Transport and Separation of Zn(II)/Mn(II) in a Multimembrane Hybrid System (MHS)

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In this paper the recovery, concentration and/or separation of an equimolar mixture of Zn(II) and Mn(II) sulfates by multimembrane hybrid system (MHS) were evaluated, in which the organic phase is placed between the two solid cation-exchanges membrane. Di(2-ethylhexyl)phosphoric acid (henceforth D2EHPA) dissolved in kerosene was selected as the carrier in the membrane phase,because it is a good extractant of divalent transition metals in hydrometallurgy. Solutions of di(2-ethylhexyl)phosphoric acid in organic solvents are widely used as membranes when metal-containing cations are in the process of separation or concentration. Its ability to selectively and reversibly bind metal ions may enable a liquid membrane to perform difficult separations. All the experiments made in our laboratory demonstrated that MHS is stable over time and is effective for separating and transporting some divalent ions, such as Mn or Zn. The studies of pertraction in the multimembrane hybrid system indicate the feasibility of water removal from the organic liquid membrane phase by pervaporation. It was also found, that the selectivity of Zn^{2+} *pertraction increases when the liquid membrane dehydration (pervaporation) is applied.* ***Continuous pervaporation of water increases the concentration of the metal-carrier complexes in the organic liquid membrane.***

Keywords: multimembrane hybrid system (MHS), liquid membranes, cations separation, pervaporation

The vast majority of industrial effluents and waste water, such as mining water, etching or pickling baths, dilute leach solution generated during hydrometallurgy, electroplating rinse liquors, etc. may carry Co(II), Ni(II), Mn(II), Zn(II), etc. in low concentrations. A secondary source of Zn and Mn contamination are zinc-carbon and alkaline zinc-manganese dioxide batteries which are widely used as they have good electrical properties/price ratio. Heavy metals are not biodegradable; they tend to accumulate in living organisms causing various diseases and disorders [1].

Liquid membranes have shown great potential, especially in cases where solute concentrations are relatively low and other techniques cannot be applied efficiently, since they combine the processes of extraction and stripping in a single unit operation [1-2]. The use of liquid membranes containing specific metal ion carriers offers an alternative method to the solvent extraction processes for selective separation and concentration of the metal ions from aqueous dilute solutions. Depending on their specific composition, liquid membranes allow effective recovery, active concentration (uphill transport), and/or separation of various metals or organic compounds from aqueous media. This process provides maximum yield of the extracted solute with minimum inventory and power consumption.

A lot of technologies that were developed and tested in the last decade have to be included in the bulk liquid membrane (BLM) group. The following systems, such as hybrid liquid membrane (HLM) [3], hollow-fiber liquid membrane (HFLM) [4], flowing liquid membranes (FLM) [5], multimembrane hybrid system (MHS) [6] and membrane contactor systems [7-8] are the similar BLM system.

Recently, many applications of the hybrid liquid membranes have been described [9–13].This method was patented by Ho et al. [9] and renewed by Kedem *et al.* [10]. The multimembrane hybrid system (MHS) has been developed and used for the transportation and separation of divalent metal ions from multicomponent solutions [11]. The concept of the method is the introduction of the bulk liquid membrane between two solid ion-exchange membranes (IEMs). In this case both IEMs are barriers, which physically separate organic and aqueous liquid phases. Moreover, the ability of IEM to metal cations sorption from aqueous solution causes a high accumulation of reacting species at the interfaces.

A similar system with a cation-exchange membrane (CEM) polymer has been recently studied and classified as the hybrid membrane extraction [14]. The mechanism of hybrid membrane extraction operation involves a series of coupled process such as:

a) cations exchange sorption of cations from the feed solution into cation-exchange membrane;

b) ion exchange dialysis across cation-exchange membrane;

c) extraction of cations from cation-exchange membrane by a specific reagent dissolved in an organic phase;

d) finally diffusion of extractant in its free and loaded form into the organic phase.

A remark of V. Kislik and Eyal is that, in comparison with liquid-liquid extraction (LLX), supported liquid membrane (SLM), and emulsion liquid membrane (ELM), hybrid liquid membrane(HLM) has the potential to provide many economic and operational advantages, such as: low carrier losses, long membrane lifetime, ''once through'' continuous operation, compact equipment, application of different driving forces (chemical potential, pressure,

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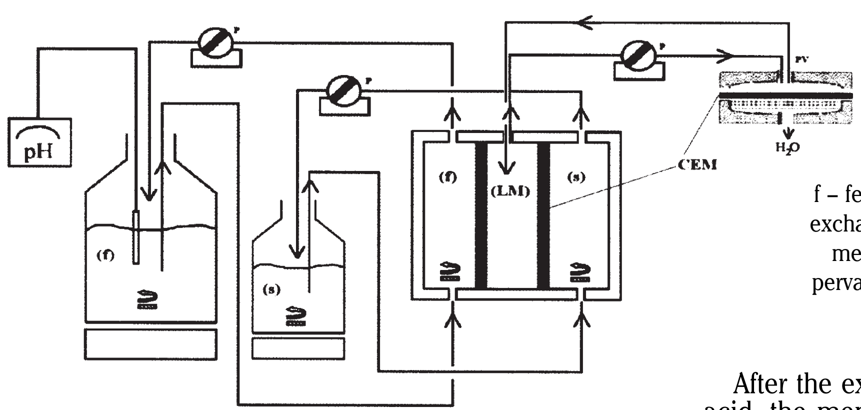

Fig.1. Scheme of the experimental MHS: f – feed solution, s – stripping solution, CEM – cation-exchange membrane, LM – liquid membrane, pH – pH meter, P –peristaltic pump, p – piston pump, PV – pervaporation module with vacuum system and water receiver

temperature gradients between different compartments, electric field, etc.), no need of surface formation, impregnation, gravity gradients, high membrane capacity, etc. [15-20].

The transport mechanism involves a series of coupled cation-exchange difussion processes in cation-exchange membranes and counter transport of cations as mediated by this ionic carrier. The membrane systems combine some advantageous properties of polymer and liquid membranes with its high stability in time.

The first experiments were carried out without a standard pervaporation module. It was observed that after 1 day working, inside organic phase on cation-exchange membrane appear water bubbles and then in whole liquid membrane. If the feed containing sodium cations at *p*H>5, the surface active properties of the sodium salt of D2EHPA lead to the formation of water in oil emulsion and reverse micelles [21-23], are the explication. The first phenomenon destroys the bulk liquid membrane system; whereas the second intensifies the fluxes unselectively, e.g. zinc versus sodium and other metals ions, which result in the loss of selectivity and basic membrane properties [24].

Wodzki et al. [25] specified and demonstrated that to enhance the liquid membrane stability and performance it is necessary to reconstruct the MHS by adding a system which continuously removes water from liquid membrane phase, and for this purpose a standard pervaporation (PV) module can be exploited [26].

In this paper the recovery, concentration and/or separation of an equimolar mixture of Zn(II) and Mn(II) sulfates by multimembrane hybrid system were evaluated, in which the organic phase is placed between the two solid cation-exchanges membrane. Di(2-ethylhexyl) phosphoric acid (henceforth D2EHPA) dissolved in kerosene was selected as the carrier in the membrane phase,because it is a good extractant of divalent transition metals in hydrometallurgy. Solutions of di(2-ethylhexyl) phosphoric acid in organic solvents are widely used as membranes when metal-containing cations are in the process of separation or concentration. Its ability to selectively and reversibly bind metal ions may enable a liquid membrane to perform difficult separations.

Experimental part

Materials and reagents

The experiments were carried out in a transport system including two cation-exchange membranes.

The Nafion-117 (Du Pont De Nemours, USA) perfluorosulfonic cation-exchange membranes were used as separators between organic and aqueous phases.Nafion-117 membrane is composed of a perfluorinated polymer with fixed sulfonic acid groups.The concentration of sulfonic acid groups in the membrane (H^+ form) is 1 mol/dm^3, thickness 0.019 cm and water content 13.5 wt. %. Additional, another one Nafion-117 CEM were used at pervaporation module.

After the experiment, for removing the absorbed free acid, the membranes were regenerated by soaking in sulfuric acid solution (2 mol dm^{-3}) and by further washing in double distillated water.

The liquid membrane was prepared by using the carrier/ extractant bis(2-ethylhexyl)phosphoric acid (D2EHPA, Sigma Chem. Co., USA, 95%), which was dissolved in kerosene (Maker, Poland, boiling point 124-174°C, viscosity 0.69 mPa s, and density 0.783 g cm^{-3}) to a concentration between 0.001 and 0.1 mol/dm^3.

Sulfuric acid with the concentration 1 mol/dm^3 was used as a stripping solution.

Aqueous feed solution were prepared by dissolving the $ZnSO_4$ and $MnSO_4$ in double distillated water.The feed *p*H was adjusted by adding the appropriate amount of NaOH or HCl, and then controlled by using a pH-meter (Elmetron CX721). The initial concentration was between 0.0001-0.01 mol dm^3.

Samples of the 0.1-5 cm^3 volume were taken from the feed solution and 1cm^3 volume from the stripping solution, and analyzed off-line using a Varian atomic absorption spectrophotometer. All experiments were carried out at temperature of 25 ± 1°C.

Transport cell and operating conditions

All transport experiments were performed in the multimembrane hybrid system constructed as presented in figure 1.

The transport cell was made of plexiglass. The cell was composed of three compartments filled with the stated liquids and separated by 2 cation-exchange membranes. The effective volume of each compartments was 17 cm^3. The cation-exchange membranes were held in place between plexiglass gaskets and clamped together. Were used silicon rubber rings surrounding the gaskets, to prevent possible leakage of liquids.

First experiments were performed without pervaporation module.The external solutions, i.e. feed solution of 1000 cm^3 volume and stripping solution of 100 cm^3 volume were pumped from an external reservoir through compartment 1 and 3 at a flow rate of 13 cm^3/ min, and were agitated with a magnetic bar at 500 rpm. Compartment 2 was filled with 30 cm^3 liquid membrane. Separately all the compartments were magnetically agitated too with 300 rpm.

When the experiments were carried out coupled to a pervaporation module the liquid membrane had 68 cm^3 and was pumped with a Teflon piston pump (150 cm^3/ min , OSI France) in a closed circuit composed of the piston pump, MHS cell and the pervaporation unit.

In addition, another Nafion-117 membrane were used in the pervaporation module for continuous liquid membrane dehydration. The Nafion-117 membrane were used in the PV module because of their high mechanical and chemical resistance as well as their good hydrophilic properties [27].The PV membrane was supported by stainless steel porous plate. The receiver chambers of the pervaporation unit were connected to a glass vacuum system operating at the pressure of 5–10 mm Hg. Water pervaporated into the low pressure side was frozen in one of the two receivers cooled by solid carbon dioxide and thereafter determined by subsequent weighing.

Results and discussions

To find the amount species transported from feed to strip phase after time *t*, the feed $[M]_f$ and strip $[M]_s$ solutions concentration were used.

$$\frac{[M]_{s,t}V_s}{1000A_s} = Qmol/cm^2) \quad (1)$$

where :$[V]_s$ denotes the volume of stripping solution and $[A]_s$ the output membrane area (cm^2).

The fluxes were calculated from *Q* versus time dependence. If we considered that the transport was quasi-stationary, the respective fluxes were calculated as:

$$J_M = \frac{\Delta[Q]_{M,s}}{\Delta t}(mol/cm^2 s) \quad (2)$$

Other characteristic associated with MHS fluxes is "up-hill" transport which can be evaluated by concentration (3) factor (CF) and efficiency factor (EF) defined as follows:

$$CF_M = \frac{[M(II)]_{s,t}}{[M(II)]_{f,0}} \quad (4)$$

$$EF_M = \frac{[M(II)]_{s,t}}{[M(II)]_{f,t}} \quad (3)$$

where [M(II)] denotes the concentration of divalent metal ions in feed (f) or strip (s) solution at the initial feed concentration of M(II) species (0) or after time (t).

Pumping the M(II) species from the feed into strip phase is characterized by the recovery factor (RF) calculated as:

$$RF_M = 100(\frac{[M(II)]_{f,0} - [M(II)]_{f,t}}{[M(II)]_{f,0}}) \quad (5)$$

The ability of this system to separate cations is characterized by the separation coefficients (α). In our case of multicomponent feed solutions, the overall separation coefficient $\alpha^{M_k}_{\Sigma M}$, can be calculated:

$$\alpha^{M_k}_{\Sigma M} = \frac{[M(II)]_{k,s}\,\Sigma[M(II)]_{i,f} \quad i \neq k}{[M(II)]_{k,f}\,\Sigma[M(II)]_{i,s} \quad i \neq k} \quad (6)$$

where the separation factors for *k* and *i* ionic species should indicate how far the composition of the stripping solution is different from that of the feed.

In this case the separation ability is usually measured by selectivity coefficients $\beta^{M_k}_{M_p}$ defined as the ratio of stationary fluxes corresponding to two different cations *k* and *p*:

$$\beta^{M_k}_{M_p} = \frac{J_{M_k}}{J_{M_p}} \quad (7)$$

Transport and separation of zinc and manganese cations from multicomponent solutions

In order to check MHS performance in recovering and concentrating the Zn^{2+} and Mn^{2+} salts simultaneously have been carried out some tests with this aqueous feed phase containing $ZnSO_4$ and $MnSO_4$ (1000 cm^3) with concentration ranging from 0.0001 – 0.01 M and aqueous stripping solution of 1M H_2SO_4 (100 cm^3). A solution of D2EHPA (30cm^3) (di(2-ethylhexyl)phosphoric acid, c_{D2EHPA} =0.1 M) in kerosene was applied as a liquid membrane.

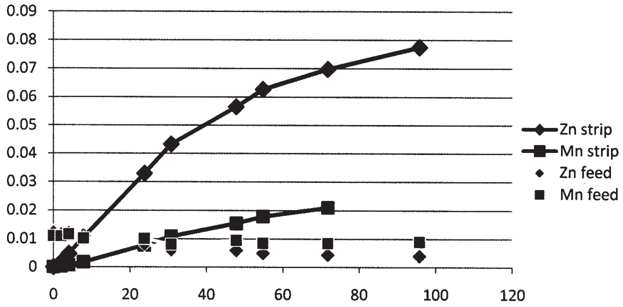

Fig. 2. Transport of cations in MHS

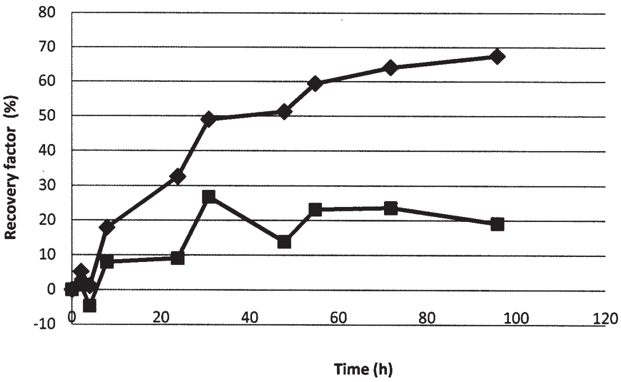

Fig. 3. Recovery factor values: Zn ◆ Mn ■

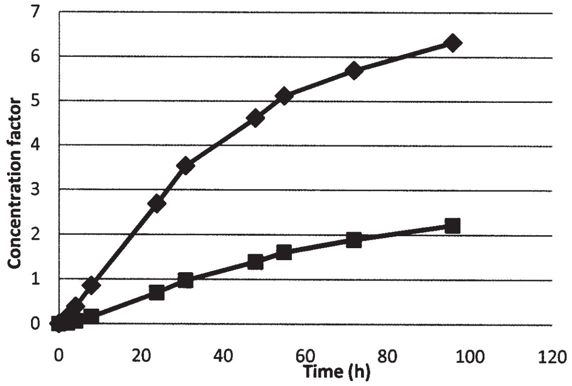

Fig. 4. Concentration factor: Zn ◆ Mn ■

Typical experimental results corresponding with the system with 0.01 M solution of Zn^{2+} an Mn^{2+} salts as the feed phase are presented in figures 2-4.

The flux of Zn(II) and Mn(II) for this system was 2.69x 10^{-9} and 6.24 x 10^{-10} mol/cm^{2}s, respectively. Recovery factor (fig. 3) was found in this experiment to reach 60% for Zn(II) and 20% for Mn(II), and the selectivity coefficients β^{Zn}_{Mn} = 50.1. All the results presented (fig 4- the concentration factor) confirm the usefulness of MHS for transporting and recovery Zn(II) ions from their dilute solutions.

In figure 5 the metal species show that the effect of feed concentration can be qualitatively different. An increased selectivity toward Zn(II) ions can be seen when feed concentration increased. Therefore 0.01 M feed concentration was selected as optimum feed concentration for this system and was used for the following experiments.

The following experiments were performed with and without pervaporation module with feed phase containing $ZnSO_4$ and Mn (1000cm^3) with concentration of 0.01 M and aqueous stripping solution of 1M (100 cm^3). For this experiments, the solution of D2EHPA (68 cm^3) dissolved in kerosene had concentration ranging 0.001- 0.1 M.

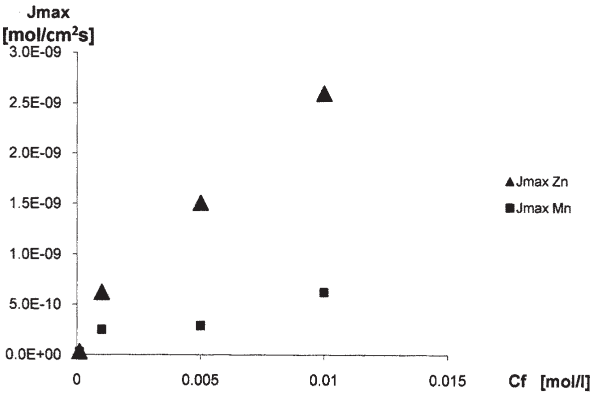

Fig. 5. Effect of feed concentration on fluxes in MHS

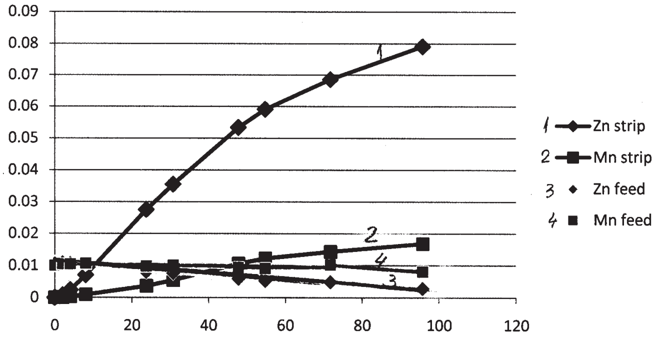

Fig. 6. Transport of cations in MHS without pervaporation

In figure 6 are represented the cations transport trough MHS without pervaporation module containing 0.01 M feed solution, 1M stripping solution and 0.1 M D2EHPA.

From figure 6 the active (up-hill) transport is observed after 7 and 15 h for Zn^{2+} and Mn^{2+} cations, respectively.

The formation of emulsion in the bulk liquid membrane phase as a consequence of the water transport, can results in the loss of selectivity [25]. It was found that continuous removal of water from an organic liquid membrane phase (realized by coupling the pertraction to the pervaporation process) leads to a small reduction in the Zn^{2+} and Mn^{2+} concentrationof the stripping solution (fig. 7). So,the higher concentration of the complex in the liquid membrane phase reduces the fluxes in stripping solution and an increase in the selectivity of the D2EHPA towards preferentially transported Zn(II) cations was observed.

Compared to other liquid membrane systems (bulk, supported or emulsion), MHS exhibits some advantages i.e. high stability in a long time operation and high selectivity [11, 27-30].

Metal ions are actively concentrated in the strip solution or removed from the feed solution (8-11) which demonstrates that MHS can be a useful tool for the separation, recovery and concentration these metals, for example the recovery factor for Zn(II) overcome 70%.

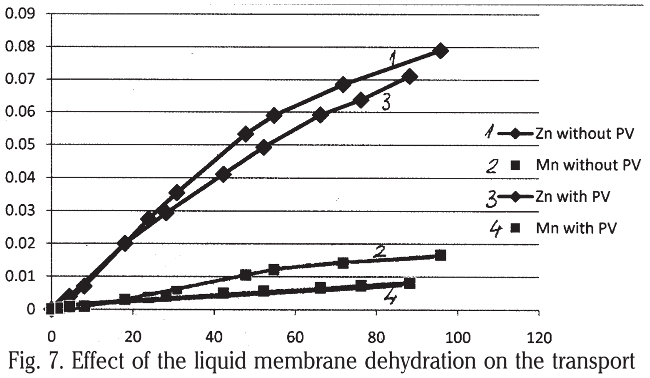

Fig. 7. Effect of the liquid membrane dehydration on the transport in the MHS

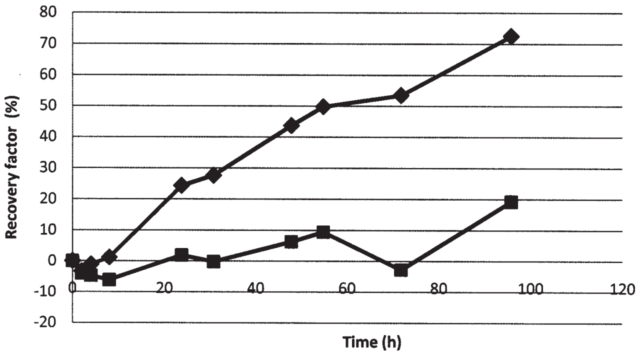

Fig. 8. Recovery factor on the transport in MHS without pervaporation: Zn ◆ Mn ■

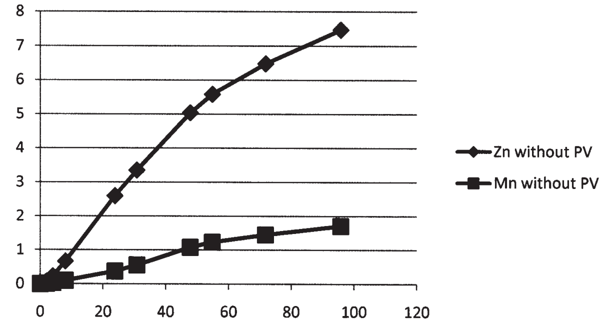

Fig. 9. Concentration factor on the transport in MHS

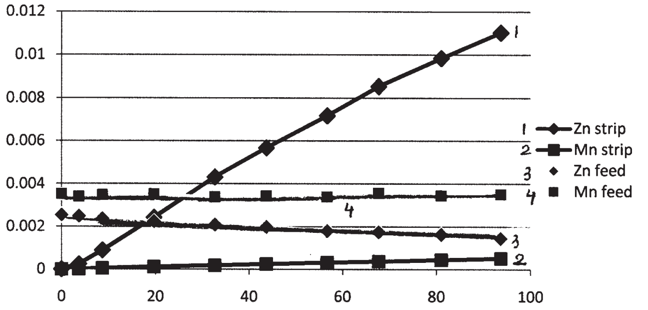

Fig. 10. Transport of cations from a real spent battery solution after leaching in concentrated H_2SO_4 and dilution in MHS with pervaporation

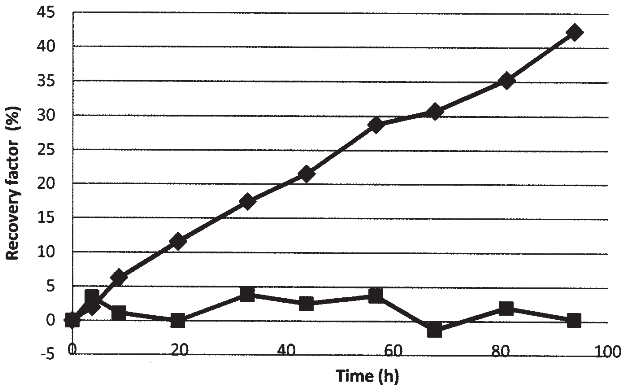

Fig. 11. Recovery factor from a real spent battery in MHS with pervaporation

Additionally, a real spent battery solution after leaching in concentrated H_2SO_4 and dilution, was also applied as the feed solution, because separation of Zn^{2+} from Mn^{2+} is one of the fundamental problems in the disposal of zinc-carbon spent batteries.

The MHS equipped with the pervaporation unit was also applied for recovery and separation of Zn^{2+} from Mn^{2+} a real spent battery. For example the flux of Zn^{2+} and Mn^{2+} for the system with pervaporation with real spent battery solution was 2.3×10^{-10} and 8.1×10^{-12} mol/ cm^{2}s, respectively and recovery factor reached 40 % for Zn(II).

Conclusions

All the experiments made in our laboratory demonstrated that multimembrane hybrid system (MHS) is stable over time and is effective for separating and transporting some divalent ions, such as Mn or Zn.

The studies of pertraction in the multimembrane hybrid system indicate the feasibility of water removal from the organic liquid membrane phase by pervaporation.

It was also found, that the selectivity of Zn^{2+} pertraction increases when the liquid membrane dehydration (pervaporation) is applied**.**

Continuous pervaporation of water increases the concentration of the metal-carrier complexes in the organic liquid membrane.

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