regions are covered in the figure: a region where the thermistor does not have a hot spot, a transition region, and a region where a hot spot is present. It was possible to obtain data before and after a hot spot had formed for only a few runs, since the transition region was very unstable.

Static voltage characteristic curves were taken between the maximum and minimum limits of cooling for the thickest thermistor and are shown in Figure 2. These clearly show the thermistor breakdown to occur earlier with greater cooling. At the low power dissipation level needed when the thermistor is suspended in still air at 25°C., the thermistor does not break down and no temperature irregularities are observed.

In conclusion the study showed that the temperature of a thermistor will depend on the heat flux as well as its resistance when the thermistor is used as a power source and that care must be exercised when using thermistors as power sources of known surface temperature. If they are used at high heat fluxes, a nonuniform radial temperature will exist and the thermistor will eventually break down with the formation of a hot spot. Thermistors, when they contain a hot spot, exhibit a practically constant voltage drop and there is the possibility of their use as constant voltage electrical components.

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Effect of a Surface Active Agent on the Velocity of Rise of Benzene Drops in Water

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Previous work has shown that the presence of small quantities of surface active agents in liquid-liquid extraction processes reduces the rate of mass transfer (*1, 2, 3, 4, 5, 6, 7, 8*), while large quantities of detergent may cause an increase in the rate (*2, 4*). The reduction in the mass transport rate has been attributed to either a reduction in the internal circulation of the drops (*5, 7, 8*) or to a true barrier effect caused by a surface layer of detergent (*4, 6*). The increase in mass transfer has been ascribed to an increase in the oscillation of the drops caused by a reduction in the surface tension (*4*), or simply to a reduction in the drop size (*2*) where this was unknown. The purity of the surfactants used was found to have no effect (*8*).

Although numerous workers had observed the effects of detergents on mass transfer, Garner and Skelland (*5*) and also Lindlan and Terjesen (*7*) were the first to note that surface active agents also reduce the velocity of fall of drops, although Stuke (*9*) had already demonstrated that surface active agents had a pronounced effect on the rate of rise of bubbles in water. Garner and Skelland (*5*) found that a 0.003 wt. % solution of sodium dodecyl sulfate 6 reduced the velocity of fall of nitrobenzene drops (3.0 to 5.4-mm. diameter) in water, and their technique of visual observation with aluminum particles showed that the effect of the detergent was to reduce the internal circulation in the drops. About the same time Lindlan and Terjesen (*7*) found that 0.003 wt. % sodium oleyl *p*-anisidinesulfonate could lower the velocity of fall of carbon tetrachloride drops (2.0 to 3.5-mm. diameter) in water by as much as 7 to 10%; they also found that the amount of detergent necessary to produce the maximum reduction in the velocity of fall was only 30 to 50% of that required to cause the maximum reduction in the mass transfer rate of iodine. The reduction in the velocity of fall was also attributed to a suppression of the internal circulation in the drops. Recently Boye-Christensen and Terjesen (*8*) used sodium oleyl *p*-anisidine sulfonate and sodium hexadecanyl sulfate to inhibit the extraction of both iodine and *o*-nitrophenol from water by carbon tetrachloride drops and again inferred that the action of the detergents was to reduce the velocity of internal circulation, which in turn caused a reduction in the velocity of rise and rocking motion.

In most of the above work the reduction in velocity of fall of drops was observed as incidental to the effects on mass transfer or internal circulation, so that only a narrow range of drops sizes was used. Although no work has been done with detergents over a wide drop-diameter range, such work (*10, 11*) has been carried out with pure liquids with a wide variety of physical properties, so that the effect of interfacial tension on the velocity of rise could be correlated empirically. The object of the present work is to investigate the effect of small quantities of a detergent on velocity of rise over as large a diameter range as possible, since Stuke (*9*) in his work on bubbles observed that the effects of the surface active agents capric and caproic acids depended on the bubble diameter. Small quantities of detergents were used to avoid significantly changing the bulk properties of the liquid phase, such as density and viscosity. In this connection Houghton, Ritchie, and Thomson (*12*) have used the effect of detergents on the velocity of bubbles to demonstrate that trace quantities of surfactants are present in sea water; they also showed that, depending on the bubble diameter, surfactants may also have a pronounced effect on the spiral motion of bubbles.

EXPERIMENTAL

The apparatus was similar to that described by Houghton et al (*12*). The method used was to time the rise of benzene drops in water over a distance of 200.0 cm. by means of a stopwatch. The drops were formed and released one at a time, and sufficient time was allowed to elapse for the decay of the wake of the previous drop before allowing another to rise.

By using jets of various diameters it was possible to produce drops with diameters in the range 1 to 10 mm. However in the case of strong detergent solutions it was found difficult to form single drops on the large size jets, since they tended to form inside the jet rather than on the tip and then break up into a number of smaller drops on release. The column of water was 5.6 cm. in diameter and 228 cm. long, a distance of 28 cm. being allowed for the drops to reach their terminal velocity before starting the stopwatch, the measurement being culminated when the drop broke through the water surface. De-ionized water was used, and as a precaution against any mass transfer effects the water was saturated with benzene (analytical grade). The jets could be exchanged without emptying the column. The jets in use were kept completely filled with benzene through a silicone rubber stopper at their base by a micrometer hypodermic syringe also filled with benzene. A long needle was used so that the benzene used to form the drops did not come in contact with the silicone stopper. For large drops the syringe could be used to measure the volume of single drops, while for small drops it was necessary to measure the volume of a number of drops, even though each was timed singly. In this way the volume of the drops could be obtained with an accuracy of better than ± 1%. By timing a large number of drops, usually about thirty of each size, the velocity of rise could be measured to better than ± 1%. The water temperature was recorded to within 0.1°C. by a mercury thermometer.

The detergent solutions were made by dissolving the commercial surface active agent Teepol (an alkyl aryl sulfonate) in de-ionized water saturated with benzene. Three concentrations of 0.003, 0.015, and 0.3 wt.% Teepol were used. A tensiometer was used to measure the interfacial tensions of the solutions; the results are recorded in Table 1.

RESULTS AND DISCUSSION

Figure 1 illustrates the effect of drop diameter on the terminal velocity of rise of benzene drops in pure water and Teepol solutions of three different concentrations. The velocities of rise in pure water are about 10% higher than those reported by Klee and Treybal (*11*) for the same system, indicating perhaps that in the latter work some impurity may have been present, especially since the authors state that some technical grade materials were used without purification. That impurities were probably present is indicated also by the reported interfacial tension for benzene-water, which was 30.0 dynes/cm. as compared with 35.0 dynes/cm. for the present work. Furthermore the discrepancy cannot be explained on the basis of a wall correction, since such a correction would probably make velocities from the present work even higher than those of Klee and Treybal. However since generalized corrections for wall effects at high Reynold's numbers are not available as yet, and since Hu and Kintner (*10*) have demonstrated that the effect was negligible for cylinders with diameters in the range 2.14 to 6.99 cm. and drops of diameters in the range 0.1 to 1.2 cm., it was considered unnecessary to make a correction for the proximity of the wall. It is interesting to note that West et al. (*3*) have demonstrated that the use of plastic connecting tubing is sufficient to affect the extraction rate in benzene-acetic acid-water systems, so that in the present experiments care was taken to avoid direct contact of the liquids with materials other than glass or stainless steel. As the concentration of Teepol was increased, it was found difficult to prevent the drops from breaking up as they were formed, so that in these cases it was impossible to form single drops above a certain diameter.

With respect to observations on the motion of the individual drops it was noted that as benzene drops in pure water traveled up the column, there was pronounced rocking with a large superimposed spiral motion, especially for large sizes. However when detergents were added, even at the lowest concentrations used (0.003 wt.%), the rocking motion and the diameter of the spiral were both decreased as found by Houghton et al. (*12*) for bubbles. In both pure water and detergent solutions the large drops also exhibited pronounced oscillation with changes in shape from oblate to prolate spheroidal through various intermediate but less well-defined shapes. It was difficult to ascertain visually whether the amplitude of the oscillation was more pronounced in detergent solutions than in pure water [as observed by Lindlan and Terjesen (*7*)], since the large drops tended to break up into smaller ones, presumably because of the lower interfacial tension. The interfacial tensions are listed in Table 1.

Figure 2 shows the data of Figure 1 replotted in terms of the drag coefficient. In calculating the drag coefficients the physical properties of the continuous phase were taken as those of pure water even when detergent was present. At low Reynold's num-

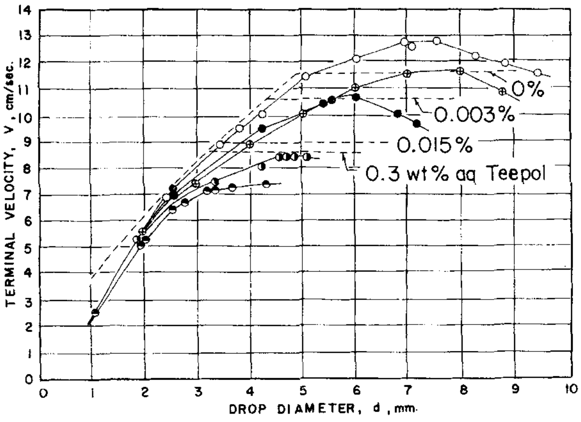

Fig. 1. Terminal velocities of benzene drops. Open circle, pure water. Darkened circle, 0.003 wt. % aq. Teepol. Half open circle, darkened on right side, 0.015 wt. % aq. Teepol. Half open circle, darkened on top, 0.30 wt. % aq. Teepol. Open circle with cross, data of Klee and Treybal (*10*). — — — — equations of Klee and Treybal (*10*).

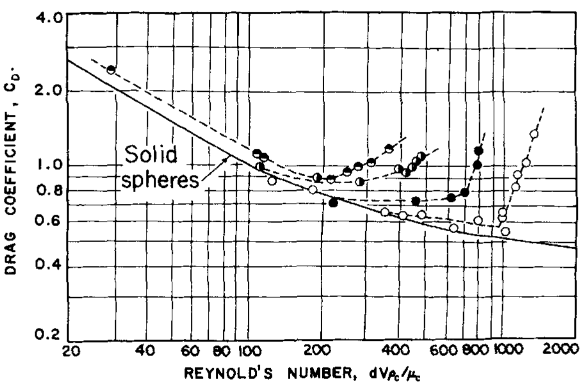

Fig. 2. Drag coefficients for benzene drops. Open circle, pure water. Darkened circle, 0.003 wt. % aq. Teepol. Half open circle, darkened on right side, 0.015 wt. % aq. Teepol. Half open circle, darkened on top, 0.30 wt. % aq. Teepol.

TABLE 1. SYSTEMS STUDIED

Disperse phase	Continuous phase	Temp., °C.	σ, dynes/cm.	μ_C, centipoise	ρ_C,* g./cc.	ρ_D,* g./cc.
Benzene	Water	23.8	35.0	0.919	0.9974	0.8747
Benzene	0.003 wt. % aq. Teepol	26.2	23.4	0.870	0.9968	0.8721
Benzene	0.015 wt. % aq. Teepol	24.6	8.6	0.902	0.9972	0.8738
Benzene	0.30 wt. % aq. Teepol	25.4	6.8	0.886	0.9970	0.8730

* "International Critical Tables," Vol. 3, pp. 24-33.

bers it is evident that drops behave like solid spheres. However as the Reynold's number is increased, the drag coefficient shows a sharp rise roughly at the point where the velocities in Figure 1 reach a constant or maximum value. The sharp rise in the drag coefficient-Reynold's number curve begins at lower Reynold's numbers as the interfacial tension is decreased by increasing the amount of surfactant. It is interesting to note that this general effect of interfacial tension has been observed by Hu and Kinter *(10)* and Klee and Treybal *(11)* for the case of pure liquids without the addition of detergents. However in the present experiments it is possible to distinguish the effects of interfacial tension from those of the other physical variables such as bulk density and viscosity, which remain substantially constant. In the experiments of Klee and Treybal *(11)* there was, in most cases, a portion of the drag-coefficient curve lying below that for solid spheres, indicating pronounced circulation, although this was not true for their data on the benzene-water system. It is interesting that neither the present data nor the data of Hu and Kinter *(10)* indicate the presence of internal circulation by exhibiting drag coefficients lower than those for solid spheres. The discrepancy may be due to the presence of impurities throughout the measurements of Hu and Kinter (the organic liquids were in direct contact with rubber) or to the fact that these workers formed their drops singly while Klee and Treybal used a slow stream of drops. Figure 2 also shows that at low Reynold's numbers with the highest detergent concentrations (0.3 wt.%) the drag coefficient curve is about 20% higher than, but still parallel to, that for solid spheres. This indicates perhaps that, with excessive amounts of surfactant, the drop surface may become so modified by adsorbed Teepol that the drop behaves as a rough sphere. That the behavior at high detergent concentrations is somewhat anomalous can also be confirmed by comparing the present experimental results with the following empirical equations for pure liquids given by Klee and Treybal:

$$V_I = 38.3\, \rho_C^{-0.45}\, \Delta\rho^{0.58}\, \mu_C^{-0.11}\, d^{0.70} \tag{1}$$

$$V_{II} = 17.6\, \rho_C^{-0.55}\, \Delta\rho^{0.28}\, \mu_C^{0.10}\, \sigma^{0.18} \tag{2}$$

V_I represents the velocity of drops in the region where the velocity increases with diameter, whereas V_{II} represents the value in the region where the velocity remains approximately constant with increasing diameter. Equations (1) and (2) were obtained by correlating empirically the data from eleven pure immiscible liquids covering a wide range of physical properties; for example the interfacial tension varied from 0.3 to 42.4 dynes/cm., although no detergents were added. The broken lines in Figure 1 represent equations (1) and (2) plotted for an average temperature of 25.0°C. for the present experiments, with the interfacial tensions and physical properties given in Table 1. It is apparent from Figure 1 that the general effect of detergents can be explained on the same basis that explains the effect of interfacial tension in pure liquid systems, except at very high detergent concentrations where the velocity seems to be somewhat lower than that predicted on the basis of the correlation for pure liquids.

It would seem from the above discussion that the behavior of pure liquids and detergent solutions may be interpreted by some common effect that is linked to the interfacial tension in both cases. At least four possible explanations for the effect of interfacial tension on the velocity of rise of drops may be visualized.

1. Lower interfacial tensions may enhance the oscillation of the drops from the prolate to the oblate spheroidal forms, thus producing an increase in resistance to forward motion.
2. Using complex mixtures of various organic liquids, Garner and Skelland *(13)* have shown that whenever the interfacial tension is lowered, there is a reduction in the internal circulation of a drop and that the Reynold's numbers required to start circulation are also lower. They concluded that surface viscosity would be a major factor in determining the degree of internal circulation.
3. Interaction between oscillation and internal circulation might itself inhibit internal circulation and affect forward motion.
4. An interesting explanation that is perhaps implied, but not actually stated by Garner and Skelland *(13)*, is that there is some connection between interfacial tension and surface viscosity. The present work tends to indicate that surface viscosity is governed by a phenomenon that is common to interfaces between pure liquids and to interfaces containing adsorbed surfactant.

However no definite conclusions with respect to any of the above hypotheses may be reached from the present experiments.

NOTATION

C_D = $4\Delta\rho g d/3\, \rho_C V^2$

d = equivalent spherical diameter of drop, cm.

V = terminal velocity of rise, cm./sec.

V_I = terminal velocity of rise in region I, cm./sec.

V_{II} = terminal velocity of rise in region II, cm./sec.

Greek Letters

ρ_C = density of continuous phase, g./cc.

ρ_D = density of disperse phase, g./cc.

$\Delta\rho$ = $\rho_C - \rho_D$ = difference in density, g./cc.

μ_C = viscosity of continuous phase, poise

σ = interfacial tension, dynes/cm.

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