Pertraction of Silver through Bulk Liquid Membranes*

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Extraction equilibrium of silver for the solvent containing Cyanex 471X in a mixture of alkanes and isodecanol as both diluent and modifier in the mass ratio of 40 : 60 was studied. The value of the distribution coefficient of Ag increased with increasing concentration of the extractant in the solvent and concentration of HNO_3 in the aqueous phase, but it decreased with increasing concentration of Ag in the aqueous phase. The value of the loading of the extractant is independent of its concentration and at higher aqueous concentrations of Ag it approaches the value 0.5. This suggests the mole ratio of silver to carrier in the complex to be 1:2. The model based on this complex and the extraction constant defined on concentrations of species did not describe equilibrium data well and therefore activities of species should be used. In the present paper the transport of Ag through layered bulk liquid membranes (BLM) was studied. A simple model of the transport through the BLM to the stripping phase with diffusional resistances in series described experimental data relatively well. With increasing concentration of the carrier in the solvent, the mass flux through the extraction interface increased only 1.2 times, while the distribution coefficient of Ag increased 3.3 times. The maximum mass flux through the stripping interface was much lower (6 to 8 times) than the initial mass flux through the extraction interface. The concentration of the carrier in the solvent, concentration of HNO_3 in the aqueous phase, and composition of the stripping solution did not influence these fluxes. This suggests that the kinetics of the stripping determine the overall transport rate.

Recovery, separation or removal of metals is a frequent task in many technologies applied in hydrometallurgy and environmental protection. Solvent extraction [1, 2] and pertraction [3—6] can be employed in these applications. A carrier diluted in the organic phase forms a complex with a metal or a metallic compound well soluble in this phase. This complex could be stripped (reextracted) from the organic phase into a suitable aqueous solution containing a component decomposing the complex and/or strongly binding the metal. Pertraction combines extraction and stripping in one equipment [6]. Pertraction of silver through supported membranes was studied in works [3, 7] and through bulk liquid membrane in paper [4]. The process was carried out with the use of triisobutylphosphine sulfide (Cyanex 471X) [4, 7, 8] and macrocyclic carriers of Ag [3].

The aim of this work was to study the transport of silver across layered bulk liquid membranes from acidic nitrate solutions using triisobutylphosphine sulfide as a carrier, and related L/L equilibria.

THEORETICAL

L/L Equilibrium

Some extractants (carriers) can coextract in addition to metallic cations also anions, as it is also the case of Ag^+ cations and NO_3^- anions, extracted by sulfide extractants. The formation of the silver complexes can be described by the overall reaction scheme

$$m Ag^+ + m NO_3^- + n \overline{P} \xleftrightarrow{K_{m,n}} \overline{(AgNO_3)_m P_n} \quad (A)$$
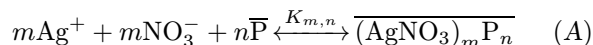
The equilibrium constant of this reaction is defined by the equation

$$K_{m,n} = \frac{[\overline{(AgNO_3)_m P_n}]}{[Ag^+]^m [NO_3^-]^m [\overline{P}]^n} \quad (1)$$

For $m = 1$ eqn (1) can be rewritten into the form

$$K_{1,n} = \frac{c_S^*}{c_F^* c_{NO_3} c_P^n} \quad (2)$$

or into the transformed form

$$\log\{Y\} = \log\{K_{1,n}\} + \log\{c_F^*\} \tag{3}$$

where

$$Y = \frac{c_S^*}{c_{NO_3} c_P^n} \tag{4}$$

The concentrations of free extractant and nitrate ions can be expressed as follows

$$c_P = c_{P,0} - n c_S^* \tag{5}$$

$$c_{NO_3} = (c_{NO_3})_0 - c_S^* \tag{6}$$

where $(c_{NO_3})_0$ is the initial concentration of NO_3^- in the feed phase. Eqn (3) is a basis for the statistical analysis of the model with the suggested chemism of the complex formation ($m = 1$). Thus the slope estimated from the correlation of experimental data by eqn (3) should be equal to one. The partition of silver between the aqueous and organic phases is characterized by the distribution coefficient

$$D = \frac{c_S^*}{c_F^*} \tag{7}$$

The loading of the extractant, the number of the permeant ions or molecules per one molecule of the extractant, is defined by the relationship

$$z = \frac{c_S^*}{c_{P0}} \tag{8}$$

where c_{P0} is the initial (overall) concentration of the extractant.

Transport through a Bulk Liquid Membrane

A simple model, considering only diffusional resistances in series and a constant volume of all phases [9], was used for the modelling of time courses of mass concentrations of Ag in all phases in pertraction through layered bulk liquid membranes

$$\frac{d\rho_F}{dt} = -\frac{k_F k_M A_F (D\rho_F - \rho_M)}{V_F(k_F + k_M D)} \tag{9}$$

$$\frac{d\rho_M}{dt} = \frac{k_F k_M A_F}{V_M}\left[\frac{D\rho_F - \rho_M}{k_F + k_M D}\right] - $$
$$- \frac{k_M A_R}{V_M}(\rho_M - \rho_{MR}) \tag{10}$$

$$\frac{d\rho_R}{dt} = \frac{k_M A_R}{V_R}(\rho_M - \rho_{MR}) \tag{11}$$

where k_F and k_M are individual mass-transfer coefficients in the feed and membrane phases. The concentration of Ag in the membrane phase was calculated from the mass balance

$$\rho_M = \frac{V_{F0}\rho_{F0} - V_F\rho_F - V_R\rho_R}{V_M} \tag{12}$$

The value of the distribution coefficient was estimated from the empirical eqn (15). The concentration of the permeant in the membrane at the stripping interface, ρ_{MR}, is supposed to have a value close to zero because of a strong action of the reagent in the stripping solution and effective decomposition of the complex.

The initial mass flux of acid through the extraction interface, which is also the maximum one, and the maximum mass flux of acid through the stripping interface were estimated from the following equations

$$J_{F0} = -\frac{V_F}{A_F}\left(\frac{d\rho_F}{dt}\right)_{t=0} \tag{13}$$

$$J_{Rmax} = \frac{V_R}{A_R}\frac{d\rho_R}{dt} \tag{14}$$

where the values of derivatives were estimated from empirical functions correlating experimental data. The second-order polynomial relationship was used to describe the time course ρ_F in the initial period, whereas a linear approximation was applied for the evaluation of the maximum time derivative of ρ_R.

EXPERIMENTAL

Chemicals

Triisobutylphosphine sulfide (Cyanex 471X, Cyanamid Inc., Ont., Canada) of technical quality (molar mass of 234.36 kg kmol^{-1}) was used as an extractant (carrier) as received. A dodecane fraction of n-alkanes (Slovnaft, Slovakia) was used as a diluent. The composition (w_i/%) estimated by GC was C_{10} 7.18, C_{11} 32.39, C_{12} 33.11, C_{13} 26.84, C_{14} 0.28, and others 0.2. The mean molar mass was 166.9 kg kmol^{-1}, density and viscosity at 25°C were 741.4 kg m^{-3} and 1.183 mPa s, respectively. Isodecanol (Isopar, Holland) of technical quality was used as a modifier as received. Other chemicals (AgNO$_3$, NH$_3$, Na$_2$S$_2$O$_3$ · 5H$_2$O, Na$_2$SO$_3$, CH$_3$COOH, H$_3$BO$_3$, KAl(SO$_4$)$_2$ · 12H$_2$O, KI, AgI) used were of anal. grade. Aqueous solution of AgNO$_3$ ($\rho_{F0} \cong 500$ g m^{-3}) with a concentration of HNO$_3$ 0.10 kmol m^{-3}, if not otherwise stated, was used as feed.

Stripping solution A: NH$_4$OH with a concentration of 0.5 kmol m^{-3} if not otherwise stated. This solution was used in the experiments if not otherwise stated.

Stripping solution B: Aqueous solution with a following composition (w_i/%): Na$_2$S$_2$O$_3$ 13.6, Na$_2$SO$_3$ 1.4, CH$_3$COOH 1, KAl(SO$_4$)$_2$ 0.9, H$_3$BO$_3$ 0.7, H$_2$O 82.4 [8].

In the membrane phase the carrier was dissolved in alkanes and isodecanol was used as a modifier in the mass ratio m(alkanes)/m(isodecanol) = 40/60. The viscosity and density of this mixture at 25°C were 3.88 mPa s and 796 kg m^{-3}, respectively.

Equipment and Methods

Transport through a Bulk Liquid Membrane

The two-compartment contactor used is described in detail elsewhere [9]. The feed solution (volume $V_F \cong 250$ cm^3) was placed in the left arm of the contactor, the stripping solution ($V_R \cong 135$ cm^3) was in the right arm of the contactor and the horizontal space above aqueous phases joining both compartments was filled with the organic phase – liquid membrane ($V_M \cong 90$ cm^3), which formed a layer thickness of about 18 mm. All phases were vigorously stirred and the temperature of the phases was kept at 25 °C ± 0.5 °C. The rotational frequency of the mixing bars in the feed and stripping phase was 120 min^{-1} and the rotational frequency of the two flat disc teflon mixers in the membrane phase was 100 min^{-1}. The interfacial areas of the extraction and stripping interfaces were 21.79 cm^2 and 20.77 cm^2, respectively.

At chosen times, samples of the feed and the stripping solutions were withdrawn. The mass of these samples estimated from differential weighing was around 2 g. The same amount of the feed or the fresh stripping solutions was immediately added to both compartments to keep the volumes of the solutions constant.
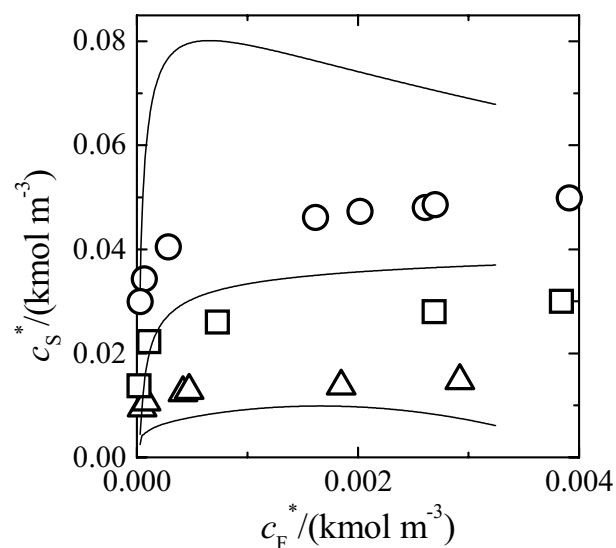
L/L Equilibrium

For the determination of equilibrium between the aqueous phase containing diluted AgNO$_3$ (feed phase) and the solvent containing carrier (Cyanex 471X with concentrations of 0.03 kmol m^{-3}, 0.06 kmol m^{-3}, 0.1 kmol m^{-3}), both phases were poured into an Erlenmeyer flask and stirred around 4 h in a thermostatic shaker at 25 °C. After this period the phases were carefully separated and the content of Ag was determined in both phases (in the membrane phase after stripping into the stripping solution).

The concentration of Ag in the feed and in the stripping phase was estimated by potentiometric titration with a solution of KI with a concentration of 0.0004 kmol m^{-3} by the Mettler Toledo DL53 autotitrator (Schwarzenbach, Switzerland). The sample was diluted to 20 cm^3 with a saturated solution of AgI, then HNO$_3$ with a concentration of 5 kmol m^{-3} was added to adjust pH to about 1. The concentration of Ag in the stripping solution B was determined by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

L/L Equilibrium

Extraction equilibria of silver for the solvent with triisobutylphosphine sulfide (Cyanex 471X) as an extractant were studied at 25 °C. Cyanex 471X is solu-

Fig. 1. Equilibrium concentration of silver in the solvent with Cyanex 471X *vs.* silver concentration in the aqueous nitrate solution with a concentration of HNO$_3$ 0.10 kmol m^{-3}. Lines are calculated according to eqn (*2*) for the model with $m = 1$ and $n = 2$ and extraction constant $\{K_{1,2}\} = 1.01 \times 10^7$ estimated from the slope analysis. Concentration of Cyanex 471X in the solvent (c/(kmol m^{-3})): 0.03 ($\triangle$), 0.06 ($\square$), 0.10 ($\bigcirc$).
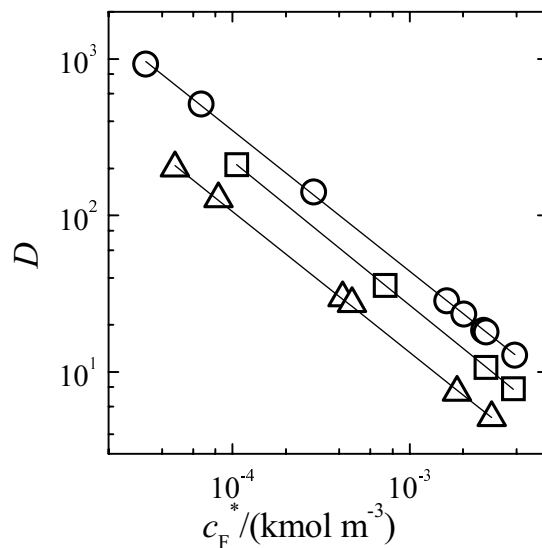
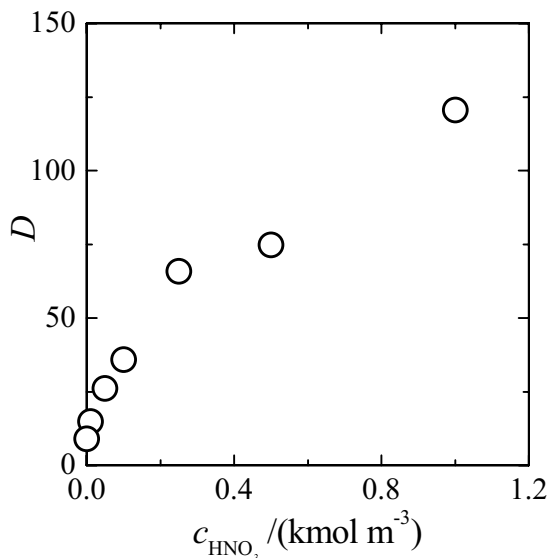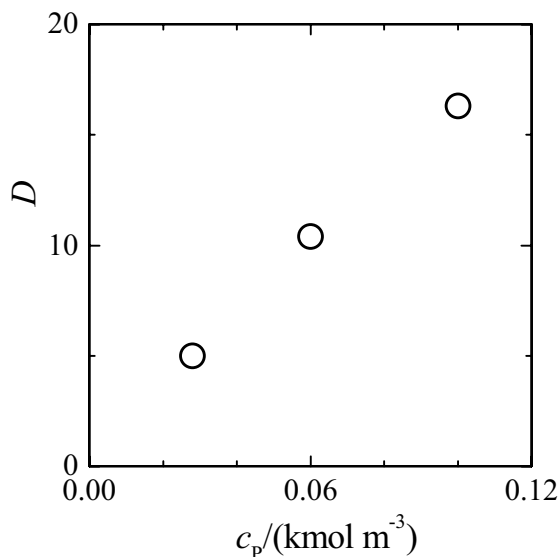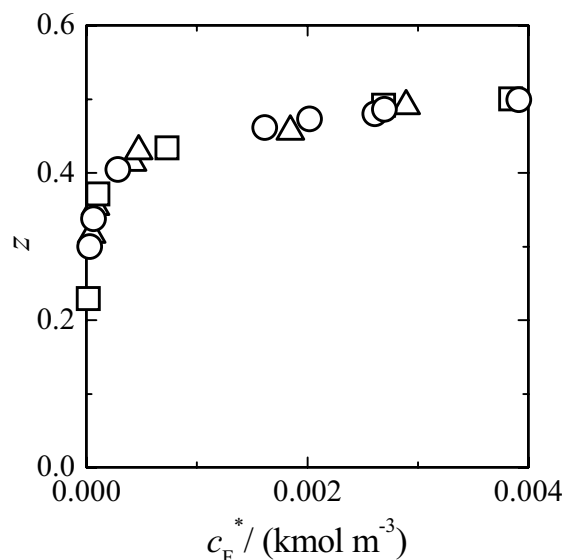**Fig. 2.** The distribution coefficient of silver *vs.* equilibrium concentration of Ag in 0.10 kmol m^{-3} HNO$_3$. Lines are calculated as linear fit to experimental data ($r = -0.9999$ for all lines). Legend as in Fig. 1.

ble in alkanes, however, its complexes with silver are partially insoluble in alkanes. It was found that isodecanol is a suitable modifier to dissolve complexes. The appropriate mass ratio of alkanes to isodecanol was estimated as 40:60 and this ratio was used in all experiments. The equilibrium concentration of Ag in the solvent *vs.* aqueous concentration of Ag is presented

Table 1. Values of the Coefficients of the Empirical Equation (15) Correlating the Distribution Coefficient Y and Concentration of Ag in the Feed Phase

c_{P0}	a	b	r
kmol m^{-3}	(kmol m^{-3})$^{-b}$		
0.03	0.02641	-0.90091	-0.9999
0.06	0.04682	-0.91878	-0.9999
0.1	0.08839	-0.89914	-0.9998

Fig. 5. Loading of the extractant *vs.* concentration of Ag in the feed. Legend as in Fig. 1.

Fig. 3. Dependence of the distribution coefficient on the concentration of HNO$_3$ in the aqueous phase. Concentration of Cyanex 471X in the solvent was 0.06 kmol m^{-3}.

Fig. 4. Dependence of the distribution coefficient on the concentration of Cyanex 471X in the solvent at $\rho_{F0}^* = 205$ g m^{-3} and $c_{HNO_3} = 0.10$ kmol m^{-3}.

in Fig. 1. The values of the distribution coefficient of silver strongly decreased with increasing aqueous concentration of Ag (Fig. 2). This dependence is linear in the log-log coordinates, see Fig. 2, and by the linear fit of the experimental data parameters of the empirical relationship

$$D = a(c_F^*)^b \qquad (15)$$

were estimated. The coefficients a and b are shown in Table 1. These coefficients are function of carrier concentration in the solvent.

The value of the distribution coefficient of Ag increases with increasing concentration of HNO$_3$ in the feed (Fig. 3). An increasing concentration of Cyanex 471X in the solvent resulted in a proportional increase in the value of the distribution coefficient of Ag (Fig. 4) and of the coefficients in the empirical equation (15), as shown in Table 1.

The value of the loading, defined by eqn (8), *i.e.* the number of the permeant ions (Ag$^+$) per one molecule of the extractant, was independent of the extractant concentration, see Fig. 5, what implied the value of $m = 1$. At the aqueous concentrations of Ag close to the solvent saturation, the loading approached the value 0.5 (Fig. 5). This suggested the value of the mole ratio of silver to carrier in the complex to be 1:2. Various mechanisms of complex formation with values of $m = 1$ and $n = 1, 1.5, 2$, and 3 have been tested by slope analysis using a linear fit to experimental data according to eqn (3) with results shown in Table 2. Since for $n = 3$ the value of concentration of the free carrier (c_P) in the denominator of eqn (4) is approaching zero, so mechanism with $m = 1$ and $n = 3$ is unrealistic. Fig. 6 shows the linear fit to experimental data for $n = 2$, including 95 % confidence

Table 2. Slope Analysis of Equilibrium Data according to Eqn (*3*). Results of the Linear Fit to Experimental Data

m	n	$\log\{K_{1,2}\}$	Slope	r
1	1.0	1.38	0.161	0.988
1	1.5	2.92	0.318	0.901
1	2.0	7.0065	1.02	0.956
1	3.0	Unreal	Unreal	–
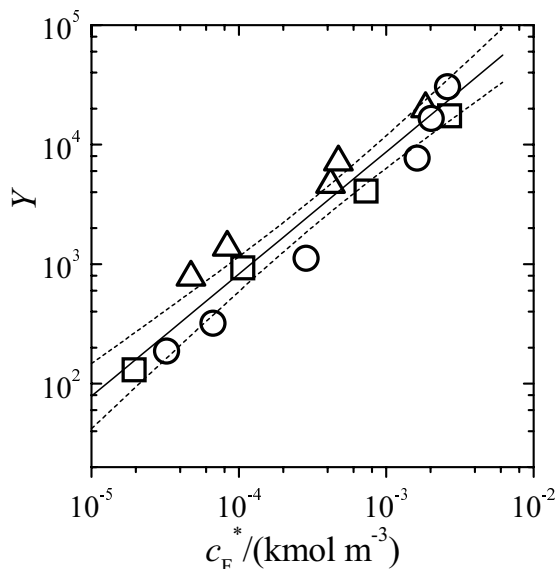
Fig. 6. Statistical analysis of equilibrium data for mechanisms of formation of the complexes with $m = 1$ and $n = 2$ including 95 % confidence bands. Legend as in Fig. 1.

bands, with a slope equal to 1.02, which is quite close to the required value of 1. The intercept of this correlation line yields the value of extraction constant $K_{1,2}$ = 1.01×10^7 (kmol m^{-3})$^{-3}$. The relatively great variance of the correlating data is much more reflected in the dependences of the distribution coefficient (shown as lines in Fig. 1), calculated from eqns (*2*) and (*7*), using the above-mentioned value of $K_{1,2}$. This figure shows that eqns (*2*) and (*7*) do not correlate experimental data well, especially at higher concentrations of the extractant. This deviation could be explained by the formation of several complexes of silver with an extractant of different structure with dominance of the (1,2) complex or by concentration-dependent value of activity coefficients in both phases. Taking into account the value of the loading which approaches 0.5 (Fig. 5), the second explanation is more probable.

Transport through Liquid Membranes

The transport of silver through layered bulk liquid membranes was studied in a two-compartment contactor. For the modelling of the concentration depen-
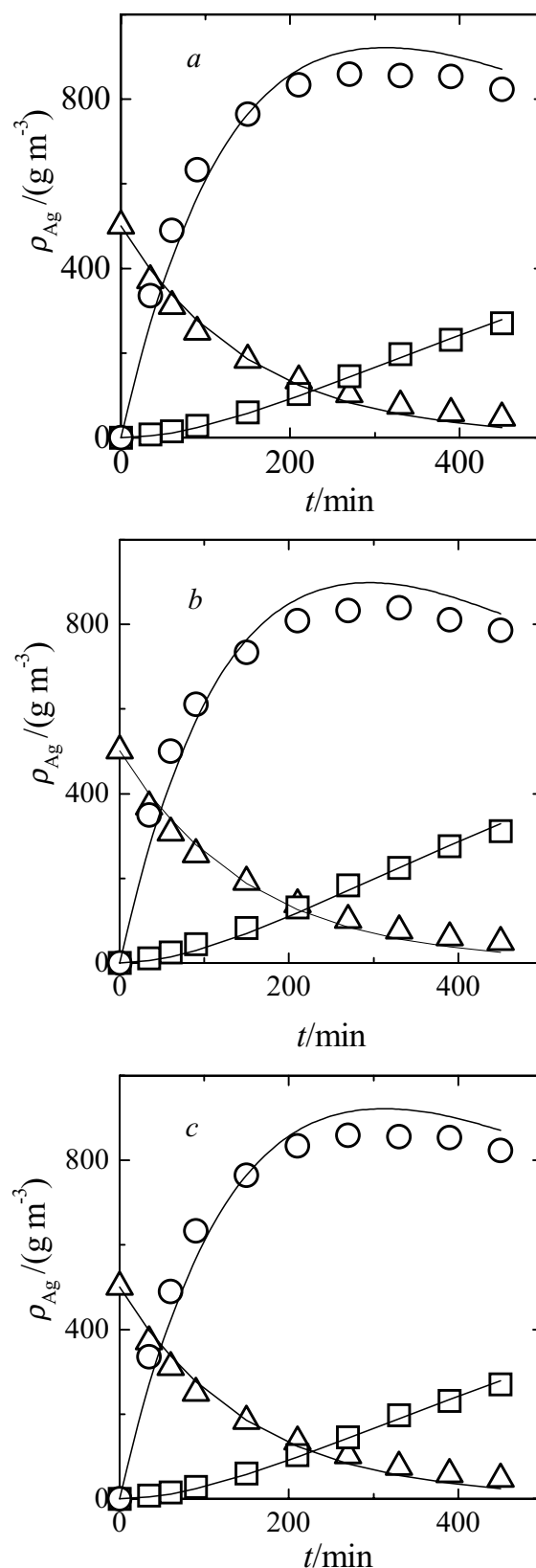
Fig. 7. Time courses of Ag concentration in three phases of the two-compartment contactor. (Carrier concentration (kmol m^{-3}): *a*) 0.03, *b*) 0.06, *c*) 0.10.) Lines are calculated according to the suggested model. Feed phase ($\triangle$), stripping solution A ($\square$), membrane phase ($\circ$).

Table 3. Parameters of the Model of Ag Transport through LM

| c_{P0}	$k_F \cdot 10^6$	$k_M \cdot 10^6$
kmol m^{-3}	m s^{-1}	m s^{-1}
0.03	10.4	1.20
0.06	13.2	1.08
0.10	12.6	0.97

dences of Ag, the presented model with diffusional resistances in series (eqns (9—12) and (15)) was used. This model fits experimental data well, with values of model parameters presented in Table 3, as shown in Fig. 7. With increasing concentration of the carrier in the solvent, the value of the individual mass-transfer coefficient in the boundary layers in the membrane, k_M, slightly decreased, as Table 3 revealed. As it will be shown below, the kinetics of stripping play an important role in the overall transport rate and a related term has to be included into the model.

The initial flux of Ag through the extraction interface, J_{F0}, was much higher than the maximum value of the flux through the stripping interface, J_{Rmax}. Fig. 9 reveals that this initial flux is higher by a factor of 6 for the lowest carrier concentration and by a factor of 8 for the highest concentration. This suggests that the overall transport rate of silver through the liquid membrane, represented by J_R, is limited by the rate of the stripping. The initial mass flux through the extraction interface increased only 1.2 times with increasing concentration of Cyanex 471X in the membrane phase from 0.03 to 0.10 kmol m^{-3} (Fig. 9). This increase is not proportional to the increase of the value of the distribution coefficient by a factor of 3.3, as follows from Fig. 4. The mass flux through the stripping interface remained practically unchanged with the carrier concentration. This suggested that kinetics of the stripping strongly influenced the overall transport rate, as it was observed also in the pertraction of butyric acid [9].

With increasing concentration of HNO$_3$ in the feed from 0.01 to 1.0 kmol m^{-3}, no influence on the mass fluxes through the extraction and stripping interfaces, J_{F0} and J_{Rmax}, was found (Fig. 8), despite the fact that the value of the distribution coefficient increased remarkably, as shown in Fig. 3.

The effect of concentration of NH$_3$ in the stripping solution on the flux through the stripping interface is negligible. No change was observed in the time courses of concentrations in all phases and also in the mass fluxes through the extraction and stripping interfaces, when different stripping solutions A and B were used, see Fig. 9.
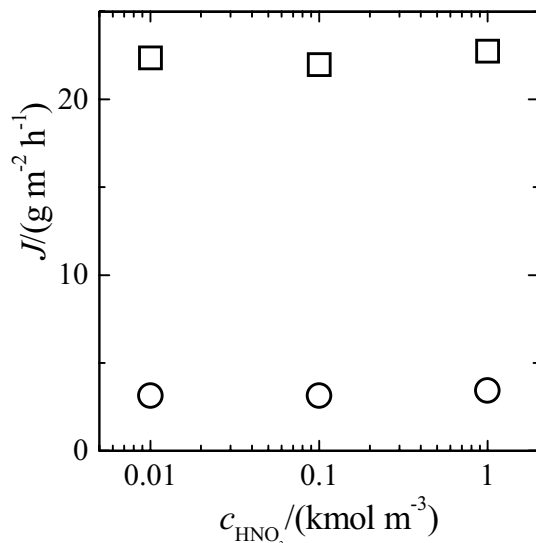
Fig. 8. Initial mass flux through the extraction interface, J_{F0} ($\square$) and maximum mass flux through the stripping interface, J_{Rmax} ($\circ$) *vs.* concentration of HNO$_3$ in the feed phase. The concentration of Cyanex 471X in the solvent was 0.06 kmol m^{-3}.
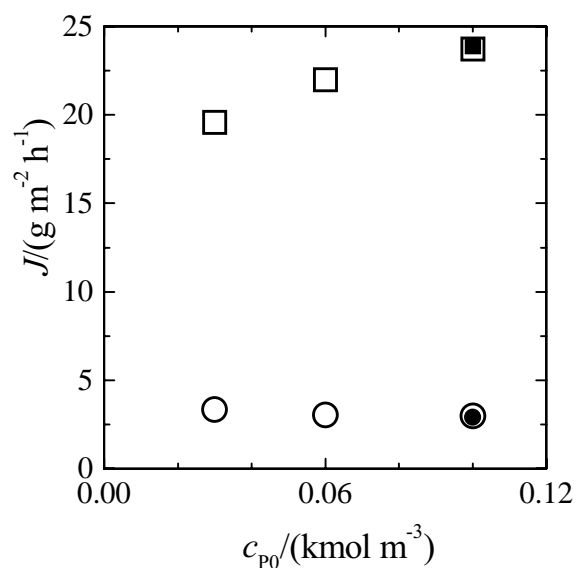
Fig. 9. Initial mass flux through the extraction interface, J_{F0} ($\square$) and maximum mass flux through the stripping interface, J_{Rmax} ($\circ$) *vs.* concentration of Cyanex 471X. The solid points represent results of experiments carried out with stripping solution B.

SYMBOLS

a	coefficient in eqn (15)	(kmol m^{-3})$^{-b}$
A	surface area	m^2
b	exponent in eqn (15)	
c	molar concentration of the permeant	kmol m^{-3}
c_P	molar concentration of the free carrier	kmol m^{-3}

D	distribution coefficient, defined by eqn (7)	
J	mass flux of the permeant	$\mathrm{g\ m^{-2}\ h^{-1}}$
k	individual mass-transfer coefficient	$\mathrm{m\ s^{-1}}$
$K_{m,n}$	extraction constant, defined by eqn (1)	$(\mathrm{kmol\ m^{-3}})^{-(2m+n-1)}$
$K_{1,n}$	extraction constant for stoichiometric coefficients $(1,n)$, defined by eqn (2)	$(\mathrm{kmol\ m^{-3}})^{-(n+1)}$
r	correlation coefficient	
t	time	min; h
V	volume	$\mathrm{m^3}$
Y	value defined by eqn (4)	$(\mathrm{kmol\ m^{-3}})^{-n}$
z	loading, defined by eqn (8)	
[ ]	molar concentration of the species in brackets	$\mathrm{kmol\ m^{-3}}$
ρ	mass concentration of the permeant	$\mathrm{g\ m^{-3}}$

Indices

F	feed phase
M	membrane phase
0	initial value
P	carrier (extractant)
R	stripping solution
S	solvent
*	equilibrium value

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