An Application of Supported Liquid Membranes for Removal of Inorganic Contaminants from Groundwater

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This review paper summarizes the results of an investigation on the use of supported liquid membranes for the removal of uranium(VI) and some anionic contaminants (technetium(VII), chromium(VI) and nitrates) from the Hanford site groundwater. As a membrane carrier for U(VI), bis(2,4,4-trimethylpentyl)phosphinic acid was selected because of its high selectivity over calcium and magnesium. The water soluble complexing agent 1-hydroxyethane-1,1-diphosphonic acid was used as stripping agent. For the anionic contaminants the long-chain aliphatic amines Primene JM-T (primary), Amberlite LA-2 (secondary) and trilaurylamine (tertiary) were investigated as membrane carriers. Among these amines, Amberlite LA-2 proved to be the most effective carrier for the simultaneous removal of the investigated anion contaminants. A good long-term stability (at least one month) of the liquid membranes was obtained, especially in the uranium(VI) removal.

A supported liquid membrane (SLM) process has been considered, among other possible options, for the removal of contaminants from groundwater, because of the following advantages of SLM's over competing techniques (solvent extraction, ion exchange, polymeric membrane processes, etc.):

1. high concentration factors achieved through a high feed to strip volume ratio
2. low carrier inventory required
3. no phase separation problems
4. negligible organic phase entrainment in the feed and strip aqueous phases (although loss of organic phase due to solubility is still inevitable)
5. simplicity of operation of membrane modules.

These advantages, however, are balanced by typical drawbacks of SLM processes, such as the lack of a scrub stage, which makes more stringent the need of a high

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selectivity, and the lack of long-term stability, which allows for a practical application. With these considerations in mind, we have performed an investigation on the use of SLM's to remove selected contaminants from the Hanford site groundwater, as an application of the basic knowledge previously acquired at the Chemistry Division of Argonne National Laboratory (1-4). The detailed results of this investigation have been the subject of a number of publications (5-8). In the present paper we review the most important results and conclusions.

Groundwater

The detailed analysis of the Hanford groundwater has been reported in ref. (6). In Table I we report the typical concentrations of the species relevant for our investigation.

Table I.   Concentration of Selected Contaminants in Hanford Groundwater

| Contaminant | Concentration | | MCL |
	low	high	(maximum contaminant limit)
nitrate (ppm)	46	1,460	45
chromate (ppb)	51	437	50
^{99}Technetium (pico Ci/L)	906	29,100	900
Uranium (ppb)	8,590		10

SOURCE : Adapted from ref. (7).

To perform our SLM experiments, a synthetic groundwater solution (SGW), simulating the composition of the groundwater from a specific Hanford monitoring well, was prepared using the procedure reported in ref. (5). The composition of the SGW is reported in Table II. The pH of the SGW was adjusted to 2 with H_2SO_4 for reasons that will be discussed later. For distribution and/or permeation experiments, the SGW was spiked with U-233, or Tc-99, or made 10^{-3} M with Na_2CrO_4. From Table II it appears that, apart from sodium, the major cationic constitutents of SGW are calcium and magnesium. Any method devised to remove uranium from the solution, must therefore exhibit a very high selectivity over these two components. Similarly, a good selectivity for nitrates over sulfate-bisulfate species is required.

Table II.   Composition of Synthetic Groundwater at pH 2

Constituent	Molarity
Calcium	0.012
Magnesium	0.0062
Sodium	0.017
Silicon	0.0009
Chloride	0.0016
Sulfate-bisulfate	0.017
Nitrate	0.030
Uranium	0.0004
Sum of Molarities	0.094

Membrane Supports

The liquid membrane supports were used both in flat-sheet and hollow-fiber configurations. In the flat-sheet membrane experiments Celgard or Accurel polypropylene membranes were used, with a thickness ranging from 25 to 100 microns, a pore size from 0.02 to 0.1 microns, and a porosity from 38 to 75%. The hollow-fibers were obtained from Enka. They were also made of propylene, with a porosity of 75%, a pore size of 0.1 microns, a wall thickness of 200 microns (I.D. = 0.6 mm, O.D. = 1 mm). The hollow-fibers were used to fabricate small laboratory scale modules, containing from 4 to 100 fibers about 10 cm long. For the tests with real groundwater discussed in the following, large size (2,600 fibers each 45.5 cm long) commercial Enka modules were used. The technique used to impregnate the supports with the carrier solution in n-dodecane has been described in refs. (5) and (6). All hollow-fiber modules were operated in recirculating mode, with feed and strip solutions flowed through the lumen and the shell side of the fibers, respectively, by calibrated peristaltic pumps. Other experimental details concerning the hydrodynamic conditions used in the flat-sheet and hollow-fiber experiments can be found in (5-8).

Uranium(IV) Removal from Synthetic Groundwater

The challenge of uranium(VI) removal from groundwater consists in finding a compromise between the two somewhat contradictory requirements of high selectivity for U(VI) over Ca(II) and Mg(II) and minimum adjustment of the feed composition. The latter requirement means that neutral and basic extractants (for example, mono- or bi-functional organophosphorus compounds and tertiary amines), showing a high affinity for U(VI), cannot be used as carriers, because they require high concentrations of anions such as nitrate for an effective uranium extraction. Organophosphorous acids, on the other hand, would extract from groundwater at neutral pH not only U(VI) but at least some significant amounts of all other cations with very little selectivity. A compromise solution, suggested by us in (5), was to add sulfuric acid to the groundwater lowering the pH to about 2, where very little Ca and Mg extraction takes place with organophosphorus acids. We thought that this low pH value would not only provide the required selectivity for U(VI) removal, but would also provide the hydrogen ions needed for the subsequent removal of the anionic contaminants in the form of acids by means of a basic carrier in a second membrane module. Of course, at the end of the process, the groundwater should undergo a neutralization step, befoꞋe ᵇeing again pumped under ground.

Among some organophosphorous acids tested as U(VI) carriers from SGW at pH 2, bis(2,4,4-trimethylpentyl)phosphinic acid (H[DTMPeP]), contained in the commercial extractant Cyanex 272, was selected for its superior ability to reject calcium and magnesium. For example, with a 0.1 $\underline{M}$ solution of Cyanex 272 in n-dodecane, it was determined, from distribution experiments, that the selectivity for U(VI) over Ca(II), measured as the ratio of distribution ratios, was ~ 10^9. The next step was to find a suitable stripping agent capable of removing U(VI) from the SLM at the membrane-strip solution interface. The water soluble strong uranium(VI) complexing agent 1-hydroxyethane-1,1-diphosphonic acid, HEDPA, was found to be very effective. The distribution ratio of U(VI) between 0.1 $\underline{M}$ Cyanex 272 in n-dodecane and 0.1 $\underline{M}$ HEDPA in water was measured to be 6×10^{-3}, that is, at least 3 orders of magnitude lower than with a 0.1 $\underline{M}$ solution of oxalic acid. Note here that the use of sodium carbonate, the traditional stripping agent for U(VI) in many solvent extraction studies, produced very short-lived liquid membranes, and, therefore, cannot be considered for the present application. The

detailed description of the equilibria involved in the extraction of U(VI) by Cyanex 272 from SGW, and in its stripping by HEDPA, is reported in (5).

Uranium(VI) Permeation Studies. Figure 1 shows some typical results of permeation experiments, where the decrease of U(VI), Ca(II) and Fe(III) concentration in the feed is reported as function of time. The concentration data fall on straight lines described by the equation

$$\ln \frac{C}{Co} = -\frac{A}{V} P t \tag{1}$$

where C and Co are the feed concentrations of transported species at time t and zero, respectively, A is the membrane area, V is the volume of the feed solution, and P the permeability coefficient (cm s^{-1}).

In the experiments of Figure 1, Fe(III) was also studied because this cation is ubiquitous and therefore its behavior is important even though it is not listed as a constituent in the Hanford site groundwater. Figure 1 shows that when 99% of U(VI) is removed from the SGW, after 2.0 hours, only 0.02% of the calcium follows the uranium. This corresponds to a membrane selectivity for U(VI) over Ca(II) equal to 1.6×10^4 (ratio of permeability coefficients). The data of Figure 1 were obtained with a membrane area equal to 9.8 cm^2 and a feed volume equal to 13 cm^3. For a much higher value of the A/V ratio, as usually provided by industrial hollow-fiber modules, the time required for the same level of uranium separation would be correspondingly shorter, but the relative contamination of uranium with calcium and iron, that depends on the selectivity, would be the same.

Figure 2 shows how the U(VI) permeability coefficients varies with the concentration of the membrane carrier (data obtained with flat-sheet supports). A striking feature of the data is the almost independence of P_U from the carrier concentration over about three orders of magnitude. A membrane initially containing 0.1 $\underline{M}$ Cyanex 272 in dodecane will continue to operate satisfactorily even when 99% of the carrier is lost due to solubility or other causes. The consequence of this result on the long-term membrane stability is evident. The continuous line of Figure 2 has been calculated with equation 2

$$P_U = \frac{D_U}{D_U \Delta_a + \Delta_o} \tag{2}$$

where D_U = distribution ratio of U(VI) between feed and liquid membrane, $\Delta_a = d_a/D_a$ = thickness of aqueous diffusion layer/aqueous diffusion coefficient, cm-s^{-1}, and $\Delta_o = d_o/D_o$ = membrane thickness/membrane diffusion coefficient, cm-s^{-1}. How Equation 2 can be used to calculate the aqueous and organic diffusion coefficients of the U(VI) containing species is discussed in detail in (5).

To demonstrate that high concentration factors of U(VI) can be reached in practice with our SLM system, experiments were performed in which a 2 L solution of SGW was circulated in a module as the feed, while the strip solution (0.1 $\underline{M}$ HEDPA) had a volume of 45 mL. After six hours, uranium had been concentrated by a factor 34 in the strip solution. Much higher concentration factors (at least 10^3) can be achieved, however, by using the same strip solution over and over again. We have demonstrated in (5) that a 0.5 $\underline{M}$ HEDPA stripping solution, containing 0.2 $\underline{M}$ U(VI), is still very effective in stripping uranium from 0.1 $\underline{M}$ Cyanex 272 in n-dodecane.

Removal of Anionic Contaminants from Synthetic Groundwater

After passing through a SLM module, in which the uranium separation has taken place, the pH of the groundwater has not been significantly changed by the UO_2^{2+} - H^+ exchange with the phosphinic acid. As a consequence, the acidic pH of the groundwater can be exploited to remove nitrate, pertechnetate and chromate anions in the form of acids in a second SLM module, containing as carrier a basic molecule capable of reacting with these acids to form membrane soluble salts. After diffusing through the liquid membrane, these salts can be released at the strip side of the membrane, where an alkaline stripping solution (NaOH) ensures that the free carrier is regenerated.

Three commercially available long-chain aliphatic amines, Primene JM-T (primary), Amberlite LA-2 (secondary), and trilaurylamine (TLA, tertiary), were tested as membrane carriers for nitrate, pertechnetate and chromate anions. Long-chain aliphatic amines, dissolved in an organic diluents, are known to extract acids according to the reaction

$$n\,H^+ + A^{n-} + n\,\overline{B} \overset{K}{\rightleftharpoons} \overline{(BH)_nA} \rightleftharpoons \overline{aggregates} \tag{3}$$

where H_nA is a generic acid in the aqueous solution, B is the amine, and the bar represents organic phase species. K is the equilibrium constants that can be taken as a measure of the affinity of the amine for the acid. Table III summarizes the physico-chemical properties of the three amines investigated, of relevance for the choice of the membrane carrier for our specific application.

Table III. Properties of Primene JM-T (I), Amberlite LA-2(II) and TLA(III)

Chemical affinity	for HNO_3	:	$K_I > K_{II} > K_{III}$
	for $HTcO_4$	:	$K_{III} \geq K_{II} > K_I$
	for H_2CrO_4	:	$K_{III} \geq K_{II} > K_I$
Solubility in water		:	$S_I > S_{II} > S_{III}$
Interfacial pressure		:	$\Pi_I > \Pi_{II} > \Pi_{III}$

The detailed determination of the equilibrium constants and of the interfacial behavior of the three amines shown in Table III are reported in refs. (7-8). From the data of Table III it appears that the primary amine would not be a good choice as a carrier because, although a better extractant for HNO_3, it is a relatively poor extractant for the other two acids. Also, its higher solubility in water and its greater lowering of the interfacial tension (higher tendency to emulsion formation) are an indication that SLM containing Primene JM-T would be more unstable. The tertiary amine, on the other hand, showing the lowest solubility in water and the best interfacial behavior, exhibits the lowest affinity for HNO_3. It seems, therefore, that the best compromise among the properties listed in Table III is the choice of Amberlite LA-2 as the membrane carrier.

Anionic Species Permeation Studies. The dependence of the HNO_3 permeability coefficient on the concentration of the three amines in n-dodecane (flat-sheet membrane experiments) is reported in Figure 3. It appears from the data that,

with the primary and secondary amine, the same limiting P value is reached. Amberlite LA-2, however, reaches the limiting value at a much lower concentration and, therefore, following the same reasoning as for the Cyanex 272 case in Figure 2, is a better carrier for nitric acid. The behavior of Primene JM-T, which has a higher equilibrium constant for HNO_3 extraction (see Table III), may be due to its higher solubility in water, or simply may reflect the extreme complexity of the aggregation equilibria in the organic phase. The HNO_3 permeability coefficient with TLA as carrier is always much lower than for the other two amines, except for very low carrier concentrations. This may indicate that a local precipitation of the nitrate-TLA salt takes place in the pores of the membrane, reducing the speed of permeation.

In the groundwater acidified at pH 2 with sulfuric acid, sulfate and bisulfate anions are present. By using an amine as the carrier in a SLM system, it is important to know what fraction of the total H^+ is transported by the liquid membrane as HNO_3, because we are interested in removing nitrates, not sulfates, from the groundwater. For this purpose a number of experiments were performed where a pH electrode and a nitrate electrode were used to follow the decrease of acidity and of nitrates in the acidified SGW used as the feed. A detailed discussion of the results is reported in (7). Here it is important only to mention that the removal of nitrates, with all three amines, followed quite closely the removal of total acid. With 0.6 $\underline{M}$ Amberlite LA-2 as carrier, for example, when 90% of H^+ was removed, about 75% of the removable nitrate ions had left the feed. This result allowed us to conclude that H^+ is removed from the SGW mainly as nitric acid and that amine based SLMs are effective in removing nitrates from SGW even in the presence of large quantities of sulfate-bisulfate anions.

Membrane experiments showed that the efficiency of the three amines as carriers for Tc(VII) parallels the sequence of equilibrium constants reported in Table III. That is, secondary and tertiary amines are better at removing Tc(VII) than primary amines.

An unexpected result was found investigating the Cr(VI) removal by the three amines. Contrary to the sequence of Table III, the use of TLA as carrier led to a very low value of the Cr(VI) permeability coefficient, even lower than with Primene JM-T. This result is probably a further indication of the poor solubility of TLA salts (in this case chromate) in n-dodecane.

In conclusion, the permeation behavior of the anionic contaminants under study through SLMs containing either one of the amines investigated, confirms that the carrier of choice for the simultaneous removal of nitrates, Tc(VII) and Cr(VI) is the secondary amine Amberlite LA-2.

Tests with Real Groundwater

Some tests with 50 gallons samples of groundwater from a specific monitoring well were performed at Hanford using two 2.2 m^2 internal surface area commercial hollow-fiber modules in series, containing a 0.1 $\underline{M}$ Cyanex 272 and a 0.1 $\underline{M}$ Primene JM-T solution in n-dodecane, respectively, as liquid membranes. The stripping solutions were 4 gallons of 0.1 $\underline{M}$ HEDPA for the first module, and 4 gallons of 0.1 $\underline{M}$ NaOH for the second one. Other experimental details are reported in (6). The result of a typical test are sumarized in Table IV.

The results show that the two modules were very effective in reducing the U(VI) and Tc(VII) concentrations by about three and two orders of magnitude, respectively. The limited success with NO_3^- is due to the fact that these tests were performed before the final choice of the best carrier for nitrates was made. The use of a 0.2 $\underline{M}$ Amberlite LA-II solution as liquid membrane in the second module would have led to much better results for the removal of nitrates.

Table IV. Results of Tests with Real Groundwater

Time (hours)	First Module Feed U(VI)(ppb)	Second Module Feed NO₃ (ppm)	Second Module Feed Tc(VII)(pCi/L)
0	3,460	38.5	786
4	257	37	361
8	30	31	139
12	7.3	24.7	51
16	2.1	20.9	18
20	1.4	18.1	9
24	—	15.3	8
36	—	10.2	4
48	—	5.2	2

Flowrates: 1.5 gal/min, shell side, feed; 1.0 gal/min, lumen side, strip.

Liquid Membrane Stability

To test the ability of our liquid membrane system to continuously operate at high efficiency, stability tests were performed. They are described in detail in ref. (6) for the uranium removal from groundwater and in ref. (8) for the removal of the anionic contaminants. Some results are shown in Figure 4, as uranium permeability vs. time (a constant permeability was the criterion for stability), for two modules that were operated without interruption (except nights and weekends) for very long times. An excellent stability, that is constant uranium permeability, was shown by the module with reservoir (it contained a small reservoir of carrier solution ensuring a continuous reimpregnation of the membrane pores). The stability test with this module was interrupted after six months because of the deterioration of the reservoir seal. However, it worked long enough to demonstrate that a properly designed self-reimpregnating module can operate for a practically unlimited time. The conventional module (without reservoir) was periodically reimpregnated with the carrier solution, when the initial permeability of uranium had declined by about 50%. The procedure was repeated seven times over a time span of almost 1.5 years. The results reported in Figure 4 show that periodic reimpregnations of the hollow-fibers are also a viable technique to have modules operating efficiently for long times. It is interesting to note that the reimpregnation procedure, described in detail in (6), while not affecting the stability of the membrane, had a postive effect on the module performance, measured by the uranium permeability, which improved substantially and progressively after each of the first three reimpregnations. Different strip solutions were used after the last two reimpregnations. In one case a 1 M (instead, of 0.1 M) HEDPA solution was used to see if a much higher osmotic pressure difference between feed and strip solution would affect the stability, in the other case a different stripping agent, a derivative of HEDPA, was tested.

Stability tests were also performed with liquid membranes containing each of the three amines investigated as carrier for anions. In the experiments involving liquid membranes adsorbed on flat-sheet supports having a thickness of only 25 microns, the order of stability tertiary > secondary > primary was measured. This is the reverse order of amine solubility in water and of the interfacial lowering at a water-dodecane interface. Both factors, solubility and interfacial tension, seem to be operative in determining the liquid membrane stability, together with the other usual factors, such as support materials, pore size, osmotic pressure gradient and flow rate, which have been kept constant in this work. An impressively high stability was measured in the experiments with flat-sheet membranes, when TLA was the carrier. We think that the high stability of the TLA-dodecane liquid

membrane is due to the low solubility of the amine salts in the membrane diluent. The formation of a solid or gelatinous phase in the membrane pores, while having a detrimental effect on the permeation speed, may have a positive effect on the membrane life, by preventing the formation of emulsion with the aqueous phase and by acting as a barrier against water bridging in the membrane pores.

Stability tests were also performed using modules containing hollow-fibers with a much higher wall thickness (200 microns). Because of the much larger inventory of organic phase contained in the pores of the fibers, a complete failure of the membrane over a time span of about 1 month was not observed for any of the three amines, although the initial flux of HNO_3 through the membranes was significantly reduced, especially with the primary amine. Also from a stability standpoint, however, the secondary amine Amberlite LA-2 exhibited the best performance, loosing only 40% of the initial HNO_3 flux after 40 days of continuous operation.

In conclusion, the stability tests performed with hollow-fiber modules containing as liquid membranes n-dodecane solutions of either Cyanex 272 (carrier for uranium(VI)) or Amberlite LA-2 (carrier for anionic contaminants) have shown that a relatively long membrane life, of the order of at least one month, can be expected in the processing of contaminated groundwater. After one month, or more, of continuous operation, the modules can be easily reimpregnated without loosing their separation efficiency. Alternatively, self-reimpregnating modules seem capable of operating without problems for much longer times.

Conclusions

The experiments reported in ref. (5-8) have shown that a few options are available for selecting a supported liquid membrane process for the removal of U(VI), Cr(VI), Tc(VII) and nitrate ions from acidified groundwater. The first option involves the use of two modules in series: the first one, containing the extractant Cyanex 272 as carrier, removes uranium, while the second one, containing the long-chain aliphatic secondary amine Amberlite LA-2 as carrier, removes the anionic contaminants. We have demonstrated that this system is highly effective in achieving the desired decontamination and that membrane lives of at least one month of continuous operation can be expected (much longer membrane lives can be obtained using the somewhat more complicated self-reimpregnating modules).

An alternative option could be the use of the tertiary amine TLA as the carrier in the second module, because of the higher stability of TLA-based liquid membranes. In this case the benefit of less frequent module reimpregnations would compensate for the lower effectiveness of TLA in removing nitrates. The TLA alternative appears especially attractive if used in a combined process where the nitrate removal from groundwater is achieved mainly by other means (for example, biological).

A third alternative, which probably deserves more investigation, is the use of a single membrane module, instead of two in series, containing the primary amine Primene JM-T as carrier. This compound has the unique property of removing from groundwater acidified with sulfuric acid not only the anionic contaminants, but also U(VI) in the form of anionic sulfato-complexes (7). In this way all the unwanted contaminants would be removed in the same module, making the process simpler. The advantage of using one single module, however, would be counteracted by the need for more frequent reimpregnations, because of the shorter lifetime of the Primene JM-T based membrane, unless a self-reimpregnating module is used.

We think that all three options discussed above can be realized in practice. The choice among them should be based mainly on economic and engineering considerations.

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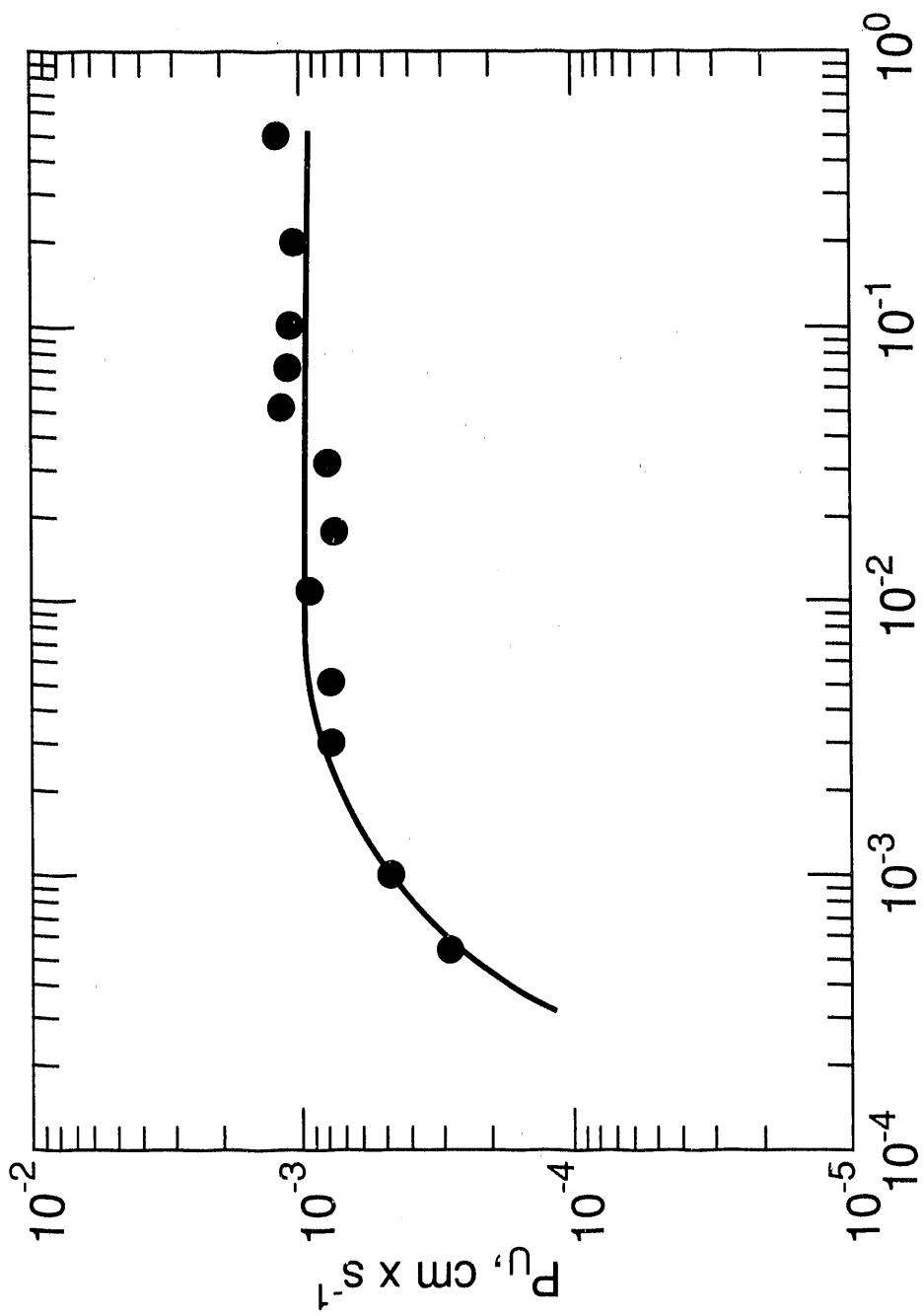8. Chiarizia, R.; *J. Memb. Sci.*, **1991**, *55*, 65.

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Figure 1. U(VI), Ca(II) and Fe(III) removal from SGW at pH 2. Liquid membrane = 0.1 $\underline{M}$ Cyanex 272 in n-dodecane; Strip = 0.1 $\underline{M}$ HEDPA; membrane area (hollow-fibers) = 9.8 cm^2; feed volume = 13 cm^3; feed linear velocity = 8.0 cm s^{-1}.

Figure 2. Permeability coefficient of U(VI) vs. carrier concentration. Feed = SGW at pH 2. Membrane: Cyanex 272 in n-dodecane on flat-sheet support; Strip = 0.1 $\underline{M}$ HEDPA. (Reproduced with permission from ref. (5). Copyright 1990 M. Dekker, Inc.)
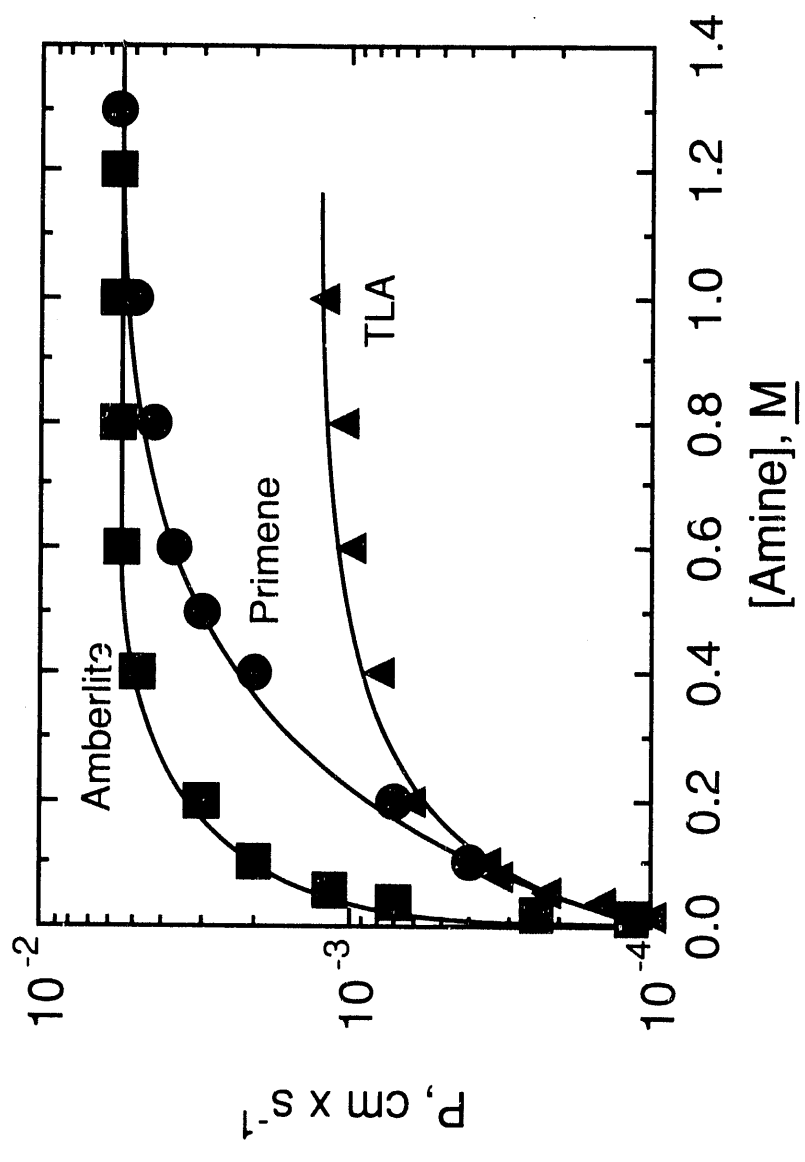
Figure 3. Permeability coefficient of HNO_3 vs. carrier concentration in n-dodecane. Feed = 10^{-2} $\underline{M}$ HNO_3; Membrane = flat-sheet support; Strip = 0.1 $\underline{M}$ NaOH. (Reproduced with permission from ref. (7). Copyright 1991 Elsevier Science Publishers B.V.)
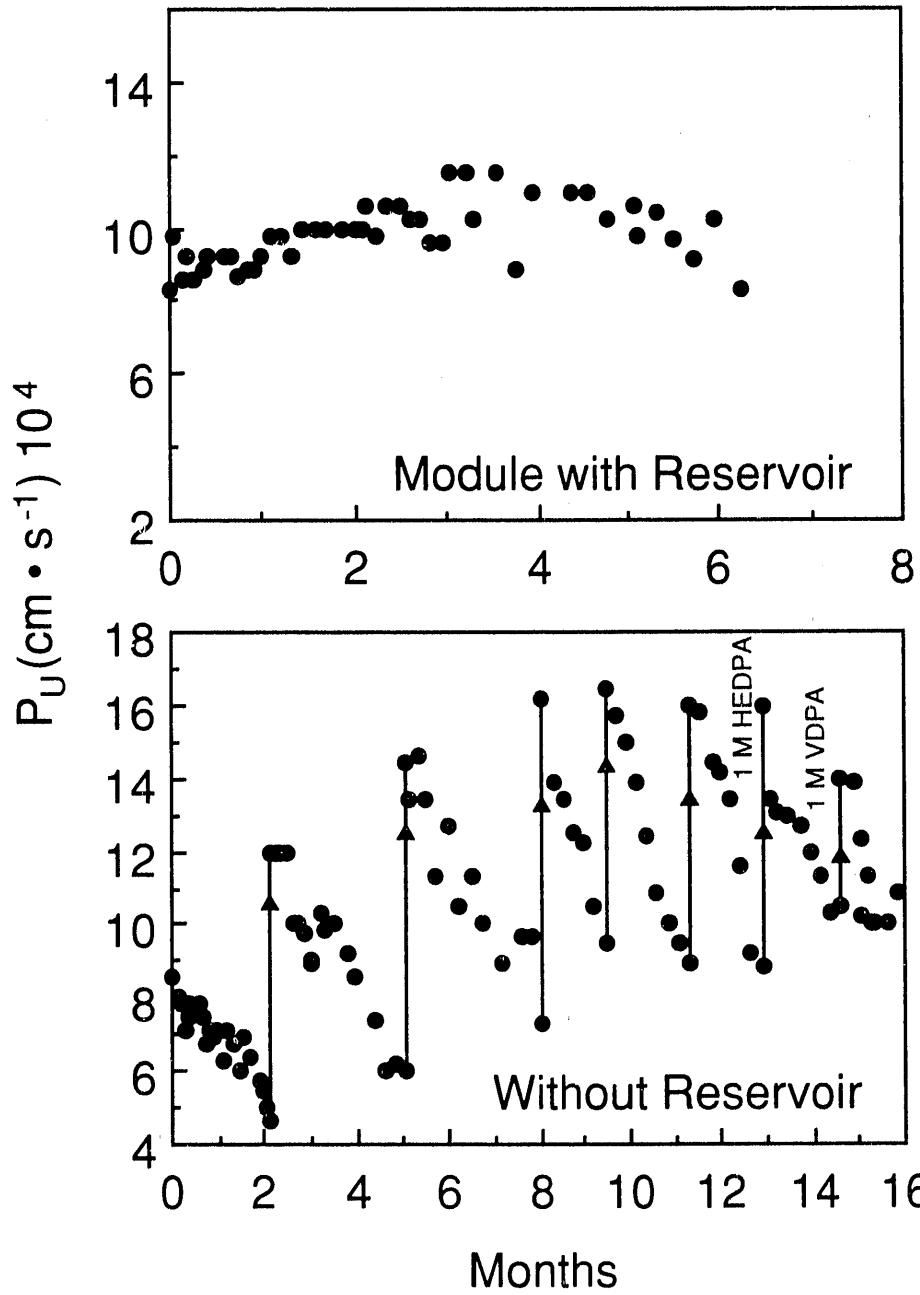
Figure 4. Permeability coefficient of U(VI) vs. time for a module with reservoir and a conventional module. Feed = SGW at pH 2, 10 mL, replaced daily; Membrane = 0.1 $\underline{M}$ Cyanex 272 in n-dodecane on hollow-fibers; Strip = 0.1 $\underline{M}$ HEDPA, 16 mL, replaced monthly. (Reproduced with permission from ref. (6). Copyright 1991 M. Dekker, Inc.)

P, cm x s⁻¹ vs [Amine], M. Curves labeled Amberlite, Primene, and TLA.

$P_U(cm \cdot s^{-1}) \, 10^4$

Module with Reservoir

1 M HEDPA

1 M VDPA

Without Reservoir

Months

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