Supporting Information

Uptake and surface reaction of methanol by sulfuric acid solutions investigated by vibrational sum frequency generation and Raman spectroscopies

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Mass balance calculations for the methyl species in the H_2SO_4 solutions

The methyl species mass balance at equilibrium was calculated in the following manner. H_{ROH} is the acidity function[2] for the alcohol, and MHS is the protonated and unprotonated methyl sulfate species.

$[CH_3OH]_{initial} = [CH_3OH]_{eq} + [CH_3OH_2^+]_{eq} + [MHS]_{eq}$

$$\log\frac{[CH_3OH_2^+]}{[CH_3OH]} = -H_{ROH} + pK_{BH^+}$$

A value of $pK_{BH+} = -2.05$ was used.[1]

The values of H_{ROH} were determined from a plot of H_{ROH} vs. wt% sulfuric acid solution. The values were taken from reference 2. Over the wt% range of interest, the relationship between H_{ROH} and wt%

H_2SO_4 is approximately linear. Therefore, the data was fit using a linear regression.

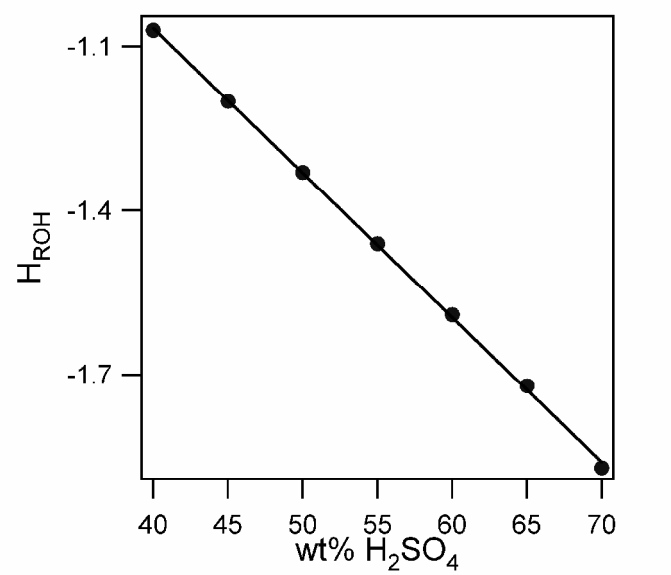

Figure S1. Plot of H_{ROH} values[2] as a function of wt% H_2SO_4.

The required values of H_{ROH} could then be calculated using the equation:

$$H_{ROH} = 0.0264 * (wt\%H_2SO_4) - 0.0093$$

The extent of MHS formation was calculated using the apparent equilibrium constant, K_{eq}.

$$K_{eq} = \frac{[MHS][H_2O]}{[H_2SO_4][CH_3OH]}$$

K_{eq} values were extrapolated from a plot of K_{eq} [3] vs wt% H_2SO_4.

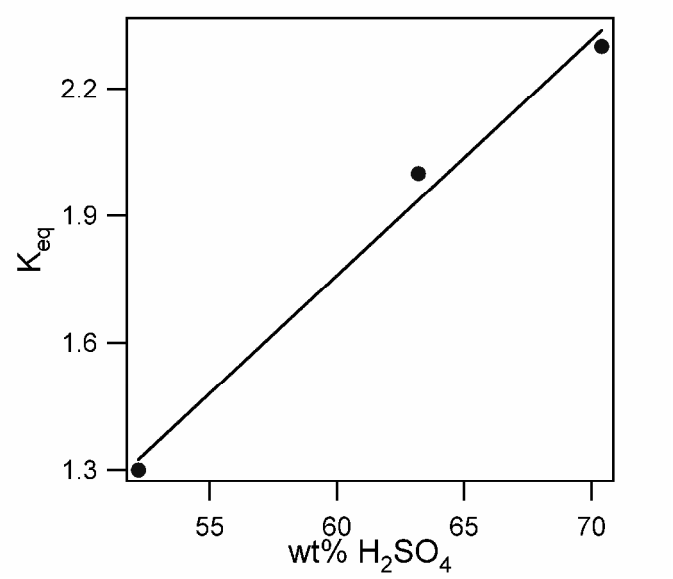

Figure S2. Plot of K_{eq} [3] as a function of wt% H_2SO_4.

Using the extrapolated values of K_{eq}, the extent of reaction was calculated for each H_2SO_4 solution.

$$K_{eq} = 0.0557x(wt\%H_2SO_4) - 1.5809$$

The percentages of CH_3OH, $CH_3OH_2^+$ and MHS were calculated and are shown in Table 2 of the main article. Using a value of pK_{BH^+} = -4.86,[4] the calculated equilibrium mass balance is shown in Table S1 below.

Table S1. Calculated equilibrium mass balance of the methyl species in 47.1 – 68.3 wt% H_2SO_4 solutions using pK_{BH+} = -4.86.

wt % H_2SO_4	% CH_3OH	% $CH_3OH_2^+$	% MHS
47.1	86.9	0.02	13.0
51.4	83.2	0.03	16.7
54.5	80.7	0.03	19.3
58.4	77.7	0.04	22.3
61.5	75.4	0.05	24.6
64.7	73.1	0.05	26.8
68.3	70.8	0.07	29.2

Comparing the values in Table S1 and Table 2 from the article show that the value of pK_{BH^+} chosen will greatly affect the predicted mass balance.

Another study investigated the esterification of ethanol in 60+ wt% H_2SO_4.[5] Using the % esterification determined in reference 5 we recalculated the mass balance.

Table S2. Mass balance determined using % conversion found in reference 5.

wt % H_2SO_4	% CH_3OH	% $CH_3OH_2^+$	% MHS
61.5	60.5	23.9	15.6
64.7	56.0	27.1	16.9
68.3	51.1	30.8	18.0

Comparing the values from Table 2 and Table S2, shows that the predicted mass balance using the different values for the % conversion to MHS remain similar within a few percent.

References

(1) Perdoncin, G.; Scorrano, G. *J. Am. Chem. Soc.* **1977**, *99*, 6983-6986.

(2) Lee, D. G.; Cameron, R. *J. Am. Chem. Soc* **1971**, *93*, 4724-4728.

(3) Deno, N. C.; Newman, M. S. *J. Am. Chem. Soc.* **1950**, *72*, 3852-3856.

(4) Weston Jr, R. E.; Ehrenson, S.; Heinzinger, K. *J. Am. Chem. Soc.* **1967**, *89*, 481 - 486.

(5) Clark, D. J.; Williams, G. *J. Chem. Soc.* **1957**, 4218-4221.