3578 *J. Chem. Eng. Data* **2010,** *55,* 3578–3589

Liquid−Liquid Equilibria of 5-Methyl-2-pyrazinecarboxylic and Sulfuric Acids for Solvents with Trioctylamine

Ján Marták, L'ubica Kubišová, and Štefan Schlosser*

Department of Chemical and Biochemical Engineering, Slovak University of Technology,
Radlinského 9, SK-812 37 Bratislava, Slovak Republic

Liquid−liquid equilibrium data of 5-methyl-2-pyrazinecarboxylic acid (MPCA) and H_2SO_4 in water + organic solvent systems with the reactive extractant trioctylamine (TOA) are presented together with the model of equilibrium. Dissociation constants of both acids were also determined. The addition of 1 $kmol \cdot m^{-3}$ of Na_2SO_4 decreased the pK_a of MPCA and pK_{a2} of H_2SO_4 from 3.09 to 2.87 and from 2.10 to 0.908, respectively. In the extraction of MPCA, the overloading of TOA indicated the formation of (*p*, 1) complexes **$(HMPCA)_p$TOA** with $p = 1$ to 3. The (1, 1) complex is more stable in n-alkanes with isodecanol. Other (*p*, 1) complexes are more stable in xylene. H_2SO_4 with TOA in xylene form (*r*, *q*) complexes, $\mathbf{(SO_4^{2-})_{q-r}(HSO_4^{-})_{2r-q}(HTOA^{+})_q}$. At low H_2SO_4 concentrations, a (1, 2) complex, TOA/sulfate, is formed. On increasing the acid concentration, the expected (1, 1) complex, TOA/hydrogen sulfate, aggregates, probably immediately, to complexes (2, 3) and (3, 3). When the ionic strength was increased by Na_2SO_4, the extraction of H_2SO_4 was less effective. High water content of the solvent loaded with H_2SO_4 with the stoichiometry (1, 2) suggests the formation of reverse micelles similarly as observed in ionic liquids.

Introduction

The recovery and separation of organic acids from aqueous solutions by organic solvents containing water insoluble extractants has already been extensively studied. Most works deal with amine extractants although there are also papers devoted to other compounds such as trialkylphosphine oxides[1−3] or tributylphosphate.[2,4−10] Recently also phosphonium ionic liquids (ILs) appeared as promising extractants of acids.[11−13] Known for a longer time, the extractant Aliquat 336, trialkylmethylammonium chloride,[14−16] is in fact also an IL.

The conception that the extraction of acids by amines is realized via the formation of stoichiometrically defined (acid + amine) complexes has been presented, for example, in papers of Tamada et al.[17−19] In these complexes, the amine can be joined with the acid, forming an ion pair, or by hydrogen bonding. Generally, the formation of an ion pair is typical for strong acids and more basic amines and of a hydrogen bond for weak acids and less basic amines. This has been explained in detail in the papers of Canari and Eyal[20−24] by analyzing a larger set of equilibrium data including also IR spectra of the organic phases. In larger (acid + amine) complexes, individual molecules of acids are joined together by hydrogen bonds between the carboxylic groups. This has been shown already by Tamada et al.[17−19] as well as in most other cited works. The hydrogen bond between acids leads to the overloading of extractant, which is more typical for hydrophobic acids, for example, butyric acid[25] or C_6 acids.[26] A higher overloading of extractant by more polar lactic acid has been observed in the extraction using the IL Cyphos IL-104 (trialkylphosphonium dialkylphosphinate).[12] However, in the case of Cyphos IL-104, much larger overloading has been achieved with butyric acid.[13]

The extractants are rarely used in pure form; they are often diluted in a suitable diluent. The reason can be, for example, the reduction of the solvent viscosity or dissolution of the complex. Most diluents can be divided into two groups:

1. Nonpolar diluents, which do not solvate the (acid + extractant) complexes. Therefore, the effect of these diluents on the interaction of inorganic or more polar organic acids (e.g., lactic acid) with the extractant is negligible so that the distribution coefficient is proportional to the concentration of the extractant.[12] In the hydrophobic environment of organic solvents, more polar complexes often tend to aggregate so that a second organic phase can be formed. Studying the extraction of inorganic acids by tributylphosphate diluted in *n*-octane, Chiarizia et al.[7,8] concluded that the (acid + tributylphosphate) complexes have the character of reverse micelles and the second organic phase is formed via their aggregation by polar interactions. Besides the acid and extractant, the micelles also contained water, and their typical diameter was about (1.0 to 1.5) nm.[8] In the case of more hydrophobic, for example, butyric or C_6, acids, the second organic phase is not formed, but the extraction is affected by the physical solubility of these acids in the diluent.[13,25,26]

2. Diluents containing polar groups which can stabilize the bond between the acid and the extractant by solvation. In this way, formation of the second organic phase can be avoided, and the extraction efficiency as well as the values of distribution coefficient increases. Such behavior has been confirmed in many works.[27−32] Solvating diluents often contain polar hydrogen, for example, chloroform or alcohols. Although they stabilize the (acid + amine) ion pair very well, their polar hydrogen can compete with protons of the carboxylic groups, thus destabilizing the hydrogen bond between the acids.[18] This leads to lower overloading and results in the distribution coefficient decrease at higher acid concentrations. Among the various types of diluents, alcohols were found to be the most solvating ones. Because of their high ability to modify the extraction by reactive extractants, they are often called *modifiers*. In the works of Qin

---

* Corresponding author. E-mail: stefan.schlosser@stuba.sk.

10.1021/je100207p

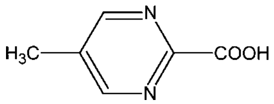

Figure 1. Structure of 5-methyl-2-pyrazinecarboxylic acid.

et al.[33] and Shan et al.[34] it has been shown that the basicity of the extractant increases with the increase in the solvating power of the diluent. Therefore it could happen that the same acid with the same extractant forms an ion pair in a solvent containing a modifier, but they form a hydrogen bond in a nonpolar diluent. This has been well-confirmed by the IR spectra.[21]

On the basis of the application of the mass action law, the model of liquid−liquid equilibrium can be derived, and the composition of (acid + extractant) complexes can be proposed. This has been proven, for example, for citric and lactic acids in the papers of Juang and Huang,[35,36] for various dicarboxylic acids in Li et al.,[37] for monocarboxylic acids in Qin et al.,[33] and for propionic acid extracted by trioctylamine (TOA) in Shan et al.[34] and Wasewar and Pangarkar.[32] Although these models do not provide a precise thermodynamic description, they correlate the experimental data very well. Such an approach was also chosen in this work. A better thermodynamic description has been done by Bízek et al.[38] and Procházka et al.[39] for citric, lactic, and malic acids and Vachtová et al.[40] and Procházka et al.[41] for sulfuric acid extracted by a mixture of various trialkylamines. The most precise thermodynamic approach to the modeling has been presented in the papers of the Maurer's research group for HCl, HNO_3, and H_2SO_4[42,43] as well as for acetic, citric, and oxalic acids[44,45] and TOA. In some complexes suggested by this model, the stoichiometric ratio of water to acid is rather high. In the case of H_2SO_4 it sometimes achieved the values of 6 or even 12. Such water content is similar to that in some phosphonium ILs saturated with water[12] and can indicate the presence of reverse micelles. These have been already proven by laser light scattering measurements for the IL Cyphos IL-104.[13]

Applications of liquid−liquid extraction and pertraction in the recovery and separation processes of organic acids have been recently discussed in papers.[46−48]

The aim of this work was to measure and model liquid−liquid equilibrium data of 5-methyl-2-pyrazinecarboxylic acid (MPCA) and H_2SO_4 in systems of (water + organic solvent containing TOA). Some equilibrium data on the extraction of the industrially important MPCA by TOA were published by Kubišová et al.[49,50] The structure of MPCA is shown in Figure 1.

Theory

Calculation of pK_a Values at Various Ionic Strengths. Potentiometric titrations with a solution of NaOH (1) + H_2O (2), $c_1 = \text{kmol}\cdot\text{m}^{-3}$, as the titrant were carried out for the determination of pK_a of MPCA and H_2SO_4 in binary solutions MPCA (1) + H_2O (2) and H_2SO_4 (1) + H_2O (2). For the determination of pK_a in solutions containing 1 kmol·m^{-3} of Na_2SO_4 the titrant was NaOH (1) + Na_2SO_4 (2) + H_2O (3), $c_1 = 0.1$ kmol·m^{-3} and $c_2 = 1$ kmol·m^{-3}. Since the concentrations of acids and NaOH were rather low and did not exceed 0.1 kmol·m^{-3}, the concentrations instead of activities were used in the model. The feasibility of this simplification was checked by determining the pK_a value of butyric acid, which is well-known from literature. pH and volume of the added titrant V_T were chosen as independent and dependent variables, respectively.

Table 1. pK_a Values of Acids at T = 25 °C

acid	I / mol·kg^{-1}	pK_{a1}	pK_{a2}	correlation coefficient
butyric acid	∼0	4.78		0.99998
MPCA[a]	∼0	3.09		0.99989
	3.083[b]	2.87		0.99994
H_2SO_4	∼0	−3[51]	2.10[51]	
	3.083	no data	0.908	0.99992

[a] 5-methyl-2-pyrazinecarboxylic acid. [b] Ionic strength I = 3.083 mol·kg^{-1} was achieved by adding 1 kmol·m^{-3} Na_2SO_4.

The first dissociation constants of H_2SO_4 are rather low (Table 1) so that, at the working pH varying between 1.5 and 6, there are no neutral H_2SO_4 molecules. Dissociation constants of MPCA and the second dissociation constant of H_2SO_4 are

$$K_{a,MPCA} = \frac{[H^+][MPCA^-]}{[HMPCA]} \tag{1}$$

$$K_{a2,H_2SO_4} = \frac{[H^+][SO_4{}^{2-}]}{[HSO_4{}^-]} \tag{2}$$

The analytical concentrations of both acids and NaOH during titration depend on the volume of added titrant V_T according to the relations

$$c_{a,H_2SO_4} = \frac{c_{a,H_2SO_4o}V_o}{V_o + V_T} \tag{3}$$

$$c_{a,MPCA} = \frac{c_{a,MPCAo}V_o}{V_o + V_T} \tag{4}$$

$$c_{a,NaOH} = \frac{c_{a,NaOH,T}V_T}{V_o + V_T} \tag{5}$$

where V_o and $c_{a,o}$ are the initial volume of sample and the initial analytical concentration of the appropriate acid before the titration. $c_{a,NaOH,T}$ is the concentration of NaOH in titrant. For the achievement of ionic strength I = 3 kmol·m^{-3} (or 3.083 mol·kg^{-1} in terms of molality), 1 kmol·m^{-3} of Na_2SO_4 was used. The same salt was also added to the titrant to avoid the decrease in ionic strength during titration. From the condition of electroneutrality follows

$$[Na^+] + [H^+] = [MPCA^-] + 2[SO_4{}^{2-}] + [HSO_4{}^-] + [OH^-] \tag{6}$$

Since the pK_a of the used acids are in the range of acidic pH, the concentration of OH^- was neglected. For the concentration of other ions in eq 6 follows

$$[Na^+] = 2c_{a,Na_2SO_4} + c_{a,NaOH} \tag{7}$$

$$[MPCA^-] = \frac{c_{a,MPCA}K_{a,MPCA}}{[H^+] + K_{a,MPCA}} \tag{8}$$

$$[SO_4{}^{2-}] = \frac{(c_{a,Na_2SO_4} + c_{a,H_2SO_4})K_{a2,H_2SO_4}}{[H^+] + K_{a2,H_2SO_4}} \tag{9}$$

$$[HSO_4{}^-] = \frac{(c_{a,Na_2SO_4} + c_{a,H_2SO_4})[H^+]}{[H^+] + K_{a2,H_2SO_4}} \tag{10}$$

Combining eqs 3 to 10, the dependence of V_T on pH can be derived

$$V_{\mathrm{T}} = V_{\mathrm{o}} \frac{2c_{\mathrm{a,H_2SO_4o}} - R(c_{\mathrm{a,Na_2SO_4}} + c_{\mathrm{a,H_2SO_4o}}) + Pc_{\mathrm{a,MPCAo}} - 10^{-\mathrm{pH}}}{c_{\mathrm{a,NaOH,T}} + Rc_{\mathrm{a,Na_2SO_4}} + 10^{-\mathrm{pH}}} \tag{11}$$

where

$$P = \frac{K_{\mathrm{a,MPCA}}}{10^{-\mathrm{pH}} + K_{\mathrm{a,MPCA}}} \tag{12}$$

$$R = \frac{10^{-\mathrm{pH}}}{10^{-\mathrm{pH}} + K_{\mathrm{a2,H_2SO_4}}} \tag{13}$$

Modeling of Liquid−Liquid Equilibria. MPCA. The physical extraction of MPCA by pure diluents (*n*-alkanes and xylene) and a modifier (isodecanol) was found negligible; thus the extraction model considers only reactive extraction by TOA. For the equilibrium in the system with binary solution MPCA (1) + H_2O (2) and organic solvent containing TOA as an extractant, the following reaction for the formation of binary (MPCA + TOA) complexes between undissociated acid HMPCA and TOA at the liquid−liquid interface was proposed:

$$p\mathrm{HMPCA} + \mathbf{TOA} \rightleftharpoons \mathbf{(HMPCA)}_{\boldsymbol{p}}\mathbf{TOA} \tag{14}$$

where the boldface font designates the species in the organic phase. Since the solubility of TOA in water is very low, it has been neglected. MPCA is a monobasic acid; therefore, it can supply only one hydrogen for the bond with TOA, and thus the formation of complexes containing only one molecule of TOA was assumed, the so-called (p, 1) complexes. Depending on the nature of the diluent, a hydrogen or ionic bond can be formed between TOA and MPCA. In the latter case, the (p, 1) complex can be schematically better written as $\mathbf{(HMPCA)_{p-1}(MPCA)^{-}(HTOA)^{+}}$. The model of equilibrium based on reaction 14 operates with the analytical equilibrium concentration of MPCA in the aqueous phase $c^{*}_{\mathrm{aF,MPCA}}$ as an independent variable. On the basis of the mass action law, the equilibrium constant of reaction 14 characterizing the complex stability, frequently called the stability constant, is

$$K_{p,1} = \frac{c_{p,1}}{[\mathrm{HMPCA}]^{p} c_{\mathrm{P}}} \tag{15}$$

where c_{P} is the concentration of free (uncomplexed) TOA and $c_{p,1}$ is the concentration of complex (p, 1) in the organic phase. In this definition, the concentrations were used instead of activities. For the modeling of equilibria in (water + organic solvent) systems such approximation is usual and commonly accepted, as can be documented by numerous publications.[17,33−37] Although such models do not provide a precise thermodynamic description, they support the theoretical suggestions related to the mechanism of extraction and hence considerably contributed to the overall comprehension of the system. On the other hand, a rigorous thermodynamic description needs more experimental data. According to eq 15, the $c_{p,1}$ is

$$c_{p,1} = K_{p,1}[\mathrm{HMPCA}]^{p} c_{\mathrm{P}} \tag{16}$$

The calculation of the concentration of undissociated acid [HMPCA] from the independent variable $c^{*}_{\mathrm{aF,MPCA}}$ can be done using the electroneutrality condition:

$$[\mathrm{H}^{+}] = [\mathrm{MPCA}^{-}] + [\mathrm{OH}^{-}] \tag{17}$$

Since the experimental values of pH in the aqueous phase did not exceed the value of 2.9, the concentration of $[\mathrm{OH}^{-}]$ was neglected. According to eq 1, the concentration of protons $[\mathrm{H}^{+}]$ is

$$[\mathrm{H}^{+}] = \frac{K_{\mathrm{a,MPCA}}[\mathrm{HMPCA}]}{[\mathrm{MPCA}^{-}]} \tag{18}$$

and $[\mathrm{MPCA}^{-}]$ is

$$[\mathrm{MPCA}^{-}] = c^{*}_{\mathrm{aF,MPCA}} - [\mathrm{HMPCA}] \tag{19}$$

A combination of the last three equations results in the quadratic equation for [HMPCA]

$$[\mathrm{HMPCA}]^{2} - (K_{\mathrm{a,MPCA}} + 2c^{*}_{\mathrm{aF,MPCA}})[\mathrm{HMPCA}] + (c^{*}_{\mathrm{aF,MPCA}})^{2} = 0 \tag{20}$$

The total equilibrium concentration of MPCA in the organic phase is a sum of concentrations of all (p, 1) complexes multiplied by p

$$c^{*}_{\mathrm{S,\,MPCA}} = \sum_{p=1}^{i} p c_{p,1} = c_{\mathrm{P}} \sum_{p=1}^{i} pK_{p,1}[\mathrm{HMPCA}]^{p} \tag{21}$$

The concentration of free extractant c_{P} can be calculated as the difference between the analytical concentration of TOA c_{aP} and the sum of concentrations of all complexes

$$c_{\mathrm{P}} = c_{\mathrm{aP}} - c_{\mathrm{P}} \sum_{p=1}^{i} K_{p,1}[\mathrm{HMPCA}]^{p} \tag{22}$$

The analytical concentration of TOA in equilibrium, c_{aP}, differs from that in pure solvent, c_{Po}, due to the volume changes of phases during the extraction according to the following relation

$$c_{\mathrm{aP}} = c_{\mathrm{Po}}\left(1 - \frac{c^{*}_{\mathrm{S,\,MPCA}} M_{\mathrm{MPCA}}}{\rho_{\mathrm{MPCA}}}\right) \tag{23}$$

where M_{MPCA} is the molar mass of MPCA and ρ_{MPCA} is the density of pure powdered MPCA. The volume changes of phases are explained in Materials and Methods in more detail. Joining the last three equations gives the relation for $c^{*}_{\mathrm{S,MPCA}}$

$$c^{*}_{\mathrm{S,MPCA}} = \frac{c_{\mathrm{Po}}\rho_{\mathrm{MPCA}} X}{\rho_{\mathrm{MPCA}}(1 + Y) + c_{\mathrm{Po}} M_{\mathrm{MPCA}} X} \tag{24}$$

where X and Y are artificial variables

$$X = \sum_{p=1}^{i} pK_{p,1}[\mathrm{HMPCA}]^{p} \tag{25}$$

$$Y = \sum_{p=1}^{i} K_{p,1}[\mathrm{HMPCA}]^{p} \tag{26}$$

From eqs 21 and 24 for the concentration of free extractant, c_{P}, follows

$$c_{\mathrm{P}} = \frac{c_{\mathrm{Po}}\rho_{\mathrm{MPCA}}}{\rho_{\mathrm{MPCA}}(1 + Y) + c_{\mathrm{Po}} M_{\mathrm{MPCA}} X} \tag{27}$$

and combining eqs 22 and 27 gives, for c_{aP},

$$c_{\mathrm{aP}} = \frac{c_{\mathrm{Po}}\rho_{\mathrm{MPCA}}(1 + Y)}{\rho_{\mathrm{MPCA}}(1 + Y) + c_{\mathrm{Po}} M_{\mathrm{MPCA}} X} \tag{28}$$

Loading of TOA by MPCA, z_{MPCA}, is defined as the ratio of acid to extractant concentrations

$$z_{\mathrm{MPCA}} = \frac{c^{*}_{\mathrm{S,MPCA}}}{c_{\mathrm{aP}}} = \frac{\sum_{p=1}^{i} p c_{p,1}}{c_{\mathrm{aP}}} = \sum_{p=1}^{i} z_{p,1} \tag{29}$$

where $z_{p,1}$ is the loading of the extractant by an individual complex (p, 1). Combining eqs 24 and 28 for loading results in

$$z_{\mathrm{MPCA}} = \frac{X}{(1 + Y)} \tag{30}$$

The saturation ratio of extractant, $z_{\mathrm{P,MPCA}}$, can be defined as the molar fraction of the extractant bound in complexes with respect to the analytical concentration of the extractant

$$z_{\mathrm{P,MPCA}} = \frac{\sum_{p=1}^{i} c_{p,1}}{c_{\mathrm{aP}}} = \sum_{p=1}^{i} z_{\mathrm{P},(p,1)} = 1 - \frac{c_{\mathrm{P}}}{c_{\mathrm{aP}}} \tag{31}$$

The distribution coefficient of MPCA, $D_{\mathrm{a,MPCA}}$, is defined as

$$D_{\mathrm{a,MPCA}} = \frac{c^{*}_{\mathrm{S,MPCA}}}{c^{*}_{\mathrm{aF,MPCA}}} = \frac{\sum_{p=1}^{i} p c_{p,1}}{c^{*}_{\mathrm{aF,MPCA}}} = \sum_{p=1}^{i} D_{\mathrm{a},(p,1)} \tag{32}$$

where $D_{\mathrm{a},(p,1)}$ is the distribution coefficient of MPCA in individual complex (p, 1).

H_2SO_4. As in the case of MPCA, the physical extraction of H_2SO_4 by diluents and a modifier was negligible. For the equilibrium of the system with the binary aqueous solution of H_2SO_4 or ternary aqueous solution of H_2SO_4 containing Na_2SO_4 and an organic solvent containing TOA, the following reaction describing the formation of binary complexes between H_2SO_4 and TOA was proposed:

$$2r\mathrm{H}^{+} + r\mathrm{SO}_4^{2-} + q\mathbf{TOA} \rightleftharpoons \boldsymbol{(\mathrm{SO}_4^{2-})_{q-r}(\mathrm{HSO}_4^{-})_{2r-q}(\mathrm{HTOA}^{+})_q} \tag{33}$$

Because pH was in all experiments fairly above the pK_{a1} of H_2SO_4 (Table 1) which forms ion pairs with TOA, only charged forms of this acid were involved here. Complexes of H_2SO_4 and TOA were designated as (r, q) complexes. Instead of MPCA, more than one molecule of TOA may participate in the complex because H_2SO_4 is dibasic. Since the calculation of proton concentration $[\mathrm{H}^+]$, in fact pH, in the aqueous phase is complicated, it was selected as an independent variable instead of the equilibrium concentration of H_2SO_4 in the aqueous phase, $c^{*}_{\mathrm{F,H_2SO_4}}$. The concentration of H_2SO_4 in the organic phase, $c^{*}_{\mathrm{S,H_2SO_4}}$, only in some cases slightly exceeded the concentration of TOA (0.4 $\mathrm{kmol \cdot m^{-3}}$) compared to $c^{*}_{\mathrm{S,MPCA}}$, which sometimes exceeded even the value of 1.2 $\mathrm{kmol \cdot m^{-3}}$. Therefore, volume changes of the phases due to the acid extraction are much lower for H_2SO_4 than for MPCA so that they were neglected. The stability constant of the (r, q) complex, $K_{r,q}$, is

$$K_{r,q} = \frac{c_{r,q}}{[\mathrm{H}^+]^{2r}[\mathrm{SO}_4^{2-}]^{r} c_{\mathrm{P}}^{q}} \tag{34}$$

Hence, the concentration of the complex, $c_{r,q}$, is

$$c_{r,q} = K_{r,q}[\mathrm{H}^+]^{2r}[\mathrm{SO}_4^{2-}]^{r} c_{\mathrm{P}}^{q} \tag{35}$$

The concentration of sulfate anions, $[\mathrm{SO}_4^{2-}]$, can be calculated from the electroneutrality condition:

$$2[\mathrm{SO}_4^{2-}] + [\mathrm{HSO}_4^{-}] = [\mathrm{Na}^+] + [\mathrm{H}^+] - [\mathrm{OH}^-] \tag{36}$$

The sodium ions originated from Na_2SO_4 in experiments at a higher ionic strength. The 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 ($[\mathrm{SO}_4^{2-}] + [\mathrm{HSO}_4^{-}]$), which originated from the initially added Na_2SO_4 and H_2SO_4. $c^{*}_{\mathrm{aF,SO_4}}$ can be calculated from the second dissociation constant of H_2SO_4 (eq 2), $K_{\mathrm{a2,H_2SO_4}}$, which may also be written as

$$K_{\mathrm{a2,H_2SO_4}} = \frac{[\mathrm{H}^+][\mathrm{SO}_4^{2-}]}{c^{*}_{\mathrm{aF,SO_4}} - [\mathrm{SO}_4^{2-}]} \tag{37}$$

After the rearrangement

$$c^{*}_{\mathrm{aF,SO_4}} = \frac{[\mathrm{SO}_4^{2-}]([\mathrm{H}^+] + K_{\mathrm{a2,H_2SO_4}})}{K_{\mathrm{a2,H_2SO_4}}} \tag{38}$$

The concentration of sodium ions is equal to the double concentration of added Na_2SO_4, $[\mathrm{Na}^+] = 2c_{\mathrm{aF,Na_2SO_4}}$, which is the double concentration of added Na_2SO_4, and the concentration of hydroxyl anions, $[\mathrm{OH}^-]$, is

$$[\mathrm{OH}^-] = \frac{K_{\mathrm{H_2O}}}{[\mathrm{H}^+]} \tag{39}$$

Finally, combining eqs 36, 38, and 39 results in

$$[\mathrm{SO}_4^{2-}] = R_1\left(2c_{\mathrm{aF,Na_2SO_4}} + [\mathrm{H}^+] - \frac{K_{\mathrm{H_2O}}}{[\mathrm{H}^+]}\right) \tag{40}$$

where R_1 is

$$R_1 = \frac{K_{\mathrm{a2,H_2SO_4}}}{[\mathrm{H}^+] + 2K_{\mathrm{a2,H_2SO_4}}} \tag{41}$$

Equation 40 can be substituted into eqs 34 and 35 to make them applicable for modeling.

The concentration of the free extractant, c_{P}, can be calculated as the difference between the analytical concentration of TOA, c_{aP}, and the sum of concentrations of all complexes multiplied by q

$$c_{\mathrm{P}} = c_{\mathrm{aP}} - \sum_{q=1}^{k}\left(q c_{\mathrm{P}}^{q} \sum_{r=1}^{j} K_{r,q}[\mathrm{H}^+]^{2r}[\mathrm{SO}_4^{2-}]^{r}\right) \tag{42}$$

This equation can be finally rearranged to the k^{th} degree polynomic equation. The total equilibrium concentration, $c^{*}_{\mathrm{S,H_2SO_4}}$, of H_2SO_4 in the organic phase is a sum of concentrations of all (r, q) complexes multiplied by r

$$c^{*}_{\mathrm{S,H_2SO_4}} = \sum_{q=1}^{k}\left(c_{\mathrm{P}}^{q} \sum_{r=1}^{j} r K_{r,q}[\mathrm{H}^+]^{2r}[\mathrm{SO}_4^{2-}]^{r}\right) = \sum_{q=1}^{k}\left(\sum_{r=1}^{j} r c_{r,q}\right) \tag{43}$$

The loading of extractant by H_2SO_4, $z_{\mathrm{H_2SO_4}}$, is

$$z_{\mathrm{H_2SO_4}} = \frac{c^{*}_{\mathrm{S,H_2SO_4}}}{c_{\mathrm{aP}}} = \frac{\sum_{q=1}^{k}\left(\sum_{r=1}^{j} r c_{r,q}\right)}{c_{\mathrm{aP}}} = \sum_{q=1}^{k}\left(\sum_{r=1}^{j} z_{r,q}\right) \tag{44}$$

The saturation ratio of extractant, $z_{\mathrm{P,H_2SO_4}}$, is

$$z_{\mathrm{P,H_2SO_4}} = \frac{\sum_{q=1}^{k}\left(q \sum_{r=1}^{j} c_{r,q}\right)}{c_{\mathrm{aP}}} = \sum_{q=1}^{k}\left(\sum_{r=1}^{j} z_{\mathrm{P}(r,q)}\right) = 1 - \frac{c_{\mathrm{P}}}{c_{\mathrm{aP}}} \tag{45}$$

and the distribution coefficient, $D_{\mathrm{a,H_2SO_4}}$, is

$$D_{a,H_2SO_4} = \frac{c^*_{S,H_2SO_4}}{c^*_{aF,H_2SO_4}} = \frac{\sum_{q=1}^{k}\left(\sum_{r=1}^{j} rc_{r,q}\right)}{c^*_{aF,H_2SO_4}} = \sum_{q=1}^{k}\left(\sum_{r=1}^{j} D_{a,(r,q)}\right) \tag{46}$$

where $D_{a,(r,\,q)}$ is the distribution coefficient of H_2SO_4 in the form of the individual complex (r, q).

Materials and Methods

Chemicals. a. Trioctylamine. TOA (Fluka, CH) with $w >$ 0.99 was used as an *extractant*.

b. Isodecanol. Isodecanol purchased from UNIPAR (NL) was used as a *modifier*.

c. Diluents. Xylene. Xylene was a mixture of ortho-, meta-, and para-isomers with analytical grade purity (Lachema, CZ).

n-Alkanes. The dodecane fraction of *n*-alkanes (Slovnaft, SK) with the following mass fractions (100 w) of C_{10}, C_{11}, C_{12}, C_{13}, and $C_{\geq 14}$ was estimated by GC: 7.18, 32.39, 33.11, 26.84, and 0.28, respectively.

d. Acids. MPCA. MPCA was received from the Research Institute of Organic Synthesis (Pardubice, CZ), in crystalline form, $w \geq 0.99$.

HCl. HCl with $w = 0.35$ and H_2SO_4 with $w = 0.96$ of analytical grade purity were purchased from Mikrochem (SK).

e. Na_2SO_4 and NaOH. Na_2SO_4 and NaOH of analytical grade purity were also purchased from Mikrochem (SK).

The density and molar mass of solvents and related components are shown in Table 2.

Determination of pK_a. The values of pK_a were measured by potentiometric titration with titrant NaOH (1) + H_2O (2), $c_1 =$ 0.1 kmol·m^{-3}, in binary solutions of acid (1) + H_2O (2) or with NaOH (1) + Na_2SO_4 (2) + H_2O (3), $c_1 = 0.1$ kmol·m^{-3} and $c_2 = 1$ kmol·m^{-3}, in solutions with an increased ionic strength of about 3.1 mol·kg^{-1}. An automatic titrator DL 53 (Mettler Toledo, CH) with a pH electrode DG101-SC (Mettler Toledo, CH) was used. The electrode was calibrated using secondary reference solutions with pH of 1.68, 4.01, and 6.86, respectively (Slovak Institute of Metrology, SK). The titration was done in a vessel with a thermometer (graduation of 0.1 °C) and a tempering jacket for the adjustment of the temperature exactly to (25 ± 0.1) °C. The titration was performed stepwise with the difference of pH between the consecutive steps typically of about 0.1. Each consecutive step was allowed only when the pH remained stable on the third decimal place for at least 1 min. The dependence of the volume of added titrant, V_T, versus pH was observed. After the achievement of a plateau in such dependence, the titration was stopped, and the results were correlated by the least-squares method according to eq 11. The ionic strength of the solution in the titration vessel was calculated as follows:

$$I = m_{Na^+} + m_{H^+} + m_{HSO_4^-} + 4m_{SO_4^{2-}} + m_{MPCA^-} \tag{47}$$

The molalities of the ions can be calculated from their concentrations given by eqs 7 to 10.

Liquid−Liquid Equilibria. Twenty mL of binary aqueous solution of MPCA or H_2SO_4 or ternary aqueous solution containing H_2SO_4 and 1 kmol·m^{-3} of Na_2SO_4 were contacted with 20 mL of solvent in 500 mL Erlenmeyer flasks using a rotational shaking water bath at the frequency of 180 min^{-1} and the temperature of (25 ± 0.1) °C for 5 h. Because of the low solubility of MPCA in water, a weighted amount of pure powdered MPCA was added directly into the solvent when higher equilibrium concentrations $c^*_{aF,MPCA}$ were required. After the separation of phases, the equilibrium pH of aqueous phase (F) was measured, and the content of the acid was analyzed. The content of acids in the organic solvent phase (S) was analyzed after stripping of acids into the aqueous solution containing an excess of NaOH (stripping phase, R).

Analysis of Acids. The concentration of MPCA in both F and R phases was determined by UV spectrophotometry at the wavelength of 275 nm using an analyzer UNICAM 8625 (UK). The concentration of H_2SO_4 in the F phase was determined by the potentiometric titration with a titrant NaOH (1) + H_2O (2); $c_1 = 0.1$ kmol·m^{-3}. For phase R, back-titration of residual NaOH with a titrant HCl (1) + H_2O (2); $c_1 = 0.1$ kmol·m^{-3} was used. The titrations were performed on a titrator DL 53 with the pH electrode DG101-SC. The uncertainty of these measurements was within ± 0.5 %.

Because of the extraction and stripping of acids, initial volumes of the phases, V_o, are different from those at the equilibrium or after stripping. For the initial and equilibrium volumes of the aqueous phase, V_{Fo} and V_F, it follows:

$$V_F = V_{Fo} - \frac{(c_{aFo}V_{Fo} - c^*_{aF}V_F)M_A}{\rho_A} \tag{48}$$

where M_A and ρ_A are the molar mass and density of pure acid. The parentheses signify the difference between the initial and the equilibrium molar amounts of acid in the aqueous phase. After rearrangement

$$V_F = V_{Fo}\frac{\rho_A - c_{aFo}M_A}{\rho_A - c^*_{aF}M_A} \tag{49}$$

Stripping of the acid can be briefly described by the following reaction:

$$(\mathbf{H}_n\mathbf{A})_p\mathbf{TOA}_q + np\mathrm{OH}^- \rightleftharpoons q\mathbf{TOA} + p\mathrm{A}^{n-} + np\mathrm{H_2O} \tag{50}$$

where $n = 1$ for MPCA and 2 for H_2SO_4. The stripped acid and the released neutralization water increase the initial volume of the stripping phase V_{Ro} to V_R as follows

$$V_R = V_{Ro} + \frac{c_RV_RM_A}{\rho_A} + \frac{(c_{R,Na^+} - c_{R,TB})V_RM_{H_2O}}{\rho_{H_2O}} \tag{51}$$

where the concentration of sodium ions after the stripping, c_{R,Na^+}, can be calculated from the initial concentration of NaOH, $c_{R,NaOH}$,

Table 2. Kinematic Viscosity ν and Density ρ of Used Chemicals and Solvents at T = 25 °C

chemical or solvent	$\nu \cdot 10^6$ / m^2·s^{-1}	ρ / kg·m^{-3}
MPCA		1403
n-alkanes	1.722	743.1
isodecanol	16.32	
TOA		804.3
solvent SX[a]	0.9511	855.3
TOA (1) + *n*-alkanes (2); $c_1 = 0.4$ kmol·m^{-3}	2.202	754.3
solvent SA[b]		767.1

[a] TOA (1) + xylene (2); $c_1 = 0.4$ kmol·m^{-3}. [b] TOA (1) + isodecanol (2) + *n*-alkanes (3); $c_1 = 0.4$ kmol·m^{-3}, $c_2 = 0.8$ kmol·m^{-3}.

$$c_{\mathrm{R,Na^+}} = c_{\mathrm{aRo,NaOH}}\frac{V_{\mathrm{Ro}}}{V_{\mathrm{R}}} \tag{52}$$

and $c_{\mathrm{R,TB}}$ is the concentration of residual NaOH in phase R after the stripping (total basicity, TB). After the rearrangement, combining the last two equations gives the relation

$$V_{\mathrm{R}} = V_{\mathrm{Ro}}\frac{\rho_{\mathrm{A}}(\rho_{\mathrm{H_2O}} + c_{\mathrm{aRo,NaOH}}M_{\mathrm{H_2O}})}{\rho_{\mathrm{A}}(\rho_{\mathrm{H_2O}} + c_{\mathrm{R,TB}}M_{\mathrm{H_2O}}) - c_{\mathrm{R}}M_{\mathrm{A}}\rho_{\mathrm{H_2O}}} \tag{53}$$

Finally for the volume of the solvent phase V_{S} it follows

$$V_{\mathrm{S}} = V_{\mathrm{So}}\frac{\rho_{\mathrm{A}}}{\rho_{\mathrm{A}} - c_{\mathrm{S}}^{*}M_{\mathrm{A}}} \tag{54}$$

The equilibrium concentration of acid in the solvent phase, c_{S}^{*}, is calculated from its concentration in the stripping phase, c_{R}

$$c_{\mathrm{S}}^{*} = c_{\mathrm{R}}\frac{V_{\mathrm{R}}}{V_{\mathrm{S,samp}}} \tag{55}$$

where $V_{\mathrm{S,samp}}$ is the volume of the sample of organic phase taken for the stripping. In each experiment, the mass balance of acid, Δ, was checked by the ratio

$$\Delta = \frac{c_{\mathrm{aF}}^{*}V_{\mathrm{F}} + c_{\mathrm{S}}^{*}V_{\mathrm{S}}}{W_{\mathrm{A}}/M_{\mathrm{A}} + c_{\mathrm{Fo}}V_{\mathrm{Fo}}} \tag{56}$$

where W_{A} is the mass of pure acid added to the experiment (e.g., powdered MPCA). The ideal value of Δ should be 1. The uncertainty of this mass balance ratio can be expressed in terms of standard deviation

$$\mathrm{SD} = \left[\frac{1}{n}\sum_{k=1}^{n}(\Delta_k - 1)^2\right]^{1/2} \tag{57}$$

The uncertainty of all measurements presented here is 0.039.

The values of ionic strengths in the aqueous phases I_{F}^{*} were calculated according to the following equations:

$$I_{\mathrm{F}}^{*} = m_{\mathrm{F,MPCA^-}}^{*} \tag{58}$$

for MPCA and for H_2SO_4

$$I_{\mathrm{F}}^{*} = m_{\mathrm{F,HSO_4^-}}^{*} + 3m_{\mathrm{F,SO_4^{2-}}}^{*} \tag{59}$$

These equations are based on the definition of ionic strength and the fact that both Na^+ and H^+ cations are monovalent. Molalities of the anions can be calculated from their molar concentrations given by eqs 8 to 10.

Results and Discussion

Determination of pK_a. pK_a values are needed for the calculation of HMPCA and SO_4^{2-} concentrations in eqs 14 and 33. The relation between the volume of the added titrant, V_{T}, and pH (eq 11) was initially tested on a binary solution of butyric acid (1) + H_2O (2) (Table S1 in Supporting Information, SI) with a known value of pK_a = 4.82 at T = 25 °C. Figure 2 and the correlation coefficient in Table 1 show a very good fit of experimental data to the model. A slightly lower value of the determined pK_a compared with that published in the literature can be attributed to the additional ionic strength coming from the dissociated part of BA in the sample, sodium ions present in the titrant and protons (Table S1 in SI).

Generally, by increasing the ionic strength, pK_a values of acids decrease.[51] This could be explained by the assumption that a more polar environment supports the dissociation of acids. Experimental data from the titration of the binary solution (MPCA + H_2O) (Table S1), ternary solution H_2SO_4 (1) + Na_2SO_4 (2) + H_2O (3) with $c_2 = 1$ kmol·m^{-3}, and quaternary solution MPCA (1) + H_2SO_4 (2) + Na_2SO_4 (3) + H_2O (4) with $c_3 = 1$ kmol·m^{-3} (Table S2 of SI) were correlated for the comparison of pK_a at the ionic strength I close to zero and 3.083 mol·kg^{-1} (Figure 2). The values of estimated pK_a collected in Table 1 show that the increase in ionic strength from about 0 to about 3 mol·kg^{-1} caused the decrease in the pK_a value of MPCA by 0.22. In the case of H_2SO_4, the decrease was as high as 1.19. This occurred due to the fact that it is impossible to distinguish between the sulfates coming from 1 kmol·m^{-3} of Na_2SO_4 and H_2SO_4, so all of them are involved in the definition of pK_{a2} (eq 2). A rather low pH is needed to protonate half of all of these sulfates to hydrogen sulfates. The liquid−liquid equilibrium data at the increased ionic strength cannot be satisfactorily modeled without considering these modifications of pK_a.

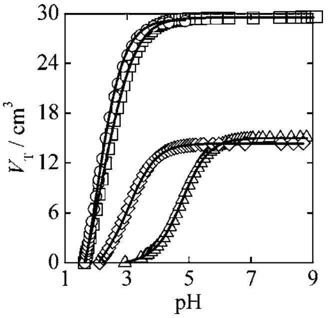

Figure 2. Correlation of experimental data from Tables S1 and S2 in the SI by eq 11 for the determination of pK_a values of the acids shown in Table 1. Samples were the following aqueous solutions: ○,15 cm^3 of H_2SO_4 (1) + Na_2SO_4 (2) + H_2O (3); c_1 = 0.0937 kmol·m^{-3}, c_2 = 1 kmol·m^{-3}. □, 10 cm^3 of MPCA (1) + H_2SO_4 (2) + Na_2SO_4 (3) + H_2O (4); c_1 = 0.1000 kmol·m^{-3}, c_2 = 0.09148 kmol·m^{-3}, c_3 = 1 kmol·m^{-3}. ◇, 15 cm^3 of MPCA (1) + H_2O (2); c_1 = 0.09599 kmol·m^{-3}. △, 15 cm^3 of BA (1) + H_2O (2); c_1 = 0.1006 kmol·m^{-3}.

Liquid−Liquid Equilibria of MPCA. In the formulation of a suitable solvent for the extraction of MPCA by TOA, *n*-alkanes, xylene, and isopropylbenzene as the diluents, as well as the modifier isodecanol, were initially tested. The distribution coefficients of MPCA in (water + diluent) systems without TOA are very close to zero, and the same has been found also for the mixture isodecanol (1) + *n*-alkanes (2) with $c_1 = 0.8$ kmol·m^{-3}.

In the extraction of MPCA with solvent TOA (1) + *n*-alkanes (2), $c_1 = 0.4$ kmol·m^{-3}, the second organic phase containing aggregated (MPCA + TOA) complexes was formed. To determine if such complexes could be regarded as reverse micelles similarly as it has been concluded by Chiarizia et al.[7,8] needs further study and measurements. In the tested range of MPCA concentrations, the formation of the second organic phase was prevented when at least 0.8 kmol·m^{-3} of isodecanol was added to *n*-alkanes. However, isodecanol is highly toxic for some microorganisms.[52,53] The replacement of isodecanol with, for example, less toxic isotridecanol leads to the increased viscosity of the solvent slowing down mass transfer in the extraction or pertraction. Therefore it was attempted to use xylene or isopropylbenzene. Because of their aromatic character possessing also some polarity, the (MPCA + TOA) complexes did not aggregate, and the second organic phase disappeared.

Overloading was observed in the reactive extraction of MPCA by TOA (1) + xylene (2) with $c_1 = 0.4$ kmol·m^{-3} (solvent SX) and TOA (1) + isodecanol (2) + *n*-alkanes (3) with c_1 = 0.4 kmol·m^{-3} and $c_2 = 0.8$ kmol·m^{-3} (solvent SA). According

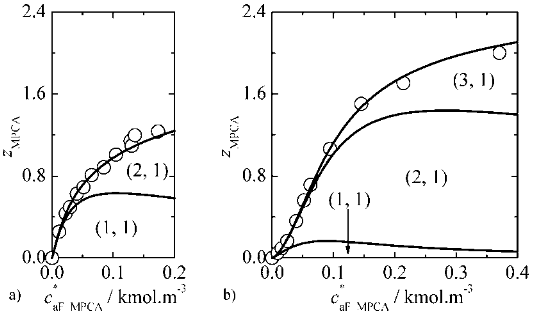

Figure 3. Concentration dependence of loading of TOA by MPCA in systems with binary aqueous solutions of MPCA and solvent SA (a) or solvent SX (b). Overall loading is depicted as a sum of partial loadings $z_{p,1}$ according to eq 29. Circles are the experimental values of loading.

Table 3. Liquid−Liquid Equilibria of MPCA Extracted from Binary Solutions (MPCA + H_2O) by TOA (1) + Isodecanol (2) + *n*-Alkanes (3) with c_1 = 0.4 kmol·m^{-3} and c_2 = 0.8 kmol·m^{-3} (Solvent SA)[a]

$c^*_{aF,MPCA}$ kmol·m^{-3}	pH^*_F	I^*_F mol·kg^{-1}	$c^*_{S,MPCA}$ kmol·m^{-3}	z_{MPCA}	$D_{a,MPCA}$	Δ
0.0116	2.92	0.0047	0.102	0.256	8.75	1.03
0.0225	2.71	0.0066	0.171	0.435	7.62	0.95
0.0294	2.56	0.0067	0.195	0.496	6.63	1.01
0.0407	2.52	0.0087	0.245	0.628	6.02	0.93
0.0516	2.39	0.0086	0.269	0.691	5.21	0.96
0.0649	2.40	0.0111	0.314	0.811	4.85	0.92
0.0847	2.27	0.0113	0.342	0.886	4.04	0.97
0.105	2.21	0.0123	0.388	1.01	3.71	0.95
0.128	2.14	0.0132	0.437	1.14	3.40	1.02
0.130	2.14	0.0134	0.420	1.10	3.23	1.00
0.136	2.13	0.0068	0.457	1.20	3.37	0.99
0.173	2.07	0.0051	0.471	1.23	2.72	1.02

[a] Experimental values of equilibrium MPCA concentrations in aqueous ($c^*_{aF,MPCA}$) and solvent ($c^*_{S,MPCA}$) phases, loading z_{MPCA} (eq 29) and distribution coefficient $D_{a,MPCA}$. Ionic strength (I^*_F) was calculated by eq 58 using pK_a = 3.09 (Table 1) and mass balance Δ by eq 56. The uncertainty of Δ (eq 57) is 0.042.

Table 4. Liquid−Liquid Equilibria of MPCA Extracted from Binary Solutions (MPCA + H_2O) by TOA (1) + Xylene (2) with c_1 = 0.4 kmol·m^{-3} (Solvent SX)[a]

$c^*_{aF,MPCA}$ kmol·m^{-3}	pH^*_F	I^*_F mol·kg^{-1}	$c^*_{S,MPCA}$ kmol·m^{-3}	z_{MPCA}	$D_{a,MPCA}$	Δ
0.00896	2.93	0.0037	0.0192	0.0481	2.14	1.04
0.0154	2.71	0.0046	0.0372	0.0933	2.42	0.99
0.0248	2.77	0.0081	0.0658	0.166	2.65	0.99
0.0394	2.63	0.0102	0.142	0.361	3.61	0.99
0.0521	2.56	0.0120	0.220	0.562	4.23	1.00
0.0627	2.53	0.0137	0.278	0.715	4.44	0.94
0.0944	2.24	0.0117	0.409	1.06	4.33	0.92
0.145	2.16	0.0157	0.568	1.50	3.90	1.03
0.214	2.08	0.0198	0.640	1.71	2.99	1.00
0.371	1.96	0.0270	0.742	2.00	2.00	1.02

[a] The meaning of symbols in column headings is the same as in Table 3. The uncertainty of Δ (eq 57) is 0.036.

Table 5. Stability Constants $K_{p,1}$ of (*p*, 1) Complexes Containing *p*MPCA and TOA

complex (*p*, 1)	$K_{p,1}$/(kmol·m^{-3})$^{-p}$ solvent SA[a]	$K_{p,1}$/(kmol·m^{-3})$^{-p}$ solvent SX[b]
(1, 1)	35.4	4.77
(2, 1)	106	136
(3, 1)		125
correlation coefficient	0.9990	0.9973

[a] TOA (1) + isodecanol (2) + *n*-alkanes (3); c_1 = 0.4 kmol·m^{-3}, c_2 = 0.8 kmol·m^{-3}. [b] TOA (1) + xylene (2); c_1 = 0.4 kmol·m^{-3}.

Table 6. pH_{hn} Values of TOA in Various Diluents from the Paper of Canari and Eyal[21]

diluent	pH_{hn}
kerosene	2.85
octanol (1) + kerosene (2) with w_1 = 0.2	4.50
octanol	6.06

to the concentration dependence of loading in Figure 3a and Table 3 in the model, (*p*, 1) complexes (1, 1) and (2, 1) were assumed for the solvent SA. For the solvent SX, the loading slightly exceeded the value of 2 (Table 4 and Figure 3b) so that also complex (3, 1) had to be involved. (*p*, 1) complexes containing only one molecule of TOA are typical for the monocarboxylic acids (see eq 14).[17]

The calculated values of stability constants $K_{1,1}$ and $K_{2,1}$ in Table 5 are by about 7.5 times higher and by about 22 % lower for solvent SA than those for solvent SX, respectively. Such differences indicate that complex (1, 1) is more stable in solvent SA and complex (2, 1) in solvent SX. Complex (1, 1) is probably an ion pair which is well-solvated by more polar isodecanol contained in solvent SA than by xylene. On the other hand, the hydrogen bond between MPCA molecules in complex (2, 1) can be destabilized by a polar hydrogen of isodecanol turning the complex (2, 1) back to the complex (1, 1). The xylene present in solvent SX does not disturb the hydrogen bond. This is in agreement with the observations of Tamada and King,[18] confirmed also by the measurements of IR spectra.

To qualify the character of the bond between the acid and the extractant, the pK_a values of acid and the extractant basicity are needed. The latter has been characterized by Canari and Eyal[21] as the pH of half-neutralization of amine (pH_{hn}) loaded with HCl. The neutralization was done by the addition of NaOH. If pK_a < pH_{hn}, then the ion-pair is formed. In the opposite case, the hydrogen bond was formed. When these values were approximately equal, both COOH and COO^- groups were detected in the IR spectra of the organic phases so that the character of the (acid + amine) bond was between the hydrogen bond and the ion pair. According to the pH_{hn} values of TOA in three diluents shown in Table 6 with the increase in polarity of the diluent, the pH_{hn} value increased. The comparison of pK_a of MPCA (3.09, Table 1) with the pH_{hn} (Table 6) indicates that, in solvent SA containing isodecanol with mass fraction w = 16.5 %, an acid forms an ion pair with an amine. Because of the xylene polarity and its aromatic character, the pH_{hn} of TOA in xylene is probably a little higher than that for kerosene in Table 6. Therefore, the pH_{hn} of TOA in solvent SX should be similar to pK_a of MPCA so that the character of the bond between MPCA and TOA in solvent SX is probably between the ion pair and the hydrogen bond. The lower strength of the hydrogen bond compared with the ion pair is also the cause why complex (1, 1) is less stable in solvent SX than in solvent SA. Another consequence is the different saturation of the extractant at the same loading. At the loading of 1 (Figure 3), TOA is saturated to 80 % in solvent SA (Figure 4a) but only to slightly above 50 % in solvent SX (Figure 4b).

At the MPCA concentration approaching zero almost all extracted MPCA is in the complex (1, 1) (Figure 5). Since it is more stable in solvent SA, at lower equilibrium aqueous MPCA concentrations ($c^*_{aF,MPCA}$), the distribution coefficient is higher for solvent SA. Contrary to this, at higher $c^*_{aF,MPCA}$, complex (2, 1) prevails, which is more stable in solvent SX. Therefore, at these concentrations, the distribution coefficient is higher for solvent SX. At $c^*_{aF,MPCA}$ = 0.08 kmol·m^{-3}, the distribution

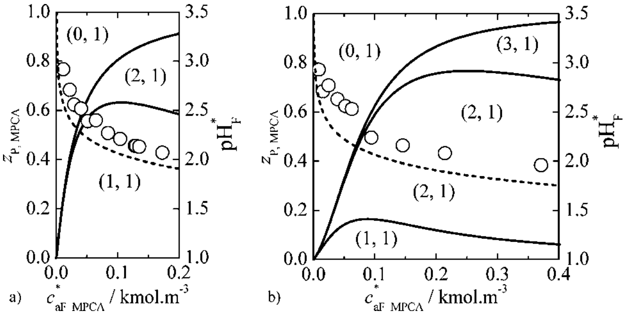

Figure 4. Concentration dependence of extractant saturation $z_{P,MPCA}$ by MPCA in systems with binary aqueous solutions of MPCA and solvent SA (a) or solvent SX (b). The overall saturation ratio is depicted as a sum of partial saturation ratios $z_{P,(p,1)}$ according to eq 31. Circles and dashed curves are the experimental and calculated values of pH in the aqueous phase.

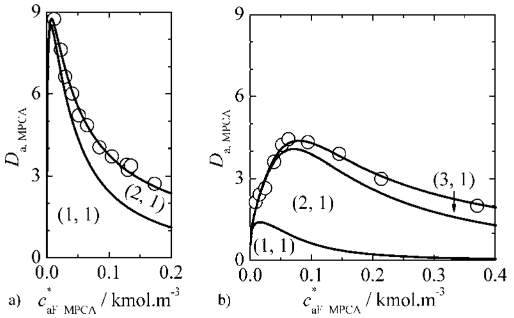

Figure 5. Concentration dependence of distribution coefficient of MPCA in systems with binary aqueous solutions of MPCA and solvent SA (a) or solvent SX (b). The overall distribution coefficient is depicted as a sum of partial distribution coefficients $D_{a,(p,1)}$ according to eq 32. Circles are the experimental values of distribution coefficient.

Table 7. Liquid−Liquid Equilibria of H_2SO_4 Extracted from Binary Aqueous Solutions by TOA (1) + Xylene (2) with $c_1 = 0.4$ kmol·m^{-3} (Solvent SX)[a]

c^*_{aF,H_2SO_4} / kmol·m^{-3}	pH^*_F	I^*_F / mol·kg^{-1}	c^*_{S,H_2SO_4} / kmol·m^{-3}	c^*_{S,H_2O} / kmol·m^{-3}	D_{a,H_2SO_4}	Δ
8.3·10^{-4}	3.16	0.0023	0.0138	0.0763	16.7	1.13
0.0014	2.78	0.0037	0.0223	0.127	15.8	0.91
0.0020	2.55	0.0050	0.0501	0.253	25.5	1.00
0.0031	2.43	0.0073	0.0947	0.579	30.4	0.95
0.0048	2.23	0.0103	0.149	0.869	31.0	0.99
0.0093	1.87	0.0162	0.196	1.15	21.0	1.00
0.0263	1.60	0.0390	0.239	1.10	9.07	1.01
0.0487	1.26	0.0611	0.254	1.03	5.22	0.99
0.0946	1.01	0.109	0.278	0.924	2.94	0.98
0.1962	0.72	0.214	0.333	0.832	1.70	1.04
0.619	0.32	0.655	0.374	0.570	0.604	1.00
1.33	0.05	1.43	0.398	0.459	0.298	1.01
3.26	−0.15	3.76	0.422	no data	0.129	no data
3.44	−0.41	3.97	0.415	0.337	0.121	1.02

[a] Ionic strength I^*_F was calculated by eq 59 using pK_{a2} = 2.10 (Table 1). The meaning of symbols in column headings is similar as in Table 3. The uncertainty of Δ (eq 57) is 0.048.

Table 8. Liquid−Liquid Equilibria of H_2SO_4 Extracted from Ternary Aqueous Solutions Containing 1 kmol·m^{-3} of Na_2SO_4 by TOA (1) + Xylene (2) with $c_1 = 0.4$ kmol·m^{-3} (Solvent SX)[a]

c^*_{aF,H_2SO_4} / kmol·m^{-3}	c^*_{aF,SO_4} / kmol·m^{-3}	pH^*_F	I^*_F / mol·kg^{-1}	c^*_{S,H_2SO_4} / kmol·m^{-3}	c^*_{S,H_2O} / kmol·m^{-3}	D_{a,H_2SO_4}	Δ
0.00430	1.00	3.07	3.07	0.0643	0.132	14.9	1.02
0.00630	1.00	2.87	3.06	0.107	0.402	17.0	1.01
0.00649	0.976	2.97	2.98	0.0925	no data	14.3	no data
0.0138	1.00	2.57	3.04	0.171	0.987	12.4	1.00
0.0287	1.02	2.13	3.00	0.220	1.02	7.68	0.99
0.0697	1.05	1.85	3.02	0.249	1.01	3.57	1.00
0.113	1.09	1.60	2.99	0.271	0.915	2.42	1.00
0.158	1.13	1.40	2.96	0.284	0.880	1.80	1.00
0.195	1.17	1.15	2.83	0.307	0.792	1.57	1.00

[a] c^*_{aF,SO_4} was calculated by eq 38 and ionic strength I^*_F by eq 59 using pK_{a2} = 0.908 (Table 1). The meaning of symbols in column headings is similar to Table 3. The uncertainty of Δ (eq 57) is 0.0087.

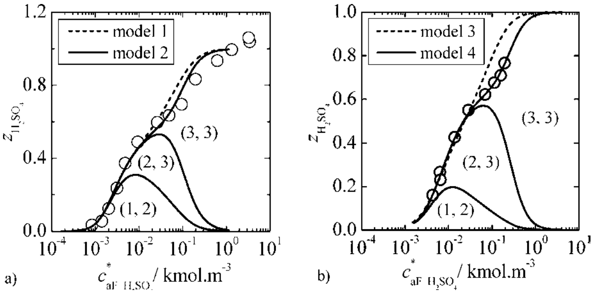

Figure 6. Concentration dependence of loading of extractant $z_{H_2SO_4}$ by H_2SO_4 in systems with solvent SX and binary solution H_2SO_4 + H_2O (a) or ternary solution H_2SO_4 (1)+ Na_2SO_4 (2) + H_2O (3) with c_2 = 1 kmol·m^{-3} (b). The overall loading is depicted as a sum of partial loadings $z_{r,q}$ according to eq 44. Models are numbered as in Table 9. Circles are the experimental values of loading.

coefficient is equal for both solvents, and for solvent SX it reaches the maximum. At this maximum, most of the extracted MPCA is in the form of complex (2, 1) (Figure 5b). For solvent SA, on decreasing $c^*_{aF,MPCA}$, the distribution coefficient increases fairly. This can be important in the extraction or pertraction from the feeds with low acid content.

Liquid−Liquid Equilibrium of Sulfuric Acid. Because of its high polarity, physical extraction of sulfuric acid by diluents *n*-alkanes or xylene was negligible. In contrast to solvent SX, in the extraction by TOA (1) + *n*-alkanes (2), the formation of the second organic phase occurred. Therefore, solvent SX was chosen for further experiments.

Both pK_a values of H_2SO_4 are lower than pH_{hn} of TOA (Table 6) so that only ionic bonds were proposed between H_2SO_4 and TOA.[22] By increasing the acid concentration, the loading $z_{H_2SO_4}$ increases much faster than in the case of MPCA as follows from the comparison of Tables 4, 7, and 8 and Figures 3 and 6. However, in the intervals of equilibrium aqueous concentration of H_2SO_4 c^*_{aF,H_2SO_4} = (0.01 to 0.1) kmol·m^{-3} and (0.03 to 0.2) kmol·m^{-3} for systems with the binary aqueous solution of H_2SO_4 (H_2SO_4 + H_2O; Figure 6a) and ternary solution of H_2SO_4 containing 1 kmol·m^{-3} of Na_2SO_4 (H_2SO_4 + Na_2SO_4 + H_2O; Figure 6b), respectively, this increase is less steep than outside these intervals. This has been usually explained as a transition interval between trialkylammonium sulfate and trialkylammonium hydrogen sulfate, in fact (*r*, *q*) complexes (1, 2) and (1, 1), respectively.[40] According to the results of Canari and Eyal,[22] the existence of such a transition interval is characteristic only in the case when the (acid + TOA) bond has ionic character. However, models 1 and 3 in Table 9, which consider only complexes (1, 2) and (1, 1), did not fit the data well as that shown by the values of the correlation coefficient and the dashed lines in Figure 6. Procházka et al.[41] considered also complex (2, 2), and Schunk and Maurer[43] proposed complexes (3, 6) and (3, 3) for toluene and (4, 8) and (4, 4) for methyl isobutyl ketone as diluents.[42] However, in all of these complexes, the acid-to-TOA ratio is the same as in complex (1, 2) or (1, 1). The problem is that for a satisfactory data fit by the model assuming complexes with such ratios, the loading at the mentioned transition interval should be close to the value of 0.5. However, Figure 6 shows that this value is slightly above 0.6. Therefore, models 2 and 4 assuming the three complexes, (1, 2), (2, 3), and (3, 3), were proposed as they correlate the

Table 9. Stability Constants $K_{r,q}$ of (*r*, *q*) Complexes Containing rH$_2$SO$_4$ and qTOA in TOA (1) + Xylene (2) with $c_1 = 0.4$ kmol·m^{-3} (Solvent SX)

model number	1	2	3	4	5	6
complex	$K_{r,q}$/(kmol·m^{-3})$^{1-3r-q}$SCT					
(*r*, *q*)	H_2SO_4 (1) + H_2O (2)		H_2SO_4 (1) + Na_2SO_4 (2) + H_2O (3); $c_2 = 1$ kmol·m^{-3}			
(1, 2)	$4.47 \cdot 10^7$	$4.64 \cdot 10^7$	$8.16 \cdot 10^5$	$7.24 \cdot 10^5$	$5.92 \cdot 10^5$	$7.25 \cdot 10^5$
(1, 1)	$9.02 \cdot 10^5$		$3.73 \cdot 10^4$		$4.55 \cdot 10^3$	
(2, 3)		$2.73 \cdot 10^{14}$		$4.12 \cdot 10^{11}$		$3.36 \cdot 10^{11}$
(3, 3)		$4.33 \cdot 10^{18}$		$1.27 \cdot 10^{14}$		$8.28 \cdot 10^{13}$
pK_{a2}	fixed 2.10		fixed 0.908		free 0.775	free 0.895
correlation coefficient	0.9887	0.9942	0.9892	0.9970	0.9966	0.9972

data much better. A possible structure of these complexes is proposed in Figure 9. Complex (2, 3) has already been proposed, for example, for HCl by Schunk and Maurer.[43] It was also attempted to unfix K_{a2} in models 3 and 4 which resulted in models 5 and 6, respectively (Table 9). In the case of model 5, the stability constants $K_{1,2}$ and $K_{1,1}$ decreased by about 27 % and 88 %, respectively, and K_{a2} increased by about 36 % compared with those in model 3. In the case of model 6, $K_{1,2}$ increased slightly by about 0.14 %, $K_{2,3}$ and $K_{3,3}$ decreased by about 18 % and 35 %, respectively, and K_{a2} increased very moderately by about 3 % compared with those in model 4. These comparisons show that unfixing of pK_{a2} caused much smaller changes in the parameters of the model assuming three complexes compared with model assuming only two complexes. Therefore, the model with three complexes is the better one. Especially the rather good resistance of pK_{a2} to modifications in model 6 should be emphasized because if the pK_{a2} changes too much (as in model 5), the concentration of the sulfate anion, in fact reactant in eq 33, is artificially changed to a value far from the real state in the aqueous phase.

Using the stability constants of model 4 in Table 9, the TOA saturation was calculated according to eq 45 as shown in Figure 7. Assuming the ionic character of all bonds between TOA and H_2SO_4, the pH$_{hn}$ of TOA can be estimated from these graphs. In Figure 7 it is shown by a broken line. Although these pH$_{hn}$ values are lower than those assumed according to Table 6, they are still higher than both dissociation constants of H_2SO_4 so that the ionic character of the (H_2SO_4 + TOA) bond is supported. Differences in the values of pH$_{hn}$ are probably due to the different methods of determination.

The extraction of H_2SO_4 from the ternary solution (H_2SO_4 + Na_2SO_4 + H_2O) is less effective compared with the binary solution (H_2SO_4 + H_2O). This is expressed by the shift of the loading curve in Figure 6b to the right compared with that in Figure 6a, although the shape of the curve remained unchanged. Such behavior can be explained by comparing the equilibrium pH. Figure 7 shows that, at the same equilibrium aqueous concentration of H_2SO_4 (c^*_{aF,H_2SO_4}), the pH is higher for (H_2SO_4 + Na_2SO_4 + H_2O). Provided that the TOA forms ion pairs with H_2SO_4, the extraction efficiency depends on the possibility of formation of the HTOA$^+$ cation. This cannot be formed sufficiently in (H_2SO_4 + Na_2SO_4 + H_2O) with the lack of protons so that the extraction efficiency decreases. The reason for higher pH in (H_2SO_4 + Na_2SO_4 + H_2O) follows from the competition between TOA and SO_4^{2-} for protons. The excess of sulfate anions originated from Na_2SO_4 binds more protons than in (H_2SO_4 + H_2O), although the analytical concentration of free H_2SO_4 is the same. Stability constants of the corresponding complexes in the system with (H_2SO_4 + Na_2SO_4 + H_2O) are from about two to almost five orders of magnitude lower compared with those in the systems with (H_2SO_4 + H_2O). This is also because of the excess of sulfate anions in the aqueous phase. The rather high concentration of SO_4^{2-} diminishes the values of stability constants because it is in the denominator of eq 34.

Another consequence is the lower value of the distribution coefficient in Figure 8b compared with Figure 8a, especially at low concentrations of H_2SO_4. The maximum value of the distribution coefficient for the system with (H_2SO_4 + Na_2SO_4 + H_2O) is almost twice lower than that for (H_2SO_4 + H_2O). Figure 8 shows that, at these maxima, in the solvent phase the major part of acid is in the form of complex (1, 2) and a minor part in that of complex (2, 3). The maximum for (H_2SO_4 + Na_2SO_4 + H_2O) was achieved at $c^*_{aF,H_2SO_4} = 0.006$ kmol·m^{-3} and for (H_2SO_4 + H_2O) at c^*_{aF,H_2SO_4} about twice lower. Both maxima are fairly higher than those for the system with binary solution (MPCA + H_2O) and solvent SX (Figure 5b), about

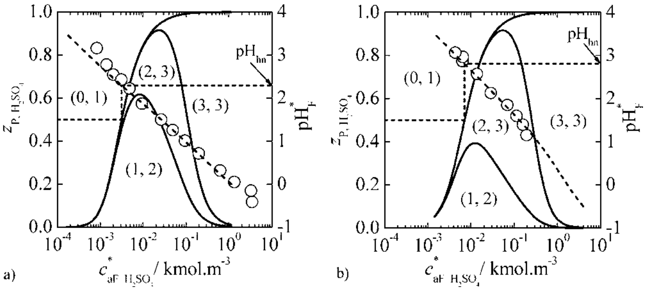

Figure 7. Concentration dependence of extractant saturation by H_2SO_4 z_{P,H_2SO_4} in systems with solvent SX and binary solution H_2SO_4 + H_2O (a) or ternary solution H_2SO_4 (1) + Na_2SO_4 (2) + H_2O (3) with $c_2 = 1$ kmol·m^{-3} (b). The overall saturation ratio is depicted as a sum of partial saturation ratios $z_{P,(r,q)}$ according to eq 45. Circles and the associated dashed lines are the experimental and calculated values of pH in the aqueous phase. A broken line illustrates the method of pH$_{hn}$ estimation, which was 2.29 (a) and 2.81 (b).

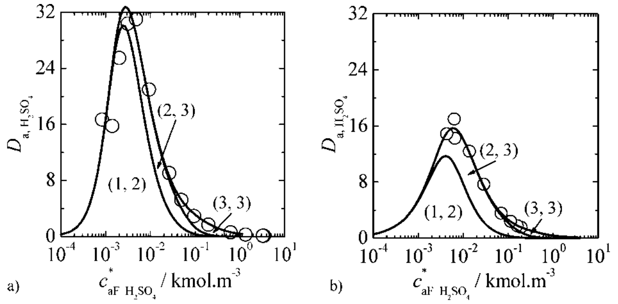

Figure 8. Concentration dependence of the distribution coefficient of H_2SO_4 in systems with solvent SX and binary solution H_2SO_4 + H_2O (a) or ternary solution H_2SO_4 (1) + Na_2SO_4 (2) + H_2O (3) with $c_2 = 1$ kmol·m^{-3} (b). The overall distribution coefficient is depicted as a sum of partial distribution coefficients $D_{a,(r,q)}$ according to eq 46. Circles are the experimental values of the distribution coefficient.

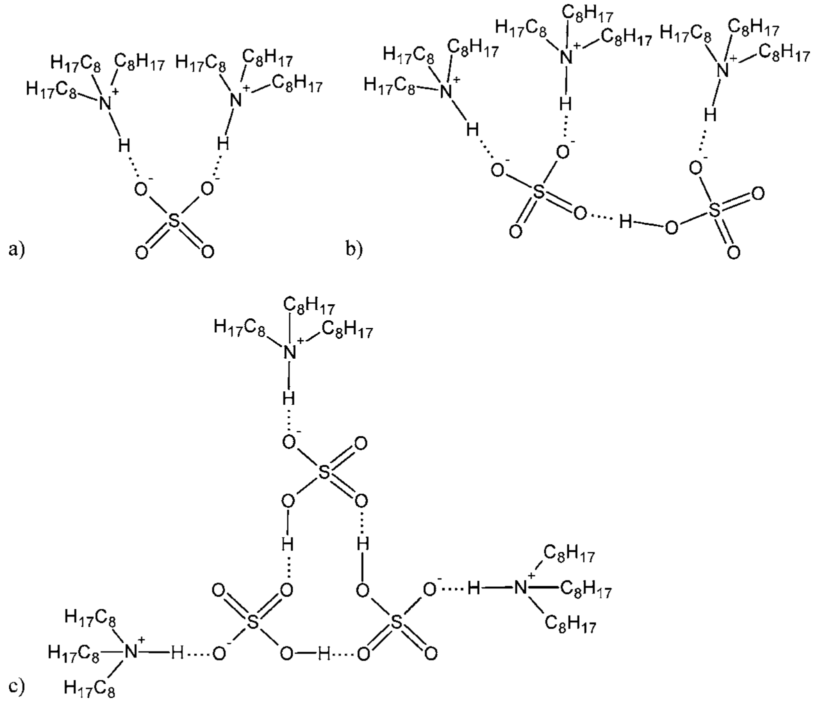

Figure 9. Proposed structures of (H_2SO_4 + TOA) complexes. (a) Complex (1, 2), (b) complex (2, 3), (c) complex (3, 3).

7.3 and 3.6 times for (H_2SO_4 + H_2O) and (H_2SO_4 + Na_2SO_4 + H_2O), respectively. The related $c^*_{aF,MPCA}$ shown in Figure 5 (0.08 $kmol \cdot m^{-3}$) is about 27 and 13 times higher than the corresponding H_2SO_4 concentrations, respectively. These differences in the distribution of acids indicate that the affinity of strong acid H_2SO_4 to TOA is much higher than that of weak MPCA. The acidities of H_2SO_4 and MPCA follow from the comparison of their pK_a shown in Table 1. The difference between the affinities of both acids to TOA is more evident when comparing Figures 7a and 4b where the saturation ratios of extractant z_P versus c^*_{aF} are drawn. At the value of c^*_{aF} of about 0.02 $kmol \cdot m^{-3}$, more than 90 % of TOA is loaded when it comes into contact with (H_2SO_4 + H_2O), but less than 10 % of TOA is complexed when it comes into contact with (MPCA + H_2O). The comparison of Figures 8 and 5b shows that the distribution coefficient of H_2SO_4 is lower than that of MPCA at c^*_{aF} of above 0.06 $kmol \cdot m^{-3}$. This is not caused by lower stability of (H_2SO_4 + TOA) complexes compared with the (MPCA + TOA) ones but by the fact that, unlike MPCA, in the case of H_2SO_4 overloading does almost not occur as can be seen when Figures 6 and 3b are compared. Therefore, the maximal concentration of H_2SO_4 in the solvent is limited by the TOA concentration. This can be explained on the basis of assumption that the overloading can only appear when the hydrogen bond is formed between the undissociated molecules of acids. Contrary to MPCA, the undissociated molecules of H_2SO_4 exist only at very low pH. Some hydrogen bonds between H_2SO_4 molecules are assumed in the structure proposals of complexes (2, 3) and (3, 3) in Figure 9 , parts b and c. However, as the H_2SO_4 is dibasic, besides hydrogen donated to such a hydrogen bond, the second hydrogen must be dissociated at moderate acidic conditions. The only possibility of how to dissociate it is the formation of an ion pair with another TOA molecule. In the modeling the lack of overloading led to the fact that the larger (H_2SO_4 + TOA) complexes could be understood as aggregated smaller complexes (Figure 9).

Complex (2, 3) can be regarded as aggregated complexes (1, 2), TOA/sulfate, and (1, 1), TOA/hydrogen sulfate, and complex (3, 3) as three aggregated hydrogen sulfates. A little overloading can be seen in Figure 6a. The last two points achieve the values of $z_{H_2SO_4}$ = (1.06 and 1.04). Since the corresponding equilibrium pH are rather low, −0.15 and −0.41, respectively (Figure 7a and Table 7), there are probably satisfactory acidic conditions in both aqueous and organic phases for the existence of some undissociated H_2SO_4.

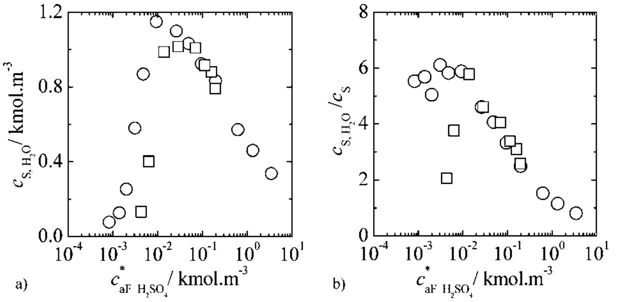

Figure 10. Concentration dependence of water concentration (a) and molar ratio of water to H_2SO_4 (b) in the organic phase in systems with solvent SX and aqueous phases: ○, binary solution H_2SO_4 + H_2O. □, ternary solution H_2SO_4 (1) + Na_2SO_4 (2) + H_2O (3) with $c_2 = 1\ kmol \cdot m^{-3}$.

Figure 10a indicates that pure solvent SX equilibrated with water is almost water-free. By increasing the acid concentration, the water content in the solvent increases up to the maximum, which was achieved at $c^*_{aF,H_2SO_4} = 0.009\ kmol \cdot m^{-3}$ for (H_2SO_4 + H_2O), and for (H_2SO_4 + Na_2SO_4 + H_2O) there was a plateau at c^*_{aF,H_2SO_4} = (0.014 to 0.07) $kmol \cdot m^{-3}$ (Figure 10a and Tables 7 and 8). Comparing Figures 10a and 6 it can be said that the maxima of the water concentration correspond to the loading value very close to 0.5. This indicates that regardless of the complex distribution, the overall stoichiometric ratio of H_2SO_4 and TOA in the solvent phase is 1:2. This is in fact trioctylammonium sulfate which can be regarded as an IL with the stoichiometric formula $[(C_8H_{17})_3NH^+]_2SO_4^{2-}$. Such polar sites may have a tendency to aggregate, forming a particle with alkyl chains oriented to the hydrophobic diluent, xylene, in fact a reverse micelle. This presumption is in coherence with the aggregation of polar (H_2SO_4 + TOA) complexes indicated by modeling. The low polarity of xylene should be unable to prevent such structuring. From Figure 10a it can be easily calculated that at the maximum of the water content in the solvent phase there are about six and five water molecules per one $[(C_8H_{17})_3NH^+]_2SO_4^{2-}$ for the systems with $(H_2SO_4 + H_2O)$ and $(H_2SO_4 + Na_2SO_4 + H_2O)$, respectively. These values are rather high and also indicate the formation of reverse micelles. For comparison, in the water-saturated ILs tetraalkylphosphonium chloride (Cyphos IL-101),[11] octanoate (unpublished), and dialkylphosphinate (Cyphos IL-104)[11,12] there are 5, 5.7, and 7.6 water molecules per one molecule of IL, respectively. These ILs are insoluble in water (hydrophobic), although the water solubility in them is high. The reverse micelles have been proven in a water-saturated solution of 0.1 $kmol \cdot m^{-3}$ of Cyphos IL-104 in *n*-dodecane.[13] On the other hand, the (p, 1) complexes of rather hydrophobic and weak organic acids, for example, butyric[26] or dimethylcyclopropanecarboxylic[25] acids where p may exceed 5 or 10, respectively, contain very little water, typically 1 water molecule per 10 acid molecules.

By a further increase in the H_2SO_4 concentration above the value corresponding with the maximum water concentration (Figure 10a), the water concentration decreased. This can be explained as destabilization and the splitting of reverse micelles because the formation of $(H_2SO_4 + TOA)$ complexes removes an IL (in this case trioctylammonium sulfate) from the protective adsorption layer on the surface of reverse micelles. A similar phenomenon was observed in the extraction of lactic and butyric acids by phosphonium ILs.[11−13] In the model published in papers of Schunk and Maurer[42,43] no reverse micelles were supposed, and the water was considered as a part of the $(H_2SO_4 + TOA)$ complexes. However, for toluene diluent, 18 and 6 molecules of water were assigned to complexes (3, 6) and (3, 3), respectively, and for diluent methyl isobutyl ketone, 48 and 12 molecules were assigned to complexes (4, 8) and (4, 4), respectively. From this follows the ratio of $6H_2O$ per one H_2SO_4 in TOA/sulfate in the case of toluene diluent provided that complex (3, 6) can be regarded as an aggregate of three complexes (1, 2). This is similar to the findings presented here (Figure 10b) for xylene which is structurally very close to toluene. For TOA/sulfate in methyl isobutyl ketone, this ratio was as high as 12:1. In the extraction of inorganic acids by tributylphosphate (TBP) Chiarizia et al.[8] detected the reverse micelles with the composition $(4HNO_3 + 4TBP)$, $(3HCl + 7TBP + 3H_2O)$, $(HClO_4 + 4TBP + 3H_2O)$, $(2H_2SO_4 + 6TBP + 4H_2O)$, and $(9H_3PO_4 + 10TBP + 5H_2O)$ using small-angle neutron scattering. The size of these micelles is probably comparable with that of the mentioned complexes proposed by Schunk and Maurer. From this point of view there seems to be no reason why not to call them also reverse micelles. The interpretation based on the formation of reverse micelles in systems with TOA is supported also by recent data on ILs.[12,13]

Conclusions

By increasing the ionic strength, the pK_a values of MPCA and H_2SO_4 decreased from 3.09 to 2.87 and from 2.10 to 0.908, respectively. The physical extraction of MPCA and H_2SO_4 by *n*-alkanes and xylene as well as by isodecanol as a modifier is negligible.

In reactive extraction of MPCA, overloading of TOA by MPCA occurred so that the formation of (acid + TOA) complexes with the stoichiometry (p, 1), where $p = 1$ to 3, has been proposed. Two diluents of TOA avoiding the formation of the second organic phase were used for the reactive extraction of MPCA from the binary aqueous solutions. In solvent SX with xylene as diluent, the character of the (MPCA + TOA) bond is probably between a hydrogen bond and an ion pair because the pH_{hn} of TOA is similar to the pK_a of MPCA. For solvent SA containing *n*-alkanes as a diluent and isodecanol as a modifier, this bond is probably ionic because pH_{hn} of TOA is fairly higher than pK_a of MPCA. The second and third molecule of MPCA in complexes (2, 1) and (3, 1) are coupled via a hydrogen bond.

Modeling of the MPCA data indicates that complex (1, 1) is more stable in solvent SA than in solvent SX. For complex (2, 1) and probably also for complex (3, 1) it is vice versa. This difference is due to the fact that isodecanol can inhibit the formation of hydrogen bonds between the molecules of MPCA. This is well-reflected in the values of the distribution coefficient. These are, at lower MPCA concentrations, higher for solvent SA compared with solvent SX because at lower MPCA concentrations, complex (1, 1) prevails. At higher MPCA concentrations, above 0.08 $kmol \cdot m^{-3}$, it is vice versa because at these concentrations complexes (2, 1) and (3, 1) prevail.

The affinity of H_2SO_4 to TOA is much higher compared with MPCA as follows from the concentration dependencies of TOA saturations by MPCA and H_2SO_4. The bond between H_2SO_4 and TOA in the complexes is probably ionic as follows from the comparison of both pK_a of H_2SO_4 and pH_{hn} of TOA. Complex (1, 2), TOA/sulfate, is formed at lower H_2SO_4 concentrations. At higher H_2SO_4 concentrations, the formation of complex (1, 1), TOA/hydrogen sulfate, was expected. However, modeling indicates that it probably immediately aggregated with complex (1, 2) resulting in the formation of complex (2, 3). Complex (3, 3) is also formed probably by aggregation of smaller complexes. This behavior differs from that of MPCA where larger complexes were formed by an addition of further molecules of MPCA to smaller complexes. When ionic strength was increased by the addition of Na_2SO_4, the extraction of H_2SO_4 by TOA was not so effective because higher pH in the solution with Na_2SO_4 inhibits the formation of the $HTOA^+$ cation.

The maximum water content in the solvent in the equilibrium was obtained when 2 mol of H_2SO_4 per 1 mol of TOA were present in the organic phase. In this state, the molar ratio of water to H_2SO_4 was about 6, indicating the formation of reverse micelles. H_2SO_4 forms ion pairs with TOA, de facto an IL, where formation of reverse micelles was observed.

Supporting Information Available:

Tables of experimental data and volume of added titrant and figure of the dissociation of HMPCA and HSO_4^- in binary and ternary aqueous solutions vs pH. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Watson, E. K.; Rickelton, W. A.; Robertson, A. J.; Brown, T. J. A liquid phosphine oxide: solvent extraction of phenol, acetic acid and ethanol. *Solvent Extr. Ion Exch.* **1988**, *6*, 207–220.
(2) Fahim, M. A.; Qader, A.; Hughes, M. A. Extraction Equilibria of Acetic and Propionic Acids from Dilute Aqueous Solution by Several Solvents. *Sep. Sci. Technol.* **1992**, *27*, 1809–1821.
(3) Scheler, C.; Popovic, M.; Bajpai, R. Reaktiv-Extraktion von Milchsäure aue einer Fermentationsbrühe in einem Hohlfasermembranmodul. *Chem. Ing. Tech.* **1997**, *69*, 951–955.
(4) Ingale, M. N.; Mahajani, V. V. Recovery of carboxylic acids, C2-C6, from an aqueous waste stream using tributylphosphate (TBP): Effect of presence of inorganic acids and their sodium salts. *Sep. Technol.* **1996**, *6*, 1–7.
(5) Matsumoto, M.; Takahashi, T.; Fukushima, K. Synergistic extraction of lactic acid with alkylamine and tri-*n*-butylphosphate: effects of amines, diluents and temperature. *Sep. Purif. Technol.* **2003**, *33*, 89–93.

(6) Morales, A. F.; Albet, J.; Kyuchoukov, G.; Malmary, G.; Molinier, J. Influence of extractant (TBP and TOA), diluent, and modifier on extraction equilibrium of monocarboxylic acids. *J. Chem. Eng. Data* **2003**, *48*, 874–886.

(7) Chiarizia, R.; Briand, A. Third phase formation in the extraction of inorganic acids by TBP in *n*-octane. *Solvent Extr. Ion Exch.* **2007**, *25*, 351–371.

(8) Chiarizia, R.; Briand, A.; Jensen, M. P.; Thiyagarajan, P. Sans study of reverse micelles formed upon the extraction of inorganic acids by TBP in *n*-octane. *Solvent Extr. Ion Exch.* **2008**, *26*, 333–359.

(9) Kyuchoukov, G.; Morales, A. F.; Albet, J.; Malmary, G.; Molinier, J. On the possibility of predicting the extraction of dicarboxylic acids with tributylphosphate dissolved in a diluent. *J. Chem. Eng. Data* **2008**, *53*, 639–647.

(10) Labbaci, A.; Kyuchoukov, G.; Albet, J.; Molinier, J. Detailed Investigation of Lactic Acid Extraction with Tributylphosphate Dissolved in Dodecane. *J. Chem. Eng. Data* **2010**, *55*, 228–233.

(11) Marták, J.; Schlosser, Š. Phosphonium ionic liquids as new, reactive extractants of lactic acid. *Chem. Pap.* **2006**, *60*, 395–398.

(12) Marták, J.; Schlosser, Š. Extraction of lactic acid by phosphonium ionic liquids. *Sep. Purif. Technol.* **2007**, *57*, 483–494.

(13) Marták, J.; Schlosser, Š. Liquid-Liquid Equilibria of Butyric Acid for Solvents Containing a Phosphonium Ionic Liquid. *Chem. Pap.* **2008**, *62*, 42–50.

(14) Kyuchoukov, G.; Marinova, M.; Molinier, J.; Albet, J.; Malmary, G. Extraction of lactic acid by means of a mixed extractant. *Ind. Eng. Chem. Res.* **2001**, *40*, 5635–5639.

(15) Kyuchoukov, G.; Marinova, M.; Albet, J.; Molinier, J. New method for the extraction of lactic acid by means of a modified extractant (Aliquat 336). *Ind. Eng. Chem. Res.* **2004**, *43*, 1179–1184.

(16) Kyuchoukov, G.; Yankov, D.; Albet, J.; Molinier, J. Mechanism of lactic acid extraction with quaternary ammonium chloride (Aliquat 336). *Ind. Eng. Chem. Res.* **2005**, *44*, 5733–5739.

(17) Tamada, J. A.; Kertes, A. S.; King, C. J. Extraction of Carboxylic Acids with Amine Extractants. 1. Equilibria and Law of Mass Action Modeling. *Ind. Eng. Chem. Res.* **1990**, *29*, 1319–1326.

(18) Tamada, J. A.; King, C. J. Extraction of Carboxylic Acids with Amine Extractants. 2. Chemical Interactions and Interpretation of Data. *Ind. Eng. Chem. Res.* **1990**, *29*, 1327–1333.

(19) Tamada, J. A.; King, C. J. Extraction of Carboxylic Acids with Amine Extractants. 3. Effect of Temperature, Water Coextraction and Process Considerations. *Ind. Eng. Chem. Res.* **1990**, *29*, 1333–1338.

(20) Eyal, A. M.; Canari, R. pH-Dependence of Carboxylic and Mineral Acid-Extraction By Amine-Based Extractants - Effects of pKa, Amine Basicity, and Diluent Properties. *Ind. Eng. Chem. Res.* **1995**, *34*, 1789–1798.

(21) Canari, R.; Eyal, A. M. Extraction of carboxylic acids by amine-based extractants: Apparent extractant basicity according to the pH of half-neutralization. *Ind. Eng. Chem. Res.* **2003**, *42*, 1285–1292.

(22) Canari, R.; Eyal, A. M. Effect of pH on dicarboxylic acids extraction by amine-based extractants. *Ind. Eng. Chem. Res.* **2003**, *42*, 1293–1300.

(23) Canari, R.; Eyal, A. M. Selectivity in monocarboxylic acids extraction from their mixture solutions using an amine-based extractant: Effect of pH. *Ind. Eng. Chem. Res.* **2003**, *42*, 1301–1307.

(24) Canari, R.; Eyal, A. M. Selectivity in the extraction of lactic, malic, glutaric, and maleic acids from their binary solutions using an amine-based extractant: Effect of pH. *Ind. Eng. Chem. Res.* **2003**, *42*, 1308–1314.

(25) Sabolová, E.; Schlosser, Š.; Marták, J. Liquid-liquid equilibria of butyric acid in water plus solvent systems with trioctylamine as extractant. *J. Chem. Eng. Data* **2001**, *46*, 735–745.

(26) Marták, J.; Schlosser, Š. L/L equilibria of dimethylcyclopropanecarboxylic acid in water - Solvent systems with trioctylamine as an extractant. *Chem. Pap.* **2000**, *54*, 413–422.

(27) Senol, A. Extraction equilibria of formic, levulinic and acetic acids using (Alamine336/diluent) and coventional solvent systems: modeling considerations. *J. Chem. Eng. Jpn.* **1999**, *32*, 717–737.

(28) Senol, A. Effect of diluent on amine extraction of acetic acid: Modeling considerations. *Ind. Eng. Chem. Res.* **2004**, *43*, 6496–6506.

(29) Marinova, M.; Albet, J. L.; Molinier, J.; Kyuchoukov, G. Specific influence of the modifier (1-decanol) on the extraction of tartaric acid by different extractants. *Ind. Eng. Chem. Res.* **2005**, *44*, 6534–6538.

(30) Kyuchoukov, G.; Labbaci, A.; Albet, J.; Molinier, J. Simultaneous influence of active and "inert" diluents on the extraction of lactic acid by means of tri-n-octylamine (TOA) and tri-iso-octylamine (TIOA). *Ind. Eng. Chem. Res.* **2006**, *45*, 503–510.

(31) Senol, A. Influence of diluent on amine extraction of pyruvic acid using Alamine system. *Chem. Eng. Process.* **2006**, *45*, 755–763.

(32) Wasewar, K. L.; Pangarkar, V. G. Intensification of propionic acid production by reactive extraction: Effect of diluents on equilibrium. *Chem. Biochem. Eng. Q.* **2006**, *20*, 325–331.

(33) Qin, W.; Li, Z. Y.; Dai, Y. Y. Extraction of monocarboxylic acids with trioctylamine: Equilibria and correlation of apparent reactive equilibrium constant. *Ind. Eng. Chem. Res.* **2003**, *42*, 6196–6204.

(34) Shan, X. C.; Qin, W.; Dai, Y. Y. Dependence of extraction equilibrium of monocarboxylic acid from aqueous solutions on the relative basicity of extractant. *Chem. Eng. Sci.* **2006**, *61*, 2574–2581.

(35) Juang, R. S.; Huang, W. T. Equilibrium Studies on the Extraction of Citric-Acid from Aqueous-Solutions with Tri-*N*-Octylamine. *J. Chem. Eng. Jpn.* **1994**, *27*, 498–504.

(36) Juang, R. S.; Huang, R. H. Equilibrium Studies on Reactive Extraction of Lactic-Acid with an Amine Extractant. *Chem. Eng. J.* **1997**, *65*, 47–53.

(37) Li, Z. Y.; Qin, W.; Wang, M.; Huang, Y.; Dai, Y. Y. Equilibrium of extraction of succinic, malic, maleic and fumaric acids with trioctylamine. *Chin. J. Chem. Eng.* **2002**, *10*, 281–285.

(38) Bízek, V.; Horaček, J.; Rericha, R.; Koušova, M. Amine Extraction of Hydroxycarboxylic Acids 0.1. Extraction of Citric-Acid with 1-Octanol *N*-Heptane Solutions of Trialkylamine. *Ind. Eng. Chem. Res.* **1992**, *31*, 1554–1562.

(39) Procházka, J.; Heyberger, A.; Bízek, V.; Koušová, M.; Volaufová, E. Amine Extraction of Hydroxycarboxylic Acids 2. Comparison of Equilibria for Lactic, Malic, and Citric Acids. *Ind. Eng. Chem. Res.* **1994**, *33*, 1565–1573.

(40) Vachtová, J.; Heyberger, A.; Mrnka, M.; Procházka, J. Extraction of sulfuric acid with trialkylamine in a mixed diluent. *Ind. Eng. Chem. Res.* **1999**, *38*, 2028–2035.

(41) Procházka, J.; Heyberger, A.; Volaufová, E. Sulfuric acid extraction with trialkylamine-effect of xylene and *n*-octanol as modifiers. *Ind. Eng. Chem. Res.* **2003**, *42*, 5305–5311.

(42) Schunk, A.; Maurer, G. Distribution of hydrochloric, nitric, and sulfuric acid between water and organic solutions of tri-*n*-octylamine Part II. Methylisobutylketone as organic solvent. *Fluid Phase Equilib.* **2003**, *211*, 189–209.

(43) Schunk, A.; Maurer, G. Distribution of hydrochloric, nitric, and sulfuric acids between water and organic solutions of tri-n-octylamine Part I. Toluene as organic solvent. *Fluid Phase Equilib.* **2003**, *207*, 1–21.

(44) Kirsch, T.; Maurer, G. Distribution of Oxalic-Acid Between Water and Organic Solutions of Tri-*N*-Octylamine. *Ind. Eng. Chem. Res.* **1996**, *35*, 1722–1735.

(45) Kirsch, T.; Ziegenfuss, H.; Maurer, G. Distribution of citric, acetic and oxalic acids between water and organic solutions of tri-*n*-octylamine. *Fluid Phase Equilib.* **1997**, *129*, 235–266.

(46) Schlosser, Š.; Kertész, R.; Marták, J. Recovery and separation of organic acids by membrane-based solvent extraction and pertraction: An overview with a case study on recovery of MPCA. *Sep. Purif. Technol.* **2005**, *41*, 237–266.

(47) Schlosser, Š. *Extractive Separations in Contactors with One and Two Immobilized L/L Interfaces: Applications and Perspectives. In Membrane Operations. Innovative Separations and Transformations*; Drioli, E., Giorno, L., Eds.; Wiley-VCH: Weinheim, 2009; pp 513−542.

(48) Blahušiak, M.; Schlosser, Š.; Marták, J. Simulation of a hybrid fermentation-separation process for production of butyric acid. *Chem. Pap.* **2010**, *64*, 213–222.

(49) Kubišová, Ľ.; Marták, J.; Schlosser, Š. *Competitive Transport of Mineral Acids in Pertraction and Membrane Based Solvent Extraction of Heterocyclic Carboxylic Acid*, Proceedings of 28th Conference of Slovak Society of Chemical Engineering, Tatranské Matliare, Slovakia, May 21−25, 2001; Markoš, J., Štefuca, V., Eds.; Slovak University of Technology: Tatranské Matliare, Slovakia, 2001; full text on CD ROM 12 p, printed abstracts p 196.

(50) Kubišová, Ľ.; Sabolová, E.; Schlosser, Š.; Marták, J.; Kertész, R. Membrane Based Solvent Extraction and Stripping of a Heterocyclic Carboxylic Acid in Hollow Fiber Contactors. *Desalination* **2002**, *148*, 205–211.

(51) Kotrlý, S.; Šucha, L. *Chemical equilibria in analytical chemistry* (in Czech); SNTL: Praha, 1988.

(52) Marták, J.; Rosenberg, M.; Schlosser, Š.; Krištofíková, Ľ. Toxicity of Organic-Solvents Used in-Situ in Microbial Fermentation. *Biotechnol. Tech.* **1995**, *9*, 247–252.

(53) Marták, J.; Sabolová, E.; Schlosser, Š.; Rosenberg, M.; Krištofíková, Ľ. Toxicity of organic solvents used in situ in fermentation of lactic acid by Rhizopus arrhizus. *Biotechnol. Technol.* **1997**, *11*, 71–75.

Received for review March 5, 2010. Accepted May 25, 2010. Support of the Slovak Grant Agency VEGA 1/0876/08 is acknowledged.

JE100207P