A METHOD FOR CONTINUOUS OPERATION OF SUPPORTED LIQUID MEMBRANES

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Supported liquid membranes (SLM) have some advantages for the separation and concentration of metal ions from aqueous solutions, but membrane stability becomes a problem in practical application. Membrane liquids in SLMs are held in the pore structure of support solids solely by capillary force. Hence in a situation of SLM separations, it is inevitable that the solvent and/or carrier as the constituent of membrane liquid would be more or less washed or forced out of the support solid in addition to the dissolving loss to the process stream.

Most recently, two methods for continuous regeneration of SLMs have been developed with single hollow-fiber (HF)[1,7] and a laminated nonwoven film;[2] the stabilities of these SLMs have been demonstrated in continuous operation for one to several weeks. Danesi and Rickert[1] used a vertical, single HF-SLM module with a reservoir for membrane solvents at the top of the module, from which the solvent continuously soaked into the porous support by capillary action. Tanigaki et al.[7] and Fujinawa and Hozawa,[2] on the other hand, utilized a pressure flow of membrane solvents throughout the SLM of single-fiber and laminated film in horizontal configuration, respectively, where the pressure flow comes from sucking under reduced pressures at the one end of the SLM and soaking into it at the other end.

To renew the membrane phase in SLMs, apart from these two methods, we utilized the buoyant force of membrane solvent in continuum-pore of support solids. This view will be demonstrated in the present paper with the object of confirming its applicability to a multifibers module.

1. Experimental

A schematic drawing of the experimental apparatus for a single hollow-fiber SLM is shown in **Fig. 1**. The SLM module is composed of glass and Teflon tubes without use of adhesive. Goretex hollow fiber TA002

(Japan Goretex Co. Ltd.) was used as a support solid of the SLM. The module had a pool for membrane liquid at the bottom of the fiber, which was connected with a device for canceling out the pressure between the membrane liquid (hatched in Fig. 1) and strip solution stream. Membrane liquid in the pool soaks into the pore of supported solid, and then moves up through the continuum-pore or creeps up the lumen side of the fiber by buoyant force and capillary action. Thus the liquid membrane phase in the SLM can be forced to continuously renew itself as a continuous regenerating SLM (*CR*-SLM). Also, it might be expected to contribute the permeation of ions across the membrane as well as to stabilize the SLM. In the present experiments, upflow mode was adopted for the channels of both feed and strip solutions.

Nickel or cobalt was permeated from the feed solution of each nitrate into a strip solution of nitric acid through the SLM. Permeation fluxes based on the logarithmic mean of the external and internal surface areas were determined from measurements of the metal ion concentration in the strip solution at time intervals by atomic absorption spectroscopy.

As a mobile carrier, two commercial extractants were used: di-(2-ethylhexyl)phosphoric acid (HDEHP) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHPNA), which were supplied from Daihachi Chemical Co. under the trade names DP-8R and PC-88A, respectively. Each extractant was diluted with *n*-heptane or toluene to a 0.08 M or 0.16 M monomer concentration without further purification.

Experiments were made for three systems: (1) HDEHP/toluene-Ni, (2) HDEHP/*n*-heptane-Ni and (3) EHPNA/*n*-heptane-Co. All aqueous solutions were saturated with the organic diluent used in each system.

2. Results and Discussion

The lifetime of SLMs with toluene as the membrane solvent is so short that it is difficult to apply the SLM to membrane separation.[3] However, the application of continuous regeneration of SLM might make it
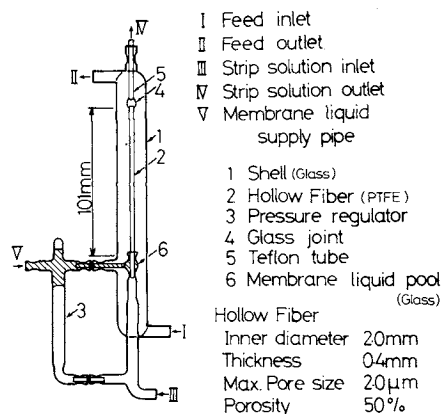
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Fig. 1. Single hollow-fiber module for continuous regeneration of the liquid membrane.

possible to operate such an unstable solvent system. **Figure 2** shows typical results for the HDEHP/toluene-Ni system, wherein the two dashed lines represent the permeation fluxes calculated by assuming that the diffusion of nickel complex in the membrane is rate-determining. Here we used the equilibrium constant by Komasawa et al.,[4,5] though it was outside of their experimental conditions, together with the diffusion coefficient estimated by the Wilke-Chang equation. As Fig. 2 shows, the flux data are in satisfactory agreement with the respective calculation lines. Such agreement suggests that stable SLM operations can be attained in the continuous regeneration mode used in the present study, even for unstable SLM systems.

Figure 3 shows the results for the HDEHP/n-heptane-Ni system. It can be seen from Fig. 3 that for the non-regenerating SLM a decline in the permeation flux begins after a short period of time, while the breakthrough time of the aqueous solution into the SLM was ca. 12 hr. Such behavior is probably because the Ni-complex has water molecules as a ligand[6] and the water is liberated from the complex in the membrane during the diffusion in accordance with equilibria between the complexes. In the case of the CR-SLM, on the other hand, the fluxes of nickel were maintained at a constant value over the entire one-week duration of the experiment.

Typical results for the EHPNA/n-heptane-Co system are shown in **Fig. 4**. The SLM operation for the present system was relatively stable even in the non-regenerating mode, since Co-EHPNA complex is not coordinated with water unlike the Ni-HDEHP complex mentioned above. However, the membrane began to degrade at ca. 25 h, being broken out after two days; while in the CR-SLM the membrane was completely stable over a period of one week. As Fig. 4 shows, the short-term permeation flux in the non-regenerating mode was equal to that in the CR-SLM, against an expectation that the latter may be higher
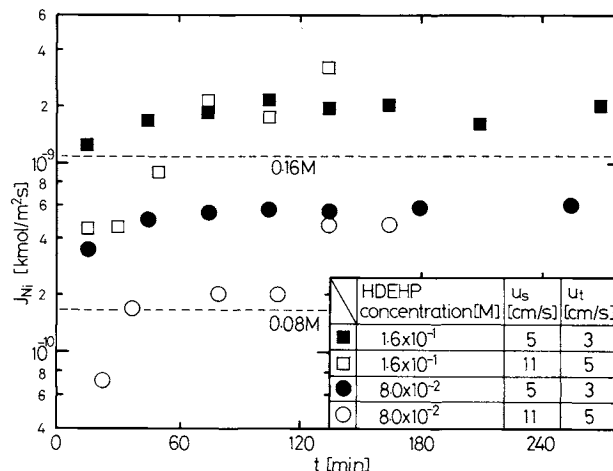
HDEHP concentration [M]	u_s [cm/s]	u_t [cm/s]
1.6×10^{-1}	5	3
1.6×10^{-1}	11	5
8.0×10^{-2}	5	3
8.0×10^{-2}	11	5

Fig. 2. Plots of permeation flux of nickel against operation time for SLMs with toluene solutions of HDEHP. Feed solution, $[Ni^{2+}] = 1.0 \times 10^{-2}$ mol/dm^3, pH 4.2; strip solution, HNO_3 1.0×10^{-2} mol/dm^3. Dashed lines represent calculated values assuming membrane diffusion controlling.
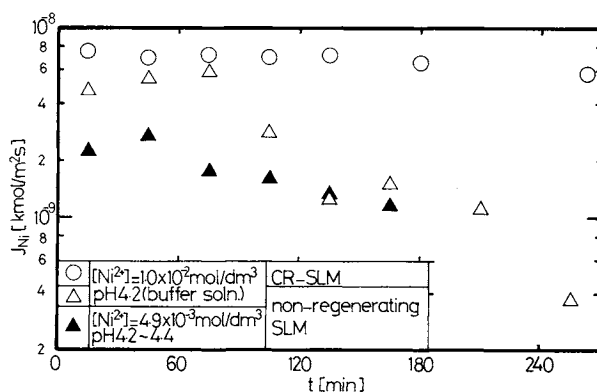
○ $[Ni^{2+}] = 1.0 \times 10^{-2}$ mol/dm^3
△ pH 4.2 (buffer soln.)
▲ $[Ni^{2+}] = 4.9 \times 10^{-3}$ mol/dm^3 pH 4.2~4.4
CR-SLM
non-regenerating SLM

Fig. 3. Plots of permeation flux of nickel against operation time for SLM with n-heptane solution of HDEHP (0.08M). Feed solution, $u_s = 5$ cm/s; strip solution, HNO_3 1.0×10^{-2} mol/dm^3, $u_t = 3$ cm/s.
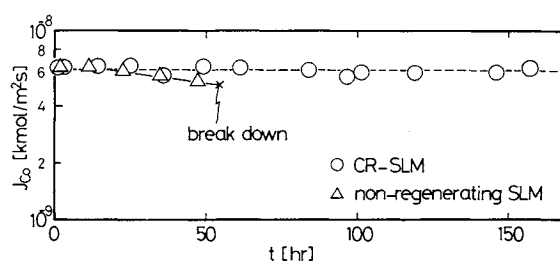
break down

○ CR-SLM
△ non-regenerating SLM

Fig. 4. Plots of permeation flux of cobalt against operation time for SLM with n-heptane solution of EHPNA (0.08M). Dash line represents calculated values assuming membrane diffusion controlling. Feed solution, $[Co^{2+}] = 1.0 \times 10^{-2}$ mol/dm^3, pH 4.1–4.5, $u_s = 5$ cm/s; strip solution, HNO_3 1.0×10^{-1} mol/dm^3, $u_t = 3$ cm/s.

than the former. Taking into consideration a permeation mechanism, we expected that the diffusion rate of Co-complex through the membrane could be enhanced by a flow of the membrane liquid. Although such a flow contribution to the permeation flux can be

inferred from the difference between the flux data for the HDEHP/n-heptane-Ni system (see Fig. 3), further information might be drawn from the difference in the interfacial tension.

In conclusion, we found that the present continuous regeneration is useful in prolonging the lifetime of SLMs, which utilize the buoyancy of membrane liquid. Thus the application of the present regeneration method to a multi-fibers module has been undertaken.

Nomenclature

J	= permeation flux of metal ion	[kmol/m$^2\cdot$s]
t	= operation time	[min] or [h]
u_s	= shell-side flow velocity	[cm/s]
u_t	= tube-side flow velocity	[cm/s]
[ ]	= concentration of ion	[mol/dm^3]

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DYNAMIC FORMATION OF POLYION AND POLYION COMPLEX MEMBRANES, AND THEIR SOLUTE REJECTION

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In recent years, the formation of dynamic membranes for ultrafiltration use have been reported.[3,5] Polyion is one of the candidates for membrane material because of its conformational versatility.[1] There are some studies concerning solid membranes of polyion complex (PIC) prepared by the casting method, but only a few studies of dynamic polyion and PIC membranes have been reported.[2]

In this work, two dynamic polyion membranes and two types of dynamic PIC membranes were formed and their solute rejections were investigated.

1. Experimental

1.1 Apparatus

Figure 1 shows the cross section of the module (TDK Corp., Dynaceram DC-0005) used and a schematic diagram of the experimental setup. The module has one porous ceramic tube (O.D. = 5 mm, I.D. = ca. 2 mm, length = 500 mm) and an effective membrane area of 74.5 cm^2. The mean pore size of the surface layer of the tube is 50 nm. Operating pressure, liquid linear velocity, and temperature were kept at 0.49 MPa, 2.07 m$\cdot$s^{-1}, and 298 K, respectively.

1.2 Membrane formation procedure

Polyions used were sodium polyacrylate (SPA, linear polymer, average $M_W = 3 \times 10^6$) for polyanion and polyethylene imine (PEI, branched polymer, average $M_W = 1 \times 10^5$) for polycation.
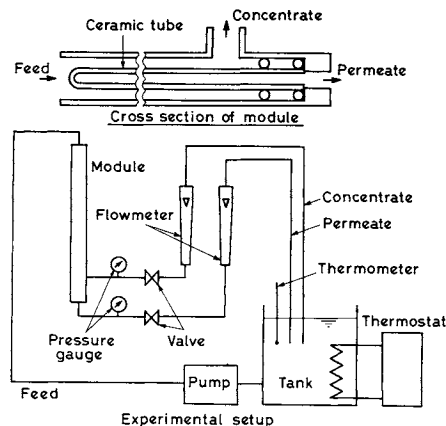

Fig. 1. Cross section of module used and schematic diagram of experimental setup.