The Extraction of Water and Sulfuric Acid by Trilaurylamine Dissolved in Toluene. Batch and Emf Titration Studies at 298 K

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The extraction of sulfuric acid by long-chain amines has been subject to numerous studies, they are reviewed in Ref. 1. Most workers in the field have neglected the coextraction of water by sulfuric acid as well as the aggregation equilibria. Some disagreement exists between various studies. For that reason we have studied the extraction of sulfuric acid by trilaurylamine (TLA) dissolved in toluene at 25 °C using both the two-phase emf-titration method [2] controlled by computer [3] as well as batch experiments.[1] In the present paper a brief report is given of the results obtained.

Batch experiments. Both phases were analysed for acid by titration with alkali. Water in the organic phase was analysed using the Karl Fischer method. From the equilibrium concentration of sulfuric acid in water, the corresponding activities of water and acid were obtained from data by Giauque *et al.*[4]

Results. Fig. 1 gives a plot of $Z_{H_2SO_4}$ and Z_{H_2O} against $\log\{H^+\}^2\{SO_4^{2-}\}$. These quantities are defined by

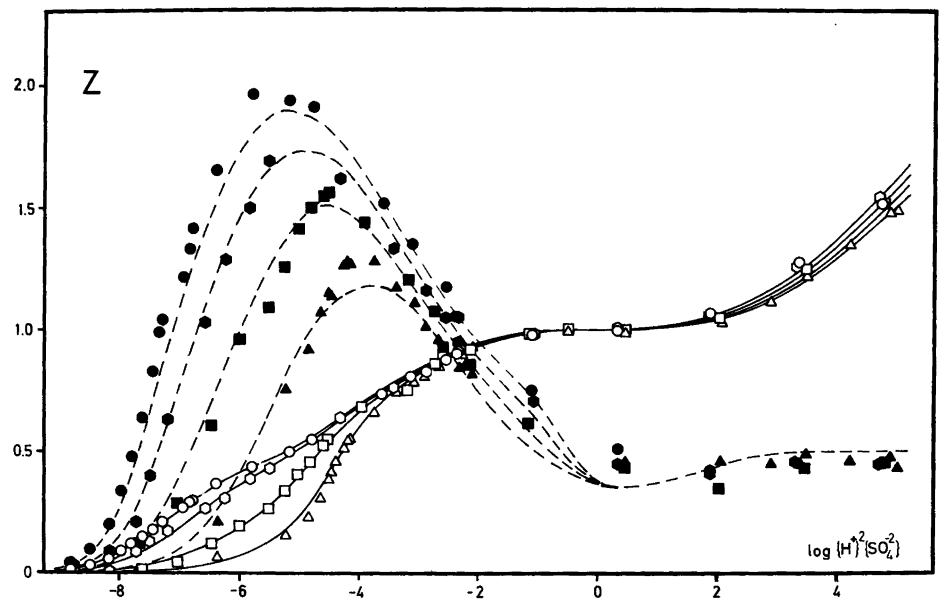

Fig. 1. $Z_{H_2SO_4}$ and Z_{H_2O} plotted against $\log\{H^+\}^2\{SO_4^{2-}\}$ for the range of sulfuric acid activity covered. △ ▲ $[TLA]_{tot}$=0.0100 M; □ ■ $[TLA]_{tot}$=0.0493 M. Benzene rings $[TLA]_{tot}$=0.100 M; ○ ● $[TLA]_{tot}$=0.1572 M. Open circles refer to H_2SO_4 the other to H_2O. The fulldrawn curves refer to H_2SO_4, the dashed refer to H_2O. The curves have been computed from the model in Table 1.

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Table 1. Constants K_{pqr} for reaction (2) in toluene at 298 K.

Species	$\log K_{pqr}$
$(TLA)_2(H_2SO_4)(H_2O)_2=(TLAH^+)_2SO_4^{2-}(H_2O)_2$	$\log K_{212}$ = 7.52±0.22
$(TLA)_4(H_2SO_4)_2(H_2O)_{10}=(TLAH^+)_4(SO_4^{2-})_2(H_2O)_{10}$	$\log K_{4210}$=16.89±0.19
$(TLA)_5(H_2SO_4)_4(H_2O)_6$	$\log K_{546}$ =27.88±0.20
$(TLA)_3(H_2SO_4)_3(H_2O)_=(TLAH^+HSO_4^-)_3(H_2O)$	$\log K_{331}$ =17.40±0.05
$(TLA)_2(H_2SO_4)_3(H_2O)$	$\log K_{231}$ = 7.43±0.17

$$Z_{H_2SO_4}=([H_2SO_4]_{org}-[H_2SO_4]_{dil})/[TLA]_{tot} \quad (1a)$$

$$Z_{H_2O}=([H_2O]_{org}-[H_2O]_{dil})/[TLA]_{tot} \quad (1b)$$

The amounts of water and acid extracted by the diluent have been obtained by separate studies. For amine concentrations have been used: 0.0100 M, 0.0493 M, 0.100 M and 0.1572 M in toluene.

The curves in Fig. 1 have been computed with the species and equilibrium constants given in Table 1. This model was arrived at by using the version ZEHTA of the computer program LETAGROP.[5]

The constants K_{pqr} given in Table 1 refer to the reaction

$$p\text{TLA(org)}+2qH^+ + qSO_4^{2-} + rH_2O \rightleftarrows (\text{TLA})_p(H_2SO_4)_q(H_2O)_r(\text{org}) \quad (2)$$

In Fig. 2 the fraction of amine present in each species, α_{pqr}, is plotted against $\log\{H^+\}^2\{SO_4^{2-}\}$ for $[TLA]_{tot}$=0.0493 M. The quantity α is given by

$$\alpha_{pqr}=p[(TLA_p(H_2SO_4)_q(H_2O)_r]/[TLA]_{tot}$$

Emf work. In order to find support for the existence of the species found at low acidities, an emf study was performed at 298 K using a computer controlled system with a HP-85A micro-computer. The ionic strength (I) was kept at 1.00 M (Na,H)SO_4. In Fig. 3 $Z_{H_2SO_4}$ is plotted against $\log[H_2SO_4]$ for the following amine concentrations: 0.0314 M, 0.0493 M, 0.1000 M and 0.1527 M in toluene. The curves have been computed with the species and equilibrium constants given in Table 2. The constants K_{pq} refer to the reaction

$$p\text{TLA(org)}+qH_2SO_4(aq) \rightleftarrows (\text{TLA})_p(H_2SO_4)_q(\text{org}) \quad (3)$$

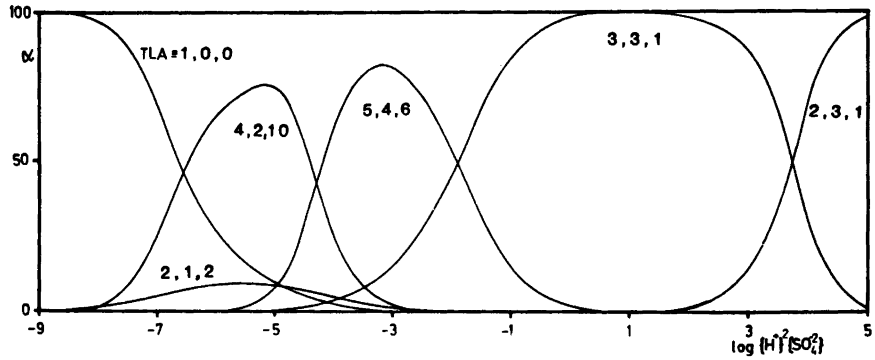

Fig. 2. The fraction of amine, α_{pqr}, present in each species plotted against $\log\{H^+\}^2\{SO_4^{2-}\}$ for $[TLA]_{tot}$=0.0493 M.

Table 2. Equilibrium constants for reaction (3) at 298 K and the ionic strength I=1.00 M (Na,H)SO_4.

Species	$\log K_{pq}$
$(TLAH^+)_2SO_4^{2-}$	$\log K_{21}$=1.9 ±0.3
$(TLAH^+)_4(SO_4^{2-})_2$	$\log K_{42}$=6.44±0.08

$[H_2SO_4]$ refers to total sulfate, *i.e.*

$$[H_2SO_4]=[HSO_4^-]+[SO_4^{2-}]$$

Since the water activity is kept constant by the ionic medium, no information about water in the species is obtained from the emf study. For that reason water is excluded from reaction (3).

From Table 2 a value of the dimerization constant of $(TLAH^+)_2SO_4^{2-}$ equal to $10^{2.6}$ is obtained. This value refers to the reaction

$$2(TLAH^+)_2SO_4^{2-}(H_2O)_2(org)+6H_2O(aq)\rightleftarrows(TLAH^+)_4(SO_4^{2-})_2(H_2O)_{10}(org) \quad (4)$$

According to reaction (4) water promotes aggregation. Similar results have been found for liquid cation exchangers of the sulfonic acid type.[6]

The importance of dimer formation is illustrated by Fig. 4 where the fractions of monomer and dimer are plotted against the total concentration of sulfuric acid in the organic phase for two concentrations of this acid in the aqueous phase A discussion of these results in relation to the literature is given in Ref. 1.

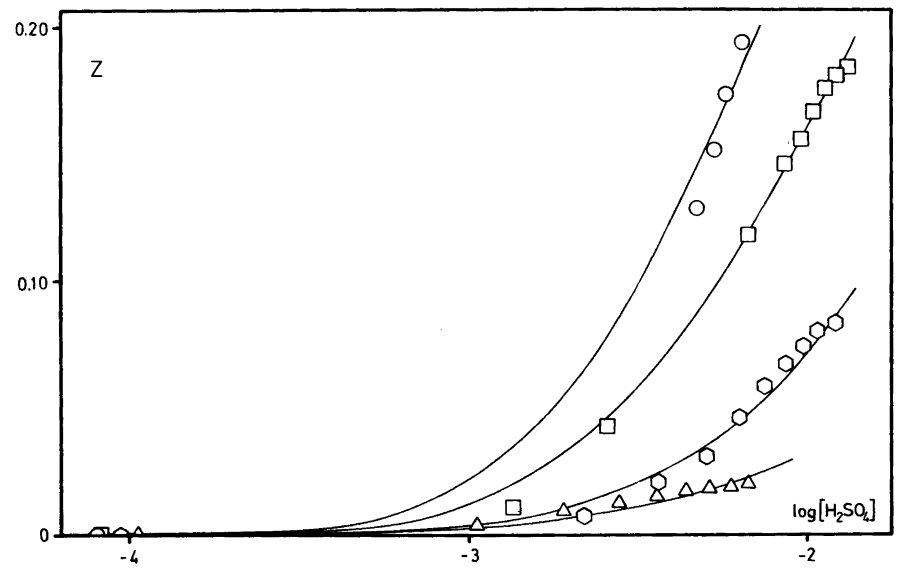

Fig. 3. $Z_{H_2SO_4}$ plotted against $\log[H_2SO_4]$ for the four amine concentrations studied. △ $[TLA]_{tot}$=0.0314 M. Benzene rings $[TLA]_{tot}$=0.0493 M; □ $[TLA]_{tot}$=0.1000 M; ○ $[TLA]_{tot}$=0.1572 M.

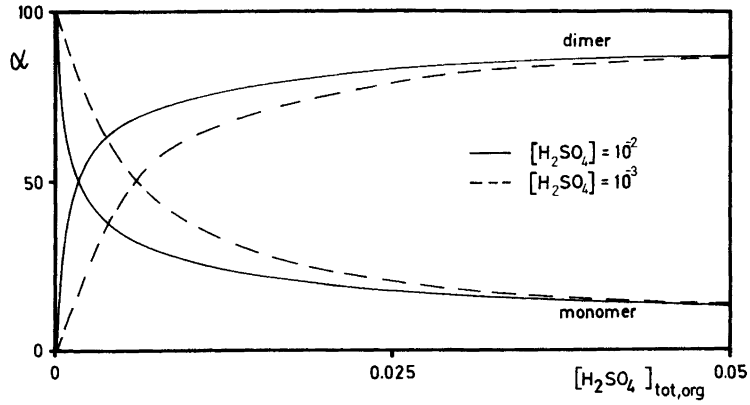

Fig. 4. The fractions of monomer and dimer plotted against $[H_2SO_4]_{tot,org}$ for two different concentrations of sulfuric acid in the aqueous phase: ——— $[H_2SO_4]_{aq}=1\cdot10^{-2}$ M; --------- $[H_2SO_4]_{aq}=1\cdot10^{-3}$ M.

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