BOND-GRAPH DESCRIPTION AND SIMULATION OF MEMBRANE PROCESSES: HYBRID MEMBRANE EXTRACTION

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Abstract

The bond-graph method was applied to study the hybrid membrane extraction, which occurs in the system with an ion-exchange polymer membrane placed between an aqueous and organic liquid phase. The numerical calculations were carried out to describe the time evolution of the transport systems as dependent on initial conditions for pH and the aqueous solution concentration as well as the carrier concentration in a liquid membrane. The results of the numerical calculations were compared with the experimental results.

1. INTRODUCTION

The classic, common methods of dispersive liquid-liquid extraction are affected by various inconvenient phenomena due to water uptake, loss of active components, instability, short time of operation, etc. These drawbacks can be overcome by applying the non-dispersive extraction with the interface immobilized by a porous membrane [1,2]. In the case of ionic substances, this type of membrane can be replaced by dense ion-exchange membrane which leads to the system of the hybrid membrane extraction (HME) [3,4]. Ion-exchange membranes (IEM) are expected to mediate the extraction occuring as the ion-exchange processes between the external aqueous solution and the reactive extractant (liquid ion-exchanger-specific reagent dissolved in the organic phase).

The hybrid membrane extraction can be theoretically studied by a quantitative description of the involved processes by thermodynamic network analysis (TNA) with the formalism of the bond-graph method [5]. On this basis, the mathematical model in the form of a set of ordinary differential equations was proposed and used for calculating the evolution of local concentrations and fluxes. Having assumed model parameters and experimentally estimated transport conditions, the mathematical model was numerically solved using the Berkeley Madonna (ver.8.0.1.) program. The numerical calculations were carried out to describe the time evolution of the transport systems as dependent on the initial conditions for pH and the

aqueous solution concentration as well as the carrier concentration in a liquid membrane. To verify the model correctness and applicability, the calculations were compared with the experimental results.

2. EXPERIMENTAL

The experiments were performed in the system with the Nafion-117 (17 cm^2) cation-exchange polymer membrane (CEM) separating the aqueous solution of KNO_3 (1000 cm^3) and the organic phase (50 cm^3) composed of D2EHPA (di(2-ethylhexyl)phosphoric acid) dissolved in kerosene. In the system, extracted cations are transported by cation exchange groups in the polymer membrane and then desorbed into the organic phase by a liquid exchanger (extractant).

3. RESULTS AND DISCUSSION

3.1. EXPERIMENTAL VERIFICATION OF THE NUMERICAL CALCULATIONS

The comparison of theoretically calculated and typical experimental dependence of the concentration $[K]^{oc}$ of extracted K^+ cations in the organic phase (in the form of $CK \cdot 3(CH)$ complex) vs. time of transport is presented in Fig.1a-b. The results correspond with the organic containing D2EHPA of the concentration equal to 0.01 or 0.325 mol/dm^3, respectively. The first dependence (Fig.1a) exhibits a maximum of experimental concentrations which can be ascribed to the system changes caused by the osmotic permeation of water. In the second case (Fig. 1b) a regular, typical extraction curve with the concentration $[K]^{oc}$ attaining an equilibrium was observed.
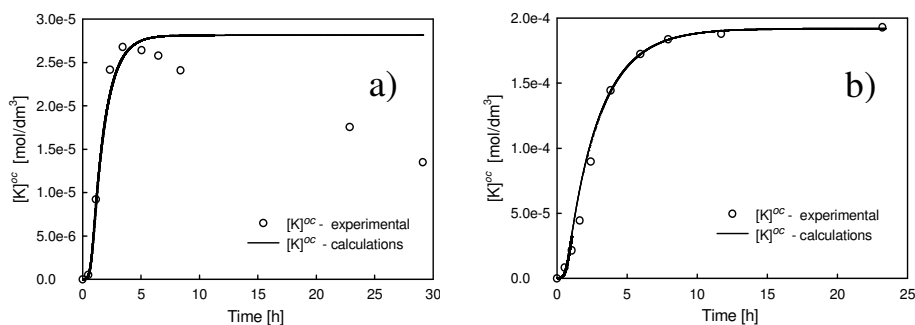

Fig.1. Concentration of K^+ - D2EHPA complex in organic phase *vs.* time of extraction; concentration of the aqueous phase: 0.01 mol KNO_3/dm^3, pH=5.95, concentration of D2EHPA in the organic phase: (a). 0.1 and (b). 0.325 mol/dm^3 Continuous lines were calculated by respective TNA model.

In order to verify the hypothesis concerning negative influence of water uptaken into the organic phase on the HME efficiency, an additional experiment with the same system but with water pervaporation (PV) from the organic phase was carried out. The results in Fig.2 indicate that the HME-PV system exhibits a regular shape typical for the extraction kinetics curves. This means that osmotic permeation of water can diminish equilibrium concentration of extracted species, although the maximum of extraction rates in the HME and HME-PV systems are comparable, i.e. 1.45 and 1.38 mol/cm^{2}s, respectively.
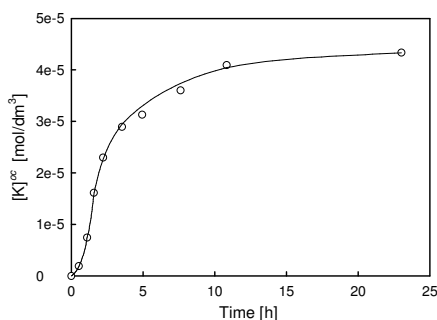

Fig.2. Extraction of K^+ into organic phase with water pervaporation: aqueous feed solution: 0.01 mol KNO_3 /dm^3; pH$_{f,t=0}$ =5.95, organic phase: 0.1 mol D2EHPA/dm^3, cation exchange membrane: Nafion-117, pervaporation membrane: Nafion-120.

3.2. INFLUENCE OF FEED CONCENTRATION

The properties of the HME system were studied as dependent on the feed concentration with KNO_3 conc. changing in the range: 0.005-0.1 mol/dm^3 (with pH$_{f, t=0}$ = 5.95). The results of the investigation are presented in Fig.3 as a dependence of the maximum extraction rate (mol/cm^{2}s) on the initial feed KNO_3 concentration.
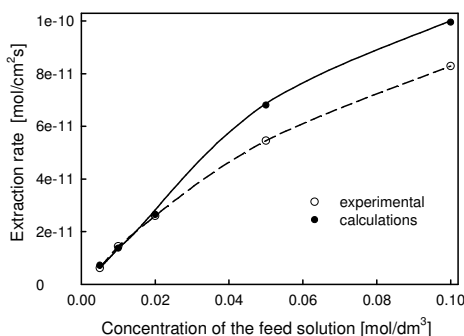

Fig.3 Experimental and theoretical (from TNA) dependence of maximum extraction rate on KNO_3 concentration in the feed solution; organic phase: 0.1 mol D2EHPA/dm^3 of kerosene; pH$_{f, t=0}$ =5.95.

It can be concluded from the plots in Fig.3 that the model calculations and experimental results coincide in the region of relatively low concentrations, i.e. up to 0.02 mol/dm^3. Qualitatively however, the both dependencies are similar and characteristic for consecutive processes.

3.3. INFLUENCE OF FEED pH

One of most frequently studied extraction property of D2EHPA is its dependence on the pH of the feed solution. Therefore, a similar investigation was carried out for the HME system using the KNO_3 feed solution of 0.01 mol/dm^3 concentration and pH ranging from 2 to 6. The corresponding results are presented and compared with the results of model calculations in Fig.4.
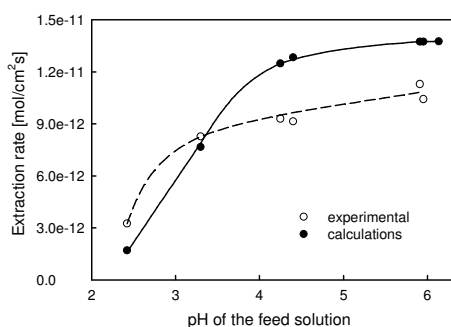

Fig.4. Dependence of maximum extraction rate on pH of feed solution: 0.01 mol KNO_3 /dm^3, organic phase 0.1 mol D2EHPA/dm^3 of kerosene.

The results of experiments and model investigations confirm that the extraction in the HME system is fast for pH_f ranging from 3.5 to 6. Below this region extraction rate significantly decreases, and for $pH_f > 6$ the formation of emulsion in the organic phase was observed.

3.4. INFLUENCE OF D2EHPA CONCENTRATION ON EXTRACTION RATE

The extraction rates in the HME system as dependent on the extractant concentration were studied. The experimental and calculated results are presented in Fig.5.
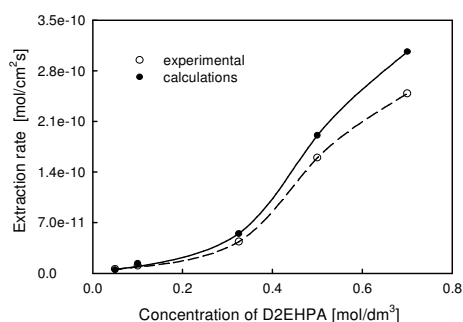

Fig.5 Dependence of maximum extraction rate on extractant concentration; feed solution: 0.01 mol KNO_3/dm^3, $pH_{f, t=0} = 5$.

From the results presented in Fig.5, one can conclude that the extraction rate in the HME system is strongly dependent on D2EHPA concentration above

0.4 mol/dm^3. For very high concentrations (0.7 mol/dm^3), an increase of the organic phase viscosity can diminish the extraction rate which is observed as convex curvature of the studied dependence.

3.5. DEPENDENCE OF DISTRIBUTION COEFFICIENTS ON REACTION CONDITION

The extraction properties of D2EHPA are known to depend on the composition of a reaction medium. However, the HME system differs from the classic one because the organic phase is not immediately contacted with the aqueous solution of the known composition but with the internal solution of the cation exchange membrane. From this reason, some calculations were carried out to correlate pH of the bulk feed solution with the local pH at the organic phase and cation exchange membrane (reaction sub-layer). The calculations were carried out for $pH_{(t=0)}^{f\,b}$ =2.4÷7 with other model constants and parameters assumed to be the same. The results of calculations are presented in Fig.6.
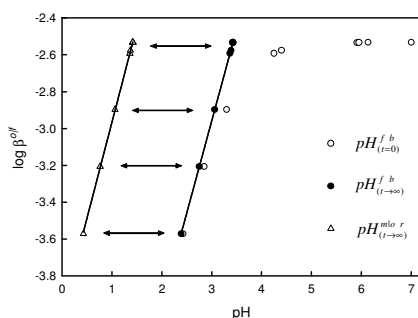

Fig.6. Dependence of K$^+$ distribution coefficient $\beta^{o|f}$ on $pH_{(t=0)}^{f\,b}$ and equilibrum $pH_{(t\to\infty)}^{f\,b}$ of feed solution and equilibrium $pH_{(t\to\infty)}^{m|o\,r}$ at the interface cation exchange membrane | organic solution m|o (model calculations).

The calculated linear dependence of $\log\beta^{o|f}$ on equilibrium $pH_{(t\to\infty)}^{f\,b}$ and $pH_{(t\to\infty)}^{m|o\,r}$ complies with a general theory and D2EHPA properties. Also, the results of calculations indicate that an increase of $pH_{(t=0)}^{f\,b}$ above 4 does not change significantly its equilibrium value $pH_{(t\to\infty)}^{f\,b}$ and respective distribution coefficients $\beta^{o|f}$. This effect seems to be caused by a stabilizing function of the acidic cation exchange membrane. The plots in Fig. 6 allow predicting the lower distribution coefficients for the HME in comparison to the classic L-L extraction because of lower pH in the reaction medium.

4. CONCLUSION

According to the results of this study, thermodynamic network analysis can be successfully exploited for the qualitative or quantitative description and prediction of the hybrid membrane extraction. For example, the results of calculations simulating the HME system properties comply with experimentally observed dependencies of extraction rates on quantities such as feed or stripping solution concentration, its pH, and the concentration of an extractant in the organic phase.

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