SIMPLE KINETIC ANALYSIS OF CONTINUOUS MEMBRANE EXTRACTION

Piotr SZCZEPAŃSKI and Romuald WÓDZKI

Faculty of Chemistry, Nicholas Copernicus University,
87-100 Toruń, Poland
e-mail: piotrs@chem.uni.torun.pl

INTRODUCTION

The scheme of consecutive reactions has been applied for describing the recovery of Cu^{2+} in a continuous membrane extraction (CME) process. The procedure is facilitated by an extractant/carrier dissolved in an organic phase (liquid membrane) whereas the interfacial extraction and re-extraction processes are mediated by the polymer cation-exchange membranes located between the liquid membrane and the feed (f) and stripping (s) solution respectively. The overall process can be roughly represented by a simple scheme involving irreversible reactions of the first order:

$$M_f \xrightarrow{\ k_1\ } M_{LM} \xrightarrow{\ k_2\ } M_s \tag{1}$$

In Eq.(1) M_f, $M_{LM,}$ and M_s denote the metal cation in the feed, liquid membrane (complexed by the carrier) and stripping solution respectively.

According to Eq.(1) the corresponding kinetics can be expressed by the set of first order differential equations, which after integration result in Eq.(2-4) representing the time evolution of reduced concentrations (R) [1,2] of M species in each of the system compartment (i.e. the feed, membrane system and stripping solution):

$$R_f = e^{-k_1 \cdot t} \tag{2}$$

$$R_{LM} = \frac{k_1}{k_2 - k_1}(e^{-k_1 \cdot t} - e^{-k_2 \cdot t}) \tag{3}$$

$$R_s = 1 + \frac{1}{k_1 - k_2}(k_2 e^{-k_1 \cdot t} - k_1 e^{-k_2 \cdot t}) \tag{4}$$

In Eqs.(2-3), the reduced concentrations are defined as follows:

$$R_f = C_f/C_{f,0}, \quad R_{LM} = C_{LM}/C_{f,0}, \quad R_s = C_s/C_{f,0}, \tag{5}$$

where $C_{f,0}$ is the concentration of the metal cations in the feed at the time t=0, and C_f, C_{LM}, C_s − are the time dependent concentrations of M in the particular solution.

The above phenomenological model was successfully applied to interpret the properties of several bulk liquid membranes in general [2,3], and the liquid membranes containing Acorga reagents in particular (for the Cu^{2+} pertraction processes) [1,2-4]. Therefore, we have expected the model to be feasible also in the case of the CME as a more complex system. The main goal of this investigation was to answer the question how far the CME behaves as a classic liquid membrane system by comparing the values of respective kinetic constants to those reported in the literature. On the other hand, the comparison of k_1 and k_2 can indicate which of macroscopic processes limits the overall pertraction rate in the membrane system.

EXPERIMENTAL

The experiments were performed in the CME system composed of two contactors with the cation exchange membranes (FKS FuMa Tech, Germany) and the organic phase circulating between. The organic phase (250 cm^3) was prepared from Acorga P-50 (94% 5-nonylsalicylaldoxime, Acorga Ltd.) dissolved in technical kerosene (Maker, Poland, b.p. 124-174 ^0C) to the concentration of 0.1 mol/dm^3. The liquid membrane was contacted to the cation exchange membranes of the area 200 cm^2, each. The aqueous feed solution (10 dm^3) contained Zn^{2+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, Na^+ and K^+ nitrates, each of the concentration 0.01 mol/dm^3. The sulfuric acid solution (0.5, 1, 3 mol/dm^3, 100 cm^3) has been applied as the stripping phase in the CME system.

RESULTS AND DISCUSSION

The curves representing the dependence of the metal concentrations in the feed and stripping solutions on time have been used as the primary experimental data. The respective "membrane concentrations" have been calculated using the mass balance equation. The experimental extraction and re-extraction data for Cu^{2+} are presented in Figs. 1-3. They cover the time period up to 100 hr when the process was clearly nonstationary ($dJ/dt \neq 0$). After this time (100-800 hrs) the pertraction was observed to occur as a quasi-stationary process. The dependence of Cu^{2+} reduced concentrations a liquid membrane on time takes a characteristic shape indicating the following interrelations between the extraction (J_f) and re-extraction (J_s) rates in time: $J_f > J_s \rightarrow J_f = J_s \rightarrow J_f < J_s$. These relations trivially prove that the process at its beginning stage is limited by a slow re-extraction (due to the accumulation of Cu^{2+} in the organic phase and a lack of substrates for respective stripping reaction), and after passing a maximum with instantaneous equalization of the rates, the overall process, in turn, is limited

by the slower extraction rate. This sequence has been experimentally observed as characteristic accumulation and depletion of Cu^{2+} cations in the liquid organic phase.
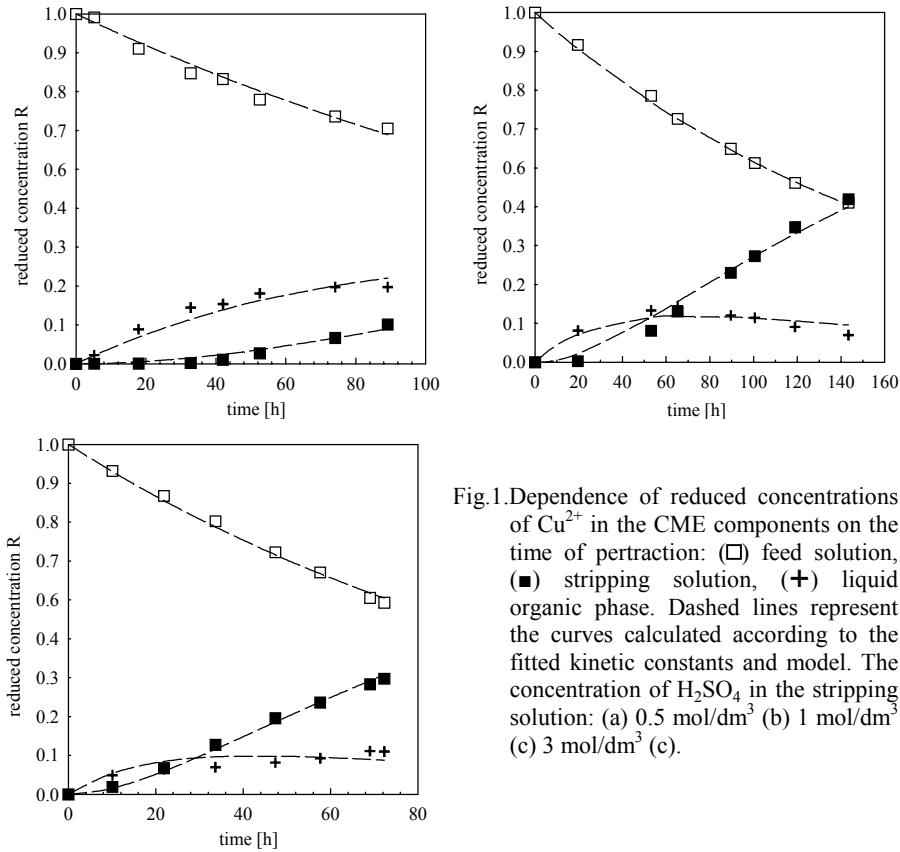

Fig.1. Dependence of reduced concentrations of Cu^{2+} in the CME components on the time of pertraction: (□) feed solution, (■) stripping solution, (+) liquid organic phase. Dashed lines represent the curves calculated according to the fitted kinetic constants and model. The concentration of H_2SO_4 in the stripping solution: (a) 0.5 mol/dm^3 (b) 1 mol/dm^3 (c) 3 mol/dm^3 (c).

The kinetic constants k_1 and k_2 were calculated by applying a non-linear regression method An additional rate constant k_{max} has been calculated from:

$$k_{max} = k_2 \cdot \left(\frac{k_1}{k_2}\right)^{-\frac{k_2}{k_1-k_2}} \qquad (4)$$

The values of particular rate constants are listed in Tab.1. The curves resulting from fitting procedure are drawn in respective figures as dashed lines. They agree sufficiently well with the experimental data giving in any case the squared correlation coefficients higher than 0.94. The results presented in Tab.2 show that the increase in the stripping solution concentration leads to the 6.5 – fold increase of the k_2 re-extraction rate constant. At the same time only 2-fold increase of the k_1 extraction rate constant was observed. These constants increase with increasing the concentration of sulfuric acid in the stripping solution and seem to be

correlated. However any independence of these apparent constants cannot be postulated because the extraction and re-extraction processes are additionally coupled by diffusion phenomena in the organic phase, which are not specified in the simple kinetic model. The assumption underlying the model calculations requires the homogeneous liquid membrane phase. However, diffusion phenomena create some gradients of concentration and the R_{LM} used for calculations is only a respective integral and the real concentrations R_{LM} at the strip and feed interface can be drastically different and time dependent [5]

Tab. 1. The apparent kinetic rate constants k_1, k_2 i k_{max} for continuous membrane extraction of Cu^{2+} as mediated by Acorga P-50

Concentration of the sulfuric acid in the stripping solution [mol/dm^3]	k_1 [s^{-1}]	r^2	k_2 [s^{-1}]	r^2	k_{max} [s^{-1}]
This work					
0.5	$1.32\pm0.14\times10^{-6}$	0.938	$2.11\pm0.19\times10^{-6}$	0.942	6.02×10^{-7}
1	$1.55\pm0.02\times10^{-6}$	0.999	$7.61\pm0.64\times10^{-6}$	0.983	1.03×10^{-6}
3	$2.27\pm0.06\times10^{-6}$	0.996	$1.37\pm0.06\times10^{-5}$	0.994	1.59×10^{-6}
Literature data					
Szpakowska et al. [6]	$1.92\text{-}2.16\times10^{-5}$		$0.87\text{-}1.61\times10^{-5}$		(BLM/kerosene)
Szpakowska [4]	1.14×10^{-4}		6.9×10^{-5}		(BLM/n-octane)
	4.16×10^{-5}		8.33×10^{-7}		(BLM/mesitylene)

The comparison of the data in Tab.1 show that the kinetic constants for the CME process are approx. one order of magnitude lower than in the case of a classic process. This is a simple consequence of slow diffusion processes in the polymer phase of the cation exchange membranes.

The kinetic constants k_1 and k_2 enabled us to calculate maximum rate of stripping (J_{max}) according to Eq.(5).

$$J_{max} = \frac{V_f}{A_s} C_{f,0} \cdot k_{max} \qquad (mol/cm^2 s) \qquad (5)$$

This rate amounts 3.77×10^{-10} mol/cm^{2}s in the case of the extraction system with 0.5 mol/dm^3 solution of H_2SO_4, and increases to 6.45×10^{-10} mol/cm^{2}s and 9.93×10^{-10} for 1 mol/dm^3 and 3 mol/dm^3 H_2SO_4, respectively. After passing this maximum the stripping rates diminish step by step to zero value due to disappearing of driving forces for the overall process. In practice the kinetic model can be exploited to optimize time and operational conditions for the CME system. The practical application of any membrane system needs of stabile and continuous working that would be acceptable from a

technological point of view. Therefore, the experiment has been prolonged in time to get an operation characteristic for 800 hrs of performance. The results presented in Fig.2 show that the kinetic model of consecutive reactions can be applied only in the first stage of the changes of Cu^{2+} concentrations in the system compartments. After gaining pseudo-stationary conditions the model based on the first order kinetic (or I-Fick's law for diffusion) is a better approximation for interpreting respective experimental data. Alternatively, a universal network-thermodynamic model generating the accumulation and depletion curves of the shape presented in Fig.2 can be applied as described elsewhere [5].
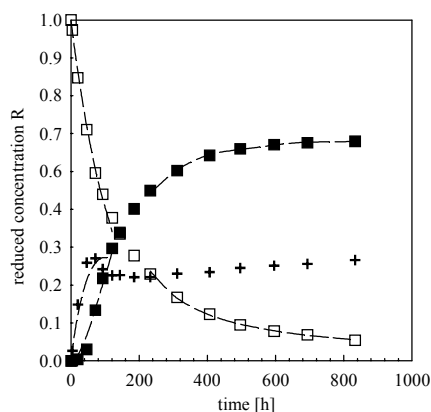
Fig.2. Long-time extraction process of Cu^{2+} in the CME system.

CONCLUSION

Taking together the results of experiments and calculations one can conclude that the simple phenomenological model represented by two adjustable parameters k_1 and k_2 is sufficient for describing Cu^{2+} pertraction phenomena, (mediated by Acorga P-50) in the continuous membrane extraction system operating under non-stationary conditions. The application of the model allows to predict time evolution of the system and to compare the system by the values of calculated kinetic rate constants. The comparison of CME with other membrane systems indicate that the presence of additional polymer membranes stabilizig the interfaces makes the interfacial processes lower by approx. one order of magnitude.

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