Surface Tensions and Surface Segregation of *n*-Butanol in Sulfuric Acid[†]

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The surface tensions of *n*-butanol in water and 20, 38, 58, and 72 wt % H₂SO₄ were recorded at 294 K in order to compare the segregation of the alcohol at the water–air and acid–air interfaces. The surface tensions of each solution decrease steadily as butanol is added, yielding nearly constant surface concentrations of butyl-containing species between 0.2 and 0.4 M butanol. These surface concentrations range from ~3.5 × 10¹⁴ cm⁻² (~73% of maximum packing) at the surface of water to ~2.0 × 10¹⁴ cm⁻² (~41% of maximum packing) at the surface of 72 wt % H₂SO₄. The reduction in surface coverage with increasing acidity may be driven by butanol protonation, changes in solvent size, and the conversion of butanol to C₄H₉OSO₃H and C₄H₉OSO₃⁻. The alcohol surface coverage on 72 wt % acid is nearly doubled by cooling the acid from 294 to 208 K or by substituting *n*-hexanol for *n*-butanol.
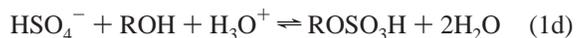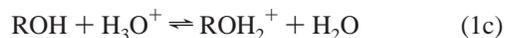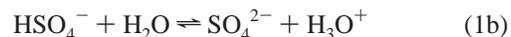
Introduction

Many organic molecules containing polar and nonpolar groups segregate to the surface of water,[1,2] often forming compact hydrocarbon films that impede gas transport through the interface.[3] The composition and packing of these films may differ significantly in environments where the water is acidic.[4] Water droplets in the upper troposphere and lower stratosphere, for example, often contain sulfuric acid at concentrations of 40–80 wt % H₂SO₄ and temperatures of 210–240 K.[5,6] These acid aerosols may be exposed to organic surfactants[7,8] that segregate to the surface of the particles, potentially altering the rates of gas dissolution and reaction.[5,9] In particular, the evaporation of water from sulfuric acid aerosols and the reaction of these aerosol particles with ammonia are impeded by monolayer and multilayer organic films.[10–13]

As a further step toward investigating organic surfactants in sulfuric acid,[14] we have measured the surface tensions of *n*-butanol in 0–72 wt % H₂SO₄, where the extent of surface segregation can be determined from the Gibbs adsorption equation. Although butanol molecules are not long enough to form an effective surfactant barrier,[3] their high solubility and absence of aggregation[15] make the alcohol useful for exploring how protonation and reaction in sulfuric acid control the formation of a surface hydrocarbon layer. We hope to use these surface tension measurements to determine coverages of longer chain alcohols on sulfuric acid for molecular beam studies of reactive gases scattering from the surfactant-coated acid.

The extent of alcohol segregation will be governed in part by the bulk and surface properties of sulfuric acid. For the four acid concentrations employed here, 20, 38, 58, and 72 wt % H₂SO₄, the bulk composition is dominated by H₂O, HSO₄⁻, and H₃O⁺, with less than 3% SO₄²⁻ and very little molecular H₂SO₄.[16] Over the 0–72 wt % acid range, the H⁺ activity increases by a factor of 10¹¹, reflecting the enormous protonating power of the acid.[16] At 294 K, the surface tensions of the H₂SO₄–H₂O mixtures rise from 73 dyn cm⁻¹ for pure water to 76 dyn cm⁻¹ for 45 wt % H₂SO₄ and then drop to 74 dyn cm⁻¹

for 72 wt % H₂SO₄.[17] A Gibbs adsorption analysis based on water vapor pressures indicates that H₂SO₄ is depleted at the surface by less than 1 × 10¹³ cm⁻² below ~50 wt % acid (a 1% reduction) and is in excess by no more than 5 × 10¹² cm⁻² above this concentration.[18] Auger electron spectroscopy confirms that the atom composition of the surface and bulk are nearly equal.[19] In addition, sum frequency studies suggest that the surface species are either neutral H₂O and H₂SO₄ or closely spaced ion pairs.[18,20]

Alcohols are readily protonated in sulfuric acid and may react further in solution to produce alkyl hydrogen sulfate, ROSO₃H, and dialkyl sulfate, (RO)₂SO₂, according to the equilibria:[21–24]

$$H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+ \tag{1a}$$

$$HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+ \tag{1b}$$

$$ROH + H_3O^+ \rightleftharpoons ROH_2^+ + H_2O \tag{1c}$$

$$HSO_4^- + ROH + H_3O^+ \rightleftharpoons ROSO_3H + 2H_2O \tag{1d}$$

$$ROSO_3H + H_2O \rightleftharpoons ROSO_3^- + H_3O^+ \tag{1e}$$

$$ROSO_3H + ROH \rightleftharpoons (RO)_2SO_2 + H_2O \tag{1f}$$

^{13}C NMR studies of methanol, ethanol, and *n*-propanol in sulfuric acid indicate that protonation (step 1c) generates ROH₂⁺ equal in concentration to ROH in 76–78 wt % H₂SO₄.[25,26] Iraci, Essin, and Golden found that both protonation and low temperatures enhance the reversible solvation of methanol under conditions where steps d and f are expected to be slow.[27] In particular, they showed that the solubility of methanol rises from 10⁵ to 10⁸ M/atm as the acid concentration is increased from 45 to 70 wt % H₂SO₄ and the temperature is lowered from 231 to 197 K. Kane and Leu further showed that CH₃OSO₃H (step d) could be detected in the vapor over 40–85 wt % H₂SO₄ at 295 K,[28] and they postulated that the formation of (CH₃O)₂SO₂ (step f) becomes important in 75–85 wt % acid.[29] In addition, ethyl hydrogen sulfate has been monitored by ¹H NMR and by oxidative titration in >50 wt % H₂SO₄; roughly equal fractions

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of $CH_3CH_2OSO_3H$ and CH_3CH_2OH are observed in the 75 wt % acid at 298 K.[23,30] The sulfuric acid esters are expected to be strong acids and should be partially dissociated into $ROSO_3^-$ and H_3O^+ in sulfuric acid−water mixtures (step e).[31] The rates of methanol, ethanol, and butanol esterification are reported to occur over times of ∼1−10 h in 70 wt % acid at room temperature and over longer times at lower acid concentrations and temperatures (see ref 29 for measurements of higher methanol reaction rates).[21,23,27]

On the basis of these studies, we expect that butanol will undergo protonation and esterification in concentrated sulfuric acid solutions and, therefore, that butyl species segregating to the surface of the acid will be a mixture of C_4H_9OH, $C_4H_9OH_2^+$, $C_4H_9OSO_3H$, $C_4H_9OSO_3^-$, and possibly $(C_4H_9O)_2SO_2$. The surface tension measurements do not readily distinguish among these species, but the experiments below indicate that the total surface concentration of butyl species decreases steadily with increasing acidity. This reduction in surface coverage may be caused by the conversion of C_4H_9OH to $C_4H_9OSO_3H$ at higher acidities, by changes in solvent size, and by charge repulsion among the ionic species $C_4H_9OH_2^+$ or $C_4H_9OSO_3^-$.

Experimental Section

The Wilhelmy plate method[32] was used to measure the surface tensions γ of 0−0.4 M *n*-butanol in 0, 20, 38, 58, and 72 wt % H_2SO_4 at 294 K and of 0−0.07 M *n*-hexanol in 72 wt % acid. The downward force on a 3.36 cm perimeter platinum plate was measured using a balance with a precision of 0.1 mg (0.05%). The contact angle was observed to be nearly zero for each solution. All measurements were made in a closed environment purged with N_2 to minimize water uptake. The solutions were prepared from doubly distilled sulfuric acid (GFS Chemicals), Millipore water, and ACS or spectroscopic grade butanol and hexanol (HPLC grade butanol was found to contain surface-active impurities). Typically, 50 μL of *n*-butanol were stirred into a 50 mL acid sample contained in a 5.5 cm diam by 4.5 cm tall Teflon flask. After each addition, the Pt plate was submersed in the acid and stabilized for five minutes before three consecutive measurements were recorded over a fifteen minute period. Typically, 7 h were required to make a complete set of surface tension measurements. The maximum spread in values was usually ±0.3 dyn cm^{-1}. We also found that solutions prepared by adding butanol in one aliquot rather than through successive addition yielded the same surface tension values. Last, the surface tension of a 0.2 M butanol/72 wt % acid solution did not change by more than ±0.3 dyn cm^{-1} during a 4 h time period, indicating that further esterification did not measurably alter the surface tension over this time. The miscibility of *n*-butanol in water is limited to 1.0 M, but it appears to be miscible in 72 wt % H_2SO_4 in all proportions.[21,33]

We also recorded the surface tension of *n*-butanol in 72 wt % H_2SO_4 cooled to 208 K with a dry-ice−ethanol bath. The viscosity of the supercooled acid at 208 K is 8000 cP,[34] making it difficult to submerse and stabilize the Pt plate. Stable readings were obtained instead by submersing a 0.083 cm diam Pt wire, which has a perimeter 13 times smaller than the plate.[35] These measurements were recorded by adding butanol to the cold acid over a 7 h time period, during which significant esterification may not have occurred.[27]

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Figure 1 displays the surface tensions of 0−0.4 M butanol in water and 38, 58, and 72 wt % sulfuric acid. The values
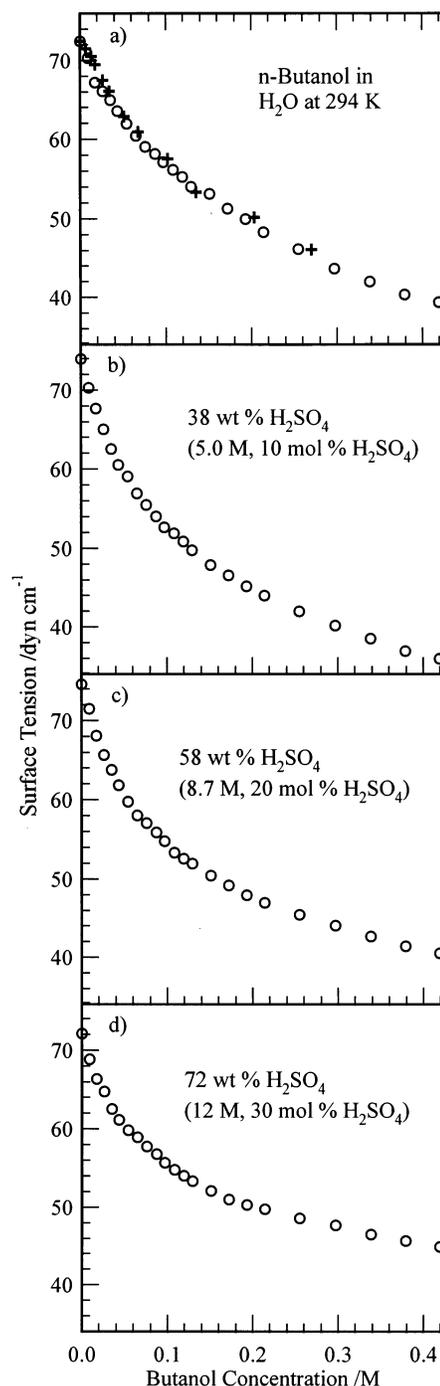
Figure 1. Surface tensions of butanol-sulfuric acid solutions at 294 K as a function of sulfuric acid and *n*-butanol concentrations. The mol % H_2SO_4 values in each panel are the stoichiometric (undissociated) concentrations. The + symbols in panel a are data from Posner et al.[36]

decrease steadily as butanol is added to each solution, but they remain above the pure butanol surface tension of 25 dyn cm^{-1}. The minimum 39 dyn cm^{-1} surface tension for 0.4 M butanol in pure water drops to 36 dyn cm^{-1} for 38 wt % H_2SO_4 and then rises to 45 dyn cm^{-1} for the 72 wt % acid. The surface tensions of the butanol−water solutions in the top panel are nearly identical to earlier measurements by Posner et al.[36] (+ symbols); Harkins and Wampler;[37] Addison;[38] Dynarowicz;[39] and Donaldson and Anderson.[2]

The surface excess of butyl-containing species in each solution is calculated from the Gibbs adsorption equation at constant temperature, $-d\gamma = \sum_{i=2}^{n} \Gamma_i^{(H_2O)} d\mu_i$, where μ_i is the

chemical potential of component i and $\Gamma_i^{(H_2O)}$ is the surface excess of component i relative to the surface excess of component 1, chosen to be H_2O.[32,40] The $\Gamma_i^{(H_2O)}$ are equal to a weighted difference between absolute surface excesses, $\Gamma_i^{(H_2O)} = \Gamma_i - \Gamma_{H_2O}(c_i/c_{H_2O})$, where c_i and c_{H_2O} are liquid-phase concentrations and the gas-phase concentrations are neglected.[40] The relative excesses $\Gamma_i^{(H_2O)}$ are independent of the position of the dividing surface between gas and solution.

The $C_4H_9OH-H_2O-H_2SO_4$ system potentially contains at least 10 different species: H_2O, H_2SO_4, HSO_4^-, SO_4^{2-}, H_3O^+, ROH, ROH_2^+, $ROSO_3H$, $ROSO_3^-$, and $(RO)_2SO_2$, where R = C_4H_9. As described in the Appendix, these species are related by eqs 1a−f and by overall charge balance, which allow −dγ to be rewritten in terms of dμ_{ROH}, d$\mu_{H_2SO_4}$, and dμ_{H_2O}. We estimate that variations in $\mu_{H_2SO_4}$ and μ_{H_2O} contribute less than 10% to the change in surface tension over the 0−0.4 M butanol range, permitting the relative surface excess to be computed approximately from

$$\Gamma_{butyl}^{(H_2O)} \approx \frac{-a_{butanol}}{RT}\left(\frac{\partial\gamma}{\partial a_{butanol}}\right)_T \qquad (2)$$

where $a_{butanol}$ is the activity of butanol, the partial derivative refers only to constant temperature, and the relative surface excess of all butyl-containing species is (see the Appendix)

$$\Gamma_{butyl}^{(H_2O)} \equiv \Gamma_{ROH}^{(H_2O)} + \Gamma_{ROH_2^+}^{(H_2O)} + \Gamma_{ROSO_3H}^{(H_2O)} + \Gamma_{ROSO_3^-}^{(H_2O)} + 2\Gamma_{(RO)_2SO_2}^{(H_2O)} \qquad (3)$$

Equation 2 may be simplified by determining the relation between $a_{butanol}$ and the formal butanol concentration $c_{butanol}$. Harkins and Wampler showed that Henry's Law is valid to within 5% for 0−0.4 M butanol in water (0−0.007 butanol mole fraction).[37,41] In addition, capacitance manometer and mass spectroscopic measurements of a degassed sample of *n*-butanol in 72 wt % H_2SO_4 at 296 K indicate that the butanol vapor pressure $P_{butanol}$ increases linearly from 0 to 0.4 M alcohol. The absolute pressure is 0.1 ± 0.05 Torr over the 0.4 M solution. The activity $a_{butanol} = P_{butanol}/P_{butanol}^0$ should therefore also vary linearly with $c_{butanol}$ in concentrated sulfuric acid, enabling the surface tension data to be analyzed using

$$\Gamma_{butyl}^{(H_2O)} \approx \frac{-c_{butanol}}{RT}\left(\frac{\partial\gamma}{\partial c_{butanol}}\right)_T \qquad (4)$$

On the basis of the 0.1 Torr increase in pressure over the 0.4 M butanol range, the effective solubility of butanol in 72 wt % H_2SO_4 is roughly 3×10^3 M/atm at 296 K, which is 20 times greater than the 150 M/atm value for butanol in water.[42]

Figure 2 shows the surface excess $\Gamma_{butyl}^{(H_2O)}$ at each acid concentration, calculated by approximating the derivative in eq 4 by a finite difference. In each panel, the surface excess rises sharply to $2-4 \times 10^{14}$ cm^{-2} as the butanol concentration is increased to 0.2 M and then varies only weakly from 0.2 to 0.4 M butanol. The error bars in panel d represent 90% confidence intervals for nine measurements and are close to ±0.3 × 10^{14} cm^{-2}; the fluctuations in $\Gamma_{butyl}^{(H_2O)}$ below 0.2 M butanol arise from small changes in the slope in Figure 1d and are likely due to errors in measurement.

We can interpret the data further by assuming that the segregated butyl species lie solely at the outermost layer of the solution and that the acid below this layer has the same composition as the bulk solution (see the Appendix).[43] At low bulk concentrations of butanol, the total surface coverage of
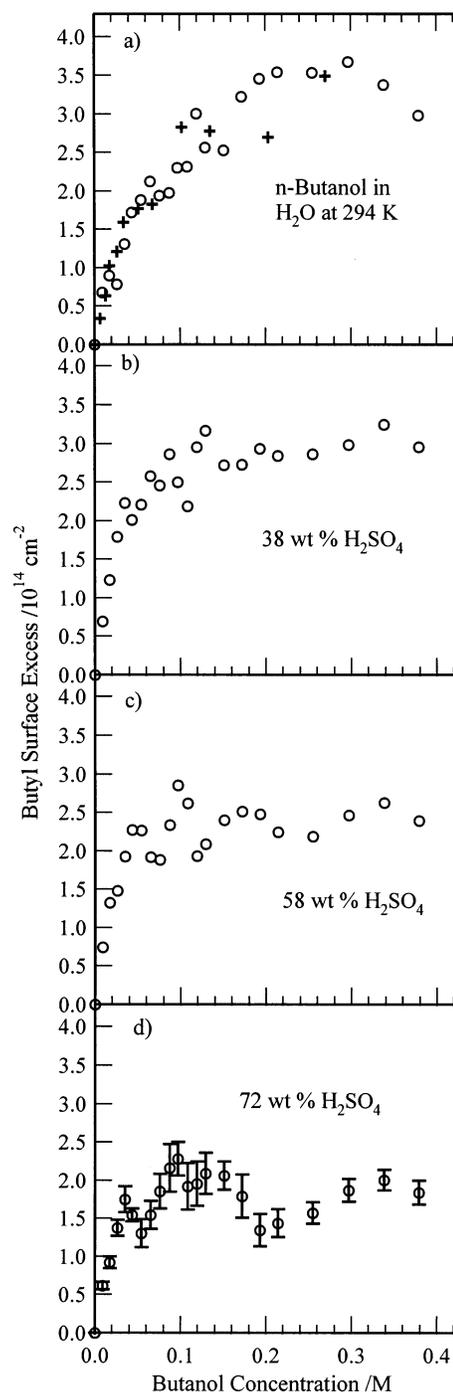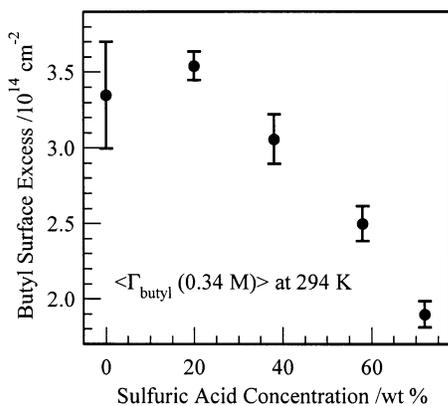

Figure 2. Butyl surface excess $\Gamma_{butyl}^{(H_2O)} \approx -(c_{butanol}/RT)(\Delta\gamma/\Delta c_{butanol})_T$ as a function of sulfuric acid and *n*-butanol concentrations. The + symbols in panel a are the surface excesses calculated from the Posner et al. data in Figure 1a.[36]

butyl species, n_{butyl}^{surf}, is then equal to the sum of the relative surface excess $\Gamma_{butyl}^{(H_2O)}$, and the number of butyl species per unit area, n_{butyl}^{2D}, in a slice through the bulk. n_{butyl}^{2D} is given by

$$n_{butyl}^{2D} \approx \frac{c_{butanol}}{A_{water}c_{water} + A_{acid}c_{acid}} \qquad (5)$$

where $A_{water} \approx 1 \times 10^{-15}$ cm^2 is the approximate area of H_2O and H_3O^+, $A_{acid} \approx 2 \times 10^{-15}$ cm^2 is the approximate area of H_2SO_4, HSO_4^-, and SO_4^{2-}, and c_{water} and c_{acid} are the formal molar concentrations of water and acid in the bulk solution.

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Figure 3. Average butyl surface excess at 294 K as a function of sulfuric acid concentration (including a value for 20 wt % H_2SO_4). The average was calculated from the last three points in each panel in Figure 2, corresponding to *n*-butanol concentrations of 0.30, 0.34, and 0.38 M. The total surface concentrations of butyl-containing species are 2% to 4% higher than the average surface excesses.

For 0.4 M butanol (0.007 mole fraction), n_{butyl}^{2D} varies from 7 to 8×10^{12} cm^{-2} for pure water and 72 wt % H_2SO_4, respectively. These values yield $n_{butyl}^{surf} \approx 1.02\ \Gamma_{butyl}^{(H_2O)}$ for water to ≈ 1.04 $\Gamma_{butyl}^{(H_2O)}$ for 72 wt % H_2SO_4, indicating that the total surface concentration of butyl-containing species is just slightly higher than the relative surface excess in Figure 2.

Figure 3 summarizes the main result: the average surface excess between 0.3 and 0.4 M butanol, $\langle\Gamma_{butyl}^{(H_2O)}\rangle$, drops steadily from ∼3.4 × 10^{14} to ∼1.9 × 10^{14} cm^{-2} as the acid concentration increases from 0 to 72 wt % H_2SO_4. The value for butanol in pure water is close to the 3.5 × 10^{14} cm^{-2} excess measured by Harkins and Wampler at 0.4 M[37,39] and corresponds to an average surface area per butanol molecule of 29 Å^2 (from $\langle n_{butyl}^{surf}\rangle^{-1} \approx [1.02\langle\Gamma_{butyl}^{(H_2O)}\rangle)]^{-1}$). This area is 38% greater than the close-packed value of 21 Å^2 for long chain alcohols,[1] indicating that butanol molecules segregating from a 0.4 M water solution do not cover the surface in tightly packed, vertically oriented chains.[44] The butyl surface concentration in 72 wt % acid corresponds to an average surface area of 51 Å^2, or 75% more than the area occupied by butanol on the surface of pure water. This area is sufficient for a butanol molecule to adopt a wide range of orientations, including ones parallel to the surface, where it would cover approximately 35 Å^2.[45]

Figures 4 and 5 illustrate how changes in temperature and chain length alter the alcohol surface coverage. Figure 4a compares the surface tensions of butanol in 72 wt % H_2SO_4 at 294 and 208 K, measured by using the Pt plate and Pt wire, respectively. The surface tension drops faster at 208 K than at 294 K, but the data is noisier because of the smaller mass changes associated with the Pt wire. The surface excess in Figure 4b is 50−100% higher at 208 K than at 294 K at concentrations beyond 0.15 M butanol, corresponding to surface densities of 3−4 × 10^{14} cm^{-2}. The effect of adding two CH_2 groups to butanol is shown in Figure 5, which compares *n*-butanol and *n*-hexanol in 72 wt % H_2SO_4 at 294 K. The surface tension decreases more sharply for the longer chain alcohol, yielding a surface excess of ∼3 × 10^{14} cm^{-2} at 0.06 M hexanol, or 50% higher than for butanol.

Discussion

The chief observation is shown in Figure 3: the surface coverage of butyl species, $\langle n_{butyl}^{surf}\rangle \approx (1.02-1.04)\langle\Gamma_{butyl}^{(H_2O)}\rangle$, decreases from 3.5 × 10^{14} cm^{-2} to 2.0 × 10^{14} cm^{-2} as the acidity
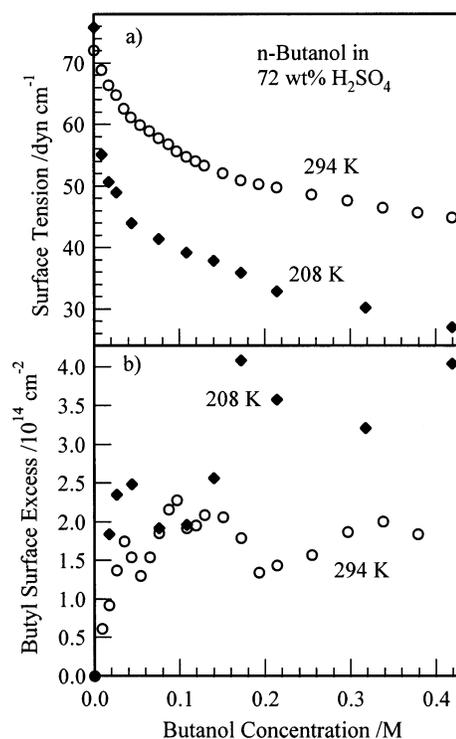
Figure 4. Surface tension (a) and surface excess (b) of *n*-butanol in 72 wt % H_2SO_4 at 294 K (○) and 208 K (◆) as a function of butanol concentration.
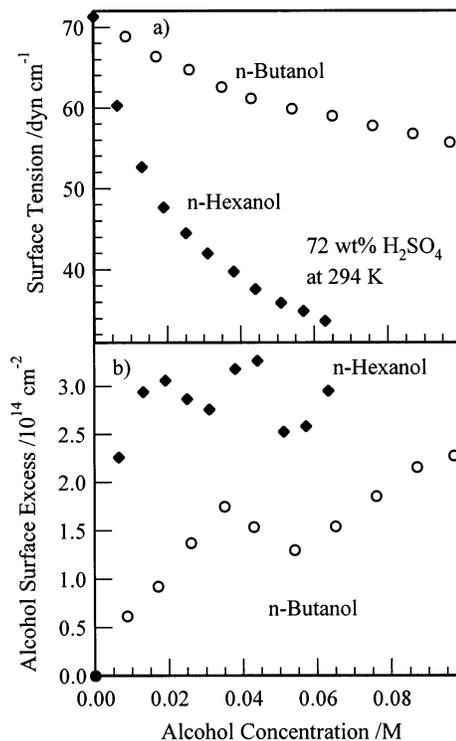
Figure 5. Surface tension (a) and surface excess (b) of *n*-butanol (○) and *n*-hexanol (◆) in 72 wt % H_2SO_4 at 294 K as a function of alcohol concentration.

of the 0.3−0.4 M butanol solutions increases from 0 to 72 wt % H_2SO_4 at 294 K. This 43% decline in surface coverage implies that alcohols at the surfaces of sulfuric acid solutions are not likely to provide more compact barriers than on pure water at the same temperature and bulk alcohol concentration. A similar conclusion was reached by Rubel for solid hexadecanol monolayers on 73 and 95 wt % phosphoric acid, based

on measured water uptake probabilities of 1×10^{-4} and 4×10^{-4}, respectively.[4] The 4-fold higher water uptake rate for the more acidic subphase was attributed to an unspecified ionization of the OH headgroup, which leads to a loss of cohesion among the hexadecanol molecules.

The addition of sulfuric acid to water most likely suppresses the surface segregation of butanol through a similar ionization mechanism that includes protonation of the OH group and conversion of some butanol to ionic or neutral butyl hydrogen sulfate. Changes in solvent size and the increased solubility of butanol in more acidic solutions may also play a role. In particular, the formation of ROH_2^+, $ROSO_3H$, and $ROSO_3^-$ makes *n*-butanol 20 times more soluble in 72 wt % H_2SO_4 than in water. The surface tension data, however, does not immediately indicate that this greater solubility drives butyl species from the surface to positions deeper in the bulk. Figure 2 shows that $\Gamma_{butyl}^{(H_2O)}$ increases linearly in the low concentration region of 0–0.04 M butanol, with slopes $\Gamma_{butyl}^{(H_2O)}/c_{butanol}$ close to 8×10^{-6} cm^{-2}/cm^{-3} in each panel. The slopes are not statistically different in 0, 20, 38, 58, and 72 wt % H_2SO_4, implying that the surface segregation of butyl species at low surface coverages (less than 1.5×10^{14} cm^{-2}) does not vary with acidity as strongly as does the limiting surface coverage above 0.2 M butanol. This observation supports the idea that interactions between butyl species at high surface coverages, including charge repulsion[1,4,46] among neighboring ROH_2^+ or $ROSO_3^-$ species, inhibit close packing at the surface. At the submonolayer concentrations shown in Figure 3, the segregated butyl species will also occasionally be separated by solvent molecules. The substitution of H_2O by molecular or dissociated H_2SO_4 between the chains should increase the spacing from roughly 3 to 4.5 Å,[47] thereby expanding the film in regions where the solvent has not been squeezed out.

The addition of sulfuric acid to water may also increase the effective surface area of a butanol molecule as some ROH and ROH_2^+ species are converted into $ROSO_3H$ or $ROSO_3^-$. However, the minimum cross-sectional area of an $-OSO_3H$ group is only ~20 Å^2,[47] implying that neutral $ROSO_3H$ molecules should be compressible to areas smaller than the 51 Å^2 observed in Figure 3 for 72 wt % H_2SO_4. Figures 4 and 5 demonstrate that changes in temperature and chain length do reduce the occupied surface area: the alcohol monolayer can be made 50–100% more compact by cooling the 72 wt % acid from 294 to 208 K or by substituting *n*-hexanol for *n*-butanol and thereby increasing the attractive forces between the chains, each in parallel with trends observed for alcohol segregation on the surface of pure water.[38,48,49] These trends suggest that alcohols much longer than butanol may segregate densely enough onto the surface of supercooled sulfuric acid aerosols to impede gas transport significantly, just as observed on concentrated phosphoric acid.[4] This hypothesis will be tested by determining the segregation of long chain alcohols in 72 wt % H_2SO_4 at 294 and 208 K and by measuring the uptake rates[13] as a function of chain length.

Appendix: The Gibbs Equation for Butanol Segregation in Sulfuric Acid

Butyl Surface Excess. The equation relating the surface tension γ to the relative surface excesses $\Gamma_i^{(H_2O)}$ at fixed temperature, $-d\gamma = \sum_{i=2}^{n} \Gamma_i^{(H_2O)} d\mu_i$, can be simplified by imposing relations among the chemical potentials μ_i. The ROH–H_2O–H_2SO_4 system (R = C_4H_9) consists of potentially 10 species (ROH, H_2O, H_2SO_4, HSO_4^-, SO_4^{2-}, H_3O^+, ROH_2^+, $ROSO_3H$, $ROSO_3^-$, and $(RO)_2SO_2$). The Gibbs equation for this system is (dropping the H_2O superscripts on $\Gamma_i^{(H_2O)}$)

$$-d\gamma = \Gamma_{H_3O^+} d\mu_{H_3O^+} + \Gamma_{H_2SO_4} d\mu_{H_2SO_4} + \Gamma_{HSO_4^-} d\mu_{HSO_4^-} +$$
$$\Gamma_{SO_4^{2-}} d\mu_{SO_4^{2-}} + \Gamma_{ROH} d\mu_{ROH} + \Gamma_{ROH_2^+} d\mu_{ROH_2^+} +$$
$$\Gamma_{ROSO_3H} d\mu_{ROSO_3H} + \Gamma_{ROSO_3^-} d\mu_{ROSO_3^-} + \Gamma_{(RO)_2SO_2} d\mu_{(RO)_2SO_2}$$
(A.1)

The relative surface excess of species i can be obtained from $\Gamma_i = -(\partial\gamma/\partial\mu_i)_{T,\mu_j(j \neq i,H_2O)}$ if the chemical potentials of the other species could be fixed. We control only the temperature and initial concentration of sulfuric acid, and thus the μ_j may vary as the alcohol is added. Equation A.1 can still by simplified by relating the chemical potentials through eqs 1a–f and by imposing electrical neutrality, $\Gamma_{H_3O^+} + \Gamma_{ROH_2^+} = \Gamma_{HSO_4^-} + \Gamma_{ROSO_3^-} + 2\Gamma_{SO_4^{2-}}$. These conditions allow eq A.1 to be recast in terms of $d\mu_{ROH}$, $d\mu_{H_2SO_4}$, and $d\mu_{H_2O}$ as

$$-(\partial\gamma/\partial\mu_{ROH})_T = \Gamma_{butyl} + [\Gamma_{HSO_4^-} + 2\Gamma_{SO_4^{2-}} - \Gamma_{ROSO_3H} - $$
$$\Gamma_{ROH_2^+} - 2\Gamma_{(RO)_2SO_2}] (\partial\mu_{H_2O}/\partial\mu_{ROH})_T + [\Gamma_{H_2SO_4} + \Gamma_{HSO_4^-} +$$
$$\Gamma_{SO_4^{2-}} + \Gamma_{ROSO_3H} + \Gamma_{ROSO_3^-} + \Gamma_{(RO)_2SO_2}] (\partial\mu_{H_2SO_4}/\partial\mu_{ROH})_T$$
(A.2)

Equation A.2 demonstrates that the change in surface tension depends not only on Γ_{butyl}, the sum of the relative surface excesses of all butyl containing species (eq 3), but also on changes in the chemical potentials of H_2SO_4 and H_2O with added butanol. The change in μ_{H_2O} has been measured for the addition of *n*-butanol to pure water[37] and of 2-butanol to 0.1 M Na_2SO_4.[37] In both cases, $(\partial\mu_{H_2O}/\partial\mu_{ROH})_T$ is smaller than 0.005 over the 0.4 M butanol range. The effect of added butanol on the chemical potentials of H_2O and H_2SO_4 in 72 wt % H_2SO_4 is more difficult to assess. Studies of the dissolution of *tert*-butyl alcohol in 0–55 wt % H_2SO_4 at 298 K indicate that 0.4 M butanol does not alter the Hammett acidity function H_0 by more than 0.1 units, implying that the activity of H_3O^+ is relatively unaffected.[50] One indirect method for estimating $(\partial\mu_{H_2SO_4}/\partial\mu_{ROH})_T$ is to assume that the addition of butanol is equivalent to the addition of water, according to the formal reaction $HSO_4^- + ROH \leftrightarrow ROSO_3^- + H_2O$, and to assume that $ROSO_3^-$ behaves like $HOSO_3^-$.[21] A 0.4 M butanol solution in 72 wt % H_2SO_4 would then be equivalent to pure 71.7 wt % H_2SO_4. Thermodynamic calculations[16] indicate that this dilution lowers $P_{H_2SO_4}$ from 4.5×10^{-9} to 4.0×10^{-9} Torr and raises P_{H_2O} from 0.57 to 0.60 Torr, yielding $(\Delta\mu_{H_2SO_4}/\Delta\mu_{ROH})_T$ of -0.06 and $(\Delta\mu_{H_2O}/\Delta\mu_{ROH})_T$ of $+0.03$. Equation A.2 reduces approximately to $-(\partial\gamma/\partial\ln c_{ROH})_T \approx \Gamma_{butyl} - (^1/_{11})[(^2/_3)\Gamma_{H_2SO_4} + (1/3)\Gamma_{HSO_4^-} + \Gamma_{ROSO_3H} + (^2/_3)\Gamma_{ROSO_3^-} + (^1/_3)\Gamma_{ROH_2^+} - (^4/_3)\Gamma_{(RO)_2SO_2}]$. The term in brackets is smaller than Γ_{butyl} due to partial cancellation of the excess of butyl species and the deficit of sulfuric acid species (dibutyl sulfate should be present in

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only very small amounts). The coefficient of $^1/_{11}$ further limits the correction term to no more than 9% of Γ_{butyl}.

Butyl Surface Concentration. As shown in ref 40, the relative surface excess $\Gamma_i^{(\text{H}_2\text{O})}$ for a multicomponent, gas–liquid system can be expressed approximately as $n_i - n_{\text{H}_2\text{O}}(c_i/c_{\text{H}_2\text{O}})$, where c_i is the liquid-phase concentration of species i and n_i is the total number of species i in solution per unit area of surface, integrated from above the gas–liquid interface to a cutoff position deep within the bulk. For the special case in which the excesses and deficits are limited to the outermost layer of the solution, this cutoff position can be placed just below the outer monolayer and n_i becomes the surface concentration of species i, n_i^{surf}. The expression for $\Gamma_{\text{butyl}}^{(\text{H}_2\text{O})}$ can then be combined with the constraint $n_{\text{butyl}}^{\text{surf}}A_{\text{butyl}} + n_{\text{water}}^{\text{surf}}A_{\text{water}} + n_{\text{acid}}^{\text{surf}}A_{\text{acid}} = 1$, where A_i is the surface area per molecule. We also assume that $n_{\text{water}}^{\text{surf}}/n_{\text{acid}}^{\text{surf}}$ equals $c_{\text{water}}/c_{\text{acid}}$ (which holds for sulfuric acid, where there is little surface segregation[18,19]), and we set $-(\partial\gamma/\partial\mu_{\text{ROH}})_T = \Gamma_{\text{butyl}}^{(\text{H}_2\text{O})}$ in eq A.2. In the limit of low bulk butanol concentration, the total surface concentration of butyl species is given by $n_{\text{butyl}}^{\text{surf}} \approx \Gamma_{\text{butyl}}^{(\text{H}_2\text{O})} + n_{\text{butyl}}^{\text{2D}}$, where $\Gamma_{\text{butyl}}^{(\text{H}_2\text{O})}$ and $n_{\text{butyl}}^{\text{2D}}$ are determined from eqs 4 and 5, respectively. The second term contributes only 2–4% to the sum.

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