

TRANSPORT AND SEPARATION OF Zn(II) AND Cu(II) IN AN AGITATED BULK LIQUID MEMBRANE

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Abstract

Pertraction of Zn(II) and Cu(II) ions from binary solutions across a bulk liquid membrane (BLM) containing di(2-ethylhexyl)phosphoric acid (D2EHPA) as the carrier was investigated. The influence of the pH, D2EHPA concentration, feed and stripping phase concentration was evaluated. The enhancement of the separation effects in unsteady state pertraction of Zn(II) was observed.

1. INTRODUCTION

The application of liquid membranes is an important alternative to the standard processes of wastewater treatment or separation and recovery of metal cations. LM is composed of an organic liquid phase placed between two aqueous phases. Concentration of the feed and stripping solution, carrier concentration and the type of organic solvent are the most important factors influencing the pertraction process.

Organophosphorous compound, such as D2EHPA, have been widely used as the extraction agent (carrier) in transport and separation of a number of metals such as Zn(II), Cu(II), Co(II), Ni(II), Cd(II), etc. [1-3]. The separation of Zn(II)/Cu(II) cations has been investigated by many researchers because of great importance to hydrometallurgy and environmental protection [3-7].

The aim of this study was to investigate the influence of the carrier (D2EHPA) concentration, feed and stripping concentration and pH of the feed phase on transport and separation of Zn²⁺ and Cu²⁺ cations in BLM with D2EHPA as the carrier in non-stationary conditions.

2. EXPERIMENTAL

The experiments were performed in a beaker-in-beaker type pertractor at 25°C (Fig. 1). The experimental device consisted of two concentric beakers, containing the feed solution (external beaker) and stripping solution (internal beaker). Volumes of the feed (solution of Zn²⁺ and Cu²⁺ nitrates), organic (D2EHPA in kerosene) and stripping phases (sulfuric acid

solution) were 125, 30, 25 cm³, respectively. The membrane contacting area was 16.45 cm² (f/LM interface) and 5.8 cm² (LM/s interface). The solutions were agitated with a glass stirrer (LM) at 375 rpm and magnetic stirrer (the feed and stripping solution) at 150 rpm. The concentrations of metals in the feed and stripping solutions were determined by a Varian 20-ABQ absorption spectrophotometer.

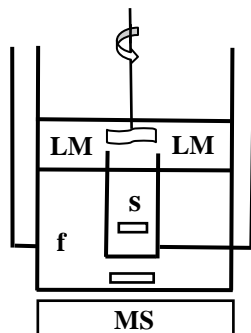


Fig. 1. Scheme of experimental bulk liquid membrane (BLM), f - feed solution, LM-liquid membrane, s-stripping solution, MS-magnetic stirrer

3. CALCULATIONS

Under the experimental conditions studied, non-stationary pertraction of Zn(II) was observed. Therefore, nonlinear equation was applied for fitting the experimental results:

$$c(t) = (a \cdot b + c \cdot t^d) (b + t^d)^{-1} \quad (1)$$

The flux of Zn(II), $J(t)$ was then calculated by differentiating the curve-fit functions, Eq. (1):

$$J(t) = \frac{V}{A} \cdot \frac{dc(t)}{dt} \quad (2)$$

where V denotes volume of the stripping solution, A – the interphase contact area. The plot of $J(t)$ vs. t corresponding to Zn(II) pertraction exhibits a maximum characterized by J_{max} . The stripping phase concentrations of Cu(II) ($[M]_{s,Cu}$) was used for calculating the amount of species transported effectively from the feed to the stripping phase after the time t :

$$Q = \frac{[M]_{s,Cu} \cdot V_s}{1000 \cdot A_s} \quad [\text{mol/cm}^2] \quad (3)$$

where V_s denotes the volume of the strip solution, A_s denotes the output membrane area (cm^2). In the case of a linear relationship Q vs. t , the transport was considered as quasi-stationary, and respective fluxes were calculated as:

$$J_{\text{Cu}} = \Delta Q / \Delta t \quad [\text{mol}/\text{cm}^2\text{s}] \quad (4)$$

4. EXPERIMENTAL RESULTS

The effect of the feed phase concentration (0.005 M-0.1 M) on the pertraction of Zn(II) and Cu(II) cations is presented in Fig. 2. Under these experimental conditions it was observed that the fluxes of Zn(II) are higher than the fluxes of Cu(II). An increase in the feed concentration causes an increase of Zn(II) fluxes and decrease in Cu(II) fluxes. This effect was interpreted elsewhere by Juang [4] in this way that decreasing of J_{Cu} at higher feed concentrations region is caused by much higher distribution ratio of Zn(II) than Cu(II) cations (at the F|LM interface). Also, for the extraction of Cu(II) in the system with D2EHPA a decrease of distribution coefficient of Cu(II) with increasing initial concentration was observed [8].

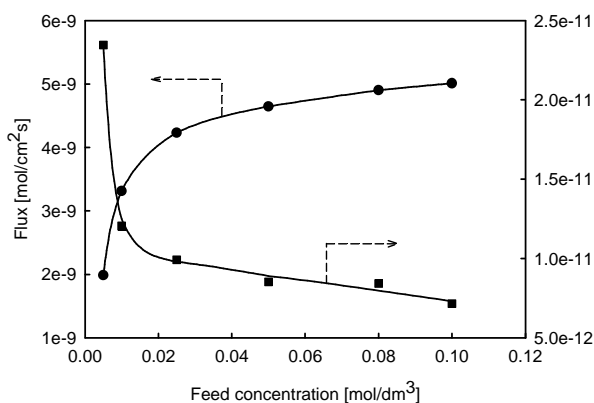


Fig. 2. Dependence of Zn^{2+} and Cu^{2+} fluxes on the feed phase concentration in BLM with 0.1 M D2EHPA as a carrier

Results in Fig.3 indicate that the flux of Zn(II) and Cu(II) increases with an increase of pH of the feed phase. In the case of low pH of the feed solution, the pertraction is governed by diffusion of complex in the membrane, and to some degree by an equilibrium distribution of transported species at the feed/membrane interface [9].

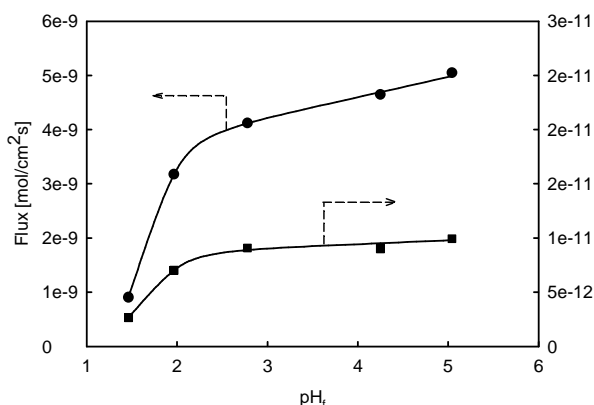


Fig. 3. Effect of pH in the feed phase on the fluxes of Zn^{2+} and Cu^{2+} in BLM with 0.1 M D2EHPA as a carrier

The influence of H_2SO_4 concentration in the stripping phase was studied at the concentration range from 0.05 to 1 M. Under the conditions, an increase of J_{Zn} with increase of acid concentration in the stripping solution was observed. This effect results from an increase of the driving force for the pertraction.

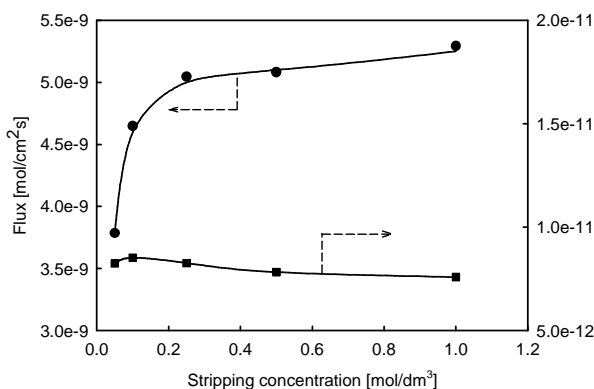


Fig. 4. Fluxes of Zn^{2+} and Cu^{2+} in BLM system with D2EHPA as carrier, at different H_2SO_4 concentration in the stripping phase

Fig. 5 shows the effect of the feed D2EHPA concentration on J_{Zn} and J_{Cu} . The flux of Zn(II) and Cu(II) increases with increasing in the carrier concentration. Moreover, the fluxes reach a plateau in the region of which the pertraction process is controlled by diffusion of metal ions in the feed solution [4]. The transport properties of the liquid membrane itself become

more important in the case of lower D2EHPA concentrations. The largest difference between J_{Zn} and J_{Cu} was observed for 0.01 M D2EHPA.

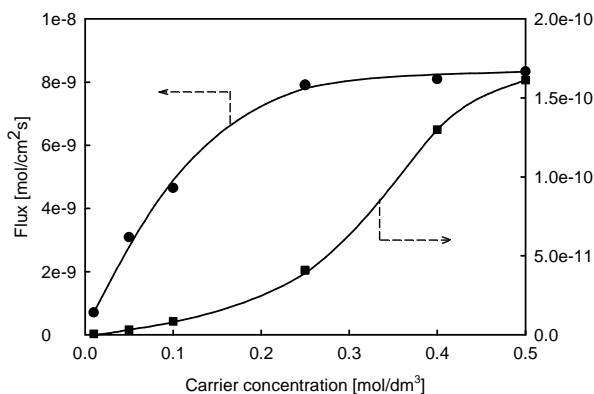


Fig. 5. Dependence of Zn^{2+} and Cu^{2+} fluxes on the carrier concentration in BLM with 0.1 M D2EHPA as a carrier

The extraction of Zn^{2+} and Cu^{2+} from aqueous solution with D2EHPA can be expressed as follows [4]:



where $n=1$ for Zn^{2+} and 2 for Cu^{2+} . Overbars refers to the organic phase. The selectivity of Zn^{2+} over Cu^{2+} in extraction can be defined as [5]:

$$\beta_1 = D_{Zn}/D_{Cu} = 2.14 \cdot 10^3 \overline{(HR)}_2^{-1/2} \quad (5)$$

where D denotes a distribution ratio. A change of the monomeric D2EHPA concentration from 0.01 - 0.5 M lowers the value of β_1 decreases from 957 to 135. These values are much higher than the ratio of J_{Zn}/J_{Cu} in the steady state pertraction through a supported liquid membrane [4]. Higher values of the ratio of J_{Zn}/J_{Cu} for concentration of D2EHPA below 0.25 M, were observed in the case of studies presented herein (non-stationary conditions for Zn(II) transport).

5. CONCLUSIONS

The influence of various experimental parameters on the transport and separation of Zn(II) and Cu(II) was evaluated. Zn(II) can be effectively transported and separated through a bulk liquid membrane containing D2EHPA as the carrier. The increase of the carrier concentration in the liquid membrane phase, counter-ion concentration in the stripping phase, concentration and pH of the feed solution led to an increase in flux of Zn(II). Under the conditions, it was found that a higher selectivity in the

separation of Zn(II) over Cu(II) can be obtained for high feed concentration (and $\text{pH} \approx 5$), stripping phase concentration of 0.25 M and low D2EHPA concentration. Enhancement of the separation effects was observed for unsteady state transport of Zn(II) in BLM,

REFERENCES

- [1] M. Resina, J. Macanas, J. de Gyves, M Munoz, *J. Membr. Sci.*, 2006, 268, 57.
- [2] R.-S. Juang, *J. Membr. Sci.*, 1993, 85, 157.
- [3] R.-S. Juang, J.-D. Jiang, *Sep. Sci. Technol.*, 1994, 29(2), 223.
- [4] R.-S. Juang, *Ind. Eng. Chem. Res.*, 1993, 32, 911.
- [5] R.-S. Juang, H.-Ch. Huang, *J. Membr. Sci.*, 1999, 156, 179.
- [6] R.-S. Juang, H.-L. Huang, *J. Membr. Sci.*, 2002, 208, 31.
- [7] R.-S. Juang, H.-L. Huang, *J. Membr. Sci.*, 2003, 213, 125.
- [8] S. Raharimalala, E. Nakache, G. Cote, *J. Chim. Phys.*, 1995, 92, 1286.
- [9] P. Plucinski, W. Nitsch, *J. Membr. Sci.*, 1988, 39, 43.