Korean J. Chem. Eng., **19**(1), 93-98 (2002)

Extraction of Strontium Ion from Sea Water by Contained Liquid Membrane Permeator

Suk-Ki Jeong and Chang-Sik Ju†

Department of Chemical Engineering, Pukyong National University, Busan 608-739, Korea

(*Received 22 March 2001 • accepted 8 September 2001*)

Abstract−To develop a liquid membrane permeator that extracts strontium ion from sea water effectively and continuously, we investigated the extraction of strontium ion from artificial and natural sea water in a contained liquid membrane permeator. The permeator consists of a liquid membrane and two cells for aqueous solutions. The liquid membrane containing D_2EHPA(di-2-ethylhexyl-phosphoric acid) and DCH18C6(dicyclohexano-18-crown-6) is trapped between two hydrophobic microporous polyethylene films and separates sea water and the 0.2 M H_2SO_4 aqueous stripping solution. The effects of various operating parameters on the extraction of strontium ion were experimentally examined. The extractant of DCH18C6 - D_2EHPA mixture in kerosene had a synergistic effect on the extraction of strontium ion. The permeator extracted strontium ion from sea water effectively and continuously with long membrane lifetime.

Key words: Contained Liquid Membrane, Strontium Ion, Sea Water

INTRODUCTION

Sea water has been a very popular research object because of the tremendous amount and abundance of dissolved components; and many researchers have been engaged in the separation and utilization of valuable components from it [Botterill, 1982; Kabil et al., 1995]. As a result of their work, several economical processes, such as sea-salt manufacturing processes and the Dow Seawater Process [Kirk et al., 1981a] for magnesium, have been developed and in operation. Although these processes are in successful economical operation, more research should be done on the use of sea water for many valuable components therefrom.

The extraction of strontium ion from sea water is one of the interesting research subjects because not only is strontium the 5th richest metallic cation in sea water whose average concentration is 80 mg/L [Kirk et al, 1981b], but it is also relatively expensive with an increasing industrial demand.

Liquid membrane technology is one of the promising methods for extracting solutes from aqueous solutions. Common liquid membranes extracting metal ions from aqueous solutions are emulsion liquid membrane (ELM), supported liquid membrane (SLM) and hollow fiber contained liquid membrane (HFCLM).

In the early stage of liquid membrane study, many researchers were engaged in the extraction in the ELM [Izatt et al., 1983; Casamatta et al., 1978]. ELM involves a laborious process including emulsification and de-emulsification, the latter step being especially problematic. Furthermore, ELM suffers from swelling instability of the inner phase.

In the SLM, the organic membrane liquid is present in the pores of a polymeric support membrane where the metal is extracted into the pore liquid at the feed solution-membrane interface. At the stripping solution - membrane interface, the metal is back extracted and concentrated in the stripping solution for recycle [Yi, 1995; Chaudry et al., 1997; Yang and Fane, 1999]. However, SLM suffers from instability resulting from the loss of membrane liquid by solubility, osmotic flow of water across the membrane, progressive wetting of the support pores, and a pressure differential across the membrane.

A novel liquid membrane technique has been recently developed. Here the organic membrane liquid is contained in the interstices of two well-packed sets of microporous hollow fibers in the shell side of a hollow fiber permeator. In this HFCLM technique [Sengupta et al., 1988; Park et al., 1999], the dilute aqueous feed solution flows inside of one set of fibers. The aqueous stripping solution passes through the inside of the other fiber set. Each aqueous-organic phase interface is immobilized at the pore-mouths of the respective fiber. For hydrophobic fibers, the aqueous feed and stripping solutions flow at pressures higher than the organic liquid membrane pressure. Any membrane liquid loss to the feed and stripping solutions is automatically compensated for by the membrane liquid reservoir.

The HFCLM technique can offer a practical alternative to current techniques and processes for removal of heavy metals. However, in the case of waste water with solid suspension, HFCLM does not operate properly because of the small diameter of hollow fibers.

The contained liquid membrane permeator with two microporous films could be an alternative to HFLCM. This permeator consists of a liquid membrane and two cells for aqueous solutions. The membrane liquid is trapped between two microporous hydrophobic films and this liquid membrane separates the feed and stripping solutions.

In this study, for the purpose of developing liquid membrane permeator extracting Sr^{2+} ion from sea water effectively and continuously, its extraction from artificial and natural sea water in the contained liquid membrane permeator with two microporous films was investigated. The effect of various operating parameters, such as extractant, extracting temperature, initial pH of feed solution, etc. on the extraction was experimentally examined.

---

†To whom correspondence should be addressed.
E-mail: csju@pknu.ac.kr

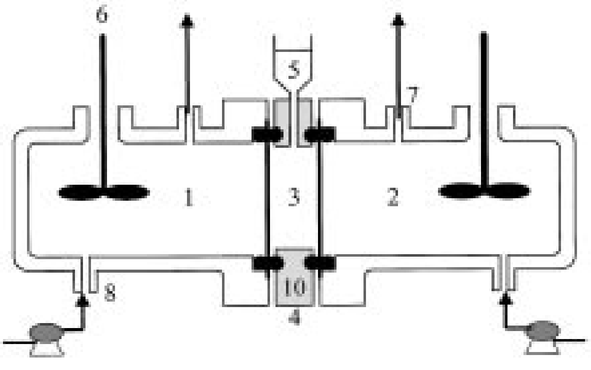

Fig. 1. Schematic diagram of liquid membrane permeator configuration.

1. Extracting solution
2. Stripping solution
3. Membrane liquid
4. Teflon cell for membrane liquid
5. Membrane liquid reservoir
6. Stirrer
7. Drain tap
8. Feeding tap

EXPERIMENTAL

Extraction of Sr^{2+} ion from artificial and natural sea water in the contained liquid membrane permeator shown in Fig. 1 was performed. The configuration and size of the permeator are similar to these used in the prior batch study [Ju et al., 2000] on zinc ion extraction from aqueous solutions.

The liquid membrane permeator consists of a liquid membrane and two glass cells for aqueous solutions. The liquid membrane consists of membrane liquid in a teflon cell holding a membrane liquid reservoir and two microporous hydrophobic polyethylene films trapping membrane liquid. The membrane liquid reservoir automatically compensates for the loss of membrane liquid during the operation and eventually prolongs the membrane lifetime. Two 80 ml glass cells for feed and stripping solutions are tightly combined on both sides of the liquid membrane with the aid of a Teflon ring seal.

For continuous operation, feeding taps on the both glass cells are connected to the extracting and stripping solution reservoir tanks.

The membrane liquid was an organic solution of D_2EHPA and/or crown ether in kerosene. Some combinations of extractants at different concentraions were tried. The feed solution was artificial sea water whose concentrations of Na^+, Mg^{2+} and Sr^{2+} ion were the same as those of natural sea water. The extraction from natural sea water was also examined. The stripping solution was 0.2 mol/L aqueous sulfuric acid solution.

After assembling the Teflon cell for liquid membrane, we filled two microporous films and two glass cells for aqueous solutions, a Teflon cell with membrane liquid through the membrane liquid reservoir. The permeator assembly was placed in a thermostated water bath and the feed and stripping solutions were also filled in glass cells to start extraction. During the extraction, both aqueous solutions in the glass cells were continuously stirred.

The variation of Sr^{2+} ion concentration in the feed and stripping solutions with time were measured by an AA analysis.

The effect of operating conditions (extractant and its composition, extraction temperature, initial pH and concentration of the feed solution) on the extraction was experimentally examined.

RESULTS AND DISCUSSION

1. Membrane Liquid

Crown ethers consist of hydrophilic cavities and hydrophobic exteriors, and form stable complexes particularly with alkali and alkaline earth metal ions by holding the ions in the central cavity. And the selectivity of crown ethers for metal ions in solvent extraction systems largely depends on the relation between the size of the metal ion and the cavity of the crown ether; in other words, the metal ion which fits the crown ether cavity best is the most extractable [Vogtle and Webe, 1984]. The extraction can therefore be controlled by varying the number of oxygen atoms in the crown ether ring, the presence of cyclohexane or benzene rings in the crown ether structure, and the length, branching and chemical nature of the substituents groups of the carbon chains attached to the cyclohexane or benzene rings.

Ramadan and Danesi [1988] and some other researchers reported the mixture of crown ethers and long chain, water insoluble organophillic acids strongly synergized the extraction of metal ions. The synergistic effect of membrane liquid can be adjusted by the proper selection of organophillic acids and the cavity size of crown ether corresponding to the diameter of the metal ion being extracted.

To select a proper membrane liquid composition for the extraction of Sr^{2+} ion from sea water, some mixtures of D_2EHPA and crown ethers, 18C6 and DCH18C6, whose cavity diameter is 2.6-3.2 Å were tested considering the ionic diameter of Sr^{2+} ion of 2.26 Å. D_2EHPA is one of the most common and easily obtainable extractants for metal ions. Among the mixtures we tested, D_2EHPA (30 vol%) and DCH18C6 (3×10^{-3} mol/L) in kerosene showed good characteristics on the extraction of Sr^{2+} ion from artificial sea water. Fig. 2 shows the variations in the concentrations of Sr^{2+} ion in the feed and stripping solutions with time. From it, we could observe the equilibrium extraction efficiency of 0.735 for the mixed extractant of D_2EHPA and DCH18C6, which was bigger than the sum (0.48) of the equilibrium extraction efficiencies for single extractants of D_2EHPA and DCH18C6, and we can conclude this extractant mixture shows a synergistic effect on the extraction of Sr^{2+} ion from artificial sea water. This conclusion is meaningful considering

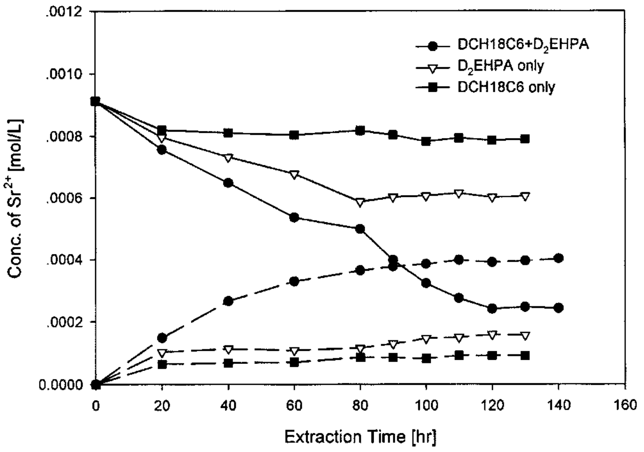

Fig. 2. The effect of extractants on the extraction of Sr^{2+} ion from artificial sea water in batch liquid membrane permeator (dashed lines represent stripping solutions).

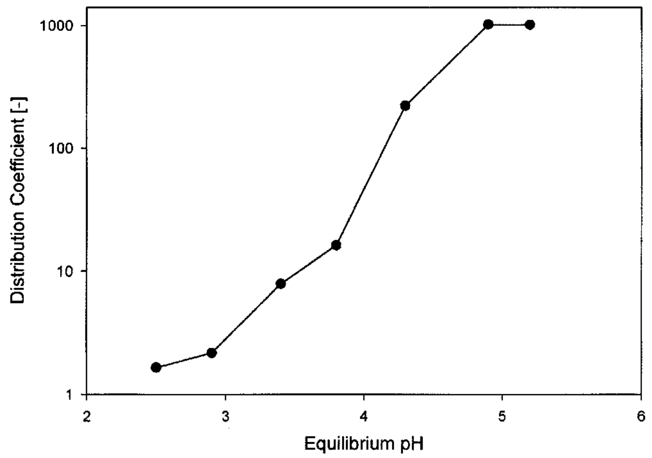

Fig. 3. The variation of distribution coefficients of Sr^{2+} ion with equilibrium pH of extracting solutions for the mixed extractant of D_2EHPA and DCH18C6 in kerosine.

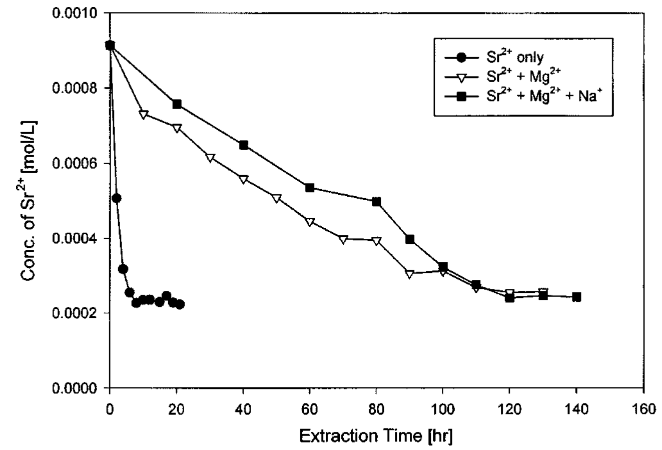

Fig. 4. The effect of composition of extracting solutions on the extraction of Sr^{2+} ion in the batch liquid membrane permeator.

Ramadan and Danesi [1988] used extractant mixture of dinonylnaphthalene sulfonic acid (HD) and DCH18C6 in n-dodecane to extract Sr^{2+} ion, because D2EHPA is cheaper and more easily obtainable than HD.

Prior to the extraction of Sr^{2+} ion from sea water in the contained liquid membrane permeator with the extractant mixture as a membrane liquid, distribution coefficients of Sr^{2+} ion for the extractant mixture were measured at various equilibrium pH's of aqueous Sr^{2+} solutions. The initial concentration of Sr^{2+} ion in the aqueous solution was 80 ppm. As shown in Fig. 3, the distribution coefficients of Sr^{2+} ion increased with the equilibrium pH until it reached around 5. These distribution coefficients were high enough for the extraction of Sr^{2+} ion, considering the pH of natural sea water is 8.0. And this type of distribution coefficient curve which shows an increase in distribution coefficient at increasing pH but has a plateau is for the case when complexes of the form MR_n and $MR_n(RH)_m$ are formed and extracted and no nonextractable complexes of the form $M(OH)_p$ are formed [Lo et al., 1983]. On the basis of the extraction-stripping reaction mechanism proposed by Ramadan and Danesi [1988] which forms $SrR_2(HR)_{m-2}(DCH18C6)$, it's possible to predict a similar form of complex might be formed even though different acidic extractant is applied.

2. Batch Extraction

To verify the ability of the liquid membrane permeator with an extractant of D_2EHPA and DCH18C6 in kerosene as a membrane liquid for extraction of Sr^{2+} ion from sea water, the effect of composition of the feed solution in the batch liquid membrane permeator was examined. Three kinds of the feed solutions were tested. The first one was an aqueous Sr^{2+} solution with initial concentration of 80 ppm. As shown in Fig. 4, the permeator extracted Sr^{2+} ion fast from the aqueous solution and reached extraction equilibrium within 10 hours. However, as the 1,290 ppm of Mg^{2+} ion and 5,385 ppm of Na^+ ion were added to the aqueous Sr^{2+} solution successively, the extraction rates definitely decreased and it took about 120 hours to reach extraction equilibrium. There was no significant increase in the equilibrium concentration of Sr^{2+} ion in the feed solution after extraction equilibrium was reached. The concentrations of Mg^{2+} and Na^+ were the same as those of natural sea water. The addition of Mg^{2+} and Na^+ to the feed solution dramatically increased the total concentration of solutes in the feed solution and these ions hindered Sr^{2+} ions from extracting to reduce the extraction rate. Considering the equilibrium extraction efficiency of Sr^{2+} ions from artificial sea water was 0.726 and the membrane lifetime of this permeator was much longer than 120 hours, this permeator could be an alternative choice for extraction of Sr^{2+} ion from sea water if it is installed beneath a sailing ship and extracts Sr^{2+} ions continuously.

The major operating parameters affecting the extraction in the liquid membrane permeator were initial concentration and pH in the feed solution, and extracting temperature. Figs. 5-7 represent the effect of these parameters.

Fig. 5 represents the effect of initial concentration of Sr^{2+} ion in the feed solution on the equilibrium extraction efficiency. As shown, the equilibrium extraction efficiency decreased with the initial concentration when the initial concentration was low, and became constant as the initial concentration increased. The increase in the initial concentration of Sr^{2+} ion in feed solution results in the increase in the transport of Sr^{2+} ion to stripping solution, which enhances the

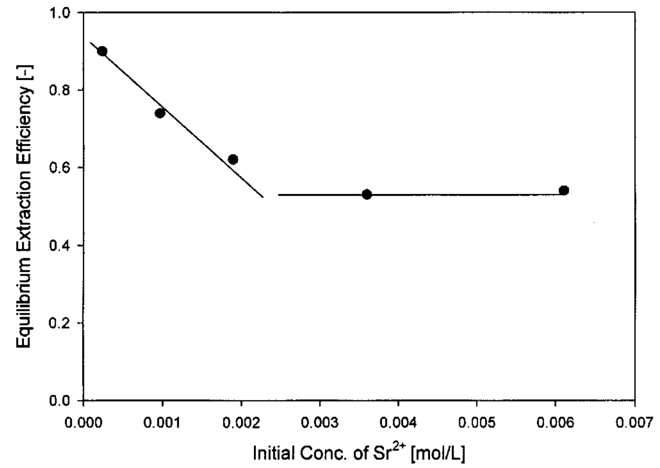

Fig. 5. The effect of initial concentration of Sr^{2+} ion in extracting solutions on the equlibrium extraction efficiency in the batch liuqid membrane permeator.

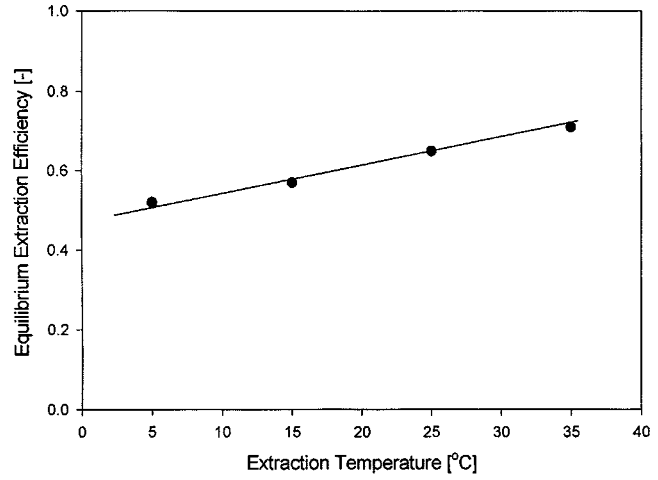

Fig. 6. The effect of extraction temperature on the equilibrium extraction efficiency in the batch liquid membrane permeator.

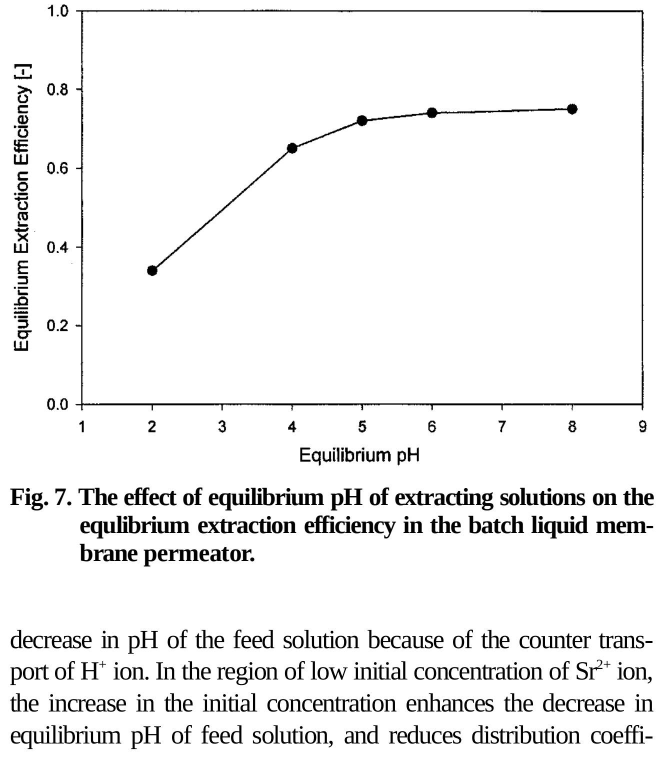

Fig. 7. The effect of equilibrium pH of extracting solutions on the equlibrium extraction efficiency in the batch liquid membrane permeator.

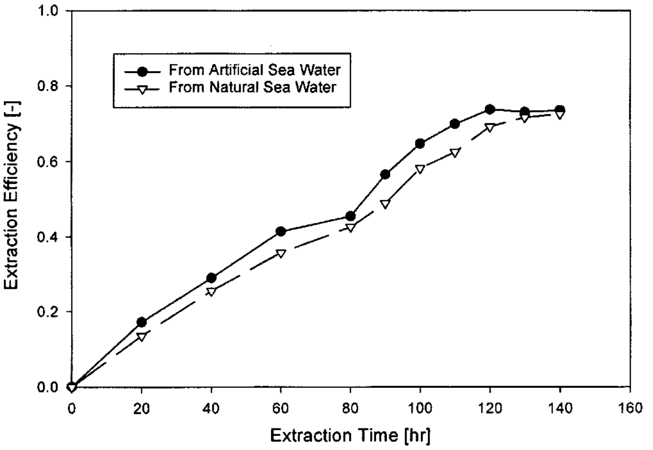

Fig. 8. The comparision of time profiles of extraction efficiency of Sr^{2+} ion from natural and artificial sea water in the batch extractor.

decrease in pH of the feed solution because of the counter transport of H^+ ion. In the region of low initial concentration of Sr^{2+} ion, the increase in the initial concentration enhances the decrease in equilibrium pH of feed solution, and reduces distribution coefficient and equilibrium extraction efficiency. However, a high initial concentration of Sr^{2+} ion makes a significant decrease in equilibrium pH of the feed solution and causes a low distribution coefficient. Even though the transport of Sr^{2+} ion to stripping solution is stimulated by high concentration of Sr^{2+} ion in the feed solution, the equilibrium extraction coefficient remains almost constant.

Fig. 6. shows the equilibrium extraction efficiency was proportional to the extraction temperature. The temperature range in this study was 5-35 °C, and this may be the actual whole range in the large scale extraction of metal ions from natural sea water. The increase in the equilibrium extraction efficiency is mainly due to the increase in equilibrium constant because the equilibrium constant of extraction reaction generally increases with extraction temperature. And this increase may be partly due to the change in the distribution coefficient because the variation of temperature can also affect the distribution. It is known that the distribution coefficient of some metal complexes increases with the increase in temperature, but some complexes do not show this behavior at all [Lo et al., 1983]. Because the actual change in the temperaure of sea water is insignificant, detailed research on this was not performed.

Fig. 7 represents the effect of equilibrium pH of the feed solution on the equilibrium extraction efficiency. It sharply increased with equilibrium pH when the pH was low. However, the increasing tendency decreased with the pH and finally the equilibrium extraction efficiency became constant. This result is closely related to the variation of distribution constants with equilibrium pH shown in Fig. 3.

Fig. 8 shows the comparison of time profiles of extraction efficiencies of Sr^{2+} ion from artificial and natural sea water in the batch permeator. It shows that the extraction rate of Sr^{2+} ion from natural sea water was slightly smaller than that from artificial sea water, and the time to reach extraction equilibrium is lengthened by 20 hours. However, the equilibrium extraction efficiencies from the two sea waters were nearly same. These results, similar to that of Fig. 4, are due to the higher total concentration of solutes in the natural sea water than that in the artificial sea water.

3. Continuous Extraction

The extraction of Sr^{2+} ion from artificial sea water in the continuous contained liquid membrane permeator was performed to examine the effect of some operating parameters on the extraction flux. In the continuous operation, it normally took about 40-50 hours to reach a steady state if the space time of the permeator was 5 hours. The extraction fluxes of Sr^{2+} ion were evaluated from the steady state concentration of Sr^{2+} ion at the exit of extraction cell.

Fig. 9 represents the effect of equilibrium concentration of Sr^{2+} ion in the feed solution on the extraction flux in the continuous liquid membrane permeator. As shown, the extraction flux increased with equilibrium concentration of Sr^{2+} ion up to near 0.0025 mol/L and became constant above that value. This result corresponded to the theoretical model proposed by Rovira and Sastre [1998] saying the extraction flux of metal ion in the supported liquid membrane permeator is proportional to the concentration of metal ion in the feed

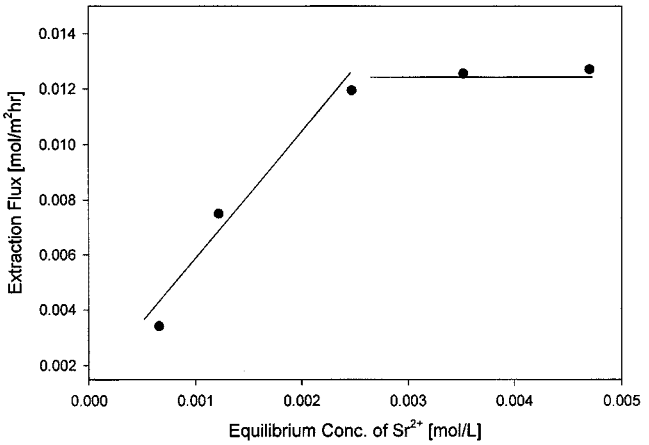

Fig. 9. The effect of equilibrium concentration of Sr^{2+} ion in extracting solution on the extraction flux in the continuous liquid membrane permetor.

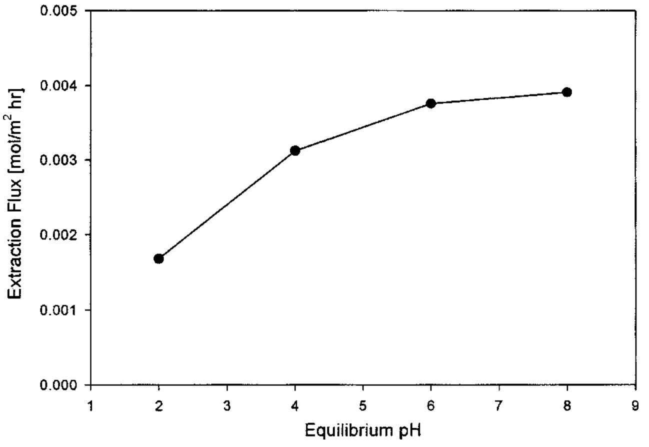

Fig. 10. The effect of equilibrium pH of extracting solutions on the extraction flux of Sr^{2+} ion in the continuous liquid membrane permeator.

solution when the concentration is extremely small and becomes constant as the concentration increases. This means the flux is controlled by diffusion in an aqueous film in the first portion of the graph, and becomes entirely controlled by diffusion in the membrane as the concentration increased.

Fig. 10 shows the effect of equilibrium pH of the feed solution on the extraction flux of Sr^{2+} ion. As shown, the extraction flux increased with equilibrium pH at the low equilibrium pH. But the increasing tendency diminished as the pH increased to get constant extraction flux. This result is also closely related to the variation of distribution constant with equilibrium pH as shown in Fig. 3.

CONCLUSIONS

As an effective liquid membrane permeator for extracting Sr^{2+} ion from sea water, a contained liquid membrane permeator with two microporous films, was proposed. The extraction of Sr^{2+} ion from artificial and natural sea waters in the batch and continuous contained liquid membrane permeators was performed. The results obtained are summarized as follows:

1. The liquid membrane permeator with an extractant of DCH18C6 and D$_2$EHPA mixture in kerosene as a membrane liquid extracted Sr^{2+} ion from sea water effectively with a long membrane lifetime.
2. The extraction rate decreased with the increase in the total concentration of solutes in the extraction phase, but the equilibrium extraction efficiency did not definitely change.
3. The equilibrium extraction efficiency increased with the extraction temperature in the range of this study. The efficiency decreased with the initial concentration of Sr^{2+} ion in the feed solution when the concentration was low, but it tended to be constant as the concentration increased.
4. The extraction flux in a continuous permeator increased with the equilibrium concentration of Sr^{2+} ion and pH of the feed solution, but the increasing tendency diminished toward constant extraction flux.

REFERENCES

Botterill, J. S. M., Teoman, Y. and Yuregir, K. R., "New Aspects of Uranium Recovery from Seawater," *Ind. Eng. Chem. Proc. Res. Dev.*, **21**, 781 (1982).

Casamatta, G., Chavarie, C. and Angelino, H., "Hydrocarbon Separation Through a Liquid Water Membrane: Modeling of Permeation in an Emulsion Drop," *AIChE J.*, **24**(6), 945 (1978).

Chaudry, M. A., Ahmad, S. and Malik, M. T., "Supported Liquid Membrane Technique Application for Removal of Chromium from Tannery Wastes," *Waste Management*, **17**(4), 211 (1997).

Guha, A. K., Yun, C. H., Basu, R. and Sirkar, K. K., "Heavy Metal Removal and Recovery by Contained Liquid Membrane Permeator," *AIChE J.*, **40**(7), 1223 (1994).

Izatt, R. M., Dearden, D. V., McBride, Jr., D. W., Oscarson, J. L., Lamb, J. D. and Christensen, J. J., "Metal Separations Using Emulsion Liquid Membranes," *Sep. Sci. & Technol.*, **18**(12&13), 1113 (1983).

Ju, C. S., Cheon, J. K. and Ha. H. D., "Separation of Zinc Ion from Aqueous Solutions by Liquid Membrane Permeator with Two Microporous Films," *HWAHAK KONGAK*, **38**, 13 (2000).

Kabil, M. A., Ghazy, S. E., Abeidu, A. M. and Metwaly, N. M., "Comparative-Study of Selective Separation of Magnesium from Brine and Seawater," *Sep. Sci. Technol.*, **30**(20), 3787 (1995).

Kirk, R. E., Othmer, D. F., Grayson, M. and Eckroth, D., "Encyclopedia of Chemical Technology," John Wiley & Sons, New York, **14**, 577 (1981a).

Kirk, R. E., Othmer, D. F., Grayson, M. and Eckroth, D., "Encyclopedia of Chemical Technology," John Wiley & Sons, New York, **16**, 279 (1981b).

Lo, T. C., Baird, M. H. I. and Hanson, C., "Handbook of Solvent Extraction," John Wiley & Sons, New York, 61 (1983).

Park, S. W., Sohn, I. J., Suh, D. S. and Kumazawa, H., "Separation of CO$_2$ by 2-Amino-2-Methyl-1-Propanol Aqueous Solution in Microporous Hydrophobic Hollow Fiber Contained Liquid Membrane," *Korean J. Chem. Eng.*, **16**, 549 (1999).

Ramadan, A. and Danesi, P. R., "Transfer Rate and Separation of Sr^{2+} and Cs+ by supported Liquid Membranes Utilizing Synergized Crown Ether Carriers," *Solv. Extr. and Ion Exch.*, **6**(1), 157 (1988).

Rovira, M. and Sastre, A. M., "Modeling of Mass Transfer in Facilitated Supported Liquid Membrane Transport of Palladium(II) Using

Di-2-ethylehexyl Thiophosphoric Acid," *J. Memb. Sci.*, **149**, 241 (1998).

Sengupta, A., Basu, R., Prasad, R. and Sirkar, K. K., "Separation of Liquid Solutions by Contained Liquid Membranes," *Sep. Sci. Tech.*, **23** (12,13), 1735 (1988).

Vogtle, F. and Webe, E., "Host Guest Complex Chemistry III," 2, Springer-Verlag, Berlin (1984).

Yang, X. J. and Fane, A. G., "Performance and Stability of Supported Liquid Membranes Using LIX 984N for Copper Transport," *J. of Membr. Sci.*, **156**, 251 (1999).

Yi, J. H., "Effects of the Boundary Layer and Interfacial Reaction on the Time Lag in Supported Liquid Membranes," *Korean J. Chem. Eng.*, **12**, 391 (1995).