Desalination of seawater with supported liquid membrane

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Abstract. Seawater contains a lot of dissolved substances which are important chemicals. Broadly speaking the chemical composition of seawater is the main constituents of salinity, trace elements, gases, organic compounds, and suspended material. Desalination techniques have long been known and carried out, among others, by distillation, reverse osmosis, ion exchange (ion exchange) and electrodialysis. SLM is a separation technique consisting of two homogeneous phases, namely the feed phase and the receiving phase. Separation with SLM techniques is largely determined by the effectiveness and selectivity of the carrier compound. In this study using D2EHPA-TBP and HTTA-TBP as a carrier compound which was then applied in decreasing salinity levels of seawater. Seawater desalination with the SLM technique for carrier compounds was 81.690% and 84.504%, respectively.

1. Introduction

Since ancient times, the resolution of problems caused by the quality and quantity of water supplies has been crucial for human survival. Rapid population growth has led to an increase in water demand, the development of industries and expansion has increased the need for water. Not to mention the existence of water pollution by industry and households and the presence of seawater intrusion in several large cities near the coast that can reduce the existing water supply.

There is not enough water in a certain amount, the water must be of good quality. Good quality water can be met, among others, by finding new sources, processing dirty water into clean water or removing salt from seawater (desalination). Desalination techniques have long been known and carried out, among others, by distillation, reverse osmosis, ion exchange, and electrodialysis. In the process of seawater desalination, the membrane technology used is electrodialysis and reverse osmosis. The use of liquid membranes offers a new alternative for seawater desalination processes. Liquid membranes that can be used are emulsion liquid membranes (ELM) and liquid supported membranes (SLM). Desalination using ELM obtained 98% water recovery, where more than 99% of the salt was transferred in the receiving phase, while desalination by SLM technique was slower than by the ELM technique. However, with the optimum conditioning in the SLM technique desalination can take place (Naim, M.M, 2002). The weakness of the ELM technique is the need for an emulsion stabilizing agent and an effort to solve the emulsion (demulsification).

SLM is a separation technique consisting of two homogeneous phases, namely the feed phase and the receiving phase. The two phases are separated by a semipermeable membrane (Mulder, 1996). The advantages of separating with the SLM technique are that it is relatively simple, uses a relatively little
extractor, has a high flux, is selective and the extraction stage and is separated into one unit (Wolkowiak and Gega, 1996).

Separation with SLM techniques is largely determined by the effectiveness and selectivity of the carrier compound. The presence of a carrier compound is expected cations and anions in seawater can be transferred in the receiving phase. Tri-n-butyl phosphate or TBP is a non ionic (neutral) extractant. TBP is known to have a good ability to extract negative and neutral metal ions (De Anil, 1997). 2-thenoyltrifluoroacetone (HTTA) is used as another name for diketone is very widely used as a chelating agent in metal ion extraction (Kim Young-Sang, et al., 2000).

Cation exchange extractants including organophosphorus acid, phosphonic acid, and phosphonic acid or carboxylic acids can be used for hydrochloric, nitric or sulfuric acid media, and anion exchange extractants such as quaternary ammonium salts. Of this large number of extracting reagents, organophosphates are one of the most studied for metal extraction, especially D2EHPA acid (Ryberg, 1992; Moreno, 1993). D2EHPA is a cation exchange acid extractant.

Sometimes a mixture of two extractants will raise the extracted individual elements (Rydberg, 1992). Djunaïdi, et al (2000-2004) developed a synergy carrier compound between D2EHPA-TBP for metal extraction in the form of anions or cations, and the results obtained as expected were that the extracted metal experienced an increase when compared to a single carrier compound.

Djunaïdi, et al (2000) examined the synergy effect of two D2EHPA-TBP carriers with solvent extraction techniques for lanthanum metal and obtained the optimum composition of D2EHPA-TBP synergy that is 4: 1 (1M). Kurniasih, Y (2001) also obtained the optimum composition of 4: 1 D2EHPA-TBP synergy for uranium metal. Because HTTA is a chelating extractant for the extraction of metal ions such as D2EHPA, it is assumed that the synergy of HTTA-TBP with a composition of 4: 1 can also increase the extracted metal. The 4: 1 composition is expected to be the optimum composition for HTTA-TBP synergy. Thus the synergy of D2EHPA-TBP and HTTA-TBP is expected to be able to extract a mixture of metals and anions in seawater.

2. Experimental

2.1. Preparation of supported liquid membranes

2.1.1. Preparation of mixed carrier compounds in a ratio of 4: 1, the total concentration of 1M. A total of 6.92 ml of 2.89 M D2EHPA plus 1.36 ml of TBP 3.676 M was put into a 25 ml flask and then added kerosene little by little and shaken to be homogeneous. After that, add kerosene to the boundary mark, 4.44 g HTTA added with 1.36 ml of TBP 3.676 M put into a 25 ml measuring flask then added kerosene little by little and shaken to be homogeneous. After that, add kerosene to the boundary mark.

2.1.2. Preparation of a single carrier compound, 1M. 8.62 ml of 2.89 M D2EHPA was put into 25 ml measuring flask and then added kerosene little by little and shaken to be homogeneous. After that, add kerosene to the boundary mark. 6.8 ml of TBP 3.676 M was put into a 25 ml measuring flask and then added kerosene little by little and shaken to be homogeneous. After that, add kerosene to the boundary mark. 5.55 g HTTA was put into a 25 ml measuring flask and then added kerosene little by little and shaken to be homogeneous. After that, add kerosene to the boundary mark. Impregnation process The carrier compound was used to impregnate the PTFE membrane for 2 hours. The impregnated membrane is ready-made.

2.2. Sample preparation

The sample as the feed phase is a seawater simulation solution, which is prepared by dissolving 30.6 mg of NaCl and 2.2 mg of MgSO4 in 1L volume with aqua dest. Before being used as the feed phase of this solution, the salinity level was determined by argentometric titration of the Volhard method, and the pH was measured by a pH meter.
2.3. Desalination with SLM technique
The ready-made membrane is installed between the feed phase and the receiving phase in a set of SLM devices. The prepared sample is then poured into one glass as the feed phase and the other glass is poured into the receiving phase solution namely HNO₃ solution and NH₃ dilute with pH variations 1-7. The two phases are stirred with a stirring time variation of 6-24 hours with sampling time intervals every 6 hours. The solution of the feed phase and the receiving phase after stirring is analyzed by argentometric titration of the Volhard method to determine the salinity level.

2.4. Application in seawater
From the results of the above study used for desalination in seawater.

2.5. Determination of salinity levels
Determination of salinity is carried out using the argentometry method including the following stages:

2.5.1. Standardize AgNO₃ solution
5 mL 0.01 M NaCl solution was added to the Erlenmeyer, then a K₂CrO₄ indicator solution was added. The solution is titrated with AgNO₃ solution to form a red precipitate (the endpoint of the titration). The molarity of the AgNO₃ solution was calculated by the formula:

\[ M_{AgNO_3} = \frac{M_{NaCl} \cdot M_{NaCl}}{V_{AgNO_3}} \]

Standardize the NH₄CNS solution in the same way as above using the solution AgNO₃ with a Fe(NO₃)₃ solution indicator.

2.5.2. Determination of chlorinity by argentometric titration volhard method
2 mL sample was put into Erlenmeyer, plus an AgNO₃ solution until it was excessive so that all the chloride precipitated. HNO₃ solution is added to the solution so that the solution becomes acidic. The precipitate formed was filtered with filter paper then the precipitate was washed with 1% HNO₃. The filtrate is added to the Fe³⁺ indicator and titrated with the NH₄CNS solution to form an orange-red color (the endpoint of the titration). Chlorinity is calculated by the formula:

\[ \text{Chlorinity} = \frac{(V_{AgNO_3} - V_{NH_4CNS} \cdot M_{NH_4CNS}) \text{mmol}}{V_{\text{sampel}}} \times 35.45 \frac{mg}{\text{mmol}} \]

Chlorinity is usually expressed in g / kg, so the equation above must be converted to density so the above formula becomes:

\[ \text{Chlorinity} = \frac{\text{g}}{\text{L}} \times \frac{1}{\text{densitas} \left( \frac{kg}{L} \right)} \]

From this chlorinity the amount of salinity can be determined:

\[ \text{Salinity} = \text{Klorinitas} \times 1.80655 \frac{g}{kg} \]

3. Results and discussion
Seawater contains a lot of dissolved substances which are important chemicals. Broadly speaking the chemical composition of seawater is the main constituents of salinity, trace elements, gases, organic compounds, and suspended material (Evans, S.M; Hutabarat, S., 1985). Salts in seawater are not only composed of chloride ions and sodium ions but are also composed of quite dominant magnesium, potassium, calcium, and sulfate ions. Therefore the decrease in salts in seawater cannot be determined solely based on the decrease in chloride levels. SLM technique is a combination of extraction and stripping processes (Misra,
1996), so that it can be applied to the desalination process, namely by separating salts in seawater into the receiving phase so that water with relatively lower salinity is obtained. For the desalination process with the SLM technique to take place optimally, the pH variations of the receiving phase and carrier compounds are used. A decrease in salinity is determined by the argentometry method of the Volhard method in the feed phase and the receiving phase after 24 hours of mixing with an interval of sampling every 6 hours.

3.1. The effect of the pH of the receiver phase

The transport process that occurs in seawater cations and anions in the membrane due to the thrust that causes the seawater cations and anions can move from the feed phase to the receiving phase. The main cause that causes the thrust in the cations and anions of seawater is the hydrogen ion concentration gradient. The difference in the concentration of hydrogen ions between the feed phase and the receiving phase allows the process of transport both cations and anions in seawater. Changes in pH in the feed phase and the receiving phase indicate the process of transport of cations and seawater anions to the receiving phase. Changes in the pH of the feed phase and the receiver phase are presented in Table 1. From the two tables, there is a noticeable decrease in pH in both the receiving phase and the feed phase. This shows the involvement of hydrogen ions in the process of transport cations and anions from the feed phase to the receiving phase.

| Carrier       | Feed Phase | Receiving phase |
|---------------|------------|-----------------|
|               | pH₀ | pH₂₄  | pH₀ | pH₂₄  |
| D2EHPA-TBP, 4:1 | 5.820 | 3.115 | 3.908 | 3.945 | 3.887 | 4.101 | 3.944 | 4.947 | 3.830 | 5.917 | 3.938 | 6.900 |
| D2EHPA-TBP, 4:1 | 5.820 | 3.115 | 3.908 | 3.945 | 3.887 | 4.101 | 3.944 | 4.947 | 3.830 | 5.917 | 3.938 | 6.900 |
| HTTA-TBP, 4:1   | 5.820 | 1.268 | 2.405 | 3.302 | 4.686 | 4.490 | 4.335 | 4.041 |
| HTTA-TBP, 4:1   | 5.820 | 1.268 | 2.405 | 3.302 | 4.686 | 4.490 | 4.335 | 4.041 |

Information : pH₀: pH of the solution before stirring, pH₂₄: pH of the solution after stirring 24 hours

Setting the pH of the receiver phase causes a difference in hydrogen concentration between the feed phase and the receiving phase. The pH of the receiver phase is set at pH 1-7 to find out the optimum pH of the receiver phase so that the desalination process takes place optimally, shown in Table 2.
Table 2. Changes in chloride levels, salinity, and bait phase desalination in the desalination process

| Carrier                  | pH₀   | Feed Phase | Receiving phase |
|--------------------------|-------|------------|-----------------|
|                          | CT    | Salinity   | % Desalinasi    | pH₀ | CT | Salinity |
| D2EHPA-TBP, 4:1          | 5.820 | 1.991      | 3.597           | -   | -  | -        |
|                          | 0.925 | 1.671      | 53.543          | 1.172 | 1.176 | 2.124 |
|                          | 0.862 | 1.558      | 56.693          | 2.084 | 1.176 | 2.124 |
|                          | 0.799 | 1.444      | 59.843          | 3.020 | 1.364 | 2.464 |
|                          | 0.894 | 1.614      | 55.118          | 4.101 | 1.458 | 2.634 |
|                          | 0.078 | 0.142      | 96.063          | 4.947 | 1.489 | 2.690 |
|                          | 0.141 | 0.255      | 92.913          | 5.917 | 1.176 | 2.124 |
|                          | 0.172 | 0.312      | 91.339          | 6.900 | 1.458 | 1.634 |
| HTTA-TBP, 4:1            | 5.820 | 1.933      | 3.493           | -   | -  | -        |
|                          | 0.707 | 1.278      | 63.415          | 1.001 | 1.470 | 2.565 |
|                          | 0.802 | 1.448      | 58.537          | 2.080 | 1.379 | 2.490 |
|                          | 0.802 | 1.448      | 58.537          | 3.020 | 1.317 | 2.380 |
|                          | 0.707 | 1.278      | 63.415          | 4.087 | 1.317 | 2.380 |
|                          | 0.362 | 0.653      | 81.301          | 5.032 | 1.501 | 2.712 |
|                          | 0.802 | 1.448      | 58.537          | 5.917 | 1.287 | 2.324 |
|                          | 0.487 | 0.880      | 74.797          | 6.900 | 1.317 | 2.380 |

Figure 1: Changes in salinity levels in the feed phase at various pH variations of the receiving phase with the carrier compounds D2EHPA-TBP (a) and HTTA-TBP (b) to the stirring time (hours).

The role of hydrogen ions is very important in reactive transport aided by carrier compounds. D2EHPA and HTTA as cation exchange carriers release hydrogen ions in the feed-membrane interface phase and bind to positively charged metal ions. Metal ions are carried to the membrane interface with the receiving phase which is then released into the receiving phase. D2EHPA and HTTA bind H⁺ ions back to the process of releasing metal ions to the receiving phase (Prakorn, R and Ura, P, 2003). The process goes back and forth and continuously so that the pH of the receiver phase and the feed phase equilibrium after 24 hours of stirring are shown in Table 2. The process of cation and anion transport causes an increase in salinity levels in the
receiving phase both with D2EHPA-TBP and HTTA-TBP carrier compounds shown in Figure 1. This cation and anion transport process is maximized by the presence of TBP which provides a synergistic effect because TBP will bind cations and anions in seawater thereby increasing the desalination percent.

\[ \text{Figure 2} \] Changes in salinity levels in the receiving phase at various pH variations of the recipient phase with D2EHPA-TBP (c) and HTTA-TBP (d) carrier compounds to the stirring time (hours).

Figure 3 shows the effect of the pH of the receiver phase on salinity in both the feed phase and the receiving phase. Based on the graph, the higher the pH of the receiving phase, salinity in the feed phase decreases both D2EHPA-TBP and HTTA-TBP carrier compounds and the optimum occurs at the pH of the receiving phase ± 5. This is because the extraction of the alkali metal is effective at the pH of the solution approaching the base or a little base (Kim, Young-Sang et al., 2003). Whereas at pH 6 and 7 the salinity level decreased relatively constant for D2EHPA-TBP carrier compounds. This is due to the presence of hydrogen ions which helps transport cations and anions in relatively small amounts when compared to pH 1-5. At the receiver phase pH 5, percent desalination obtained for D2EHPA-TBP carrier compounds (96,063%) and HTTA-TBP (81,301%). So that pH ± 5 is used for the desalination process with a single carrier compound in simulated seawater and seawater and mixed carrier compounds for applications in seawater.
3.2. Influence of Carrier Compounds (Synergy Effect on Desalination Process)

The synergy effect is a mutually reinforcing effect which results in an increase in extraction yield by utilizing the extracting solvent. To find out the effects of synergy on this desalination process, then a single carrier compound is used to determine the effectiveness of cation and anion transport in seawater it can be seen that the D2EHPA-TBP carrier compound. HTTA-TBP with a ratio of 4:1 gives a synergy effect on the desalination process which is shown by the high percentage of desalination when compared with the single carrier compounds. This is reinforced by Figure 4 and Figure 5 illustrates the comparative effects of synergy on the seawater desalination process. In the desalination process using the synergy of D2EHPA-TBP and HTTA-TBP there is a decrease in salinity levels when compared to desalination using a single carrier compound. The length of time of stirring causes greater salinity levels to decrease. Percentage of desalination with D2EHPA-TBP carrier compounds (96.063%) is higher when compared to HTTA-TBP (81.301%). This result is almost the same as the transport of sodium and chloride using the D2EHPA carrier compound and tri-n-octyl methyl ammonium hydroxide (TOMAH) where more than 95% is transported to the receiving phase by Leon. G. et al (2004). Based on the transport mechanism as well as and the counterpoint, the reaction that occurs follows the reaction equation:

\[
M^{n+} + n(HDEHP) \rightleftharpoons M(H(DEHP)_2)n + nH^+ \quad (1)
\]

\[
M^{n+} + nX^- + nTBP \rightleftharpoons M(X)n(TBP)n \quad (2)
\]

\[
M^{n+} + n(HTTA) \rightleftharpoons M(TTA)n + nH^+ \quad (3)
\]

In desalination using D2EHPA and HTTA carrier compounds. hydrogen and chloride ions with water also react with D2EHPA with the reaction equation:

\[
H^+ + Cl^- + 2H_2O + (D2EHPA)_2 \rightleftharpoons (D2EHPA.H_2O)_2 \cdot HCl \quad (4)
\]

\[
H^+ + Cl^- + 2H_2O + (HTTA)_2 \rightleftharpoons (HTTA. H_2O)_2 \cdot HCl \quad (5)
\]

Hydrogen and chloride can also react with TBP by the reaction equation:

\[
H^+ + Cl^- + nTBP \rightleftharpoons HCl \cdot nTBP \quad (6)
\]
By using a combination of D2EHPA-TBP and HTTA-TBP carrier compounds, then the possible reactions that occur are as follows:

\[
\text{M}^{n+} + 2\text{Cl}^- + n(\text{DEHPA})_2 + n\text{TBP} \rightleftharpoons \text{M}[\text{DEHPA}]_2[\text{Cl}]_2.n\text{TBP} + 2\text{H}^+ \quad (7)
\]

\[
\text{M}^{n+} + 2\text{Cl}^- + n(\text{HTTA})_2 + n\text{TBP} \rightleftharpoons \text{M}[\text{TTA}]_2[\text{Cl}]_2.n\text{TBP} + 2\text{H}^+ \quad (8)
\]

(Kurniasih, Y., 2001). Based on the reaction mechanism above, cation and anion transport processes in seawater are maximized by the presence of TBP which provides a synergistic effect. This will increase the transport of cations and anions to the receiving phase. Based on the use of D2EHPA-TBP and HTTA-TBP carrier compounds it increases cation and anion transport to the receiving phase. which is indicated by high desalination percent for D2EHPA-TBP carrier compounds (96.063%) and HTTA-TBP (81.301%).

![Figure 4](image)

**Figure 4.** Comparison of percent desalination with variations of carrier compounds.

![Figure 5](image)

**Figure 5** Changes in salinity levels in the feed phase (a) and the receiving phase (b) for the synergy test

### 3.3. Application in seawater

The many compositions of seawater compilers cause the carrier compounds not only to transport the cations or anions making up salinity but also other metals present in seawater. Synergy carriers of D2EHPA-TBP
and HTTA-TBP are not selective enough for one cation or anion, so that all cations and anions present in seawater will be transported to the receiving phase.

Seawater application also provides a synergy effect for D2EHPA: TBP and HTTA: TBP carrier compounds when compared to a single carrier compound. This is shown in table 3. Figure 7 shows the synergy effect on the seawater desalination process. The presence of cation and anion transport in seawater is presented in Figure 6 which shows an increase in desalination in the feed phase due to the combined use of two carrier compounds. This is also shown in Figure 7 which shows a decrease in salinity levels in the feed phase and an increase in salinity levels in the receiving phase. Percentage of desalination used SLM technique with HTTA-TBP and D2EHPA-TBP synergy carrier compounds respectively 84.507% and 81.069%. HTTA-TBP synergy carrier compounds tend to transport more sodium and chloride in seawater than the D2EHPA-TBP synergy carrier. This is because HTTA carrier compounds tend to transport more sodium than D2EHPA carrier compounds (De Anil. 1997).

| Carrier | Cl⁻ | Salinity | % Desalination |
|---------|-----|----------|----------------|
| D2EHPA  | 2.738 | 4.946 | 31.169 |
| HTTA    | 1.829 | 3.304 | 54.026 |
| TBP     | 3.565 | 6.440 | 10.390 |
| D2EHPA : TBP, 4 : 1 | 0.557 | 1.007 | 81.690 |
| HTTA : TBP, 4 : 1 | 0.471 | 0.852 | 84.507 |

Figure 6 Percent desalination graph for seawater applications
4. Conclusion
Seawater desalination with the SLM technique for D2EHPA-TBP carrier compounds obtained desalination percent by 81.690% and HTTA-TBP by 84.504%. The use of mixed carrier compounds D2EHPA-TBP and HTTA-TBP with a concentration ratio of 4:1 provides a synergy effect on the desalination process.

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