Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Molinari, Raffaele , Drioli, Enrico and Pantano, Giuseppe(1989) 'Stability and Effect of Diluents in Supported Liquid Membranes for Cr(III), Cr(VI), and Cd(II) Recovery', Separation Science and Technology, 24: 12, 1015 — 1032
To link to this Article: DOI: 10.1080/01496398908049886
URL: http://dx.doi.org/10.1080/01496398908049886

SEPARATION SCIENCE AND TECHNOLOGY, 24(12 & 13), pp. 1015-1032, 1989

Stability and Effect of Diluents in Supported Liquid Membranes for Cr(III), Cr(VI), and Cd(II) Recovery*

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Abstract

Some results obtained with the aim of optimizing the permeation fluxes, separation factors, and stability of SLM's are described. A flat sheet polypropylene membrane was used in all the experiments. The ions on which the SLM's were tested were Cr(III), Cr(VI), and Cd(II). The carriers were dinonylnaphthalene sulfonic acid (DNNSA), Aliquat 336, and Alamine 336. The diluents were *o*-xylene, kerosene, *n*-heptane, and their mixtures. Among the various mixtures tested for membrane impregnation, a maximum separation factor of 15.0 by using the SLM 50% v/v DNNSA + 25% v/v *o*-xylene + 25% v/v kerosene was obtained. The stability of this membrane was greater than 70 hours of continuous operation. The effect of temperature in the 25-35°C range was also investigated.

INTRODUCTION

The requirement for a world with minimum pollution has brought about the need for clean technologies in industrial production. A way to accomplish this could be the recovery and recycling of substances not

*Part of this work was presented at the 2nd Annual National Meeting of the NAMS, Syracuse, New York, June 1-3, 1988.

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used in industrial cycles. As an alternative to conventional unit operations, processes using supported liquid membranes (SLM's) could become very competitive when the species used for separation and concentration are ions in aqueous solutions (*1–10*).

A SLM is expected to be one of the most efficient membranes for separation processes since facilitated transport is more effective than passive transport. Also, they have a great potential for low cost and energy savings. High permeability and high selectivity can be attained through selective enhancement of the permeant fluid induced by a reversible reaction with a carrier species contained in the membrane matrix. This type of transport has been experimentally successful in the hydrometallurgical field for the recovery and separation of metal ions (*11–13*).

A supported liquid membrane in general is made with a solution of a specific carrier in a diluent medium adsorbed in a microporous polymer (e.g., hydrophobic polypropylene). The diluent is required to be immiscible with the solutions on the two sides of the membrane.

The transport of chemical species through the SLM (*14–18*) occurs when a chemical potential gradient is established between the feed and strip solutions. The chemical gradient is generated from the concentration difference of the chemical species which influences the chemical equilibrium of extraction and stripping at the feed side and strip side of the membrane interfaces, respectively.

Variously configurated membrane supports are available: plate and frame, spiral, tubular, and hollow fibers.

Hollow fiber supported liquid membranes are a very attractive solution to the need for membrane modules with very high throughputs and modules packaging densities as high as 1000 m^2/m^3. Another interesting geometry could be the spiral-type module, since a packaging density close to that of the hollow fiber modules can be reached if the thickness of the spacer is 1 mm (*19*).

Important parameters in the use of SLM's on an industrial scale are the stability, lifetime, and facility of regeneration. Those problems have been studied in terms of the leakage of water across the membrane under an applied hydrostatic pressure difference (*20*), in terms of volume and salt flow under an applied osmotic gradient and no hydrostatic pressure (*21*), and in terms of the initial flux (*10*) or feed concentration in the outlet (*19*) under normal operative conditions.

Stable SLM's can be obtained by selecting the solid support and the membrane solvent while taking into account the force holding the solvent within the pores of the support itself.

Referring to the solvent, it seems that aliphatic hydrocarbons with a high boiling point give a long lifetime of a SLM compared to aromatic hydrocarbons. On the other hand, stability is not the only parameter to be considered, since the industrial application of SLM's also depends on the membrane surface area needed for certain applications. In fact, the minimization of capital and operational costs is related to a small membrane surface area, something that can be attained by using SLM's with good stability, low diffusional resistences (high fluxes), and high separation factors. A mathematical model taking into account the solubility and the viscosity effect on the transport of metals across SLM's has also been reported in the literature (*22*, *23*).

In the present paper some experimental aspects of stability and membrane regeneration, transmembrane ion flux, and separation factor by using flat sheet SLM's are described. The examples reported concern the separation and concentration of Cr(III), Cr(VI), and Cd(II) ions from aqueous solutions using dinonylnaphthalene sulfonic acid (DNNSA), Aliquat 336, and Alamine 336 as carriers. Three types of diluents, *o*-xylene (aromatic), kerosene (industrial mixture), and *n*-heptane (aliphatic), or their mixtures, have been used. The temperature effect in the 25–35°C range has been also studied.

EXPERIMENTAL

Materials

The extractants used in this study as carriers were dinonylnaphthalene sulfonic acid (DNNSA) for Cr(III), Aliquat 336 for Cr(VI), and Alamine 336 for Cd(II). The first extractant is commercially available from Alpha Products, the other two from Henkel Corporation.

K_2CrO_4, $CrK(SO_4)_2 \cdot 12H_2O$ and $CdCl_2$ were used for the preparation of aqueous feed solutions of Cr(VI), Cr(III), and Cd(II), respectively.

Other chemicals used were HCl, NaOH, H_2SO_4, NaCl, CH_3COONa, NH_4Cl, and CH_3COOH. All were analytical purity grade reagents.

The polymeric flat sheet support used in all the experiments was a microporous hydrophobic polypropylene membrane Accurel (Enka A.G.) of nominal porosity 70%, 150 μm thick, and of 0.2 μm pore size.

Methods

The organic solution used as the liquid membrane was prepared by mixing the carrier, in an appropriate ratio, with a water-immiscible low dielectric constant organic diluent. The SLM was prepared by simple imbibition dipping of the flat sheet membrane into the organic solution for about half an hour or an hour.

The experiments were carried out by assembling the flat sheet SLM in a two compartment cell. The membrane surface was 21 cm^2 and the volume of the aqueous solution in each compartment was 0.110 dm^3. The cell was immersed in a thermostatic water bath and maintained at the chosen temperature.

The solutions were mechanically stirred by using a glass impeller equipped with motors and speed regulators.

An Orion combined electrode was used in all the experiments for measuring the pH of the feed and strip solutions and, if necessary, to correct them to a constant pH value by the addition of highly concentrated basic or acidic solutions.

A Perkin-Elmer 380 Atomic Absorption Spectrophotometer was used to measure the concentrations of Cr(III), Cr(VI), and Cd(II) in the feed and strip solutions.

The initial flux J_0 was evaluated from the C–t curves by using the equation

$$J_0 = (dC/dt)_0(V_f/A)$$

where $(dC/dt)_0$ is the slope at $t = 0$, V_f is the volume of the feed solution, and A is the membrane permeation surface area.

Results and Discussion

From previous experiments (*10*, *18*, *24*) the chemical conditions for extractions of Cr(VI), Cr(III), and Cd(II) were found.

The extraction (or stripping) of Cr(VI), as the CrO_4^{2-} anion, from aqueous solutions can be accomplished by using Aliquat 336 as the carrier and a low (or high) concentration of chloride ion according to the following stoichiometric interfacial equilibrium equation for the feed side and the strip side:

$$2R_3CH_3NCl + CrO_4^{2-} \underset{\text{stripping}}{\overset{\text{extraction}}{\rightleftharpoons}} (R_3CH_3N)2CrO_4 + 2Cl^- \qquad (1)$$

The extraction (or stripping) of Cr(III) and Cd(II) can be accomplished by using the acidic extractants DNNSA and Alamine 336 as carriers, respectively, and a low (or high) concentration of H^+ ion at the interfaces according to the general following stoichiometric equation:

$$C^{n+} + nHX \underset{\text{stripping}}{\overset{\text{extraction}}{\rightleftharpoons}} CX_n + nH^+ \quad (2)$$

The transport mechanisms of both Eqs. (1) and (2) are referred to as countercoupled transport because the chemical species which influence the chemical equilibrium of extraction and stripping move inversely on opposite sides of the membrane.

In previous experiments on Cr(III) (*10*, *18*), comparison of the initial flux through a SLM made with a mixture of DNNSA + *o*-xylene (50% v/v) and one made with a mixture of DNNSA + kerosene (50% v/v) showed a greater flux for the SLM made with *o*-xylene as diluent. Moreover, a maximum initial permeation flux was observed when the pH difference between the feed and strip solutions was greater than 4, so 0–0.5 was selected as the pH value for the strip and 4.2–4.5 was selected as the pH value for the feed. This was done because Cr^{3+} precipitates as $Cr(OH)_3$ at a pH value of about 4.8.

Those chemical conditions and a Cr(III) concentration in the feed of 4.1 g/L, close to what is present in some industrial wastewaters, were used, with the SLM made by impregnating the polymer into the DNNSA + *o*-xylene solution. The experiments, all run for more than 6 days, always gave an initial fast decrease in the time for chromium concentration in the feed compartment, followed by a small decrease of chromium concentration with time until 50% of the initial concentration was reached (Fig. 1).

In Fig. 1 the complete absence of ion transport against the gradient of the same ion is attributed to degradation of the SLM due to the loss of the liquid membrane solution from the membrane pores.

There are various causes for the degradation or the diminution of the stability (or lifetime) of a SLM; for example, the hydrostatic pressure gradient (*20*), the osmotic pressure gradient (*21*), etc. The stability probably depends on the capillary forces that hold the organic membrane solvent within the pores, as implied by the Young-Dupré equation:

$$P_c = (2\gamma/a) \cos \theta$$

where P_c is the capillary pressure, γ is the solvent-water interfacial tension, a is the membrane pore size, and θ is the contact angle.

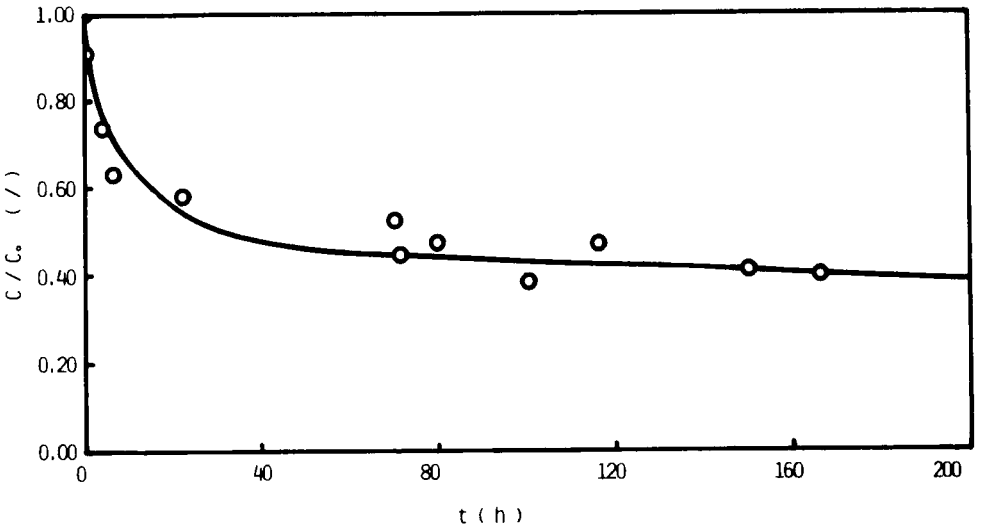

FIG. 1. Decrease of the feed concentration with time while using *o*-xylene as the diluent. Feed: $[Cr^{3+}]$ = 4.1 g/L, pH = 4.2. Strip: 1 *N* H_2SO_4, pH = 0. SLM: 50% DNNSA + 50% *o*-xylene. T = 25°C.

Aromatic solvents are reported in the literature (*20*) to have lower interfacial tension than aliphatic hydrocarbons, and this could explain the fast degradation of the SLM made by using *o*-xylene as the solvent. Figure 2 shows the results of using kerosene as diluent of DNNSA for transport through the SLM. Furthermore, by replacing the solution in the feed side by fresh feed solution when its value is about 20% of the initial concentration, 22 days of operation were possible with a further increase of the concentration in the strip until a value about 1.5 times the initial feed concentration was reached. It can also be observed that a decrease of the feed concentration in the two sequential runs is practically independent of the increasing strip concentration.

Figures 3 and 4 compare the stability of the SLM DNNSA + *o*-xylene and of the SLM DNNSA + kerosene, respectively, when used in continuous operation. Figure 3 shows a loss of about 50% of the initial flux of the SLM DNNSA + *o*-xylene after 120 h of continuous operation. The SLM DNNSA + kerosene, however, practically keeps its initial flux after 96 h of continuous operation and, looking at Fig. 2, the stability can be extended to at least a period of 22 days.

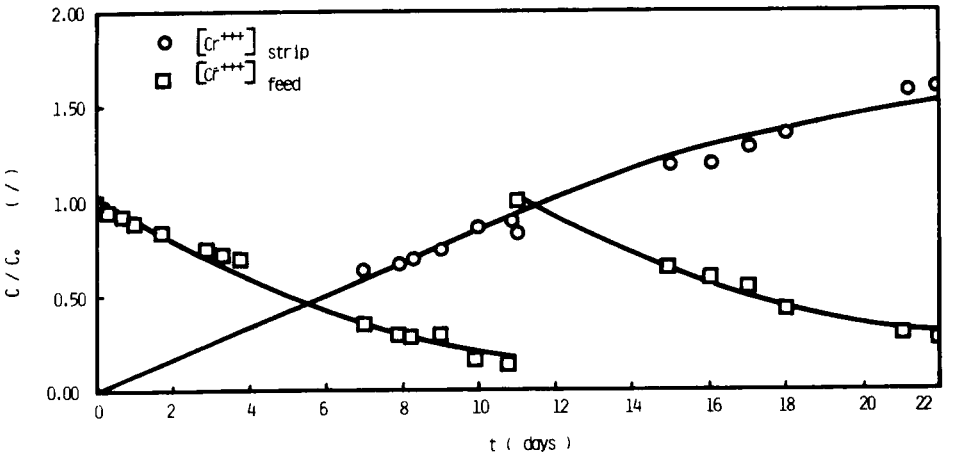

FIG. 2. Decrease of the feed concentration (□) and increase of the strip concentration (○) with time while using kerosene as the diluent in two sequential runs. Feed: $[Cr^{3+}]$ = 4.1 g/L, pH = 4.2. Strip: 1 *N* H_2SO_4, pH = 0. SLM: 50% DNNSA + 50% kerosene. T = 25°C.

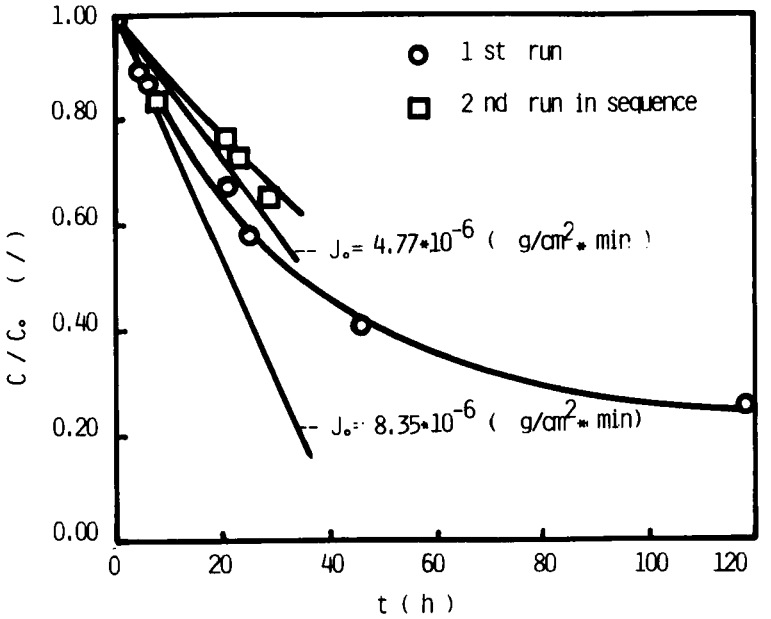

FIG. 3. Test of the initial flux of the SLM in which *o*-xylene was used as the diluent in two sequential runs. Feed: $[Cr^{3+}]$ = 4.1 g/L, pH = 4.2. Strip: 1 *N* H_2SO_4, pH = 0. SLM: 50% DNNSA + 50% *o*-xylene. T = 25°C.

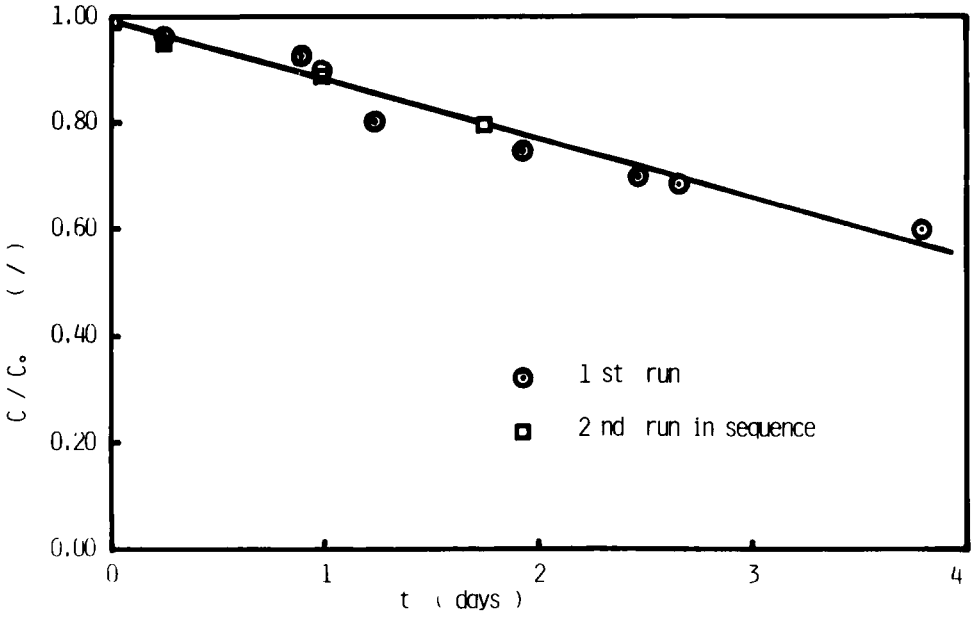

FIG. 4. Test of the initial flux of the SLM in which kerosene was used as the diluent in two sequential runs. Feed: $[Cr^{3+}]$ = 4.1 g/L, pH = 4.2. Strip: 1 N H_2SO_4, pH = 0. SLM: 50% v/v DNNSA + 50% v/v kerosene. T = 25°C.

In contrast to the good stability, the SLM DNNSA + kerosene gave an initial flux about 5 times lower than the SLM DNNSA + *o*-xylene. This behavior probably occurs because the viscosity of kerosene is greater than that of *o*-xylene, and therefore the diffusion coefficient in the membrane (estimated from the Stokes-Einstein equation, $D = kT/6\pi r\mu$, where k is the Boltzmann constant, T is the absolute temperature, r is the molecular radius of the diffusing species, and μ is the viscosity of the organic phase) decreases with an increase of the viscosity of the diluent.

In order to investigate the conditions needed for a SLM with long stability and high diffusion coefficients, we tested some diluents and their mixtures.

In Fig. 5 a comparison is made of the initial fluxes at various feed concentrations of the diluents *o*-xylene, kerosene, *n*-heptane, and kerosene + *o*-xylene. The initial fluxes were obtained by calculating the slope at $t = 0$ from a series of experiments as reported, for example, in Fig. 6.

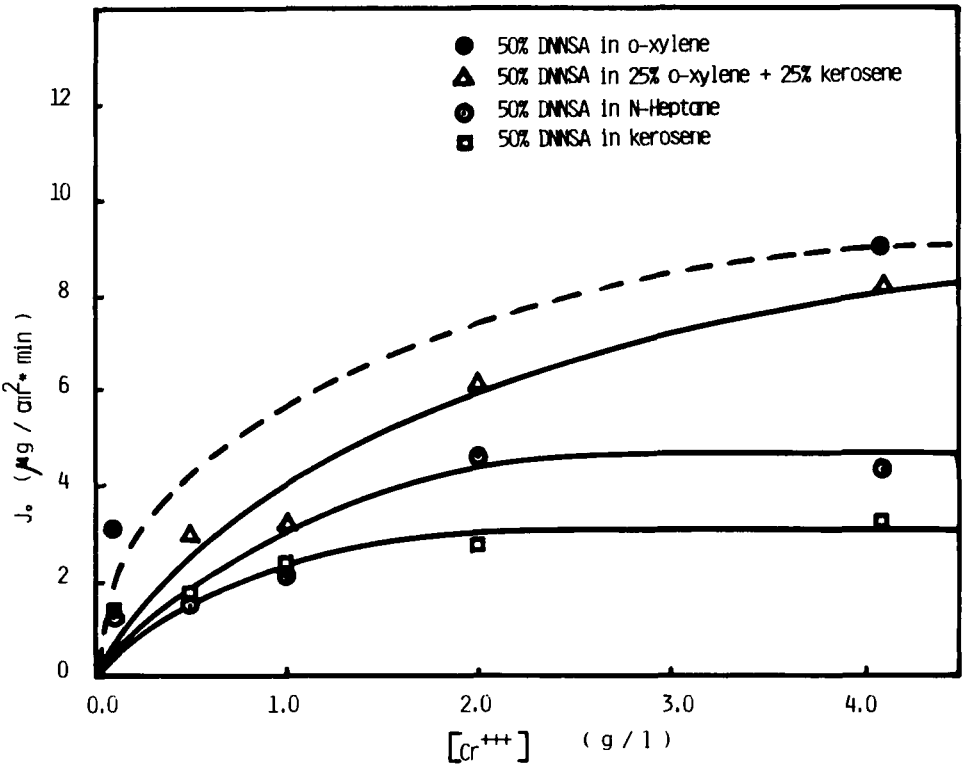

FIG. 5. Initial flux vs chromium concentration while using various solvents as the diluents. Feed: $[Cr^{3+}]$ = 0.0–4.1 g/L, pH = 4.2. Strip: 1 *N* H_2SO_4, pH = 0. T = 25°C.

From Fig. 5 it can be seen that by using the mixture *o*-xylene + kerosene as the diluent, the initial chromium flux is about 2.5 times greater than when kerosene is used alone, and it is very close to what was obtained with *o*-xylene as the diluent. These results mean that by changing the physicochemical characteristics of the solvent, an SLM with simultaneous good ion flux and good stability can be obtained, as reported in Fig. 7. In fact, a significant improvement in the effectiveness of the SLM DNNSA + *o*-xylene + kerosene is seen with respect to the SLM DNNSA + kerosene, reported in Fig. 2.

The separation factor (ratio between the concentration of an ion in the strip and the concentration of the same ion in the feed at the same time) is greater than 15.0 after 70 h of operation in Fig. 7 and 5.1 after 22 days of

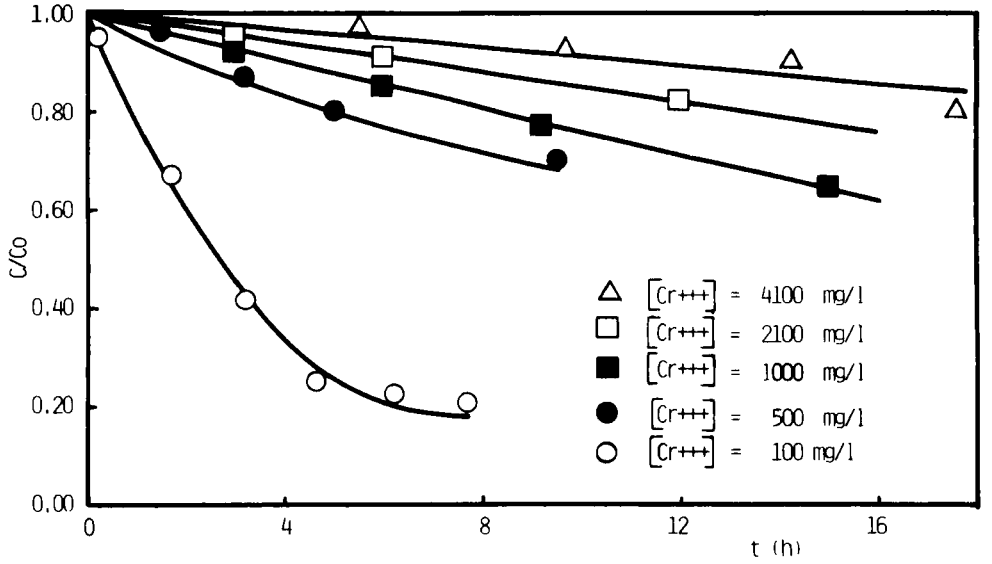

FIG. 6. Decrease of the feed concentration with time while varying the chromium concentration in the feed. Feed: $[Cr^{3+}]$ = 0.1–4.1 g/L, pH = 4.2. Strip: 1 *N* H_2SO_4, pH = 0. SLM: 50% v/v DNNSA + 50% v/v kerosene. T = 25°C.

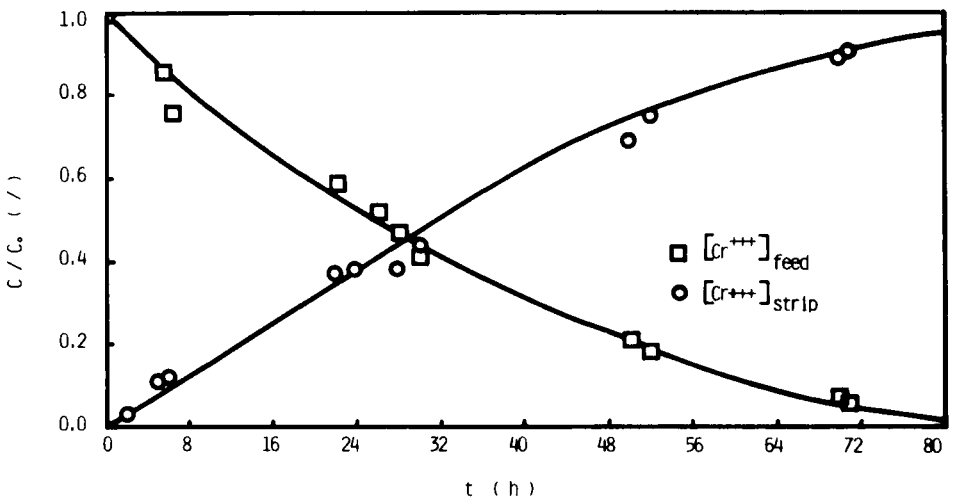

FIG. 7. Decrease of the feed concentration (□) and increase of the strip concentration (○) with time while using *o*-xylene + kerosene as the diluent. Feed: $[Cr^{3+}]$ = 2.0 g/L, pH = 4.2. Strip: 1 *N* H_2SO_4, pH = 0. SLM: 50% DNNSA + 25% *o*-xylene + 25% kerosene. T = 25°C.

operation in Fig. 2. Also, the presence of active transport after 70 h means that the stability of the SLM DNNSA + *o*-xylene + kerosene is greater than 70 h.

The trend of the C/C_0 vs t curves in Fig. 7, and similar figures, is a consequence of the diminution of the feed concentration due to transport through the SLM. This behavior is typical if we remember that it is the chemical equilibrium reactions at the membrane interface which influence how well an SLM works: decreasing the feed concentration decreases the concentration of the complex carrier-metal into the liquid membrane, so that the diffusive transport is decreased; at the same time, increasing the concentration of the ion of interest in the strip solution decreases the rate of the decomplexation reaction and therefore the complexive flux decrease.

Figure 8 illustrates this last effect for Cd(II) separation and concentration by using alamine in the diluents *o*-xylene and kerosene. These experiments were performed by utilizing strip solutions with Cd con-

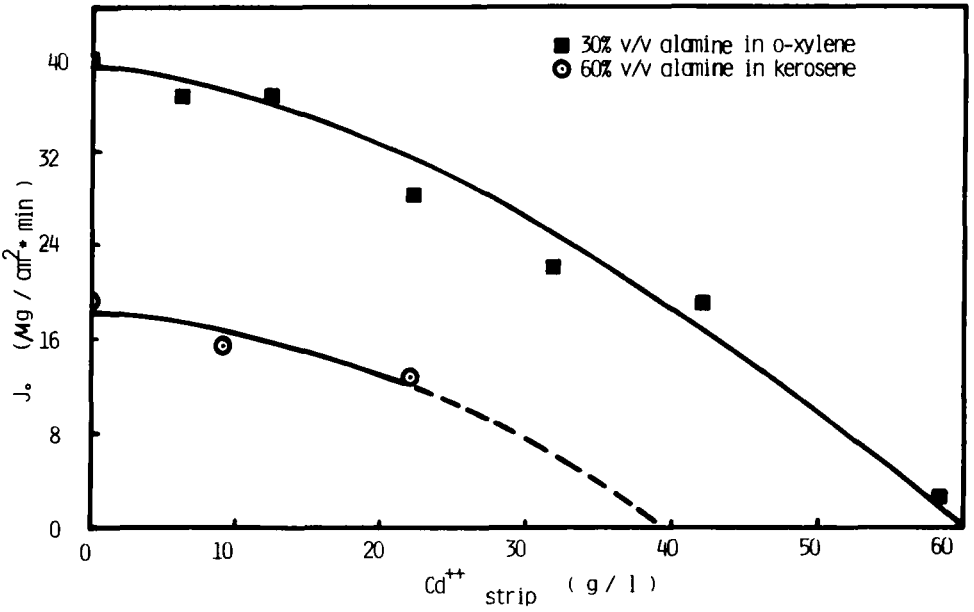

FIG. 8. Influence of the permeating ion concentration in the strip solution on the initial permeation flux. Feed: $[Cd^{2+}]$ = 0.5 g/L, [NaCl] = 1 *M*, pH = 1. Strip: $[Cd^{2+}]$ = 0–58 g/L, $[CH_3COONa + NH_4Cl]$ = 0.5–0.25 *M*, pH = 7. SLM: Alamine in *o*-xylene (30% v/v) and Alamine in kerosene (60% v/v). T = 25°C.

centration variable in the 0–60 g/L range and the feed solution at a constant initial concentration of 0.5 g/L in each run. The initial flux was calculated by following the decrease of the Cd^{2+} concentration in the feed side. In this figure there again appears a higher flux when using *o*-xylene with respect to kerosene and also a maximum concentration of cadmium in the strip solution of 40 or 80 g/L, corresponding to zero flux.

A comparison of chemical stability among different SLM's can be made by looking at Figs. 3, 4, 9, and 10. Figures 3 and 9 show a significant decrease of the initial flux, J_0, when using *o*-xylene as the diluent.

A different behavior is observed when kerosene is used as the diluent (Figs. 4, 9, and 10). There is practically no appreciable degradation of the SLM DNNSA + kerosene (Fig. 4), a sensible degradation of the SLM alamine + kerosene (Fig. 9), and very little degradation of the SLM

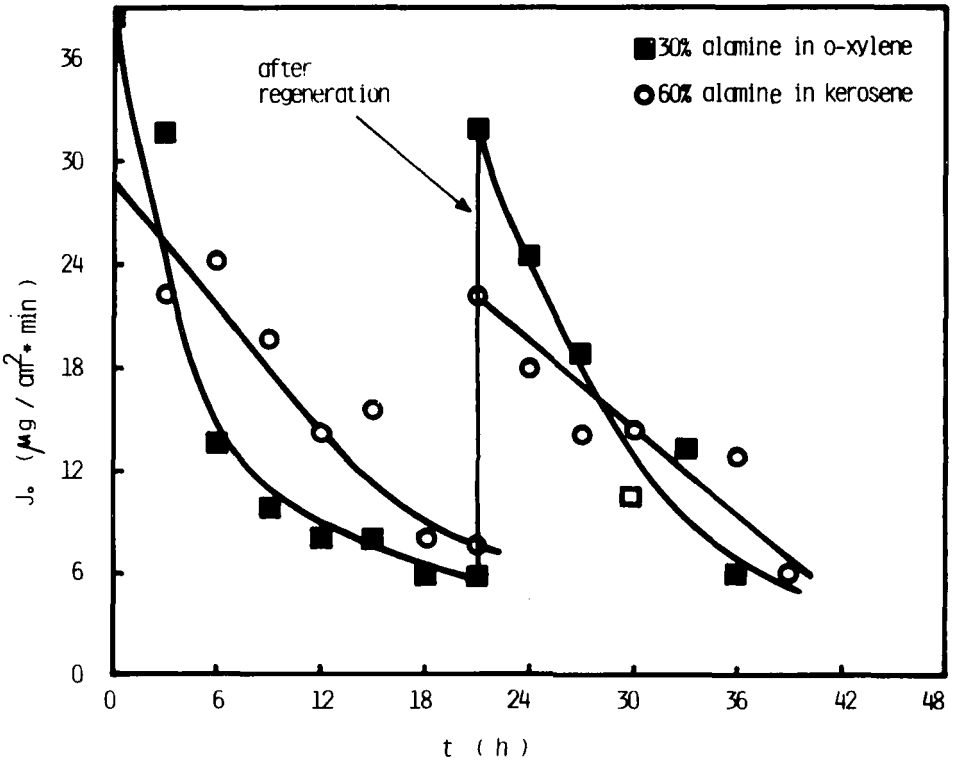

FIG. 9. Behavior of the initial flux as a function of the operating time of the SLM. Feed: $[Cd^{2+}]$ = 0.5 g/L, [NaCl] = 1 *M*, pH = 1. Strip: $[CH_3COONa + NH_4Cl]$ = 0.5 *M*, pH = 7. SLM: Alamine in *o*-xylene (30% v/v) and Alamine in kerosene (60% v/v). T = 25°C.

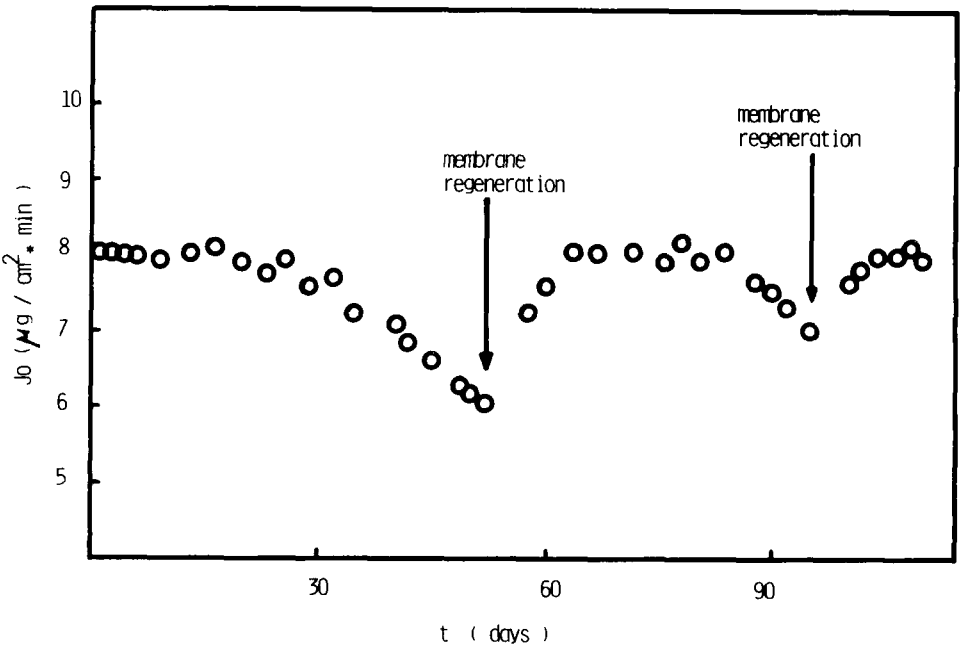

FIG. 10. Behavior of the initial flux as a function of the operating time of the SLM. Feed: $[CrO_4^{2-}]$ = 0.1 g/L. Strip: [LiCl] = 4 *M*. SLM: Aliquat in kerosene (25% v/v). T = 25°C.

aliquat + kerosene (Fig. 10). These differences can probably be attributed to changes in the chemical-physical characteristics of the liquid membrane mixtures, so the stability of each SLM is dependent on the carrier-solvent mixture used on the same polymer.

In order to verify the chemical resistence of the polypropylene membrane to the solvent *o*-xylene, an experiment was carried out on the flat sheet membrane used as the SLM support. An SLM membrane alamine + *o*-xylene was periodically tested in the permeation cell for a total time of more than a month. At the end of each test the SLM was washed with *o*-xylene and the support was stored in *o*-xylene. Figure 11 shows no influence of the solvent on the polymer because the metal permeation flux remain practically constant for the entire period.

Another parameter investigated was the effect of temperature in the 25–35°C range. As can be seen in Fig. 12, a rise of temperature increases the initial flux, probably due to the fast kinetics of the complexation and decomplexation reactions at the interfaces and the lower diffusional

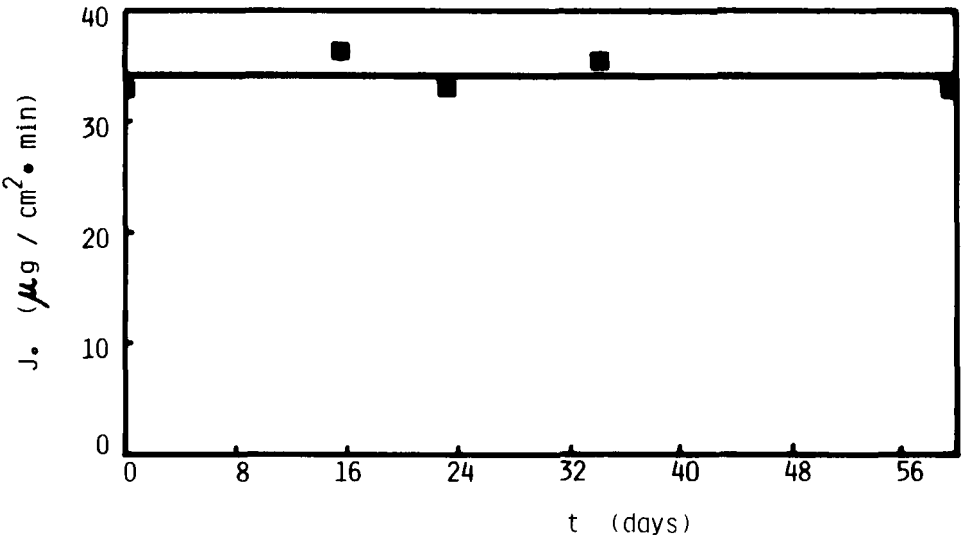

FIG. 11. Chemical resistence of a flat sheet polypropylene membrane to *o*-xylene. Feed: $[Cd^{2+}]$ = 0.5 g/L, [NaCl] = 1 *M*, pH = 1. Strip: $[CH_3COONa + NH_4Cl]$ = 0.5 *M*, pH = 7. SLM: Alamine in *o*-xylene (30% v/v). T = 25°C.

resistance of the metallo-organic complex into the immobilized liquid membrane.

It is interesting to observe in Fig. 12 a strong dependence of the flux on the temperature. In particular, for the SLM DNNSA + kerosene + *o*-xylene the initial flux at 35°C is twice that at 25°C.

The operation of the SLM at 35°C can significantly decrease the time required for certain separations, as can be seen in Fig. 13, if the membrane area is constant. However, the stability of the SLM at this higher temperature needs to be tested.

CONCLUSIONS

These experiments on SLM's show that the stability and the transmembrane flux are dependent on the chemical-physical characteristics of the carrier-diluent mixture and not on the characteristics of the diluent only if the polymer is the same.

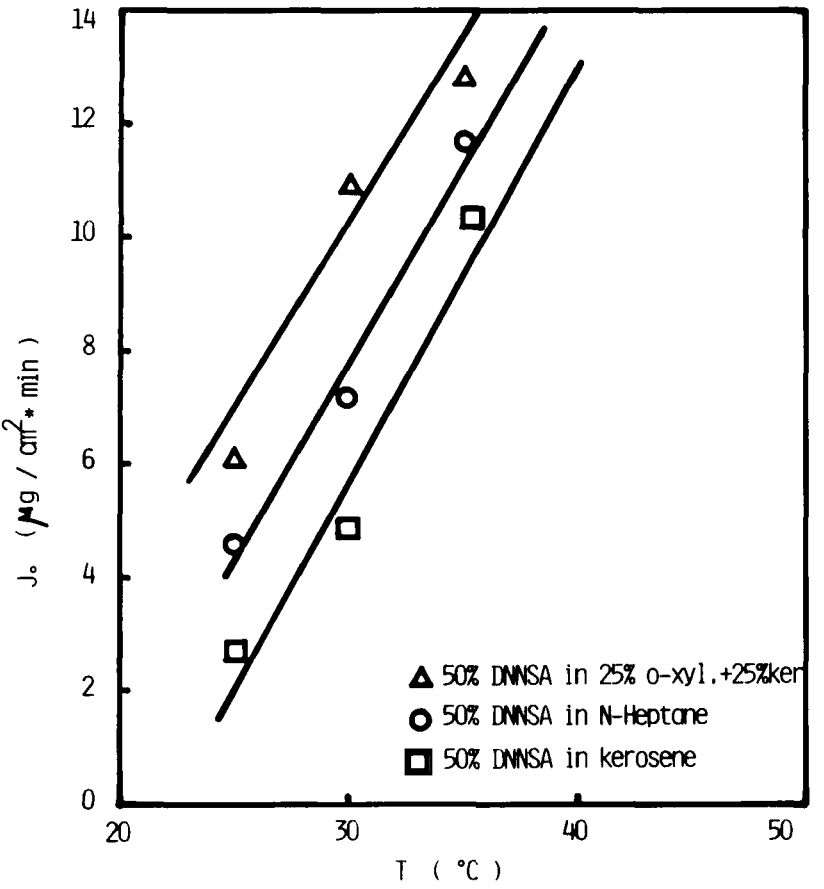

FIG. 12. Initial flux vs temperature while using various solvents as the diluent. Feed: $[Cd^{2+}] = 0.5$ g/L, [NaCl] = 1 *M*, pH = 1. Strip: $[CH_3COONa + NH_4Cl] = 0.5$ *M*, pH = 7. SLM: Alamine in *o*-xylene (30% v/v) and Alamine in kerosene (60% v/v). $T = 25°C$.

The initial flux of the SLM prepared with the mixture 50% v/v DNNSA + 25% v/v *o*-xylene + 25% v/v kerosene is about 2.5 that of 50% v/v DNNSA + 50% kerosene. The separation factor of the first SLM was about 15.0 in 70 h of continuous operation versus 5.1 in 22 days of continuous operation for the second SLM. These results show that a broad investigation is needed to determine the optimal formulation of the mixture to use when designing a good SLM.

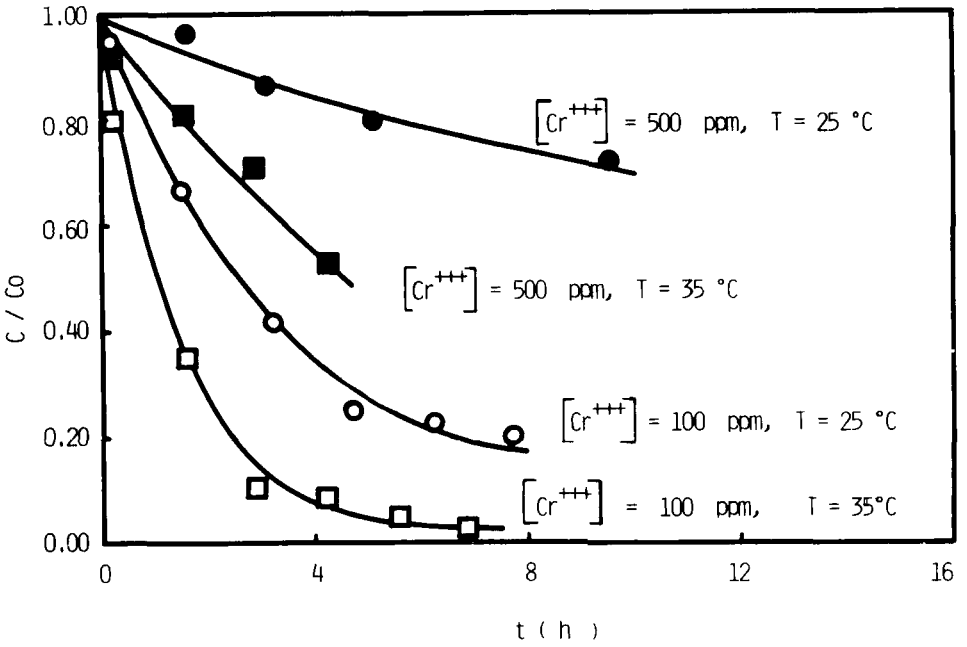

FIG. 13. Decrease of the feed concentration with time at two temperatures and two feed concentrations. Feed: $[Cr^{3+}]$ = 0.1 and 0.5 g/L, pH = 4.2. Strip: 1 *N* H_2SO_4. SLM: 50% v/v DNNSA + 50% v/v kerosene.

The use of an appropriate carrier-solvent mixture can give fast separations.

All these aspects, if optimized, will lead to a low membrane area, small equipment, and low energy consumption.

Acknowledgments

This research was partially supported by the P. F. Chimica Fine e Secondaria of C.N.R. We thank Enka A.G. and Henkel Co. for having kindly supplied the polypropylene support and the carrier, respectively.

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Received by editor October 3, 1988