BOND-GRAPH DESCRIPTION AND SIMULATION OF MEMBRANE PROCESSES: HYBRID PERTRACTION IN MULTIMEMBRANE SYSTEM

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Abstract

Thermodynamic network analysis (TNA) was applied for modeling and theoretical description of the hybrid pertraction of univalent cations in the multimembrane hybrid system (MHS). Some numerical calculations were carried out to describe the evolution of the transport systems as dependent on the initial conditions for pH, aqueous solutions concentration, and the carrier (D2EHPA) concentration in a liquid membrane. The results of the theoretical calculations were experimentally verified.

1. INTRODUCTION

The subject of this investigation was the hybrid pertraction (HP) of univalent cations occurring in the multimembrane hybrid system (MHS) composed of two polymer cation-exchange membranes (CEMs) and a liquid membrane placed between. [1-3]. The transport mechanism involves a series of coupled cation exchange-diffusion processes in CEMs and counter transport of cations as mediated by the ionic carrier

A fundamental description of this process can be formulated in the framework of the thermodynamic network analysis after taking into consideration all the specific physicochemical and phenomenological relationships that govern the membrane phenomena. The network of the local fluxes and capacitances (based on the bond-graph approach) allows the formulation of a relevant mathematical description of the time-evolution of all the concentrations resulting from the operation of MHS system. Having assumed or measured model parameters and experimental transport conditions, the mathematical model was numerically solved using the Berkeley Madonna (ver.8.0.1.) solver of ordinary differential equations.

The results of model calculations of the transport characteristics as dependent on the initial conditions for pH, the aqueous solutions concentrations, and the carrier concentration in a liquid membrane were compared with the corresponding experimental results.

2. EXPERIMENTAL

The experiments were performed with the organic phase composed of D2EHPA (di(2-ethylhekxyl)phosphoric acid) dissolved in kerosene, the aqueous solution of KNO_3 and H_2SO_4 as the feed and stripping phase, respectively, and Nafion 117 cation-exchange polymer membrane (CEM).

3. RESULTS AND DISCUSSION

3.1. Experimental verification of the numerical calculations

The comparison of numerical calculations with the experimental data for a typical dependence of K^+ concentration in the feed and stripping solution vs. time of transport is presented in Fig.1.

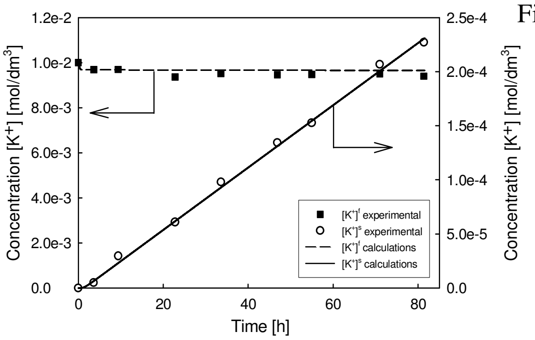

Fig.1. Experimental and calculated dependence of K^+ concentration in feed and stripping solution on pertraction time; feed soln.: 0.01 mol KNO_3/dm^3, $pH_{f,t=0}$ =5.9; stripping soln.: 1mol H_2SO_4/cm^3; liquid membrane: 0.1 mol D2EHPA /dm^3 of kerosene.

The results in Fig.1 indicate good accordance of experimental and calculated pertraction characteristics. Under the studied conditions, the pertraction exhibits an apparent pseudo-stationary course represented by a linear dependence of K^+ concentration vs. time dependence.

3.2. The effect of feed solution concentration

To evaluate the effect of the feed solution concentration on K^+ output fluxes, the pertraction processes with KNO_3 feed concentration ranging from 0.005-0,2 mol/dm^3 were carried out. The results of experiments and corresponding model calculations are presented in Fig.2 as the plots of maximum output fluxes on the feed concentration.

The plots in Fig.2 have typical nonlinear shapes similar to that observed for hybrid membrane extraction. [4]. They can be considered as a fragment of a hyperbolic dependence which is observed for consecutive reaction-diffusion phenomena. However, the effectiveness (maximum rates or fluxes) of HME and HP is lower in the case of HP. This is caused by an additional stripping cation exchange membrane and large volume of the bulk liquid membrane used which slow down the overall process.

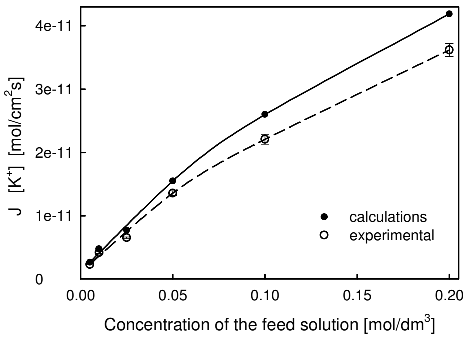

Fig.2. Experimental and calculated dependence of maximum output fluxes on the feed concentration; stripping soln.: 1 mol H_2SO_4/dm^3, liquid membrane: 0.1 mol D2EHPA/dm^3, feed $pH_{f,t=0}$ =5.9.

3.3. The effect of feed pH

The feed phase pH is another factor influencing the rate of hybrid pertraction in a multimembrane hybrid system because of D2EHPA properties. The experiments and calculations were carried out for $pH_{t=0}$ changed in the interval 2.42÷5.89 and constant initial KNO_3 concentration equal to 0.01 mol/$dm^{3.}$ The results of this investigation are presented in Fig.3.

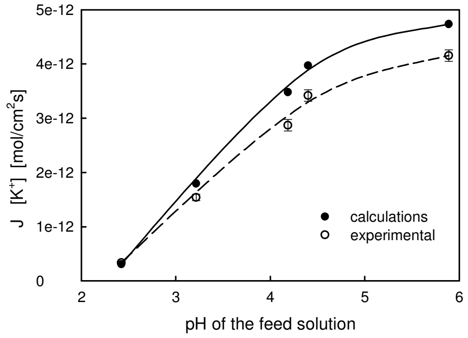

Fig.3. Experimental and calculated dependence of maximum output fluxes on feed pH; stripping soln.: 1mol H_2SO_4/dm^3; liquid membrane 0.1 mol D2EHPA/dm^3.

The results in Fig.3 indicate that typically for the membrane systems with D2EHPA as the carrier, the fluxes increase with an increase in the feed pH.

3.4. The effect of carrier concentration in liquid membrane

The carrier concentration is one of main factors which determine the pertraction effectiveness. To evaluate this effect experimentally and theoretically, the investigation of the pertraction with the liquid membrane containing D2EHPA of the concentration from 0.05 to 0.7 mol/dm^3 was carried out. The corresponding results are presented in Fig.4.

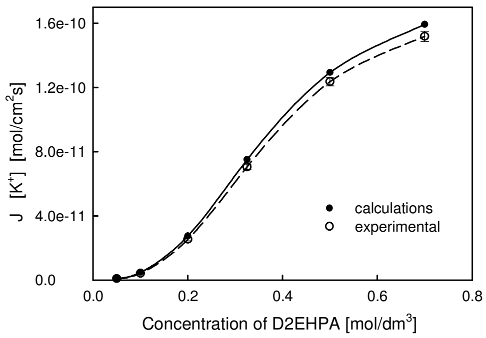

Fig.4. Experimental and calculated dependence of K^+ maximum output fluxes on D2EHPA concentration in liquid membrane; feed soln.: 0.01 mol KNO_3/dm^3, feed $pH_{f,t=0}$ =5.9; stripping soln.: 1 mol H_2SO_4 /dm^3.

The plots in Fig.4 indicate very good accordance of experimental and calculated curves. The curves themselves are typical for this kind of dependence and exhibit a tendency to saturate fluxes when feed concentration increases.

3.5. The effect of stripping solution concentration

To verify the effect of the stripping solution on the output fluxes in MHS, the hybrid pertraction processes were carried out using feed solutions of the H_2SO_4 concentration varying in the range: 0.01÷2 mol/dm^3. These concentrations are equivalent to the hydronium cations concentration range of 0.0165÷2.15 mol/dm^3. The results of the experiments and calculations are presented and compared in Fig.5.

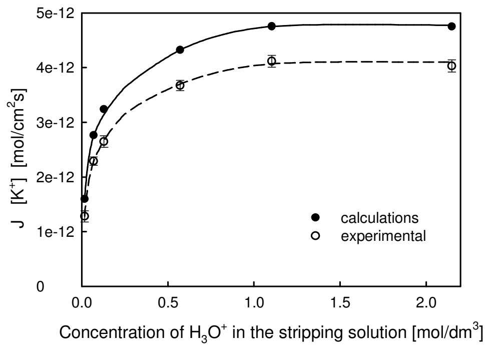

Fig.5. Experimental and calculated dependence of K^+ maximum fluxes on the stripping solution concentration; feed soln.: 0.01 mol/dm^3 KNO_3, feed $pH_{f,t=0}$ =5.9; liquid membrane: 0.1 D2EHPA mol/dm^3

The experimental and calculated dependencies in Fig.5 exhibit saturation of output fluxes typical for liquid membrane systems. Under the studied conditions, this effect appears for H_2SO_4 concentration exceeding 1 mol/dm^3.

4. CONCLUSIONS

The results of network modeling and respective numerical calculations indicate that it is possible to generate the behavior of the multimembrane hybrid system being qualitatively comparable with that observed experimentally. The applied methods of pertraction modeling can be used for prediction of fluxes in the multimembrane hybrid system as dependent on initial conditions, pH, and the carrier concentration in a liquid membrane.

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