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Liquid−Liquid Equilibria of 5-Methyl-2-Pyrazinecarboxylic Acid in Systems (Aqueous Solution with Increased Ionic Strength) + (Solvent with Trioctylamine)

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Liquid−liquid equilibrium data of 5-methyl-2-pyrazinecarboxylic acid (MPCA) in two-phase systems with acidic aqueous solution containing Na_2SO_4 and/or NaCl and organic solvent (trioctylamine (TOA) + xylene) are presented. Data from systems containing Na_2SO_4 were successfully correlated using an equilibrium model. Modeling of systems with chlorides needs more data. MPCA and inorganic acids are extracted simultaneously via two mechanisms. The first is competitive extraction of MPCA and inorganic acids for free TOA. This results in the formation of binary (MPCA + TOA) and (inorganic acid + TOA) complexes. The second mechanism is coextraction of acids resulting in ternary complexes (MPCA + inorganic acid + TOA). Competitive extraction dominates in the presence of NaCl. This suppressed the extraction of MPCA because its affinity to TOA is much lower compared to HCl. Coextraction dominates in the presence of Na_2SO_4. In this case, extraction of MPCA is comparable or even better than in systems without inorganic species. A solvent with (H_2SO_4 + TOA) complexes which are de facto ionic liquids provides better extraction of MPCA from aqueous solutions.

Introduction

Technological solutions from various industrial processes and fermentations often contain a significant amount of organic acids. These can be recovered by extractive separations based on partitioning in liquid−liquid systems like solvent extraction, membrane based solvent extraction, and pertraction through liquid membranes.[1,2] In systems also containing inorganic salts, at acidic pH, these salts behave as inorganic acids, and they are simultaneously extracted together with organic acids. Depending on the mechanism of extraction, this can positively or negatively affect the efficiency of organic acid extraction.

The influence of inorganic acids and salts on the extraction of organic acids is documented in various papers. Kim et al.[3] found that sodium chloride decreases the extraction of succinic acid by trioctylamine (TOA). A similar effect of inorganic acids HCl, HNO_3 and H_2SO_4 as well as of their sodium salts on the extraction of acetic and citric acids was found by Schunk et al.[4−7] Modeling of data with the precise thermodynamic approach revealed that besides binary (acid + TOA) complexes also ternary complexes (organic acid + inorganic acid + TOA) had to be proposed. Canari and Eyal proposed the ternary complex (propionic acid + HCl + TOA).[8] Kirsch and Maurer[9−11] modeled the extraction from ternary mixtures containing acetic (Ac), citric (Cit), and oxalic (Ox) acids, (Ac + Cit + H_2O), (Ac + Ox + H_2O), and (Cit + Ox + H_2O). Values of distribution coefficients predicted by the thermodynamic model which considered only binary complexes were occasionally lower than the experimental ones. Therefore, ternary complexes were assumed. The composition of complexes proposed by Schunk et al.[4−7] as well as by Kirsch and Maurer[9−11] are summarized in Tables S1 and S2 in the Supporting Information. This summary shows that the composition of ternary complexes depends also on the character of used diluent. Ternary complexes containing two organic acids and TOA were proposed also by Canari and Eyal.[12] An attempt to extract lactic acid (LA) from binary (LA + H_2O) solution as well as from a simulated fermentation broth by TOA partially loaded with hydrochloric acid was evaluated in works of Kirsch and Maurer[9−11] and Yankov et al.[13] A significant increase in the distribution coefficients of lactic acid at pH above the pK_a of lactic acid was observed.

A case study on recovery of 5-methyl-2-pyrazinecarboxylic acid (MPCA) from process mother liquor by membrane based solvent extraction and stripping with design of production pilot plant is presented in the paper of Schlosser et al.[1] Kinetic studies on the pertraction through layered bulk liquid membranes and membrane based solvent extraction[15] of MPCA with TOA as a carrier realized by Kubišová et al.[14] revealed that hydrochloric acid slowed down the transport of MPCA more than H_2SO_4.

Data on the equilibrium extraction of MPCA and H_2SO_4 from binary solutions (MPCA + H_2O) and (H_2SO_4 + H_2O) by TOA were presented by Marták et al.[16] in a previous study. It has been shown that H_2SO_4 interacts with TOA much stronger than MPCA. Therefore, it was expected that the extraction of organic acids from acidic solutions (organic acid + inorganic acid(s) or salt(s) + H_2O) can be markedly affected by the inorganic acid. Similar solutions are frequently released from various technological processes.

This work is a continuation of the previous study.[16] Its aim was to investigate the influence of inorganic salts NaCl and Na_2SO_4 on the liquid−liquid equilibria of MPCA in systems (acidic aqueous solution with increased ionic strength) + (solvent containing TOA). The model based on mass action law correlating the liquid−liquid equilibrium data from simultaneous extraction of MPCA and H_2SO_4 by TOA has also been formulated.

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Table 1. Liquid−Liquid Equilibria of 5-Methyl-2-Pyrazinecarboxylic Acid (MPCA) Extracted by Solvent (TOA + Xylene), $c_{Eo} = 0.4$ kmol·m^{-3}[a]

no.	$c_{aF,MPCA}$ kmol·m^{-3}	c_{aF,Cl^-} kmol·m^{-3}	$c_{F,TA}$ kmol·m^{-3}	c_{aF,SO_4} kmol·m^{-3}	pH_F	I_F kmol·m^3	$c_{S,MPCA}$ kmol·m^{-3}	$c_{S,HCl}$ kmol·m^{-3}	$c_{S,TA}$ kmol·m^{-3}	c_{S,H_2SO_4} kmol·m^{-3}	$D_{a,MPCA}$	S	Δ_{MPCA}	Δ_{Cl}	Δ_{TA}	Δ_{SO_4}
1[16]	0.0944	0	0.0944	0	2.24	0.0116	0.409	0	0.409	0	4.33		0.92			
2	0.111	0.337	0.0890	0	2.20	0.351	0.116	0.330	0.426	0	1.04		1.15	1.00	0.99	
3	0.0859	0.693	0.0703	0	2.29	0.706	0.0829	0.356	0.446	0	0.965		1.09	1.02	1.03	
4	0.0702	0.995	0.0490	0	2.41	1.009	0.0646	0.360	0.428	0	0.921		1.11	1.03	1.02	
5	0.0896	1.425	0.0604	0	2.42	1.445	0.0824	0.347	0.420	0	0.919		1.17	1.02	1.00	
6	0.0819	2.029	0.0533	0	2.34	2.046	0.0766	0.358	0.418	0	0.935		1.16	1.02	0.99	
7	0.0740	2.669	0.0439	0	2.34	2.685	0.0720	0.3620	0.421	0	0.973	7.17	1.15	1.03	0.98	
8	0.0757	1.058	0.0591	0.647	2.47	2.934	0.0962	0.365	0.472	0.0053	1.27	7.96	1.00	0.93	0.94	1.06
9	0.0745	0.663	0.0681	0.837	2.48	3.128	0.120	0.357	0.478	0.0008	1.61	10.5	1.02	0.93	0.93	1.03
10	0.0715	0.391	0.0760	0.921	2.44	3.108	0.146	0.312	0.495	0.0181	2.05	13.1	1.03	0.97	0.97	1.03
11	0.0806	0	0.0773	0.998	2.49	2.967	0.324	0	0.565	0.121	4.02	33.2	1.02		0.98	0.99
12	0.0799	0	0.0817	1.001	2.50	2.976	0.362	0	0.622	0.130	4.53	34.9	1.07		1.06	1.00
13	0.0183	1.011	0.0278	0.612	2.48	2.764	0.0306	0.398	0.438	0.0080	1.67		1.11	1.00	0.91	1.04
14	0.0353	1.020	0.0722	0.645	2.15	2.790	0.0567	0.386	0.485	0.0233	1.61		1.04	1.00	1.08	1.09
15	0.0757	1.058	0.0591	0.647	2.47	2.934	0.0962	0.365	0.472	0.0053	1.27		1.00	0.93	0.94	1.06
16	0.126	1.040	0.114	0.703	2.45	3.098	0.150	0.357	0.517	0.0050	1.19		1.03	0.99	0.99	1.21
											SD (eq 18)		0.096	0.038	0.047	0.084

[a] Aqueous phases: ternary solution (MPCA + NaCl + H_2O) (nos. 1 to 7, see Figure 2), quaternary solution (MPCA + Na_2SO_4 + NaCl + H_2O) with various ratios of Na_2SO_4 and NaCl at average ionic strength of about 3.10 mol.kg^{-1} (nos. 7 to 12, see Figure 2) and with $c_{Fo,Na_2SO_4} = 0.4$ kmol·m^{-3} and $c_{Fo,NaCl} = 1.4$ kmol·m^{-3} (nos. 13 to 16, see Figure 3). The meaning of the symbols is elucidated in Figure 1. $D_{a,MPCA}$ is the distribution coefficient of MPCA defined by eq 9. c_{aF,Cl^-} and $c_{S,HCl}$ are equilibrium concentrations of chlorides in the aqueous and solvent phases. Ionic strength (I_F) and selectivity (S) were calculated by eqs 19 and 13. Equilibrium pH (pH_F) was adjusted to approach the value of 2.4. The mass balances Δ were calculated by eqs 14 to 17.

Materials and Methods

The same chemicals as in previous study[16] were used. Furthermore, HNO_3 with mass fraction $w = 65$ % required for the determination of chlorides and NaCl with analytical grade purity were purchased from Lachema (Czech Republic).

L/L Equilibria. All experiments were carried out at the atmospheric pressure and the temperature $T = (25 \pm 0.1)$ °C. A total of 20 mL of aqueous solution were contacted with 20 mL of solvent (TOA + xylene) in 500 mL Erlenmeyer flasks. This two-phase system was agitated for at least 5 h using a rotational shaking water bath GFL 1092 (Germany) at the frequency of 180 min^{-1}. For the preliminary experiments the systems with following phases were investigated:

1. (MPCA + NaCl + H_2O) and (TOA + xylene) with $c_{Eo} = 0.4$ kmol·m^{-3} (Table 1, nos. 2 to 7). The subscript “E” means “extractant” that is TOA, and “o” means initial value before the phases were contacted.
2. (MPCA + Na_2SO_4 + NaCl + H_2O) with variable concentrations of Na_2SO_4 and NaCl provided that the resulting ionic strength, I_F, is close to 3 kmol·m^{-3} and (TOA + xylene) with $c_{Eo} = 0.4$ kmol·m^{-3} (Table 1, nos. 8 to 16). The subscript “F” means aqueous “feed” phase.

From Table 1 follows that the extraction of MPCA from aqueous phase to organic solvent was much better in systems with Na_2SO_4 than in systems with NaCl. Therefore, the further work was focused only to the systems containing sulfates without chlorides:

3. (MPCA + H_2SO_4 + Na_2SO_4 + H_2O) with $c_{Fo,H_2SO_4} = 0.1$ kmol·m^{-3} and $c_{Fo,Na_2SO_4} = 1$ kmol·m^{-3}, and (TOA + xylene) with $c_{Eo} = (0.2, 0.4 \text{ and } 0.6)$ kmol·m^{-3} (Table 2).
4. (MPCA + Na_2SO_4 + H_2O) with $c_{Fo,\,Na_2SO_4} = 1$ kmol·m^{-3} (Tables 3 and 4).

The desired equilibrium pH was adjusted by concentrated solutions of sulfuric ($w = 0.96$) or hydrochloric ($w = 0.35$) acids and/or sodium hydroxide ($w = 0.50$) followed by equilibration. Due to the low solubility of MPCA in water, which depends on the ionic strength, a solid powdered MPCA ($w > 0.99$) was added into the solvent when higher equilibrium concentrations, $c_{aF,MPCA}$, were needed (the letter “a” in subscript refers to “analytical concentration” including both dissociated and undissociated MPCA). After the separation of the phases, the equilibrium pH of the aqueous phase was measured and the content of the acids and salts was analyzed. The content of acids in the organic solvent phase (S) was analyzed after stripping of the acids to the solution of NaOH (stripping or recovery phase, R).

Analyses. Concentrations of MPCA, $c_{aF,MPCA}$ and $c_{R,MPCA}$, in both F and R phases were determined by UV spectrophotometry at a wavelength of 275 nm using an analyzer UNICAM 8625 (U.K.). The concentration dependencies of absorbance appeared the same for solutions (MPCA + H_2O) and (MPCA + NaOH + H_2O) with $c_{NaOH} = 0.5$ kmol·m^{-3}, $A_{274} = 0.1182 c_{a,MPCA}$ (concentration in mol.m^{-3}). Therefore, the same calibration was used for both F and R phases. The concentration of all acid equivalents in the aqueous phase, in fact the total acidity, $c_{F,TA}$, and the concentration of the excess NaOH in the R phase after stripping, in fact total basicity, $c_{R,TB}$, were determined by potentiometric titrations with 0.1 kmol·m^{-3} of NaOH and HCl as titrants, respectively, using a pH electrode DG101-SC (Mettler Toledo, Switzerland). Concentrations of chlorides in F and R phases, c_{aF,Cl^-} and c_{R,Cl^-}, were measured by potentiometric titration with a titrant ($AgNO_3$ + H_2O); $c_{AgNO_3} = 0.1$ kmol·m^{-3} using an argentometric electrode DM 141-SC (Mettler Toledo, Switzerland). The sample was diluted in a mixture of (ethanol + water + HNO_3 with $w = 0.325$) with volume ratios of 5:5:1 so that the final mass fraction of HNO_3 was 0.0295. All potentiometric titrations were performed using a titrator DL 53 (Mettler Toledo, Switzerland). The uncertainty of these measurements was within ± 0.5 %.

Since the solutes are transferred from one phase to another until the equilibrium is reached, the initial and equilibrium volumes of the phases differ. The volume changes due to transfer of H_2SO_4 and HCl were neglected as discussed in the previous study.[16] The influence of MPCA transfer on the phases volumes was considered assuming the additivity of volumes of the solid MPCA and liquid solutions (ideal mixing). The possibility of such approach was tested experimentally observing the volume and density changes when solid MPCA was mixed with water and NaOH solution. The additivity of volumes was also applied

Table 2. Liquid−Liquid Equilibria of MPCA Extracted from Quaternary Solution (MPCA + H_2SO_4 + Na_2SO_4 + H_2O), $c_{Fo,H_2SO_4} = 0.1$ kmol·m^{-3}, $c_{Fo,Na_2SO_4} = 1$ kmol·m^{-3} with Solvent (TOA + Xylene), $c_{Eo} = (0.2, 0.4, \text{and } 0.6)$ kmol·m^{-3}[a]

$c_{aF,MPCA}$ kmol·m^{-3}	$c_{F,TA}$ kmol·m^{-3}	c_{aF,SO_4} kmol·m^{-3}	pH_F	I_F kmol·m^3	c_{Eo} kmol·m^{-3}	$c_{S,MPCA}$ kmol·m^{-3}	$c_{S,TA}$ kmol·m^{-3}	c_{S,H_2SO_4} kmol·m^{-3}	$D_{a,\,MPCA}$	Δ_{MPCA}	Δ_{TA}	Δ_{SO_4}
0.00794	0.0389	0.989	2.39	2.905	0.2	0.029	0.176	0.0739	3.59	1.01	0.90	0.99
0.0495	0.0818	1.003	2.22	2.923	0.2	0.129	0.282	0.0765	2.60	0.99	0.95	0.99
0.0875	0.120	1.011	2.23	2.957	0.2	0.187	0.357	0.0846	2.14	0.99	1.00	1.00
0.133	0.171	1.019	2.07	2.942	0.2	0.218	0.343	0.0628	1.63	0.98	0.92	0.98
0.168	0.201	1.020	2.08	2.955	0.2	0.255	0.407	0.0753	1.52	1.01	0.98	0.99
0.214	0.247	1.033	2.00	2.969	0.2	0.278	0.378	0.0502	1.29	0.88	0.83	0.97
0.274	0.313	1.028	1.80	2.872	0.2	0.339	0.500	0.0795	1.24	1.11	1.08	1.00
0	0.0130	0.976	2.97	2.912	0.4	0	0.185	0.0925			0.97	1.00
0.00919	0.0153	0.979	2.93	2.923	0.4	0.0449	0.271	0.113	4.88	1.04	1.03	1.01
0.00976	0.0171	0.978	2.91	2.921	0.4	0.0442	0.228	0.0917	4.53	1.12	0.97	0.99
0.0375	0.0305	0.998	2.90	2.992	0.4	0.170	0.362	0.0954	4.54	1.04	0.97	1.00
0.0614	0.0405	0.988	2.90	2.974	0.4	0.272	0.483	0.0959	4.43	0.96	0.97	1.01
0.0760	0.0511	1.004	2.85	3.027	0.4	0.346	0.537	0.0944	4.55	1.00	0.96	1.00
0.0661	0.0470	1.002	2.82	3.013	0.4	0.292	0.529	0.118	4.42	0.95	1.01	1.03
0.00985	0.0201	0.987	2.80	2.941	0.4	0.0960	0.316	0.110	9.75	1.02	1.10	1.01
0.0964	0.0702	1.015	2.75	3.057	0.4	0.420	0.605	0.0912	4.35	1.00	0.96	1.00
0.175	0.159	1.032	2.47	3.092	0.4	0.522	0.705	0.0915	2.97	1.04	0.97	0.99
0.132	0.122	1.027	2.44	3.058	0.4	0.489	0.694	0.100	3.70	1.09	1.07	1.00
0	0.00495	0.972	3.17	2.906	0.6	0	0.193	0.0962			0.96	1.00
0.00411	0.00576	0.973	3.18	2.910	0.6	0.0179	0.212	0.0971	4.35	1.09	0.97	0.99
0.00961	0.00737	0.974	3.18	2.917	0.6	0.0432	0.238	0.0975	4.50	1.11	0.97	1.00
0.0333	0.0116	0.978	3.35	2.952	0.6	0.155	0.325	0.0847	4.64	1.05	0.88	0.98
0.0665	0.0203	1.002	3.32	3.048	0.6	0.390	0.588	0.0978	5.86	0.98	0.92	0.98
0.0856	0.0288	1.013	3.16	3.083	0.6	0.492	1.144	0.132	5.74	1.00	1.03	1.01
0.118	0.0477	1.044	3.05	3.188	0.6	0.720	1.010	0.141	6.10	1.02	1.05	1.02
0.166	0.0894	1.060	2.76	3.221	0.6	0.841	1.104	0.125	5.05	1.05	1.05	1.00
0.176	0.1057	1.072	2.70	3.252	0.6	0.862	1.144	0.134	4.89	1.02	1.05	1.02
0.242	0.1603	1.099	2.62	3.343	0.6	1.004	1.193	0.0856	4.15	1.01	0.96	0.96
								SD (eq 18)		0.057	0.063	0.015

[a] See also Figures 6 and S1. The meaning of the symbols is as in Table 1.

Table 3. Liquid−Liquid Equilibria of MPCA Extracted from Ternary Solution (MPCA + Na_2SO_4 + H_2O), $c_{Fo,\,Na_2SO_4} = 1$ kmol·m^{-3} with Solvent (TOA + Xylene), $c_{Eo} = 0.4$ kmol·m^{-3}, at Three Different Average Values of pH_F 2.03 (Exp. Nos. 1 to 6), 2.43 (Exp. Nos. 7 to 19), and 2.87 (Exp. Nos. 20 to 28)[a]

no.	$c_{aF,MPCA}$ kmol·m^{-3}	$c_{F,TA}$ kmol·m^{-3}	c_{aF,SO_4} kmol·m^{-3}	pH_F	I_F kmol·m^3	$c_{S,MPCA}$ kmol·m^{-3}	$c_{S,TA}$ kmol·m^{-3}	c_{S,H_2SO_4} kmol·m^{-3}	c_{S,H_2O} kmol·m^{-3}	$D_{a,MPCA}$	S	Δ_{MPCA}	Δ_{TA}	Δ_{SO_4}
1	0	0.0574	1.015	2.13	2.930	0	0.440	0.220	no data				0.97	0.99
2	0.0139	0.0749	1.003	2.16	2.904	0.0911	0.486	0.197	no data	6.57	33.4	1.05	0.95	0.99
3	0.0324	0.102	1.018	2.08	2.929	0.173	0.576	0.202	no data	5.34	26.9	1.03	0.99	1.00
4	0.0672	no data	∼1	1.99	no data	0.289	no data	no data	no data	4.30	no data	0.99	no data	no data
5	0.0895	0.166	1.046	1.94	2.970	0.333	0.742	0.204	no data	3.71	19.1	0.98	1.00	1.02
6	0.131	0.219	1.060	1.90	2.998	0.389	0.782	0.195	no data	2.96	16.1	0.98	0.99	1.02
7	0	0.0276	1.004	2.57	2.970	0	0.341	0.171	0.987				1.02	1.00
8	0.0153	0.0406	1.013	2.45	2.985	0.0937	0.399	0.153	0.819	6.13	40.7	0.98	0.94	0.97
9	0.0202	0.0433	1.012	2.48	2.987	0.119	0.422	0.151	0.818	5.89	39.4	0.98	0.97	0.99
10	0.0206	0.0585	1.019	2.33	2.987	0.1208	0.471	0.176	0.594	5.83	33.8	0.99	1.25	1.04
11	0.0371	0.0565	1.010	2.42	2.978	0.195	0.476	0.141	0.695	5.25	37.6	0.95	0.93	0.98
12	0.0588	0.0640	1.003	2.49	2.973	0.254	0.527	0.137	0.509	4.33	31.8	1.01	0.99	1.00
13	0.0799	0.0817	1.001	2.50	2.976	0.362	0.622	0.130	0.564	4.53	34.9	1.07	0.97	1.00
14	0.0806	0.0773	0.999	2.49	2.968	0.324	0.565	0.121	0.516	4.02	33.2	1.02	0.98	0.99
15	0.103	0.0933	0.995	2.48	2.963	0.404	0.627	0.112	0.391	3.93	35.0	1.02	1.01	1.00
16	0.109	0.107	0.999	2.40	2.961	0.399	0.620	0.110	0.578	3.65	33.1	0.96	0.97	0.99
17	0.132	0.122	1.027	2.44	3.058	0.489	0.694	0.100	no data	3.7	37.9	1.09	1.07	1.00
18	0.145	0.147	1.001	2.40	2.978	0.467	0.671	0.102	0.560	3.22	31.5	0.99	0.99	1.00
19	0.175	0.159	1.032	2.47	3.092	0.517	0.704	0.0915	no data	2.95	33.3	1.04	0.97	0.99
20	0	0.0126	1.001	2.87	2.981	0	0.213	0.107	no data				1.10	1.01
21	0	0.0130	0.976	2.97	2.912	0	0.185	0.0925	no data				0.97	1.00
22	0.00919	0.0153	0.979	2.93	2.923	0.0449	0.270	0.113	no data	4.88	42.4	1.04	1.03	1.01
23	0.00976	0.0171	0.978	2.91	2.921	0.0442	0.228	0.0917	no data	4.53	48.3	1.12	0.97	0.99
24	0.0375	0.0305	0.998	2.90	2.992	0.169	0.362	0.0954	no data	4.62	47.3	1.04	0.97	1.00
25	0.0614	0.0405	0.988	2.90	2.974	0.272	0.483	0.0959	no data	4.43	45.6	0.96	0.97	1.01
26	0.0661	0.0470	1.002	2.82	3.013	0.292	0.529	0.118	no data	4.42	37.7	0.95	1.01	1.03
27	0.0760	0.0511	1.004	2.85	3.027	0.346	0.537	0.0944	no data	4.55	48.4	1.00	0.96	1.00
28	0.0964	0.0702	1.015	2.75	3.057	0.420	0.605	0.0912	no data	4.35	48.4	1.00	0.96	1.00
										SD (eq 18)		0.044	0.061	0.014

[a] See also Figures 7, 10a, and S2. The meaning of the symbols is as in Table 1.

for concentrated solutions of HCl, H_2SO_4 and NaOH used for pH adjustment.

Assuming ideal mixing for the initial and equilibrium volumes of aqueous phase, V_{Fo} and V_F, it follows

$$V_F = V_{Fo} + V_{H_2SO_4} + V_{HCl} + V_{NaOH} - \frac{(c_{aFo,\,MPCA}V_{Fo} - c_{aF,\,MPCA}V_F)M_{MPCA}}{\rho_{MPCA}} \quad (1)$$

Table 4. pH-Dependence of Liquid−Liquid Equilibria of MPCA Extracted from Ternary Solution (MPCA + Na_2SO_4 + H_2O), $c_{Fo,Na_2SO_4} = 1$ $kmol \cdot m^{-3}$, with Solvent (TOA + Xylene), $c_{Eo} = 0.4$ $kmol \cdot m^{-3}$[a]

$c_{aF,MPCA}$ $kmol \cdot m^{-3}$	$c_{F,TA}$ $kmol \cdot m^{-3}$	c_{aF,SO_4} $kmol \cdot m^{-3}$	pH_F	I_F $kmol \cdot m^3$	$c_{S,MPCA}$ $kmol \cdot m^{-3}$	$c_{S,TA}$ $kmol \cdot m^{-3}$	c_{S,H_2SO_4} $kmol \cdot m^{-3}$	$D_{a, MPCA}$	S	Δ_{MPCA}	Δ_{TA}	Δ_{SO_4}
0.126	0.553	1.201	1.23	2.833	0.290	0.813	0.261	2.29	10.5	0.99	0.98	1.02
0.0525	0.338	1.117	1.43	2.837	0.192	0.717	0.262	3.65	15.5	0.99	0.87	0.97
0.0813	0.199	1.082	1.78	2.997	0.288	0.628	0.170	3.54	22.5	1.05	0.97	0.98
0.0672	no data	no data	1.99	no data	0.289	no data	no data	4.30	no data	0.99	no data	no data
0.0799	0.0817	1.002	2.50	2.980	0.362	0.619	0.128	4.53	35.6	1.07	0.97	1.00
0.0661	0.0470	1.002	2.82	3.013	0.292	0.529	0.118	4.42	37.7	0.95	1.01	1.03
0.0736	0.0352	0.992	3.08	3.008	0.271	0.419	0.0732	3.68	49.9	0.95	0.99	1.02
0.103	no data	no data	3.28	no data	0.253	no data	no data	2.45	no data	0.98	no data	no data
0.0793	0.0214	0.968	3.39	2.959	0.162	0.214	0.0258	2.04	76.4	0.97	0.95	1.00
								SD (eq 18)		0.039	0.056	0.021

[a] Average $c_{aF,MPCA} = 0.081$ $kmol \cdot m^{-3}$. See also Figure 9a, 10b, and S3. The meaning of the symbols is as in Table 1.

where $V_{H_2SO_4}$, V_{HCl}, and V_{NaOH} are the volumes of the concentrated solutions of H_2SO_4, HCl, and NaOH used for the adjustment of pH. In parentheses stands the difference between the initial ($c_{aFo,MPCA}V_{Fo}$) and equilibrium ($c_{aF,MPCA}V_F$) molar amounts of MPCA in the aqueous phase. M_{MPCA} and ρ_{MPCA} are molar mass (138.13 $g \cdot mol^{-1}$) and density of the solid MPCA (1.403 $kg.m^{-3}$, $T = 25$ °C). After rearrangement

$$V_F = \frac{(V_{Fo} + V_{H_2SO_4} + V_{HCl} + V_{NaOH})\rho_{MPCA} - V_{Fo}c_{aFo, MPCA}M_{MPCA}}{\rho_{MPCA} - c_{aF, MPCA}M_{MPCA}} \tag{2}$$

Since the concentration of sulfates was not determined directly, this had to be calculated using the concentrations of MPCA, $c_{aF,MPCA}$, chlorides, c_{aF,Cl^-}, and total acidity, $c_{F,TA}$, in the F phase. Then, total equilibrium concentrations of both hydrogensulfate and sulfate anions, $c_{aF\ SO_4}$, in the F phase is

$$c_{aF,SO_4} = c_{Fo,Na_2SO_4}\frac{V_{Fo}}{V_F} + \frac{1}{2}\left(\frac{c_{NaOH}V_{NaOH} + c_{Fo,NaCl}V_{Fo}}{V_F} + c_{F,TA} - c_{aF,MPCA} - c_{aF,Cl^-}\right) \tag{3}$$

where c_{Fo,Na_2SO_4} and $c_{Fo,NaCl}$ are the initial concentrations of Na_2SO_4 and NaCl in the F phase. c_{NaOH} is the concentration of added NaOH with $w = 0.50$ for pH adjustment.

Stripping of MPCA causes the formation of neutralization water. Both stripped MPCA and neutralization water increase the initial volume of the stripping phase, V_{Ro}, to the final volume, V_R

$$V_R = V_{Ro} + \frac{c_{R,MPCA}V_RM_{MPCA}}{\rho_{MPCA}} + \frac{(c_{R,Na^+} - c_{R,TB})V_RM_{H_2O}}{\rho_{H_2O}} \tag{4}$$

where ρ_{H_2O} and M_{H_2O} are the density and molar mass of water and

$$c_{R,Na^+} = c_{Ro,NaOH}\frac{V_{Ro}}{V_R} \tag{5}$$

$c_{Ro,NaOH}$ is the concentration of NaOH in the solution for stripping. Combining the last two equations gives the relation

$$V_R = V_{Ro}\frac{\rho_{MPCA}(\rho_{H_2O} + c_{Ro,NaOH}M_{H_2O})}{\rho_{MPCA}(\rho_{H_2O} + c_{R,TB}M_{H_2O}) - c_{R,MPCA}M_{MPCA}\rho_{H_2O}} \tag{6}$$

Equilibrium concentration of MPCA in the S phase, $c_{S,MPCA}$, must be calculated from $c_{R,MPCA}$

$$c_{S,MPCA} = \frac{V_R}{V_{S,samp}}c_{R,MPCA} \tag{7}$$

where $V_{S,samp}$ is the sample volume of the S phase taken for stripping. An analogical equation follows also for the concentration of HCl, $c_{S,HCl}$. For the concentration of sulfuric acid, c_{S,H_2SO_4}, which was not measured directly, it follows

$$c_{S,H_2SO_4} = \frac{V_R}{2V_{S,samp}}(c_{R,Na^+} - c_{R,TB} - c_{R,MPCA} - c_{R,Cl^-}) \tag{8}$$

Distribution coefficient of MPCA, $D_{a,MPCA}$, is defined as a ratio of overall MPCA concentrations in the solvent and aqueous phases, $c_{S,MPCA}$ and $c_{aF,MPCA}$

$$D_{a,MPCA} = \frac{c_{S,MPCA}}{c_{aF,MPCA}} \tag{9}$$

For the volume of the solvent phase (S) in equilibrium, V_S, it follows

$$V_S = V_{So} + \frac{c_{S,MPCA}V_SM_{MPCA}}{\rho_{MPCA}} \tag{10}$$

The fraction on the right side means the volume of extracted MPCA. Due to volume changes of the solvent phase the equilibrium concentration of TOA, c_{aE}, differs from the initial one, c_{Eo} according to the equation

$$c_{aE} = c_{Eo}\frac{V_{So}}{V_S} = c_{Eo}\left(1 - \frac{c_{S,MPCA}M_{MPCA}}{\rho_{MPCA}}\right) \tag{11}$$

The relation for V_{So}/V_S follows from eq 10. The loading of TOA by H_2SO_4 defined as molar ratio of H_2SO_4 and TOA in the organic phase is

$$z_{H_2SO_4} = \frac{c_{S,H_2SO_4}}{c_{aE}} \tag{12}$$

Selectivity of the extraction, S, was evaluated as a distribution coefficient of MPCA, $D_{a,MPCA}$, divided by the ratio of sums of all acid equivalents related to inorganic acids in the organic and aqueous phases, $D_{a,IA}$.

$$S = \frac{D_{a,MPCA}}{D_{a,IA}} = D_{a,MPCA}\frac{(c_{aF,Cl^-} + 2c_{aF,SO_4})}{(c_{S,HCl} + 2c_{S,H_2SO_4})} \tag{13}$$

In each experiment, the mass balances of MPCA, Δ_{MPCA}, sulfates, Δ_{SO_4}, chlorine, Δ_{Cl}, and total acidity, Δ_{TA}, were checked by the ratios

$$\Delta_{MPCA} = \frac{c_{aF,MPCA}V_F + c_{S,MPCA}V_S}{W_{MPCA}/M_{MPCA} + c_{Fo,MPCA}V_{Fo}} \tag{14}$$

where W_{MPCA} is the mass of solid MPCA added to the solvent

$$\Delta_{SO_4} = \frac{c_{aF,SO_4}V_F + c_{S,H_2SO_4}V_S}{(c_{Fo,H_2SO_4} + c_{Fo,Na_2SO_4})V_{Fo} + c_{H_2SO_4}V_{H_2SO_4}} \tag{15}$$

where c_{Fo,H_2SO_4} is the initial concentration of H_2SO_4 in the F phase and $c_{H_2SO_4}$ and is the concentration of H_2SO_4 in the concentrated solution used for the pH adjustment.

$$\Delta_{Cl} = \frac{c_{aF,Cl^-}V_F + c_{S,HCl}V_S}{(c_{Fo,HCl} + c_{Fo,NaCl})V_{Fo} + c_{HCl}V_{HCl}} \tag{16}$$

and

$$\Delta_{TA} = \frac{c_{aF,TA}V_F + c_{S,TA}V_S}{(c_{Fo,MPCA} + 2c_{Fo,H_2SO_4} + c_{Fo,HCl})V_{Fo} + W_{MPCA}/M_{MPCA} + 2c_{H_2SO_4}V_{H_2SO_4} + c_{HCl}V_{HCl} - c_{NaOH}V_{NaOH}} \tag{17}$$

Uncertainty of this mass balance ratio can be expressed in terms of standard deviation from the ideal value of $\Delta = 1$

$$\mathrm{SD} = \left[\frac{1}{n}\sum_{k=1}^{n}(\Delta_k - 1)^2\right]^{1/2} \tag{18}$$

The values of SD are listed in Tables 1 to 4 on the bottom of the appropriate columns. Unfortunately, some values of Δ differ more than by 10 % from the ideal value. This concerns especially the preliminary experiments collected in Table 1. The aqueous phases of the most of these experiments were prepared by mixing concentrated solution of MPCA with $c_{MPCA} = 0.4$ kmol·m^{-3}, water and solid salts. This way of preparation appeared inappropriate from the material balance point of view. Therefore, in the next experiments the aqueous phases were prepared by mixing aqueous solutions (MPCA + Na_2SO_4 + H_2O) with $c_{MPCA} = 0.4$ kmol·m^{-3} and (Na_2SO_4 + H_2O), provided that both of them have the same concentrations of Na_2SO_4. This resulted in the improvement of the material balances although they were in some cases still far from ideal. The present idea is to prepare the phases gravimetrically from solutions with known density, with subsequent density measurements of the equilibrium phases. However, this needs equipment for the fast density measurement, which was not available in the times when the experiments were done. Another problem followed from the pH adjustment which was done using highly concentrated solutions of H_2SO_4, HCl, and NaOH with w = 0.96, 0.35, and 0.50, respectively. Rather little volumes of these solutions contain rather large amounts of these agents. Therefore, just little inaccuracy in measurement of the added volumes may cause increased inaccuracy in the mass balances. This is manifested especially in experiment no. 10 in Table 3. The volume of added H_2SO_4 was not measured precisely so that the material balance of total acid, Δ_{TA}, in the system differs from the ideal value by 25 % and although the material balance of sulfates, Δ_{SO_4}, differs only by 4 %, it is still much worse than Δ_{SO_4} of other experiments in Table 3.

On the basis of the definition of ionic strength and the fact that both Na^+ and H^+ cations are monovalent, the following equation was derived for ionic strength in the aqueous phases

$$I_F = [Cl^-] + [HSO_4^-] + 3[SO_4^{2-}] + [MPCA^-] \tag{19}$$

The chlorides were determined argentometrically and the concentrations of other ions can be calculated using the dissociation constants of the related acids. Some of them are derived in the following section, for example eqs 29 and 31 to 33.

Model of Liquid−Liquid Equilibrium

The preliminary experiments summarized in Table 1 revealed that the extraction of MPCA in systems containing Na_2SO_4 is fairly more effective compared to systems with NaCl as can be seen from the distribution coefficient of MPCA, $D_{a,MPCA}$. Therefore, the next experiments (Tables 2 to 4) were done only with systems containing Na_2SO_4 without NaCl. The amount of data from few experiments with NaCl is not sufficient to perform their modeling, so that the equilibrium model based on the mass action law has been derived only for systems with the acidic solution (MPCA + Na_2SO_4 + H_2O) or (MPCA + H_2SO_4 + Na_2SO_4 + H_2O) with constant concentration of Na_2SO_4, c_{Fo,Na_2SO_4} = 1 kmol·m^{-3}, corresponding to the ionic strength $I_{Fo} = 3$ kmol·m^{-3}, and organic solvent (TOA + xylene). As the physical extraction of MPCA by xylene is negligible[16] only reactive extraction by TOA is considered according to the following reaction:

$$p\mathrm{HMPCA} + 2r\mathrm{H}^+ + r\mathrm{SO}_4^{2-} + q\mathbf{TOA} \rightleftharpoons \mathbf{(HMPCA)}_p\mathbf{(HSO_4^-)}_{2r-q}\mathbf{(SO_4^{2-})}_{q-r}\mathbf{(HTOA^+)}_q \tag{20}$$

where the boldface designates the species in the organic phase. This reaction describes the coextraction of H_2SO_4 and MPCA by TOA via the formation of ternary complexes (p, r, q). The formula of the ternary complex on the right side of the equation assumes the formation of ion pair between TOA and H_2SO_4 and hydrogen bond between H_2SO_4 and MPCA. Binary complexes (H_2SO_4 + TOA) and (MPCA + TOA) are (0, r, q) and

(p, 0, 1), respectively. The latter are formed according to eq 14 in the previous study,[16] where the hydrogen bond between MPCA and TOA is considered. The equilibrium constant of reaction 20, $K_{p,r,q}$ (extraction constant), is

$$K_{p,r,q} = \frac{c_{p,r,q}}{[\mathrm{HMPCA}]^p[\mathrm{H}^+]^{2r}[\mathrm{SO_4}^{2-}]^r c_\mathrm{E}^q} \tag{21}$$

where $c_{p,r,q}$ and c_E are the concentrations of complex (p, r, q) and free extractant in the organic phase, respectively. The following simplifications were done:

(a) Equilibrium activities were substituted with molarities (molar concentrations). Such an approximation is usual and commonly accepted as can be documented by numerous publications.[17−22] Although these models do not provide a precise thermodynamic description, they support theoretical suggestions related to the mechanism of extraction and hence considerably contribute to the overall comprehension of the system. On the other hand, a rigorous thermodynamic description needs more experimental data.

(b) Extractant (TOA), diluent (xylene), and the complexes are insoluble in water.

(c) Difference between the initial (V_o) and equilibrium volumes (V) of phases due to the mass transfer of acids was considered for MPCA, for H_2SO_4 it was neglected as explained in the previous study.[16] The difference in volumes caused that the equilibrium concentration of TOA, c_aE, differs from the initial one, c_Eo (eq 11).

(d) Coextraction of water was not considered in the model. As it will be shown in the final part of Results and discussion, water interacts with (TOA + acids) complexes in two ways. It appeared rather difficult to qualify exactly which part of water extraction should be assigned to the hydration of complex (stronger interaction) and which part to the formation of the suggested reverse micelles (weaker interaction). More detailed data are needed for such determination.

(e) Xylene was considered as an inert diluent with no influence on the extraction.

Such a system can be regarded as a three-component one with two phases. According to the Gibbs law of phases, there are three degrees of freedom. Therefore, the model operates with three independent variables which were chosen as follows:

1 total (analytical) equilibrium concentration of MPCA in the aqueous phase, $c_\mathrm{aF,MPCA}$

2 equilibrium pH ($\mathrm{pH_F}$) which was chosen instead of the analytical concentration of sulfates, $c_\mathrm{aF,SO_4}$, for the reduction of the model complexity

3 initial concentration of TOA (extractant) in the organic solvent before the contact of phases, c_Eo.

In fact, the model considers also the fourth independent variable - equilibrium concentration of sodium ions, $[\mathrm{Na}^+]$, in the aqueous phase. Although the initial concentration of Na_2SO_4, $c_\mathrm{Fo,\,Na_2SO_4}$, was always 1 $\mathrm{kmol \cdot m^{-3}}$ (i.e., 2 $\mathrm{kmol \cdot m^{-3}}$ of sodium ions), volume changes due to the mass transfer during the achievement of equilibrium and occasional addition of concentrated NaOH for the adjustment of pH (see Materials and Methods) caused deviations of this value. Since these deviations are small, for a more transparent presentation, the curves in all Figures were calculated with the approximation that $[\mathrm{Na}^+]$ is a constant value of 2 $\mathrm{kmol \cdot m^{-3}}$.

The model operated with the following parameters:

a equilibrium reaction constants of (p, 0, 1) and (p, r, q) complexes, $K_{p,0,1}$ and $K_{p,r,q}$, as fitting parameters

b equilibrium reaction constants of (0, r, q) complexes, $K_{0,r,q}$, as fixed parameters. The values of them were taken from a previous study on systems composed from (H_2SO_4 + Na_2SO_4 + H_2O) with $c_\mathrm{Fo,Na_2SO_4} = 1\ \mathrm{kmol \cdot m^{-3}}$ and (TOA + xylene) with $c_\mathrm{Eo} = 0.4\ \mathrm{kmol \cdot m^{-3}}$ (model 4 in Table 9 in the previous study[16])

c dissociation constants of MPCA and H_2SO_4, $\mathrm{p}K_{a,\mathrm{MPCA}}$ 2.87 and $\mathrm{p}K_{a2,\mathrm{H_2SO_4}}$ 0.908, as fixed parameters. These values were determined in solutions containing 1 $\mathrm{kmol \cdot m^{-3}}$ of Na_2SO_4 with $I = 3\ \mathrm{kmol \cdot m^{-3}}$ (Table 1 in the previous study[16]). Since the deviations in I_F from this value are rather moderate, within the interval of (−5.6 to +11.4) %, their influence on both dissociation constants was neglected.

Other quantities are dependent variables. Experimental values of five of them were fitted using the least-squares method:

1 equilibrium concentration of MPCA in the organic phase, $c_\mathrm{S,MPCA}$ (eq 7)

2 distribution coefficient of MPCA, $D_\mathrm{a,MPCA}$ (eq 9)

3 equilibrium concentration of H_2SO_4 in the organic phase, $c_\mathrm{S,H_2SO_4}$ (eq 8)

4 total acidity in the aqueous phase, $c_\mathrm{F,TA}$, measured by acidobasic titration, which is in fact

$$c_\mathrm{F,TA} = [\mathrm{H}^+] + [\mathrm{HMPCA}] + [\mathrm{HSO_4^-}] \tag{22}$$

5 total equilibrium concentration of acid equivalents in the organic phase, $c_\mathrm{S,TA}$, defined as

$$c_\mathrm{S,TA} = c_\mathrm{S,MPCA} + 2c_\mathrm{S,H_2SO_4} \tag{23}$$

These quantities, except $D_\mathrm{a,MPCA}$, are summarized in Figure 1. Results of fitting of $c_\mathrm{S,MPCA}$, $c_\mathrm{S,H_2SO_4}$, $c_\mathrm{F,TA}$, and $c_\mathrm{S,TA}$ are shown in the Supporting Information (Figures S1 to S3). $D_\mathrm{a,MPCA}$ vs $c_\mathrm{aF,MPCA}$ is shown in Figures 3, 6, 7, and 9a.

According to eq 21, concentration of complex (p, r, q) $c_{p,r,q}$ is

$$c_{p,r,q} = K_{p,r,q}[\mathrm{HMPCA}]^p[\mathrm{H}^+]^{2r}[\mathrm{SO_4}^{2-}]^r c_\mathrm{E}^q \tag{24}$$

Dependent variables in this equation, [HMPCA], $[\mathrm{SO_4}^{2-}]$, and c_E, were calculated as described below:

[HMPCA] was estimated using the dissociation constant of MPCA, $K_\mathrm{a,MPCA}$

$$[\mathrm{HMPCA}] = \frac{c_\mathrm{aF,MPCA}[\mathrm{H}^+]}{[\mathrm{H}^+] + K_\mathrm{a,MPCA}} \tag{25}$$

$[\mathrm{SO_4}^{2-}]$ can be calculated using the electroneutrality condition in the equilibrium:

$$2[\mathrm{SO_4}^{2-}] + [\mathrm{HSO_4}^-] = [\mathrm{Na}^+] + [\mathrm{H}^+] - [\mathrm{MPCA}^-] - [\mathrm{OH}^-] \tag{26}$$

Left side of this equation is equal to ($[\mathrm{SO_4}^{2-}] + c_\mathrm{aF,SO_4}$), where $c_\mathrm{aF,SO_4}$ is the sum of concentrations of sulfates and hydrogen sulfates ($[\mathrm{SO_4}^{2-}] + [\mathrm{HSO_4}^-]$), originating from Na_2SO_4 and

H_2SO_4. c_{aF,SO_4} can be calculated from the second dissociation constant of H_2SO_4, K_{a2,H_2SO_4}

$$K_{a2,H_2SO_4} = \frac{[H^+][SO_4^{2-}]}{c_{aF,SO_4} - [SO_4^{2-}]} \tag{27}$$

After rearrangement

$$c_{aF,SO_4} = \frac{[SO_4^{2-}]([H^+] + K_{a2,H_2SO_4})}{K_{a2,H_2SO_4}} \tag{28}$$

For [MPCA$^-$] follows

$$[MPCA^-] = \frac{c_{aF,MPCA}K_{a,MPCA}}{[H^+] + K_{a,MPCA}} \tag{29}$$

and the concentration of hydroxyl anions is

$$[OH^-] = \frac{K_{H_2O}}{[H^+]} \tag{30}$$

When eqs 26, 28, 29, and 30 are combined, it follows for $[SO_4^{2-}]$

$$[SO_4^{2-}] = R\left([Na^+] + Pc_{aF,MPCA} + [H^+] - \frac{K_{H_2O}}{[H^+]}\right) \tag{31}$$

where

$$P = \frac{K_{a,MPCA}}{[H^+] + K_{a,MPCA}} \tag{32}$$

$$R = \frac{K_{a2,H_2SO_4}}{[H^+] + 2K_{a2,H_2SO_4}} \tag{33}$$

The equilibrium concentration of MPCA in the organic phase, $c_{S,MPCA}$, is a sum of $c_{p,r,q}$ (eq 24) multiplied by p

$$c_{S,MPCA} = \sum_{p=1}^{i}\left[p\sum_{r=0}^{j}\left(\sum_{q=1}^{k} c_{p,r,q}\right)\right] \tag{34}$$

Combining eqs 11 and 34 gives the following relation for the total (analytical) concentration of the extractant in the equilibrium, c_{aE}:

ORGANIC SOLVENT PHASE (S)

composition:

extractant: TOA,
diluent: xylene
complexes: $(p, 0, 1)$, i.e. $(HMPCA)_p TOA$
$(0, r, q)$, i.e. $(HSO_4^-)_{2r-q}(SO_4^{2-})_{q-r}(HTOA^+)_q$
(p, r, q), i.e. $(HMPCA)_p(HSO_4^-)_{2r-q}(SO_4^{2-})_{q-r}(HTOA^+)_q$

equilibrium concentrations of acids:

equation based on sum of complexes (used in model) — *experimental determination from concentrations in stripping phase (R)*

$$\sum_{p=1}^{i}\left[p\sum_{r=0}^{j}\left(\sum_{q=1}^{k} c_{p,r,q}\right)\right] + 2\sum_{r=1}^{j}\left[r\sum_{p=0}^{i}\left(\sum_{q=1}^{k} c_{p,r,q}\right)\right] = c_{S,TA} = \frac{V_R}{V_{S,samp}}\left(c_{R,Na^+} - c_{R,TB}\right)$$

$$\sum_{p=1}^{i}\left[p\sum_{r=0}^{j}\left(\sum_{q=1}^{k} c_{p,r,q}\right)\right] = c_{S,MPCA} = \frac{V_R}{V_{S,samp}} c_{R,MPCA}$$

$$\sum_{r=1}^{j}\left[r\sum_{p=0}^{i}\left(\sum_{q=1}^{k} c_{p,r,q}\right)\right] = c_{S,H_2SO_4} = \frac{V_R}{2V_{S,samp}}\left(c_{R,Na^+} - c_{R,TB} - c_{R,MPCA}\right)$$

AQUEOUS PHASE (F)

composition:

neutral molecules: HMPCA and H_2O
cations: Na^+ and H^+
anions: $MPCA^-$, HSO_4^-, SO_4^{2-} and OH^-

equilibrium concentrations of acids:

equation based on sum of components (used in model) — *experimental determination*

$[H^+]+[HMPCA]+[HSO_4^-] = c_{F,TA}$ measured directly
$[HMPCA]+[MPCA^-] = c_{aF,MPCA}$ measured directly

$$[HSO_4^-]+[SO_4^{2-}] = c_{aF,SO_4} = c_{Fo,Na_2SO_4}\frac{V_{Fo}}{V_F} + \frac{1}{2}\left(\frac{c_{NaOH}V_{NaOH}}{V_F} + c_{F,TA} - c_{aF,MPCA}\right)$$

Figure 1. Schematic description of the composition of aqueous and organic phases in systems with aqueous phase (MPCA + H_2SO_4 + Na_2SO_4 + H_2O) or (MPCA + Na_2SO_4 + H_2O) and solvent (TOA + xylene) with relation to concentrations.

$$c_{\mathrm{aE}} = c_{\mathrm{Eo}}\left\{1 - \sum_{p=1}^{i}\left[p\sum_{r=0}^{j}\left(\sum_{q=1}^{k} c_{p,r,q}\right)\right]\frac{M_{\mathrm{MPCA}}}{\rho_{\mathrm{MPCA}}}\right\} \tag{35}$$

Another relation for c_{aE} is a sum of all $c_{p,r,q}$ (eq 24) multiplied by q together with concentration of free extractant in the solvent phase, c_{E}

$$c_{\mathrm{aE}} = \sum_{q=1}^{k}\left[q\sum_{p=0}^{i}\left(\sum_{r=0}^{j} c_{p,r,q}\right)\right] \tag{36}$$

c_{E} is the last dependent variable in eq 24. In eq 36 it is included as $c_{0,0,1} = c_{\mathrm{E}}$. When eqs 24, 35, and 36 are combined, c_{E} can be calculated as a solution of the kth degree polynomic equation

$$\sum_{p=0}^{i}\left\{\sum_{r=0}^{j}\left[\sum_{q=1}^{k}\left(c_{\mathrm{Eo}}\frac{M_{\mathrm{MPCA}}}{\rho_{\mathrm{MPCA}}}p + q\right) \times K_{p,r,q}[\mathrm{HMPCA}]^{p}[\mathrm{H}^{+}]^{2r}[\mathrm{SO}_4^{2-}]^{r}c_{\mathrm{E}}^{q}\right]\right\} - c_{\mathrm{Eo}} = 0 \tag{37}$$

For equilibrium concentration of H_2SO_4, $c_{\mathrm{S,H_2SO_4}}$, experimentally determined by eq 8, follows from the model

$$c_{\mathrm{S,H_2SO_4}} = \sum_{r=1}^{j}\left[r\sum_{p=0}^{i}\left(\sum_{q=1}^{k} c_{p,r,q}\right)\right] \tag{38}$$

Similarly as concentrations, also the distribution coefficient of MPCA, $D_{\mathrm{a,MPCA}}$, defined by eq 9, can be expressed as a sum of contributions related to the individual complexes (p, r, q), $D_{\mathrm{a,MPCA}(p,r,q)}$ as it is shown in Figures 6, 7, and 9a

$$D_{\mathrm{a,MPCA}} = \sum_{p=1}^{i}\left[\sum_{r=0}^{j}\left(\sum_{q=1}^{k} D_{\mathrm{a,MPCA}(p,r,q)}\right)\right] \tag{39}$$

where

$$D_{\mathrm{a,MPCA}(p,r,q)} = \frac{p c_{p,r,q}}{c_{\mathrm{aF,MPCA}}} \tag{40}$$

The same follows also for saturation of the extractant, z_{E}, defined as a molar ratio of the extractant bound in complexes to the overall amount of the extractant

$$z_{\mathrm{E}} = 1 - \frac{c_{\mathrm{E}}}{c_{\mathrm{aE}}} \tag{41}$$

In Figures 8 and 9b, z_{E} is depicted using the relation

$$z_{\mathrm{E}} + \frac{c_{\mathrm{E}}}{c_{\mathrm{aE}}} = \frac{\sum_{p=0}^{i}\left[\sum_{r=0}^{j}\left(\sum_{q=1}^{k} q c_{p,r,q}\right)\right]}{c_{\mathrm{aE}}} = 1 \tag{42}$$

Similarly as in eq 36 also here $c_{0,0,1}$ is not a complex but it is equal to the concentration of free TOA, c_{E}. In Figures 6 to 9 the area between two curves always belongs to the contribution of one complex and the vertical distances between curves are the contributions of the individual complexes at the given concentration of MPCA, $c_{\mathrm{aF,MPCA}}$. These contributions are always ordered from bottom to top as follows: first are (p, 0, 1) complexes (1, 0, 1) and (2, 0, 1), then (0, r, q) complexes (0, 1, 2), (0, 2, 3) and (0, 3, 3) (only z_{E}, i.e., Figures 8 and 9b), then (p, 1, 2) complexes (1, 1, 2), (2, 1, 2) and (3, 1, 2) and finally (p, 2, 3) complexes (1, 2, 3), (2, 2, 3). The borders between the sets of (p, 0, 1), (0, r, q) and (p, r, q) complexes are boldfaced. The area related to the contribution of the given complex is sometimes very narrow. However, in most cases, these complexes cannot be neglected because in other conditions (pH, concentration) much wider area indicates considerable contribution. For example, complex (2, 2, 3) has rather big area at pH 2.03 (Figure 7a and 8a). At pH 2.87, the area of the same complex is almost negligible (Figure 7c and 8c).

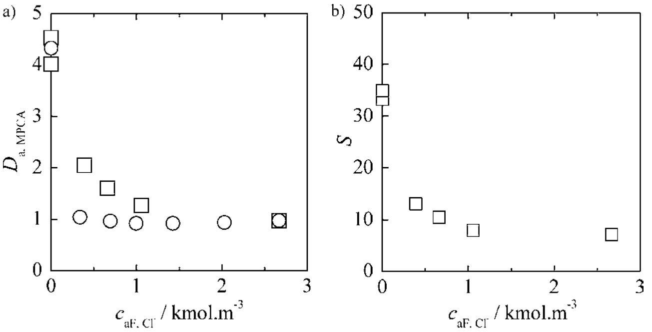

Figure 2. Influence of NaCl concentration on the distribution coefficient of MPCA, $D_{\mathrm{a,MPCA}}$ (a), in extraction by (TOA + xylene), $c_{\mathrm{Eo}} = 0.4$ kmol·m^{-3}. Aqueous phases: ○, ternary solutions (MPCA + NaCl + H_2O) at average equilibrium $\mathrm{pH_F}$ 2.32 and $c_{\mathrm{aF,MPCA}} = 0.087$ kmol·m^{-3} (see Table 1, experiment nos. 1 to 7) and □, quaternary solutions (MPCA + Na_2SO_4 + NaCl + H_2O) with various ratios of Na_2SO_4 and NaCl at average ionic strength $I_{\mathrm{F}} = 3.10$ kmol·m^{-3}, pH 2.45, and $c_{\mathrm{aF,MPCA}} = 0.076$ kmol·m^{-3} (see Table 1, experiment nos. 7 to 12). (b) Selectivity (S) related to quaternary solution.

Results and Discussion

Comparison of MPCA Extraction from Aqueous Solutions Containing Na_2SO_4 and/or NaCl. The ternary acidic solution (MPCA + inorganic salt + H_2O) can be in fact regarded as a solution of two acids. Reactive extractants extract these acids simultaneously (see eq 20). Two mechanisms of such extraction have been proposed:

A Competitive extraction which can be explained as a competition between organic and inorganic acids for the free TOA. This results in the formation of binary complexes (MPCA + TOA) and (inorganic acid + TOA) with the stoichiometry (p, 0, 1) and (0, r, q), respectively.

B Coextraction, when ternary complexes (p, r, q) containing both acids and TOA are formed.

These two mechanisms proceed simultaneously (see eq 20 and text below).

For preliminary testing of the influence of ionic strength on MPCA extraction by solvent (TOA + xylene), the ternary solutions (MPCA + NaCl + H_2O) with various concentrations of NaCl were examined. Figure 2 and experiments 1 to 7 in Table 1 show that already at the aqueous concentration of chlorides $c_{\mathrm{aF,Cl^-}} = 0.34$ kmol·m^{-3}, the value of the distribution coefficient of MPCA, $D_{\mathrm{a,MPCA}}$, dropped from 4.3 to 1.0. With a further increase in the chloride concentration, $D_{\mathrm{a,MPCA}}$ remained almost unchanged. This effect, as well as the data on concentrations of HCl in the solvent, $c_{\mathrm{S,HCl}}$, shown in Table 1 indicate

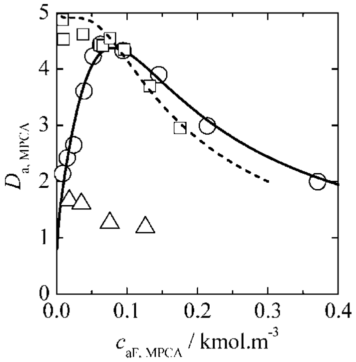

Figure 3. Concentration dependence of the distribution coefficient of MPCA, $D_{\mathrm{a,MPCA}}$, in extraction by solvent (TOA + xylene); $c_{\mathrm{Eo}} = 0.4$ kmol·m^{-3}. Aqueous phases: ○, —, binary solution (MPCA + H_2O),[16] □, – –, quaternary solutions (MPCA + H_2SO_4 + Na_2SO_4 + H_2O), $c_{\mathrm{Fo,H_2SO_4}} = 0.1$ kmol·m^{-3}, $c_{\mathrm{Fo,Na_2SO_4}} = 1$ kmol·m^{-3} (Table 2) and △, (MPCA + Na_2SO_4 + NaCl + H_2O), $c_{\mathrm{Fo,Na_2SO_4}} = 0.4$ kmol·m^{-3} and $c_{\mathrm{Fo,NaCl}} = 1.4$ kmol·m^{-3} (Table 1). Lines were correlated according to the model presented in the previous study[16] (binary solution) and model 2 in Table 5 (quaternary solution).

that hydrochloric acid is competitively bonded to TOA in a large extent at the expense of MPCA. The extraction of MPCA was suppressed because the affinity of strong inorganic acids to TOA is much higher compared to MPCA.[16] However, it will be shown below that a minor part of acids was extracted also by coextraction. Further experiments were carried out using a quaternary solution (MPCA + Na_2SO_4 + NaCl + H_2O) with various concentrations of Na_2SO_4 and NaCl, provided that the ionic strength remained similar, in fact within the interval from (2.69 to 3.13) kmol·m^{-3} (Table 1, experiments 7 to 12). Figure 2a shows that at zero concentration of chlorides, $D_{\mathrm{a,MPCA}}$ was the same as in extraction from binary solvent (MPCA + H_2O). Increasing the chloride concentration, $D_{\mathrm{a,MPCA}}$ did not decrease so sharply as it was observed with (MPCA + NaCl + H_2O). Figure 2b shows that the selectivity of the MPCA extraction (eq 13) was about five times higher when only sulfates without chlorides were present compared to the point when it was vice versa. These results indicate that in spite of the similar ionic strengths, the extraction of MPCA from solutions containing Na_2SO_4 is much better compared to those containing NaCl.

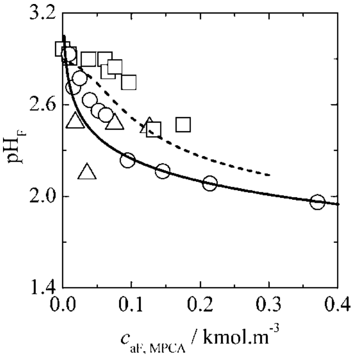

Figure 4. Concentration dependence of the equilibrium pH in liquid−liquid equilibria of MPCA in systems with solvent (TOA + xylene), $c_{\mathrm{Eo}} = 0.4$ kmol·m^{-3}. Meaning of symbols and lines are the same as in Figure 3.

Table 5. Chemical Reaction Equilibrium Constants, $K_{p,r,q}$, of (p, r, q) Complexes Containing pHMPCA, $r$$H_2SO_4$, and qTOA for Systems with Acidic Aqueous Solution (MPCA + H_2SO_4 + Na_2SO_4 + H_2O) or (MPCA + Na_2SO_4 + H_2O) with $c_{\mathrm{Fo,Na_2SO_4}} = 1$ kmol·m^{-3} and Organic Solvent (TOA + Xylene)

model number	1	2
complex	$K_{p,r,q}$	
(p, r, q)	(kmol·m^{-3})$^{1-p-3r-q}$	
(0, 1, 2)	fixed $7.24 \cdot 10^5$	
(0, 2, 3)	fixed $4.12 \cdot 10^{11}$	
(0, 3, 3)	fixed $1.27 \cdot 10^{14}$	
(1, 0, 1)	13.0	16.9
(2, 0, 1)	832	772
(1, 1, 1)	$3.04 \cdot 10^5$	
(1, 1, 2)	$8.38 \cdot 10^7$	$6.33 \cdot 10^7$
(2, 1, 2)	$4.29 \cdot 10^8$	$1.16 \cdot 10^8$
(3, 1, 2)	$1.08 \cdot 10^9$	$6.22 \cdot 10^9$
(1, 2, 3)		$1.86 \cdot 10^{13}$
(2, 2, 3)		$5.66 \cdot 10^{14}$
p$K_{\mathrm{a2,MPCA}}$	fixed 2.87	
p$K_{\mathrm{a2,H_2SO_4}}$	fixed 0.908	
correlation coefficient	0.9923	0.9926

For better elucidation of differences in the influence of Na_2SO_4 and NaCl on extraction of MPCA by (TOA + xylene) the dependences of $D_{\mathrm{a,MPCA}}$ on MPCA concentration was investigated with quaternary solutions (MPCA + H_2SO_4 + Na_2SO_4 + H_2O) with $c_{\mathrm{Fo,H_2SO_4}} = 0.1$ kmol·m^{-3} and $c_{\mathrm{Fo,Na_2SO_4}} =$ 1 kmol·m^{-3} and (MPCA + Na_2SO_4 + NaCl + H_2O) with constant ratio of Na_2SO_4 to NaCl. They are depicted in Figure 3. As expected, a less effective extraction was observed for system with chlorides in the whole range of tested MPCA concentrations. Comparison of systems with (MPCA + H_2SO_4 + Na_2SO_4 + H_2O) and with binary solution (MPCA + H_2O)[16] is also shown in Figure 3. It was revealed, that at MPCA concentrations $c_{\mathrm{aF,MPCA}} > 0.1$ kmol·m^{-3}, $D_{\mathrm{a,MPCA}}$ is slightly higher for (MPCA + H_2O) and at $c_{\mathrm{aF,MPCA}} < 0.05$ kmol·m^{-3}, $D_{\mathrm{a,MPCA}}$ is markedly higher for (MPCA + H_2SO_4 + Na_2SO_4 + H_2O). This indicates that at $c_{\mathrm{aF,MPCA}} < 0.05$ kmol·m^{-3} the addition of H_2SO_4 increases the extraction of MPCA. Moreover, Figure 4 shows that, in the equilibrium with (MPCA + H_2SO_4 + Na_2SO_4 + H_2O), pH was higher compared to (MPCA + H_2O). Such behavior indicates that, contrary to systems with NaCl, in the systems with Na_2SO_4 coextraction is very important. In the interval of $c_{\mathrm{aF,MPCA}} = (0.05$ to $0.1)$ kmol·m^{-3}, $D_{\mathrm{a,MPCA}}$ is similar for both (MPCA + H_2SO_4 + Na_2SO_4 + H_2O) and (MPCA + H_2O). This is in agreement with the similarity of $D_{\mathrm{a,MPCA}}$ in Figure 2a at zero concentration of chlorides.

Modeling of Liquid−Liquid Equilibria with Simultaneous Extraction of MPCA and H_2SO_4. Since the results of the preliminary experiments indicate that the extraction of MPCA from aqueous solutions containing sulfates could be more effective compared to solutions containing chlorides, further work was focused only on the systems with solutions (MPCA + H_2SO_4 + Na_2SO_4 + H_2O), in which $c_{\mathrm{Fo,Na_2SO_4}} = 1$ kmol·m^{-3}. In this way, a satisfactory set of data has been obtained for their correlation using the model based on the mass action law. The few experiments with chlorides do not provide sufficient information for such modeling. The problem may arise at least from the fact that the number of independent values should be close to the number of fitted parameters. Moreover, since the concentration of NaCl differs from experiment to experiment, the dependencies of equilibrium constants, $K_{p,r,q}$, as well as dissociation constant, p$K_{\mathrm{a,MPCA}}$, on ionic strength are necessary. We were not able to determine them from such little amount of data.

Experiments with Na_2SO_4 can be divided in two main sets.

1. Experiments oriented on the influence of TOA concentration on the extraction of MPCA. Dependencies on MPCA concentration, $c_{\mathrm{aF,MPCA}}$, at three different concentrations of TOA $c_{\mathrm{Eo}} = (0.2, 0.4$ or $0.6)$ kmol·m^{-3} were measured (Table 2, Figure 6). The initial concentration of H_2SO_4 was always constant, $c_{\mathrm{Fo,H_2SO_4}} = 0.1$ kmol·m^{-3}.

2. Experiments oriented on the influence of equilibrium pH. Dependencies on $c_{aF,MPCA}$ at three different equilibrium pH (pH_F) adjusted close to 2.03, 2.43, or 2.87 (Table 3, Figures 7, 8, and 10a) were measured. The initial concentration of TOA was always constant, $c_{Eo} = 0.4\ \mathrm{kmol \cdot m^{-3}}$. This set of experiments was finished by pH-dependence at average $c_{aF,MPCA}$ of about $0.081\ \mathrm{kmol \cdot m^{-3}}$ and $c_{Eo} = 0.4\ \mathrm{kmol \cdot m^{-3}}$ (Table 4, Figures 9 and 10b).

Both data sets were correlated simultaneously. Initially, the equilibrium constants $K_{p,r,q}$ with $p = (1\text{ to }3)$, $r = (1\text{ to }3)$, and $q = (1\text{ to }2)$ and $K_{p,0,1}$ with $p = (1\text{ to }3)$ were chosen as fitting parameters. Correlation by the least-squares method reduced the initial 21 fitting parameters to the final six as shown in Table 5, model 1. Four of them are the equilibrium constants of ternary complexes containing both MPCA and H_2SO_4. These (p, r, q) complexes could be considered as formerly (0, r, q) with added MPCA molecules. This is evident mainly for the three (p, 1, 2) complexes and complex (1, 1, 1) should be considered as formerly (0, 1, 1) with one added molecule of MPCA, whereas complex (0, 1, 1) could be formed by the splitting of (0, 2, 3) to TOA/sulfate, (0, 1, 2), and TOA/hydrogensulfate, (0, 1, 1).[16] Equilibrium constants of other (p, r, q) complexes, were turned to zero value. Therefore, for the next model, only $K_{p,r,q}$ of complexes (p, 1, 2), (p, 2, 3), (p, 3, 3) and (p, 0, 1) with $p = (1\text{ to }3)$ were selected as initial fitting parameters. Such correlation resulted in model 2 in Table 5. The initial 12 parameters were reduced to the final seven. The correlation coefficient for model 2 is slightly better compared to that for model 1. The last attempt was the combination of models 1 and 2 considering all eight free parameters from Table 5 provided that the initial values of them were chosen as follows: for $K_{1,1,1}$ value from model 1, for $K_{1,2,3}$ and $K_{3,2,3}$ values from model 2 and for other five constants the average values from model 1 and 2. Fitting turned these values to model 2, which was therefore finally selected for all further calculations. The fact that the modeling tended to the selection of (p, r, q) complexes, which can be considered as (0, r, q) with added MPCA (Table 5), is in agreement with the concept that in all (p, r, q) complexes H_2SO_4 is joined with TOA directly in the form of an ion pair and MPCA is joined with H_2SO_4 by hydrogen bonding. Regardless to the fact that this correlation does not represent precise thermodynamic approach, such tendency supports the opinion that H_2SO_4 interacts with TOA much stronger than MPCA as it was also concluded in the previous study.[16] Hypothetical structural formulas of complexes (2, 1, 2) and (3, 1, 2) are shown in Figure 5.

Extraction of MPCA in Binary Complexes. The increased ionic strength in the aqueous phases usually supports the extraction of organic molecules with hydrophobic properties to the organic solvents. For MPCA the hydrophobicity is indicated by its limited solubility in water. In the presence of reactive extractants, such a salting-out effect can be disturbed by the parallel extraction of inorganic acid. Anyway, for that part of overall extraction, in which the inorganic acid does not participate and MPCA interacts directly with TOA, that is in the formation of the binary complexes (p, 0, 1), the salting-out effect could appear. Equilibrium constants of (p, 0, 1) complexes, $K_{1,0,1}$ and $K_{2,0,1}$, shown in Table 5, model 2 are by about 4 and 5 times higher, respectively, compared to the constants of the same complexes, $K_{1,1}$ and $K_{2,1}$, obtained by modeling of the equilibrium data measured in system with binary solution ($MPCA + H_2O$) and the same solvent (see previous study,[16] Table 6). Such increase in the equilibrium constants at the increased ionic strength supports the idea that the salting-out effect occurs. Contrary to this, the extraction of polar H_2SO_4 was worse in the systems containing Na_2SO_4 compared to systems without salt.[16]

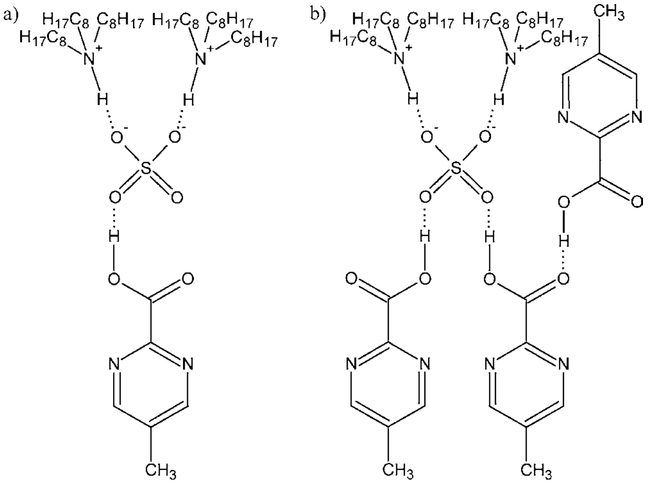

Figure 5. Hypothetical structural formulas of complexes (1, 1, 2) (a) and (3, 1, 2) (b) in systems with aqueous phase ($MPCA + H_2SO_4 + Na_2SO_4 + H_2O$) or ($MPCA + Na_2SO_4 + H_2O$) and solvent ($TOA$ + xylene).

Table 6. Concentration of Chloride-Free TOA and Values of Chloride-Free TOA Loading by MPCA Calculated using Experimental Data ($z_{MPCA,Cl-free,exp}$) and Data from Correlation ($z_{MPCA,Cl-free,calc}$) According to eqs 43 and 44, Respectively, for Experiment Nos. 2 to 7 in Table 1

no.	$c_{aE} - c_{S,HCl}$ $\mathrm{kmol \cdot m^{-3}}$	$z_{MPCA,Cl-free,exp}$	$z_{MPCA,Cl-free,calc}$
2	0.0656	1.76	1.56
3	0.0408	2.03	1.64
4	0.0380	1.70	1.50
5	0.0501	1.65	1.35
6	0.0388	1.98	1.50
7	0.0353	2.04	1.46

Extraction of MPCA from Ternary Solutions (MPCA + NaCl + TOA). In this system, the competitive mechanism dominates. However, experimental results in confrontation with equilibrium constants $K_{1,0,1}$ and $K_{2,0,1}$ obtained from correlation of the systems with sulfates (Table 5, model 2) indicate that for a minor part of MPCA also coextraction occurs. In Table 1, experiments 1 to 7, the concentration of HCl, $c_{S,HCl}$, in the solvent (TOA + xylene) with $c_{Eo} = 0.4\ \mathrm{kmol \cdot m^{-3}}$ is shown. Provided the all HCl in the solvent is in the form of complexes (p, 1, 1), $p \geq 0$, the difference between concentration of TOA (c_{aE}) and $c_{S,HCl}$, represents the extractant which did not interact with HCl. Provided the only competitive mechanism is considered, the loading of this part of TOA by MPCA, $z_{MPCA,Cl-free}$, can be calculated by two ways.

1. Using experimental values of $c_{S,MPCA}$ and $c_{S,HCl}$ (Table 1) according to the equation

$$z_{MPCA,Cl-free,exp} = \frac{c_{S,MPCA}}{c_{aE} - c_{S,HCl}} \tag{43}$$

Values of $z_{MPCA,Cl-free,exp}$ are shown in Table 6. According to the paper of Schunk and Maurer,[23] in the solvent containing TOA in toluene, which is structurally close to xylene, also complex (0, 2, 3) can be formed with HCl. This indicates that more of TOA can be blocked by chlorides than it is supposed by eq 43 assuming only formation of complexes (p, 1, 1). This fact may lead to an underestimation of $z_{MPCA,Cl-free,exp}$.

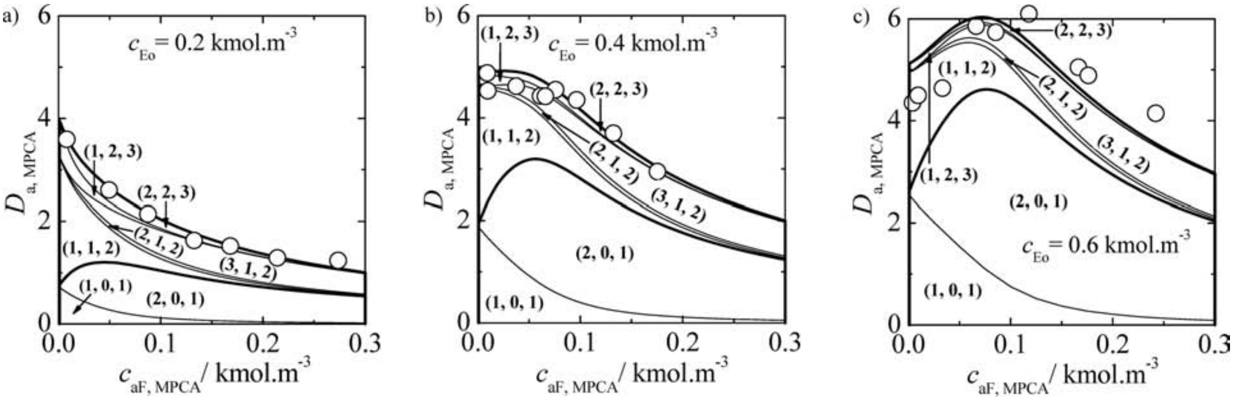

Figure 6. Influence of TOA concentration on the concentration dependence of the distribution coefficient of MPCA, $D_{a,MPCA}$ (eqs 39 and 40), in extraction from quaternary solution (MPCA + H_2SO_4 + Na_2SO_4 + H_2O), $c_{Fo,H_2SO_4} = 0.1$ kmol·m^{-3}, $c_{Fo,Na_2SO_4} = 1$ kmol·m^{-3} (Table 2) by solvent (TOA + xylene) with c_{Eo} = (0.2, a; 0.4, b; and 0.6, c) kmol·m^{-3}. The contributions of individual complexes to the values of $D_{a,MPCA}$ are explained at the end of the section “Model of Liquid−Liquid Equilibrium”.

2. Using equilibrium constants $K_{1,0,1}$ and $K_{2,0,1}$ (Table 5, model 2) and eq 30 derived in the previous study[16] for systems with binary solution (MPCA + H_2O). This equation can be applied also for systems with chlorides for that TOA which is either free or interacts directly with MPCA

$$z_{\mathrm{MPCA,Cl-free,calc}} = \frac{K_{1,0,1}[\mathrm{HMPCA}] + 2K_{2,0,1}[\mathrm{HMPCA}]^2}{1 + K_{1,0,1}[\mathrm{HMPCA}] + K_{2,0,1}[\mathrm{HMPCA}]^2} \tag{44}$$

Values of $z_{\mathrm{MPCA,Cl-free,calc}}$ are also shown in Table 6. Equilibrium constants $K_{1,0,1}$ and $K_{2,0,1}$ used in eq 44 resulted from the data correlation of experiments where the values of ionic strength (I_F, Tables 2 to 4) were fairly higher than I_F in the experiments 2 to 7 in Table 1. The conclusion from the previous section that increased I_F in the aqueous phase increases the equilibrium constants of binary complexes (MPCA + TOA) indicates that values of $K_{p,0,1}$ in eq 44 are overestimated and the real ones should be probably lower. Lower values of $K_{p,0,1}$ lead to lower loadings. Moreover, $pK_{a,MPCA} = 3.09$ was used for the calculation of [HMPCA]. This value was determined for low ionic strength, close to zero (Marták et al.[16]). However, with the increase in chloride concentration, c_{aF,Cl^-} (experiments 2 to 7 in Table 1), $pK_{a,MPCA}$ as well as the concentration of undissociated HMPCA decrease what can negatively affect the extraction. Therefore, the selection of values for $K_{p,0,1}$ and $pK_{a,MPCA}$ probably resulted in an overestimation of loadings calculated by eq 44.

In spite of the possible underestimation of $z_{\mathrm{MPCA,\ Cl-free,\ exp}}$ and the overestimation of $z_{\mathrm{MPCA,\ Cl-free,\ calc}}$, the comparison in Table 6 shows that the values of former are higher. This can only be explained by accepting the contribution of coextraction represented by formation of ternary complexes, for example, (1, 1, 1), with the proposed structure $\mathrm{TOAH^+Cl^-\cdots HMPCA}$. A similar complex containing propionic acid, $\mathrm{R_3NH^+Cl^-\cdots HOOC{-}C_2H_5}$, has already been proposed by Canari and Eyal.[8] Ternary complexes containing acetic or citric acid, HCl and TOA proposed by Schunk et al.[4−7] (Table S1), are mentioned in more detail above in Introduction.

Extraction of MPCA from Aqueous Solutions Containing Inorganic Sulfates. 1. Effect of TOA Concentration. In reactive extraction of monocarboxylic acids[24−27] from their binary aqueous solutions by solvents containing extractants diluted in a nonpolar diluent the distribution coefficient related to the reactive extraction is usually directly proportional to the extractant concentration. However, Figure 6 shows that in extraction of MPCA from solutions containing also sulfates by solvents containing TOA in various concentrations diluted in xylene, such proportionality was not preserved. Especially at MPCA concentrations approaching zero, the distribution coefficient, $D_{a,MPCA}$, approaches similar values for all concentrations of TOA. It is not likely that such event is caused by the polarity of xylene, which is low but rather by coextraction resulting in the formation of ternary complexes (*p*, *r*, *q*).

The analysis of $D_{a,MPCA}$ shown in Figure 6 indicates that the partial distribution coefficient related to the contributions of (MPCA + TOA) binary complexes (1, 0, 1) and (2, 0, 1), $D_{a,MPCA(p,\ 0,\ 1)} = D_{a,MPCA(1,\ 0,\ 1)} + D_{a,MPCA(2,\ 0,\ 1)}$, is more or less proportional to the TOA concentration rather satisfactorily. The rest of extracted MPCA should be attributed to the formation of ternary (*p*, *r*, *q*) complexes. Since the correlation of the data indicated that these could be regarded as (0, *r*, *q*) complexes with added molecules of MPCA, it can be concluded that in addition to the free TOA, (0, *r*, *q*) complexes also should act as a rather effective extractants for MPCA.

2. Effect of pH. Influence of pH on the extraction of MPCA by TOA from aqueous solutions containing inorganic sulfates is very complex. Figure 7 indicates that increasing pH from 2.03 to 2.87, the contribution of ternary (*p*, *r*, *q*) complexes to the overall distribution coefficient decreases in favor of the binary complexes. This can be elucidated as follows: at pH = 2.03, TOA can be protonated to $\mathrm{HTOA^+}$ at the interface. Cations of TOA necessarily need anions. Since at pH 2.03 almost all MPCA is undissociated, the only available ones are $\mathrm{SO_4^{2-}}$, eventually $\mathrm{HSO_4^-}$. This results in preferential formation of complexes containing H_2SO_4 (Figure 7a). Increasing pH, TOA is neutralized so that dissociated H_2SO_4 cannot be extracted effectively. The only possibility for TOA is to extract neutral HMPCA molecules by forming binary complexes (*p*, 0, 1). These are still available even at pH 2.87 = $pK_{a,MPCA}$[16] (Figure 7c), when MPCA is only half-dissociated. The preferential formation of (*p*, 0, 1) complexes at higher pH seems to be supported also by the fact that more free TOA is available as follows from the comparison of Figure 8a, 8b, and 8c.

For MPCA concentrations $c_{aF,MPCA} < 0.03$ kmol·m^{-3}, the distribution coefficient is markedly higher at pH 2.03 and 2.43 (Figure 7a and 7b) when almost all TOA is occupied by H_2SO_4 (Figure 8a and 8b) compared to pH 2.87 (Figure 7c) when about half of TOA is free (Figure 8c) as well as compared to the

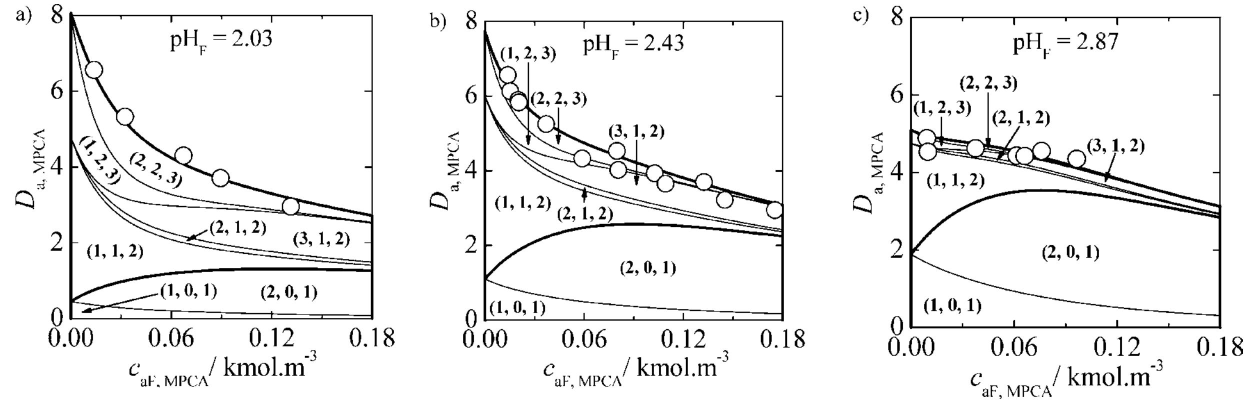

Figure 7. Concentration dependence of the distribution coefficient of MPCA, $D_{a,MPCA}$ (eqs 39 and 40), at three different equilibrium pH values, 2.03 (a), 2.43 (b), and 2.87 (c), in extraction from ternary solution (MPCA + Na_2SO_4 + H_2O), $c_{Fo,Na_2SO_4} = 1$ kmol·m^{-3}, by solvent (TOA + xylene), $c_{Eo} = 0.4$ kmol·m^{-3}. Equilibrium pH was adjusted by concentrated H_2SO_4 and/or NaOH. The contributions of individual complexes to the values of $D_{a,MPCA}$ are explained at the end of the section "Model of Liquid−Liquid Equilibrium".

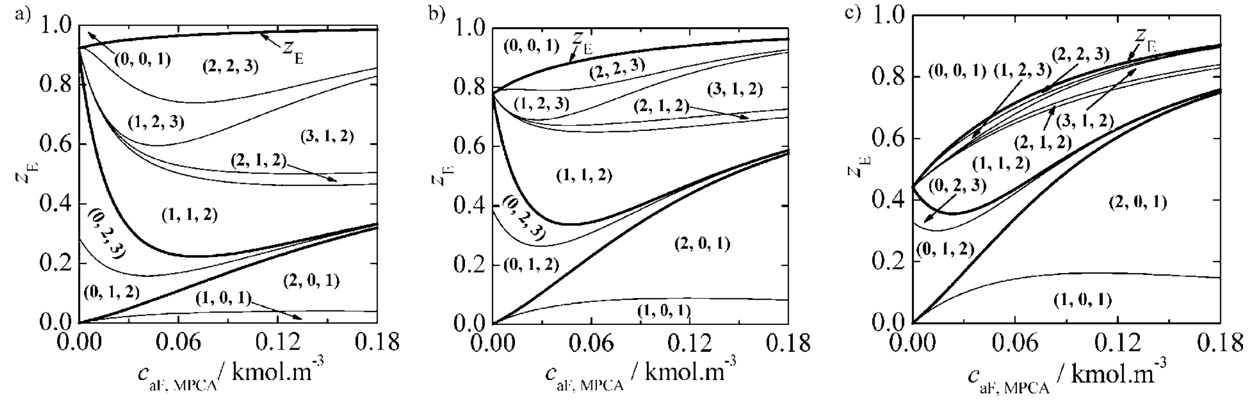

Figure 8. Saturation of TOA by MPCA and H_2SO_4, z_E (eq 41 and 42), as a function of MPCA concentration at three different equilibrium pH values: (a) 2.03, (b) 2.43, and (c) 2.87. The same experiments as in Figure 7 are presented. The contributions of individual complexes to z_E are explained at the end of the section "Model of Liquid−Liquid Equilibrium". (0, 0, 1) is free TOA.

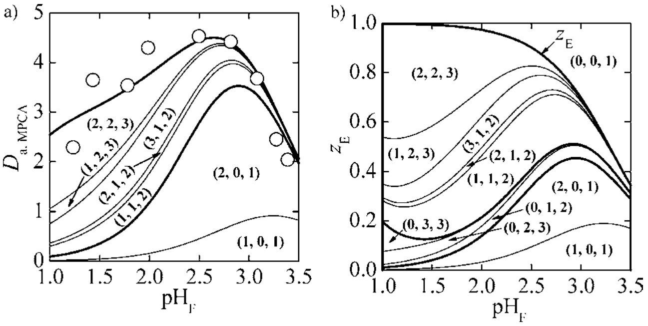

Figure 9. pH dependence of the distribution coefficient of MPCA, $D_{a,MPCA}$ (eqs 39 and 40) (a), and the saturation of TOA by MPCA and H_2SO_4, z_E (eq 41 and 42) (b), at constant equilibrium concentration of MPCA in the aqueous phase, $c_{aF,MPCA} = 0.081$ kmol·m^{-3}. Similar 2-phase systems as in Figures 7 and 8 were used. Equilibrium pH adjustment as well as the calculation of contributions of complexes to the overall values of $D_{a,MPCA}$ and z_E was done by the same way as in Figures 7 and 8. (0, 0, 1) is free TOA.

system with binary solution (MPCA + H_2O) without sulfates (Figure 3). This indicates that the solvent with (H_2SO_4 + TOA) complexes, which are de facto ionic liquids, provides better extraction of MPCA from aqueous solutions.

Figure 7 shows that for $c_{aF,MPCA} > 0.06$ kmol·m^{-3}, the increase of pH value from 2.03 to 2.87 increased the distribution coefficients slightly. This is better illustrated in Figure 9a showing the pH dependence of the distribution coefficient at constant $c_{aF,MPCA} = 0.081$ kmol·m^{-3}. The maximum distribution coefficient at pH 2.65 could be attributed to the domination of complex (2, 0, 1). Among all complexes, this one has the highest MPCA to TOA ratio, 2/1. Although the majority of complexes containing H_2SO_4 favored at lower pH contain also MPCA (Figure 9b), the MPCA to TOA ratio in them is lower, in interval from 1/3 to 3/2. Increasing pH above 2.65, which is close to $pK_{a,MPCA} = 2.87$,[16] the MPCA dissociates so that the availability of HMPCA decreases. At higher pH there is also a lack of protons. The result is that neither (*p*, 0, 1) nor (*p*, *r*, *q*) complexes can be formed so that the $D_{a,MPCA}$ steeply decreases and the amount of free TOA increases (Figure 9b).

The dependence of selectivity, *S*, on equilibrium pH is illustrated in Figure 10 where the same experiments are shown as in Figures 7 to 9. In Figure 10b it can be seen that at higher pH, the selectivity is also higher. This is important mainly for $c_{aF,MPCA} > 0.06$ kmol·m^{-3} (Figure 10a). At these concentrations, the equilibrium pH around the value of 3 could be selected as a compromise between good distribution coefficient and selectivity (compare Figures 9a and 10b). Compared to higher MPCA concentrations, for $c_{aF,MPCA} < 0.03$ kmol·m^{-3}, the differences between the selectivity at various pH values are not so high, A compromise between good distribution coefficient and selectivity should be pH of about 2.5, as follows from comparison of Figures 7 and 10a.

Coextraction of Water. A previous study[16] in systems with (H_2SO_4 + Na_2SO_4 + H_2O) and (TOA + xylene) without MPCA revealed that at loading of TOA by H_2SO_4, $z_{H_2SO_4}$, close to 0.5, the molar ratio of water to H_2SO_4 reached its maximal value, $c_{S,H_2SO_4}/c_{S,H_2O} = 6$. Since H_2SO_4 is a strong acid it forms ion

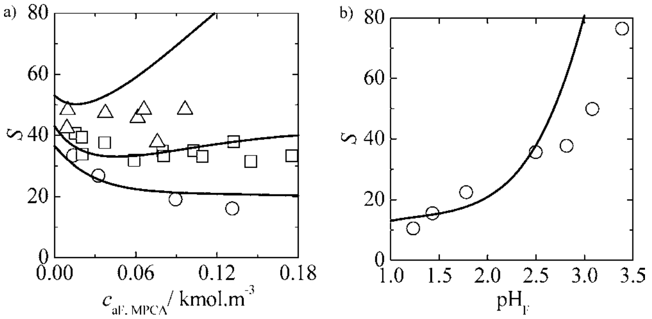

Figure 10. Concentration dependence of the selectivity (*S*) of MPCA extraction at three different equilibrium pH values: ○, 2.03; □, 2.43; and △, 2.87 (a), and pH dependence of *S* at $c_{aF,MPCA} = 0.081$ kmol·m^{-3} (b). The same experiments as in Figures 7 to 9 are presented.

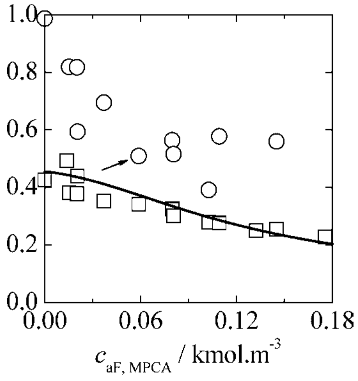

Figure 11. Concentration of water, c_{S,H_2O} (○), and loading of TOA by H_2SO_4, $z_{H_2SO_4}$ (□) vs MPCA concentration. The same experiments as in Figures 7b and 8b are presented. The arrow shows the point when the suggested reverse micelles are already broken.

pairs with TOA[16] so that at $z_{H_2SO_4} = 0.5$, in the solvent phase the structure similar to ionic liquid (IL) should be formed with formula $[(C_8H_{17})_3NH^+]_2SO_4^{2-}$, in fact TOA/sulfate. On the basis of analogy with some phosphonium ILs, especially tetradecyl(trihexyl)phosphonium 2,4,4-trimethylpentylphosphinate (Cyphos IL-104)[26−29] it was suggested that the high excess of 6 H_2O per one $[(C_8H_{17})_3NH^+]_2SO_4^{2-}$ indicates the presence of reverse micelles.[16] In the case of Cyphos IL-104 these have been already confirmed by laser light scattering in solution of Cyphos IL-104 in *n*-dodecane with various water content.[27] Another suggestions also supporting this idea are presented in the previous study.[16]

The coextraction of water was investigated in experiments 7 to 16 and 18 in Table 3. Unfortunately, there are no data on water concentration in earlier experiments because the method for its determination has not yet been established. In Figure 11, which presents the same experiments as in Figures 7b and 8b, at zero value of $c_{aF,MPCA}$, the water and H_2SO_4 concentrations in the solvent are $c_{S,H_2O} = 0.99$ kmol·m^{-3} and $c_{S,H_2SO_4} = 0.171$ kmol·m^{-3} (Table 3, no. 7). Therefore, there is about 6 H_2O per one H_2SO_4 and the loading $z_{H_2SO_4} = 0.43$, which is close to 0.5 This indicates that the solvent phase is in the state close to that with maximal water content. Increasing $c_{aF,MPCA}$ the water content decreases up to $c_{aF,MPCA} = 0.06$ kmol·m^{-3} (the point marked by arrow). Such decrease in the water content corresponds to the decrease in $z_{H_2SO_4}$, also shown in Figure 11. However, at $c_{aF,MPCA} > 0.06$ kmol·m^{-3}, the water content seems to remain at the same value of about (0.5 to 0.6) kmol·m^{-3} although $z_{H_2SO_4}$ continues to decrease. This indicates that (*p*, 0, 1) complexes which are formed especially at higher MPCA concentrations are also hydrated.

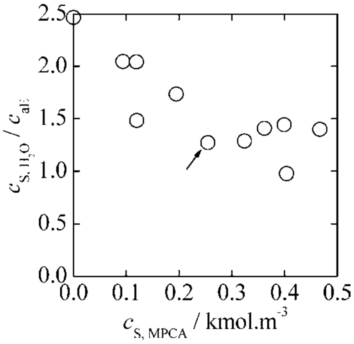

Figure 12. Molar ratio of water and TOA as a function of MPCA concentration in the organic phase $c_{S,MPCA}$. The same experiments as in Figures 7b and 8b are presented. The arrow means the same as in Figure 11.

The dependence of water concentration on $c_{aF,MPCA}$ in Figure 11 shows that water interacts with (TOA + acids) complexes at least in two ways. This is better illustrated in Figure 12, where the molar ratio of water to extractant is shown as a function of MPCA concentration in the solvent, $c_{S,MPCA}$. The point marked by arrow at $c_{S,MPCA} = 0.25$ kmol·m^{-3}, which corresponds to the point at $c_{aF,MPCA} = 0.06$ kmol·m^{-3} in Figure 11 (see Table 3, experiment no. 12), represents a break in this dependency. At $c_{S,MPCA} < 0.25$ kmol·m^{-3} besides the stronger bonded hydration water of complexes there is probably also weaker interaction with water. The MPCA concentration of 0.25 kmol·m^{-3} is needed to release all weakly bound water to the aqueous phase. The experiences with phosphonium ILs mentioned above indicate that such release of water as a consequence of acid extraction could be caused by destruction of the adsorption film of IL molecules stabilizing the reverse micelles. Confirmation of this theory should be the matter of future work. Figure 12 shows that for $c_{S,MPCA} > 0.25$ kmol·m^{-3} the water to TOA ratio is relatively stable. This indicates that only the hydration water of complexes remained in the solvent phase. The constant ratio of the water to TOA also indicates that the hydration water is needed only for stabilization of polar (acid + TOA) bond and not for the hydrogen bonds between MPCA molecules and, according to the comparison with Figure 8b, also between MPCA and H_2SO_4.

Conclusions

Extraction of MPCA and HCl from acidic aqueous solutions containing MPCA and NaCl to a solvent containing TOA in xylene is realized mainly by competitive mechanism. In systems with Na_2SO_4 instead of NaCl, coextraction dominates resulting in the preferential formation of ternary complexes (MPCA + H_2SO_4 + TOA).

The proposed model based on the mass action law for simultaneous extraction of MPCA and H_2SO_4 by TOA assuming both binary and ternary complexes fitted the data very well. The modeling resulted in a set of equilibrium reaction constants of two binary (MPCA + TOA) complexes, (1, 0, 1) and (2, 0, 1) and five ternary (MPCA + H_2SO_4 + TOA) complexes (1, 1, 2), (2, 1, 2), (3, 1, 2), (1, 2, 3), and (3, 2, 3). All ternary complexes can be regarded as formerly (H_2SO_4 + TOA) complexes (0, 1, 2) and (0, 2, 3) where H_2SO_4 is joined with TOA in the form of ion pairs and molecules of MPCA are joined with H_2SO_4 by hydrogen bonding. The (H_2SO_4 + TOA) complex (0, 3, 3) was also needed for modeling.

Ion-pairs of H_2SO_4 with TOA are de facto an ionic liquid. High water content in the solvent loaded with H_2SO_4 suggests the formation of reverse micelles. With the increasing MPCA concentration, the water content decreases analogically as in systems with phosphonium ionic liquids where the existence of reverse micelles has already been confirmed.

At the increased ionic strength of about 3 kmol·m^{-3}, equilibrium reaction constants of complexes (1, 0, 1) and (2, 0, 1) are by four to five times higher compared to the corresponding constants in the extraction from binary aqueous solutions of MPCA. This phenomenon could be regarded as a salting out effect.

At the ionic strength increased by Na_2SO_4, the increase in concentration of TOA contributes to the increase in the MPCA distribution coefficient. However, the distribution coefficient of MPCA is not directly proportional to the TOA concentration as it is usual for reactive extraction of pure monocarboxylic acids. This is evident especially at low MPCA concentrations approaching zero. This also supports the idea that ternary complexes are formed.

The effect of pH on the extraction of MPCA from solutions containing Na_2SO_4 is very complex. To achieve a good selectivity of extraction together with good distribution coefficient, optimal pH of extraction should be about 3 for MPCA concentrations above 0.06 kmol·m^{-3} and about 2.5 for MPCA concentrations below 0.03 kmol·m^{-3}. At MPCA concentrations between 0.03 and 0.06 kmol·m^{-3}, optimal pH should be between 2.5 and 3.

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Supporting Information Available:

1. Summary tables of ternary complexes (acid$_1$ + acid$_2$ + extractant) published by Schunk, Kirsch, Maurer, and their co-workers. 2. Results of data fitting from systems with aqueous phase (MPCA + H_2SO_4 + Na_2SO_4 + H_2O) or (MPCA + Na_2SO_4 + H_2O) and solvent (TOA + xylene). This material is available free of charge via the Internet at http://pubs.acs.org.

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