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Lithium Extraction from a Multicomponent Mixture Using Supported Liquid Membranes

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ABSTRACT

Increasing demand for lithium metal is expected to rise above the current production levels. Most lithium production is currently from mining and recovery of pegmatite ores. Recent research has emphasized recovery from brine sources such as geothermal water and seawater. A novel liquid-membrane-extraction process is investigated here for the recovery of lithium metal from these natural resources. Different carriers and combinations of carriers were tried for lithium selectivity. A carrier combination of LIX54 (main component is α-acetyl-*m*-dodecylacetophenone) and TOPO (tri-octyl phosphine oxide) had a synergistic effect for lithium extraction and was found to be most effective. This combination was used to extract lithium in a supported liquid membrane (SLM) process. Variables considered were pH, carrier concentrations, initial lithium concentration, type of organic solvent and stripping phase, and presence of sodium and potassium ions in the feed and flow rates of both aqueous phases. The optimal extraction efficiency of the system was higher than 95% for a model feed solution containing Na^+, K^+, and Li^+ at pH greater than 12.5. The permeability of the system was maintained at a constant value for a maximum period of 2 days and dropped below 50% after 4 days. Empirical mathematical models for lithium extraction were derived from the results of SLM experiments.

Key Words. Lithium extraction; Geothermal water; Synergistic effect; Supported liquid membrane

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INTRODUCTION

Supported liquid-membrane systems have been studied for extraction and pre-concentration of several metals (1–6). The system uses a thin polymer membrane impregnated with organic solution that separates two aqueous phases and transports selectively a "target" solute from a multicomponent feed phase to the strip phase. The advantage of SLM is the ability to transport against a concentration gradient and to continuously extract and strip solutes simultaneously. Furthermore, in comparison with other separation techniques, SLM has the advantages of low cost, high efficiency, low product contamination, and small amounts of extractant used (7). The synergistic extraction of lithium has been reported for an emulsion–liquid-membrane system using a combination of LIX54 (main component is α-acetyl-*m*-dodecylacetophenone) and TOPO (tri-*n*-octylphosphine oxide) (8, 9). The percentage of extraction was as high as 95%. Although research was carried out for the mechanism of synergistic lithium extraction using LIX54 and TOPO, the results so far have not been applied to a "real" process situation. The aim of this work is to derive the extraction kinetics and obtain some experimental results for selective lithium extraction from a multicomponent feed using LIX54 and TOPO in a SLM system. Also a mathematical model for predicting the permeability of lithium ions in a SLM system for extraction is presented.

THEORY

Extraction Mechanism

LIX54 is a chelating agent in which the extraction–stripping reaction can be described as (10)

$$n[R\text{–}H]_{org} + [M^{n+} + A]_{aq} \rightleftharpoons [R_nM]_{org} + [H^{n+} + A]_{aq} \qquad (1)$$

in which, R–H represents LIX54, M is the metal ion, A is the anion, and n is the number of electrons transferred. The subscripts *org* and *aq* denote, respectively, the organic and aqueous phases. TOPO, on the other hand, is a neutral-type extractant that reacts with solutes by replacing water of hydration in a neutral complex (10). Because lithium ions exist in water as cations and not complexes, this suggests single-carrier extraction is not possible with TOPO but is possible if it is combined with LIX54. The reaction for lithium ion extraction with LIX54 is as follows

$$[R\text{–}H]_{org} + [\mathrm{Li}^+]_{aq} \rightleftharpoons [\mathrm{Li}\text{–}R]_{org} + \mathrm{H}^+ \qquad (2)$$

A hydrogen ion in the LIX54 molecule is replaced by the lithium ion in a substitution reaction.

Further reaction with TOPO is now possible because of the formation of the [Li–R] complex. TOPO can react by forming a complex with [Li–R] according to the following equation

$$[\mathrm{Li}\text{–}R]_{org} + a[S]_{org} \rightleftharpoons [\mathrm{Li}\text{–}R\text{–}S_a]_{org} \tag{3}$$

Combining Eqs. (2) and (3) to give an overall synergistic extraction equation

$$[R\text{–}H]_{org} + [Li^+]_{aq} + a[S]_{org} \rightleftharpoons [Li\text{–}R\text{–}S_a]_{org} + \mathrm{H}^+ \tag{4}$$

The equilibrium constants for LIX54 extraction are defined as

$$K_{E,1} = \frac{[\mathrm{Li\text{–}R}]\,[\mathrm{H}^+]}{[\mathrm{Li}^+]\,[\mathrm{R\text{–}H}]} \tag{5}$$

For synergistic extraction of LIX54 and TOPO

$$K_{E,2} = \frac{[\mathrm{Li\text{–}R\text{–}S_a}]\,[\mathrm{H}^+]}{[\mathrm{R\text{–}H}]\,[\mathrm{Li}^+]\,[\mathrm{S}]^{\mathrm{a}}} \tag{6}$$

Given that the distribution ratio, D_E, is defined as the ratio of the concentration of solute in the organic phase to that in the aqueous phase at equilibrium

$$D_E = \frac{[\mathrm{Li}^+]_{\mathrm{org}}}{[\mathrm{Li}^+]_{\mathrm{aq}}} \tag{7}$$

the equilibrium constants can be expressed in terms of D_E

$$K_{E,1} = \frac{D_E[\mathrm{H}^+]}{[\mathrm{R\text{–}H}]} \tag{8}$$

and for synergistic extraction

$$K_{E,2} = \frac{D_E[\mathrm{H}^+]}{[\mathrm{R\text{–}H}]\,[\mathrm{S}]^{\mathrm{a}}} \tag{9}$$

Take the log of both sides of Eq. (9) and rearrange so that

$$\log(D_E) = \log(K_{E,2}) + \log(\mathrm{R\text{–}H}) + \mathrm{a}\log(\mathrm{S}) + \mathrm{pH} \tag{10}$$

The concentrations of the carriers do not decrease significantly and can be approximated as constants. This is due to the much lower solute concentration in comparison with the carrier concentrations. The pH and D_E can be measured at equilibrium. Thus by varying each variable independently and plotting the appropriate log plots, the extraction equilibrium can be established.

PERMEABILITY CALCULATION FOR SLM SYSTEM

For the extraction processes where interfacial reactions are faster than the diffusion process, the permeability coefficient (P) can be given by applying

Fick's law at steady state

$$P = -\frac{d[C_{Af}]}{dt} x(V/a) \times 1/C_{Af} \tag{11}$$

in which C_{Af} is the lithium concentration on the feed side at time t, V is the volume of the solution, and a is the effective membrane area. Eq. (11) can be integrated using the initial condition at $t = 0$, $C_{Af} = C_{A0}$, and the following equation is obtained

$$\ln\left[\frac{C_{Af}}{C_{A0}}\right] = -\frac{Pa}{V}t \tag{12}$$

Therefore by plotting the log of the ratio of metal concentration to that of initial feed against time, a straight-line correlation will be obtained. The slope of the line can then be used to calculate the permeability of the system if the volume of the feed solution and the total membrane surface area are known.

EXPERIMENTAL

For partitioning experiments the organic phase was prepared by dissolving the appropriate amounts of carriers LIX54 and TOPO in kerosene. Equal volumes of the model feed solution and the organic phase were mixed and shaken in a water bath at constant temperature. The feed was analyzed for lithium concentrations using a 703 Perkin-Elmer AA spectrophotometer. For multicomponent experiments, sodium and potassium were also analyzed for comparison of selectivity with lithium. All experiments were carried out at 20°C.

The organic solution was prepared by adding various amounts of carriers (LIX54 and TOPO) to the solvent and mixing until both TOPO and LIX54 were completely dissolved. As a membrane support Celgard 2500 was used, and its characteristics are porosity of 37–48%, pore size of 0.05×0.19 μm, and thickness of 20 μm. The thin sheet polymer membrane was cut into 10-cm diameter circular discs using scissors. The membrane was then soaked in the organic solution and placed in a dessicator under vacuum for at least 30 minutes. The vacuum enhances the overall permeation of the organic phase into the pores of the membrane. Rubber gloves were always worn when handling the membranes to avoid fouling the solution and blocking the pores. After soaking, the membrane was removed from the dessicator and the surface organic solution dried off with tissue paper. The membrane was then quickly placed between the two half cells. The cells were then screwed tight to avoid leakage of solution from the sides of the cell and also to ensure that the flow of solutions followed the spiral path. In the batch experiments, the feed and strip phases were recycled, and the volumes used for the two phases were kept low to reduce overall time for each run. For each experiment 100 mL of solu-

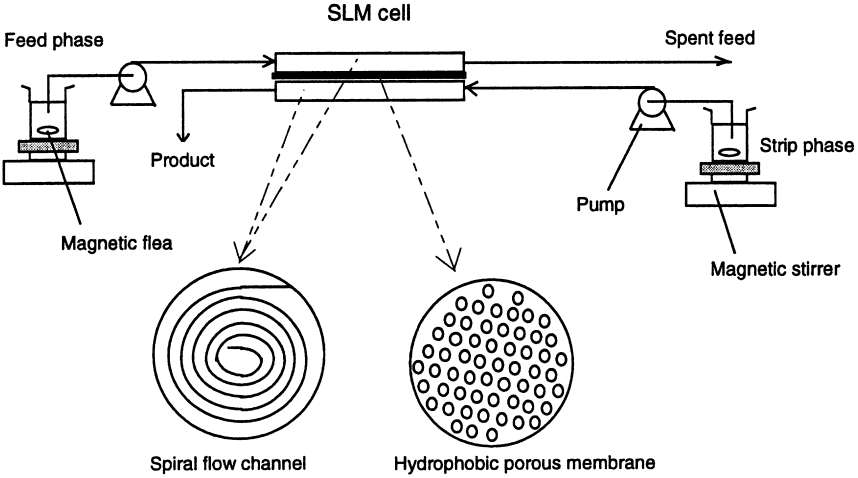

FIG. 1 Schematic of the supported liquid membrane process.

tion (identical for the feed and strip) were used. Depending on the flow rate required, either a peristaltic pump with a maximum flow rate of 3.5 mL/min or a larger pump capable of flow rates up to 30 mL/min was used. The two phases were pumped through the channels in a countercurrent direction to increase the transfer of ions (11). Samples of the feed and strip phases were taken at regular intervals. More samples were taken at the start of the runs because the driving force for mass transfer is the greatest at the start owing to a higher concentration gradient between the two phases. This initial period of transfer was monitored carefully because the accuracy of the results depends strongly on the initial rate of transfer. A schematic of the setup is shown in Fig. 1. The dimensions of the SLM cell are 3.16 mM (width), 1.6 mM (depth), and 940 mM (length). This gives a cell area of 29.7 cm^2 and a volume of 4.75 cm^3.

The runs to determine the stability of the membrane support were carried out over several days in a recirculating batch process. One liter batches of feed solution were used and changed with fresh solution every 2 days. The continuous experiments were carried out with the same setup. The strip phase was recycled while the spent feed was collected for analysis.

RESULTS

Partitioning Experiments

Three types of solvents were intended for comparison: kerosene, toluene, and hexane. A direct comparison between kerosene and toluene showed no significant difference between the two solvents with respect to distribution ratio. However, toluene was rejected because of higher cost and potential health problems. The comparison between hexane and kerosene showed a slight advantage for hexane, an approximately 15% increase in distribution ratio. This, however, is heavily offset by the high volatility of hexane that is expected to cause operational problems when applied in a SLM system. Therefore, hexane was also rejected in favor of kerosene. Furthermore, previous work with extraction using LIX54 and TOPO also used kerosene as the solvent (8, 9).

The solvent extraction and carrier-facilitated transport of Li^+ ions have previously been carried out using pentaethylene glycol (PEG) as the carrier with chloroform as the solvent (12). This combination for the organic phase was used here to determine its effectiveness for lithium transport. Both aqueous and organic phases were placed in a beaker and stirred with a magnetic stirrer at 600 rpm for 1 hour. The distribution coefficient was found to be 0.08, much lower than desired. Therefore, this combination was rejected for use in further experiments.

Extraction of lithium was possible with LIX54 alone but not with TOPO alone. The distribution ratio reached a maximum of 0.71 with LIX54 concentration at 0.58 M (20% v/v) and pH at 13.0. Figure 2 shows log–log plots of D_E versus LIX54 concentration. From the linear correlations, the expected slope of 1.0 was found for both cases. The equilibrium constant calculated for the optimum extraction of lithium using LIX54 was 1.42×10^{-12}. For the combined TOPO and LIX54, this constant becomes 2×10^{-10} M^{-1}.

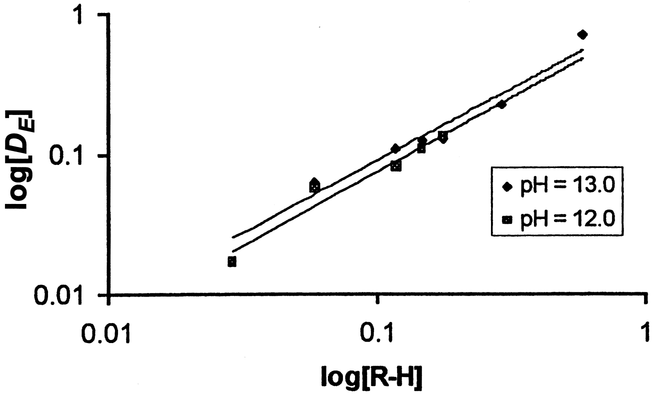

FIG. 2 Extraction of lithium with LIX54 alone, LIX54 denoted as R-H. Initial $[Li^+]$ = 20 ppm.

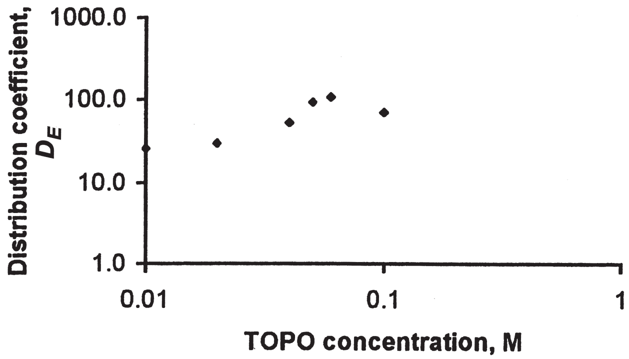

FIG. 3 Effect of TOPO concentration on the distribution coefficient for lithium extraction. Initial $[Li^+] = 20$ ppm, pH = 13.0, LIX54 concentration = 0.146 M.

For the case of synergistic extraction, the LIX54 concentration was fixed at 0.146 M, while the TOPO concentration was varied from 0.02 to 0.10 M. Figure 3 shows the log–log plot of D_E versus TOPO concentration. A straight-line correlation with a slope of 0.5 for Li^+ ion extraction was obtained. Therefore the synergistic extraction equation for lithium is

$$[R\text{–}H]_{org} + [Li^+]_{aq} + 0.5[S]_{org} \rightleftharpoons [Li\text{–}R\text{–}S_{0.5}]_{org} + H^+ \qquad (13)$$

The stoichiometric coefficient obtained for the extraction reaction was 1.3 (8, 9). Smaller concentrations of LIX54 and TOPO were used for extraction of lithium from a high concentration feed, and that required more than the stoichiometric proportion of the extractant.

The distribution ratio was calculated and this was approximately 50.0 at optimum extractant concentrations, 100 times higher than the D_E obtained for single-extractant LIX54 extraction. In most cases, more than 95% of initial Li^+ ions was extracted.

Effect of Initial Lithium Concentration

The initial lithium concentration was varied from 10 to 100 ppm with the carrier concentrations kept constant at 0.15 M LIX54 and 0.05 M TOPO. The results are plotted as $\log[D_E]$ versus $\log[C_i]$ in Fig. 4, which indicates a slight decrease in distribution ratio with increasing lithium concentration. However, for geothermal water where the lithium concentration is on the order of 20 ppm, the distribution ratio can be approximated to be independent of initial lithium concentration.

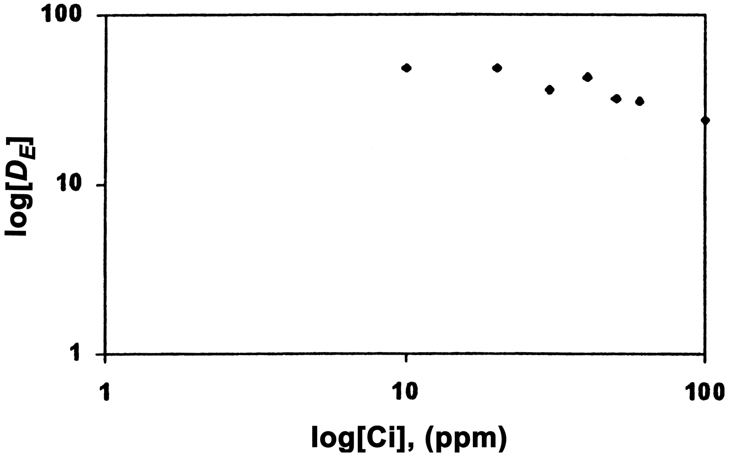

FIG. 4 Effect of initial lithium concentration on distribution coefficient. pH = 13.0, LIX54 concentration = 0.146 M, TOPO concentration = 0.05 M.

Effect of pH

The pH was varied from 6.0 to 13.5 and the log of D_E was plotted against pH. This is shown in Fig. 5. Negligible extraction occurred below a pH of 11.5. Between pH of 11.5 and 13.5, extraction increased with increasing pH (i.e., D_E varied as the inverse of the hydrogen ion concentration) reaching a maximum at approximately 13.0. The increase in distribution ratio slowed down beyond pH 13.0 because of the competition of various ions, especially Na^+ that was used in 5 M concentration to adjust the pH to a higher value. All subsequent experiments were carried out at pH 13.0 because it was determined as optimum. With geothermal water at a pH of approximately 8.5, extraction would not be possible. The pH of geothermal water will need to be raised to at least 12.0 before lithium extraction can occur. The cost of chemicals would have to be compromised against the selectivity and recovery of lithium to justify the economics of SLM technology. The other extractants work in the acidic region, i.e., pH less than 7 (13) and would need the pH adjustment as well. Furthermore, the recovery of lithium from geothermal water with the acidic extractant (13) was not as high as that achieved in this system of synergistic extraction.

Effect of Temperature

The temperature was varied from 25 to 50°C to determine the effect of temperature on lithium extraction. The conditions for extraction were set for optimum lithium extraction. The log of K_E was plotted against $1/T$; this is shown

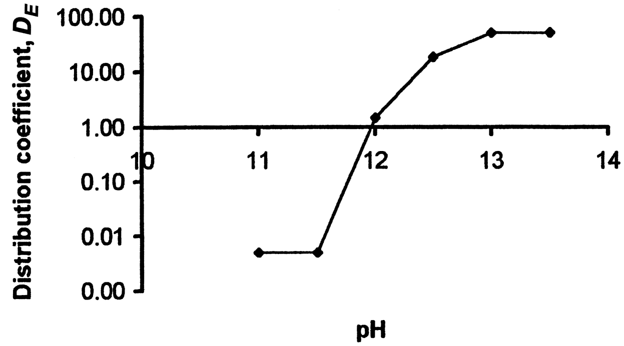

FIG. 5 Effect of pH on the distribution coefficient. Initial [Li^+] = 20 ppm, LIX54 concentration = 0.146 M, TOPO concentration = 0.05 M.

in Fig. 6. Because the entropy change for the reaction is negative, it is exothermic.

Extraction of Sodium and Potassium

Single-component extraction of sodium and potassium with LIX54 were carried out at pH 12.0 and 13.0. Concentration ranges of 1000 to 7000 ppm

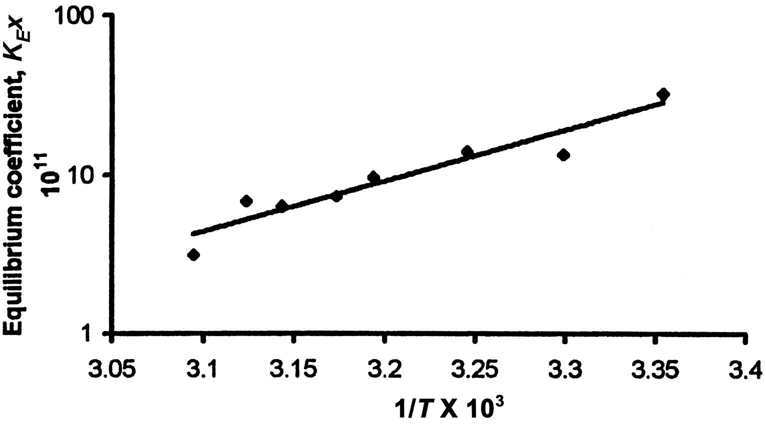

FIG. 6 Effect of temperature on equilibrium constant. Initial [Li^+] = 20 ppm, LIX54 concentration = 0.146 M, TOPO concentration = 0.05 M.

and 30 to 500 ppm were used for sodium and potassium, respectively. The plots of D_E versus concentration are shown in Fig. 7(a) and (b) for Na^+ and K^+, respectively. It can be seen from these results that lithium is selectively extracted over Na^+ and K^+ in the ion concentration range specified. Essentially, they mean that $D_E(K^+)$ and $D_E(Na^+) < 0.1$ and $D_E(Li^+) > 10$.

Multicomponent Synergistic Extraction

Multicomponent extraction of Li^+, K^+, and Na^+ ions was carried out with an ammonia solution or sodium hydroxide as buffer. Ammonia was used because using sodium hydroxide affects the concentration of sodium ions in solution. The concentration range examined for Na^+ was 100–3000 ppm, and for K^+ ions 50–500 ppm. To determine the effect of sodium and potassium ion

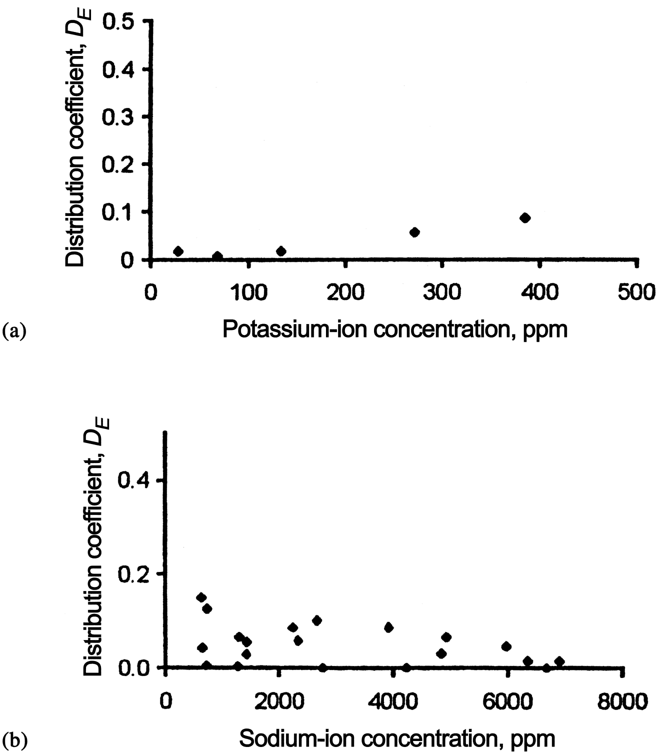

FIG. 7 (a) Extraction of sodium with LIX54 alone. pH range = 12–13.0, LIX54 concentration = 0.146 M. (b) Extraction of potassium with LIX54 alone. pH = 13.0, LIX54 concentration = 0.146 M.

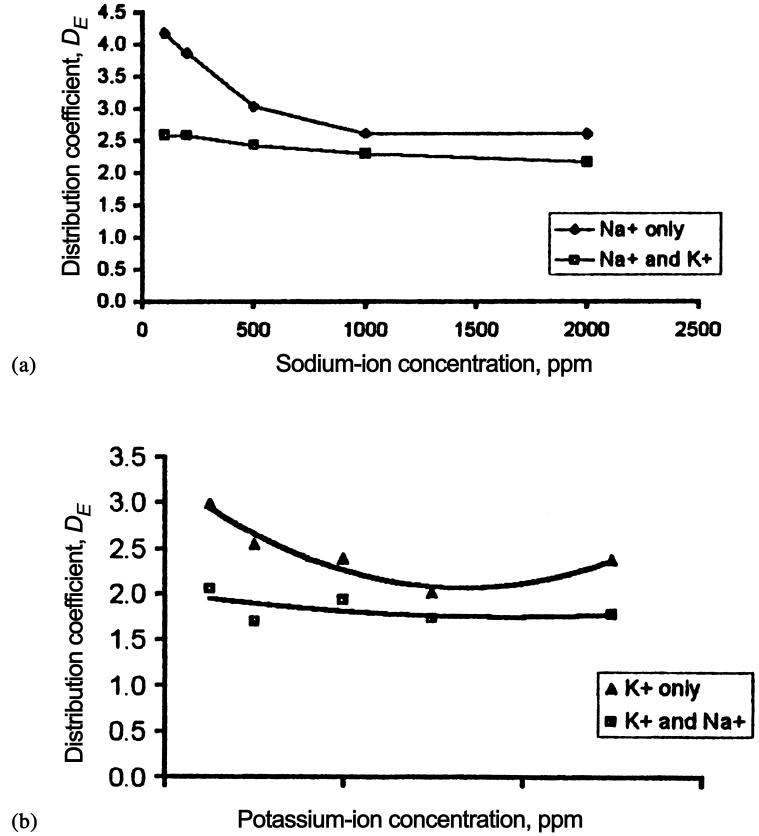

FIG. 8 (a) The effect of sodium-ion concentration on the distribution coefficient of lithium-ion extraction in multicomponent extraction. Initial $[Li^+] = 20$ ppm, pH = 13.0, $[K^+] = 300$ ppm, [LIX54] = 0.05 M, [TOPO] = 0.146 M. (b) The effect of potassium-ion concentration on the distribution coefficient of lithium-ion extraction in multicomponent extraction. Initial $[Li^+] =$ 20 ppm, pH = 13.0, $[Na^+] = 2000$ ppm, [LIX54] = 0.05 M, [TOPO] = 0.146 M.

concentration on the extraction of lithium, one metal concentration was kept constant, whereas the other was varied through the range stated. The concentration of the ions was kept at approximately the concentration present in geothermal water; 2000 and 300 ppm for sodium and potassium, respectively. For the runs with ammonia as the buffer solution, the results are shown in Fig. 8.

As can be seen from Fig. 8, the D_E of lithium ions decreases with increasing sodium concentration. This drop in lithium extraction efficiency is due to the competing reaction of sodium ions with the LIX54 carrier

$$[\mathrm{R{-}H}]_{\mathrm{org}} + [\mathrm{Na}^+]_{\mathrm{aq}} \rightleftharpoons [\mathrm{Na{-}R}]_{\mathrm{org}} + \mathrm{H}^+ \tag{14}$$

In a manner similar to that for potassium ions, the D_E for lithium ions drops with increasing potassium ion concentration. This was also due to the competing reaction of K^+ ions with the LIX54 carrier. The extraction of Li^+ from a two-component solution (with either Na^+ or K^+ ions) was also tried and the results are shown in Fig. 8. As can be seen, the effect of sodium ions on the extraction of Li^+ and K^+ is to shift the curve down by a constant amount. A similar trend was also obtained for the effect of K^+ on the extraction of Li^+ from a two-component solution.

Supported Liquid-Membrane Batch Experiments

The time to reach equilibrium was determined in order to set the length of time for the experimental runs. The concentration of lithium was measured over a period of 5 hours, and the graph of lithium concentration versus time in both aqueous phases is shown in Fig. 9. It is observed that the amount of lithium transported from the feed phase is more than that in the stripping solution. This suggests that lithium is still in the membrane phase and needs longer time or a stronger stripping solution for complete recovery.

As is observed, the extraction of lithium from the feed phase is over 90% complete in 2 hours and reaches completion in 5 hours, whereas the recovery in the strip solution is about 70–75% (Fig. 9).

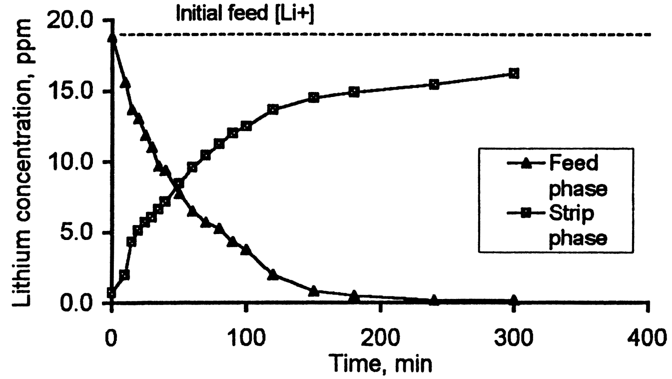

FIG. 9 Lithium concentration versus time in both aqueous phases. Initial $[Li^+]$ in feed phase = 20 ppm, pH = 13.0; organic phase: [LIX54] = 146 M, [TOPO] = 0.05 M; strip phase = 1M H_2SO_4.

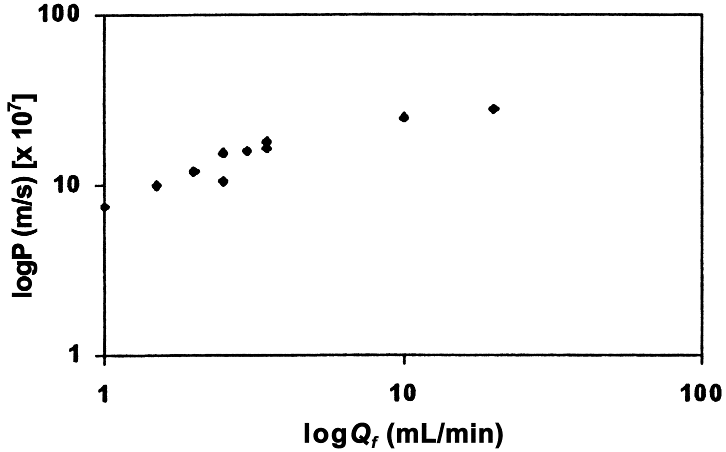

FIG. 10 Permeability versus feed-phase flow rate. Feed-phase conditions: $[Li^+]$ = 20 ppm, pH = 13.0; organic phase: solvent = kerosene, [LIX54] = 0.146 M, [TOPO] = 0.05 M; strip phase: 1 M H_2SO_4.

Effect of Feed-Phase Flow Rate

A plot of permeability versus flow rate is shown in Fig. 10. The permeability constant logarithmically increased with increasing feed-phase flow velocity, reaching a value of approximately 2.6×10^{-5} m/s at a flow rate of 20 mL/min. The initial flux was calculated from Eq. 14 and the $d[Li^+]_o/dt$ estimated from a plot of concentration versus time. The flux at 20 mL/min feed-flow rate was 1.55×10^{-4} mol/m^{2}s. These values are in the same range as those obtained by Kinugasa et al. (8, 9) in their experiments on lithium extraction. The permeability values obtained in this work are between 5.6×10^{-5} m/s (reported in ref. 14 for the extraction of platinum with Aliquat 336) and 8.3×10^{-7} m/s (reported in ref. 15 for the extraction of uranium using TOPO).

The increase in permeability could be due to the reduction of the laminar boundary layer on the surface of the membrane (8). The increase in flow rate reduces the film resistance that leads to a higher mass-transfer rate of lithium from the bulk feed phase to the surface of the supported membrane. Therefore, the overall permeability of the system is increased with increasing flow rate. Also the increasing flow rate improves the mixing of the feed phase that increases the transfer rate of ions through the bulk of the feed phase.

Effect of Feed- and Strip-Phase pH

The pH of the feed phase was varied from 11.5 to 13.5. The permeability constants were determined from the lithium concentration of the feed phase

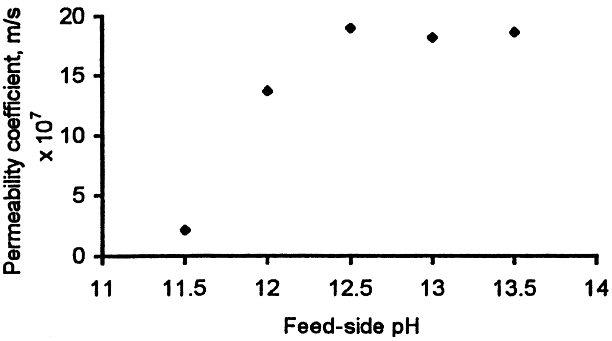

FIG. 11 Effect of feed-side pH on permeability. Feed-phase conditions: [Li^+] = 20 ppm; organic phase: solvent = kerosene, [LIX54] = 0.146 M, [TOPO] = 0.05 M; strip phase: 1 M

and plotted against the pH (Fig. 11). As can be seen, the permeability decreases sharply below a pH of 12.5 and levels out above this. This shows a similar trend to the experiments of pH variation in the phase equilibrium experiments. Therefore the cutoff pH for the feed phase for optimum extraction rate is approximately 12.5.

The uphill transport of lithium ions is driven by the reactions at the two interfaces (9). At a pH below 12.5, the reaction on the feed-side interface has a lower equilibrium constant, and this restricts the extent of lithium transported and hence lowers the permeability constant. At a higher feed-side pH, the overall mass-transfer rate is not restricted by the feed interface reaction and reaches a constant value (see Fig. 11).

Similar experiments were carried out for the strip phase with pH varied from 0.05 to 2.0. There was no significant decrease in the permeability constant for strip phase pH up to 2.0. A run was carried out with milli-Q water at pH 7.3 as the strip phase. The permeability coefficient dropped to 1.04×10^{-6} m/s for the water run. Hence as long as the H^+ concentration on the strip phase is kept relatively high, the overall mass transfer of the system will not be restricted by the stripping reaction.

Effect of Carrier Concentrations

The concentration of LIX54 was varied from 0.0292 to 0.584 M to determine the effect of LIX54 concentration on the permeability constant. The pH was fixed at 13.0 and the concentration of TOPO was kept at 0.05 M. The graph of permeability versus LIX54 concentration is given in Fig. 12. The optimum permeability was reached at LIX54 concentration of approximately 0.146 M. Increase in LIX54 concentration beyond 0.146 M had no significant

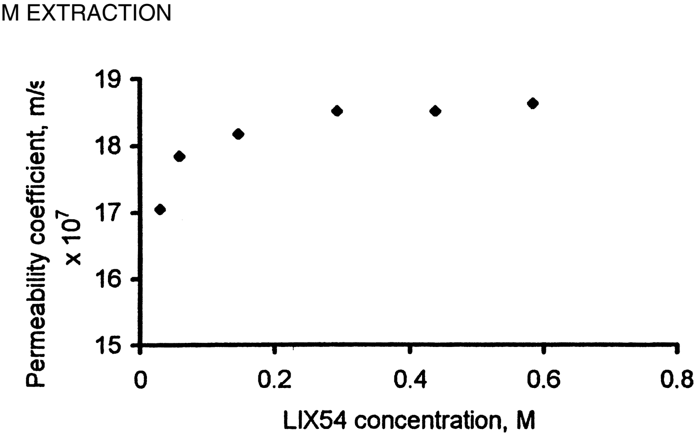

FIG. 12 Effect of LIX54 concentration on permeability coefficient. Feed-phase conditions: [Li^+] = 20 ppm, pH = 13.0; organic phase: solvent = kerosene, [TOPO] = 0.05 M; strip phase: 1 M H_2SO_4.

increase in permeability coefficient. Above this concentration, the rate of reaction is not affected by LIX54 concentration as the initial lithium concentration was kept constant at low value. The effect of increasing TOPO concentration was carried out with LIX54 concentration at 0.146 M and pH 13.0. The TOPO concentration was varied from 0 up to 0.05 M. The permeability versus TOPO concentration graph is given in Fig. 13. The optimum permeability was reached at a TOPO concentration of approximately 0.03 M.

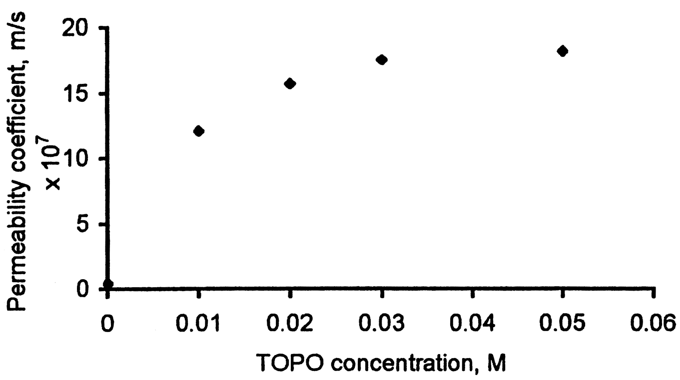

FIG. 13 Effect of TOPO concentration on permeability coefficient. Feed-phase conditions: [Li^+] = 20 ppm, pH = 13.0; organic phase: solvent = kerosene, [LIX54] = 0.146 M; strip phase: 1 M H_2SO_4.

Effect of Initial Lithium Concentration

The effect of initial lithium concentration in an SLM system was examined over the range of 20–50 ppm with optimum lithium-extraction conditions. The graph of permeability coefficient versus initial Li^+ concentration is given in Fig. 14. As can be seen, the permeability decreases with increasing concentration. The effect is in the high concentration range, i.e., 40–50 ppm. This is in agreement with the trend of the effect of initial Li^+ concentration on distribution ratio in the partitioning experiments (Fig. 4). This can be explained by the fact that the membrane phase is overloaded at higher feed concentrations as the extractant concentrations remained the same. This could change the solubility of the reaction complex formed and thus limit the recovery rate by the stripping solution. Similar results were reported for the extraction of metals (14, 15).

Stability of the SLM System

The stability of the membrane support was tested in a batch system with the recirculation of the aqueous solutions for 6 days per run. The permeability coefficient was calculated each day and a plot of permeability versus time is given in Fig. 15. Two runs were carried out with unsaturated aqueous phases. The permeability decreased after two days of operation and dropped below 50% of the original value after 4 days. As reported by Tanigaki et al. (16), the liquid membrane is more unstable when the feed and strip phases are unsaturated with the organic phase. Therefore a stability run was done with organic saturated strip and feed phases. The saturation of the aqueous phases had no significant effect on the stability of the membrane because the drop in perme-

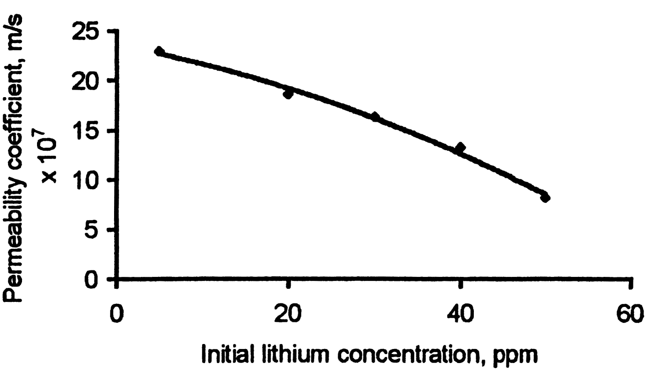

FIG. 14 The effect of initial lithium concentration on the permeability coefficient in an SLM process. Feed phase: Initial $[Li^+]$ = 20 ppm, pH = 13.0; organic phase: [LIX54] = 0.146 M, [TOPO] = 0.05 M; strip phase: 1 M H_2SO_4.

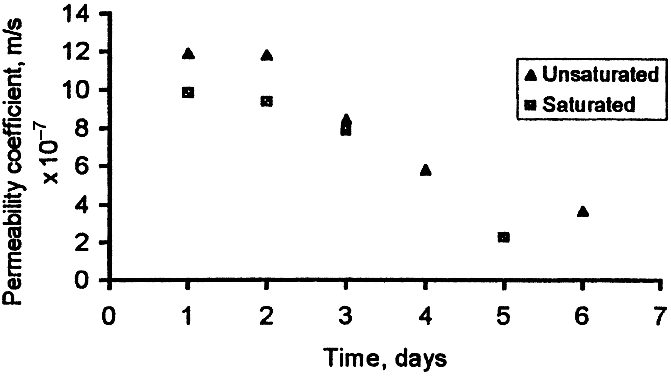

FIG. 15 Permeability coefficient versus time for trials on membrane stability. Initial [Li^+] = 20 ppm; feed phase: pH = 13.0, [LIX54] = 0.146 M, [TOPO] = 0.05 M; strip phase: = 1 M H_2SO_4.

ability occurred after 2 days, followed by a rapid decrease. The drop in the maximum permeability for the saturated case is possibly caused by a number of factors: the pressure difference over the membrane sheet, the solubility of the liquid membrane in the adjacent solutions, and emulsion formation of the liquid membrane in aqueous solutions (17–19).

Mathematical Model

An empirical mathematical model was developed from the results of the supported liquid-membrane experiments. The parameters included in the model are: feed-phase flow rate (1–15 mL/min), LIX54 concentration (0.05–0.6 M), and TOPO concentration (0–0.05), feed-phase pH (11.5–13.0) and initial feed-phase lithium concentration (5–20 ppm). A best-fit trend line was fitted to each of the results for the variables considered using the computer software Microsoft Excel 6.0. An equation and R-squared value for the accuracy of the fit was obtained from the trend line.

At optimum conditions, the permeability coefficient for the SLM system is approximately 1.86×10^{-6} m/s. Substituting into Eq. (12) with the membrane surface area, the equation becomes

$$\ln\left[\frac{C_{Af}}{C_{A0}}\right] = -\frac{(5.524 \times 10^{-9})}{V}t \qquad (15)$$

The effect of each parameter can be accounted for by multiplying Eq. (16) with a ratio of the corresponding equation to the optimum permeability coefficient of 1.86×10^{-6} m/s. This method is valid as long as each of the parameters in the equation remains constant throughout the experiment. Since the carrier concentrations are relatively high compared to the initial lithium concentration, LIX54 and TOPO remained approximately constant throughout the experiment. The pH was measured before and after each run and the change was found to be negligible. Since the flow rate can be maintained at a constant value, the method is valid for these parameters. Equation (16) is a mathematical equation for calculating the concentration of lithium with respect to time in a flat-sheet SLM system with an effective surface area of $0.00297\ \mathrm{m}^2$.

$$\ln\left[\frac{C_{Af}}{C_{AO}}\right] = -\frac{\dfrac{(5.524\times10^{-9})}{V}\times\left[\dfrac{0.485\ln[\mathrm{LIX54}]+19.006}{18.6}\right]\left[\dfrac{1.573\ln[\mathrm{TOPO}]+21.868}{18.6}\right]}{\left[\dfrac{7.5955\ln(Q_f)+7.179}{18.6}\right]\left[\dfrac{-8.08(\mathrm{p}\mathbf{H})^2+209.5(\mathrm{p}\mathbf{H})-1338}{18.6}\right]}t \tag{16}$$

Therefore for a known volume of the feed solution, the concentration of the feed phase with respect to time can be estimated from Eq. (16). The variables need to be specified and must all have a value greater than zero. However, if the pH of the solution is less than 11.0 or if the LIX54 concentration is zero,

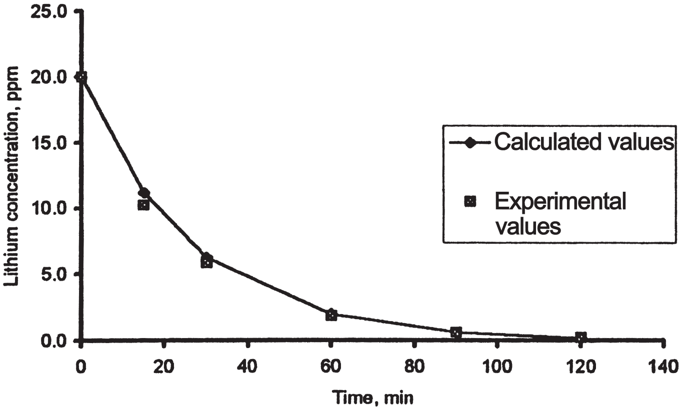

FIG. 16 Comparison of experimental results with calculated results from model. Feed phase: Initial $[\mathrm{Li}^+] = 20$ ppm; pH = 13.0; membrane phase: [LIX54] = 0.146 M; [TOPO] = 0.05 M; strip phase: 1 M H_2SO_4.

lithium extraction is not possible and the permeability coefficient should be set at zero. A plot of lithium concentration versus time in the feed phase for the model and experimental results is given in Fig. 16. As can be seen from the graph, the mathematical model is a good approximation of the experimental results.

As previously discussed, there is a significant effect of lithium concentration on permeability for concentrations above 20 ppm. The model needs to be refined to account for the effect of initial lithium concentration above 20 ppm.

CONCLUSIONS

In this paper we have described the results of an experimental study on a SLM system. It has been found that a combination of carriers, LIX54 and TOPO, can be used to extract lithium ions from dilute solutions such as sea water and geothermal water with synergistic effects. The SLM system prepared with the combined carrier in kerosene has been demonstrated to effectively extract more than 90% of the feed solute within a few hours.

The following operating conditions were determined for improved extraction

- a feed solution pH of 12.5
- a strip solution of 1M H_2SO_4
- a high feed flow rate of 3.5 mL/min and a medium flow rate of 1 mL/min for strip flow.

The performance of the SLM system was found to be stable for up to 3 days, after which the flux drops to half of the initial value. A mathematical model was developed from the results of SLM experiments and was found to be a good approximation of the experimental results.

NOMENCLATURE

a	area of SLM membrane, m^2
C_{Af}	feed-phase concentration, ppm
C_{AL}	ion concentration at $x = L$, ppm
C_{Ao}	initial concentration of ions in the feed phase, ppm
C_{As}	strip-phase concentration, ppm
C_E	equilibrium concentration of ions in feed-side reaction, ppm
D_E	distribution coefficient
J	flux of solute through membrane, $mol/m^2 \cdot s$
$K_{E,1}$	equilibrium constant for LIX54 extraction
$K_{E,2}$	equilibrium constant for synergistic extraction
M	metal ion

P	permeability coefficient, m/s
Q_f	Feed-flow rate, mL/min
R-H	LIX54 carrier
S	TOPO carrier
V	volume of feed phase, mL

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