in the bulk phase. A similar mechanism is also proposed in the present system.

In the extraction of Cd(II) and Cu(II) using Aliquat 336, Table 2.2 clearly shows a significant different between the extraction equilibrium constant for the $[R_3MeN^+CdCl_3^-]$ complex to that for the $[R_3MeN^+CuCl_3^-]$ complex. This different suggests that Cd(II) can be easily separated from Cu(II) using Aliquat 336 from chloride solutions.

Table 2.3 Predominant chloro complexes in aqueous hydrochloric acid solutions of various concentration at room temperature [144]

Central ion	1M HCl	8M HCl	13M HCl
Cu(II)	$CuCl(H_2O)_3^+$	$CuCl_2(H_2O)_2$, $CuCl_3^-$	$CuCl_4^{2-}$
Cd(II)	$CdCl_3(H_2O)^-$	$CdCl_4^{2-}$	$CdCl_4^{2-}$

The difference in the extraction ability of Aliquat 336 towards the different metals can be explained in term of the extent of hydration of these metal ions. In general, hydration of a metal ion of a smaller ionic radius is stronger than that of a larger ionic radius. Hydration of a cation is usually larger than that of an anion of the same charge [145]. Table 2.3 shows the various metal species in different HCl concentrations. It reveals the predominant chloro complexes in the various concentrations of hydrochloric acid solutions at room temperature. For Cu(II), the predominant chloro-complexes are $CuCl(H_2O)_3^+$ in 1M HCl solution, $CuCl_2(H_2O)_2$ and $CuCl_3^-$ in 8M HCl solution, and $CuCl_4^{2-}$ in 13M HCl solution. For Cd(II), the predominant chloro- complex is $CdCl_3(H_2O)^-$ in 1M HCl solution and $CdCl_4^{2-}$ in 8M and 13M HCl solutions.

Table 2.3 clearly shows that, at the concentration of HCl used in the extraction of Cu(II) for the present system, insignificant amount of the extractable anionic Cu(II) species is available in the solution, as the predominant species is the cationic species, $CuCl(H_2O)_3^+$. In contract, the predominant species of Cd(II) is the extractable anionic species, $CdCl_3(H_2O)^-$. For this reason the equilibrium extraction constant (k_{11}) for Cd(II) is significantly higher than that for Cu(II).

2.3.4 The Effect of Diluents on The Extraction of Cd(II) and Cu(II) Using Aliquat 336

The extraction of a metal complex from one phase to another is governed by intermolecular interactions between the extractant and the metal species to be extracted, the extractant and the diluent, and the metal complexes and the diluent. As mentioned previously in Section 2.1.5, several studies of the intermolecular interactions in some extraction systems have been reported [110, 111, 129-134]. However, no general rule has yet been established to predict the successfulness of a given extraction system. In the following discussion, attempts were made to interpret and explain the extraction behaviours of Cd(II) and Cu(II) using Aliquat 336 in different diluent systems.

The fundamental descriptions of the intermolecular interactions are given by van der Waals forces which include forces resulting from dispersion, dipole-dipole and dipole-induced dipole interactions [146]. The dispersion force is dependent upon the product of polarizabilities of the interacting molecules or ions [146] and is usually the largest among van der Waals forces.

For the extraction systems studied in this chapter, the extractant used was Aliquat 336 and the diluent used to form the organic phases was Shellsol AB. Shellsol AB contains approximately 99% aromatic compounds [135]. In previous study [60], the extractant used was also Aliquat 336 but the diluent used was chloroform. Under the same extraction conditions the two systems show a significant difference in the extraction equilibrium constants (Table 2.2), the extraction equilibrium constant value the of Cd(II) or Cu(II) in Shellsol AB system was found to be higher than that in the chloroform system.

According to Diamond's work [130] in which he proposed that the extraction efficiency of an extractant for the metal complex could be affected by the extractant-diluent interaction. Chloroform (being a polar solvent [147]), and Shellsol AB (being non-polar or less polar solvent [135]), are therefore expected to exhibit different interactions with the Aliquat 336 and the metal complex. Chloroform, being a polar solvent, is likely to have a stronger intermolecular interaction with Aliquat 336 than Shellsol AB. As a result, the activity of Aliquat 336 in chloroform is likely to be lower than in Shellsol AB, since Aliquat 336 is solvated to a greater extend in chloroform than in Shellsol AB. This may lead to a lower affinity of the Aliquat 336 for Cd(II) or Cu(II), resulting in the lower value of the equilibrium constant, as shown by the results.

2.4 CONCLUSION

It is shown in this chapter that the predominant extracted species for Cd(II) or Cu(II) from HCl solutions for the various concentrations of Aliquat 336 dissolved in Shellsol AB was the [1:1] complex, i.e. $R_3MeN^+CdCl_3^-$ or $R_3MeN^+CuCl_3^-$, respectively.

The experimental results in this study further confirms that the extraction of Cd(II) from HCl solutions for the various concentrations of Aliquat 336 in chloroform involved the extraction of two complexes, and they were [1:1] and [1:2] complexes (i.e. $R_3MeN^+CdCl_3^-$ and $(R_3MeN^+)_2CdCl_4^{2-}$ respectively).

The study of the organic-aqueous contact time versus the extraction efficiency indicates that the extraction rates of Cd(II) and Cu(II) by Aliquat 336 in both Shellsol AB and chloroform were high. Extraction equilibrium was found to be established in less than 1 minute of phase contact for both metal species.

This study also demonstrates that chloride ions must be present in the aqueous phase in order for the emulsion-free phase separation to occur after the phase contact.

The results also show that the extraction equilibrium constant for Cd(II) using Aliquat 336 in Shellsol AB system was significantly higher than that for the chloroform system. The difference in the extraction equilibrium constant of the two systems was likely to be related to the polarity of the solvent used.

Cd(II)/HCl/Aliquat 336/Shellsol AB system gave higher extraction efficiency than Cu(II)/HCl/Aliquat 336/Shellsol AB system. This suggests that Cd(II) can be separated from Cu(II) using Aliquat 336 from HCl solutions.

Some of the findings in this chapter have been used as guidelines for the work presented in the following chapters.

CHAPTER THREE

EXTRACTION OF Cd(II) AND Cu(II) IN HYDROCHLORIC ACID SOLUTIONS BY ALIQUAT 336 /PVC MEMBRANE

3.1 INTRODUCTION

Membrane separation technology has become increasingly important during the last two decades. Today membrane separation technology finds its applications in many fields including water and waste water treatment [29, 35-37, 148], biotechnology [30, 36, 149], pharmaceutical industry [32], food technology [29, 148] and metal separation [10-14], to name just a few. The number of such applications is still growing.

Scientifically, membrane separation processes may be classified into different categories based on the different mechanisms and principles involved in the separation or the different systems in which membrane separation technique is applied. Despite the vast variations among these applications in either separation mechanisms involved or technical details adopted, all membrane separation processes have one thing in common, they all use membranes of some kind to carry out separations.

Membrane is the heart of every membrane separation processes and can be considered as a permselective barrier between the two phases, namely the feed and the receiver phases [84]. A schematic representation of membrane separation is given in Figure 3.1.

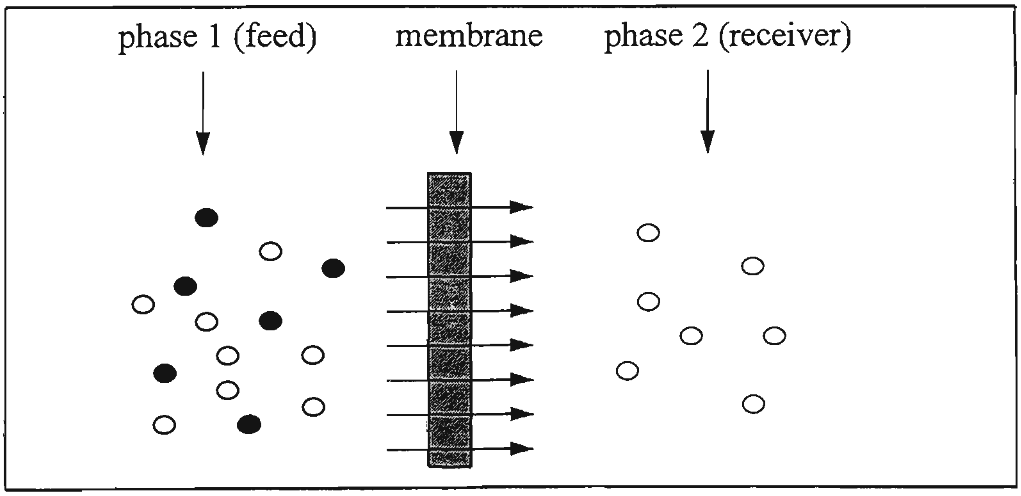


Figure 3.1. Schematic representation of membrane separation process (○ is component A, ● is component B and ➞ is the driving force.)

Phase 1 is usually considered as the feed whereas phase 2, the receiver. Separation is achieved because the membrane facilitates the transport of one component from the feed mixture more readily than of other components [84].

A general definition of a membrane is that membrane is an interphase that separates two liquid phases and restricts (or facilitates) the transport of various chemical species in a highly selective manner [154]. A membrane may be homogeneous or heterogeneous, symmetric or asymmetric in structure. It may be solid or liquid, and it may either be neutral or carry electric charge(s), which may be positive or negative or both.

The thickness of a membrane varies between less than 100 nm to more than a centimetre [154]. Mass transport through a membrane may be caused by diffusion of molecules or by convection induced by gradients of electrical potential, concentration, pressure or temperature. The performance of the membrane is determined by two parameters, the *selectivity* and the *flow* through the membrane. The latter, often denoted as the flux or the transport rate of the membrane, is defined as the volume (or mass, or number of moles) flowing through the membrane per unit area per unit time [84].

3.1.1 Flux and Driving Forces in Membrane Separation Processes

Every membrane separation process is characterized by the use of a membrane of certain properties to accomplish a particular separation. The flux of a component is determined by the driving force or forces acting on this component in the membrane. The mobility and the concentration of the solute in the membrane also determine the flux produced by a given driving force [154].

In membrane separation processes, the driving forces that cause a significant flux of a certain component are of key importance practically. These driving forces, although in most cases are ultimately connected to the chemical potential of the chemical species, can be hydrostatic pressure, concentration difference, or electrical potential difference [154]. The difference in hydrostatic pressure between two phases separated by a membrane can lead to a volume flux and to the separation of chemical species if the hydrodynamic permeability of the membrane is different for different components. The concentration difference between two phases separated by a membrane can lead to a transport of component(s) in the membrane and to the separation of various chemical species in the system if the diffusion coefficients of the various chemical species in the membrane are different. The difference in the electrical potential between two phases separated by the membrane can lead to a transport of the component(s) and to the separation of various chemical species if these species have different mobilities in the membrane due to the number (or the sign) of charge(s) they carry.

In the present membrane extraction system, the membrane used (Aliquat 336/PVC) is homogeneous in nature. The metal species transports through the membrane under the driving force of the chemical potential difference of the metal complex on two sides of the membrane. Since the pressure and temperature are held constant during extraction experiments, the chemical potential of a metal complex is determined by the concentration of the metal ion and of the ligand. The relationship between the mass flux and the concentration gradient is set by the Fick's law [154] as follow,

$$J_x = -D\, dc/dx \qquad (3.1)$$

where J_x is the mass flux along a direction denoted by x axis (in practical term, x-axis lies perpendicular to the membrane), D is the diffusion coefficient, dc/dx is the driving force, expressed as the concentration gradient along that direction (x-axis). Equation (3.1) is the theoretical basis of the mathematical modelling used in later sections of this chapter [88].

3.1.2 Membranes and Membrane Extraction

Membranes for separation processes can be classified into the following groups according to the nature of the driving forces which cause the transport of the component(s) through the membrane [155].

1. Pressure difference membranes. For example, reverse osmosis, ultrafiltration, microfiltration, membrane gas and vapour separation and pervaporation.
2. Temperature difference membranes. For example, membrane distillation.
3. Concentration difference membranes. For example, dialysis and membrane extraction.
4. Electrical potential difference membranes. For example, electrodialysis.

Membrane extraction is a relatively new separation technology which combines the membrane technology with the extraction technology [156]. In membrane extraction, an aqueous phase that contains the metal species to be extracted, or the feed phase, is in contact with a membrane on one side. The membrane may be a liquid or a solid or a polymer film. Within this membrane, an organic component, or the extractant, is held. On the other side of the membrane is the second aqueous phase, or the receiver phase, which is so formed that the metal species to be extracted would have a much lower chemical potential in this phase than in the feed phase. The metal species transports from the feed phase into the membrane. Then, driven by the difference of the chemical potential, the metal species moves across the membrane and into the receiver phase. The difference in chemical potential of the metal species between the feed and the receiver phases may be created by using a receiver phase that is initially devoid of the metal species. In this system concentration difference is naturally the driving force. However, a more effective way that can be used to maximized the difference of chemical potential is to manipulate the species and concentration of ligands in the feed and receiver phases. In this way, it is possible to concentrate the metal species in the receiver phase. This is experimentally demonstrated in a latter section.

The most popular membranes used in membrane extraction are bulk liquid membranes (BLM), emulsion liquid membranes (ELM) and supported liquid membranes(SLM). These membranes have been extensively studied in the last two decades [67, 71, 82, 149, 157-161]. However, the instability due to the 'bleeding' of the reagent from these membranes to the aqueous phase often poses problems to their industrial applications. With respect to the membrane stability, polymer membranes may be feasible [162]. The main disadvantage of the polymer membranes is their poor selectivity toward metal ions [162]. Thus, the development of the new types of membranes which possess a comparable metal extraction ability to liquid membranes and a comparable stability to polymer membranes is an important research topic which may lead to break-through in the industrial application of membrane extraction [86, 163].

3.1.3 Metal Ions Extraction Using PVC Based Membranes

The use of PVC based membranes in the extraction of metal ions has attracted considerable research interests [73-76, 83, 164]. The application of PVC based membranes in various extraction systems has been considered to have advantages over conventional solvent extraction and other liquid membrane extraction systems in the following respects: (a) PVC based membrane shows considerable mechanical strength and stability. (b) It is a 'solventless' extraction system, thus eliminates the secondary environmental pollution by organic solvents. (c) The membrane uses very small amount of extractant or reagent and is therefore economical. (d) The membrane can be used to concentrate trace amount of metals from a solution for analysis. (e) The metal extracted into the membrane can be directly analysed using methods such as spectrophotometry.

Aliquat 336/PVC membrane has been studied by Argiropoulos *et al.* for the extraction of Au(III) from hydrochloric acid solutions and for separating of Au(III) from Cu(II) [83]. In this membrane, Aliquat 336 acts as the extractant, the carrier for the metal complex and also as the plastisizer to PVC. It forms homogeneous membranes with considerable strength and stability.

Aliquat 336/PVC membrane is studied in this work for the extraction of Cd(II) and Cu(II) from hydrochloric acid solutions. Such a choice of extraction systems is based on the conclusion drawn from the previous chapter (Chapter Two) that solvent extraction of Cd(II) using Aliquat 336 in Shellsol AB has a high extraction efficiency to Cd(II) and, under similar condition, has a low extraction efficiency to Cu(II). It is of an interest to see whether Aliquat 336/PVC membrane also demonstrates such a difference in extraction efficiency of the two metal ions.

3.1.4 Transport Mechanism in Aliquat 336/PVC Membrane Extraction System

According to previous study [88], the transport mechanism of the metal ion in the Aliquat 336/PVC membrane extraction system may be schematically represented as in Figure 3.2. The following four steps were proposed to be involved in the extraction.

(1) complexation between the Aliquat 336 and metal ions at the feed/membrane interface,

(2) diffusion of the Aliquat 336-metal ion complex across the membrane,

(3) decomplexation of the Aliquat 336-metal ion complex at the membrane/the receiver interface and

(4) diffusion of the free Aliquat 336 back to the feed phase/membrane interface.

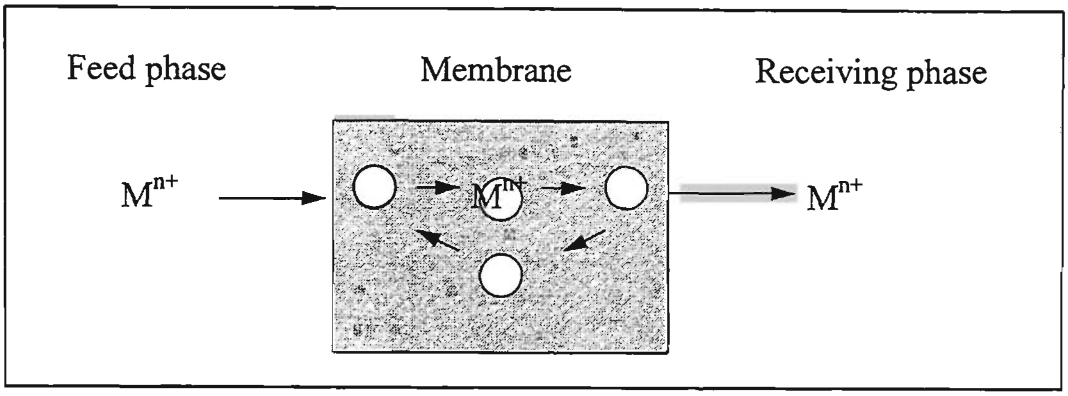


Figure 3.2. The transport mechanism of metal ions in the Aliquat 336/PVC membrane extraction system (M^{n+} = the metal ions and ○ = extractant molecules)

As can be seen from Figure 3.2, there are two factors which contribute to the transport of metal ions, one is the rate of complex formation or decomplexation at the two membrane/aqueous solution interfaces, the other is the rate of diffusion of the metal ion complex and the free Aliquat 336 across the membrane. Thus, the transport rate of the metal ions is determined by both the chemical reaction and by the diffusion factors.

Membrane extraction studies in the present work were carried out in two parts. In the first part, extraction of metal species from both phases of the system to the membrane was investigated. In the second part, extraction of metal species from the feed phase through the membrane into the receiver phase (in a continuous manner) was studied.

3.2 EXPERIMENTAL

3.2.1 Materials

3.2.1.1 <u>Reagents</u>

Aliquat 336 (tricaprylylmethylammonium chloride) was obtained from Fluka. The physical appearance of Aliquat 336 at room temperature is a straw-colored and viscous liquid. It was used as received.

Hydrochloric acid (HCl), cadmium chloride ($CdCl_2 \cdot H_2O$) and cupric chloride ($CuCl_2 \cdot 2H_2O$) were analytical reagents from BDH.

High molecular weight polyvinylchloride (PVC) was obtained from Fluka. The polymer is in the form of fine white powder.

Tetrahydrofuran (THF) was HPLC grade from BDH and was further treated by passing through an activated alumina column to remove the stabilizer and peroxides.

Cd(II) and Cu(II) standard solutions were obtained from BDH. The concentration of both standards was 1000mg/L or 1000ppm.

Milli-Q water was used for all dilutions.

3.2.1.2 Preparation of hydrochloric acid solutions

HCl solutions of 2.0M, 3.0M, 0.1M and 0.05M were used to prepare feed and receiver solutions.

3.2.1.3 Preparation of Cadmium(II) solutions

Cd(II) in 2.0M HCl solutions were prepared using cadmium chloride salt ($CdCl_2 \cdot H_2O$). The concentrations of Cd(II) solutions were 119.0 mg/L and 100.0 mg/L.

3.2.1.4 Preparation of Copper(II) solutions

Cu(II) in 3.0M HCl solution was prepared using copper(II) chloride salt ($CuCl_2 \cdot 2H_2O$). The concentration of the Cu(II) solution was 100.0 mg/L.

3.2.1.5 Preparation of membranes

The membranes used in this study were prepared by dissolving a mixture of known amounts of Aliquat 336 and PVC in a minimum volume of THF. The homogeneous solution obtained was then poured into a glass ring (90mm diameter) which was seated on a flat glass plate. A lid was used to cover the glass ring and the THF was allowed to evaporate very slowly overnight. This yielded a colourless, flexible, transparent and mechanically strong membrane. The composition of the membrane is expressed in weight percentage of Aliquat 336 in the membrane (% m/m). The membrane was then peeled from the glass surface and ready to be used for the membrane extraction study.

3.2.1.6 The compositions of membranes

Membranes containing 30%, 40% and 50% Aliquat 336 in PVC (m/m) were prepared. Membranes of Aliquat 336 content higher than 50% were not prepared, since membranes containing more than 50% Aliquat 336 were soft and sticky and mechanically too weak to be used for extraction experiments [83].

3.2.2 Measurement of Membrane Thickness

The measurement of membrane thickness was carried out using a microscope (ISSCO SZM-4) which has a internal scale. The membrane was first carefully cut into a square (54mm^2) and was then vertically mounted on a glass slide. The thickness of the membrane was then examined under the microscope. The thickness of the membrane was obtained by multiplying the measurement reading, which was an average of the readings taken from all sides of the square, with the magnification factor. The accuracy of measurement was ± 0.001 mm.

3.2.3 Membrane Extraction Procedure

Membrane extraction studies were carried out in a two-compartment cell which was thermostated at 25°C in a water bath. Each compartment has a liquid capacity of 60 ml. The membrane was sandwiched between the two compartments which were tightly clamped together. The effective extraction area of the membrane was 9.35 cm^2. Stirring rate of each compartment was controlled and kept at a constant speed. Figure 3.3 shows the schematic diagram of the membrane extraction apparatus.

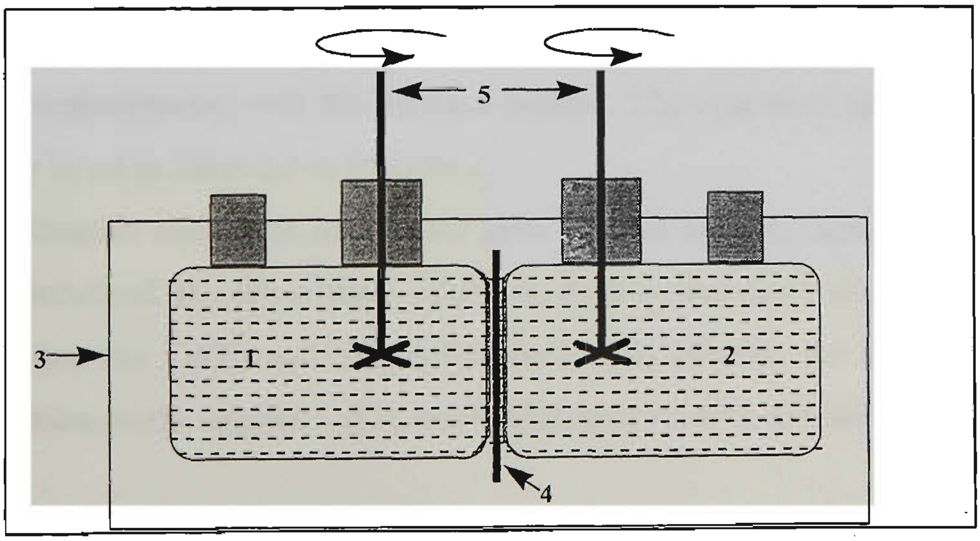


Figure 3.3. Schematic diagram of the membrane extraction apparatus.
(1) Feed phase, (2) Receiver phase, (3) Thermostated water bath,
(4) Membrane, and (5) Stirrers

3.2.3.1 Extraction of Cd(II) and Cu(II) from both phases of the system to the membrane

In the study of extraction of Cd(II) and Cu(II) from both phases of the system to the membrane, an aqueous solution of the same composition was placed in both compartments of the extraction apparatus. The extraction of Cd(II) and Cu(II) by the membrane was monitored by taking 1 ml aliquot of solutions from each compartment at certain intervals and measuring their concentrations using AAS. The analysis of the solutions taken from the two compartments was carried out separately. Each aliquot of solutions removed for analysis was replaced with equal volume of fresh metal solution.

3.2.3.2 Extraction of Cd(II) and Cu(II) from the feed phase through the membrane into the receiver phase (in a continuous manner)

An aqueous solution of Cd(II) and Cu(II) was placed in one compartment (feed phase) of the extraction cell, and a diluted HCl solution (0.05M HCl for Cd(II) and 0.1M HCl for Cu(II)) was placed in the other compartment (receiver phase). The extraction of Cd(II) and Cu(II) from the feed to the receiver phase was monitored by taking 1 ml aliquot of solution from each compartment at certain time intervals for concentration analysis of Cd(II) and Cu(II) using AAS. The analysis of the solutions taken from the two compartments were carried out separately.

3.2.3 Metal Analysis

The concentration of Cd (II) or Cu(II) samples were analyzed by AAS (GBC 902 AA spectrophotometer) with the standard method. The optimized operating parameters used were listed in Table 2.1 in Chapter 2.

A calibration curve was established prior to each analysis using a series of metal standard solutions. In each of these solutions, dilution was done using 2M hydrochloric acid solution for Cd(II) and 3M hydrochloric acid solution for Cu(II), as the HCl concentrations in the original Cd(II) and Cu(II) samples were 2M and 3M, respectively.

3.3 RESULTS AND DISCUSSION

3.3.1 The Extraction of Cd(II) and Cu(II) From Hydrochloric Acid Solutions Using Aliquat 336/PVC Membranes

3.3.1.1 The effect of the membrane composition on the extraction of Cd(II) and Cu(II)

The extraction of Cd(II) and Cu(II) from hydrochloric acid solutions using Aliquat 336/PVC membranes was studied and the decrease in the aqueous metal ion concentration with time was determined. The results of the extraction of Cd(II) using membranes of various compositions are shown in Figure 3.4. For the extraction study of 30% Aliquat 336/PVC membrane, a Cd(II) solution of 120 mg/L was initially used. For the extraction studies of 40% and 50% Aliquat 336/PVC membranes, a Cd(II) solution of 100 mg/L was initially used. The concentration data points shown in Figure 3.4 were calculated by taking the average of the concentrations of both compartments of the cell.

The extraction of Cd(II) by the membrane was evidenced by the decrease of concentrations of Cd(II) in both compartments. All membranes showed active initial extraction and then reached apparent extraction equilibrium after 20 hours of extraction (Figure 3.4). It has been found that the higher the concentration of Aliquat 336 in the membrane, the better was the extraction. In the case of 50% Aliquat 336/PVC membrane, the Cd(II) concentration was reduced to less than 50 mg/L after 20 hours of extraction, which was half of the initial Cd(II) concentration of the feed solution.

Figure 3.5 shows the results for the extraction of Cu(II) using membranes of compositions 30% and 40% Aliquat 336/PVC. The decrease in aqueous Cu(II) concentration with time was also seen for these systems. The decrease of the Cu(II) concentrations in these systems was, however, insignificant. As can be seen in Figure 3.5, only about 10% of Cu(II) was extracted into the membrane after 20 hours of extraction Both the capacity and the rate of extraction of Cu(II) were found to be independent of the composition of the membrane.

The membrane extraction results (Figure 3.4 and 3.5) are in good agreement with those of the solvent extraction using Aliquat 336 as the extractant in that Aliquat 336 extracts Cd(II) better than Cu(II).

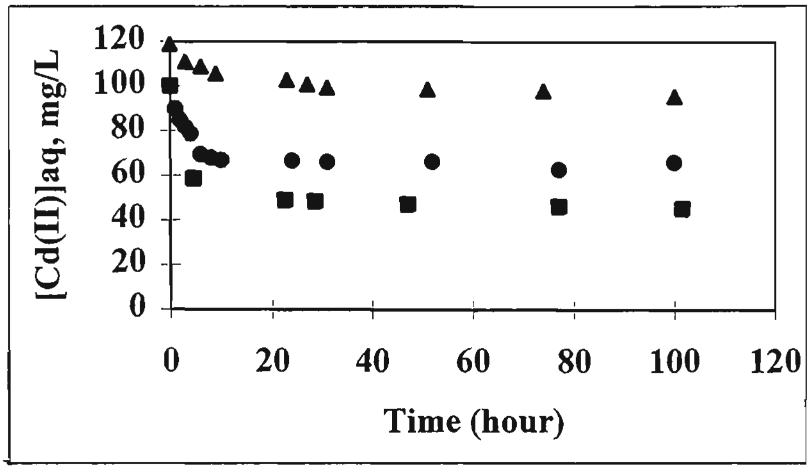


Figure 3.4. Aqueous Cd(II) concentrations vs. the extraction time for various membrane compositions (▲ 30% Aliquat 336/PVC membrane; ● 40% Aliquat 336/PVC membrane and ■ 50% Aliquat 336/PVC membrane) Initial aqueous Cd(II) concentration in 2M HCl solution - 120mg/L for 30% Aliquat 336/PVC membrane and 100mg/L for 40% and 50% Aliquat 336/PVC membranes.

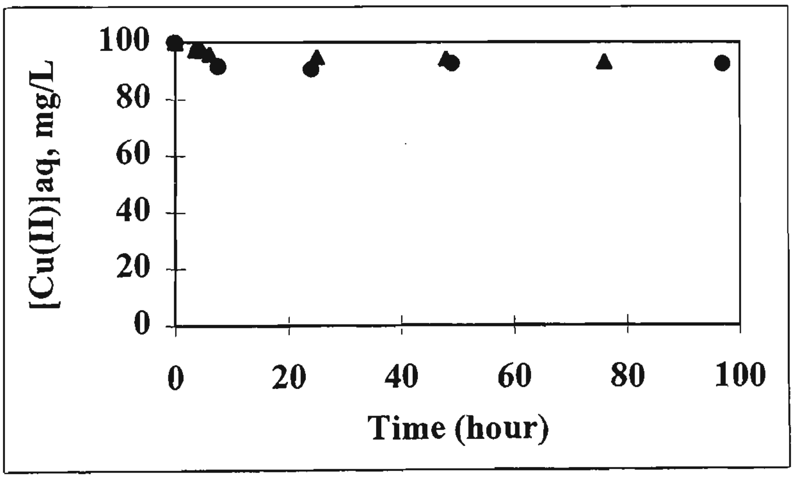


Figure 3.5. Aqueous Cu(II) concentrations vs. extraction time for various membrane compositions (▲ 30% Aliquat 336/PVC membrane; ● 40% Aliquat 336/PVC membrane). The initial Cu(II) concentration of the feed solution was 100mg/L

3.3.1.2 The effect of the membrane thickness on the extraction

Membranes of the same chemical composition but different thickness were studied for the effect of membrane thickness on the extraction of Cd(II). Figure 3.6 shows the extraction performances of a thin membrane (82μm) and a thick membrane (279μm), which were made from Aliquat 336/PVC mixture containing 30% of Aliquat 336. The results show that the extraction was improved when the thicker membrane was used, although the increase in the extraction was not directly proportional to the thickness of the membrane.

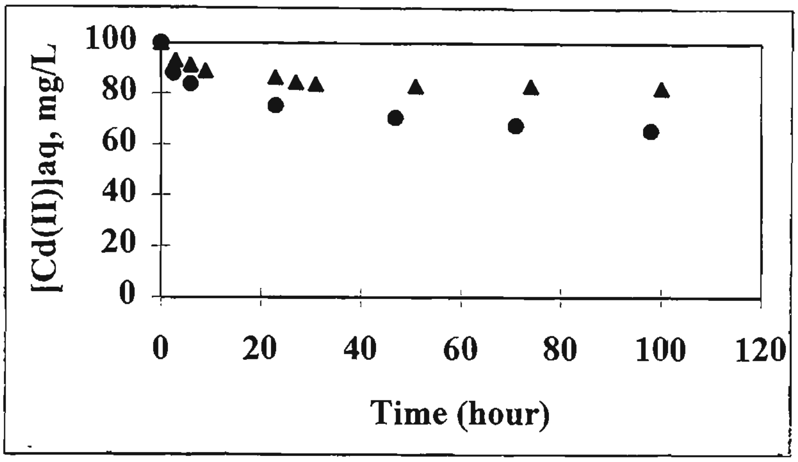


Figure 3.6. The effect of membrane thickness on the extraction of Cd(II). (the membrane composition was 30% Aliquat 336 in PVC, the initial Cd(II) concentration are 100mg/L for both 82μm membrane thickness (▲) and 279μm membrane thickness(●).)

As can be seen, the thicker membrane contained three times more Aliquat 336 than the thinner membrane but the former produced less than two times of the extraction capacity than the latter. At this point it is unclear as to why this occurred. Other investigators have also found similar phenomenon and have reported that the thickness of the membrane was one of the parameters that have significantly influenced the extraction rate and capacity of the membrane [165, 166].

3.3.1.3 The effect of the different sides of the membrane on the extraction

An interesting observation made in the study of Section 3.3.1.1 and Section 3.3.1.2 was that the extraction of Cd(II) by the two sides of the Aliquat 336/PVC membrane was not the same. This is shown in Figure 3.7 to 3.9 as unequal decrease in the concentration of Cd(II) in the two compartments of the extraction cell. Since the membrane was prepared by casting on a piece of flat glass plate, the forming conditions of the two sides of the membrane were not identical, with one side facing glass and the other facing air. Figure 3.7 shows the extraction of Cd(II) using membrane containing 30% Aliquat 336 (membrane thickness: 279μm). In this case, the aqueous phases in the two compartments were sampled and analyzed separately. It is clear from the results in Figure 3.7 that the side formed facing the glass demonstrates a higher apparent extraction capacity.

Various other experiments were conducted in order to eliminated other possibilities or errors that may have been introduced into this system. One of these was to use a thinner membrane (membrane thickness: 82μm) of the 30% Aliquat 336/PVC. The result is shown in Figure 3.8 that similar trend was also observed in this case. Another experiment was conducted such that the membrane was mounted in the reverse way, so that the two sides of the membrane were placed to face different extraction compartments. This was done in order to eliminate the possibility of uneven convection process in the two compartments due possibly to the difference in the size or shape of the two compartments of the extraction cell, although they appear visually identical. The results indicated that the glass-facing side of the membrane still showed higher extraction capacity.

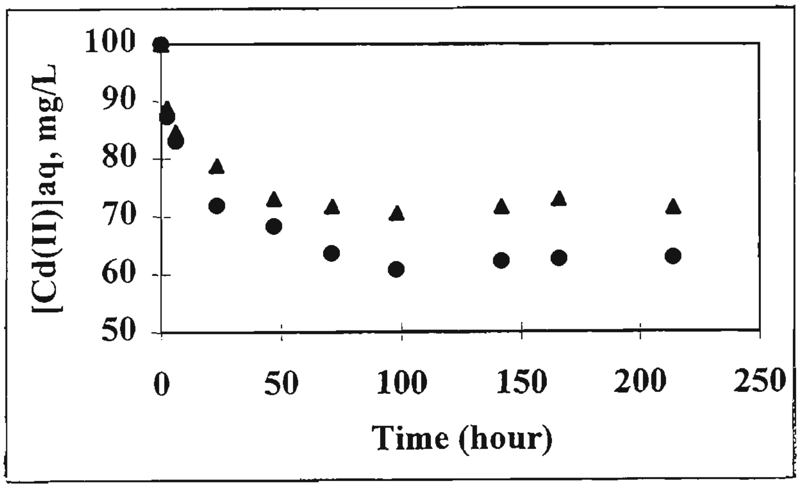


Figure 3.7. Extraction of Cd(II) using 30% Aliquat 336/PVC membrane formed facing air (▲) and facing glass (●) (The thickness of the membrane was 279μm)

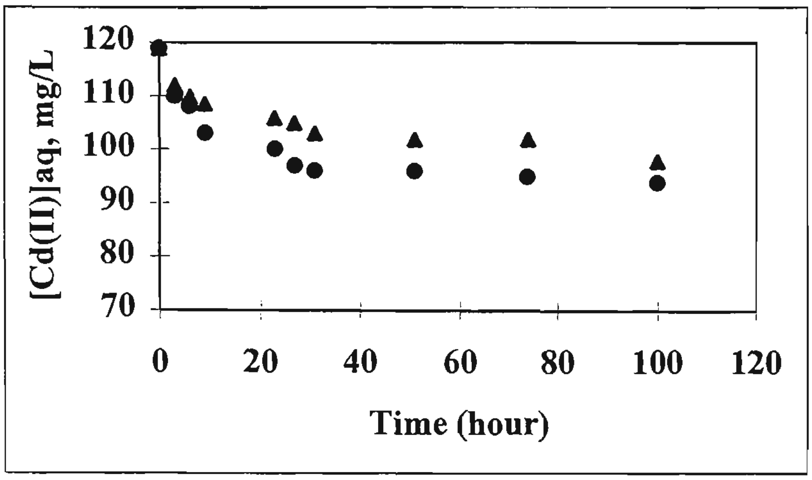


Figure 3.8. Extraction of Cd(II) using 30% Aliquat 336/PVC membrane formed facing air (▲) and facing glass (●) (The thickness of the membrane was 82μm)

The apparent difference in the extraction capacities of the two sides of Aliquat 336/PVC membrane was also observed in the extraction of Cu(II) using membranes containing 30% Aliquat 336. This is shown in Figure 3.9.

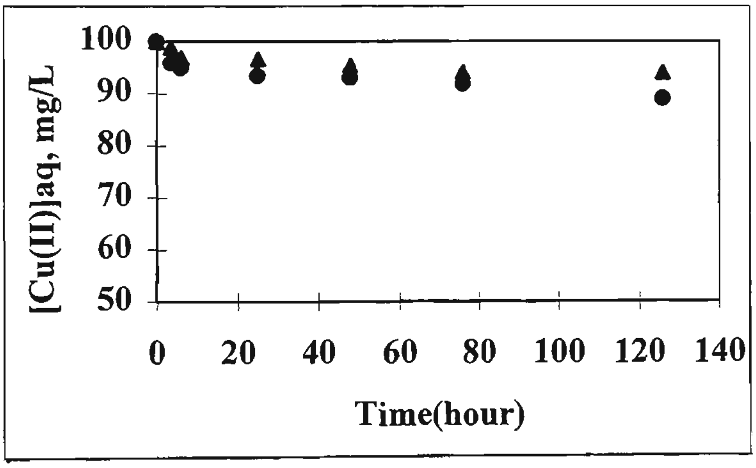


Figure 3.9. Extraction of Cu(II) using 30% Aliquat 336/PVC membrane formed facing air (▲) and facing glass (●)(The thickness of the membrane was 113μm)

For membranes containing 40% and 50% Aliquat 336, the difference in the apparent extraction capacities of the two sides diminished substantially in the extraction of Cd(II) and Cu(II) (Figures 3.10 to 3.12).

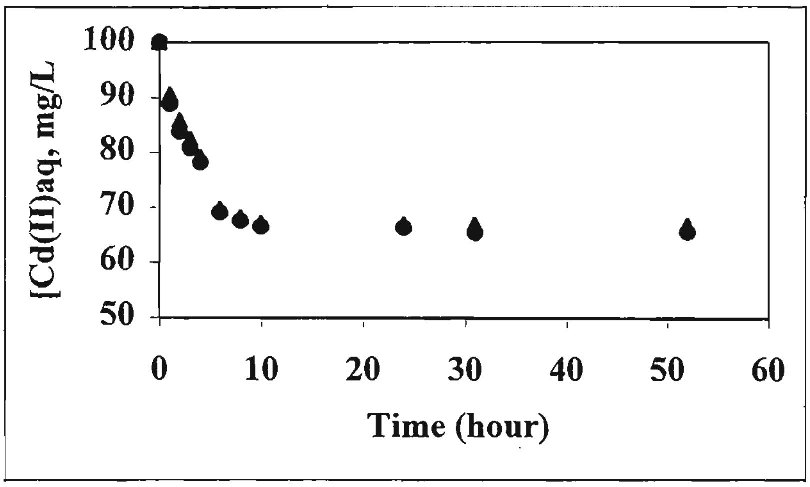


Figure 3.10. Extraction of Cd(II) using 40% Aliquat 336/PVC membrane formed facing air (▲) and facing glass (●)(The thickness of the membrane was 138μm)

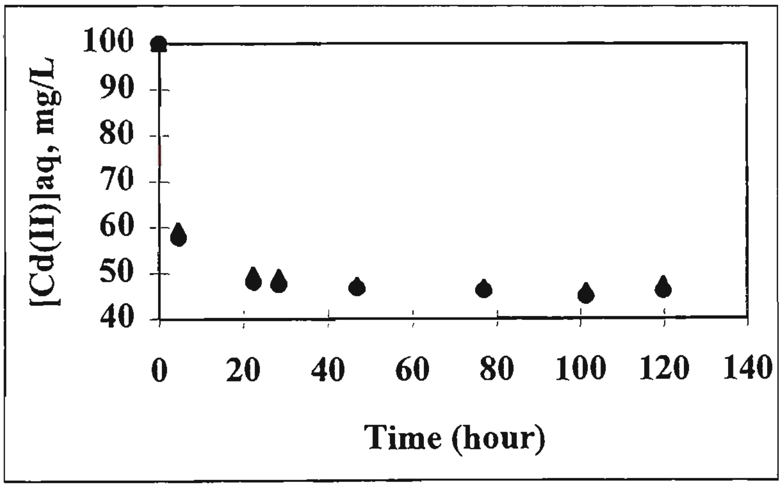


Figure 3.11. Extraction of Cd(II) using 50% Aliquat 336/PVC membrane formed facing air (▲) and facing glass (●) (The thickness of the membrane was 133μm)

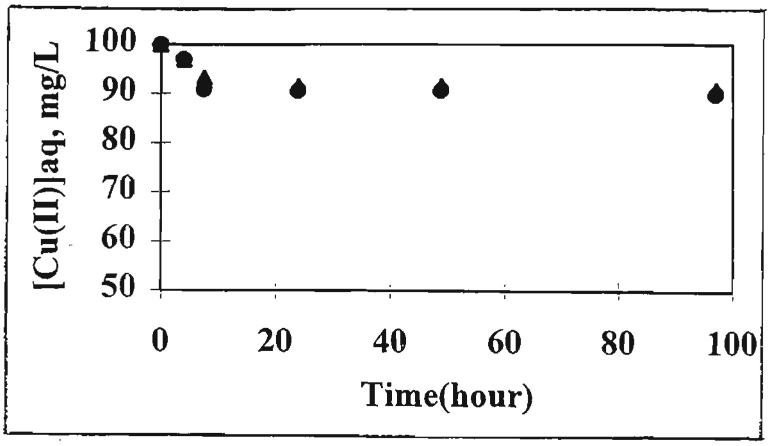


Figure 3.12. Extraction of Cu(II) using 40% Aliquat 336/PVC membrane formed facing air (▲) and facing glass (●) (The thickness of the membrane was 147μm)

Although the difference in the apparent extraction capacities of the two sides of a membrane formed under different conditions is experimentally observed beyond doubt, it is difficult to identify the cause(s) which is(are) responsible for such difference. It could be conjectured, though, that when a membrane is formed by solvent casting, some differences on the two surfaces or in the sub-surface regions close to these two surfaces may be built in due to different environments to which they face. A thorough investigation of the surfaces and the sub-surface regions of the Aliquat 336/PVC membranes would be very interesting, but is unfortunately not feasible financially for the present project. It was decided that only a preliminary surface analysis of Aliquat 336/PVC membranes would be carried out. The membrane surface analysis is presented in Chapter 4.

3.3.1.4 <u>The extraction behaviour and the mechanism for the Aliquat 336/PVC membrane extraction</u>

In the study of the solvent extraction of Cd(II) and Cu(II) from hydrochloric acid solutions with Aliquat 336 in Shellsol AB (Chapter 2), it was proposed that the extraction involved an interfacial mechanism. In this mechanism Aliquat 336 at the aqueous/organic interface undergoes a fast ion-exchange reaction with the metal chloro-anionic species, $CdCl_3^-$ or $CuCl_3^-$, to form extractable ion-pairs which then diffuse into the bulk organic phase and are replaced at the interface by fresh Aliquat 336. It should be noted that the mechanism could also include the formation of an adduct between Aliquat 336 and the neutral species $CdCl_2$ or $CuCl_2$ from the aqueous phase. This mechanism is similar to that proposed by Paimin and Cattrall [107] for the extraction of Co(II) from chloride solutions by Aliquat 336 in chloroform. They also identified that the rate determining step in the extraction was the replacement of the Aliquat 336/Co(II) complex by fresh Aliquat 336 at the interface and eliminated the possibility of diffusion as being the rate determining step.

By analogy with the solvent extraction study, a similar mechanism has been assumed for Cd(II) and Cu(II) membrane extraction. However, membrane extraction is a more complex process compared to solvent extraction since membrane extraction involves both chemical kinetics and chemical diffusion [88].

In the investigation of the extraction of Au(III) and Cu(II) using Aliquat 336/PVC membranes, Kolev *et al.* have developed a mathematical model which was used to postulate the mechanisms of the extraction [88]. In this model, it was assumed that both the kinetics of the complex formation and the diffusion of the extracted complex (as well as the diffusion of the fresh Aliquat 336 molecules) were involved in the extraction. In applying this model to the membrane extraction systems of Cd(II) and Cu(II), the following assumptions were made:

(a) the extraction rate of Cd(II) or Cu(II) was assumed to be influenced by the rate of the chemical reactions (ion-exchange) occurring at the interface and by diffusion of the Aliquat 336/Cd(II) or Aliquat 336/Cu(II) species within the membrane,

(b) fast mass transport occurred in the bulk of the aqueous phase as the aqueous solution was stirred so that the diffusion factor can be ignored,

(c) mass transport within the membrane was the result of Fickian diffusion only,

(d) the rate of ion-exchange (or complexation) between Aliquat 336 and the Cd(II)-chloro or the Cu(II)-chloro species at the interface and the diffusion of the Aliquat 336/Cd(II) complex or Aliquat 336/Cu(II) complex within the membrane were slower than the diffusion of the Cd(II)-chloro or Cu(II)-chloro species across the stagnant diffusion layer which separated the membrane from the ideally mixed aqueous solution,

(e) the overall extraction reaction can be described by the following stoichiometric equations:

$$(R_3MeN^+Cl^-)_m + (CdCl_3^-)_{aq} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (R_3MeN^+CdCl_3^-)_m + (Cl^-)_{aq} \tag{3.1}$$

or

$$(R_3MeN^+Cl^-)_m + (CdCl_2)_{aq} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (R_3MeN^+CdCl_3^-)_m \tag{3.2}$$

and

$$(R_3MeN^+Cl^-)_m + (CuCl_3^-)_{aq} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (R_3MeN^+CuCl_3^-)_m + (Cl^-)_{aq} \tag{3.3}$$

or

$$(R_3MeN^+Cl^-)_m + (CuCl_2)_{aq} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (R_3MeN^+CuCl_3^-)_m \tag{3.4}$$

where k_f and k_b are the forward and the backward kinetic rate constants and subscripts "m" and "aq" refer to the membrane and the aqueous solution, respectively.

The extraction process takes place in a considerable amount of excess of Cl^- ions. For this reason the concentration of Cl^- ions will remain constant, and the backward reaction involving the rate constant k_b described by the above equations can be considered as pseudo-first order. Under such conditions the backward kinetic rate constant will incorporate the concentration of the chloride ions. In this case the above equations can be written in a general form as:

$$B_m + M_{aq} \underset{k'_b}{\overset{k_f}{\rightleftharpoons}} (BM)_m \tag{3.5}$$

$$K_{ex} = \frac{k_f}{k'_b} \tag{3.6}$$

where B refers to Aliquat 336, M refers to the $CdCl_3^-$ or $CuCl_3^-$, MB refers to the ion-pair $R_3MeN^+CdCl_3^-$ or $R_3MeN^+CuCl_3^-$, K_{ex} is the extraction equilibrium constant and

$k'_b = k_b$ [Cl$^-$]. Detailed mathematical development of the model has been discussed, previously [88].

The experimental data points were fitted using a computer program [88] based on this model (shown as the solid curves in Figure 3.13). The parameters calculated from the mathematical modelling, viz. the diffusion coefficients (D), forward (k_f) and backward (k'_b) kinetic rate constants and the extraction equilibrium constant (K_{ex}), are listed in Table 3.1.

Table 3.1. Values of D_B, k_f, k'_b and K_{ex} obtained for the solid line fit in Figure 3.13 for the extraction of Cd(II)

Membrane composition in % Aliquat 336/PVC (m/m)	$D_B \times 10^{13}$ (m^2s^{-1})	$k_f \times 10^9$ ($m^4mol^{-1}s^{-1}$)	$k'_b \times 10^9$ ($m\ s^{-1}$)	K_{ex} ($m^3\ mol^{-1}$)
30	0.8	1.5	3.7	0.41
40	4.0	1.5	3.3	0.45
50	8.0	1.7	1.7	1.00

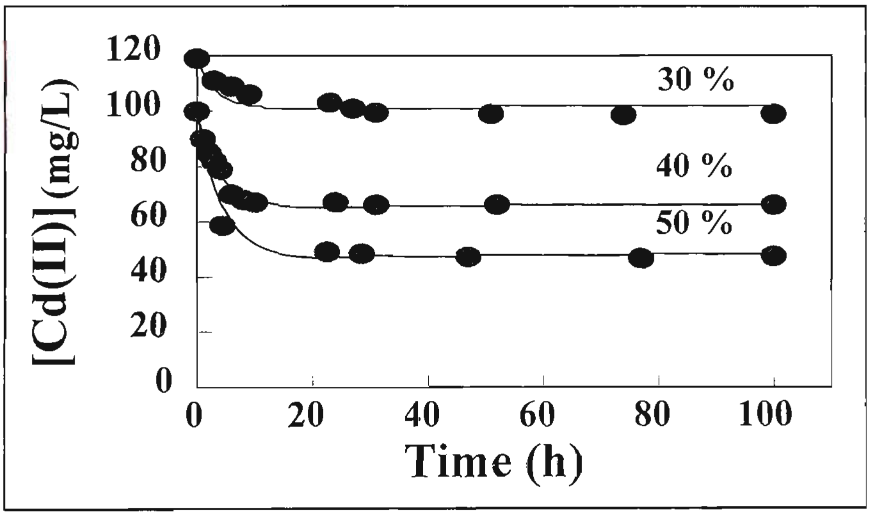


Figure 3.13. Aqueous Cd(II) concentrations vs. the extraction time for various membrane compositions (Initial aqueous Cd(II) concentration in 2M HCl solution - 120mg/L for 30% Aliquat 336/PVC membrane and 100mg/L for 40% and 50% Aliquat 336/PVC membranes. The solid dots are experiment data and the solid lines are mathematical fitting curves)

From the model, it was determined that, in the membrane extraction of Cd(II), the backward kinetic rate constant, k'_b, was larger or equal to the forward kinetic rate constant, k_f. Thus, the extraction equilibrium constant, K_{ex}, calculated from the kinetic rate constants were therefore ≤ 1.

Aliquat 336/PVC membrane was reported to extract Au(III) very strongly [88]. The K_{ex} values for Au(III) calculated using the above mathematical model were 20 m^3/mol for 30% and 40% membranes and 250 m^3/mol for 50% membrane [88]. The K_{ex} values for the extraction of Au(III) were therefore one to two orders of magnitude greater that those for the extraction of Cd(II) obtained in this study. On the other hand, the diffusion coefficients of Au(III) complex in the membrane, 2×10^{-14}, 4×10^{-14} and 1×10^{-13} m^2/s for membrane containing 30%, 40% and 50% and Aliquat 336 respectively, were more than an order of magnitude smaller than those of Cd(II) complex (see Table 3.1). [Note: Although D_B in Table 3.1 represents the diffusion coefficient of Aliquat 336 molecules in the membrane, it was assumed to be equal to D_{BM}, the diffusion coefficient of metal/Aliquat 336 complex [88]]

The small K_{ex} values for the membrane extraction of Cd(II) may mean that the activity of Aliquat 336 in the membrane could be much lower than that in a solution of an organic solvent such as Shellsol AB. In the membrane a significant portion of Aliquat 336 may be immobilized. The backward kinetic rate constant (k'_b) being smaller than the forward kinetic rate constant (k_a) suggests that it is easy to strip Cd(II) from the membrane. It may be envisaged that Aliquat 336/PVC membrane should perform well in a continuous extraction (i.e. extraction of Cd(II) from a feed solution through the membrane into a receiver solution in a continuous manner) given that Cd(II)/Aliquat 336 complex has a reasonably large diffusion coefficient, D_{AB}. This inference is investigated and discussed in the following section.

The mathematical modelling of membrane extraction of Cu(II) is not satisfactory. Due to the very low degree of extraction of Cu(II) by the membrane (Figure 3.5), it was not possible to carry out the mathematical modelling of this system.. Some qualitative hypothesis about the membrane extraction equilibrium constant and the diffusion coefficient of Cu(II) may, however, be made based on the above information and the behaviour of Cu(II) in solvent extraction system. Since Cu(II) is smaller than Cd(II) in size, Cu(II)/Aliquat 336 complex should have a greater diffusion coefficient than Cd(II).

Therefore, diffusion was unlikely to be the determining factor responsible for the poor membrane extraction performance of Cu(II). It was more likely that Cu(II) has a very low extraction equilibrium constant. Such a hypothesis was in agreement with the results observed in the solvent extraction of Cu(II), where the extraction efficiency of Cu(II) was lower than that of Cd(II).

3.3.2 Investigation of The Extraction of Cd(II) and Cu(II) From the Feed Phase Through Aliquat 336/PVC Membrane Into the Receiver Phase In a Continuous Manner

An obvious interest in the research of membrane extraction is to be able to extract metal ions from the feed phase through the membrane into the receiver phase. This requires not only that the metal species must have a reasonably high flux through the membrane (which is related to D_{BM}), but also that a large difference in chemical potential of the metal complex in the feed and the receiver phases could be maintained. Thus, in the extraction of Cd(II) and Cu(II) from the feed to the receiver by Aliquat 336/PVC membranes, a relatively high concentration of HCl solutions (2M) was used in the feed phase and a relative low concentration of HCl solution (0.05M) was used in the receiver phase. Since Cl^- was the ligand of the metal complex to be extracted, such a difference in the HCl concentrations of the feed and receiver solutions should provide a large difference in the chemical potential of the metal complex in the feed and receiver phases. The difference in chemical potentials of the metal complex between the feed and receiver phases was the driving force of the membrane extraction which caused the transport of metal complex from the feed to the receiver phase.

Figure 3.14 shows that Cd(II) was extracted from the feed to the receiver phase after ca. 7 hours. Almost a linear increase of Cd(II) concentration in the receiver phase can be seen after ca. 20 hours. Similarly, a linear decrease of metal concentration in the feed phase was also observed after ca. 20 hours of extraction. The rates of metal concentration changes of the feed and the receiver solutions were similar, suggesting that a stable (constant) metal complex transport was established. At ca. 110 hours, the Cd(II) concentrations of the feed and receiver phases equalized. Further extraction up to

167 hours resulted in an enrichment of the Cd(II) in the receiver phase. The amount of Cd(II) remains in the membrane can be calculated through mass balance.

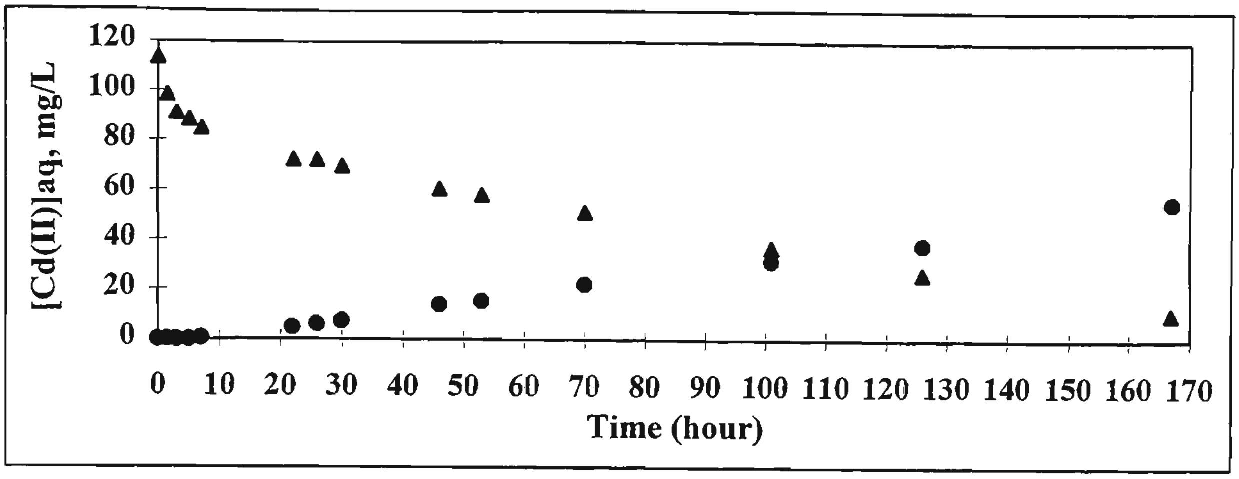


Figure 3.14. The extraction of Cd(II) from the feed phase to the receiver phase by 40% Aliquat 336/PVC membrane. (Initial Cd(II) concentration were 114mg/L in the feed phase and 0 mg/L in the receiver phase. Initial HCl concentration were 2M in the feed and 0.05M in the receiver. ▲ feed phase and ● receiver phase)

Since the concentration increase of Cd(II) of the receiver solution was a linear function of time, it might be assumed that the difference of chemical potential of Cd(II)-chloro complex, $CdCl_3^-$, in the feed and the receiver solutions did not change dramatically within the time frame of the extraction experiment. For this to be so, the HCl (or Cl^-) concentrations of the feed and the receiver solutions must not change greatly from their initial values. To verify this point, HCl concentrations of the feed and the receiver solutions were analysed by separately measuring Cl^- and H^+ concentrations and results are listed in Table 3.2. These results confirmed that, within the time frame of the experiment, no significant amount of HCl (or Cl^-) transported from the feed through the membrane into the receiver solution.

Table 3.2 The results of analyzing HCl concentrations in the feed and receiver phases for the extraction of Cd(II) using Aliquat 336/PVC membrane

Cd(II)	Feed		Receiver		Total	
	H^+(M)	Cl^-(M)	H^+(M)	Cl^-(M)	H^+(M)	Cl^-(M)
Initial	1.84	1.84	0.05	0.05	1.89	1.85
167 hrs	1.80	1.81	0.09	0.09	1.89	1.90

Assuming the duration of a constant transportation of Cd(II) was 160 hours (from hour 7 to hour 167), an average flux of Cd(II) was empirically estimated, using the total amount of Cd(II) transported into the receiver solution (including aliquots removed for analysis) divided by the membrane area and time, to be 5.77×10^{-4} μg/cm^{2}s or 5.1×10^{-12} mol/cm^{2}s. Although, according to the definition of flux given in equation (3.1), diffusion coefficient and the concentration gradient of the analyte are required to calculate the flux, in case of the concentration of the analyte in the receiver is not a constant, the flux may be calculated by dividing the total amount of the analyte transported into the receiver solution with the membrane area and time [197].

The extraction rate of Cu(II) using Aliquat 336/PVC membrane was lower compared to the Cd(II) system (Figure 3.15). After 167 hours of extraction, the concentration of Cu(II) in the feed was still higher than that of the receiver. The concentrations of Cu(II) in the two compartments did not become equal until 600 hours.

Also, the increase of Cu(II) concentration in the receiver solution (or the decrease of Cu(II) concentration in the feed solution) became non-linear after 150 hours of extraction. This suggests that there may be a significant permeation of Cl^- through the membrane. Analysis of Cl^- concentrations of the feed and receiver solutions confirmed this hypothesis. The Cl^- concentration of the feed solution decreased from 2.81 M to 2.14 M after 167 hour of extraction, and to 1.77 M after 600 hours. While the Cl^- concentration of the receiver solution increased from 0.10 M to 0.78 M after 167 hours of extraction, and to 1.15 M after 600 hours. The large degree of permeation of Cl^- through the membrane after 600 hours was likely to significantly reduce the difference of the chemical potential of Cu(II)-chloro complex in the feed and the receiver solutions. This makes a high concentration of Cu(II) in the receiver solution impossible. Assuming that the extraction behaviour of Cu(II) was linear between the hours 5 and 149, the average flux estimated within this period was 2.93×10^{-4} μg/cm^{2}s or 4.6×10^{-12} mol/cm^{2}s.

Table 3.3 The results of analyzing HCl concentrations in the feed and receiver phases for the extraction of Cu(II) using Aliquat 336/PVC membrane

Cu(II)	Feed		Receiver		Total	
	H^+(M)	Cl^-(M)	H^+(M)	Cl^-(M)	H^+(M)	Cl^-(M)
Initial	2.82	2.81	0.10	0.10	2.92	2.91
167 hrs	2.15	2.14	0.79	0.78	2.94	2.92
670 hrs	-	1.77	-	1.15	-	2.92

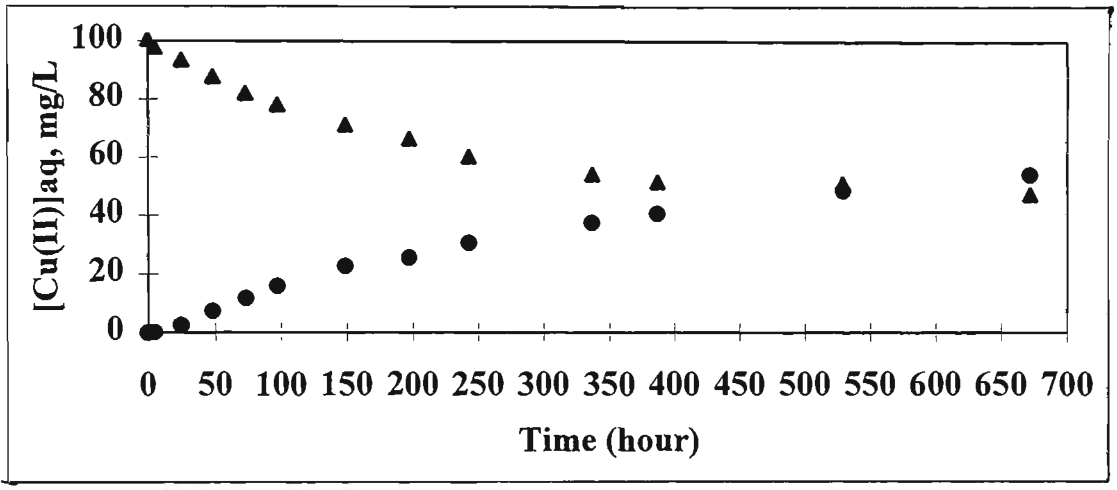


Figure 3.15. The extraction of Cu(II) from the feed phase to the receiver phase by 40% Aliquat 336/PVC membrane. (Initial Cu(II) concentration were 100mg/L in the feed phase and 0 mg/L in the receiver phase. Initial HCl concentration were 3M in the feed and 0.1M in the receiver. ▲ feed phase and ● receiver phase)

Results in this section demonstrated that it was possible to extract Cd(II) using an Aliquat 336/PVC membrane in a continuous manner. Although the membrane also extracts Cu(II), it is difficult to concentrate Cu(II) from the feed to the receiver solution using continuous extraction, since Cl^- permeates through the membrane during the extraction of Cu(II) and reduces the difference of chemical potential of Cu(II) of the two compartments, thus reduces the driving force of the extraction.

3.3.3 Stability of Aliquat 336/PVC Membranes

Aliquat 336/PVC membrane was reported to have considerable stability in the extraction of Au and Hg [83, 167]. When exposed to HCl solution, the loss of Aliquat 336 from the membrane was reported to be insignificant and no bleeding or dimensional distortion was reported. In this study, however, it was found that the stability of the membrane was dependent upon the metal being extracted.

In the extraction of Cu(II), the Aliquat 336/PVC membrane demonstrated excellent stability from hydrochloride solutions in terms of the lack of bleeding and dimensional distortion. In this case, after more than 600 hours, the membrane was still in good condition but the colour of membrane had turned from clear transparent to bright yellow, indicating that the Cu(II) complex was extracted into the membrane. Atomic Force Microscopy (AFM) imaging of the membrane surfaces before and after extraction of Cu(II) did not show obvious topographic changes (Chapter 4). Chemical analysis of the membrane surfaces before and after extraction using X-ray Photoelectron Spectroscopy (XPS) did not show any evidence of loss of Aliquat 336 from the membrane surfaces (Chapter 4). These results strongly suggest that the membrane can be reused after the extraction of Cu(II).

However, when the membrane was used in the extraction of Cd(II) from hydrochloric acid solution, it showed very poor stability. The membrane obtained after being loaded with Cd(II) was light brown in colour. Dimensional distortions (wrinkles) were visible from the surface of the membrane. A viscous material seeped out through very fine cracks and tiny pin holes on the Cd(II)-loaded membrane surfaces. The bleeding of the Cd(II) loaded membrane was observed by AFM (Chapter 4). XPS analysis of the Cd(II) loaded membrane surface was not performed due to concerns of the potential contamination of the vacuum chamber by the sample. In the extraction of Cd(II), the poor dimensional and structural stabilities of the membrane after extraction offer slim possibility of it being reused.

3.4 CONCLUSION

In this study, the performance of the Aliquat 336/PVC membrane in the extraction of Cd(II) and Cu(II) was investigated. The membrane showed a higher extraction capacity to Cd(II) than to Cu(II). The extraction capacity of the membrane to Cd(II) was found to be dependent upon the thickness and the Aliquat 336 content of the membrane. The extraction of Cd(II) was greater for the thicker membrane and for the membranes of greater Aliquat 336 content. The diffusion coefficients (D_B), forward (k_f) and backward (k_b') extraction rate constants for the extraction of Cd(II) were calculated using the mathematical model developed by Kolev *et al.* [88]. The extraction capacity of the membrane to Cu(II) was very low and was independent of the Aliquat 336 content of the membrane. The mathematical modelling was not applied to this system because of its impracticality.

Although Aliquat 336/PVC membrane of the present formation exhibited excellent stability in the extraction of Cu(II) and was also reported previously to be very stable in the extraction of Au(III), the membrane stability was not universally observed in all metals extraction since the membrane has shown poor stability when it was used in the extraction of Cd(II).

In the extraction of the metals from the feed phase to the receiver phase, the HCl transport through the membrane was found to be slow, which was shown to be important for these systems. The extraction of Cd(II) from the feed to the receiver phase in this continuous manner was feasible, but not in the case of the extraction of Cu(II).

The problems associated with the Aiquat 336/PVC membrane extraction systems mentioned above require further investigation before the membrane can be used in the industrial applications.

CHAPTER FOUR

PRELIMINARY STUDY OF SURFACE PROPERTIES OF ALIQUAT 336/PVC MEMBRANES

4.1 INTRODUCTION

One of the major differences between membrane extraction and conventional solvent extraction is that in the former, the metal ions transport across the interface of the aqueous phase and a polymer matrix, whereas in the later, the metal ions are transported across the interface of the aqueous and the organic phases. The chemical and physical properties of the membrane may therefore affect the membrane extraction behaviour towards the metal ions. Experimental evidence presented in Chapter 3 indicated that the two sides of Aliquat 336/PVC membranes formed under different conditions, i.e. membrane sides formed against the glass plate and facing air, have apparently different extraction rates. Therefore, characterization of the two sides of the membrane is necessary in order to understand the extraction behaviour displayed by this system. It was also observed that Aliquat 336/PVC membrane showed different dimensional stability in the extraction of Cd(II) and Cu(II) from HCl solutions. This further motivated the surface characterization of the Aliquat 336/PVC membrane. It is envisaged that the physical properties and chemical composition of the sub-surface region of the membranes may also affect their metal ion extraction performance and dimensional stability.

The techniques chosen for the surface characterization of the Aliquat 336/PVC membrane were Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS). AFM was invented by Binning *et al.* in mid-1980's as a high resolution imaging technique [89]. Now, AFM is used in many areas including biological science [168, 169], surface science [98, 99], materials and polymer sciences [170-173], membrane science [93, 174, 175] and pulp and paper [176, 177]. In its application in membrane science, AFM revealed surface microscopic structures of various membranes which were helpful in understanding the functions and behaviour of the membranes [93, 174, 175]. One of the main advantages of AFM technique over traditional surface analysis techniques such as Scanning Electron Microscopy (SEM) is that AFM imaging can be carried out under ambient conditions and does not require a conductive surface coating and vacuum.

XPS was developed by K. Siegbahn [178] in the 1960s and commercial instrumentation began to appear in the mid-1970s. It is also known as Electron Spectroscopy for Chemical Analysis (ESCA). The principle of XPS is based on the photoelectric effect [179]. A beam of monochromatic X-ray irradiates the sample, generates photoelectrons by ejecting electrons from various shells of atoms of the sample. The chemical information of the sample surface may then be obtained by determining the binding energy of the (E_B) of the ejected electrons [178, 179]. XPS has been used as a surface chemical analysis technique in areas of metallurgy [19], adhesion technology [181], semi-conductor materials [182], catalysis [183], inorganic materials [184, 185], polymers [90, 104, 105] and biomedical materials [186].

In this work, a preliminary membrane surface characterization using AFM and XPS techniques was carried out so as to achieve some basic understanding of the physical properties and chemical composition of the surfaces of Aliquat 336/PVC membranes. These properties include the surface topography, surface chemical composition and chemical and physical stabilities of the membranes.

4.2 BACKGROUND OF AFM AND XPS

4.2.1 The Principle of AFM

4.2.1.1 Operation principles

Atomic force microscopy (AFM) is the term used to describe a scanning probe microscopy which produces an image by measuring a force between the tip and the specimen. Generally, AFM scans the surface of the sample in a raster manner with a sharp tip. The tip senses the molecular forces (i.e. the van der Waals forces, either repulsive or attractive, depending on the operation mode [187, 188]). AFM scans the tip over a surface and adjusting its height above the surface according to the feed back photo current signal so that the force sensed by the tip can be kept constant [189]. The topographic image is then obtained by plotting the height signal against the scanning area. This technique can be used for studying both conducting and non-conducting materials.

The major components of an atomic force microscope are [190]: (a) a sharp tip mounted on a cantilever, (b) a laser beam and a photodetector that senses the deflection of the cantilever, (c) a feedback system to monitor and control the deflection of the cantilever, (d) a mechanical scanning system (driven by piezoelectric elements) that moves the tip with respect to the sample in a raster pattern and, (e) a display system which converts the measured data into an image. A schematic diagram of an AFM is shown in figure 4.1.

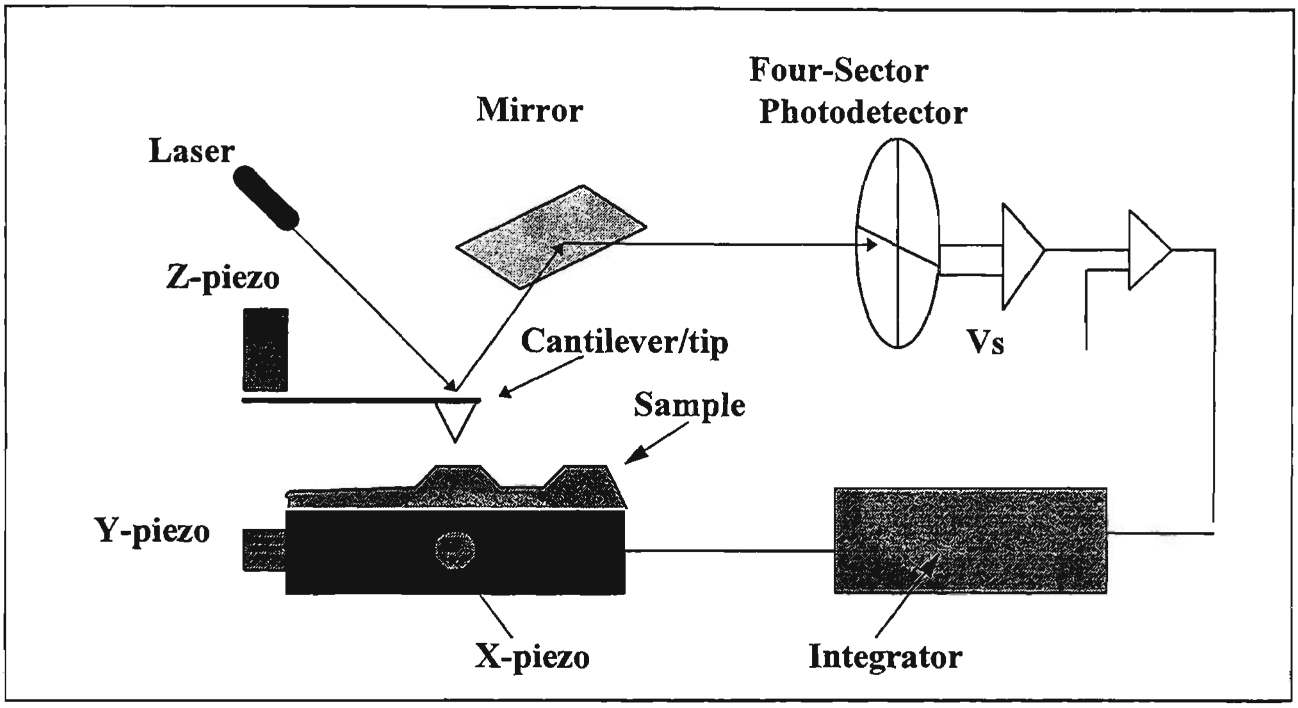


Figure 4.1 Schematic diagram of an atomic force microscope

A laser focused on the back of the cantilever is reflected onto a segmented photodetector (usually four domains) to monitor the deflection of the cantilever due to surface topography. The cantilever acts as a microscopic force sensor. As the tip approaches the sample surface, the force between the tip and the molecules (or atoms) on the sample surface changes, causing the deflection of the cantilever. The deflection of the cantilever, in turn, causes the deflection of the laser beam that shines on the back of the cantilever and a change of the photodetector current is detected. The photocurrent is used as the feed back to the piezoelectric component that control the distance between the tip and the sample surface (or Z-piezo) by exerting a voltage to the Z-piezo. By controlling the photocurrent constant during a scan and then plotting the scanning area (xy) against the Z-piezo voltage (V), a sample surface topographic image is obtained. This scanning mode is called the constant force mode [190]. Likewise, AFM can also scan with the Z-piezo voltage fixed and sensing the force or the photocurrent variation. This mode is called the constant height mode.

Commercial AFM instruments are equipped with the state-of-the-art scanning mechanism and software which can provide many other capabilities such as non-contact scanning mode, lateral force mapping and liquid cells which allow the scanning of samples that are immersed in a liquid.

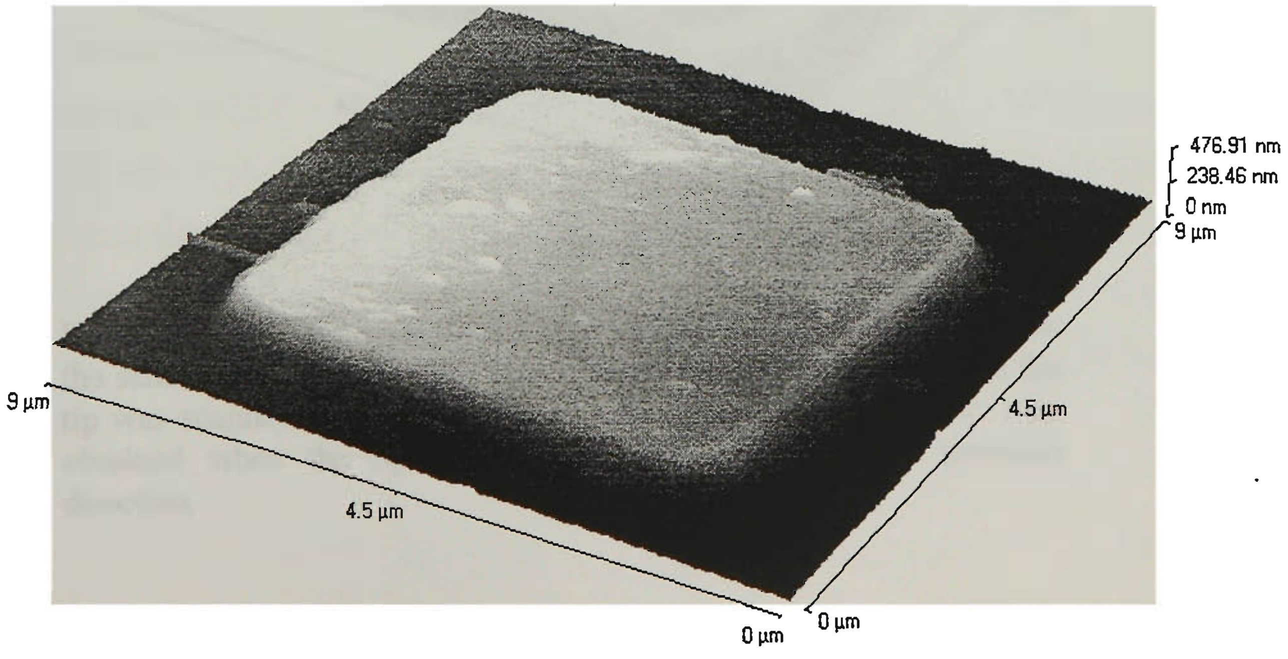
4.2.1.2 Contact, non-contact imaging and lateral force mapping

AFM imaging modes can be classified as "contact" or "non-contact" depending on the net forces between the probe and the sample [191]. In contact mode, also known as repulsive mode, the tip is very close (in contact) to the surface being imaged and is responding to very short range repulsive interactions with the sample. This mode can be used to acquire the sample surface topography as well as the lateral force information. In non-contact mode the tip instead responds to attractive long range van der Waals interactions with the sample. Therefore, in non-contact mode, the tip is generally at a distance of 5-10nm away from the surface while imaging. Non-contact imaging is not widely used without modification to the technique as the attractive van der Waals forces are substantially weaker than the repulsive forces used in contact mode and attenuates very rapidly with the tip-sample distance. Due to the above reasons, contact mode tends to give better resolution of the surface topography than does the non-contact mode. Since the purpose of the present preliminary study of the Aliquat 336/PVC membranes using AFM was to acquire membrane surface topographic and lateral force information, contact mode was used for all imaging.

During contact imaging, the cantilever twists slightly as a result of changes in the lateral force on the tip. The torsion, or twisting, of the cantilever will increase or decrease depending on the frictional characteristics of the surface in contact with the tip (greater torsion results from increased friction). The cantilever can also be twisted quite significantly if the material on the surface is viscous and has great adhesion power [192]. In contact AFM imaging, movement of the cantilever in response to changes in surface topography is detected by changes in relative amounts of laser light striking the upper and lower halves of the photodetector. Lateral force data can be obtained by measuring the difference of the signals between the left and the right halves of the photodetector. Therefore, the lateral force mapping detects the changes of the twisting direction of the cantilever as the scanning direction of the cantilever changes. Modern AFM apparatus can record the lateral force data collected from the forward and the backward scans. These data may be used collectively to interpret the lateral force character of the sample. Since output from all four sectors of the photodetector can be measured simultaneously, topographic and lateral force data can be obtained during the same scan. Hence lateral force data are generally used in conjunction with topographic imaging. These data show changes in the (chemical) composition of the probed material as reflected by changes in surface friction or surface adhesion. Lateral force data are therefore useful in mapping out areas of different chemical composition on the surface of materials.

It is necessary to note that topographic features may also contribute to the torsion of the cantilever. In many cases, the torsion of the cantilever caused by topographic features can be distinguished from lateral forces of frictional and adhesive nature. The following images taken from a semiconductor grid (a standard sample supplied with a TMX2000 AFM instrument) illustrate this point.

(a)



(b)

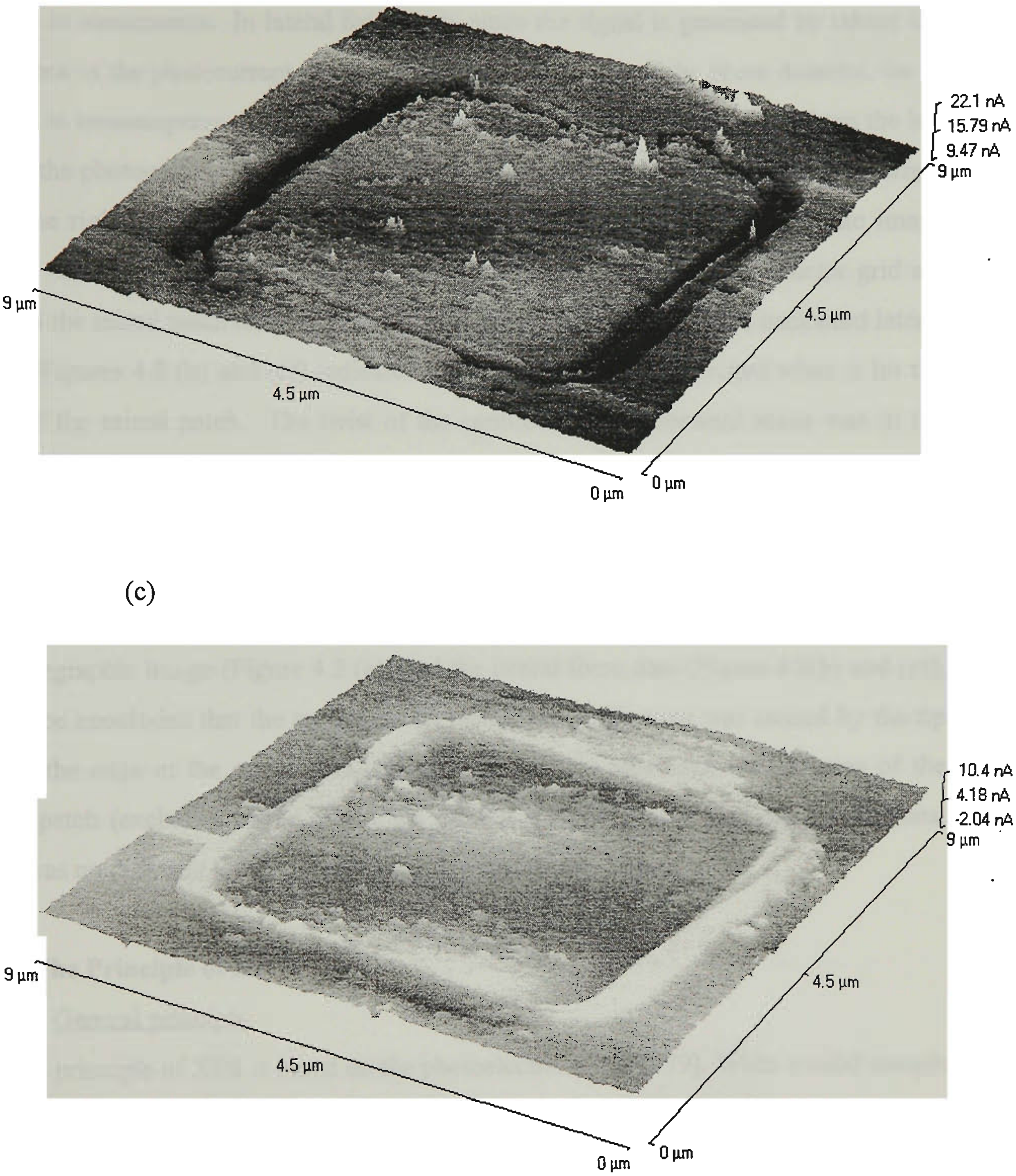


Figure 4.2 (a) The topographic image of the raised patch of SiO_2 on the semiconductor grid. (b) The lateral force map obtained when the tip was scanned in the forward direction. (c) The lateral force map obtained when the tip was scanned in the backward (reverse) direction.

The brightness of the grey scale shows the vertical profile of the surface, with the bright region being the raised areas and dark regions the depressions and pores. The z-scale is in nanometres. In lateral force map, since the signal is generated by taking the difference of the photocurrent of the left and the right halves of the photo detector, the z-scale is in nanoamperes. The bright region indicates a greater photocurrent from the left half of the photocell compare to the right half and the dark area, the greater photocurrent from the right half of the photocell compare to the left half. The topographic image (Figure 4.2 (a)) shows that the base and the raised patch of the semiconductor grid are flat and the raised patch has a well defined edge. Both the forward and backward lateral scans (Figures 4.2 (b) and (c)) indicated that the cantilever was twisted when it hit the edge of the raised patch. The twist of the cantilever in the forward scans was in the opposite direction to that in the backward scans, since the tip hit the raised patch from the opposite directions when scanning forward and backward respectively. The twist of the cantilever in the opposite directions was well reflected by the increase (in forward scan) and decrease (in backward scan) of the photocurrent signal. By jointly examining the topographic image (Figure 4.2 (a)) and the lateral force data (Figure 4.2(b) and (c)), it may be concluded that the torsion of the cantilever in this scan was caused by the tip hitting the edge of the raised SiO_2 patch. Since in the base area and the area of the raised patch (exclusive of the edge), the cantilever showed a similar degree of twists, there was no different lateral forces being detected in these areas.

4.2.2 The Principle of XPS

4.2.2.1 General principle

The principle of XPS is based on the photoelectric effect [179]. When a solid sample is irradiated with X-ray photons, some of these photons collide elastically with the inner shell electrons and these electrons are ejected from the sample. The kinetic energy of the ejected electron equals that of the photon minus the binding energy, E_B, which held the electron to its parent atom. In practice, for a conducting sample, the electron binding energy can be written as follow [179]:

$$E_B = h\nu - E_K - \phi_{\text{spect.}} \tag{4.1}$$

Where, E_B and E_K are the binding energy and the kinetic energy of the electron, respectively, $h\nu$ is the X-ray photon energy and $\phi_{\text{spect.}}$ is the work function of the spectrometer. For non-conducting samples such as a polymer, E_B needs to be corrected for sample charging.

Each electronic shell of an element has a characteristic binding energy. When atoms form a molecule, their inner shell electron binding energy may change slightly, depending on the nature of bonding and the number of bonds with the neighbouring atoms. Such a change in the binding energy is called "chemical shift". The binding energy and the chemical shift measured by XPS provide not only chemical composition information but also information about chemical bonds. Because of the low escape depth for photoelectrons in solid, XPS is one of the most surface sensitive techniques for polymers [102, 103, 193].

4.2.2.2 XPS instrumentation

An XP spectrometer consists of a soft X-ray source(s) (usually Mg K_α (1253.6 eV) or Al K_α (1486.6 eV) [193]), an electron energy analyzer, a sample holding mechanism which allows accurate sample positioning for angle resolved work, a sample introduction system and a data analysis system. A modern XP spectrometer is also equipped with an X-ray monochromator, which is essential for high quality polymer surface analysis [194].

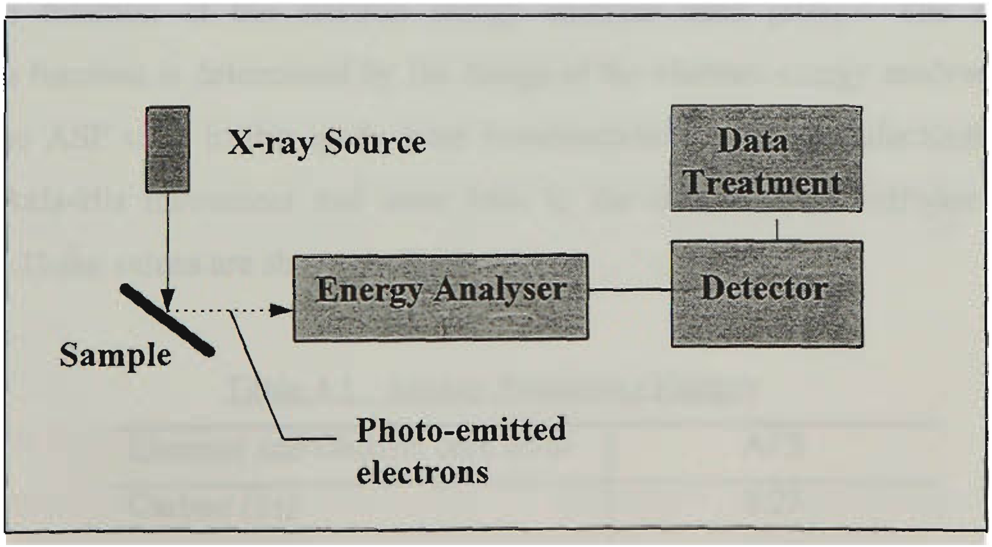


Figure 4.3 A schematic experimental set-up of XPS

All these components (except for the sample introduction and data analysis systems) are housed in an ultra-high vacuum (UHV) and magnetic-field-free stainless steel chamber, with a background pressure of 10^{-7}-10^{-8} Pa. A schematic diagram of XPS instrument is shown in Figure 4.3.

The XPS measurements of the Aliquat 336/PVC membrane were performed at the National Nanotechnology Facility & Network, CSIRO Clayton Site (Division of Molecular Science). The Spectrometer (KRATOS AXIS-His) was equipped with a monochromated Al K_α source. The sampling area was ca. 3mm^2. The photoelectron emission angle was 0° with respect to the surface normal. This corresponds to a sampling depth of ca. 10nm.

Quantitative surface analysis using XPS requires the knowledge of the atomic sensitivity factors (ASF) of the elements of interest [195]. The surface atomic ratio of one chemical species versus another is determined using the following equation:

$$\frac{N_1}{N_2} = \frac{I_1}{I_2} \times \frac{ASF_2}{ASF_1} \tag{4.2}$$

N_1/N_2 is the atomic ratio of the two elements, I_1 and I_2 are their photoelectron intensities and ASF_1 and ASF_2 are their atomic sensitivity factors. The ASF is governed by the X-ray ionization cross section of the electrons in a core level of an element from which photoelectrons are ejected and analysed. It is also determined by the electron transmission function of the electron energy analyser used [103]. The electron transmission function is determined by the design of the electron energy analyser. The values of the ASF used in this study were recommended by the manufacturer of the KRATOS Axis-His instrument and were built in the data analysis software of the instrument. These values are shown in Table 4.1.

Table 4.1 Atomic Sensitivity Factors

Element and electron core level	AFS
Carbon (1s)	0.25
Nitrogen (1s)	0.42
Oxygen (1s)	0.66
Chlorine ($2p_{3/2}$)	0.73

4.3 EXPERIMENTAL

4.3.1 Materials

Membranes containing 1, 30, 40 and 50% of Aliquat 336 were studied. These membranes were solvent cast on a piece of flat glass sheet (See Chapter 3). Since the two sides of the membrane were formed under different conditions (i.e. one side was formed facing the glass and the other to air), for clarification, they are referred to as the glass-facing and air-facing surfaces in the following discussions as shown in Figure 4.4.

Four samples of 1 cm^2 were cut from each membrane. Two of the samples were used for AFM and the other two for XPS analysis. In each surface analysis experiment, both air- and glass-facing surfaces were studied. The samples were mounted onto the sample holder using a piece of double sided sticky tape of the same size as the sample. Sample holder for XPS is made of Cu (a relatively inert, conducting and non-magnetic material) and that for AFM is made of steel. After mounting the samples onto the sample holder, the sample was cleaned for loose dust particles using a jet of high purity dry nitrogen. No further treatment was applied to the sample surfaces.

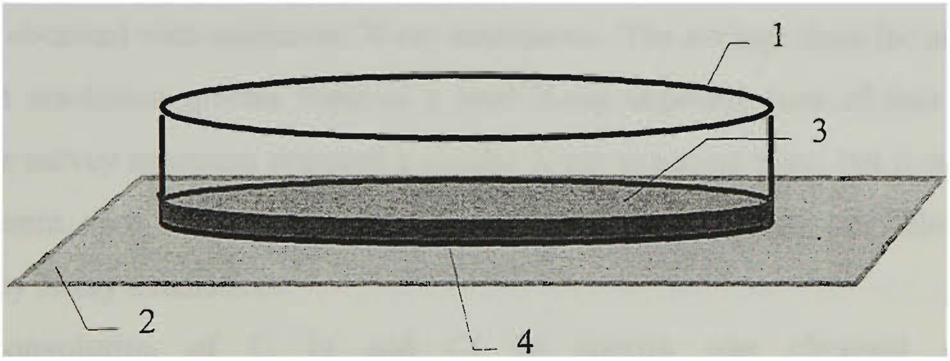


Figure 4.4. Schematic diagram of the membrane surfaces formed under different conditions. (1. glass ring, 2. The glass plate, 3. the air-facing surface and 4. the glass-facing surface)

4.3.2 Atomic Force Microscopy (AFM)

Preliminary studies of the Aliquat 336/PVC membranes were carried out using a Topometrix Explorer Atomic Force Microscope (TMX 2000). This was mounted on an Olympus IMT inverted optical microscope to facilitate the location of the tip on the membrane. The sample holder that carries the membrane sample was placed onto a magnetic platform where it was tightly held. The position of the tip on the membrane could be viewed using reflected light in the inverted optical microscope by a monitor connected to a CCD camera focused on the tip within the AFM. Standard 100μm silicon nitride V shaped cantilevers (13μm width) with pyramidal tips were used for contact mode imaging. Scanning of the membrane surface was carried out in air using piezoelectric scanners capable of 12 μm z-direction movement and 100 μm x- and y-direction movements.

4.3.3 X-Ray Photoelectron Spectroscopy (XPS)

After performing the above mentioned sample preparation, the samples were then introduced into the XPS spectrometer via a multi-stage sample introduction system. The samples were allowed to degas in the first and second stage of the sample introduction system before being introduced into the main chamber. The pressure of the main chamber during the analysis was 2×10^{-6} Pa. For each sample, a survey scan was first performed. Then, high resolution scans were performed for C 1s, Cl 2p, N 1s and O 1s levels. Since PVC has a large degradation index under X-ray irradiation [194], the spectra were obtained with minimum X-ray exposures. The average time for collecting the four high resolution spectra required a total X-ray exposure time of less then 15 minutes. The survey spectrum required a similar X-ray exposure time, but it was taken from a different spot on the sample surface for minimizing the possible sample degradation by X-ray irradiation.

The deconvolution of C 1s and Cl 2p spectra was obtained using a Gaussian/Lorentzian ratio of 0.70 and a preset FWHM (full width half maximum) of 1.1 ± 0.05 eV.

4.4 RESULTS AND DISCUSSION

4.4.1 General Surface Characteristics of The Aliquat 336/PVC Membranes Studied by AFM Technique

The surface topography of the Aliquat 336/PVC membranes was acquired using the constant force contact mode. All membranes analysed using AFM were either freshly cast or completely dried (under ambient conditions) after being used in the extraction surfaces of membranes containing 1% Aliquat 336, respectively. Topographic differences between air-facing and glass-facing surfaces of the membranes were clearly observed. Whereas gentle ripples were observed for both surfaces, the air-facing surface was rougher and more grainy than the glass-facing surface.

On the air-facing surface of the 1% Aliquat 336 membrane, some "blister-like" structures of 1 to 5 μm in diameter were found. These structures were not found in the glass-facing surface of the membrane or any surfaces of any other membranes. A closer imaging (Figure 4.7, (5.6×5.6 μm^2)) of one "blister" reveals that the surface of the blister was smoother than its surrounding areas. This leads to a possibility that this structure could perhaps have different chemical composition from its surrounding areas. For example, it may be an aggregate of one of the components used in the preparation of the membrane. Lateral force scan was then performed to clarify this point. In doing so, the forward and the backward lateral force maps were obtained and are presented in Figures 4.8 and 4.9, respectively. Both maps revealed that the frictions the tip experienced in the "blister" like area were similar to that of its surrounding areas.

The most likely cause of these "blister-like" structures was that they were fine PVC particles that were not significantly dissolved when forming the membrane and were *not* Aliquat 336 aggregates, since the later would cause significantly greater lateral deflections of the tip due to the viscous and sticky physical nature of Aliquat 336. It would have been desirable to use XPS to further analyze the chemical composition of the "blister-like" structures to support the conclusion drawn based on the lateral force measurement. Unfortunately the XPS instrument used in this study was not equipped with the zooming facility for such analysis.

Figure 4.6 shows the image of the glass-facing surface of the membrane containing 1% Aliquat 336. It was smoother than the air-facing surface. The only observable features of the glass-facing surface were many holes of diameters less than 1 μm.

These remarkable topographic differences between the two surfaces of the membrane (i.e. the glass-facing surface being smoother than the air-facing surface) were consistently observed from membranes containing 30%, 40% and 50% of Aliquat 336 (Figures 4.10 to 4.15). It is therefore apparent that the topography of the glass-facing surface is affected by conditions in which the membrane was cast. The air-facing surface therefore represents the "naturally formed" surface.

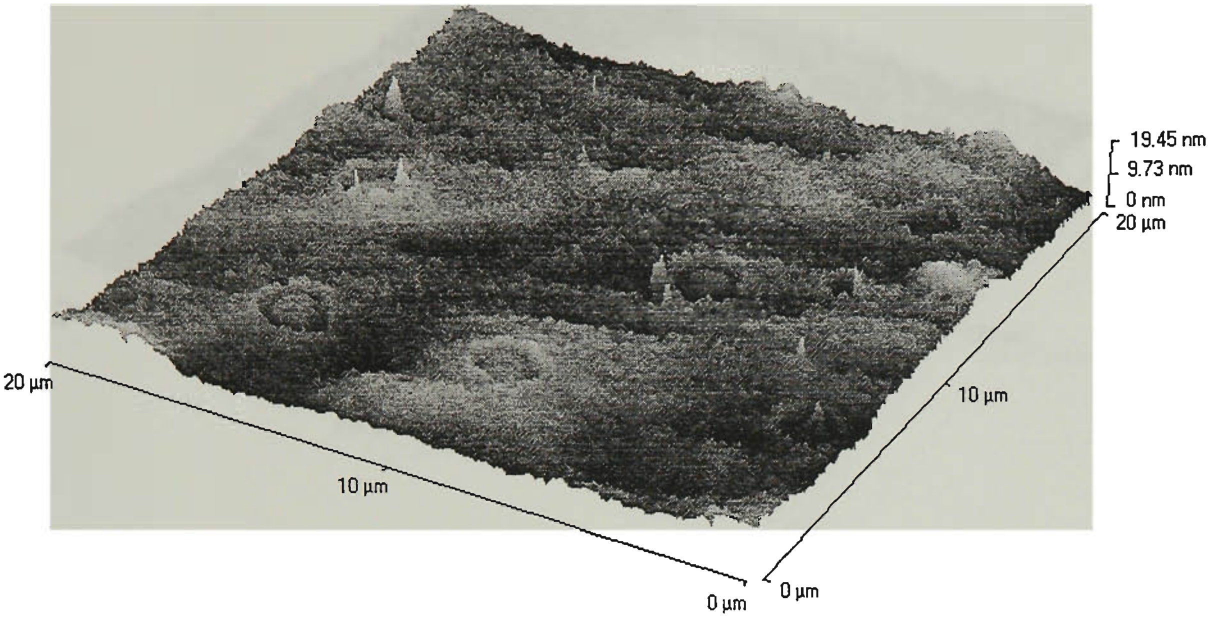


Figure 4.5 AFM image (20×20 µm^2) of the air-facing surface of 1% Aliquat 336/PVC membrane.

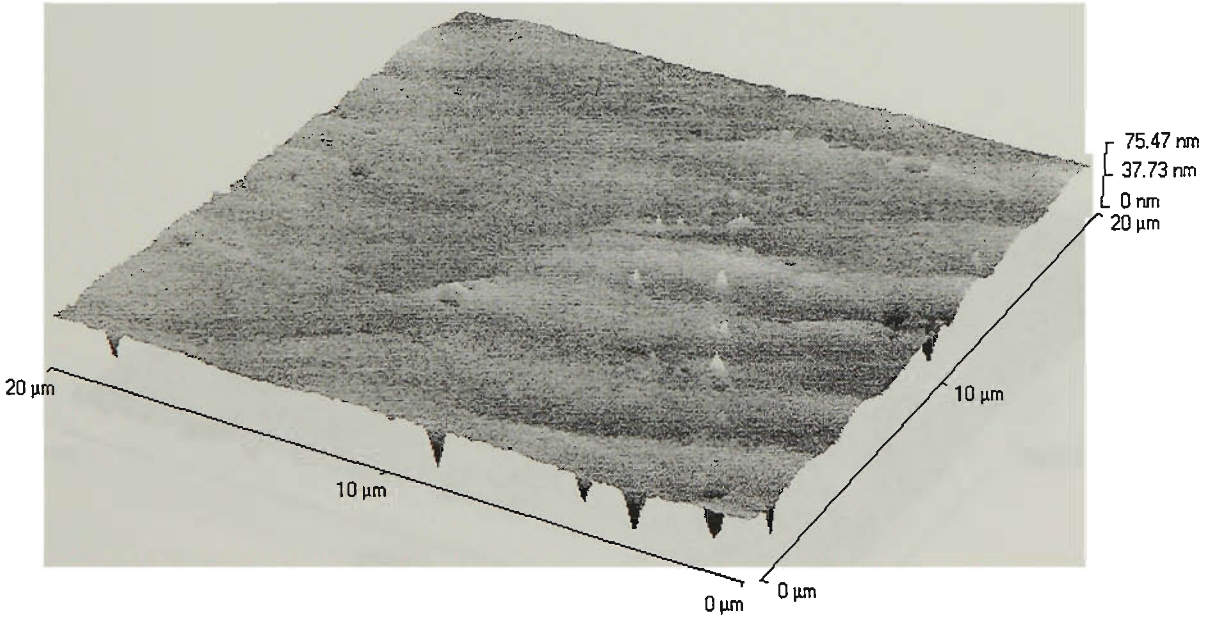


Figure 4.6 AFM image (20×20 µm^2) of the glass-facing surface of 1% Aliquat 336/PVC membrane.

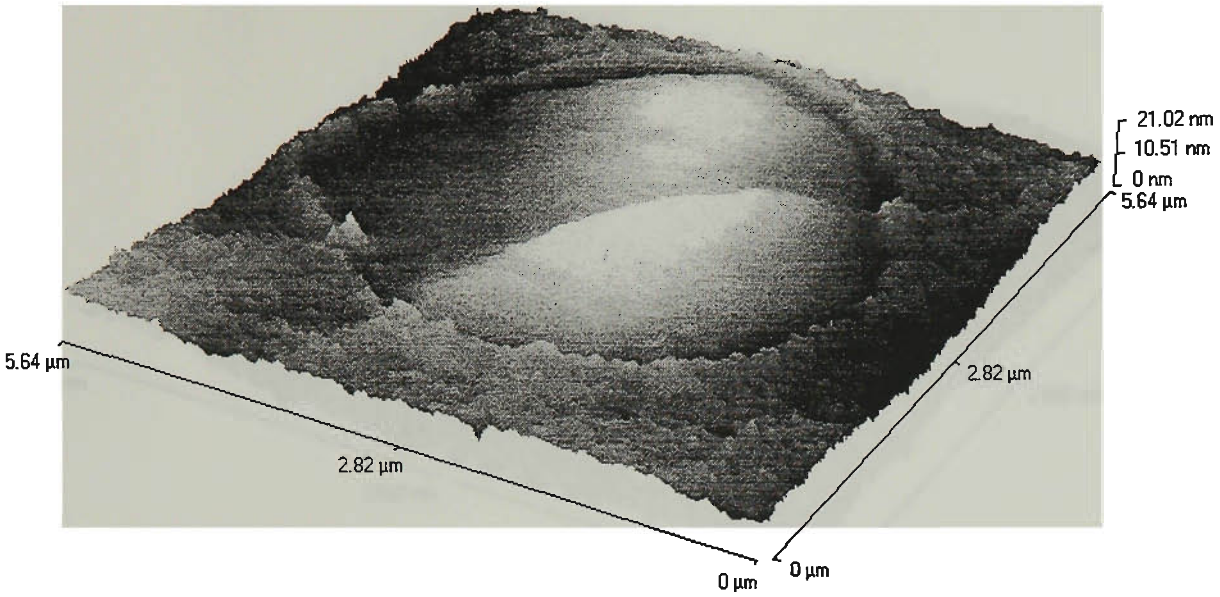


Figure 4.7 AFM image (5.6×5.6 µm^2) of a "blister" like spot on the air-facing surface of 1% Aliquat 336/PVC membrane.

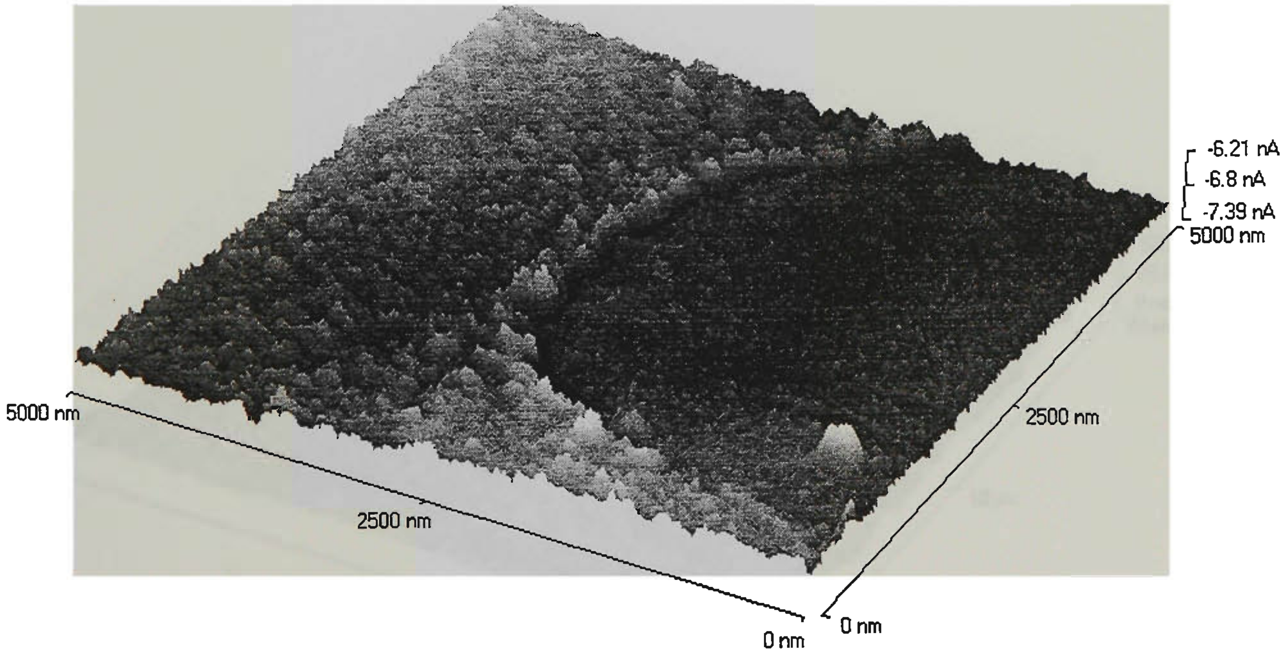


Figure 4.8 Lateral force (forward) map (5×5 µm^2) of the "blister" like spot and its surrounding areas on the air-facing surface of 1% Aliquat 336/PVC membrane.

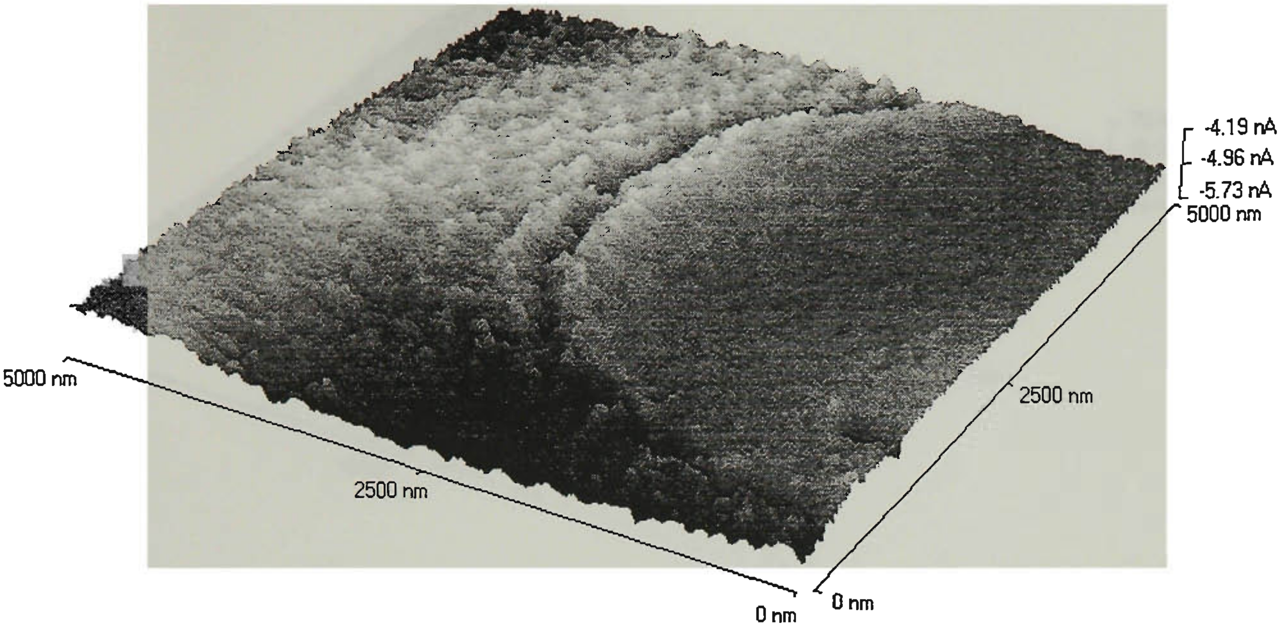


Figure 4.9 Lateral force (backward) map (5×5 μm^2) of the "blister" like spot and its surrounding areas on the air-facing surface of 1% Aliquat 336/PVC membrane.

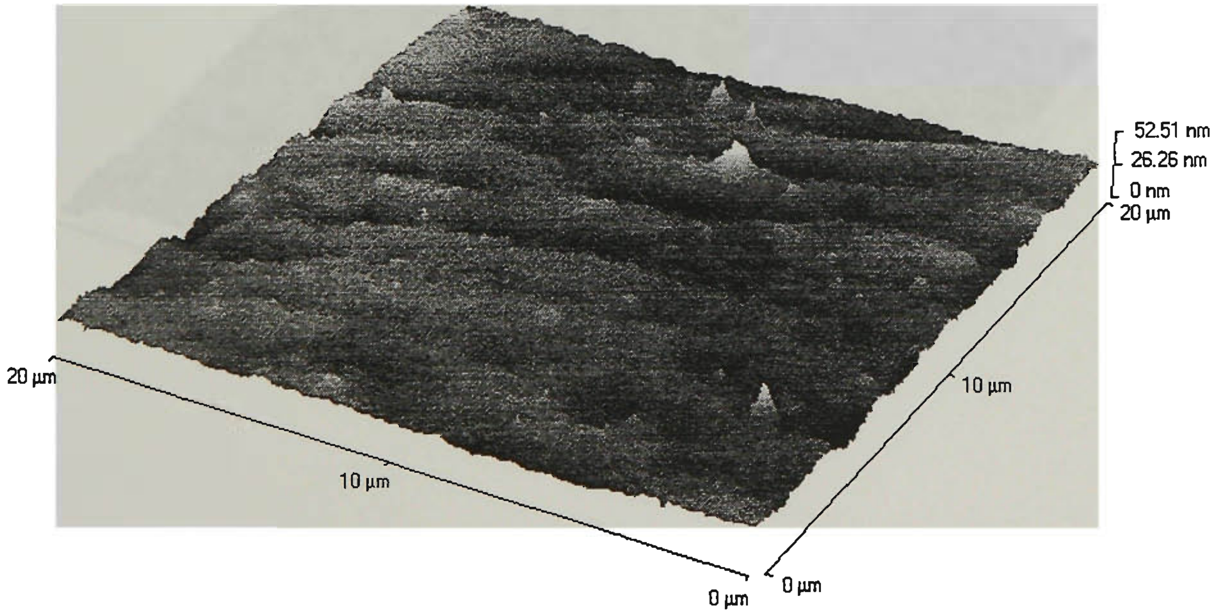


Figure 4.10 AFM image (20×20 μm^2) of the air-facing surface of 30% Aliquat 336/PVC membrane.

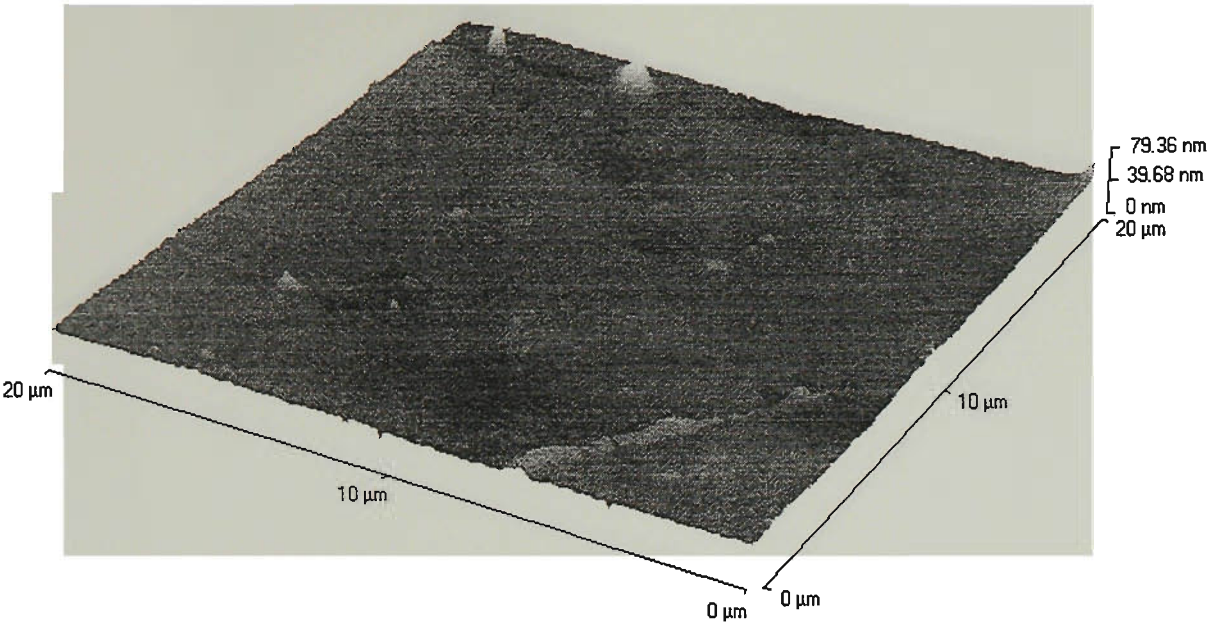


Figure 4.11 AFM image (20×20 µm^2) of the glass-facing surface of 30% Aliquat 336/PVC membrane.

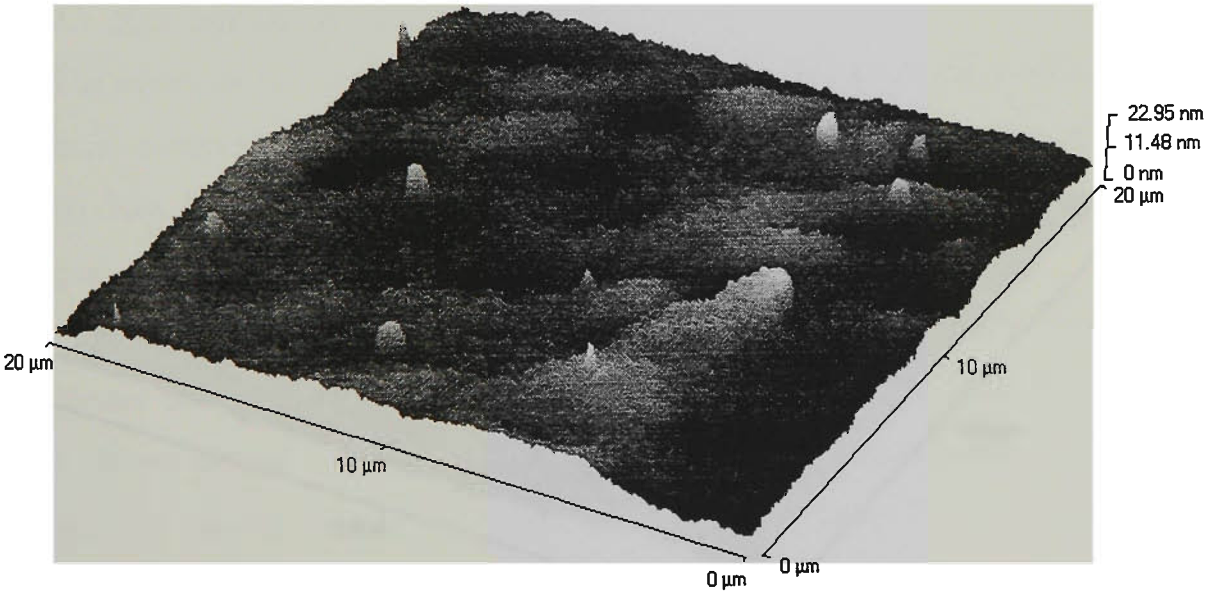


Figure 4.12 AFM image (20×20 µm^2) of the air-facing surface of 40% Aliquat 336/PVC membrane.

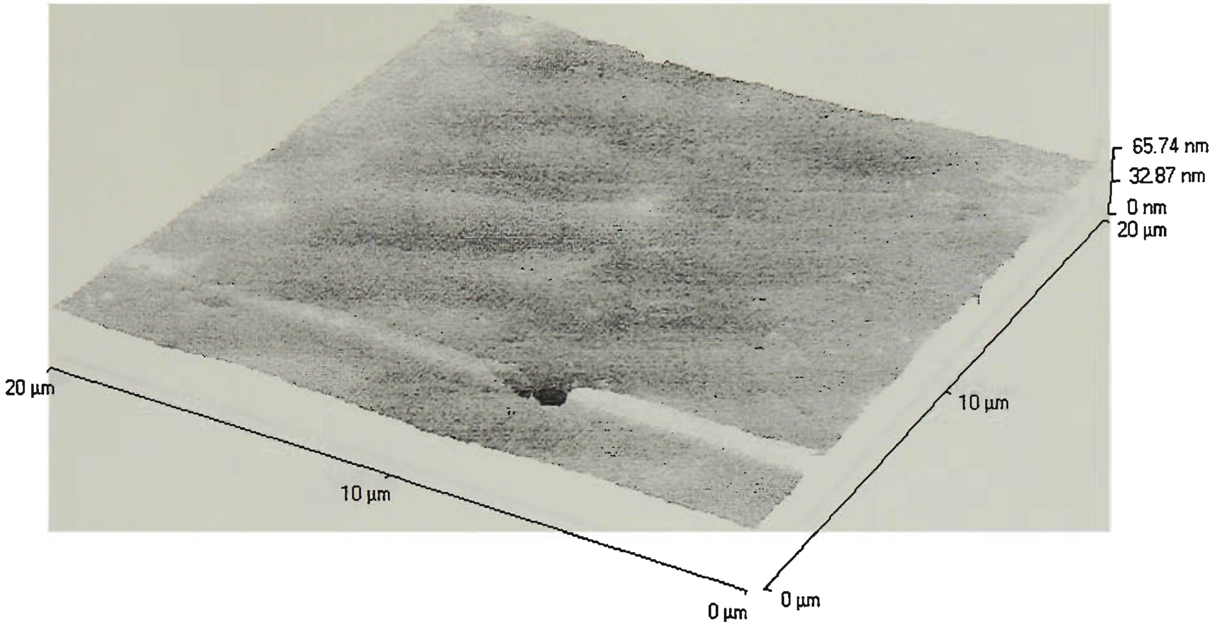


Figure 4.13 AFM image (20×20 µm^2) of the glass-facing surface of 40% Aliquat 336/PVC membrane.

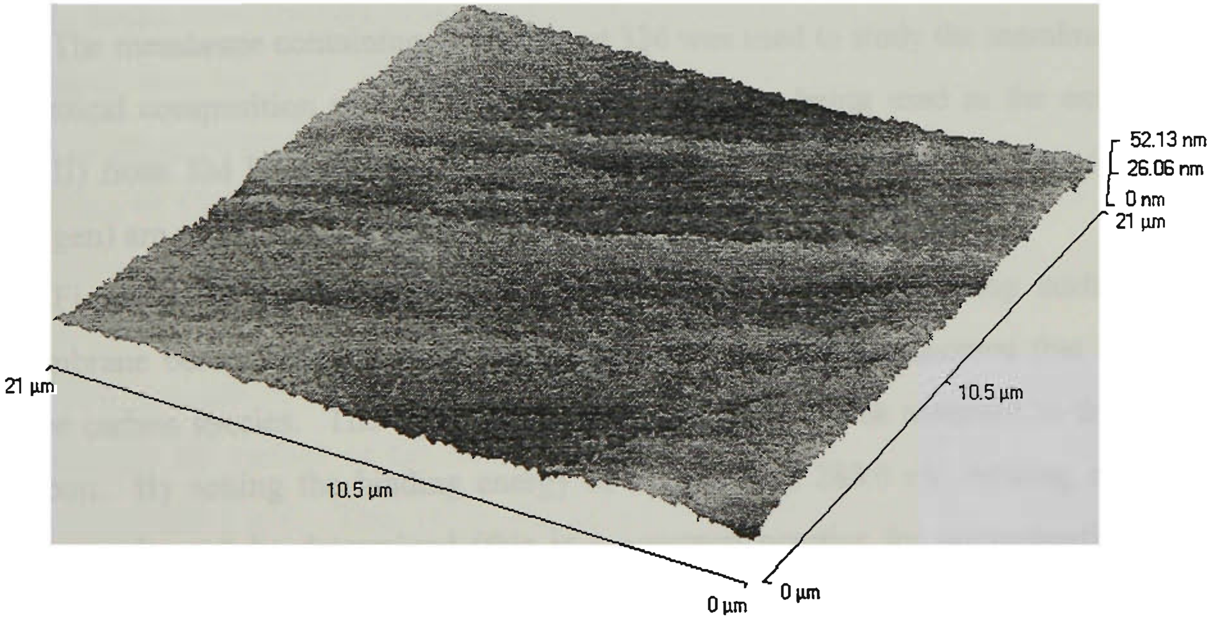


Figure 4.14 AFM image (21×21 µm^2) of the air-facing surface of 50% Aliquat 336/PVC membrane.

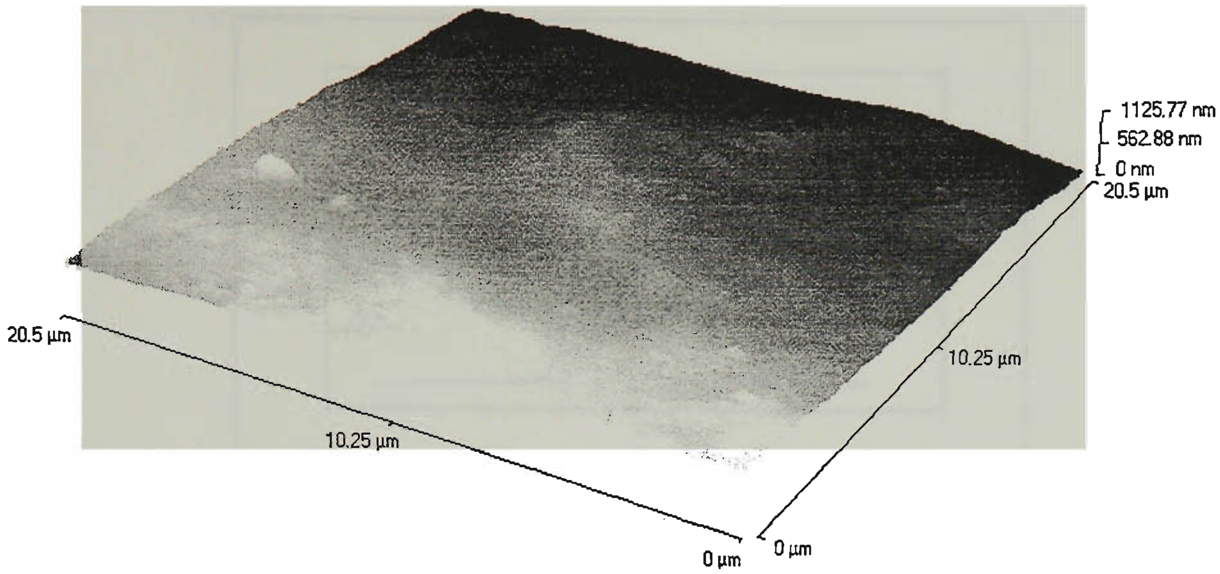


Figure 4.15 AFM image (20×20 μm^2) of the glass-facing surface of 50% Aliquat 336/PVC membrane.

4.4.2 XPS Study of Aliquat 336/PVC Membranes

4.4.2.1 XPS band assignments

The membrane containing 30% Aliquat 336 was used to study the membrane surface chemical composition using XPS for before and after being used in the extraction of Cu(II) from 3M HCl solution. The XP spectra of all detectable elements (except for oxygen) are presented in Figures 4.16 to 4.19.

Figure 4.16 shows the C 1s spectrum taken from the air-facing surface of the membrane before being used in the extraction. Deconvolution showed that there were three carbon species. The lowest binding energy peak can be assigned to the aliphatic carbon. By setting the binding energy of this peak to 285.0 eV, binding energies of other peaks can be determined (this is a common practice for compensating sample surface charging shift [194]). The other two C 1s peaks of similar intensity were assigned to -$\underline{C}H_2$- (285.7 eV) and -$\underline{C}$HCl- (286.8 eV) of the PVC. Both of these peaks in the PVC shifted up-field with respect to aliphatic carbon peak due to the presence of Cl on the hydrocarbon chain [194]. The large amount of aliphatic carbon found on the surface of the membrane was due obviously to the Aliquat 336 as it is a surface active agent (see Table 4.2).

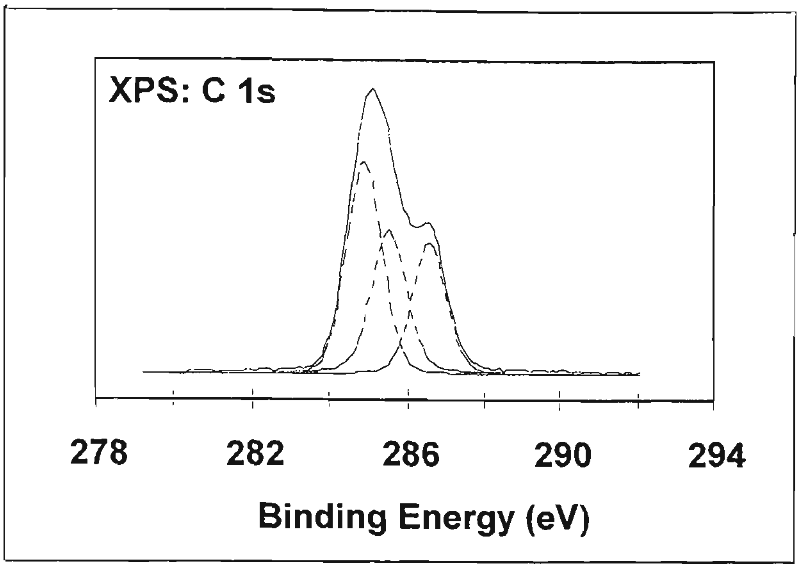


Figure 4.16 C 1s XP spectrum acquired from the air-facing surface of a 30% Aliquat 336/PVC membrane before extraction. The solid line is the photoelectron signal and broken lines are the deconvoluted components of the spectral envelope.

The Cl 2p spectrum is presented in Figure 4.17. The spectrum contains two *pairs* of Cl 2p peaks, with one pair of the peaks located at higher binding energy having a greater intensity than the other. [Each *pair* of Cl 2p peaks has two separate peaks, viz. Cl $2p_{3/2}$ and Cl $2p_{1/2}$, respectively. The intensity of Cl $2p_{3/2}$ is about twice that of Cl $2p_{1/2}$. The splitting of Cl 2p photoelectrons into Cl $2p_{3/2}$ and Cl $2p_{1/2}$ components is due to the coupling of the angular momentum and the spin momentum of Cl 2p photoelectron [194, 195].

The presence of the *two pairs* of Cl 2p peaks indicates that there were two chlorine species on the surface of the membrane. The binding energy of the stronger Cl $2p_{3/2}$ peak was 200.5 eV. This value was in good agreement with the published binding energy (200.8 eV) of -CH$\underline{\text{Cl}}$- in PVC [194] and hence can be assigned to this chlorine species. The binding energy of the weaker Cl $2p_{3/2}$ shifted down-field to 197.0 eV. A similar down-field shift of binding energy was reported for a quaternary ammonium chloride polymer, for example, poly(vinylbenzyltrimethylammonium chloride) [194]. Therefore the weaker Cl 2p peaks can be assigned to the Cl^- in Aliquat 336. The complete resolution of the two sets Cl 2p peaks enabled the quantitative analysis of both species (See Table 4.2).

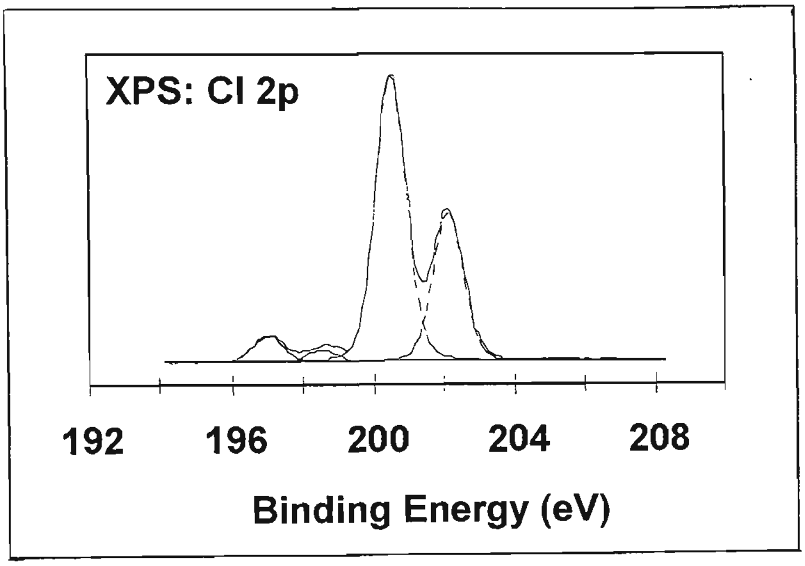


Figure 4.17 Cl 2p XP spectrum acquired from the air-facing surface of a 30% Aliquat 336/PVC membrane before extraction. The solid line is the photoelectron signal and broken lines are the deconvoluted components of the spectral envelope.

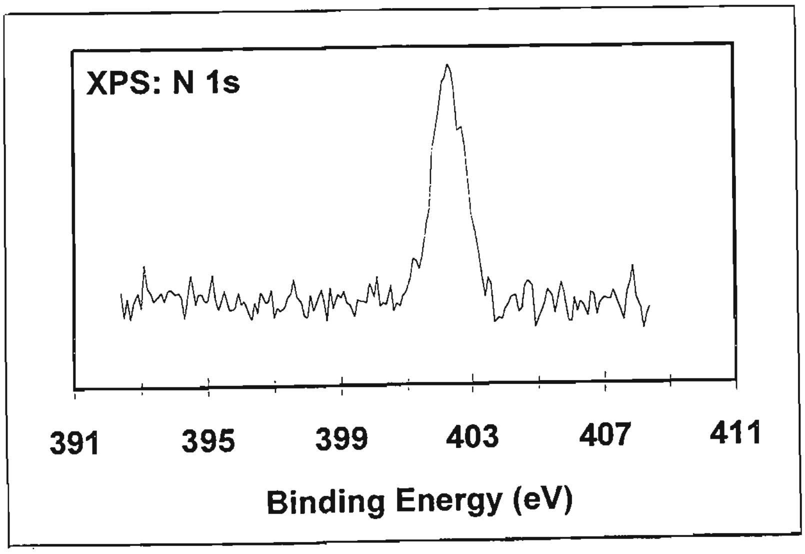


Figure 4.18 N 1s XP spectrum acquired from the air-facing surface of a 30% Aliquat 336/PVC membrane before extraction.

Figure 4.18 shows the N 1s peak detected from the membrane surface and the binding energy of this peak was 402.3 eV. This value was again in good agreement with that reported for the N^+ (402.1 eV) in poly(vinylbenzyltrimethylammonium chloride) [194] and hence can be assigned to the N^+ in Aliquat 336.

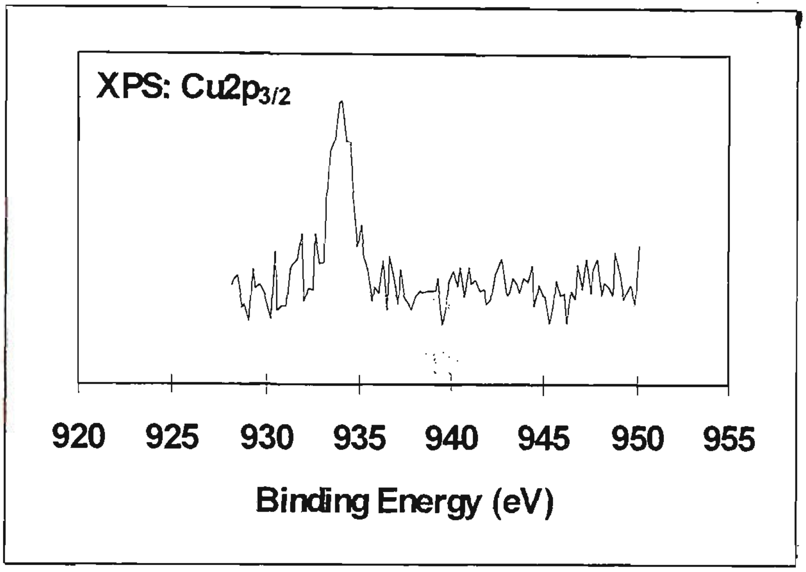


Figure 4.19 Cu 2p XP spectrum acquired from the air-facing surface of a 30% Aliquat 336/PVC membrane after extraction.

XPS study of the membrane surface was also carried out on the membrane which was used for the extraction of Cu(II). Copper was detected from both surfaces of the membrane after it was used in the extraction. Figure 4.19 shows the Cu $2p_{3/2}$ peak obtained from this membrane. The binding energy of the Cu $2p_{3/2}$ peak detected from the membrane was 934.0 eV. This value was slightly higher than that of the elemental copper which was 932.8 eV[196], indicating that the Cu detected from the membrane surface was chemically bonded to anions of high electronegativity (in this case, Cl^-).

4.4.2.2 Quantitative XPS study of the membrane surfaces

Quantitative information of the surfaces of the Aliquat 336/PVC membrane can also be obtained through the XPS study. The results (Table 4.2) show the atomic ratios of all detectable elements on the two surfaces of the membrane. For comparison, the atomic ratios of all the elements found in the bulk of the membrane were also calculated and presented in Table 4.2. For this study, it was necessary to know the chemical composition of Aliquat 336. This information was obtained from the previous study carried out by Paimin [108].

The results show that the atomic ratios of nitrogen (N^+) and Chloride (Cl^-) on the surfaces of the membrane were twice as high as that for the bulk of the membrane. This clearly indicates that Aliquat 336 concentrated on both surfaces of the membrane. For membranes before and after the extraction, the atomic ratios obtained for N^+ indicated that the surfaces of the membranes were covered by almost a complete layer of Aliquat 336. This results also support the mechanism proposed for the studies in Chapters 3 and 4 for the extraction of Cd(II) and Cu(II) from chloride solutions by Aliquat 336. The mechanism postulated that the extraction occurred by means of an interfacial mechanism in which Aliquat 336 at the interface underwent a fast ion-exchange reaction with the metal complex species, which then diffused into the bulk of the membrane and was replaced at the interface by fresh Aliquat 336. The high concentration of Aliquat 336 at the surfaces of the membrane means that the interface ion-exchange reaction can be facilitated.

Table 4.2 Atomic ratios of the surfaces and the bulk of the membrane(a)

Elements	$A_{b.ext.}$ (b)	$G_{b.ext.}$ (b)	$A_{a.\ ext.}$	$G_{a.ext.}$	Bulk
Carbon (total)	1.000	1.000	1.000	1.000	1.000
$Chlorine_{(PVC)}$	0.201	0.170	0.165	0.183	0.307
Chlorine (Cl^-)	0.019	0.020	0.020	0.021	0.011
Nitrogen (N^+)	0.024	0.023	0.026	0.026	0.011
Oxygen	0.011	0.025	0.027	0.020	0.085
Copper	nil	nil	0.001	0.001	nil

(a) The atomic ratios are normalized against carbon.

(b) A and G indicate the surfaces of the membrane formed facing air and glass, respectively. The subscripts "b. ext." and "a. ext" indicate before and after extraction.

The smaller atomic ratios of $\text{chlorine}_{(\text{PVC})}$ on the surfaces of the membrane compared to that of the bulk also indicate that the concentration of Aliquat 336 on the surface was higher than that in the bulk of the membrane.

In general, the XPS characterization of the Aliquat 336/PVC membrane suggested that the chemical composition of the very top layer of the glass- and air-facing surfaces of the membrane was similar.

4.4.3 Micro-structures of The Membrane Surface Studied Using AFM

Smaller scale scans (2×2 μm^2) were taken from both the air- and glass-facing surfaces of the membrane containing 30% Aliquat 336 (Figures 4.20 and 4.21). The smaller scale scans show that both surfaces were porous and have similar appearance of some typical amorphous polymer surfaces such as that found for the ultrafiltration film [174]. It appears that, even in 2×2 μm^2 scans, the glass-facing surface still looks smoother than the air-facing surface. Scans of 2×2 μm^2 scale did not, however, reveal further difference between these surfaces.

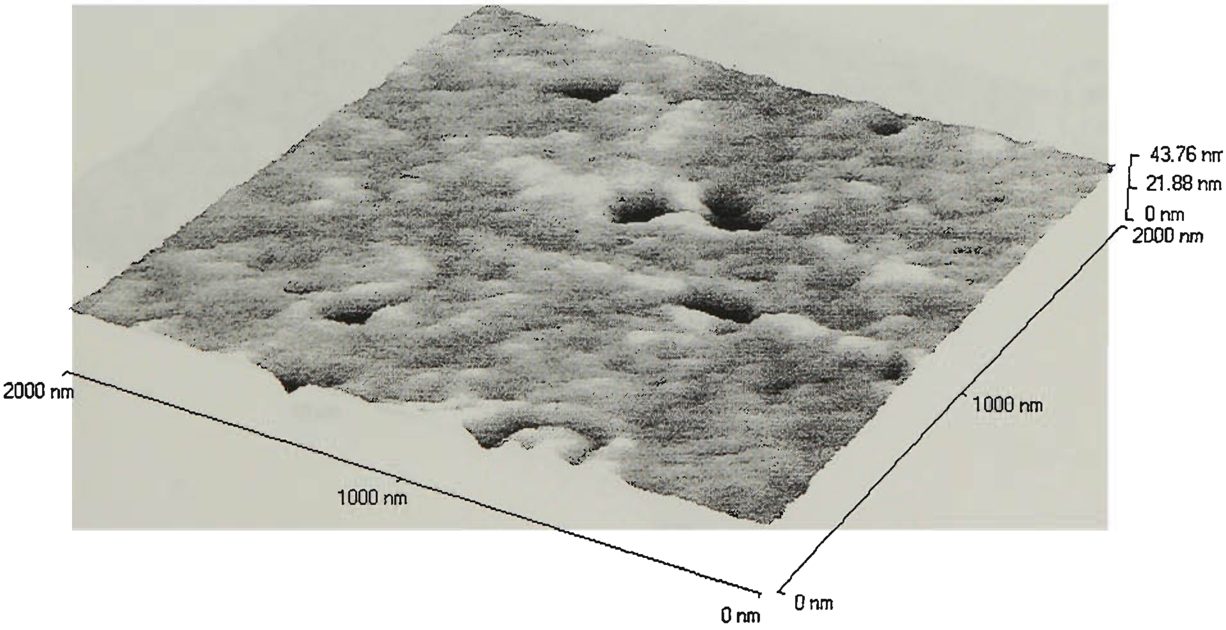


Figure 4.20 AFM image (2×2 μm^2) of the air-facing surface of the membrane containing 30% Aliquat 336.

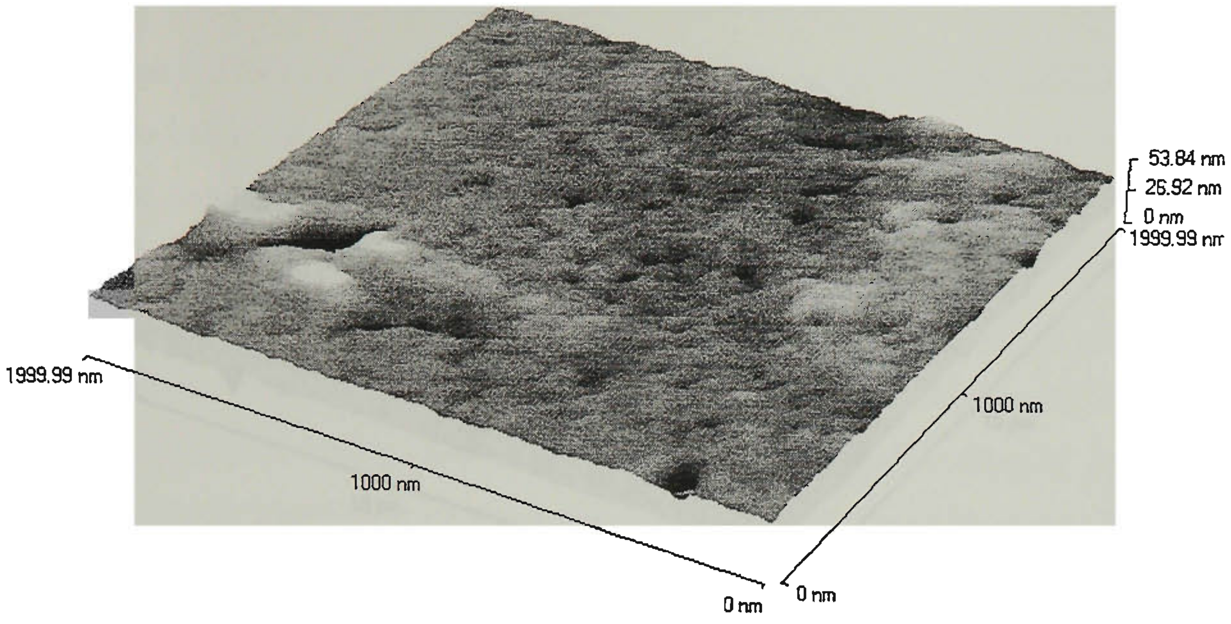


Figure 4.21 AFM image (2×2 μm^2) of the glass-facing surface of the membrane containing 30% Aliquat 336.

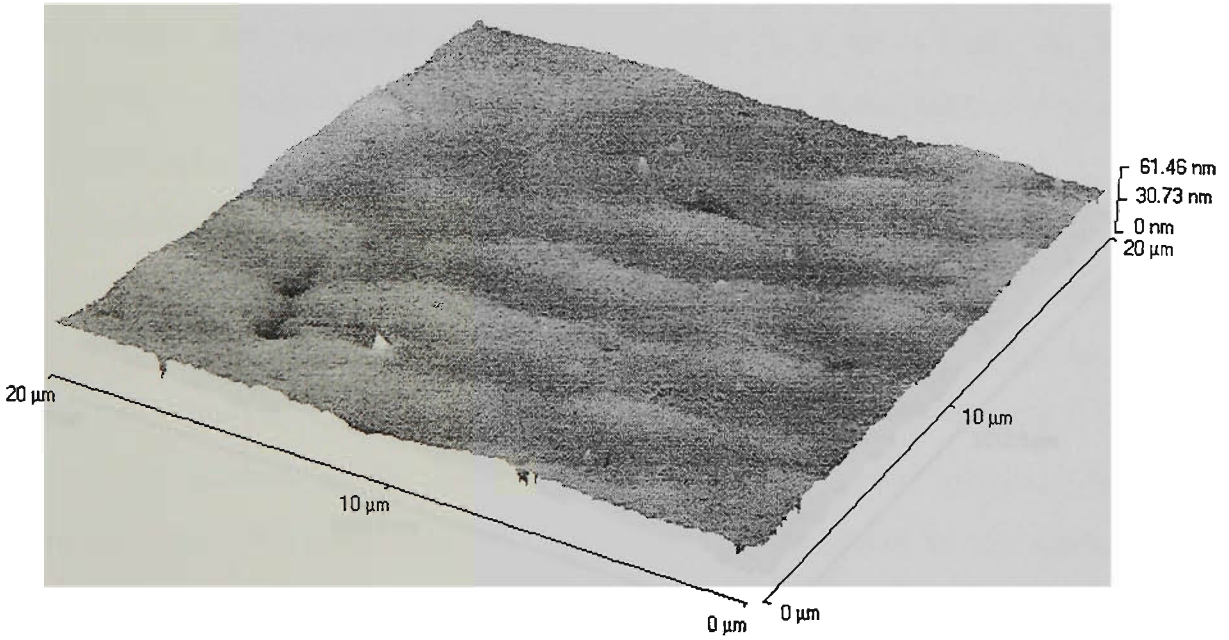


Figure 4.22 AFM image (20×20 μm^2) of the air-facing surface of the membrane containing 30% Aliquat 336 after extracting Cu(II).

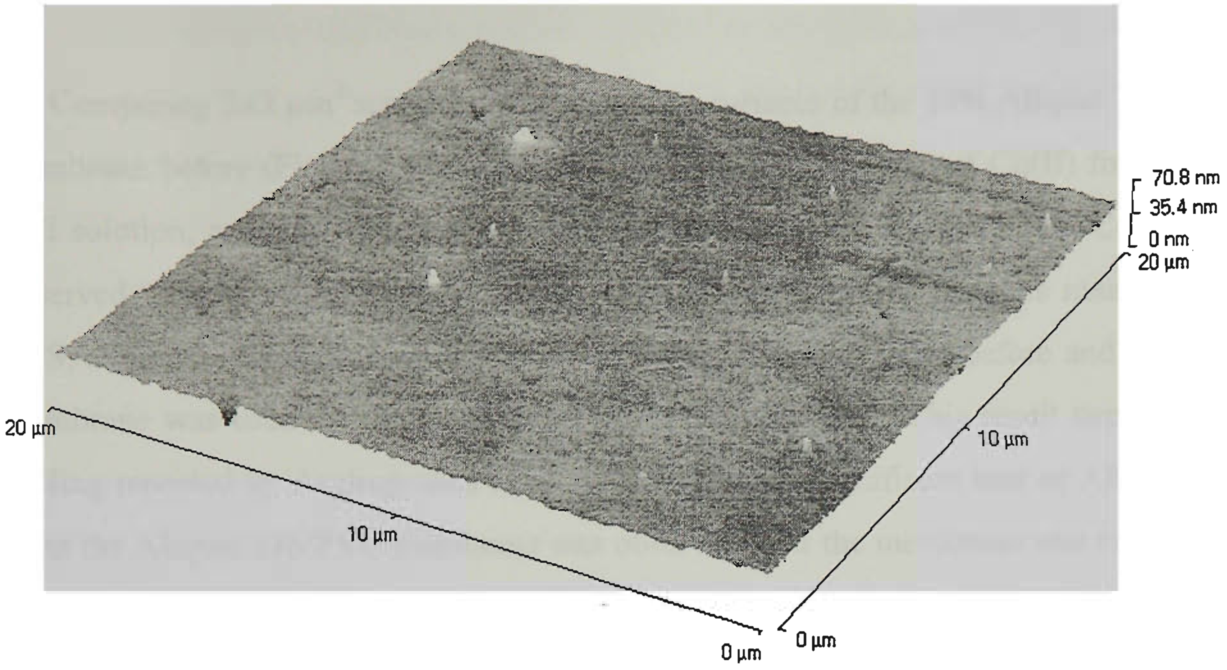


Figure 4.23 AFM image (20×20 µm^2) of the glass-facing surface of the membrane containing 30% Aliquat 336 after extracting Cu(II).

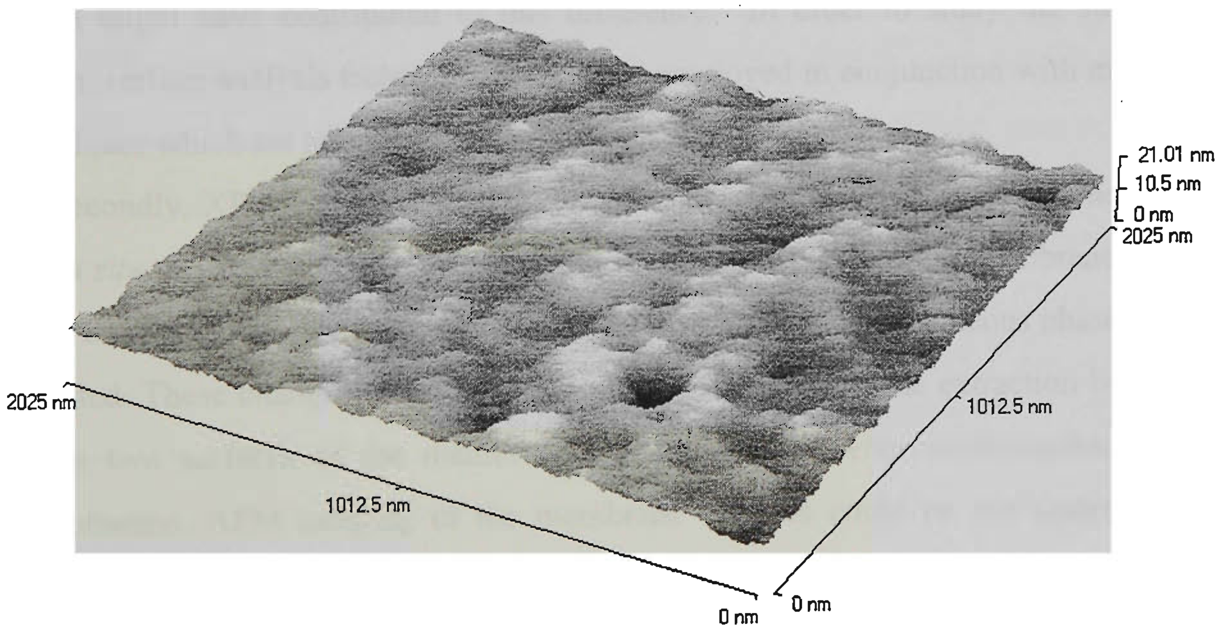


Figure 4.24 AFM image (2×2 µm^2) of the glass-facing surface of the membrane containing 30% Aliquat 336 after extracting Cu(II).

Comparing 2×2 μm^2 scans of the glass-facing surfaces of the 30% Aliquat 336/PVC membrane before (Figure 4.21) and after (Figure 4.24) extraction of Cu(II) from a 3M HCl solution, a minor decrease of the surface porosity after the extraction Cu(II) was observed. The surface chemical composition of the membrane surfaces measured by XPS, as previously discussed, also showed no significant changes before and after the membrane was used for the extraction of Cu(II) (Table 4.2). This result supports the finding reported by Argiropoulos *et al.* [83], in which insignificant loss of Aliquat 336 from the Aliquat 336/PVC membrane was observed after the membrane was exposed to the HCl solution for a prolonged period of time.

Whereas the characterization of the dry membrane surfaces using AFM and XPS has provided valuable physical and chemical information about general surface conditions of the membrane, it did not provide experimental evidence suggesting the possible cause(s) of the different extraction performance of the air- and the glass-facing sides of the membrane. However, as pointed out in Chapters 3 and 4, there could have been some physical and chemical differences in the sub-surface regions of the membrane which might have contributed to this difference. In order to study the sub-surface region, surface analysis techniques have to be employed in conjunction with microtome techniques which are not available in this Department.

Secondly, XPS and AFM imaging of the dry membrane surfaces were not carried out *in situ*. It is possible that physical and chemical changes of the membrane surfaces could have occurred when the membrane was in contact with the aqueous phase and was hydrated. These changes could have caused the difference in the extraction behaviours of the two surfaces of the membrane. To achieve a better understanding of this phenomenon, AFM imaging of the membrane surfaces could be run under aqueous solution condition.

4.4.4 Membrane Stability

Aliquat 336/PVC membrane was reported to have high stability in the extraction of Au and Hg [83, 167]. When exposed to the HCl solution, the loss of Aliquat 336 from the membrane was insignificant and no bleeding or dimensional distortion was found [83]. In this study, however, it was found that the stability of the membrane was dependent upon the metal being extracted.

In this study, The Aliquat 336/PVC membrane has demonstrated excellent stability in the extraction of Cu(II) from HCl solutions, in terms of the lack of bleeding and dimensional distortion. After extracting Cu(II), the membrane changed from totally colourless to a bright yellow colour. AFM imaging of the membrane surfaces before and after extraction of Cu(II) showed only a minor topographic difference between these membranes (Figure 4.21 to 4.24). Chemical analysis of the membrane surfaces before and after extraction using XPS showed no evidence of the loss of Aliquat 336 from the membrane surfaces (Table 4.2). These results suggest that the membrane could be reused.

When the membrane was used in the extraction of Cd(II), however, the membrane showed very poor stability. This was shown by the dimensional distortion (visible wrinkles shown in the topographic image, Figure 4.25) which appeared on the surface of the Cd(II) loaded membrane and its surfaces appeared sticky. Figure 4.25 shows an AFM image (50×50 μm^2) of the glass-facing surface of a Cd(II) loaded 40% Aliquat 336/PVC membrane. An irregular topographic pattern with some fine lines can be observed from the upper part of figure 4.25. Both forward and backward lateral force mapping (Figures 4.26 and 4.27) of the same area of the membrane produced large deflections of the cantilever by the fine lines and a circular patch on their right hand side (see also Figure 4.28). It is most likely that those fine lines were micro-cracks developed on the surface membrane during the extraction of Cd(II) and a viscous material bled out through these micro-cracks. The circular patch that registered a large lateral force was most likely to be a patch of viscous material bled out of a small hole on the membrane surface which was developed during the extraction of Cd(II). This viscous material interacted with the tip more strongly than the rest of the areas of the surface and therefore contributing to larger lateral forces sensed by the tip. Macroscopically, this viscous material also contributed to the stickiness of the Cd(II) loaded membrane.

XPS analysis of the Cd(II) saturated membrane surface was not performed due to concerns of the potential contamination of the vacuum chamber by the sample. In the extraction of Cd(II), the poor dimensional and structural stability of the membrane of the present formation offers slim possibility of being reused. More study is therefore required in order to achieve a full understanding of the mechanism of the membrane surface change after extracting Cd(II).

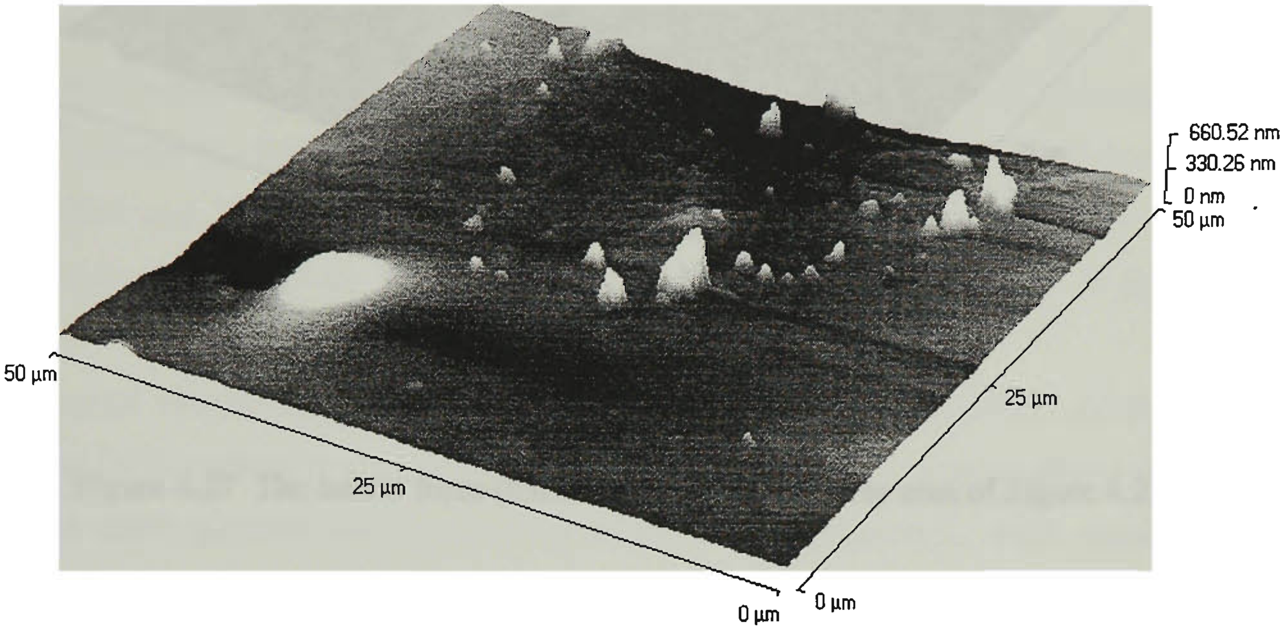


Figure 4.25 AFM image (50×50 μm^2) of the glass-facing surface of the membrane containing 40% Aliquat 336 after extracting Cd(II).

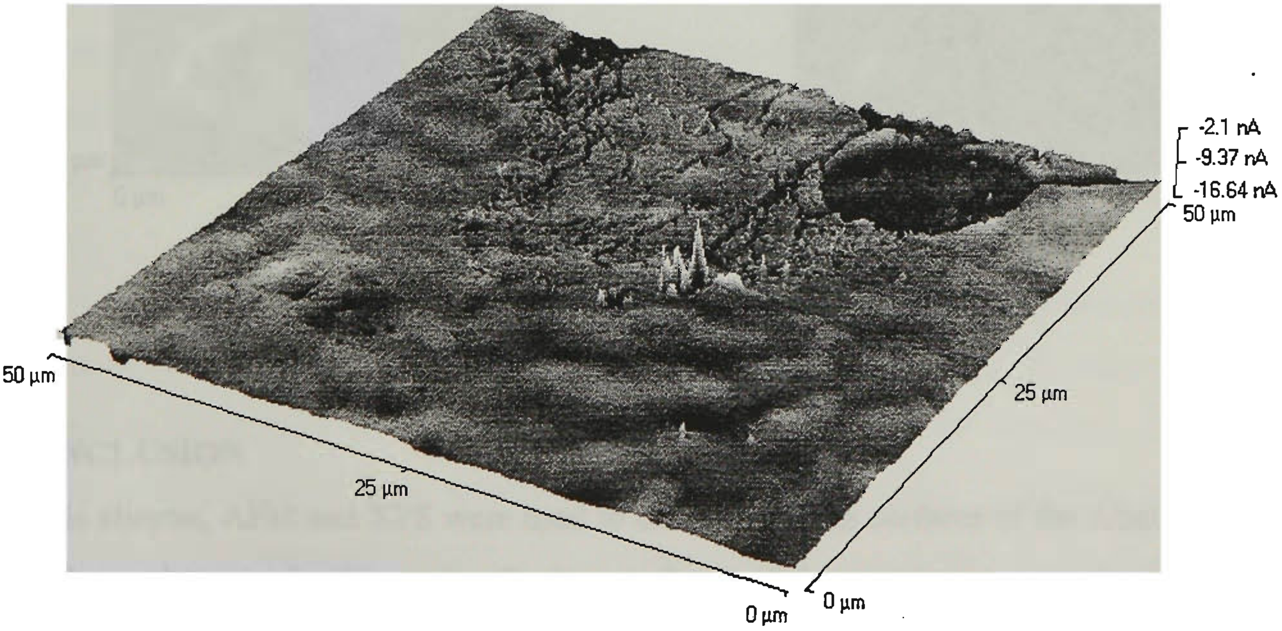


Figure 4.26 The lateral force (forward) map of the same area of Figure 4.25.

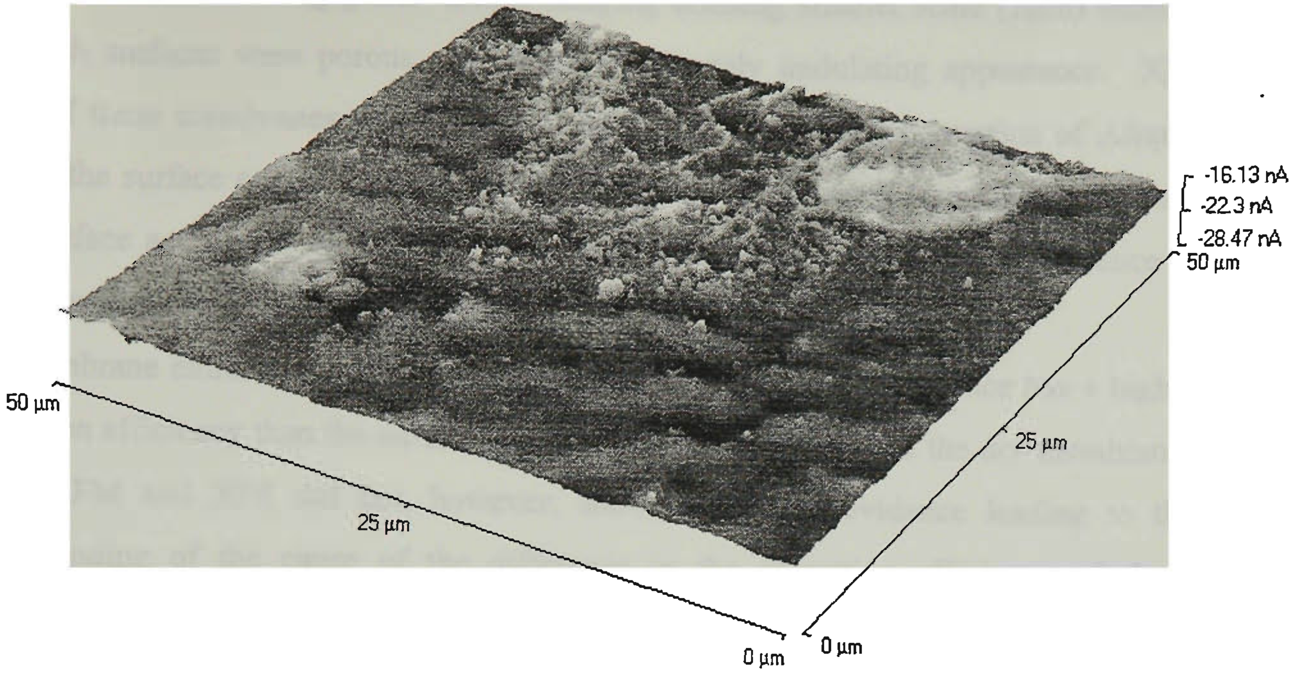


Figure 4.27 The lateral force (backward) map of the same area of Figure 4.25.

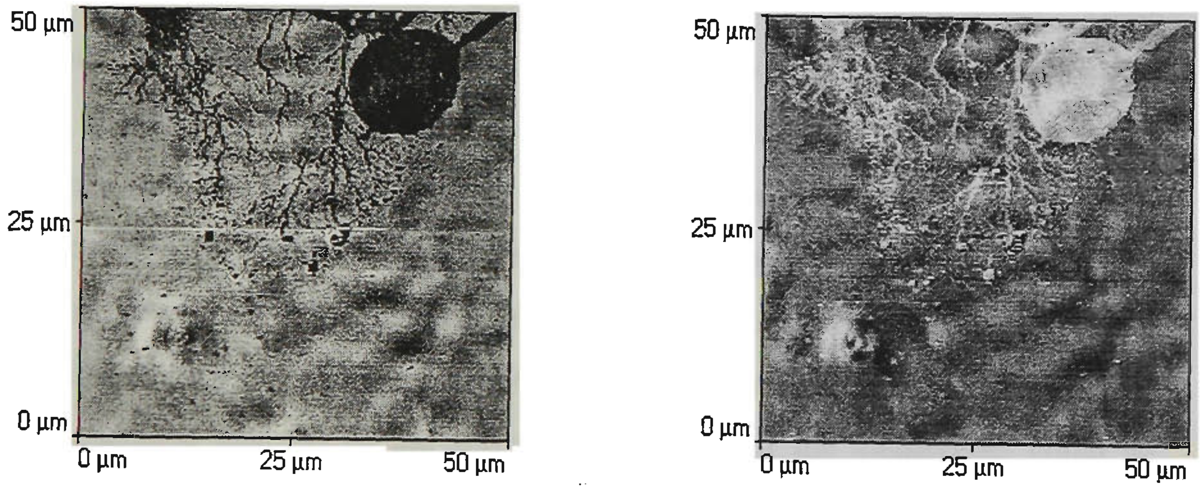


Figure 4.28 Top views of figures 4.26 and 4.27, respectively.

4.4 CONCLUSION

In this chapter, AFM and XPS were used to characterize the surfaces of the Aliquat 336/PVC membranes. In this study, the two surfaces of the membrane were formed under different conditions, with one surface formed naturally facing air and the other, against glass surface. AFM images acquired from these surfaces showed that, for all the membranes containing various amount of Aliquat 336, the surfaces facing air were rougher than those facing glass. Detail imaging utilising smaller scale (2μm) showed that both surfaces were porous and have a moderately undulating appearance. XPS study of these membranes showed that there was substantial concentration of Aliquat 336 on the surface compared to the bulk of the membrane which was attributed to the high surface activity of Aliquat 336 molecules. There was insignificant difference in their chemical composition between the air- and glass-facing surfaces.

Membrane extraction experiment showed that the glass-facing surface has a higher extraction efficiency than the air-facing surface. Surface analysis of the dry membranes using AFM and XPS did not, however, show convincing evidence leading to the understanding of the cause of the difference in the extraction efficiency of these surfaces.

A logical analysis of the results may lead to the following possibilities: (a) Both AFM and XPS analysis of the dry membrane were not carried out *in situ*. Whilst they provided useful physical and chemical information of the membrane, these methods were not able to further elaborate the possible physical and chemical changes of the membrane surface when membranes were in contact with an aqueous phase. These changes could have had an effect on the extraction behaviour of the two surfaces of the membrane. (b) The top layer of the membrane surfaces might not have contributed to the difference in the extraction capacities of the two surfaces that were formed under different conditions. Instead, it might be the *sub-surface regions* of the membrane surfaces that determined the apparent capacities of these surfaces. To achieve a better understanding of this phenomenon, AFM imaging of the membrane surfaces under water and chemical analysis of the sub-surface regions of the membranes could be carried out.

Although the Aliquat 336/PVC membrane exhibited excellent physical and chemical stability in the extraction of Cu(II) and was also reported previously to be very stable in the extraction of Au(III) and Hg(II) ions from hydrochloric acid solutions, the membrane however showed poor stability in the extraction of Cd(II). This indicated that the physical and chemical stability of the membrane in the extraction of metal ions was dependent upon the metal complex being extracted. In this case, the problems associated with the instability of the Aliquat 336/PVC membrane towards the Cd(II) ion require further research in order to meet requirements for the industrial application of this membrane.

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