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# On-line extractive separation in flow injection analysis based on polymer inclusion membranes: A study on membrane stability and approaches for improving membrane permeability

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## ABSTRACT

The effect of temperature on the sensitivity and sampling rate is studied for a flow injection analysis (FIA) system that uses a membrane separation cell fitted with a polymer inclusion membrane (PIM) for the determination of Zn(II). A temperature of 50 °C for the flowing donor and acceptor solutions and the membrane separation cell improves the sensitivity and the sampling rate relative to 20 °C up to 10-fold and 2-fold, respectively.

Studies on the stability of the PIM are reported that show a limited loss of the membrane liquid phase into the aqueous phases used in the FIA system but this has exhibited a negligible effect on the amount of Zn(II) transported across the membrane.

Most importantly, the extent of leaching of the PIM components is shown to depend on the nature of the aqueous phase with the membrane eventually reaching a stable composition.

It is also shown that the application of ultrasound to the membrane separation cell leads to a slight increase in sensitivity without affecting the long term membrane stability.

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## 1. Introduction

In a recent paper we described for the first time the use of a polymer inclusion membrane (PIM) for on-line separation in flow injection analysis FIA [1]. The PIM consisted of 40% (m/m) di(2-ethylhexyl) phosphoric acid (D2EHPA) as carrier, 10% dioctyl phthalate (DOP) as plasticizer and 50% poly(vinyl chloride) (PVC) as the base polymer and was used for the on-line separation and determination of Zn(II).

The FIA system developed, after optimization, gave a linear calibration for Zn(II) in the range of 1.0 to 30 mg L<sup>-1</sup>, a detection limit of 0.05 mg L<sup>-1</sup> and a relative standard deviation of 3.4% with a sampling rate of 4 h<sup>-1</sup>. This system was applied successfully to the determination of Zn(II) in pharmaceuticals and samples from the galvanizing industry.

We have continued our study of this system with the focus being placed on increasing the sampling rate and sensitivity and testing the long term stability of the membrane. The factors that affect the sampling rate are the rate of accumulation of Zn(II) in the acceptor phase as well as the time required to recondition the membrane between sample injections. Reconditioning is required in order to remove all traces of Zn(II) from the membrane after each measurement to avoid memory effects. Both these factors are

largely determined by the kinetics of the transport of Zn(II) through the membrane. However, due to the entangled nature of the structure of PIMs, membrane diffusion coefficients are low [2–6].

Faster accumulation of Zn(II) can be achieved by reducing the membrane thickness. However, it was found that 22 μm was the thinnest membrane that could be used in the FIA flow cell without the membrane being punctured due to the pressure difference generated by the flowing streams on both sides of the PIM [1].

In the present study we have explored two approaches involving temperature and sonication to enhance the overall mass transfer process in the PIM separation cell. Diffusion coefficients are dependent on temperature and we describe the effect of temperature on the sensitivity and sampling rate of the PIM-based FIA system. Ultrasound is known to enhance mass transfer in various processes such as extraction [7] and ultrafiltration [8]. In addition to causing mechanical vibration, sonication is known to generate acoustic cavitation in liquids, which involves the formation, growth, and collapse of gas–vapor filled bubbles in liquids [9]. We have recently described the use of sonication to increase mass transport in PIMs due to the elimination of the interfacial stagnant layer at the membrane/solution interface [10]. Sonication has also been shown to improve the sensitivity in pervaporation FIA by enhancing mass transfer in the pervaporation cell [11]. In this paper we describe the effect of sonication on the sensitivity of Zn(II) determination in the PIM-based FIA system.

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Our previous study of this FIA system demonstrated acceptable reproducibility over 20 replicate injections of the same Zn(II) standard over 5 h [1]. However, PIMs are susceptible to some degree of leaching of the membrane components into the adjacent aqueous phases, although this is considered to be substantially lower than for supported liquid membranes (SLMs) [2]. A study of the extent of loss of membrane liquid phase of membranes exposed to various aqueous phases is also reported in this paper.

## 2. Materials and methods

### 2.1. Membrane preparation

D2EHPA, dioctyl phthalate (DOP) (both purchased from Sigma-Aldrich) and high molecular weight PVC (Selectophore, Fluka, Switzerland) dissolved in tetrahydrofuran (THF) (Chem-Supply, Australia) were used to prepare PIMs containing 40% (m/m) D2EHPA, 10% (m/m) DOP and 50% (m/m) PVC according to the procedure described previously [1].

### 2.2. FIA system and experimental procedure

A FIA manifold (Fig. 1), similar to the one reported previously [1], was used in the present study. For conducting the sonication experiments, a stainless steel block and an ultrasonic transducer were attached to the donor half of the separation cell. The transducer was connected to an amplifier/generator (T&C Power Conversion, Model AG 1006, USA) and a function generator (Hameg Instruments, Model HM 8131-2, France). A home-made microphone chip was attached directly underneath the transducer cell to measure the transported resonance frequency with an oscilloscope (Digital Storage Inc. Canada, Model OS 1420 COULD 20 MHz). An external electric fan was placed next to the membrane separation cell to reduce the transducer temperature (Fig. 1). A home-made thermistor flow-through cell connected to a digital multimeter (Micronta, Model 22–185) was positioned downstream of the donor channel of the membrane separation cell. This cell consisted of a short piece of Tygon tubing (1 cm) with a circular opening where the temperature sensing part of the thermistor (47 k $\Omega$ , RS Components, Australia) was inserted and glued on. The thermistor flow-through cell was calibrated by passing aqueous solutions at constant temperature in the range from 20 to 30 °C.

The FIA procedure, similar to the one outlined in our previous study [1], involved the injection of 500  $\mu$ L of 10 mg L<sup>-1</sup> Zn(II) (ZnCl<sub>2</sub>, Unilab, Australia) standards into the donor stream (R<sub>1</sub>, Fig. 1), which consisted of 0.20 M H<sub>2</sub>SO<sub>4</sub> (Scharlau Chemie, Australia) adjusted to pH 2.6 using 3.0 M NaOH (Unilab, Australia). The acceptor stream (R<sub>2</sub>), containing 1.0 M HCl (Scharlau Chemie, Australia), was stopped for 5 min after the injection of the Zn(II) standard by turning Pump 2 off (Fig. 1). This allowed the accumulation of Zn(II) in the static acceptor solution located in the acceptor channel of the membrane separation cell. After the stop-time, Pump 2 was turned on again. This resulted in the neutralization of the acceptor stream R<sub>2</sub> after its merger with the 1.0 NaOH reagent stream R<sub>3</sub>. The combined stream was subsequently merged with a second reagent stream (R<sub>4</sub>) containing 0.20 mM 4-(2-pyridylazo)resorcinol (PAR) (Sigma Aldrich) in pH 9.3 borate buffer (0.045 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (Chem-Supply, Australia) and 0.050 M H<sub>3</sub>BO<sub>3</sub> (Ajax Chemicals, Australia)). The maximum peak absorbance at 491 nm was used as the analytical signal. Reconditioning of the membrane was then carried out by continuously passing the donor and acceptor solutions through the membrane separation cell for 10 min. The reconditioning of the membrane resulted in complete stripping of all Zn(II) extracted after the previous injection which was retained by the membrane. In this way memory effects were avoided.

To investigate the effect of temperature on the sensitivity and sampling rate, the membrane separation cell and the donor and receiver solutions were immersed in a water bath equipped with a thermoregulator (Ratek, Model TH5, Australia).

Two series of sonication experiments were conducted. In the first series sonication was conducted at 4 different frequencies (103, 119, 124, or 132 kHz). In these experiments, sonication was applied for 5 min after injection and the sonication power was kept at 1 W. In a second series of experiments the effect of the power of sonication (1–5 W) was studied at the optimal frequency of 124 kHz. The temperature of the donor stream was continuously monitored in the thermistor flow-through cell. After each sonication period, the membrane separation cell was allowed to cool down to room temperature by the continuous flow of the donor and acceptor solutions.

All measurements were conducted in triplicate.

The flow rates in the FIA manifold channels were adjusted as in our previous study [1] to 0.30 mL min<sup>-1</sup> for stream R<sub>1</sub> (Fig. 1) and 0.85 mL min<sup>-1</sup> for the remaining streams (R<sub>2</sub>–R<sub>4</sub>). The flow

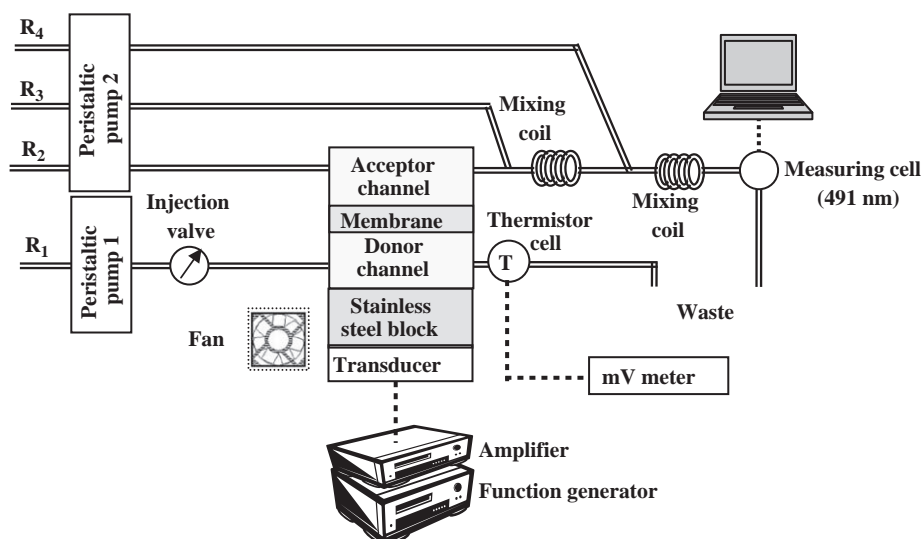


Fig. 1. Schematic of the experimental FIA system.

rates were determined at regular time intervals by weighing the effluent collected over a 5 min period.

Deionised water (18 M $\Omega$  cm, Millipore, Synergy 185, France) was used in the preparation of all solutions.

### 2.3. Investigation of the membrane stability

All extraction and transport experiments outlined in the following sections were conducted in triplicate and the results discussed are an average of these.

#### 2.3.1. Batch extraction and back-extraction experiments

A series of 20 Zn(II) extraction and back extraction cycles were carried out using solutions having the same composition as the donor and acceptor solutions used in the FIA experiments. For the extraction cycle, a circular PIM (4.5 cm diameter) of  $75 \pm 3$  mg initial mass was immersed in a 100 mL solution containing  $50 \text{ mg L}^{-1}$  Zn(II) which was located in a conical flask and shaken for 5 h at 150 rpm using an orbital shaker (Platform mixer OM6, Ratek, Australia). For back-extraction, a 100 mL solution of 1.0 M HCl was used. The extraction and back-extraction of Zn(II) were monitored by taking 0.5 mL aliquots of the aqueous phase in contact with the membrane at various time intervals, and measuring the Zn(II) concentration using atomic absorption spectrometry (AAS, Hitachi Z-2000 Series Polarized Zeeman, Japan) after dilution to 10 mL with deionized water. The mass of the membrane was recorded between each cycle. The solutions from the first extraction and back-extraction cycle were analyzed for phosphorus using inductively coupled plasma optical emission spectrometry (ICP-OES, Vista-AX-CCD Simultaneous, Varian Australia) under the following experimental conditions: power level, 1.20 kW; coolant flow, 15.0 L min $^{-1}$ ; auxiliary flow, 1.50 L min $^{-1}$ ; nebulizer flow, 0.90 L min $^{-1}$ ; and sample aspiration rate, 2.00 mL min $^{-1}$ .

#### 2.3.2. Transport experiments in a two-compartment transport cell

For this study, the transport cell shown in Fig. 2 was used in which the membrane (exposed surface area  $1.81 \times 10^{-3} \text{ m}^2$ ) was sandwiched between the two compartments. Each compartment had a volume of 100 mL and the cell was thermostated at  $25 \pm 0.1$  °C. The donor and acceptor solutions were of the same composition as those used in the batch and FIA experiments outlined above except for

the initial concentration of Zn(II) in the donor phase which was  $50 \text{ mg L}^{-1}$ . The solutions were stirred mechanically (1200 rpm) and their transient Zn(II) concentration was monitored by AAS following the procedure outlined above. Ten consecutive transport experiments were carried out with the same membrane and the membrane mass was measured between experiments after rinsing it lightly with deionized water and drying it in air overnight.

#### 2.3.3. Experiments involving membrane exposure to solutions of various electrolytes

A study was also carried out to investigate the long term loss of the membrane liquid phase after 270 h (11 day) of continuous contact between the membrane and a number of aqueous solutions not containing Zn(II). This study involved placing membranes in conical flasks containing 100 mL of deionized water, 1.0 M HCl, 0.2 M H $_2$ SO $_4$ , or 0.2 M NaCl at pH 2.60. The flasks were shaken at 150 rpm using an orbital mixer incubator (Platform mixer OM11, Ratek, Australia) thermostated at 25 °C. At the end of each day, the membrane was removed from the solution, lightly rinsed in deionized water and air dried overnight. In the morning the membrane was weighed and returned to the conical flask and the procedure was repeated.

## 3. Results and discussion

### 3.1. Effect of temperature on the sensitivity and sampling rate of the FIA system

As mentioned above, the rate of transport of Zn(II) across the PIM in the FIA membrane separation cell (Fig. 1) affects the amount of Zn(II) accumulated in the acceptor stream during the 5 min stop-time. The transport rate of Zn(II) across the membrane is governed by the diffusion coefficient of the Zn-D2EHPA complex. Since diffusion coefficients increase with temperature it can be expected that an increase in the temperature of the membrane will increase the amount of Zn(II) accumulated in the static acceptor solution and shorten the period required for the regeneration of the membrane, thus leading to improvement in both sensitivity and sampling rate. Therefore, the temperature effect was studied in the range between 20 and 80 °C. The results are presented in Fig. 3 where the values of the analytical signal and the sampling rate are quoted in relation to the corresponding values at 20 °C. An increase in the temperature from 20 to 70 °C resulted in an increase in sensitivity and sampling rate of over 30-fold and 4-fold, respectively. However, above 50 °C it

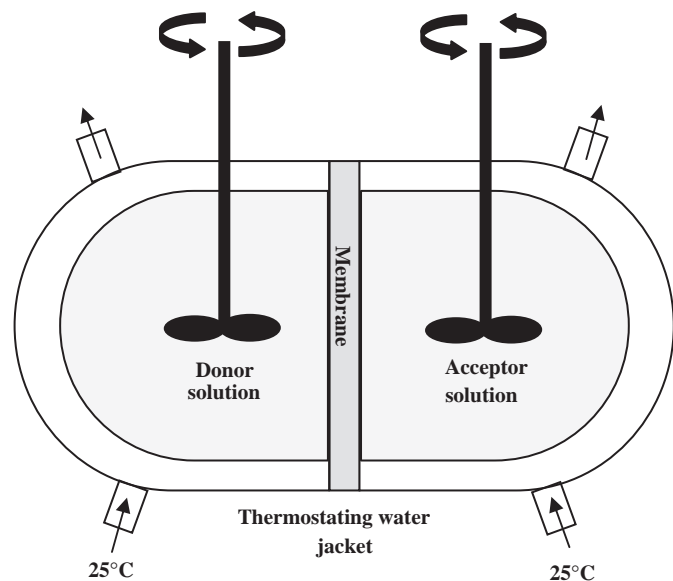


Fig. 2. Schematic of the transport cell (volume of each solution—100 mL, exposed membrane area to each solution— $1.81 \times 10^{-3} \text{ m}^2$ ).

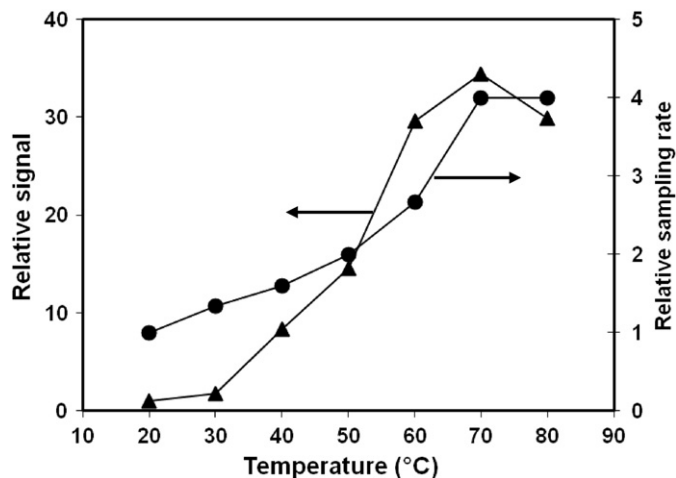


Fig. 3. Influence of temperature on sensitivity (▲) and sampling rate (●) (membrane thickness— $40 \pm 3 \mu\text{m}$ ).

was found that the membrane deteriorated rapidly resulting in poor reproducibility. This effect was probably due to enhanced leaching of the membrane liquid phase into the donor and acceptor streams. Also, very high temperatures led to unacceptable levels of evaporation of water. Nevertheless, the results demonstrate that the use of the FIA system at temperatures up to 50 °C can improve the sensitivity up to 10-fold and the sampling rate up to 2-fold with acceptable reproducibility (RSD=5.2%, 17 consecutive injections of 10 mg L<sup>-1</sup> Zn(II) standard).

### 3.2. Effect of sonication on Zn(II) mass transport

Our recent study on the application of sonication to a PIM used to extract Au(III) from hydrochloric acid solutions demonstrated an increase in the mass transport rate. This effect has been attributed to acoustic cavitation at the membrane/solution interface which eliminates the interfacial stagnant layer [2]. This finding, as well as earlier success in improving the sensitivity in pervaporation FIA [3], prompted the development of an on-line membrane separation cell utilizing ultrasound (Fig. 1) to investigate its effect on the sensitivity and sampling rate. The results for different frequencies are shown in Table 1 as the analytical signal relative to that without sonication (frequency of 0 Hz). The sonication enhanced the analytical signal at all frequencies studied with the highest enhancement of 1.8-fold obtained at 124 kHz. Table 1 also presents data regarding the temperature increase of the donor stream as a result of the application of ultrasound. Therefore, it can be expected that the overall sensitivity enhancement is partially due to the increase in temperature of the donor stream. The temperature increase at 124 kHz was 2.8 °C and in the temperature range of interest (i.e. between 20 and 30 °C, Fig. 3) such a temperature change was estimated to result in 1.2 fold increase in sensitivity. The frequency was varied in a narrow range (103–132 kHz) – this range was chosen based on the resonance frequency of the transducer–cell configuration. Within this range, the system was in resonance, meaning cavitation could be observed. As can be seen, the transducer–cell system showed a higher activity at 124 kHz, most probably due to a higher cavitation activity at this frequency due to the establishment of a better resonance of the system. Therefore, it can be concluded that sonication does improve sensitivity though with the current configuration of the sonication membrane separation cell this improvement is not substantial and further work on re-designing the configuration is necessary to control the temperature and to produce more efficient sonication of the donor and acceptor streams.

The effect of the applied ultrasonic power (1–5 W) on the analytical signal was investigated at 124 kHz. It was observed that by increasing the applied power from 1 to 5 W the sensitivity increased by only 18%.

### 3.3. Loss of membrane liquid phase during continuous contact with aqueous solutions

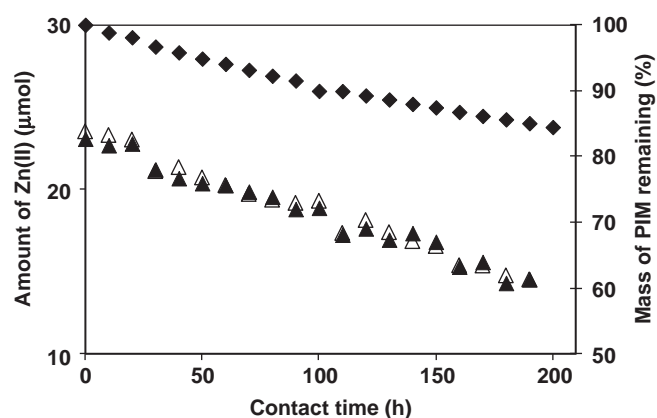
#### 3.3.1. Batch extraction/back-extraction experiments

Our earlier study on the PIM-based FIA system for the determination of Zn(II) [1] demonstrated acceptable reproducibility when

**Table 1**

Effect of sonication frequency at sonication power of 1 W on the analytical signal relative to the signal in the absence of sonication and on the temperature of the donor stream.

Frequency (kHz)	Relative signal	ΔT during sonication (°C)
103	1.06	2.9 ± 0.1
119	1.58	3.3 ± 0.1
124	1.79	2.8 ± 0.1
132	1.42	4.4 ± 0.1



**Fig. 4.** Membrane mass loss (♦) and amount of Zn(II) extracted (▲) and back-extracted (Δ) in 20 repetitive batch extraction/back-extraction cycles (Experimental conditions: orbital shaker—150 rpm; temperature—25 °C; donor solution—100 mL, 50 mg L<sup>-1</sup> Zn(II); acceptor solution—100 mL, 1.0 M HCl; PIM—75 ± 3 mg).

20 replicate measurements of the same Zn(II) standard over a 5 h period were conducted. This result suggested reasonably high membrane stability.

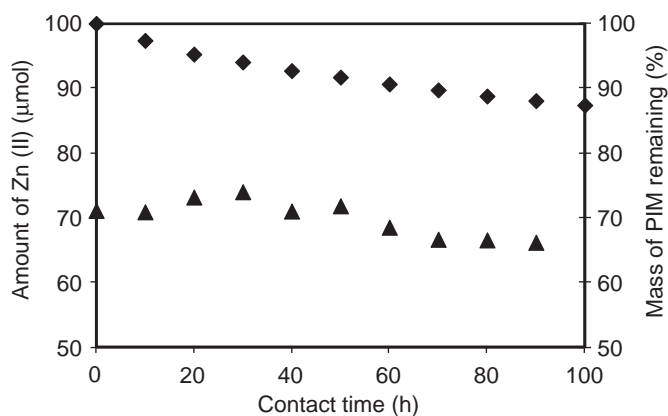
It was of interest to study the stability of the PIM over a much longer time scale viz. 200 h. This was carried out by conducting repetitive batch-wise extractions (each taking 5 h) and back-extractions (each taking 5 h) over 20 cycles using fresh solutions for each cycle and the mass of the membrane was measured between cycles. The results presented in Fig. 4 illustrate how the membrane mass and amount of Zn(II) extracted into the membrane during each extraction/back-extraction cycle changed with time.

It can be seen that there is a decrease in the amount of Zn(II) extracted during successive cycles over the 200 h period studied and this decrease correlates well with a decrease in the membrane mass. This suggests leaching of the membrane components (D2EHPA as carrier and DOP as plasticizer) into the aqueous phases. Since the data did not allow identification of the extent of leaching of each individual component (i.e. D2EHPA and DOP), the concentration of phosphorus in the aqueous phases after the first extraction and back-extraction cycle was measured by ICP-OES. This enabled the determination of the amount of D2EHPA leached and then the amount of DOP leached was calculated from the mass difference.

The total mass loss was 15.5% of the initial membrane mass and 83.6% of this was due to the loss of D2EHPA and 16.4% due to DOP. These mass losses are in the ratio of approximately 4:1 which is in agreement with the mass ratios of the corresponding components in the original membrane (i.e. 40% (m/m) D2EHPA, 10% (m/m) DOP). One interesting observation was that over 7 times the amount of D2EHPA was leached during the extraction step compared to the back-extraction step. This effect was due to the fact that the back-extraction phase was 1.0 M HCl and the presence of a high concentration of H<sup>+</sup> in the aqueous phase inhibited the dissociation D2EHPA at the membrane/solution interface and its subsequent dissolution into the aqueous phase. It is important to note that the membrane mass loss seems to approach a plateau after 200 h which suggests that there is a stable membrane composition that depends on factors such as solution pH and ionic composition of the contacting aqueous phase(s). This suggestion has been confirmed and the relevant data are discussed in Section 3.3.3.

#### 3.3.2. Transport experiments

PIMs are commonly used in transport cells with the membrane sandwiched between the donor and acceptor phases and so it was



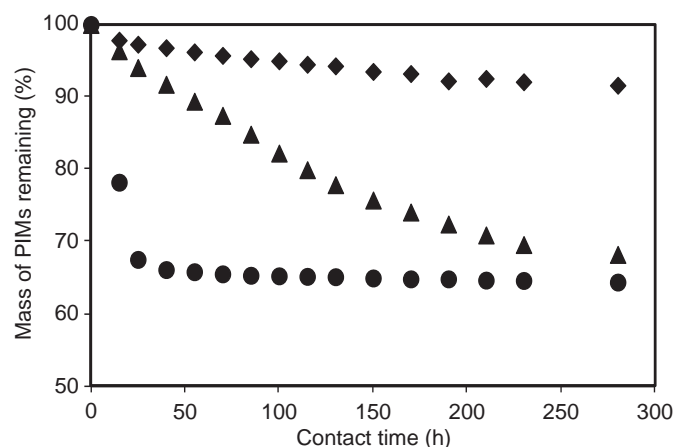
**Fig. 5.** Membrane mass loss (◆) and amount of Zn(II) transported (▲) in a 2-compartment transport cell in 10 consecutive transport experiments (Experimental conditions: stirring rate—1200 rpm; temperature—25 °C; donor solution—100 mL, 50 mg L<sup>-1</sup> Zn(II); acceptor solution—100 mL, 1.0 M HCl; PIM exposed area—1.81 × 10<sup>-3</sup> m<sup>2</sup>).

of interest to examine if the loss of the membrane components observed in the batch experiments, outlined above, affected the amount of Zn(II) transported. Ten consecutive transport experiments were carried out using the same membrane but fresh donor and acceptor solutions for each experiment and the membrane mass was measured after each experiment. Each transport experiment lasted 10 h. The results are presented in Fig. 5. The expected loss in the initial membrane mass after 100 h was found to be lower than that observed in the corresponding batch extraction and back-extraction experiments (12.6% compared to 15.5%). However, despite this mass loss the amount of Zn(II) transported remained relatively unaffected (Fig. 5) which is in stark contrast to the batch extraction/back-extraction experiments (Fig. 4). The lower mass loss of the membrane liquid phase in the transport experiments in comparison to the batch experiments is most probably due to the continuous exposure of one side of the membrane to 1.0 M HCl.

### 3.3.3. Membrane exposure to aqueous solutions of different composition

As mentioned in Section 3.3.1, it appears that, even though a PIM loses appreciable amounts of its components to an aqueous phase, it eventually reaches a composition which is at equilibrium with that aqueous phase after which there is practically no further mass loss. It can be expected that this equilibrium ('stable') composition will be determined by the ionic composition of the aqueous phase. In order to test this hypothesis, a series of experiments were conducted in which a PIM was contacted under batch conditions for 270 h (11 day) with 3 different aqueous phases, i.e. deionized water, 1.0 M HCl, and a solution identical to the donor solution in an earlier study (0.2 M H<sub>2</sub>SO<sub>4</sub>, and 0.2 M NaCl adjusted to pH 2.6 [1]).

The results, presented in Fig. 6, show that for deionized water most of the mass loss (35%) occurred within 24 h of contact and a stable membrane composition was reached after 50 h. In the case of 1.0 M HCl, the mass loss (5%) was considerably lower than in the case of deionized water but it took almost 200 h for the membrane to reach a stable composition. For the third aqueous phase composition (0.2 M H<sub>2</sub>SO<sub>4</sub> and 0.2 M NaCl adjusted to pH 2.6) the mass loss was 18% and the time required for a stable composition to be reached was close to 250 h. The corresponding membrane compositions are presented in Table 2 and are based on the ICP-OES measurements outlined earlier which suggest that D2EHPA and DOP are leached in a ratio of approximately 4:1.



**Fig. 6.** Membrane mass loss in deionized water (pH 6.80) (●), 1.0 M HCl (◆) and a solution containing 0.2 M H<sub>2</sub>SO<sub>4</sub> and 0.2 M NaCl (pH 2.60) (▲) over a period of 270 h of exposure (Experimental conditions: orbital shaker—150 rpm; temperature—25 °C; solution volume—100 mL; PIM—75 ± 3 mg).

**Table 2**

Stable compositions of D2EHPA/DOP/PVC PIMs (initial PIM composition: 40% (m/m) D2EHPA, 10% (m/m) DOP and 50% (m/m) PVC) exposed to aqueous solutions of different ionic composition.

	D2EHPA (%, m/m)	DOP (%, m/m)	PVC (%, m/m)
Deionized water	19	5	76
1.0 M HCl	38	9	53
0.2 M H <sub>2</sub> SO <sub>4</sub> and 0.2 M NaCl (pH 2.6)	31	8	61

These results confirm the important role played by the ionic species in the aqueous phase and in particular by the H<sup>+</sup> ion in reducing the loss of membrane liquid phase as a result of suppressing the dissociation of D2EHPA and reducing the solubility of both D2EHPA and DOP in the aqueous phase. It can also be concluded that conditioning of a PIM in an aqueous solution of the same or similar composition to the one to be used in the separation or transport system is recommended. This recommendation is more important for batch separation where the extraction and back-extraction processes take place sequentially at both sides of the membrane. In this case, the conditioning solution should contain an ionic concentration similar to that of the lower ionic concentration solution used in the extraction/back-extraction system. Conditioning of the membrane is less important for transport systems where the extraction and back-extraction processes take place simultaneously since it has been demonstrated in this study that a relatively small loss of membrane liquid phase has very little effect on the separation performance of such systems.

## 4. Conclusions

This work has demonstrated that the use of higher temperatures (up to 50 °C) can increase the sensitivity (10-fold at 50 °C compared to 20 °C) and sampling rate (2-fold at 50 °C compared to 20 °C) in the FIA system studied through an increase in the rate of transport of Zn(II) across the separation PIM without affecting its stability.

The application of sonication to the PIM separation cell has shown a modest increase in sensitivity which can be expected to be further improved by optimizing the configuration of the cell.

Many researchers have commented that PIMs have a relatively high resistance to leaching of the membrane components to the aqueous phase, particularly compared to SLMs. However, to the best of our knowledge no quantitative studies have been made of this phenomenon [2]. In this paper, we have shown that appreciable leaching of the carrier (D2EHPA) and plasticizer (DOP) in a 4:1 ratio (identical to the ratio of these components in the original membrane) does take place in repetitive batchwise Zn(II) extraction and back-extraction experiments lasting over a 200 h period. The resulting decrease in membrane mass has been found to correlate well with the decrease in the amount of Zn(II) extracted. However, in stark contrast to these findings, we have established that a comparable loss of membrane components in transport experiments had a relatively insignificant effect on the amount of Zn(II) transported.

Perhaps the most important conclusion drawn from this work is that the extent of leaching of the PIM components depends on the nature of the aqueous phase and that the membrane eventually reaches a stable composition with negligible further leaching taking place. Due to the limited set of membrane and solution compositions used in this study it is important that a wider range of both solution and membrane compositions are investigated in order to establish that this phenomenon is common for other PIMs. Such a study is currently in progress.

## Acknowledgments

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