Transport of 5-Methyl-2-pyrazinecarboxylic Acid through a Layered Bulk Liquid Membrane*

Ľ. KUBIŠOVÁ, J. MARTÁK, and Š. SCHLOSSER**

Department of Chemical and Biochemical Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology, SK-812 37 Bratislava
e-mail: schlosser@cvt.stuba.sk

Received 5 April 2002

Pertraction of 5-methyl-2-pyrazinecarboxylic acid (MPCA) through a layered liquid membrane and parameters influencing the transport with trioctylamine (TOA) carrier have been studied. A simple diffusion model correlates concentration dependences in all three phases relatively well. By increasing concentration of the carrier from 0.2 to 0.6 kmol m^{-3} an increase of the transport rate of MPCA does not occur despite the fact that the value of the distribution coefficient of MPCA increases 2.68 times. While H_2SO_4 and sulfates in the feed do not influence much the transport of MPCA, the addition of sodium chloride slows down the flux of MPCA markedly and increases the co-transport of mineral acids. In pertraction of MPCA from one-molar sulfate solution the ratio of molar fluxes of sulfuric acid and MPCA is equal to one. In pertraction from the feed containing 1 kmol m^{-3} of NaCl the value of this ratio is equal nearly to four. However, the flux of MPCA is four times lower.

Separation and concentration of organic acids by extraction or pertraction through liquid membranes from fermentation broths and waste solutions are of great interest in the last decade. Solvent extraction [1—5], membrane-based solvent extraction (MBSE) [6—10], and pertraction [6, 8, 11—13] of carboxylic acids by solvents containing higher tertiary amines have been studied. Extraction and L/L equilibria of 5-methyl-2-pyrazinecarboxylic acid (MPCA), which is of industrial interest, have been reported by *Marták et al.* [14]. Recently [10, 15], simultaneous MBSE and membrane-based solvent stripping (MBSS) of MPCA in hollow-fibre contactors were investigated.

Waste solutions from technological processes often contain a significant amount of organic acids together with mineral acids and their salts. The presence of inorganic salts strongly influences the transport rate of organic acids, since mineral acids are co-extracted with organic acids or some mineral acids are preferably transported with the carrier [16—18]. The influence of mineral acids on the pertraction and membrane-based solvent extraction of lactic acid was reported in papers [6, 16] and the competitive transport of mineral acids in pertraction of MPCA in paper [17].

The aim of this work was to study the mechanism of the pertraction of MPCA through layered bulk liquid membranes, the parameters influencing this transport, and to test a simple diffusion model of pertraction.

THEORETICAL

The overall reaction of the formation of MPCA complexes from a pure aqueous solution can be written as

$$p\mathrm{HMPCA} + q\overline{\mathrm{TOA}} \Leftrightarrow \overline{(\mathrm{HMPCA})_p(\mathrm{TOA})_q} \qquad (A)$$

where HMPCA is an undissociated molecule of MPCA and over bars denote species in the organic phase. Based on the results of L/L equilibria the following combinations of values of stoichiometric coefficients p and q should be considered: (1,1), (2,1), and (3,1) [14]. Then, the concentration of MPCA bonded in the form of the above-mentioned complexes at the F/M interface can be expressed as

$$c_{\mathrm{MF}} = [\overline{\mathrm{TOA}}](K_{1,1}c_{\mathrm{FM}} + 2K_{2,1}c_{\mathrm{FM}}^2 + 3K_{3,1}c_{\mathrm{FM}}^3) \quad (1)$$

and the concentration of the free carrier as

$$[\overline{\mathrm{TOA}}] = c_{\mathrm{TOA},0}/(1+K_{1,1}c_{\mathrm{FM}}+K_{2,1}c_{\mathrm{FM}}^2+K_{3,1}c_{\mathrm{FM}}^3) \quad (2)$$

The formation of MPCA complexes from solutions

*Presented at the 29th International Conference of the Slovak Society of Chemical Engineering, Tatranské Matliare, 27—31 May 2002.

**The author to whom the correspondence should be addressed.

containing H_2SO_4 and related salts can be written as [14]

$$p\mathrm{HMPCA} + 2r\mathrm{H}^+ + r\mathrm{SO}_4^{2-} + q\overline{\mathrm{TOA}} \Leftrightarrow$$

$$\Leftrightarrow \overline{(\mathrm{HMPCA})_p(\mathrm{H_2SO_4})_r(\mathrm{TOA})_q} \qquad (B)$$

The results of L/L equilibria [14] show that formation of six different complexes (MPCA:H_2SO_4:TOA) can be expected. These complexes can be briefly designated as (p, r, q) complexes where p, r, and q are stoichiometric coefficients. The complexes (1,1,2) and (2,1,2) containing both the acids, the complex (2,0,1) containing only MPCA, and the three complexes (0,1,2), (0,2,3), and (0,3,3) containing only H_2SO_4 should be taken into account.

In the development of a model for pertraction of heterocyclic carboxylic acid MPCA through a well mixed layered bulk liquid membrane (BLM) in a two-compartment pertractor, the following assumptions were made [12]:

(i) Chemical reactions of the acid/carrier complex formation at the extraction interface (F/M) and acid/carrier complex decomposition at the stripping interface (M/R) are fast, *i.e.* the diffusion mass-transfer resistances in boundary layers are decisive factors at both the interfaces.

(ii) All three phases are well mixed and hydrodynamic conditions, as well as the structure of the transported species at both interfaces in the membrane are identical. Thus, $k_{\mathrm{FM}} = k_{\mathrm{MR}} = k_{\mathrm{M}}$.

(iii) Accumulation of species in the boundary layers at interfaces is negligible. Hence, the fluxes through the boundary layers on both sides of the individual interfaces are equal.

(iv) Equilibrium is reached at the extraction interface.

(v) Excess of reagent is maintained in the stripping solution so that the concentration of the undissociated MPCA in the stripping solution, as well as the concentration of MPCA bonded in the complex with the carrier is practically zero at the M/R interface.

(vi) Volumes of all three phases are constant.

Based on the above given assumptions, the following differential equations have been derived [12] for the concentration of acid in the individual phases

$$\frac{\mathrm{d}c_{\mathrm{F}}}{\mathrm{d}t} = -\frac{k_{\mathrm{F}}k_{\mathrm{M}}A_{\mathrm{F}}\left(Dc_{\mathrm{F}} - c_{\mathrm{M}}\right)}{V_{\mathrm{F}}\left(k_{\mathrm{F}} + k_{\mathrm{M}}D\right)} \qquad (3)$$

$$\frac{\mathrm{d}c_{\mathrm{M}}}{\mathrm{d}t} = \frac{k_{\mathrm{F}}k_{\mathrm{M}}A_{\mathrm{F}}}{V_{\mathrm{M}}}\frac{(Dc_{\mathrm{F}} - c_{\mathrm{M}})}{(k_{\mathrm{F}} + k_{\mathrm{M}}D)} - \frac{k_{\mathrm{M}}A_{\mathrm{R}}c_{\mathrm{M}}}{V_{\mathrm{M}}} \qquad (4)$$

$$\frac{\mathrm{d}c_{\mathrm{aR}}}{\mathrm{d}t} = \frac{k_{\mathrm{M}}A_{\mathrm{R}}c_{\mathrm{M}}}{V_{\mathrm{R}}} \qquad (5)$$

Considering the assumption (ii), the concentration c_{FM} can be expressed as

$$c_{\mathrm{FM}} = c_{\mathrm{F}} + \frac{k_{\mathrm{M}}}{k_{\mathrm{F}}}(c_{\mathrm{M}} - c_{\mathrm{MF}}) \qquad (6)$$

and the distribution ratio of undissociated MPCA on interface is given by the relation

$$D = \frac{c_{\mathrm{MF}}}{c_{\mathrm{FM}}} \qquad (7)$$

In pertraction of MPCA from pure aqueous solutions, the distribution coefficient can be calculated from the above given equations (eqns (*1*—*7*)). In pertraction from the solutions containing H_2SO_4 and related mineral salts, the exact model of pertraction should include both MPCA and mineral acid complexes. This, together with concentration and pH-dependent distribution coefficients, leads to quite a complex system of equations. Therefore, in the first approximation, the experimental MPCA equilibrium data were fitted using a third-order polynomial regression (eqn (*8*)), and implemented into the model of MPCA pertraction (eqns (*3*—*6*)).

L/L equilibria of MPCA in the studied systems are presented and discussed in more detail, together with modelling, in paper [14]. For correlation of experimental pertraction data, a simple empirical equation derived from suggested model of L/L equilibrium has been used

$$D = a + b_1 \cdot c_{\mathrm{FM}} + b_2 \cdot c_{\mathrm{FM}}^2 + b_3 \cdot c_{\mathrm{FM}}^3 \qquad (8)$$

The values of coefficients in this equation are shown in Table 1. The experimental equilibrium data for MPCA from the solutions containing Na_2SO_4 and H_2SO_4 at pH = 2.0 and 2.5, as well as their correlation by the polynomial regression of the third order resulting from the model of L/L equilibrium are shown in Fig. 1.

Table 1. Coefficients of an Empirical Equation (*8*) Describing L/L Equilibria of MPCA at Two pH_F* Values

pH_F*	a	$b_1/(\mathrm{mol}^{-1}\ \mathrm{m}^3)$	$b_2/(\mathrm{mol}^{-2}\ \mathrm{m}^6)$	$b_3/(\mathrm{mol}^{-3}\ \mathrm{m}^9)$	Correlation coefficient
2.0	7.7737	−0.07164	3.8789×10^{-4}	-8.2958×10^{-7}	0.9997
2.5	10.9777	−0.13769	0.00122	-4.3373×10^{-6}	0.9992

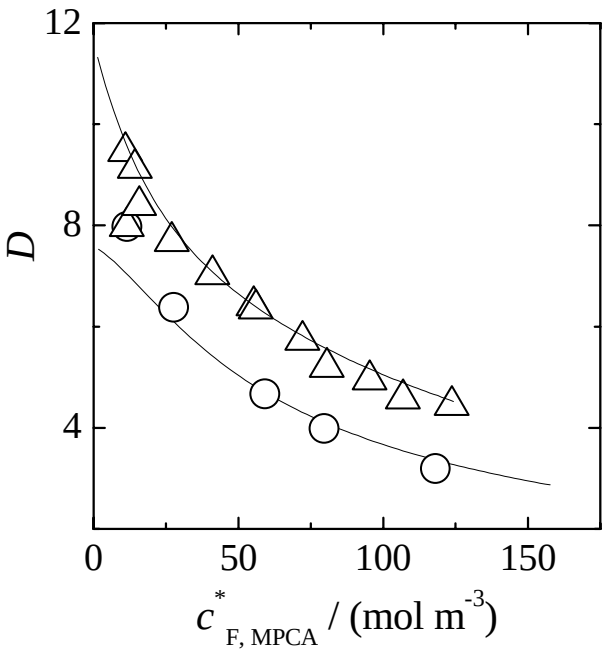


Fig. 1. Distribution coefficient of MPCA *vs.* equilibrium concentration of MPCA in the aqueous phase. Lines correlate with equilibrium data calculated by the model of L/L equilibria presented in [14] (not experimental data) by eqn (*8*). *Solvent:* 0.4 kmol m^{-3} TOA in xylene. *Aqueous phase:* MPCA in 1 kmol m^{-3} Na_2SO_4. △ $pH_F^* = 2.5$, ○ $pH_F^* = 2.0$.

EXPERIMENTAL

5-Methyl-2-pyrazinecarboxylic acid (MPCA) was received from the Research Institute of Organic Synthesis (Pardubice, CZ), in a crystalline form with purity higher than 99 mass %. Molar mass of MPCA is 138.14 g mol^{-1}. Density of MPCA at 25 °C was 1403 kg m^{-3}.

Na_2SO_4, NaOH, 25 % NH_4OH, 96 % H_2SO_4, and 35 % HCl with purity for analytical purposes were obtained from Mikrochem (SK). Anal. grade NaCl and xylene with purity over 99 % were received from Lachema (CZ).

Trioctylamine (TOA) with purity over 99 % was received from Fluka (CH).

Membrane (solvent) phase: 0.4 kmol m^{-3} TOA in xylene if not otherwise stated. Density of the membrane phase at 25 °C was 855.3 kg m^{-3}.

Stripping solution: Aqueous solution of 0.3 kmol m^{-3} NaOH if not otherwise stated. In some experiments the addition of NH_4OH (to keep an excess of alkalinity at prolonged experiments) was used.

The concentration of MPCA in the aqueous and stripping phases was determined by UV spectrophotometry using an analyzer UNICAM 8625 (UK). The concentration of MPCA in the organic phases was estimated by the same method after stripping the acid to the solution of NaOH. The total acidity or basicity (TA or TB, respectively) of the solutions was determined by potentiometric titration using the solutions of NaOH or HCl, respectively. For this purpose the microprocessor titrator DL 53 (Mettler Toledo, CH) with a glass pH electrode DG101-SC was employed.

A two-compartment glass contactor with a liquid membrane (organic phase) layered above the aqueous phases and with well mixed all phases, used in this work, is described in detail in paper [12]. Surface areas of the extraction and stripping interface were 20.13 cm^2 and 19.86 cm^2, respectively. Both the initial flux through the extraction interface and the maximum flux through the stripping interface, which represents the overall flux of solute through the liquid membrane, were estimated using the following equations

$$J_{F_0} = -\frac{V_F}{A_F}\frac{dc_{Fa}}{dt} \quad (9)$$

$$J_{R,max} = \frac{V_R}{A_R}\frac{dc_R}{dt} \quad (10)$$

The values of derivatives in these equations were estimated from empirical functions correlating experimental concentration data. The second-order power law was used for estimation of c_F in the initial period and the linear function for c_R in the linear part of this dependence, which is around the maximum in the plot of c_M *vs.* time.

RESULTS AND DISCUSSION

The time-dependent MPCA concentrations in the three phases of a two-chamber contactor during the pertraction from pure aqueous solution are presented in Fig. 2. The proposed model fits the experimental data quite well. Time courses of the MPCA concentrations during the pertraction from solutions containing Na_2SO_4 and H_2SO_4 are drawn in Figs. 3 and 4. An acceptable agreement of the model with experimental data is achieved with value of correlation coefficient in most of cases higher than 0.988, especially for aqueous phases. However, some discrepancies between the experimental and calculated data at short times and in the membrane phase (Fig. 3), and for longer times of pertraction in the feed phase (Fig. 4), can be observed. The values of individual mass-transfer coefficients in the feed and membrane phases are presented in captions of Figs. 2—4, 7, and 8.

The study of MBSE and MBSS of MPCA in hollow fibre contactors [15] demonstrates that a diffusion model, which takes into account only the diffusion mass-transfer resistances in a series in aqueous and organic boundary layers and in a stagnant solvent layer in the wall pores, overestimates the values of the overall mass-transfer coefficients in these processes and is not satisfactory. Considering the kinetics of the acid-extractant complex formation in MBSE and the complex decomposition in MBSS, the diffusion-reaction model gives a good fit to experimental data. The estimated kinetic resistances contribute to the overall

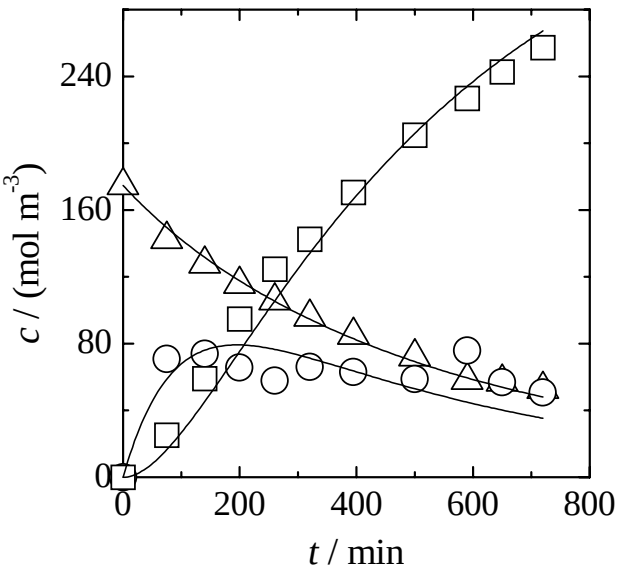


Fig. 2. Time dependences of MPCA concentration in three phases of a two-chamber contactor. △ Feed, ○ membrane phase, □ stripping solution. Lines are calculated according to the diffusion model with parameters $k_F = 6.5 \times 10^{-6}$ m s^{-1}, $k_M = 6.8 \times 10^{-6}$ m s^{-1}. *Feed:* pure MPCA in water, $pH_F = 1.89$—2.15. *Strip:* 0.3 kmol m^{-3} NaOH.

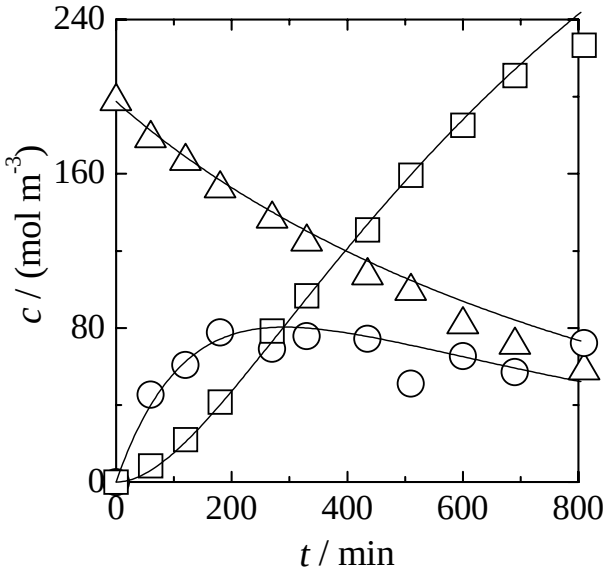


Fig. 4. Time dependences of MPCA concentration in three phases of a two-chamber contactor. △ Feed, ○ membrane phase, □ stripping solution. Lines are calculated according to the diffusion model with parameters $k_F = 3.64 \times 10^{-6}$ m s^{-1}, $k_M = 5.08 \times 10^{-6}$ m s^{-1}. *Feed*: MPCA, 1 kmol m^{-3} Na_2SO_4, $pH_F = 1.64$—2.54. *Strip*: 1.5 kmol m^{-3} NaOH.

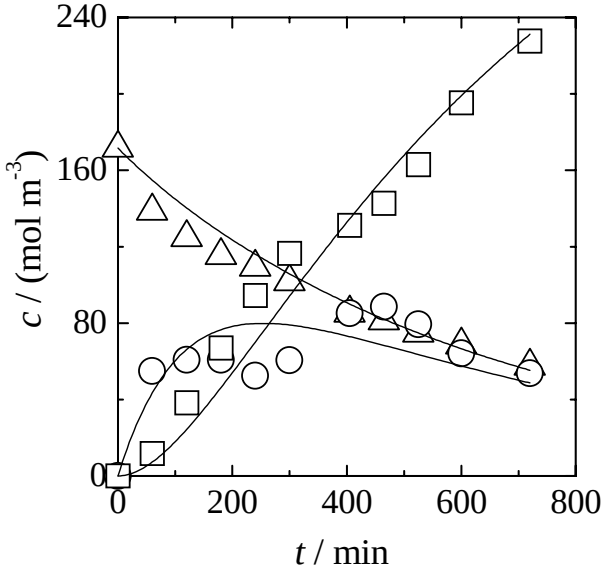


Fig. 3. Time dependences of MPCA concentration in three phases of a two-chamber contactor. △ Feed, ○ membrane phase, □ stripping solution. Lines are calculated according to the diffusion model with parameters $k_F = 4.83 \times 10^{-6}$ m s^{-1}, $k_M = 5.38 \times 10^{-6}$ m s^{-1}. *Feed*: MPCA, 1 kmol m^{-3} Na_2SO_4, $pH_{F_0} = 1.9$, pH-statted to about 2.2. *Strip*: 0.3 kmol m^{-3} NaOH and addition of 6.8 kmol m^{-3} NH_4OH after 6.8 h.

resistances in MBSE and MBSS with about 65 % and 40 %, respectively [15]. These results suggest that the complex-formation kinetic resistances should be considered also in the pertraction of MPCA through a layered bulk liquid membrane. This will be a subject of further interest.

The effect of extractant (TOA) concentration in the membrane phase in pertraction from solutions of MPCA in 1 kmol m^{-3} Na_2SO_4 and 0.1 kmol m^{-3} H_2SO_4 on fluxes through extraction and stripping interfaces is depicted in Fig. 5. From this figure it is evident that the concentration of TOA does not influence much both MPCA fluxes, despite the fact that the value of the distribution coefficient of MPCA for the solvents with 0.2 kmol m^{-3} and 0.6 kmol m^{-3} TOA increases from 2.14 to 5.74 (at aqueous equilibrium concentration of MPCA of about 0.083 kmol m^{-3}) [14]. The maximum flux of MPCA increased only by about 9 % in this interval of TOA concentrations. On the other hand, the initial flux of H_2SO_4 is proportional to the concentration of TOA, although the impact on the maximum flux of H_2SO_4 through the stripping interface is not significant. This suggests that probably saturation concentration of TOA species at both interfaces is reached at low concentration of TOA (free TOA molecules on the extraction interface and molecules of complexes MPCA—TOA on the stripping interface) and a further increase of bulk concentration of TOA does not contribute to the transport rate of MPCA. It can be concluded that because there is not any improvement in the MPCA flux, it is not advantageous to increase the concentration of TOA in the membrane phase. Therefore, any further increase in the concentration

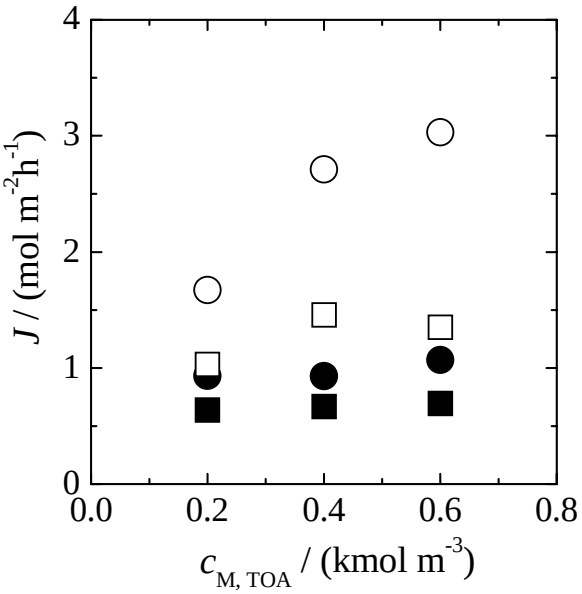


Fig. 5. Influence of the TOA concentration on the initial flux of MPCA and H_2SO_4 through the extraction interface (○ J_{F_0}) and the maximum flux of solutes through the stripping interface (□ $J_{R,\,max}$). Full points represent MPCA, open points H_2SO_4. *Feed:* 0.1 kmol m^{-3} MPCA, 1 kmol m^{-3} Na_2SO_4, pH_{F_0} = 1.45—1.65.

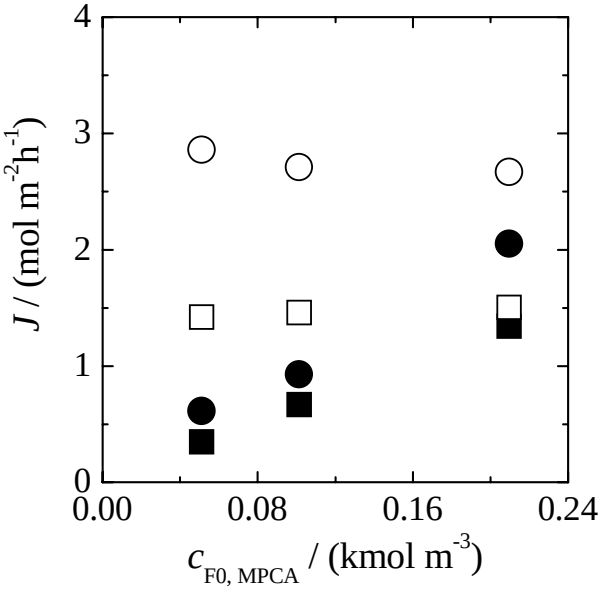


Fig. 6. Influence of the initial MPCA concentration on the initial flux of MPCA and H_2SO_4 through the extraction interface (○ J_{F_0}) and the maximum flux of solutes through the stripping interface (□ $J_{R,\,max}$). Full points represent MPCA, open points H_2SO_4. *Feed:* MPCA in 1 kmol m^{-3} Na_2SO_4 and 0.1 kmol m^{-3} H_2SO_4.

of TOA will cause only useless binding of the carrier with H_2SO_4.

The influence of the initial MPCA concentration in the feed solution is demonstrated in Figs. 6 and 7.

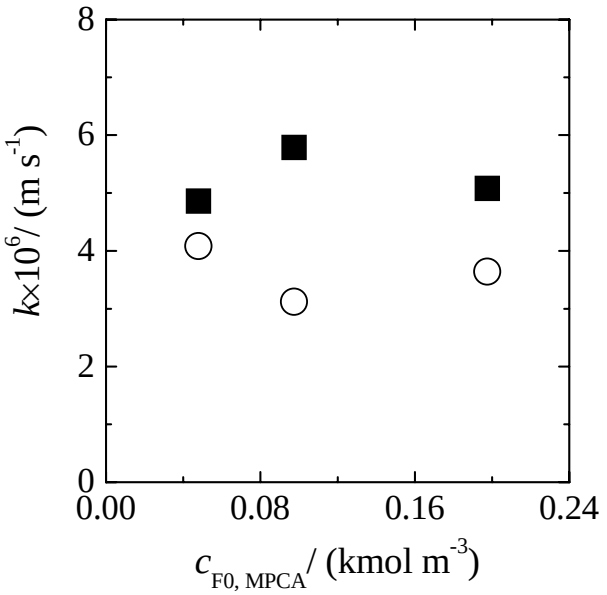


Fig. 7. Influence of the initial MPCA concentration on individual mass-transfer coefficients of MPCA. ○ k_F, ■ k_M. *Feed:* MPCA in 1 kmol m^{-3} Na_2SO_4 and 0.1 kmol m^{-3} H_2SO_4.

With increasing concentration of MPCA the driving force for the transport increases, which results in an increase of the MPCA flux through both the interfaces, as shown in Fig. 6. The initial flux of H_2SO_4 through the extraction interface and its maximum flux through the stripping interface remain constant since the driving force for H_2SO_4 pertraction did not change. The results in Fig. 6 show that for the same initial concentration of both acids (0.1 kmol m^{-3}) the maximum flux of H_2SO_4 through the stripping interface is about twice higher than the flux of MPCA. Only when the initial MPCA concentration is about twice as high as the H_2SO_4 concentration (about 0.21 kmol m^{-3}), both fluxes through the stripping interface become approximately equal. Concentration of MPCA practically does not influence the values of the individual mass-transfer coefficients of MPCA, as it is evident from Fig. 7.

With increasing concentration of H_2SO_4 and its salts in the feed solutions the value of the individual mass-transfer coefficients of MPCA in pertraction decreases (Fig. 8). However, as seen in Fig. 9, the maximum flux of MPCA through the stripping interface does not decrease and is practically constant. The maximum flux of H_2SO_4 through the stripping interface increases with increasing initial H_2SO_4 concentration in the feed (increasing driving force for the transport), as shown in Fig. 9. From this figure it is evident that the selectivity of pertraction (preferential transport of MPCA) decreases with increasing H_2SO_4 concentration.

The results demonstrating the influence of mixed salts solutions on the pertraction of MPCA are pre-

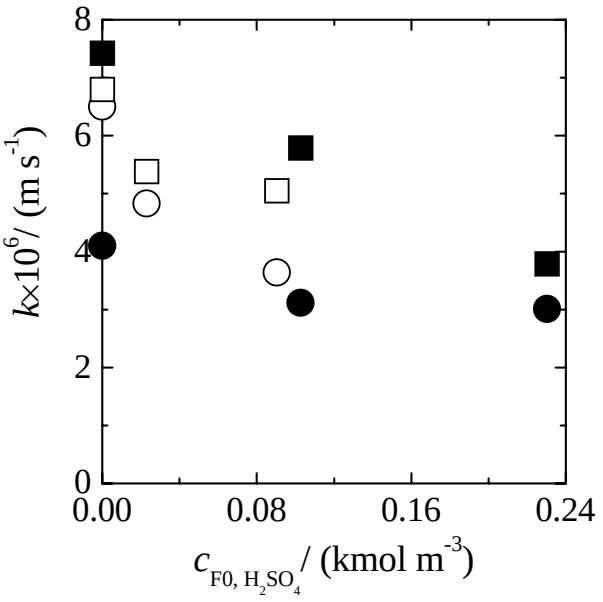


Fig. 8. Individual mass-transfer coefficients of MPCA *vs.* initial concentration of H_2SO_4 for the two feeds. ○ k_F, □ k_M. *Feed 1* (full points): 0.1 kmol m^{-3} MPCA, 1 kmol m^{-3} Na_2SO_4. *Feed 2* (open points): 0.18 kmol m^{-3} MPCA, 1 kmol m^{-3} Na_2SO_4, pH-statted (pH_F between 1.7 and 2.5).

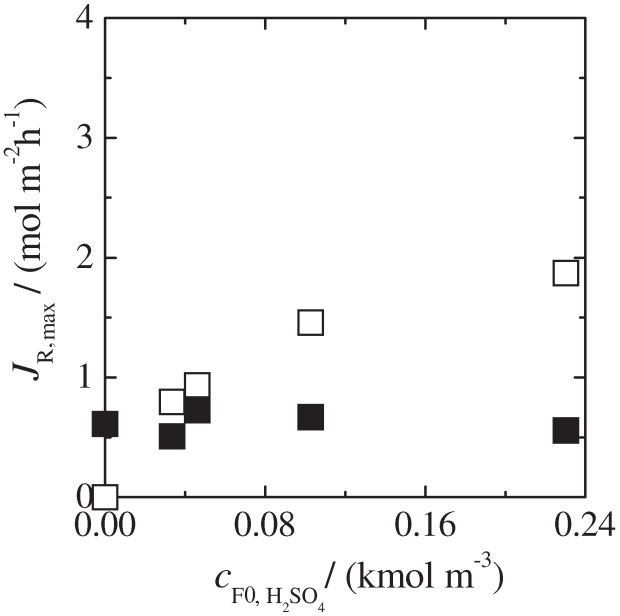
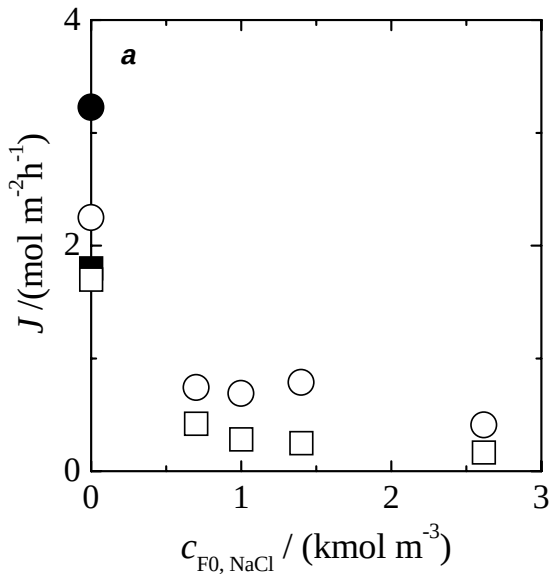


Fig. 9. Influence of the initial H_2SO_4 concentration on the maximum flux of MPCA through the stripping interface. ■ MPCA, □ H_2SO_4. *Feed*: 0.1 kmol m^{-3} MPCA, 1 kmol m^{-3} Na_2SO_4, in experiments with concentration of H_2SO_4 below 0.05 kmol m^{-3} pH was adjusted to about 2 with H_2SO_4.



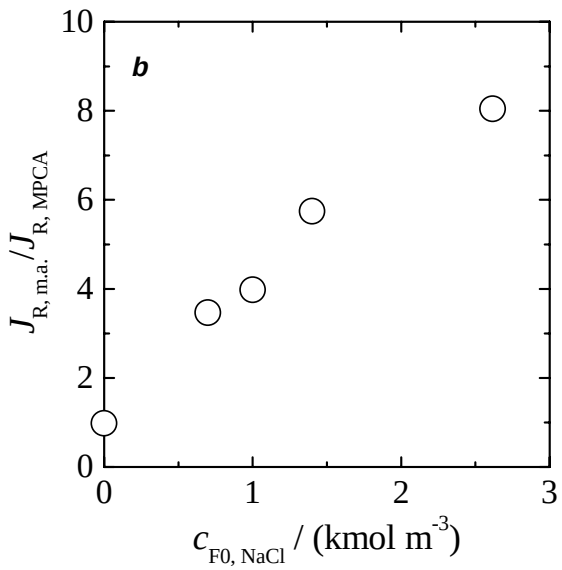


Fig. 10. Influence of the initial NaCl concentration in mixed salts solutions (Na_2SO_4, NaCl) on the initial flux of MPCA through the extraction interface (○ J_{F_0}) and the maximum flux of MPCA through the stripping interface (□ $J_{R,\ max}$) (*a*), and on the ratio of flux of mineral acids in the time interval where the maximum MPCA flux was achieved to the maximum flux of MPCA through the stripping interface ($J_{R,\ m.a.}/J_{R,\ MPCA}$) (*b*). Full points represent the fluxes in the pertraction of MPCA from aqueous solution without mineral salt. *Feed:* constant ionic strength of about 2.85 mol kg^{-1}, $c_{F_0,\ MPCA}$ = 0.18 kmol m^{-3}.

sented in Fig. 10. The flux of MPCA in the pertraction from aqueous solutions containing 1 kmol m^{-3} Na_2SO_4 is practically the same as in that from pure MPCA solutions. However, it is evident that if the feed phase contains chlorides, the pertraction rate of MPCA slows down considerably despite the fact that the ionic strength of the feed is constant. With increasing concentration of NaCl the flux of MPCA

drops rapidly, as illustrated in Fig. 10*a*. The pertraction rate of MPCA from the solution containing 2.6 kmol m^{-3} NaCl is nearly 10 times lower than that from the solution containing 1 kmol m^{-3} Na_2SO_4. This corresponds to the results from L/L equilibria, where consistently about three times lower values of the MPCA distribution coefficient were observed in chloride media in comparison with sulfate media [14]. This is connected with the competitive transport of MPCA and HCl, while H_2SO_4 is co-transported with MPCA. Co-transport and/or competitive transport of mineral acids not only decreases the transport rate of MPCA but also the separation selectivity. The mole ratio of the transported H_2SO_4 to MPCA in pertraction from pure sulfate media is about 1. The ratio of mineral acid to MPCA increases with increasing NaCl concentration and achieves the value of about 8 for the solution with 2.6 kmol m^{-3} NaCl, as can be seen in Fig. 10*b*.

Acknowledgements. Support of the Grants INCO Copernicus CT98-0147 and VEGA No. 1/9136/02 is acknowledged.

SYMBOLS

A	surface area	m^2
c	molar concentration of the permeant (undissociated acid, MPCA)	kmol m^{-3}
c_a	analytical (overall) molar concentration of permeant (MPCA)	kmol m^{-3}
D	distribution coefficient	
J	molar flux	kmol m^{-2} h^{-1}
k	individual mass-transfer coefficient	m s^{-1}
$K_{p,q}$	apparent equilibrium constant of the acid—TOA complex formation, for MPCA	$(\text{kmol m}^{-3})^{1-p-q}$
	and for H_2SO_4	$(\text{kmol m}^{-3})^{1-3p-q}$
t	time	s
V	volume	m^3
[ ]	equilibrium molar concentration of the species shown in brackets	kmol m^{-3}
$\overline{\text{overbar}}$	shows species in the solvent phase	

Subscripts

F	feed (donor) phase; extraction interface
FM	in the feed phase near extraction interface (F/M)
M	membrane phase
m.a.	mineral acid
MF	in the membrane phase near extraction interface
MR	in the membrane phase near stripping interface (M/R)
0	initial value
p	number of MPCA molecules in the acid—extractant complex
q	number of extractant (TOA) molecules in the acid—extractant complex
r	number of H_2SO_4 molecules in the acid—extractant complex
R	stripping (acceptor) solution; stripping interface
*	value at equilibrium

Abbreviations

BLM	bulk liquid membrane
HMPCA	undissociated molecule of 5-methyl-2-pyrazinecarboxylic acid
MBSE	membrane-based solvent extraction
MBSS	membrane-based solvent stripping
MPCA	5-methyl-2-pyrazinecarboxylic acid
R	stripping solution
TOA	trioctylamine

REFERENCES

1. Kertes, A. S. and King, C. J., *Biotechnol. Bioeng. 28,* 269 (1986).
2. Tamada, J. A. and King, C. J., *Ind. Eng. Chem. Res. 29,* 1333 (1990).
3. Tamada, J. A., Kertes, A. S., and King, C. J., *Ind. Eng. Chem. Res. 29,* 1319 (1990).
4. Tamada, J. A., Kertes, A. S., and King, C. J., *Ind. Eng. Chem. Res. 29,* 1327 (1990).
5. Zigová, J., Šturdík, E., Vandák, D., and Schlosser, Š., *Process Biochem. 34,* 835 (1999).
6. Kubišová, Ľ. and Schlosser, Š., in *Proc. 12th International Congress Chisa 96*, full paper No. P 3.83, 10 pp. Prague, Czech Republic, 1996.
7. Schlosser, Š., in *Integration of Membrane Processes into Bioconversions.* (Bako, K., Gubicza, L., and Mulder, M., Editors.) P. 55. Kluwer Academic, Amsterdam, 2000.
8. Schlosser, Š., Sabolová, E., and Marták, J., in *Solvent Extraction for the 21st Century.* (Cox, M., Hidalgo, M., and Valiente, M., Editors.) P. 1041. Soc. Chem. Ind., London, 2001.
9. Sabolová, E., Schlosser, Š., and Mikulová, E., *Sep. Purif. Technol.*, submitted for publication (2002).
10. Sabolová, E., Schlosser, Š., and Kubišová, Ľ., in *Proceedings of the 28th International Conference of the SSChE* (CD ROM) 13 pp. Tatranské Matliare, Slovak Republic, 2001.
11. Schlosser, Š., Kubišová, Ľ., and Marták, J., in *Proc. Euromembrane 95*, p. 398. Bath, 1995.
12. Schlosser, Š. and Sabolová, E., *Chem. Pap. 53,* 403 (1999).
13. Schlosser, Š., in *Integration of Membrane Processes into Bioconversions.* (Bako, K., Gubicza, L., and Mulder, M., Editors.) P. 73. Kluwer Academic, Amsterdam, 2000.
14. Marták, J., Schlosser, Š., and Kubišová, Ľ, in *Proceedings of the 29th International Conference of the SSChE* (CD ROM) 17 pp. Tatranské Matliare, Slovak Republic, 2002.

15. Kubišová, Ľ., Sabolová, E., Schlosser, Š., Marták, J., and Kertész, R., *Desalination 148*, 205 (2002).
16. Kubišová, Ľ., Schlosser, Š., and Marták, J., in *Proceedings of the 24th International Conference of the SSChE* (in Slovak), pp. 151. Častá – Papiernička, Slovak Republic, 1997.
17. Kubišová, Ľ., Marták, J., and Schlosser, Š, in *Proceedings of the 28th International Conference of the SSChE* (CD ROM) 11 pp. Tatranské Matliare, Slovak Republic, 2001.
18. Schlosser, Š., Sabolová, E., Kertész, R., and Kubišová, Ľ., *J. Separat. Sci. 24*, 509 (2001).