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ZINC EXTRACTION THROUGH LIQUID MEMBRANE COUPLED TO A PERVAPORATION PROCESS

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The liquid membranes have been studied under different geometrical configurations, such as: bulk, supported and emulsion liquid membranes. Liquid emulsion membrane extraction and support liquid membrane extraction are the most popular techniques. In some cases the method of volume membrane extraction can be used for the separation of various metal ions. In the case of bulk liquid membranes containing the ionic species carriers, this approach leads to the multi membrane hybrid systems (MHS) combining the properties of the bulk volume membrane and ion exchange membranes in series.

Keywords: Bulk liquid membrane, Membrane extraction, Liquid membrane pertraction, Pervaporation

1. Introduction

Selective transport of cationic substrates by membrane carriers is of great importance in chemistry, biology and separation sciences. Compared with conventional separation processes, such as liquid–liquid extraction (LLE), membrane techniques are characterized by the technical simplicity and high efficiency in separating or enriching material from gaseous or liquid mixtures. Also, these methods reduce the solvent inventory requirements and also allow the use of expensive and highly selective extractants, which otherwise would be uneconomic in solvent extractions. Membrane techniques have been widely used for carrier facilitated metal ion separations [1–8], and to a lesser degree for

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separation of organic substances [9–11]. The principle of such separation techniques was explained by Denesi [12]. The liquid membrane (LM) has been studied under different geometrical configurations, such as bulk liquid (BLM), supported liquid (SLM), emulsion liquid (ELM) membranes [13]. Emulsion membrane extraction [2, 4, 14–17] and supported liquid membrane extraction [18–21] are the most popular techniques. In some cases the method of bulk volume membrane extraction can be used for the separation of various ions [22–26]. In the case of bulk liquid membranes containing the carriers of ionic species, this approach lead to the multi membrane hybrid systems (MHS), combining the properties of the BLM and ion exchange membranes [27, 28] in series. Similar studies aim was to improve the stability of SLMs by forming microporous interfacial layers immediately on the surface of SLM [29-32]. An even more advanced solution has been proposed by Strathmann and coworkers [33] who developed a new type of composite membrane made of SLM with external, hydrophilic, charged polymer layers made of sulfonated poly(ether ether ketone). It is also noted that membrane systems composed of hydrophilic and hydrophobic membranes of various compositions and functions are frequent in natural cellular systems [34]. Such bio membrane systems are recognized as being stable, efficient and highly selective in the transport of various substances under different conditions. Thus, the biophysics of membrane transport supplies an additional motivation to design hybrid membrane systems which can also be regarded as biomimetic.

Many membrane hybrid systems are stable in time, selective and easy to handle when used for laboratory purposes. On the other hand, after the scale of the device had been increased, the time of operation prolonged and the composition and ionic strength of aqueous phase changed drastically, it was noted that the slow osmotic permeation of water into the organic phase (BLM) appears as the problem to solve. Moreover, the uptake of water by the BLM can occur because some salts of phosphoric and thiophosphoric acid derivatives, when used as extraction solvents or carriers, show a tendency to form reverse micelles [35-37]. At extreme conditions, all these factors cause the formation of emulsion in the bulk liquid membrane phase, which results in the loss of selectivity and basic membrane properties [38]. All these unrequired phenomena can be partially eliminated by careful adjustment of the feed pH, pre-treatment of the feed by removing some cations such as: K^+ Na^+ or Ca^{2+}, and a proper choice of the membrane solvent and reagent. However, such procedures may sometimes turn out to be impossible to be implemented, because of large feed volumes or variable pH and compositions of continuously produced industrial waste solutions. A much simpler approach is to reconstruct the MHS by adding a system which continuously removes water from the liquid membrane phase. For this purpose, a standard pervaporation (PV) module can be exploited [39]. Taking into account the recent report of Aouak et al. [40], it appears that this technique allows breaking the microemulsion by removing water and thus, it should improve liquid membrane stability and performance.

In the case of bulk liquid membranes containing the carriers of ionic species, this approach leads to the multi membrane hybrid systems (MHS) combining the properties of the bulk volume membrane and ion exchange membranes in series.

In this paper we compared the extraction of zinc using BLM and membrane extraction and pertraction coupled to a pervaporation process.

2. Experimental procedures

2.1. Materials and methods

$ZnSO_4$, HCl and H_2SO_4 (p.a) were purchased from POCh, Poland, Gliwice. Kerosene used as membrane solvent was supplied by CHMES Poland. Two standard carriers/extractants for zinc cations were used for the preparation of liquid membranes, di-(2-ethylhexyl) phosphoric acid (D2EHPA) and bis (2,4,4-trimethylpenthyl) thiophosphinic acid (Cyanex 302) suplied by Alfa Aesar, Fluka respectively.

The transport experiments were performed in a beaker-in-a-beaker glass type [41-43]. The transport cell was termostated. The water in the thermostated vessel was maintained at constant temperature (25˚C) by circulating water from bath through the jacket. The organic phase was agitated with a mechanical stirrer at 375 rpm. The stirring speed of the feed and stripping solutions (two Teflon-coated magnetic bars) was maintained at 200 rpm. The volume of the feed phase was 105 mL, the volume of the stripping phase - 25 mL and the volume of the liquid membrane - 25 mL. The pH=5.07 of the feed source was adjusted with HCl and measured with a glass electrode Elmetron 721. The concentration of the metal cations was determined using an atomic absorption spectrometer, Varian SpectrAA – 20 ABQ. The membrane content in the metal cations was determined using material mass balance for the three phases of the membrane system.

During all the experiments, the organic phase was prepared by dissolving the proper reagent in technical kerosene to a concentration of $0.1 mol/dm^3$. Aqueous feed solutions were prepared by dissolving the appropriate amount of $ZnSO_4$ (reagent grade) in distilled water. The feed pH was adjusted by adding the appropriate amount of HCl and controlled using a pH-meter. The initial concentration of zinc sulfate in the test solution was always $0.01 mol/dm^3$. Stripping solutions for the systems under investigation were prepared by dissolving H_2SO_4 (reagent grade) in distilled water to a concentration of 1mol/dm^3.

2.2. Transport theory

The stripping rates of ionic species were determined from the primary data in the form of the strip concentration versus time dependence. Corresponding quasi-stationary rates (J_M, eq/cm^{2}s) are defined by:

$$J_M = \frac{\Delta Qs}{\Delta t} \tag{1}$$

$$\Delta Qs\ (eq./cm^2) = z_M\, \Delta[M]_{s,t} \frac{\mathrm{Vs}}{1000\mathrm{As}} \tag{2}$$

In equations (1) and (2), Q_s denotes the amount of metal species of valence z_M transported to the receiver after the time *t*, through 1 cm^2 of the stripping area (A_s, cm^2); V_s (cm^3) the volume of the stripping solution; $[M]_{s,t}$ (mol/dm^3) the concentration of metal species at the time *t*. The PV flux of water was determined by analyzing the amount of water receivers in the analogous way. In order to evaluate the system quality, the selectivity coefficients defined as the ratio of stationary rates were calculated for binary (M_1/M_2) feed solutions:

$$SEL = \frac{JM1,s}{JM2,s} \tag{3}$$

In the case of multi-ionic solutions, the fractional rates FJ (for each M_k cation) were calculated as follows:

$$FJ_{Mk} = \frac{JMk}{\sum JMi} \quad or \quad FJ_{Mk}\,(\%) = \frac{100\,JMk}{\sum JMi} \tag{4}$$

In order to compare the results with other data published elsewhere, the permeability coefficients were calculated using Eq. (5):

$$P_{Mk} = \frac{1000\,JMk,s}{zMk}\,[M]_{k,f} \tag{5}$$

The separation ability of CME-PV and MHS [FLM-PV] and BLM with respect to a mixture of cations was evaluated through the separation factor (α):

$$\alpha_{\sum M}^{Mk} = \frac{zM\ [M]k,s\ \sum_{j\neq k} zMj\ [M]j,f}{zMk[M]k,f\ \sum_{j\neq k} zMi\ [M]j,s} \tag{6}$$

Generally, the separation factors for *k* and *j* ionic species should indicate how far the composition of the stripping solution is different from that of the feed. The mixture emerging from the membrane system should be different from that entering on the feed side, i.e. the separation factors α thought to be > 1 when the separation is reached after transferring to the strip solution or < 1 when solutes remain in the feed solution during the separation process.

3. Results and discussion

It can be expected that the separation ability of the systems studied depends mainly on the composition of the organic phase, and specifically, on the properties of the carrier. Many compounds can be exploited for selective transport of Zn^{2+}, among which, phosphoric acid derivatives are most useful. The acid-based carrier, di-(2-ethylhexyl) phosphoric acid attracts special attention due to its selectivity towards Zn^{2+}, very low solubility in water and good solubility in many organic solvents. Thus, we have tested the coupled emulsion membranes-pervaporation (CME-PV) and multi membrane hybrid (MHS) or flat liquid membranes-pervaporation [FLM-PV] systems efficiency in Zn^{2+}separation from the feed containing a mixture of zinc salts at pH ≈ 2.

Table 1

Description of the BLM system of Zn^{2+}

Lp.	Time (h)	C(f) mol / l	C(s) mol / l
1	0	1.02E-02	0.000
2	0.533	8.40E-03	5.51E-04
3	1.050	6.97E-03	2.02E-03
4	1.583	6.95E-03	3.86E-03
5	4.067	4.18E-03	1.42E-02
6	8.033	2.67E-03	2.56E-02
7	22.833	6.10E-04	3.68E-02
8	24.517	2.95E-04	3.72E-02
9	26.050	3.55E-04	3.50E-02

The results corresponding to stripping curves (Q_{Zn} versus t) and PV of water (Q_{H2O} versus t) are presented in fig.1 and fig.2. From the presented curves it is seen that both procedures results in nearly identical stripping rate curves for Zn^{2+}. In contrast, the pervaporation transport of water is markedly lower in the case of MHS [FLM-PV].

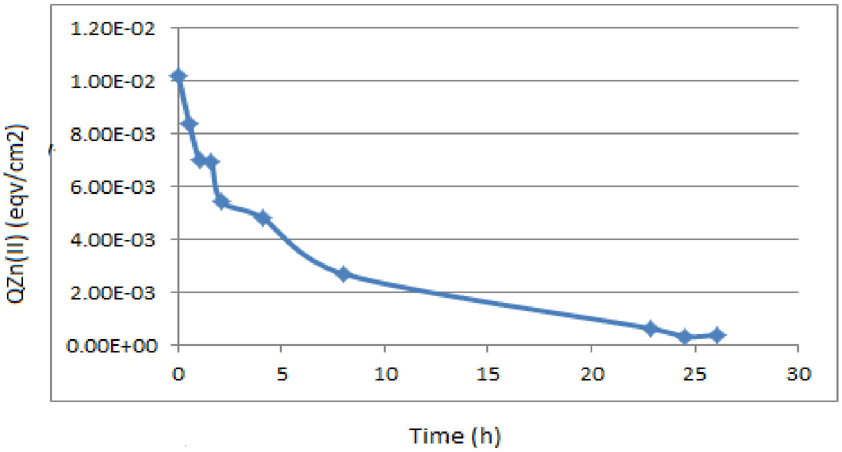

Fig.1. Efficiency of zinc separation from feed solution at different times in BLM

Additional quantitative characteristics of the studied processes are presented in table 2 and fig. 2. From the data obtained in the case of coupled emulsion membranes-pervaporation (CME-PV) and multi membrane hybrid (MHS) or flat liquid membranes-pervaporation [FLM-PV] systems, it can be concluded that the permeability coefficients, attain rather high values namely, 9.7×10^{-5} and 9.0×10^{-5} cm/s. The order of these coefficients is typical for the processes limited by diffusion phenomena, probably due to ion-exchange dialysis in cation exchange membranes.

Table 2

Transport and separation characteristics for membrane extraction, pertraction and pervaporation

Feed pH	Water pervaporation J_{H2O} (mole/cm^{2}s)	Zn^{2+} stripping J_{Zn} (eqv./cm^2/s)
Membrane extraction		
2.4	$(4.4 \pm 0.3 \times 10^{-8}$	$(1.94 \pm 0.06) \times 10^{-9}$
6.6	$(11.1 \pm 0.3) \times 10^{-8}$	$(1.12 \pm 0.04) \times 10^{-8}$
11.0	$(8.9 \pm 0.3) \times 10^{-8}$	$(6.5 \pm 0.2) \times 10^{-12}$
Pertraction		
2.3	$(2.2 \pm 0.2) \times 10^{-8}$	$(1.80 \pm 0.05) \times 10^{-9}$

The system selectivity (SEL) defined as the ratio of equivalent stripping rates (under stationary conditions) attains high values of 1662±170 and 1347±102 for the CME-PV and MHS [FLM-PV], respectively.

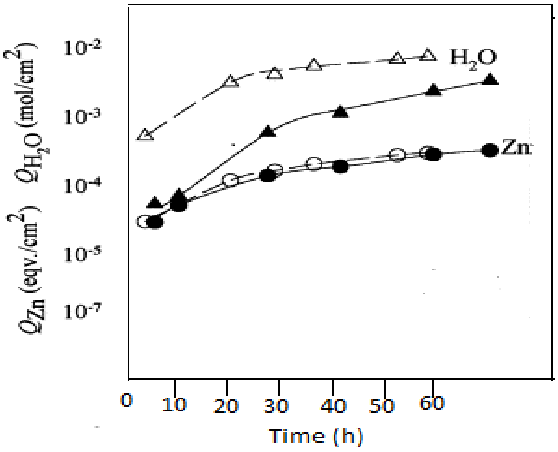

Fig. 2 Transport processes comparison in the CME-PV (empty symbols) and MHS-PV [FLM-PV] system (filled symbols): water (Δ, ▲), Zn $^{2+}$ (○●).

This means that fractional stripping rates for Zn^{2+} in both systems attain a value of 99.9%.

Simultaneously, the stripping rate of Zn^{2+} significantly decreases in the case of alkaline solutions, due to the formation of insoluble hydroxides in the feed. From the data presented in table 2, one can expect both systems to operate comparably with respect to Zn^{2+} separation. However, in the case of feeds with pH < 7, the CME-PV requires more efficient PV system than MHS [FLM-PV].

4. Conclusions

The results of this study prove that different membranes (liquid, ion-exchange and those made of neutral polymer) can be combined in complex membrane systems such as coupled emulsion membranes, and pertraction in a multi membrane hybrid systems. The combination of functions, such as ion-exchange dialysis, liquid membrane carrier transport or liquid–liquid extraction, and pervaporation of water resulted in a system which enables stable and efficient operation of systems exploiting the properties of bulk liquid organic membranes. The coupled emulsion membranes - pervaporation and multi membrane hybrid systems operating under comparable conditions, exhibit similar properties, which indicates that the difference between coupled emulsion membranes and real liquid membrane systems are about to be small. This statement can also be formulated inversely, i.e. the bulk liquid membrane systems (with flowing or agitated liquid membrane) show features of coupled emulsion membranes.

The continuous removal of water from an organic liquid membrane phase can be realized after coupling the emulsion membranes or pertraction to a pervaporation process.

Emulsion membrane-pervaporation and pertraction-pervaporation processes have the potential to provide many economical and operational advantages such as: no carrier or solvent losses, no phase mixing, long lifetime and very simple technical equipment.

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