Supporting Information V110

Effective diffusion coefficients for methanol in sulfuric acid solutions measured by Raman spectroscopy.

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To determine the concentration of CH_3OH species in both H_2O and the H_2SO_4 solutions, calibration curves were prepared. Peak areas were determined and plotted as a function of the initial mole % CH_3OH added to the solutions with the recognition that the solutions can contain up to three methyl species, CH_3OH, $CH_3OH_2^+$, and MHS (see Table 2 of the main paper for the expected distributions). The mixtures were stirred to ensure complete reaction before the Raman spectra were taken. Raman spectra were obtained using 150 mW from a 785 nm continuous wave laser (Raman Systems Inc.) The backscattered light was collected by a fiber optic probe (InPhotonics) coupled to the entrance slit of a 500 mm monochromator (Acton Research, SpectraPro 500i), using a 600 groove/mm grating blazed at 1 μm. The slit width was set at 50 μm and the bandpass was 4 cm^{-1} for the H_2SO_4 solution experiments. Spectra were acquired as the average of three thirty-second spectra.

To minimize the error in the measured peak area, the most intense peak with the least solvent interference was used for analysis. The diffusion of CH_3OH into water was monitored using the C-O symmetric stretch present at 1020 cm^{-1}.The diffusion of CH_3OH into 39.2 to 79.3 wt% H_2SO_4 solutions was monitored using the CH_3 stretching region (2800 and 3200 cm^{-1}) (due to overlapping of H_2SO_4 vibrational modes with the CO stretch of reacted CH_3OH). The diffusion of CH_3OH into 96.5 wt% H_2SO_4 was monitored using the O-S-O symmetric stretch present at 800 cm^{-1} since the reaction to MHS is both rapid and essentially complete.

The CH_3OH-water calibration curve was multiplied by a factor of 2 to account for the difference in slit width used between the calibration curve collection (50 μm) and the diffusion experiments (100 μm) after testing was completed on a methanol standard confirming that the signal does change accordingly in this slit width range.

Table S1. The intercepts, *a*, and slopes, *b*, determined using weighted linear regressions of the calibration data presented in Figs. S1 and S2. The variables *x* and *y* are the mol% CH_3OH and the peak area ratio, respectively.

$y=a+b\times x$	H_2O	39.2 wt% H_2SO_4	61.6 wt% H_2SO_4	79.7 wt% H_2SO_4	96.5 wt% H_2SO_4
	νC-O	νCH_3-ss	νCH_3-ss	νCH_3-ss	νO-S-O
		νCH_3-as	νCH_3-as	νCH_3-as	
a	78 ± 150	418 ± 180	905 ± 236	-140 ± 203	1091 ± 741
		682 ± 391	1995 ± 272	20 ± 189	
b	6443 ± 49	1442 ± 34	942 ± 31	484 ± 27	9916 ± 137
		2469 ± 71	1726 ± 37	898 ± 24	

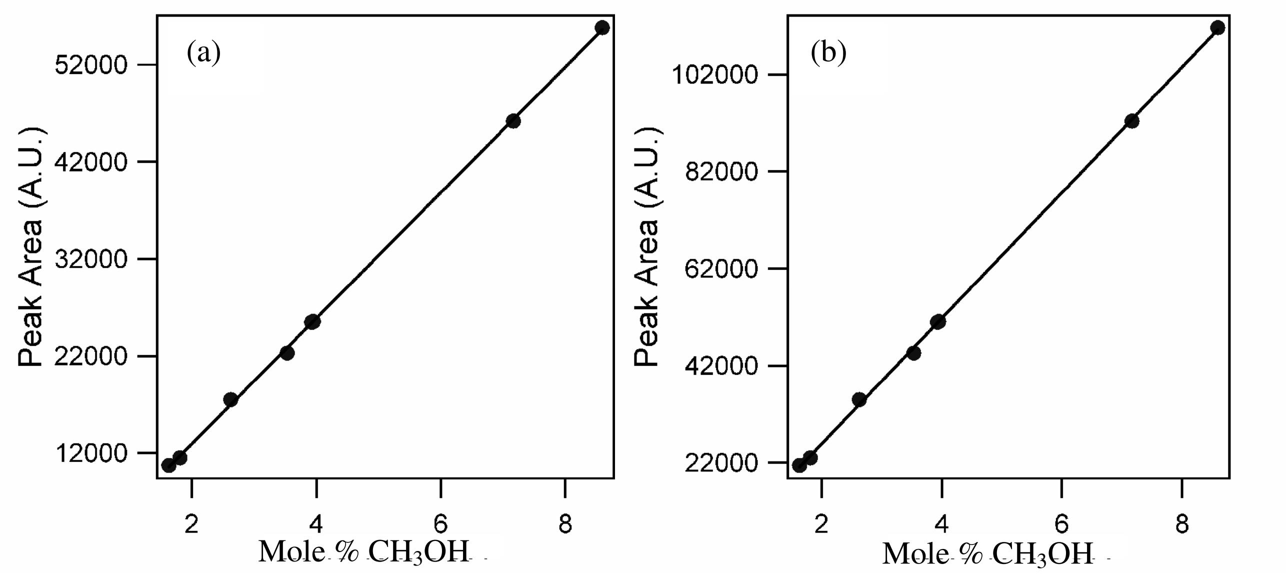

Figure S1. Calibration curves for CH_3OH-H_2O using the νCO-ss. In (a) the original curve is shown. In (b) the peak areas were multiplied by a factor of 2 to account for the increase in slit width to 100 μm in the diffusion experiments from 50 μm in the calibration experiments.

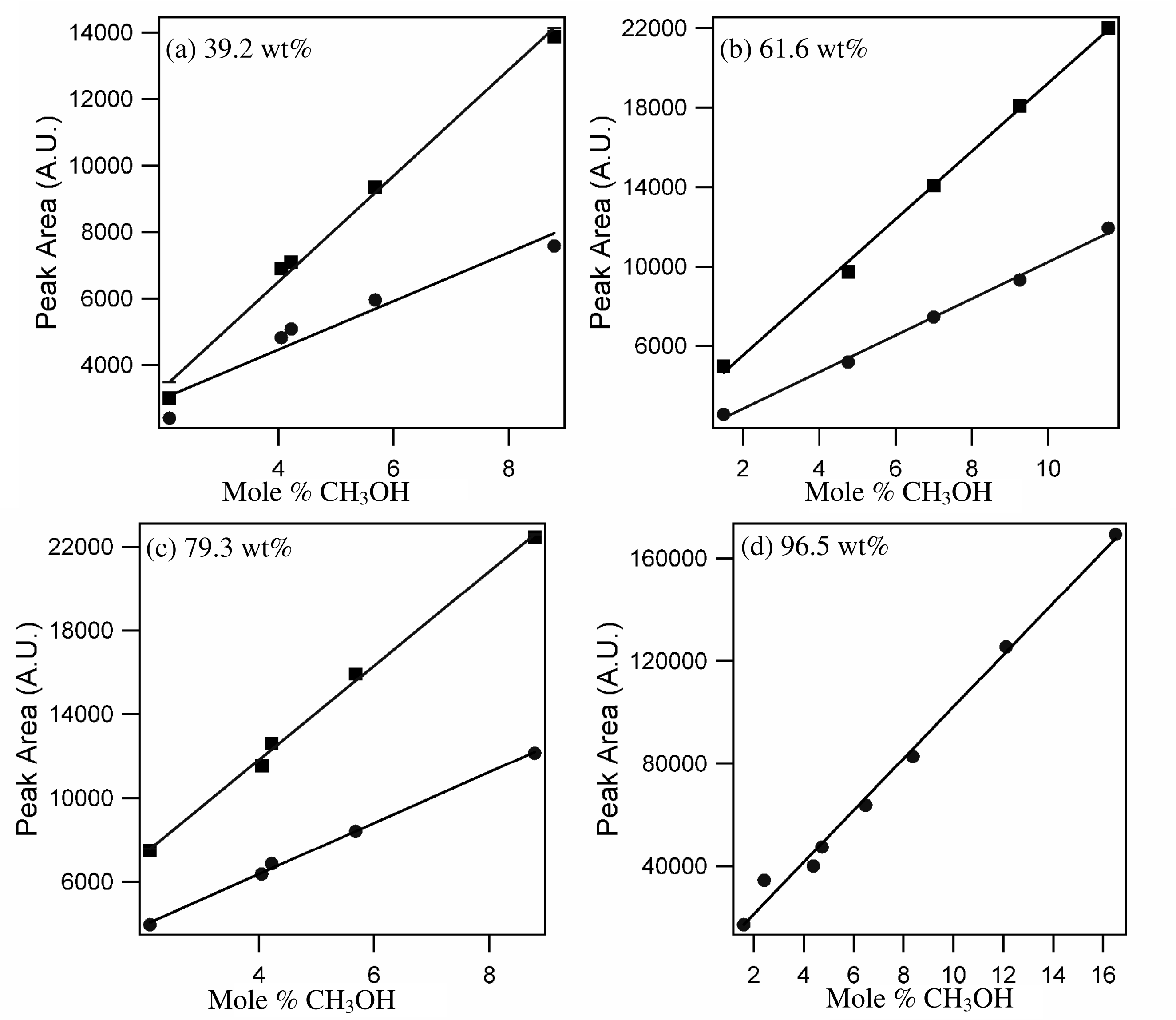

Figure S2. Calibration curves for the CH_3OH-H_2SO_4 solutions. The x-axes are labeled as the mole % CH_3OH initially added to the solution. However, in (a)-(c) CH_3OH, $CH_3OH_2^+$, and MHS are present at the time the spectra were collected and in (d) ~ all the CH_3OH is converted to MHS. In (a)-(c) the circles (●) represent the νCH_3-ss fit and the squares (■) represent the νCH_3-as fit. In (d) the νOSO stretch was used.