Polymeric Inclusion Membrane (PIM) for Thiocyanate Extraction from Acid-Neutral Solution

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Abstract. Thiocyanate can be found in the gold mine tailing that use cyanide method for gold extraction. Reaction of cyanide ion and sulphuric ion producing thiocyanate in the tailing which enhancing the environmental problem. A new polymeric inclusion membrane (PIM) has been developed to extract thiocyanate from acid to neutral solution. PIM was produced by diluting PVC as base polymer, trioctylamine (TOA) and tetraoctyl methyl ammonium chloride (TOMAC) as carriers, and 1-decanol as plasticizer in tetrahydrofurane (THF) as solvent. Thiocyanate concentration was measured based on the formation of Fe(III)-thiocyanate complex at 457 nm. As a result, thiocyanate could be extracted up to 42% using PIM technique with composition (w/w) 70% PVC, 15% TOMAC as carrier, and 15% 1-decanol as plasticizer. Feed phase was contained of 80 mg/L thiocyanate solution at pH 4. Stripping phase was contained of sodium chloride solution of 1.0 M

1. Introduction
Recent extraction methods that are used for removal, both heavy metals and anions are polymeric inclusion membranes (PIMs). PIM is a development of Supported Liquid Membrane (SLM). The loss of carrier in SLM during the extraction process can be overcome using the PIM method where carrier is firmly held in the pore of supporting polymeric materials such as PVC. In terms of economics, the number of carrier used in PIM is less than in SLM [1, 2]. Therefore, PIM is efficient and effective method for extraction of valuable materials or removal some contaminants.

PIMs are made from polymers which will produce gel-like tissue that will trap carriers and plasticizers/modifiers. Poly (vinyl chloride) (PVC) and cellulose triacetate (CTA) are often used as basic polymers in the preparation of PIMs. Plasticizers or modifiers, for example 2-nitrophenyl octyl ether (NPOE), can be added to increase the elasticity and solubility of extracted species in the liquid membrane phase of the PIM. Extraction in PIM serves to facilitate selective transport of extracted species [3]. PIM containing PVC and carrier aliquat-336 has been used for the extraction of inorganic anions such as Cl−, NO3−, SCN−, ClO4−, and SO42− and organic anions such as acetate. PIM has also been used for orthophosphate separation and preconcentration to increase the limit of online phosphate determination detection using flow analysis [4].

The important thing about a PIM is maximum flux membrane, selectivity, and extraction efficiency. Carrier in the PIM determines these. The PIM carrier functions as an extractant in the solvent extraction process as a complexing compound or ion exchanger. Complex compounds or ion pairs formed between the target ion and the carrier will then dissolve in the membrane and facilitate the transport of target ions across the membrane. The molecular structure of the carrier influences the
rate of transport of the target ion through the PIM thus determining the target ion transport efficiency and membrane selectivity. The carrier types for PIMs are divided into base carrier, acid carrier and chelating, neutral carrier or solvating carrier, macrocyclic and macromolecular carrier [3]. Base carriers used to separate metal anionic complexes are from groups of quaternary ammonium (aliquat 336-chloride), tri-n-octylamine (TOA), and pyridine, for example 4- (1-n-tridecyl) pyridine N-oxide (TDPNO). Although the nitrogen atom in the quaternary ammonium molecular structure does not contain a free electron pair, quaternary ammonium is classified as a base carrier because of the similarity of the extraction mechanism using a quaternary ammonium carrier with a carrier from the amine group [3].

The quaternary ammonium carrier will react as an anion exchanger by forming ion pairs with the target ion. Meanwhile, carriers from the amine group, for example TOA, and from the alkyl pyridine group, for example TDPNO, the carrier must be protonated first and then react with anionic target ions, or react directly with the protonated target ion. Anionic target extraction with carriers from the amine group can occur at pH below the carrier pKb. Anion exchange groups in quaternary ammonium can be replaced with other groups, such as bromide. Fructose flux through a PIM containing bromide quaternary ammonium is lower than passing a PIM with chloride ammonium as a carrier. This is possible because the size of the carrier determines mass transfer through the PIM. The nature of carrier, for example the length of the side chain of quaternary ammonium carrier, also determines the mass transfer.

Besides the nature of carrier, another factor that affects the target ion transport is the concentration of the carrier. By using a carrier trioctylammonium chloride, transport of saccharide is not visible when using carriers with concentrations of less than 20% w/w. The transport rate increases exponentially when the carrier concentration increases to 50% w/w. The carrier concentration limit for percolation threshold at lower fructose transport (17% w/w) than sucrose transport (30% w/w) through PIM-trioctylammonium chloride is due to the size of the sucrose molecule which is greater than fructose so does not require greater interaction with the carrier for transport through the solution jumping mechanism. Extraction of thiocyanate from weakly alkaline solution has been investigated [5]. This extraction was performed using PIM made of aliquat 336-chloride carrier with a concentration of 20% w/w, 70% w/w PVC as base polymer, and 10% w/w of 1-tetradecanol as plasticizer. With this PIM, the thiocyanate ion flux was 7.86 x 10^-4 mol m^-2/s. Back extraction was achieved by using a 1.0 M NaNO₃ as stripping phase solution [5]. The present work deals with the extraction efficiency of thiocyanate ion from acid to neutral solution. Independent variables investigated in this research were carriers and its concentration, plasticizer and its concentration, pH and concentration of thiocyanate solution in the feed phase.

2. Methods

2.1. Chemicals

All reagents were of analytical reagent grade unless other-wise stated. Deionized water (Milli-Q Millipore) was used for all dilutions. Potassium thiocyanate, iron (III) chloride, sodium hydroxide, nitric acid, trioctyamine (TOA), and 1-decanol were purchased from Merck. High molecular weight polyvinyl chloride, trioctylmethyl ammonium chloride (TOMAC), and tetrahydrofuran (THF) were obtained from Sigma-Aldrich.

2.2. Preparation of Polymeric Inclusion Membrane

The carrier either TOMAC or TOA, plasticizer, and PVC in varying proportions were weighed and dissolved in 15 mL of THF for the preparation of PIM as described in the previous study [6]. Total membrane mass was 360 g. The mixture was stirred by magnetic stirrer until all components had dissolved. The mixture was poured into a 75 mm diameter petri dish. The dish was covered with a filter paper to slow the evaporation of the solvent. The solvent was allowed to evaporate overnight until a thin, transparent and non-greasy membrane was produced.
2.3. Membrane extraction experiments
The diffusion cell consisted of two detachable plexiglass chambers (100 cm$^3$) separated by the PIM and clamped together. The contact surface area of PIM was 7.065 cm$^2$. The feed phase was an aqueous solution of thiocyanate at various concentrations. The pH of feed solution was adjusted from 1-8 using 0.1 M HCl. The aqueous solution of stripping phase was 1.0 M NaCl for using PIM-TOMAC and 0.1 M NaOH for using PIM-TOA. Transport experiment was conducted at room temperature. Both feed and stripping phases were stirred at 400 rpm for three hours.

The thiocyanate concentration was measured colorimetric by sampling periodically aliquots of 1.0 mL each from the feed and stripping solutions. The thiocyanate was detected as iron thiocyanate complex compound at wavelength 470 nm. The percentage of thiocyanate extraction was calculated as follow:

$$\text{Extraction efficiency (\%)} = \left( \frac{C_{\text{strip},t}}{C_{\text{feed},o}} \right) \times 100 \quad (1)$$

With the following notations: $C_{\text{strip},t}$ was the thiocyanate concentration in the stripping phase (fs) at particular time (mg/L), $C_{\text{feed},o}$ was the thiocyanate concentration in the feed phase (fp) at initial time (mg/L).

3. Results and Discussion
3.1. Effect of carrier type
PIMs produced using different carriers have different physical performance (Fig. 1). PIM with the TOMAC 20% w/w as carrier produced a thin, transparent, flexible layer and a non-oily surface. Meanwhile, PIM with a 20% w/w TOA as carrier had cloudy and oily surface, low elasticity, and rigid layer. PIM-TOA has a lower elasticity than PIM-TOMAC, i.e. 6.38 N/mm$^2$ and 3.89 N/mm$^2$, respectively. This is due to TOMAC can act as plasticizer besides as a carrier [3].

![Figure 1](image-url)

*Figure 1*. Physical performance of PIM prepared from 70% w/w PVC; 15% w/w carriers: (a) TOMAC, (b) TOA; and 15% w/w 1-decanol.

Physical properties of PIM determine the contact angle of aqueous solution to PIM so determines the hydrophilicity-hydrophobicity of the membranes. The PIM-TOMAC was more hydrophilic than PIM-TOA so the aqueous solution more easily contacted to the surface of PIM-TOMAC toward the extraction efficiency. Extraction efficiency of thiocyanate ion through PIM-TOMAC was 39.17% compared to the efficiency through PIM-TOA (20.6%).

TOMAC and TOA are classified as basic carriers [3] but the transport mechanism of thiocyanate ion through the both membranes are different. The molecular structure of the carriers influence the rate
of transport, as well as the extraction efficiency, of the targeted solutes across the membrane [3]. TOMAC, as a quartenary amines, form a complex compounds with thiocyanate ion by ion exchange mechanism. Chloride ion in the membrane phase (fm) was exchanged by chloride ion from the feed phase (fp). At the second step, the complex was across the membrane and finally the thiocyanate ion was exchanged by chloride ions in the stripping phase (fs), as follows:

\[
R_3CH_3N^+Cl^-_{(fm)} + SCN^-_{(fp)} \rightleftharpoons (R_3CH_3N)^+SCN^-_{(fm)} + Cl^-_{(fp)} \quad (2)
\]

\[
(R_3CH_3N)^+SCN^-_{(fm)} + Cl^-_{(fs)} \rightleftharpoons R_3CH_3N^+Cl^-_{(fm)} + SCN^-_{(fs)} \quad (3)
\]

Meanwhile, TOA is tertiary amines carrier. Thiocyanate ions can be extracted from the feed phase to the stripping phase by solvating mechanism. Acid condition in the feed phase forces the solvation of TOA and then interacts with thiocyanate forming an ion-pair complex compound. At the interface of membrane phase-stripping phase, the complex was dissociated and released thiocyanate ion in the stripping phase at basic condition. The transport mechanism can be formulated as follows:

\[
nH^+_{(fp)} + nSCN^-_{(fp)} + TOA_{(fm)} \rightarrow [TOAH_n]SCN_n_{(fm)} \quad (4)
\]

\[
[TOAH_n]SCN_n_{(fm)} + nOH^-_{(fs)} \rightarrow nNaSCN_{(fs)} + TOA_{(fm)} + nH_2O_{(fs)} \quad (5)
\]

### 3.2. Effect of carrier concentration

Carrier concentration influences the hydrophobic-hydrophilic performance of PIM-TOMAC in case of the contact angle. PIM-TOMAC showed practically hydrophobic character with contact angle (ϕ ) of 86° at TOMAC concentration below 1.0x10^{-5} mol/cm^2. The character changed to hydrophilic with contact angle of 28° at high concentration of TOMAC (3.0 x 10^{-5} mol/cm^2) [7]. In the present work, the concentration of TOMAC was varied from 10 - 25% (w/w) so the character of membranes was varied from hydrophobic to hydrophilic. It influences the extraction efficiency of thiocyanate ion (Table 1).

| TOMAC (% w/w) | Extraction efficiency (%) |
|---------------|---------------------------|
| 10            | 34.02                     |
| 15            | 39.17                     |
| 20            | 38.22                     |
| 25            | 33.91                     |

At carrier concentration of 10% w/w, the targeted ion extraction can be explained from the “percolation threshold” theory which this is the minimum concentration of carrier in the membrane to assess the targeted ion. At this concentration, continuous pathways (liquid micro-domains containing carrier) is created to carry out the adsorbed targeted ions across the membrane (43). For 15-20% w/w TOMAC, the quantity of carrier is sufficient to the formation of the liquid pathways inside the membranes. At these concentrations, all the reactive sites of the carrier molecule are involved in the membrane extraction. Decreasing of extraction efficiency of thiocyanate (case of 25% TOMAC) is due to carrier excess loss and steric hindrance in the membrane. The steric hindrance is realized by the voluminous alkyl groups of the carrier molecules which limit the accessible of thiocyanate ions to the active sites of the carrier. Similar behavior was also observed by Navarro et.al [8] and Martinez et.al [9]. Under these circumstances, the maximum concentration of TOMAC concentration was reached by using PIM contains 15% TOMAC: 15% 1-decanol: 70% P.
3.3. Effect of feed phase pH

The dependence of thiocyanate extraction on the pH solution at basic condition has been investigated. PIM prepared from 70% PVC, 20% TOMAC (Aliquat 336-Cl), 10% 1-tetradecanol was used in the investigation. The results showed that the extraction was not pH dependent over the investigated pH range of 7-10 [5]. In this present study, thiocyanate extraction was conducted at acid to neutral pH (1-8). As shown in Fig. 2, the effect of pH solution on the thiocyanate extraction can be neglected when the pH solution was 4-8. At pH more acid, the extraction efficiency was low.

![Figure 2](image1.png)

**Figure 2.** Effect of solution pH in the feed phase on the extraction of thiocyanate into PIMs (composition: 70% PVC, 15% TOMAC, 15% 1-decanol). Extraction was carried out for 150 minutes. Feed phase was 50 mg/L thiocyanate solution. Stripping phase was NaCl 1.0 M.

Extraction of thiocyanate can be understood as counter-transport of an anion (Fig. 3) in which thiocyanate is counter-currently transported with a coupled transport-anion, *i.e.* chloride ion.

![Figure 3](image2.png)

**Figure 3.** Counter-transport of thiocyanate passing a PIMs (adopted from Nghiem, L.D., et.al [3])

With pKa of $1.3 \times 10^{-1}$, thiocyanate mostly is in the molecule form of HSCN at pH very acidic. At pH more than 1, SCN$^-$ anions are dominant in the solution. The gradient concentrations of thiocyanate ions species and chloride ions between in two phases are driving force for thiocyanate extraction.
3.4. Effect of thiocyanate concentration

The extraction experiments performed with different initial concentration of thiocyanate in the range of 20-100 mg/L. The extraction of thiocyanate was optimum at the initial concentration of 80 mg/L (extraction efficiency was 42.2%).

![Figure 4. Effect of initial concentration on the thiocyanate extraction (feed phase of pH 4.0, stripping phase : NaCl 0.1M)](image)

Increasing initial concentration of thiocyanate solution decreased the extraction efficiency due to membrane saturation with carrier-thiocyanate complex species and as consequence the lowering extraction efficiency of thiocyanate is observed.

4. Conclusion

In the present study, PIM containing 70% PVC/15% TOMAC/15% 1-decanol was investigated towards thiocyanate extraction. In the optimal composition, the membrane has transparent, not cloudy, and elastic. The extraction of thiocyanate was influenced by various factors including the carrier type and concentration, and the feed pH and concentration. The extraction efficiency of thiocyanate was reached up to 42% by using PIM at optimal condition with initial concentration and pH of thiocyanate solution were 80 mg/L and 4.0, respectively.

References

[1] J.S. Kim, S.K. Kim, M.H. Cho, S.H. Lee, J.Y. Kim, S. G. Kwon, and E.H. Lee, Bull. Kor. Chem. Soc. 22 (10), 1076-1080 (2001).
[2] A.J. Scow, R.T. Peterson, and J.D. Lamb, J. Membr. Sci. 111 (2), 291-295 (1996).
[3] L.D. Nghiem, P. Mornane, I.D. Potter, J.M. Perera, R.W. Cattrall, and S.D. Kolev, J. Membr. Sci. 281 7-41 (2006).
[4] E.A. Nagul, C. Fontas, I.D. McKelvie, R.W. Cattrall, and S.D. Kolev, Anal. Chim. Acta 803 82-90 (2013).
[5] Y. Cho, C. Xu, R. W.Cattrall, and S. D.Kolev, J. Membr. Sci. 367 (1-2), 85-90 (2011).
[6] S. Kagaya, Y. Ryokan, R.W. Cattrall, and S.D. Kolev, Sep. and Pur. Tech. 101 69-75 (2012).
[7] M.I. Vázquez, V. Romero, C. Fontàs, E. Anticó, and J. Benavente, J. Membr. Sci. 455 312-319 (2014).
[8] R. Navarro, I. Saucedo, A. Nunez, M. Avila, and E. Guibal, React. Funct. Polym 68 337-371 (2008).
[9] S. Martinez, A. Sastre, and F.J. Alguacil, Hydrometallurgy 6 205-214 (1997).