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Characterising poly (vinyl chloride)/Aliquat 336 polymer inclusion membranes: Evidence of phase separation and its role in metal extraction

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ABSTRACT

The miscibility of the base polymer poly (vinyl chloride) (PVC) and the extractant Aliquat 336 in polymer inclusion membranes (PIMs) was investigated by characterisation of thermal transitions using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The extractions of Cd (II) and Zn (II) using PVC/Aliquat 336 PIMs with different base polymer/extractant composition and different extraction temperature were also investigated. Changes in the PIM's heat capacity measured by DSC were small, thus, could only be used to determine the glass transition temperature (T_g) of PIMs with low Aliquat 336 content. On the other hand, DMA results clearly identify the (T_g) and melting temperature (T_m) of separate PVC and Aliquat 336 rich phases in the PIMs. Results reported here indicate that the PVC/Aliquat 336 PIMs are phase separated. This phase separation has important implications to the extraction of target metallic ions by PIMs. Extraction studies showed that the extraction of metallic ions occurred only when the proportion of Aliquat 336 in PIMs was about 30 wt.% or higher. The extraction rate could be improved by increasing the temperature and thus the target ion transport in the Aliquat 336 phase.

1. Introduction

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

The mechanism of facilitated transport in PIMs is still open to speculation given the lack of understanding about the nature of their homogeneity. For a solid solution, the metal ion with the aid of an extractant is transported through a polymer matrix. For a heterogeneous solid, the metal ion with the aid of extractant is transported through continuous channels within a polymer matrix. In some instances, a combination of these two extremes may occur.

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

In this paper, PVC based PIMs were prepared with different Aliquat 336 concentrations. This work aims to determine whether the PIMs produced are a solid solution or mixture by application of differential scanning calorimetry (DSC) and dynamic mechanical

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analysis (DMA) techniques to characterise the thermal transitions. This approach clarifies the miscibility of PVC and Aliquat 336. Extraction of Cd (II) and Zn (II) were also investigated in order to observe any correlation between solid structure, thermal analysis and membrane function.

2. Materials and methods

2.1. Reagents

All reagents were obtained from Sigma Aldrich, Australia. High molecular weight poly (vinyl chloride) (PVC) and Aliquat 336 (tricaprylmethylammonium chloride) were used as the base polymer and extractant respectively. The weight-average molecular weight of this PVC is 80,000 g/mol. Aliquat 336 is a mixture of tri-alkyl methyl ammonium chloride salts produced from the methylation of Alamine 336, with the substituent alkyl chain length containing between 6 and 12 carbon atoms. HPLC grade tetrahydrofuran (THF) was used without any further purification. Cadmium (II) and zinc (II) solutions used in the membrane extraction experiments and for calibration purposes were prepared from $Cd(NO_3)_2$ and $Zn(NO_3)_2$ (analytical grade). Milli-Q grade water (Milipore, Australia) was used for the preparation of all aqueous solutions.

2.2. Preparation of PVC/Aliquat 336 PIMs

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

2.3. Extraction protocol

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

2.4. Differential scanning calorimetry (DSC) analysis

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

2.5. Dynamic mechanical analysis (DMA)

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

3. Results and discussion

3.1. Membrane characterization

3.1.1. Thermal analysis

DSC analysis of the PVC as supplied showed a glass transition temperature (T_g) of 85 °C (Fig. 1) which is consistent with literature values [15,16]. In contrast, DSC analysis of the PVC cast from THF solution exhibited a T_g of 63 °C (Fig. 1). PIMs containing 10–40 wt.% Aliquat 336 exhibited a T_g in the range of 55–63 °C (Fig. 2). PIMs containing 50–70 wt.% Aliquat 336 exhibited a T_g that was too subtle for designation using the described experimental procedure. DSC analysis of the supplied neat Aliquat 336 did not exhibit a T_g but exhibited a T_m of −19 °C (Fig. 1), which is also consistent with the report value of −20 °C [17].

The DMA is another thermal analysis technique that is frequently employed to characterise thermal transitions of polymers. The DMA isolates thermal transitions as substantial changes in the storage modulus and a corresponding peak in the dissipation of energy (tan δ).

DMA results revealed that the PVC/Aliquat 336 PIMs contained one or two thermal transitions with the number dependent on the fraction of Aliquat 336 (Figs. 3 and 4). An α transition was observed at 71 ± 8 °C for all Aliquat 336 concentrations studied here (Fig. 2). A β transition was observed at −18 ± 1 °C for PIMs samples containing 40–70 wt.% Aliquat 336 (Fig. 2). In addition, PIMs containing 10 wt.% Aliquat 336 or more started to undergo degradation at about 100 °C as evidenced in an increase in the storage modulus (Fig. 3).

3.1.1.1. α Transition. The α transition is assigned to the T_g of the PVC as it occurred in PVC cast from THF without Aliquat 336 and it was consistent with DSC T_g measurements (Fig. 1). For the PIMs

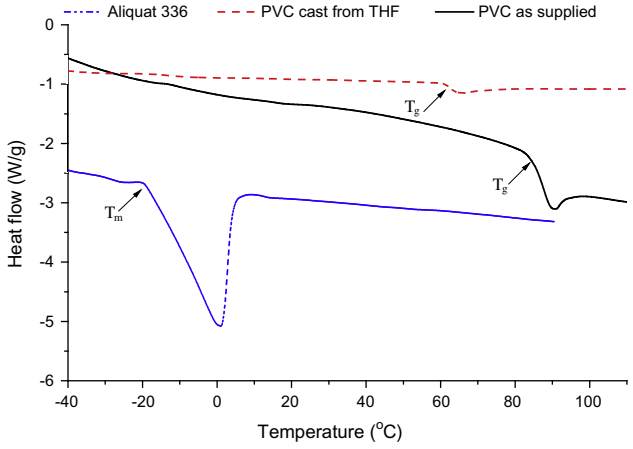

Fig. 1. DSC thermographs of Aliquat 336, PVC cast from THF and PVC as supplied.