Surface Tension of Solid-Liquid Slurries

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Introduction

The effect of solid particles on the surface tension between a liquid and a gas was experimentally observed. Two solid oxides were used, iron and silicon, in three size ranges averaging 2.5, 49 and 98 μm, up to a solid loading of 45 wt. %. Two liquids were studied, water, which wetted the two oxides, and an organic liquid, which did not. Over this range of parameters the surface tension of the liquid was essentially unaffected by the addition of solid particles.

The objective of this work was to experimentally determine the possible effect of solid particles, at the gas-liquid interface, on the surface tension between a liquid and a gas.

A knowledge of surface tension is required to design or model various equipment including boiling heat transfer and mass transfer devices. In some applications, e.g., biotechnology, and coal and heterogeneous catalytic processing equipment, knowledge of gas-liquid surface tension in the presence of finely divided solid particles (slurries) is needed. Kelkar et al. (1984) reported surface tension for a three-phase system, but these were actually gas-liquid measurements, the solid particles having settled. No published articles on the effect of added solids on gas-liquid surface tension were found.

The immediate motivation for studying the effect of solid particles addition on gas-liquid surface tension was to better predict the hydrodynamic behavior of a gas-liquid-solid bubble column. For example, studying a gas-liquid system, Hikita and Kikukawa (1974) found the surface tension to have a sizable effect on gas holdup:

$$\epsilon = k\sigma^{-2/3} \tag{1}$$

According to Eq. 1, if the solid particles decreased the surface tension to one-half its liquid value, the gas holdup would be increased 1.59 times.

From a theoretical standpoint, one would expect the slurry and liquid surface tensions to be similar. Surface tension is a measure of the entropy state of the liquid molecules at the gas-liquid interface relative to the bulk liquid. Since it is a molecular effect, only when the solid size is of the order of the liquid molecules would the added solid particles be expected to affect the surface tension. However, solid particles with a much larger diameter can cause an increase or decrease in surface tension. For example, if a surface-active agent present in the liquid is adsorbed onto the solid, then the slurry surface tension would in most cases be greater than before the solid particles were added to the liquid. Conversely, if upon addition the solid released ions to the liquid, then the slurry surface tension would in most cases be less than that of the original liquid. It thus was of interest to see if the particle size range was small enough to affect the surface tension, or if any of the above-mentioned effects were present in these systems.

System Studied

Iron and silicon oxide were used as the solid particles, in three size ranges 0.5–5, 45–53, and 90–106 μm, up to a solid loading of 45 wt. %. The smallest size iron oxide was reddish brown hematite, Fe_2O_3. The larger two sizes were black magnetite, Fe_3O_4. Two liquids were studied, tap water, which wetted the two oxides, and isoparaffin, a C_9 to C_{11} branched isomer organic liquid, which did not wet the solid particles. The choice of surface tension samples and the motivation for this study was from a large-scale fluid dynamic modeling project that used these solids and liquids. The physical properties of the two liquids and three solid types are listed in Table 1.

Experimental

Because the solid particles needed to be kept in suspension, most of the available methods for measuring surface tension were unsuitable. The maximum bubble pressure technique described by Sugden (1922) was employed. This involved pressing a gas bubble into a liquid or slurry out of two capillary tubes of different radii, Figure 1. Pressure is exerted to overcome both the surface tension and fluid static head forces according to the equation, for each tube,

$$P_i = 2\sigma/r_i + \rho_m g h \tag{2}$$

where r_i is the radius of curvature at the base of the bubble in tube i, and P_i is the maximum pressure observed just prior to bubble disengagement. By locating both capillary tube nozzles at the same height, the static head terms for the two tubes are

Table 1. Physical Properties of Liquids and Solids

Compound	Temp. °C	Surface Tension N/m	Viscosity kg/m s	Density g/cm³
Liquid				
Water	20	72.7×10^{-3}	1.00×10^{-3}	1.00
Isoparaffin	20	22×10^{-3}	1.20×10^{-3}	0.74
Solid Oxide				
Iron, hematite	20	—	—	4.9
Iron, magnetite	20	—	—	5.2
Silicon (quartz)	20	—	—	2.4

equal and cancel out when Eq. 2 is subtracted from itself, yielding:

$$P_1 - P_2 = \Delta P = 2\sigma[(1/r_1) - (1/r_2)] \qquad (3)$$

Solving for the surface tension,

$$\sigma = \Delta P/(2[(1/r_1) - (1/r_2)]) \qquad (4)$$

Sugden's method required a correction to the tube radius to obtain the correct bubble radius. However, the use of two calibrating liquids instead of one, in this case isopropyl alcohol and distilled water, bypassed the need to either know or correct for the bubble or tube radius. Thus any potential inaccuracy caused by this bubble radius correction is eliminated.

The use of two calibration liquids, A and B, also enabled the two tube heights, h_1 and h_2, to be properly adjusted. One tube height was varied until the quantity

$$h_1 - h_2 = (\sigma_A \Delta P_B - \sigma_B \Delta P_A)/[(\sigma_A \rho_B - \sigma_B \rho_A)g] = 0 \qquad (5)$$

Once the tube heights were adjusted to be at the same height, a unique ΔP could be associated with each value of the surface tension. Subtracting and then dividing Eq. 4 by itself for each calibration standard yielded:

$$\sigma = \sigma_A(\Delta P - \Delta P_B)/\Delta P_A + \sigma_B \qquad (6)$$

Equation 6 gives a linear relationship between ΔP and surface tension. Since experimental uncertainties, such as the shape of the bubble with increasing surface tension, may contribute to nonlinearies in Eq. 6, it is most accurate for the surface tension of one of the calibration standards to be as close to the sample as possible.

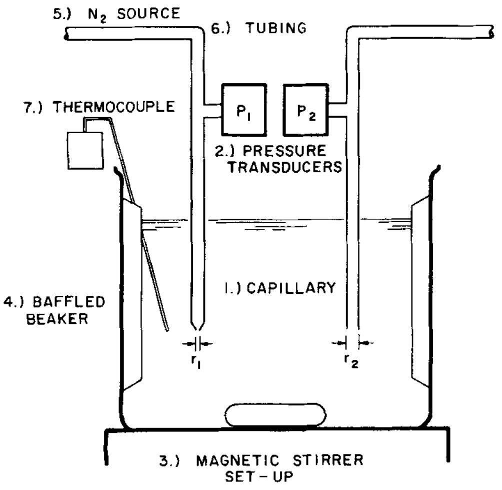

Figure 1. Experimental apparatus.

The maximum-bubble-pressure approach using two calibration standards offered several advantages for measuring slurry surface tensions. It was unnecessary to know the slurry density, which for the 100 μm particles was a function of height, or the static fluid height above the bubbling nozzle, which was difficult to measure in the opaque, agitated slurry system. It also was unnecessary to know the tube or bubble radius; all that was necessary for measuring the surface tension was the pressure difference between the two tubes. This was obtained by graphically averaging the maximum pressure reading for successive bubbles from both the 4.0 mm and 0.5 mm tubes, and then taking the difference of the two averages.

Another advantage of this method was that dynamic surface tensions could potentially be obtained. By varying the bubbling rate from the two tubes from 1 s/bubble to 30 s/bubble a surface-active, rate-limiting effect could potentially be observed, although none were.

The method used to obtain solid particle suspension was one drawback in this experiment. The larger particle slurries were stirred to keep the particles in suspension. The stirring caused shearing of the bubbles at the nozzle. Fortunately the stirring only increased the apparent surface tension by 1% and 5–10% for the water and organic systems, respectively. Even this small effect was accounted for by dividing, at the same stirrer speed, the apparent surface tension rise in the slurry samples by the apparent surface tension rise in the same liquid without solids present.

Each liquid measurement was replicated four times. Each liquid and slurry measurement was taken at four stirrer speed settings, 0, 7, 8, and 9. At zero, the stirrer was off. Nine was about the maximum possible stirring speed. Depending on agitation speed, the absolute surface tension measurements were repeatable to within 0.1 to 0.5 × 10^{-3} Nm^{-1}.

Results and Discussion

The results of the slurry surface tension measurements at the highest agitation speed are summarized in Figure 2. The results for both liquids are shown. Each point represents a different solid size and type (except for the 2.5 μm silicon oxide, which was measured at both 16 and 27 wt. %). Virtually no difference in surface tension is observed. As the solid weight loading was increased from zero to 45 wt. %, the surface tension remained constant within an experimental scatter of 3%.

The data at the highest stirrer speed (having the most uniform slurry density) were correlated to see if any variables were statistically significant. Solid loading, solid size, and temperature were analyzed for each liquid to yield:

$$\sigma_{\text{iso}} = (22.99 - 0.078 \text{ wt. \%}) \times 10^{-3}\,\text{Nm}^{-1} \qquad R^2 = 0.47 \qquad (7)$$

$$\sigma_{\text{H}_2\text{O}} = (73.37 + 0.074 \text{ wt. \%} - 0.028 \text{ SS}) \times 10^{-3}\,\text{Nm}^{-1} \qquad R^2 = 0.64 \qquad (8)$$

The low R^2 in these regressions, is an indication of the suitability of using the average value as a good estimate of surface tension.

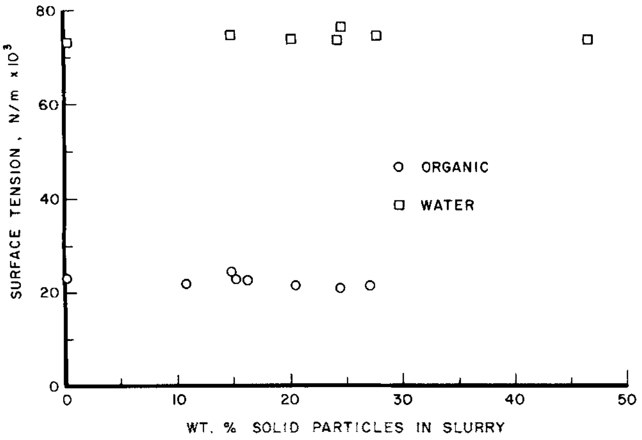

Figure 2. Slurry surface tension as a function of solid particle weight loading.

Although slight and of little practical significance, percent weight loading was found to be statistically significant for both isoparaffin and water. For the organic, nonwetting liquid, increasing the solid loading from 0 to 20 wt. % slurry **decreased** surface tension 1.4, from 22.8 to 21.4 $\mathrm{Nm}^{-1} \times 10^{-3}$. Conversely, for tap water, a wetting liquid, increasing the solid loading from 0 to a 20 wt. % slurry **increased** surface tension 1.9, from 72.8 to 74.7 dynes/cm. The high surface tension for tap water was unexpected. For the water system, an even smaller, although statistically significant effect of particle size on surface tension was observed. As particle size increased, the difference between liquid and slurry surface tension decreased. The temperature was over too narrow a range to be considered significant in the analysis, although surface tension is known to be a function of temperature.

For water, it was observed that any variable that increased the liquid-solid interfacial area increased the surface tension, even if only slightly. The converse was true for the organic liquid. Thus, the effects of particle size and solid loading on surface tension were in opposite directions for the two liquids. This may be due to the differing effects that a wetted and nonwetted solid have on the curvature of the bubble. Alternatively, it may be an artifact of this experiment. In either case, the effect is small.

The slurry surface tension at zero stirrer speed was, in reality, a liquid surface tension measurement. All solid particles had settled, and the bubbling capillary tubes could be clearly seen. Had a surface-active agent been released or adsorbed by the solid particles, then this measurement would have differed from the liquid-only measurement. The surface tensions agreed, indicating that the solid particles were not interacting with any surface active agent.

In conclusion, while some statistically significant effects were observed, for practical purposes the surface tension of the liquid was unaffected by the addition of solid particles.

Acknowledgment

We wish to thank F. J. Micale for his suggestions during the writing of this note.

Notation

g = gravitational constant = 980 g · s^{-2}
h = tube immersion depth, cm
k = constant
P = pressure, bar
r = radius of capillary tube, cm
SS = solid size, μm

Greek letters

ϵ = gas holdup, vol. %
ρ = density, g · cm^{-3}
σ = surface tension, $\mathrm{Nm}^{-1} \times 10^{-3}$

Subscripts

A = standard A
B = standard B
H_2O = water
iso = isoparaffin
1 = capillary tube 1
2 = capillary tube 2

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