

An Investigation of Solubility of Aliquat 336 in Different Extracted Solutions

Jianning Xu, Rohani Paimin¹, Wei Shen², and Xungai Wang*

School of Engineering and Technology, Deakin University, Geelong, Victoria 3217, Australia

¹Chemical Science, School of Life Sciences and Technology, Victoria University of Technology,

P.O. Box 14428, MCMC, Melbourne, Victoria 8001, Australia

²Australian Pulp and Paper Institute, Department of Chemical Engineering, Monash University, Victoria 3800, Australia

(Received November 7, 2002; Revised February 3, 2002; February 10, 2003)

Abstract: A major concern in solvent extraction processes is the loss of extractant into the aqueous phase due to its slight solubility in the aqueous phase. Similarly, in membrane extraction processes, extractant loss through extractant leakage from the membrane into the aqueous phase is also a concern. Several published membrane extraction studies using Aliquat 336 as the extractant, have expressed this concern, but none has studied extractant leakage quantitatively. It is the authors' opinion that the extractant leakage should be considered as a technical parameter of a membrane. In our laboratory active progress has been made in using Aliquat 336 'entangled' into the polymer membranes to remove heavy metal ions from wastewater samples. In this work, we studied the loss of Aliquat 336 from the point of view of its solubility in aqueous solutions. The results showed that the solubilities of Aliquat 336 in an aqueous phase acidified with 2 M HCl is about 0.1 g/100 ml of the solution. This figure provides a useful guideline for evaluating the leakage of the Aliquat 336 extractant from the membranes.

Keywords: Polymer membrane, Aliquat 336, Solubility, PVC/Aliquat 336 membrane, Separation, Membrane extraction

Introduction

It is known that the loss of extractant from the membrane to aqueous phase occurs in systems such as the Supported Liquid Membrane (SLM). SLM normally consists of an extractant and diluent held within the pores of a supporting membrane. In such a system, some 'bleeding' of the extractant from the membrane into the aqueous phase often occurs.

One way in which this problem can be reduced is by homogenizing the mixture of reagent (extractant), plasticizer and polyvinyl chloride (PVC) into an 'entangled' membrane. Studies have shown that the polymer liquid membrane consisting of the carrier species, Aliquat 336, immobilised in a polymer matrix, PVC, can be used successfully in the extraction of gold(III)[1], Cd(II)[2,3], and Pd(II)[4] from hydrochloric acid solutions. This however, is not entirely without the associated 'bleeding' problem. It is shown in this paper that small 'leakage' of the extractant from the membrane still occurs, however, this loss is minimal compared to the loss of the extractant suffered by the SLM.

In a recent paper, Xu *et al.*[3] described an experimental study on developing and characterizing a "sandwich" membrane. Whilst the authors showed that this new membrane offers higher extraction rate and capacity to heavy metal species such as Cd(II), the leakage data of this type of membrane was not available. Aliquat 336 is a surface-active compound and tends to stay at the surface of the membrane[3,5]. When the membrane is in contact with the aqueous phase, Aliquat 336 molecule at the surface orientates itself so that the ammonium ion group faces the water and the non-polar hydrocarbon groups face away from the water. Undoubtedly,

Aliquat 336 molecules leaked into aqueous phase will first occupy the interface between water and air[3,5]. In our recent work we will focus on whether Aliquat 336 could remain dissolved in the aqueous phase.

In this paper, the leakage of Aliquat 336 from the Aliquat 336/PVC 'entangled' membrane is studied by means of investigating the concentration of the extractant in the aqueous phase. As a comparison, investigation is also made on the extent of the leakage of Aliquat 336 from the sintered glass disc membrane-this membrane is similar in principle to the SLM membranes.

Experimental

Reagents

Aliquat 336 (Fluka), a complex mixture of quaternary ammonium chlorides[19], was used as received. High molecular weight (> 90000) polyvinyl chloride (PVC, Selectophore[®]) was used for membrane preparation. Tetrahydrofuran (THF) was HPLC grade (BDH) and further purified by passing through an activated alumina column to remove stabilisers and peroxides before use. Hydrochloric acid, cadmium (II) chloride were both of analytical grade (BDH). Cd(II) solution was prepared in the concentration of 2.0 M HCl. Cd(II) (Standard (BDH Spectrosol) was used for preparation of the standard solutions for the atomic absorption spectroscopy (GBC 902).

Membrane Preparation

The membranes used in this study were prepared by dissolving a mixture of Aliquat 336 and PVC in about 50 ml of THF. The homogeneous solution obtained was then poured into a glass ring on a flat glass plate. The THF was

*Corresponding author: xwang@deakin.edu.au

allowed to evaporate slowly over 12 h to yield a colourless, flexible, transparent and mechanically strong membrane. The membrane was then removed from the glass plate and used for the membrane extraction study. In this study, membranes containing 40 % Aliquat 336/PVC (m/m) were prepared. The capsulated membranes were prepared using the method detailed in a previous paper[3].

Sintered Glass Discs Membrane

The sintered porous glass discs (PYREX[®]), with a diameter of 50 mm and thickness of 4.5 mm, were acquired from a local glassware supplier. The pore size is from 40 to 100 micrometers. The sintered glass was allowed to contact the Aliquat 336 extractant and a known amount of it was absorbed into the disc via capillary penetration. The sintered glass membrane was also used for the extraction study.

The XPS (X-ray Photoelectron Spectroscopy) Measurements and Sample Preparation

The XPS measurements of the samples 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. 3 mm². The photoelectron emission angle was 0° with respect to the surface normal. This corresponds to a sampling depth of ca. 10 nm.

The XPS was used because of its surface sensitivity. When an aqueous solution saturated with Aliquat 336 was deposited on a Teflon tape, Aliquat 336 stays on the surface of the Teflon tape after the evaporation of water. This offers an easy situation for the N and Cl atoms in Aliquat 336 to be detected. It is useful to mention that although XPS has a very high surface sensitivity, measurements conducted in the present study was not intended to provide quantitative information about the solubility of Aliquat 336 in aqueous phase. Instead, it was intended to provide qualitative confirmation of the existence of Aliquat 336 in the aqueous phase. This point will be further elaborated in a later section.

Membrane Extraction

Membrane extraction studies were carried out in a two-compartment cell, at a room temperature of about 25 °C. Each compartment had a volume capacity of 220 ml. A encapsulated membrane was inserted between the two compartments. Each compartment was stirred at a constant rate throughout the extraction process by a magnetic stirrer. An aqueous solution of the same composition was placed in both compartments.

Qualitative and Quantitative Approaches for Measurement of the Solubility of Aliquat 336

Qualitative Observation of Change of Surface Pressure

Aliquat 336 is a strong surfactant and to a limited extent it

is soluble in aqueous solution. When a drop of this aqueous solution (containing dissolved Aliquat 336) was placed into solution that contained an oil droplet, the reduction in the size of the droplet can be used as a qualitative measure of the presence of Aliquat 336 in the solution. In this work, an oil-soluble and water-insoluble dye, Sudan Red, was used to colour the oil droplet in order to assist with the observation.

Qualitative XPS Measurement of Possible Deposit of Aliquat 336 on Teflon

The XPS measurement described here provides semi-quantitative data. Aqueous solution that was used in the extraction work using the capsulated Aliquat 336/PVC membrane was deposited on a Teflon film. Eight drops (ca. 0.4 ml) were deposited on an area of 1 cm². After the evaporation of water, the surface of the Teflon film was introduced into the high vacuum sample preparation chamber of the XP spectrometer for further degassing. Of course, this method is based on the assumption that the surface concentration of Aliquat 336 deposited on the Teflon exceeds the detection limit of XPS.

Gravitational Measurements of 100 ml of Aqueous Solution that was Saturated with Aliquat 336

Gravimetric measurement described in this section provides the more definitive and quantitative results for the solubility of Aliquat 336 in aqueous phase. In this measurement, predetermined masses (0.0880-70000 g) of Aliquat 336 were placed in the capsulated Aliquat 336/PVC membranes, which were made to contact with 200 ml of HCl solutions for about 168 hours at room temperature. Care was taken to avoid any loss of the HCl solution during the experiment. Any loss of the HCl solution could be confirmed by weighing the 2.0 M HCl solution at 0 hour (103.5082 g/100 ml) and 168 hour (103.5880 g/100 ml).

Results and Discussions

Qualitative Observation of Change of Surface Pressure

Figures 1-3 show the change in the size of an oil patch as an indication of the change of surface pressure. Most quaternary amines, including Aliquat 336, have surfactant properties. These molecules tend to form an oriented monomolecular layer at the water-air interface, with their hydrophobic tails pointing into the air. The existence of this layer can be qualitatively monitored by putting an oil droplet on water surface. Since oil does not dissolve in water, it forms a lens on top of water (assuming the density of oil is lower than that of water). As the number of molecules at the surface increases, the crowded mono-molecular layer will exert a surface pressure to the oil phase, causing the oil lens to decrease its size.

Figure 1(a) shows the size of the oil droplet on a 2 M HCl solution and Figure 1(b) shows the size of the oil droplet on

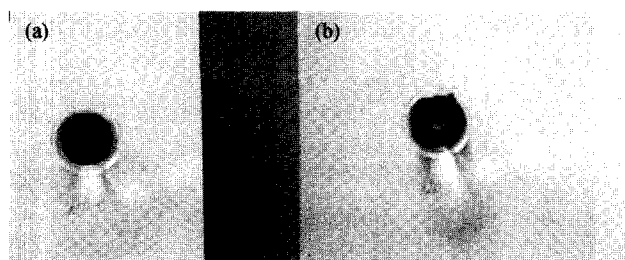


Figure 1. (a) shows the oil patch deposited on the surface of a 2 M HCl solution, (b) shows the same oil patch after the addition of 1 ml of another aqueous solution that had been extracted by using a capsulated PVC/Aliquat 336 membrane in an extracting experiment for 216.5 hours (The capsulated membrane contains 3.3047 g Aliquat 336).

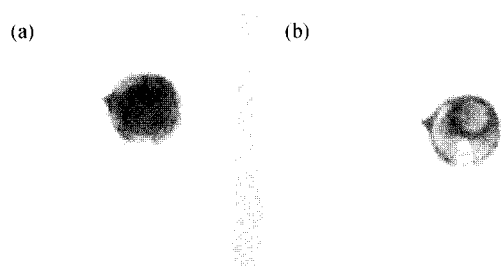


Figure 2. (a) shows the oil patch deposited on the surface of a 2 M HCl solution, (b) shows the same oil patch after the addition of 1 ml of another aqueous solution that had been extracted by using a sintered glass disc loaded with 2.0 g of Aliquat 336 via capillary imbibition in an extracting experiment for 162.5 hours.

the 2 M HCl solution that had 1 ml of the aqueous solution that was used in the membrane extraction work[3], added to it. This aqueous solution was in contact with the encapsulated Aliquat 336/PVC membrane. Figure 1(b) shows that there was a small reduction in the size of the oil droplet, indicating that surface pressure exerted by Aliquat 336 molecules on the oil droplet is detectable using this test. Therefore the change in oil droplet size indicates that Aliquat 336 is slightly soluble in the aqueous phase.

Figures 2(a) and 2(b) and Figures 3(a) and 3(b), show similar reduction in size of the oil droplet when the aqueous solution in which the oil droplet was placed in was added 1 ml of the aqueous solution. This aqueous solution had been used in the extraction of Cd(II) from 2 M HCl solution using the sintered glass membrane loaded with Aliquat 336. Qualitatively, the magnitude of the size change of the oil droplet was similar to the situation indicated in Figure 1. This suggests that Aliquat 336 is soluble to a certain extent in water.

Results Obtained Using XPS to Analyse the Solubility of Aliquat 336 in Different Extracted Solutions

XPS was used to qualitatively confirm the presence of

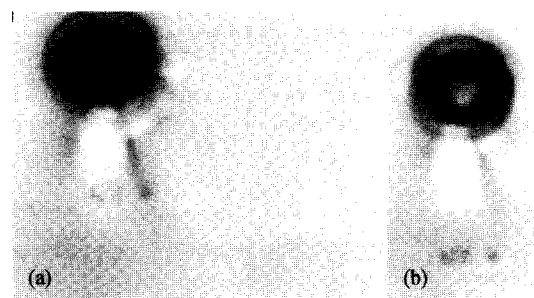


Figure 3. (a) shows the oil patch deposited on the surface of a 2 M HCl solution, (b) the same oil patch after the addition of 1 ml of another aqueous solution that had been extracted by using three pieces of sintered glass discs loaded with 6.0 g of Aliquat 336 via capillary imbibition in an extracting experiment for 167.5 hours.

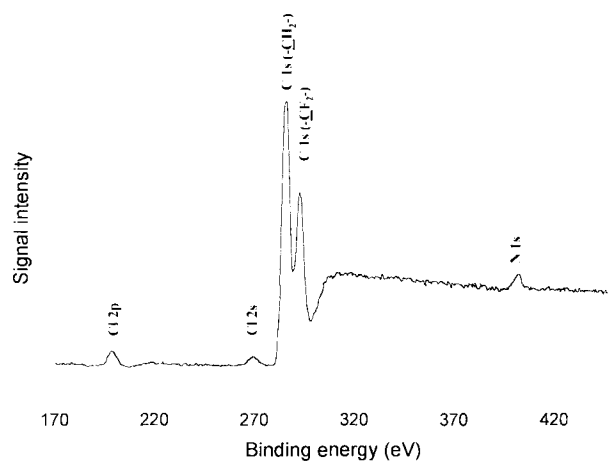


Figure 4. XPS spectrum.

dissolved Aliquat 336 in the aqueous phase. As mentioned in the experimental section, the sample was prepared by placing aqueous sample droplets on a fresh PTFE film surface to allow the evaporation of water. Due to low surface free energy of PTFE, it is not possible for a uniform layer of Aliquat 336 to form on the surface of PTFE. This makes any attempt of quantitative analysis of Aliquat 336 grossly unreliable.

Figure 4 shows the XP spectrum of Aliquat 336 deposited on the PTFE surface. The two small peaks located at 197.2 eV and 268.6 eV were due to Cl 2p and Cl 2s[6], respectively. The highest peak located at 285.0 eV was due to C 1s, which was originated from the aliphatic chains in Aliquat 336 molecule ($-\text{CH}_2-$)[6]. Immediately next to this peak and on the high binding energy side locates another C 1s peak, which has a binding energy of 292.6 eV. This peak was due to the fluorocarbon ($-\text{CF}_2-$)[6], which was originated from the PTFE substrate. The small peak located at 402.0 eV was due to N 1s.

The binding energy of the N 1s peak of 402.0 is in extremely good agreement with the N^+ (402.1 eV) in poly

(vinylbenzyltrimethylammonium chloride)[6] and therefore can be assigned to the N^+ in Aliquat 336.

Under the data acquisition conditions used, the Cl 2p band could not be resolved. This band should contain two peaks, Cl 2p_{3/2} and Cl 2p_{1/2}, with the second one at a slightly higher binding energy than the first one, but only half the height. Wang[5] have observed both the chlorine peaks from a PVC based membrane containing 30 % Aliquat 336. These authors reported that the binding energy of the Cl 2p_{3/2} peak has a binding energy of 197.0 eV. Because this binding energy is very similar to the chlorine in poly(vinylbenzyltrimethylammonium chloride)[6], it was assigned to the chloride anion in Aliquat 336[5]. In situation where the Cl 2p band cannot be completely resolved, it can be assumed the unresolved peak would skew towards that of Cl 2p_{3/2}, since its intensity is twice that of the Cl 2p_{1/2} peak. Thus, the unresolved Cl 2p band observed in this study can be assigned as the Chlorine anion in Aliquat 336.

The much greater intensity of the C peak than those of N and Cl peaks can be qualitatively interpreted as the atomic fraction of carbon in aliquat 336 molecules being much greater than that of nitrogen and chlorine, although a quantitative analysis of peak intensity would require the atomic sensitivity factors of these elements. Paimin has reported that the Aliquat 336 consists three long hydrocarbon chains, and the average number of carbon atoms in the molecule would therefore be ~25[7]. On this basis, the molecular fraction of N in Aliquat 336 (and also that of Cl) would only be ~1/(25+2). The XPS results confirmed the existence of Aliquat 336 in the aqueous phase.

Gravimetric Measurement of the Dissolved Aliquat 336 in Aqueous Phase

The prolonged contact of the membranes with the HCl solution produced the aqueous solution which was saturated with Aliquat 336. 100 ml of this solution was removed and placed into volumetric flask and weighed. Figure 5 shows the relationship between the quantity of Aliquat 336 used in

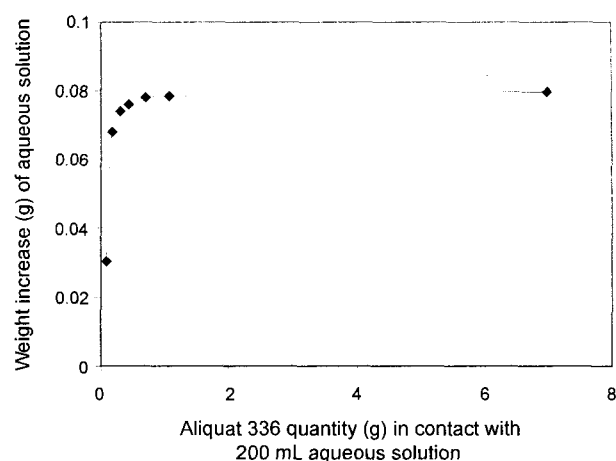


Figure 5. The plot of the quantity of Aliquat 336 in contact with 200 ml of aqueous solution against the weight increase (against the 2.0 M HCl solution) of 100 ml of aqueous solution after contacting with Aliquat 336.

the encapsulated membranes which were in contact with the aqueous solutions and the weight increase of the 2.0 M HCl solution. This result shows that saturation of the aqueous solution by Aliquat 336 has clearly been reached when the solution (200 ml) was in contact with 0.7 g of the extractant, aliquat 336. At this point, the concentration of Aliquat 336 in the solution was 0.08 g/100 ml or 800 ppm. This represents the solubility of Aliquat 336 in 2 M HCl solution at room temperature.

Results in Table 1 suggest that for systems like capsulated and sintered glass membranes where free extractant is available within the membrane, the leakage is to some extent, determined by the solubility of the extractant. However, when Aliquat 336 is incorporated as 'anentangled' component within a polymer membrane, the leakage is much lower. The total amount of Aliquat 336 present in the 'entangled' Aliquat 336/PVC membrane used in the extraction study (see Table 1) was 0.32 g and from this work, this would translate into

Table 1. The equilibrium concentration of Aliquat 336 in 2 M HCl solution after being in contact with various membranes for specified durations

| Trial number and description | Weight of 100 ml solution after extraction (g) | Solution weight increase against 2 M HCl solution (g) |
|---|--|---|
| (1) Aqueous solution extracted using capsulated membrane made of 0.8 g 40 % PVC/Aliquat 336 and 2.1703 g free Aliquat 336 | 103.5803 | 0.0721 |
| (2) Aqueous solution extracted using capsulated membrane made of 1.0 g 40 % PVC/Aliquat 336 and 3.3047 g free Aliquat 336 | 103.5812 | 0.0730 |
| (3) Aqueous solution extracted using a sintered disc loaded with 2.0 g Aliquat 336 | 103.5808 | 0.0726 |
| (4) Aqueous solution extracted using three pieces of sintered discs loaded with 6.0 g Aliquat 336 | 103.5822 | 0.0740 |
| (5) 0.8 g polymer membrane with 40 % PVC/Aliquat 336, soaked in 200 ml of 2 M HCl for 20 days. | 103.5266 | 0.0184 |
| (6) 2 M HCl solution | 103.5082 | - |
| (7) 7.0000 g Aliquat 336 dissolved in 200 ml of HCl for 7 days | 103.5880 | 0.0798 |

an Aliquat 336 concentration of 0.06 g/100 ml in the aqueous phase. The measured weight increase in the aqueous solution, however, was substantially lower (Table 1). This suggests that the entangled extractant molecules (as compare with free molecules) may have a restricted mobility within the membrane.

Conclusion

This study has focused on analysing the leakage of Aliquat 336 from various membranes that contains the extractant into the aqueous phase during a membrane extraction operation. Major findings are summarised as follows.

1. The observation of the effect of surface pressure is a reliable and convenient qualitative method to check the leakage of extractants from membranes. The gravitational measurement is a simple method to gain quantitative results of the solubility and membrane leakage information of an extractant. XPS measurement using the present sample preparation technique was also informative, as it confirms the non-evaporable residue was indeed Aliquat 336.

2. Aliquat 336 has a very low solubility in HCl solutions. Our results suggest that it is about 0.08 g/100 ml in a 2 M HCl solution at room temperature.

3. For membranes where free Aliquat 336 is incorporated,

the concentration of Aliquat 336 in the aqueous solution is governed by the solubility of the extractant. For polymer membranes in which Aliquat 336 molecules are entangled with polymer chains, the leakage is substantially less.

References

1. G. Argiropoulos, R. W. Cattrall, I. C. Hamilton, S. D. Kolev, and R. Paimin, *J. Membr. Sci.*, **138**, 279 (1998).
2. L. Wang, R. Paimin, R. W. Cattrall, W. Shen, and S. D. Kolev, *J. Membr. Sci.*, **176**, 105 (2000).
3. J. Xu, R. Paimin, W. Shen, and X. Wang, *Fibers and Polymers*, **3**(2), 68 (2002).
4. S. D. Kolev, Y. Sakai, R. W. Cattrall, R. Paimin, and I. D. Potter, *Analytica Chimica Acta*, **413**, 241 (2000).
5. L. Wang, MSc Thesis, Victoria University of Technology, 1999.
6. J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben in "Handbook of X-ray Photoelectron Spectroscopy", (J. Chastain Ed.), Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, Minnesota, U.S.A., 1992.
7. R. Paimin, Ph. D. Thesis, La Trobe University, Australia, 1984.