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Surfactant Control of Gas Uptake into Supercooled Sulfuric Acid

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Surfactant molecules on sulfuric acid droplets can potentially alter the rates of heterogeneous reactions in the upper troposphere and lower stratosphere by blocking gas molecules from entering the acid. We perform molecular beam experiments with deuterated sulfuric acid solutions (56-68 wt percent D2SO4/D2O at 213 K) containing the surfactants 1-butanol or 1-hexanol, which segregate to the surface to form a nearly complete monolayer. A beam of a protic gas HX (X = Cl or Br) is directed at a continuously renewed film of deuterated sulfuric acid in vacuum and the fraction of thermalized HX molecules that undergo HX-DX exchange is measured. This HX-DX exchange fraction is equal to the HX entry probability into the acid. Our results appear to contradict the notion that surfactants generally impede gas transport. The presence of surface butanol does not alter the rate of D2O evaporation from the liquid surface, whereas surface hexanol slightly impedes D2O transport. The most striking result is that surface butanol molecules increase the HX-DX exchange fraction, implying that HX dissociates more readily at the interface when butanol is present. This enhancement may be caused by dilution of the acid near the surface by segregated butanol molecules, which provide additional OD groups for protonation by HX.