THE DISTRIBUTION OF SULPHURIC ACID BETWEEN ISOAMYL ALCOHOL* AND WATER†

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Sulphuric acid is not extracted from water by ketones, ethers, or esters, but is by alcohols. A study has now been made of the distribution of the acid between isoamyl alcohol and water at high aqueous concentrations of the acid ($> 0 \cdot 10$M). The distribution of sulphuric acid should follow the form

$$(H_2SO_4)_A \overset{K_D}{\rightleftharpoons} (H_2SO_4)_O \tag{1}$$

where $(H_2SO_4)_A$ and $(H_2SO_4)_O$ are the undissociated acid in the aqueous and organic phases respectively.

K_D, the distribution constant or coefficient, is given by the expression

$$K_D = a(H_2SO_4)_O/a(H_2SO_4)_A \tag{2}$$

where a refers to activities.

Assuming that the activity coefficient of sulphuric acid in the organic phase is unity, the distribution can be represented by the expression

$$K' = [H_2SO_4]_O/a(H_2SO_4)_A \tag{3}$$

where $[H_2SO_4]_O$ is the molar concentration of sulphuric acid in the organic phase.

Table 1, p. 2387, shows values for the concentration of sulphuric acid in the organic phase for various activities of sulphuric acid in the aqueous phase.

Assuming that the extraction of sulphuric acid by isoamyl alcohol occurs by way of the undissociated acid molecule, it is necessary to relate the activity of the undissociated acid in the aqueous phase to the activity of dissociated acid in the aqueous phase. The concentration of undissociated acid in aqueous solution only becomes appreciable at very high concentrations, and hence the activity of the dissociated acid in the aqueous phase can be substituted by the activity of the total sulphuric acid.

$$a(H_2SO_4)_A = \frac{(\gamma_\pm^3 C_\pm^3)(H_2SO_4)_{A,\text{tot.}}}{K_1 K_2} \tag{4}$$

where K_1 and K_2 are the first and second ionization constants for sulphuric acid. $\gamma_\pm$ is the mean molal activity coefficient, and $C_\pm$ is the mean ionic molality.

The activity of undissociated acid in the aqueous phase is thus

$$a(H_2SO_4)_A = \frac{\text{activity of total sulphuric acid in aqueous phase}}{K_1 K_2} \tag{5}$$

Expression (3) becomes

$$K'' = \frac{K'}{K_1 K_2} = \frac{[H_2SO_4]_O}{a(H_2SO_4)_{A,\text{tot.}}} \tag{6}$$

A logarithmic plot of $[H_2SO_4]_O$ against $a(H_2SO_4)_{A,\text{tot.}}$ should give a straight line of slope unity. Such a plot is shown in Figure 1; a straight line is certainly obtained but the value for the slope is $0 \cdot 72$ instead of unity. The value for K'' obtained from Figure 1 is $7 \cdot 08 \times 10^{-1}$ (mole/l.)$^{-2}$.
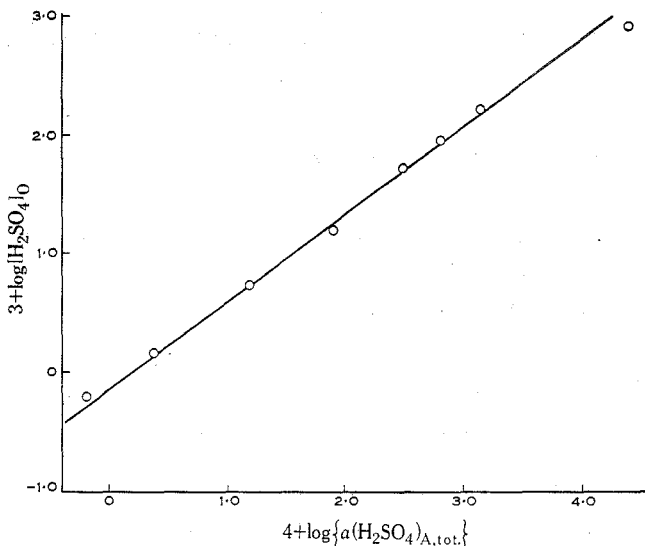
Fig. 1.—The distribution of sulphuric acid between water and isoamyl alcohol.

The low value for the slope must be due to the incorrect assumption that the activity coefficients of sulphuric acid solutions in isoamyl alcohol are unity.

Tuck[1] has obtained activity coefficients in the organic phase for the distribution of nitric acid between water and diethylene glycol dibutyl ether using the known value for the ionization constant for nitric acid. It was impossible to do this in the present work for the distribution of sulphuric acid between water and isoamyl alcohol because of the uncertainty of the first ionization constant for sulphuric acid.[2]

Diamond and Tuck[3] consider that the failure of sulphuric acid to extract into ketones, ethers, and esters, but its extraction by alcohols, illustrate the competition between water and the organic solvent for the acid. Sulphuric acid is known to have a strong primary hydration in aqueous solution arising from the presence of

[1] Tuck, D. G., *J. chem. Soc.*, 1957, 3202.
[2] Robinson, R. A., and Stokes, R. H., "Electrolyte Solutions." 2nd Edn, p. 384. (Butterworths: London 1959.)
[3] Diamond, R. M., and Tuck, D. G., *Prog. inorg. Chem.*, 1960, **2**, 155.

two oxy and two hydroxyl groups which can hydrogen bond water molecules very strongly. Extraction into alcohols is possible since such solvents can solvate the anion again by a hydrogen bonding mechanism. In non-hydroxylated solvents, however, there is no such competing hydrogen bonding reaction, and thus the sulphuric acid favours the aqueous phase. Tuck[1] has obtained considerable evidence that a hydrogen bonded complex is formed in the extraction of nitric acid by diethylene glycol dibutyl ether, and that the complex is hydrated.

TABLE 1

THE EXTRACTION OF SULPHURIC ACID BY ISOAMYL ALCOHOL

Equilibrium Aq. H_2SO_4 Molarity (M)	Equilibrium Aq. H_2SO_4 Molality C	Mean Molal Activity Coefficient* $\gamma_{\pm}$	$10^4 \times a(H_2SO_4)_{A,tot.}$	$10^3 \times$ Org. H_2SO_4 Molarity (M)
0·094	0·094	0·270	0·654	0·620
0·180	0·182	0·215	2·400	1·460
0·445	0·457	0·160	15·60	5·410
0·879	0·926	0·135	79·40	15·60
1·450	1·576	0·125	305·0	51·90
1·826	2·027	0·124	632·8	89·50
2·212	2·506	0·130	1383	160·6
3·662	4·464	0·190	24410	811·0

* Obtained from figures given in Harned, H. S., and Owen, B. B., "The Physical Chemistry of Electrolytic Solutions." 2nd Edn. (Reinhold: New York 1950.)

Experimental

Equal volumes of aqueous sulphuric acid solutions (0·1–0·4M) and isoamyl alcohol were equilibrated at 25°. The isoamyl alcohol had been saturated with water and the aqueous acid solutions with isoamyl alcohol prior to the extraction studies.

The isoamyl alcohol phases were analysed by potentiometric titration with aqueous alkali in ethanol/water mixtures. The aqueous phases were analysed by titration using phenolphthalein as indicator.

B.D.H. reagent grade isoamyl alcohol (b.p. 128–132°), specified to contain 3-methyl-butan-1-ol (b.p. 132·0°) with 15–30% of 2-methylbutan-1-ol (b.p. 128·0°), was fractionally distilled and the fraction boiling at 130–132° was collected. It was considered that this contained mostly 3-methylbutan-1-ol but certainly contained a small amount of 2-methylbutan-1-ol. In any event, it is expected that the two alcohols would have such similar extraction behaviour that the presence of a small amount of 2-methylbutan-1-ol in the 3-methylbutan-1-ol would not affect the results at all.

Acknowledgments