

Modelling of mass transfer of Zn^{2+} through supported liquid membranes (SLM)

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Abstract

Research on mass transfer in liquid membrane permeation has still left some challenging aspects to be solved. Although discussed very intensively the published models are rarely comparable and suffer from a lack of accuracy.

The program was started with research on the widely investigated and very common test system Zn^{2+}_{aqu} / Bis(2-ethylhexyl) phosphoric acid/ sulphuric acid. Based on the experimental investigation and the modelling of mass transfer in liquid/liquid extraction the target of this project has been detailed analysis of mass transfer through rigid membranes.

Besides variation of the chemical potential the influence of the composition of the mobile solvent phase on mass transfer has been determined. Several transport properties such as composition dependence of the dynamic viscosity of the solvent phase have been recorded. For modelling of the experiments an analytical model with consideration of transport and thermodynamic properties has proven advantageous over several mass transfer models.

1 Introduction

Liquid membranes have been investigated since more than 30 years and various types of applications have been proposed. Although liquid membranes are highly efficient, difficult handling and stability of liquid membranes have yet hindered successful industrial application.

Competing technologies such as precipitation or solvent extraction are not satisfying either and do suffer from different problems and limitations as well. Recent developments of new base materials and new ways of configuration allow new approaches in application of liquid membranes and offer the possibility of feasible application. Target of this project is to investigate mass transfer through supported liquid membranes and to develop appropriate tools for process and plant design.

2 Experimental Methods and Analyses

2.1 Membrane module

Investigation of mass transfer was carried out in a circular cell separated into two compartments with the membrane. The mass transfer area of the membrane was $1.38 \cdot 10^{-3} \text{ m}^2$. Membrane thickness was $100 \text{ }\mu\text{m}$ at a porosity of $\varepsilon=0.25$.

As shown in Figure 1 each compartment was equipped with a flow barrier in the center. The size of the barrier was evaluated through CFD optimization. The membrane was stabilized with the framed gasket and the central flow barrier. Correspondingly a very narrow velocity distribution of both electrolytes without dead zones was available for mass transfer experiments.

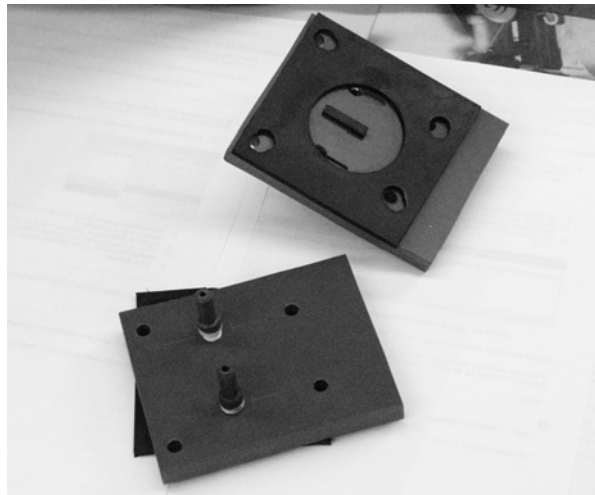


Figure 1: Membrane module

The membrane was prepared by impregnating PTFE base material of 25% porosity and a pore size of $45 \text{ }\mu\text{m}$ with solvents of different composition by evacuation of the base material and saturation with solvent during pressurization.

2.2 Chemicals

The feed solution was prepared by dissolving zinc sulfate of 99.5% purity (Merck, No 108883) in distilled water. For preparing the membrane bis(2-ethylhexyl) phosphate (Merck, No 814181) of 98% purity was dissolved in the diluent dodecane (Aldrich, No 489131) of 99% grade. The strip phase was prepared with distilled water and sulfuric acid (Roth, No 4623.5) of 95 % purity.

2.3 Apparatus and procedure

The experiments were carried out in the batch mode. Both electrolytes, the feed phase and the strip phase, were fed into the corresponding membrane chamber with a peristaltic pump. The extract phase and the raffinate phase exited the membrane module on top and were discharged into the corresponding storage tanks again to provide a batch electrolyte loop for each phase. The experimental setup is shown in the schematic of figure 2. The schematic also shows the sensors for temperature, flow rate and pH-value.

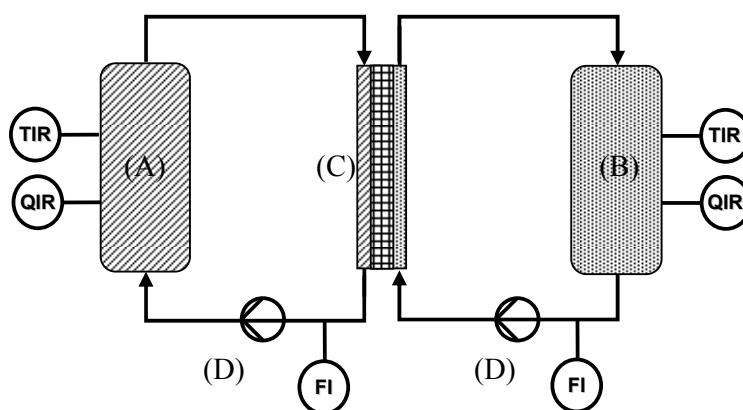


Figure 2: Schematic of the experimental set up: (A) feed vessel, (B) strip vessel, (C) membrane module with membrane, (D) peristaltic pumps; Sensors: FI (flow indicator), TIR (temperature indicator and recorder) , QIR (pH value indicator and recorder)

In order to minimize (exclude) concentration gradients in the boundary layer of the electrolyte and the membrane the shear rate was optimized prior to performing the measurement series by increasing the flow rate of both electrolyte loops. As shown in Figure 4 rate of mass transfer was constant above pump rates of >35%.

Thus it was concluded that the resistance of the boundary layers was to neglect above this rotational speed and advancing it was decided to operate the pumps at maximum speed to avoid influences of the aqueous phases.

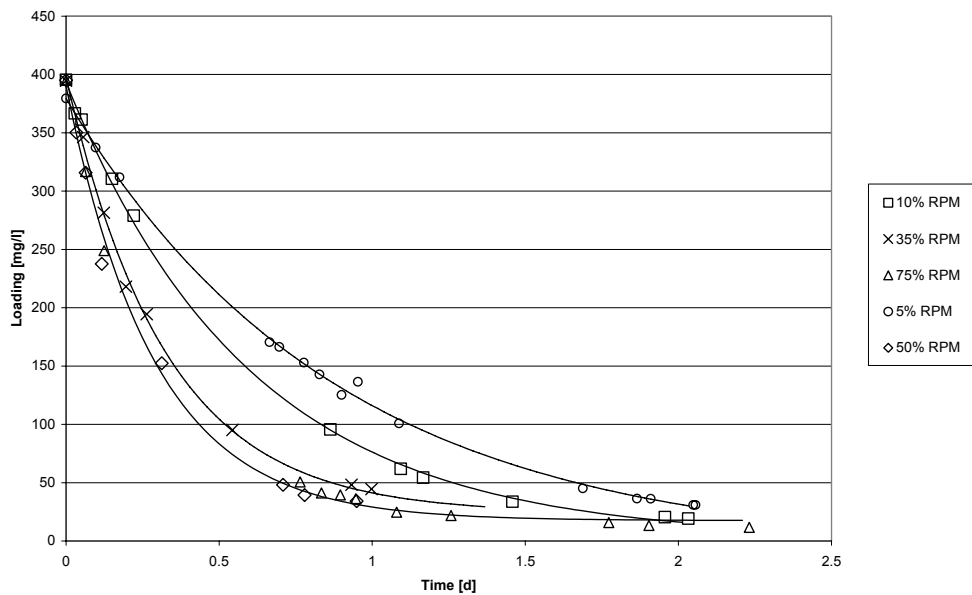


Figure 3: Influence of the pump rate on mass transfer

Mass transfer experiments were performed for several concentration levels of the aqueous feed phase, the organic membrane phase and the aqueous strip phase. During each experiment samples of the extract loop and the raffinate loop were collected for analysis. Analysis was carried out by atomic absorption spectroscopy with a Perkin Elmer AAS, model 5100. Zinc absorption was recorded at wavelength $\lambda = 210 \text{ nm}$.

3 Modeling of mass transfer

The basic idea behind industrial application of liquid membranes is the advantage of combined extraction and reextraction. The process schematic of the process is shown in Figure 4. Number III indicates the raffinate phase, number II indicates the membrane phase and number I indicates the extract (or strip) phase. Further Figure 4 schematically shows the concentration levels of Zn^{2+} and H^+ in both aqueous phases and the concentration gradient of Zn^{2+} in the membrane phase. The driving force for mass transfer of zinc from the raffinate phase into the extract phase is qualitatively indicated by the concentration difference of H^+ between phase I and phase III.

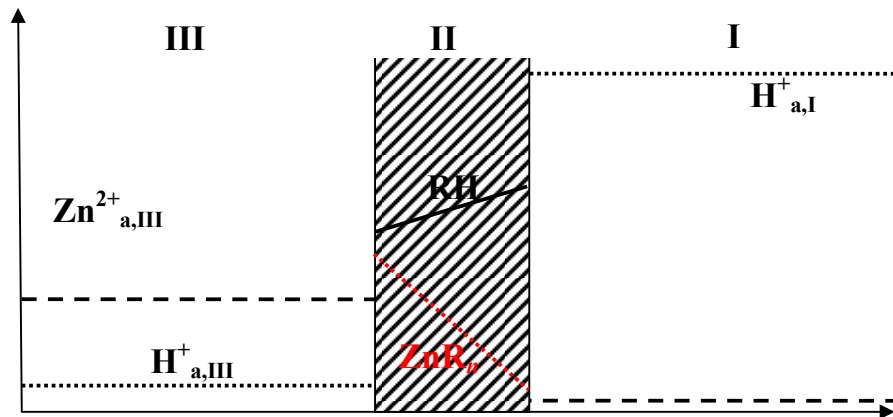


Figure 4: Mass transfer model

At both interfaces, interface II-III and interface II-I Zn^{2+} undergoes ion exchange with the solvent according to equation 1. The laden solvent is forced to diffuse through the membrane due to the difference of the chemical potential between phase I (extract phase) and phase III (raffinate phase). At the strip interface I-II the laden solvent undergoes ion exchange in the reverse direction according to equation 1 again.



In equation 2 the equilibrium constant K according to the Law of Mass Action is mentioned

$$K = \frac{\gamma_{ZnR} \cdot [ZnR_n]_o \cdot \gamma_H^n \cdot [H^+]_a^n}{\gamma_{Zn} \cdot [Zn^{2+}]_a \cdot \gamma_{RH}^n \cdot [RH]_o^n} \quad (2)$$

The concentration profile in the membrane at equilibrium can be considered as independent from diffusion coefficients and the concentration profile across the membrane can be assumed to be linear [1]. The boundary conditions are not determined by mass transfer but by the surrounding fluids.

Therefore modeling of mass transfer can be based on Fick's 1st law:

$$\dot{J} = k \cdot \varepsilon \cdot A \cdot \Delta c \quad (3)$$

The governing concentration difference of the laden solvent can be written as

$$\Delta c = [ZnR_n]_{o,II-III} - [ZnR_n]_{o,II-I} \quad (4)$$

Unfortunately the interface concentrations II-III_o and II-I_o at the membrane are not accessible, but supposing an excess of acid in the strip phase the carrier concentration at the interface II-I_o can be neglected as far as mass transfer is far off equilibrium.

$$\Delta c = [ZnR_n]_{o,II-III} \quad (5)$$

Under the same conditions it can be considered that the distribution of zinc between the two phases is constant as the concentration of complexed carrier is very low due to the excess of carrier (5 times the concentration of zinc). With the rearrangement of equation 2 according to equation 6 and

$$k_{equ} = \frac{[ZnR_n]_{o,II-III}}{[Zn^{2+}]_{a,III}} = K \frac{[RH]^n}{[H^+]^n} \quad (6)$$

combination of equations (3) and (6) to the solute flux can be expressed in terms of solute concentration in phase III as expressed in equation (7).

$$\dot{J} = k \cdot \varepsilon \cdot A \cdot k_{equ} \cdot [Zn^{2+}]_{a,III} \quad (7)$$

Equation (7) combines two constants, the mass transfer coefficient k and the equilibrium constant k_{equ} . Both constants can not be determined independently and they are summarized in the permeation coefficient k_{π} [2] as expressed in equation (8).

$$J = k_{\pi} \cdot \varepsilon \cdot A \cdot [Zn^{2+}]_{a,III} \quad (8)$$

4 Results and Discussion

As expected from equation 8 proportional dependency of solute flux and zinc concentration in the raffinate phase can be observed. Figure 6 shows the result of several tests. Parameter of these tests was the concentration of the carrier DEHPA.

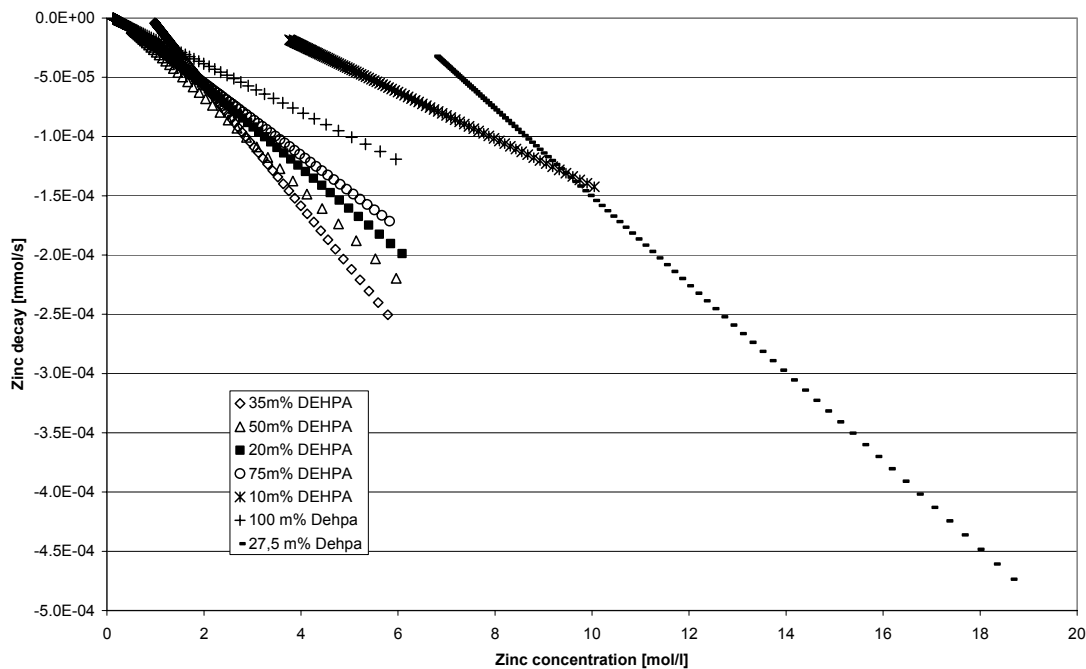


Figure 5: A dependency of the Zinc decay to the zinc concentration in the feed phase can be observed; parameter: DEHPA content of the diluent n-dodecane

According to equation 8 the permeation coefficient k_{π} can be calculated from the slope of the graphs shown in Figure 5.

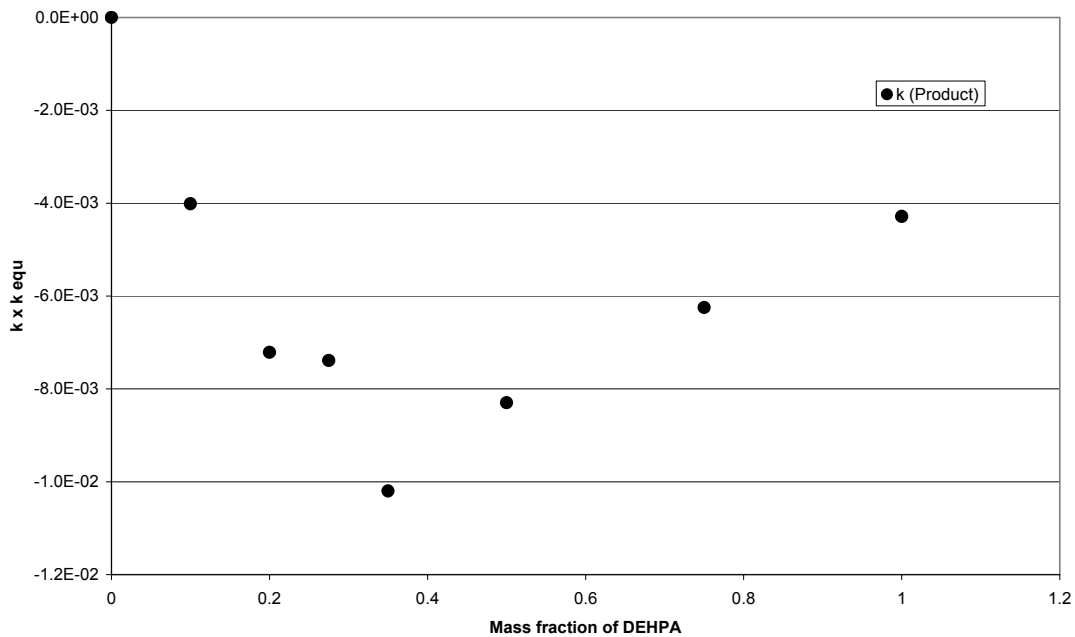


Figure 6: Dependency of k_{π} on the DEHPA content of the solvent

At low DEHPA content of the solvent mass transfer is limited by the DEHPA content. After passing a maximum mass transfer is increasingly limited by the transport properties.

4 Summary

Mass transfer of Zn^{2+} through plane supported liquid membranes was investigated. For that purpose a mass transfer cell was constructed and tested. From preliminary investigation of mass transfer the optimum operation conditions were deduced.

Finally the influence of the solvent composition on mass transfer was investigated and modeled. The apparent mass transfer coefficient, deduced from experiments passes a maximum at specific solvent composition.

References

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