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REMOVAL OF OIL FROM AQUEOUS WASTES BY FLOTATION

by

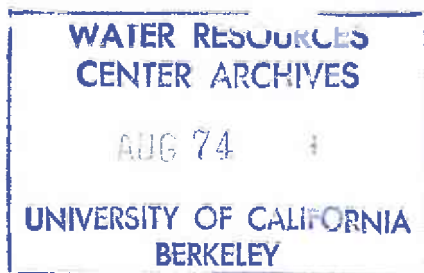
SIMON L. GOREN

Department of Chemical Engineering
University of California, Berkeley

CALIFORNIA WATER RESOURCES CENTER

University of California

Davis, California 95616



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ABSTRACT

The effects of electrolyte type and concentration on the separation of oil in water dispersions was examined experimentally. Flotation appears to be highly effective in removing droplets at high electrolyte concentrations or with aluminum sulfate under basic conditions. The efficiency of removal decreases with decreasing drop size limiting the effectiveness of flotation to droplets greater than several microns in diameter.

Introduction

A number of aqueous wastes carry micron and submicron droplets of emulsified oils which may affect the quality of the water into which the wastes are discharged. Examples include refinery wastes where water has come in direct contact with oil for purposes of chemical extraction, heat exchange, or steam distillation, ballast and bilge waters discharged from ships, some food processing wastes, and drainage carrying insecticidal, herbicidal, cleaning and other types of oils. Frequently these emulsions do not coagulate or settle out readily and are consumed only slowly by microorganisms. Techniques which have been used for separating such oil-water dispersions include centrifugation, coalescence by flow through porous media, and air flotation.

The objectives of the current research were to gain an understanding of the mechanisms involved in flotation of emulsified oils from aqueous wastes and to establish the degree and rate of clarification as functions of the droplet size, bubble size, fluid and surface properties, chemical environment and other relevant parameters. Such information is necessary for the rational design and scale-up of air flotation devices for use in the treatment of aqueous wastes either alone or in combination with other treatment procedures.

Procedures

Dilute dispersions of silicon oil in distilled water were prepared by intense mixing in a Virtis Model 23 homogenizer. Silicon oil, in these experiments Dow Corning 510 Fluid, was selected as the dispersed phase because of its very low solubility in water and because its density is very close to that of water thereby minimizing

sedimentation during the experiment; we also wished to compare the results of flotation to previously measured rates of Brownian coagulation of similar dispersions. The Virtis homogenizer had been modified by introducing larger baffles in the mixing chamber and by providing tubing for withdrawing and recirculating the dispersion. In this way oil in water dispersions with large numbers of droplets in the 1 to 5 micron size range of interest here could be prepared. The dispersion also contained larger droplets which though fewer in number accounted for much of the oil volume; for example, the number of 10μ droplets is 200 fold less than the number of 1μ droplets but they account for 5 times the volume of oil. The dispersions so prepared were stable for times of more than several hours.

Just prior to flotation, a dispersion so formed was mixed with an aqueous electrolyte solution to destabilize the dispersion. Electrolytes used were sodium chloride, calcium chloride, aluminum sulfate (alum) at various pH's controlled by addition of sodium hydroxide or hydrochloric acid, diethylamine hydrochloride, and sulfuric acid. The electrolyte concentration of the dispersions to be floated was varied from 10^{-3} to 10^{-4} moles per liter. In several experiments the surfactant lauric acid was added to yield a concentration of 1.25×10^{-4} moles per liter.

Two types of batch flotation were explored. In one series of experiments, air was bubbled through a fritted glass disc into a glass column 2-3/4 inches in diameter and 3 feet high containing the dispersion. The disc was fabricated from a Pyrex 150-C fritted disc funnel that had been chemically treated with a silicon varnish to render it preferentially air wetting. At regular time intervals samples of the dispersion were withdrawn from six inches below the

foam-dispersion interface and analyzed for the remaining oil droplets. In the second series of experiments bubbles were nucleated by introducing the corresponding electrolyte solution saturated with nitrogen gas at a pressure of 50 to 100 psig into the bottom of a column 1-3/4 inches in diameter and 4 feet high containing the dispersion. Clouds of tiny bubbles were formed owing to the sudden drop in applied pressure. Different ratios of the pressurized solution, which is analogous to the "recycle" in commercial flotation devices, to the dispersion were employed. The resulting bubbles were allowed to reach the foam-dispersion interface and then a sample was withdrawn for analysis of the remaining oil droplets.

The number and size of suspended droplets was determined by a Coulter Counter using a 30 micron aperture. Associated electronic equipment were a RIDL Model 21007 current generator, preamplifier and pulse shaper, a Northern Scientific Model NS-601 256 channel pulse height analyzer, and a Teletype Model 33 printer. In most of the pressurized experiments, oil concentration was estimated from the turbidity measured with a Hach Model 1860A Turbidimeter; to determine the efficiency of flotation from turbidity measurements it is necessary to assume that the size distribution of droplets contributing to the turbidity is unchanged by flotation.

Results

A. Bubbling experiments

Figure 1 shows typical data plotted as the remaining oil droplet concentration versus the time of flotation. The data shown here are for nominally 1.9 and 2.68 micron diameter droplets suspended in 10^{-3} molar calcium chloride solution. In this and all the other

bubbling experiments, the data closely followed straight lines on semi-log plots. This linear behavior can be explained by assuming that the rate of droplet removal is determined by collisions between bubbles and droplets. If we let V_B be the rise velocity of a bubble of diameter D_B and N_B be the number of bubbles per unit volume in the flotation column, then the total volume swept out by rising bubbles per unit time is $N_B V_B \pi D_B^2 / 4$. Let N denote the number of oil droplets per unit volume of a given size at a given time and η the efficiency of capture. Then

$$\frac{dN}{dt} = -(\eta N_B V_B \pi D_B^2 / 4) N \equiv -\frac{k}{W} N. \quad (1)$$

If the concentration and size of the continuously introduced bubbles remains constant, then k/W defined by Equation (1) also is constant and the Equation may be integrated to

$$\frac{N(t)}{N(0)} = \exp \frac{-kt}{W} \quad (2)$$

In analogy with the theory of Brownian coagulation we have introduced the stability factor W , such that $W=1$ when double layer forces are negligible, but increases above unity as double layer forces retard the attachment of droplets to the bubbles.

From graphs such as Figure (1), experimental values of k/W were determined. Unfortunately, we did not have sufficient experimental information to determine k separately. Assuming that double layer forces were completely retarded at the highest electrolyte concentrations used, i.e., $W=1$ at electrolyte concentration of 1 mole per liter, we plotted W versus the electrolyte concentration. Figure 2 shows the results for several electrolytes. The data show that

the efficiency of flotation drops markedly as the electrolyte concentration decreases. Anions with higher valence are more effective in flotation in that their fall off is much less dramatic. Also shown in Figure 2 are measurements of the stability factor determined from Brownian coagulation rates. We see that flotation is less sensitive to electrolyte concentration in coagulation, especially at lower concentrations.

B. Nucleation experiments

Most of these experiments were carried out with alum as the electrolyte at various pH's. At low pH flotation was very inefficient so that attention was paid primarily to basic solutions. An example of the data is shown in Figure 3 where we have plotted the efficiency of flotation as measured by the ratio of turbidity of the effluent to that of the feed versus pH for various concentrations of alum. For a given alum concentration there is a range of pH where flotation is effective; for example, at 2×10^{-4} moles per liter alum, the pH range for greater than 90% removal of turbidity is from about 6 to 8. As the concentration of alum decreases, higher pH's are required to achieve similar removal. With zero alum added, a pH of about 10 is required for 90% removal.

Figure 4 shows a plot of the remaining number of drops as a function of drop size. This experiment was carried out at an alum concentration of 2×10^{-5} moles per liter and a pH of 8. The figure shows that larger drops are removed much more effectively than smaller ones. For example about 78% of the 1.3 micron diameter drops are removed whereas in excess of 98% of the 5.4 micron drops are removed. Since most of the oil volume is in the larger droplets, when judged

on a volume basis flotation is a very efficient process. This behavior can be explained partly by the efficiency, η , appearing in Equation (1). Depending on the mechanism of capture, η is known to vary from the -1 to -2 power of the droplet size; for example in the coalescence of oil by flow through fibrous media a slope of about -1 was found for drop below about 3 microns in diameter. The measured slope of -1.4 found here is in fair agreement with these results.

Conclusions

Electrolytes increase the rate and degree of removal of oil from dispersions by flotation. The larger the valance of the anion, the more effective the electrolyte. Alum under basic conditions, where hydrolysis products form, is particularly effective even at low concentrations. It appears that the removal efficiency varies with the -1.4 power of drop size so that flotation is to be recommended only when droplets greater than several microns diameter are to be removed.

Publications:

1. Skocypec, Ronald, "Electrolyte Effects on Flotation of Oily-Water", U.S. Thesis, University of California, Berkeley, California.
2. Starr, Barry, "Effects of Electrolyte Concentration on the Flotation of Oil in Water Dispersions", Ph.D. Dissertation in preparation, University of California, Berkeley, California.

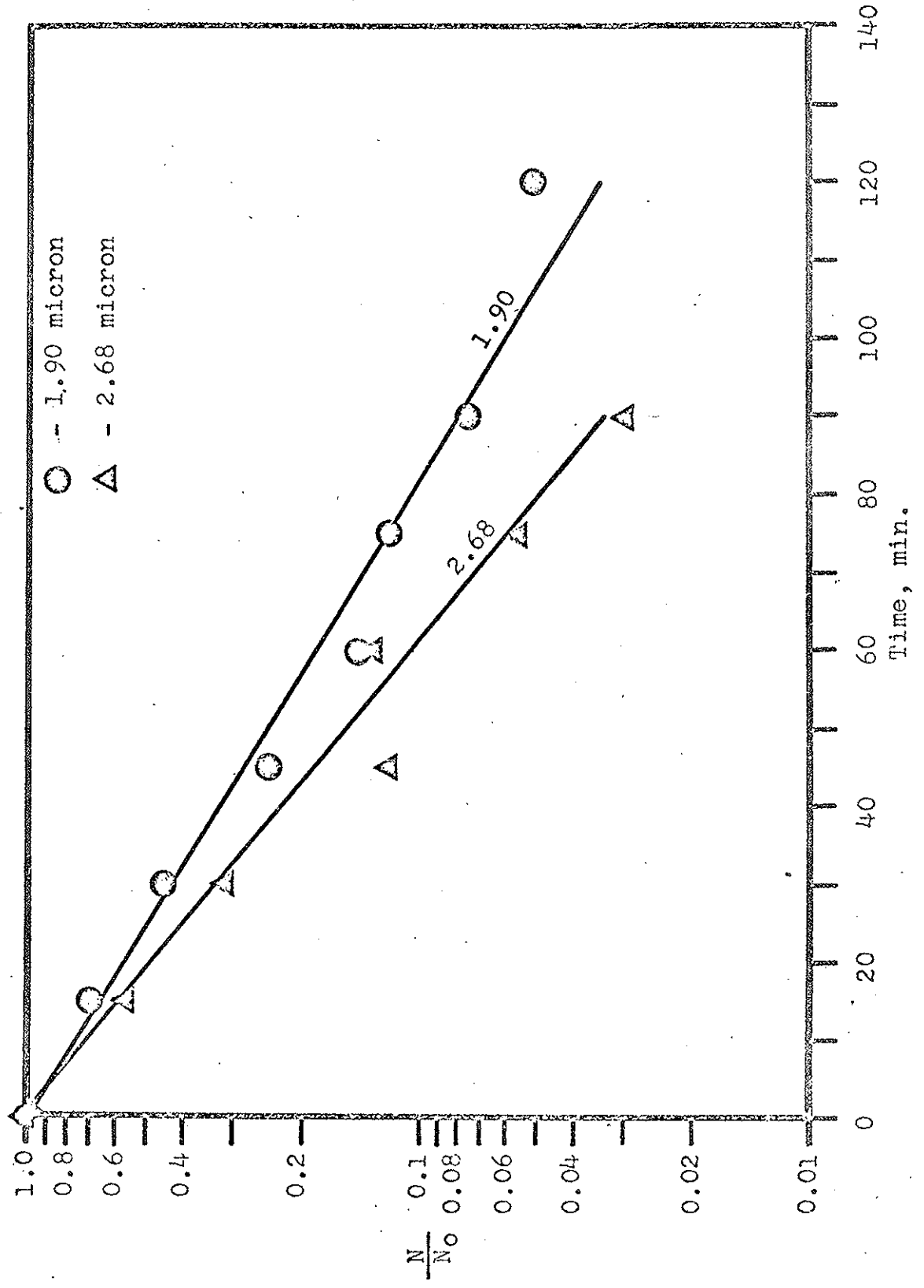


Fig. 1. Fraction of Particles Remaining with Time for 0.001 molar CaCl₂

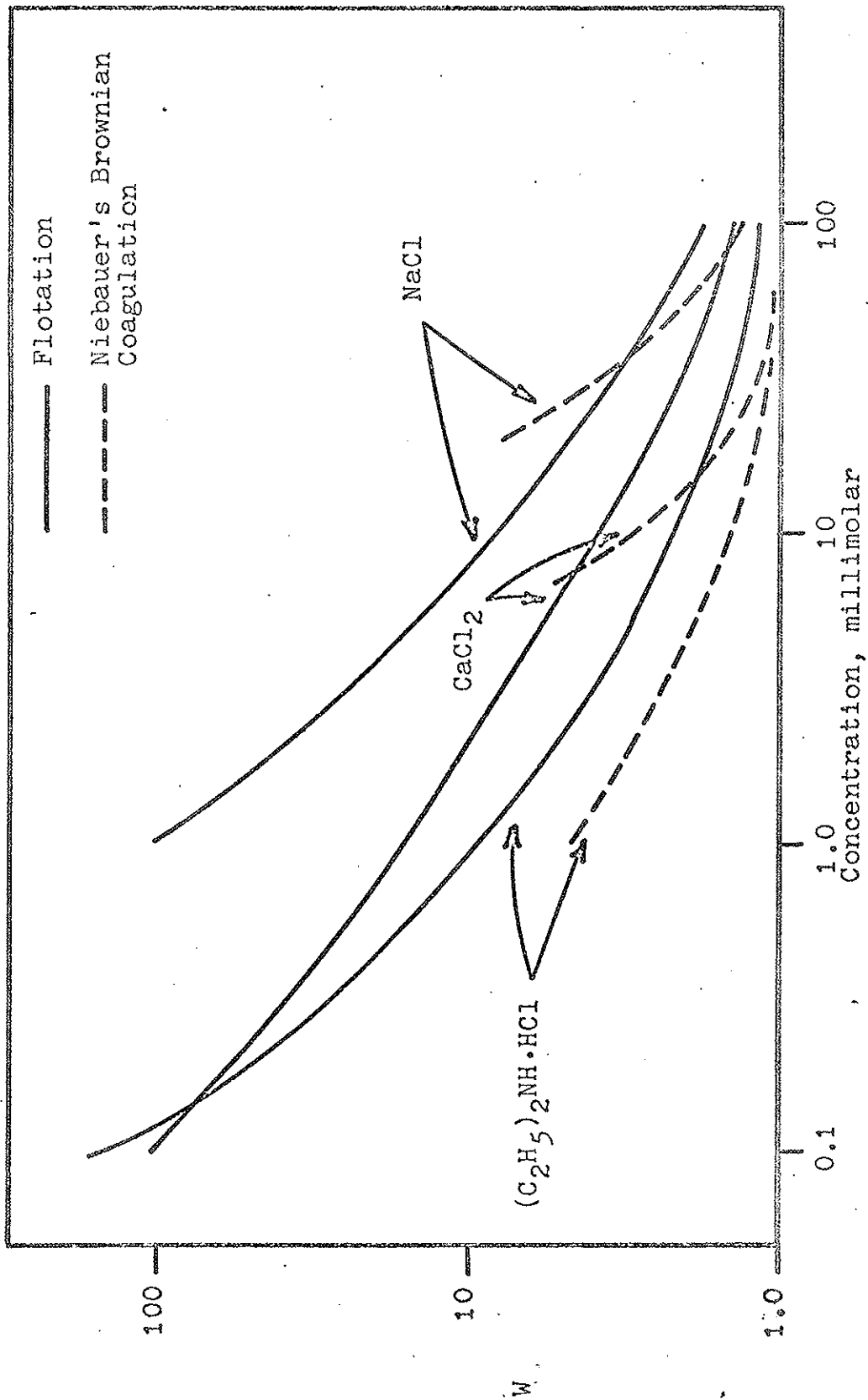


Fig. 2 Comparison of Figure 24 with Brownian Coagulation Data

FRACTION OF TURBIDITY REMOVED

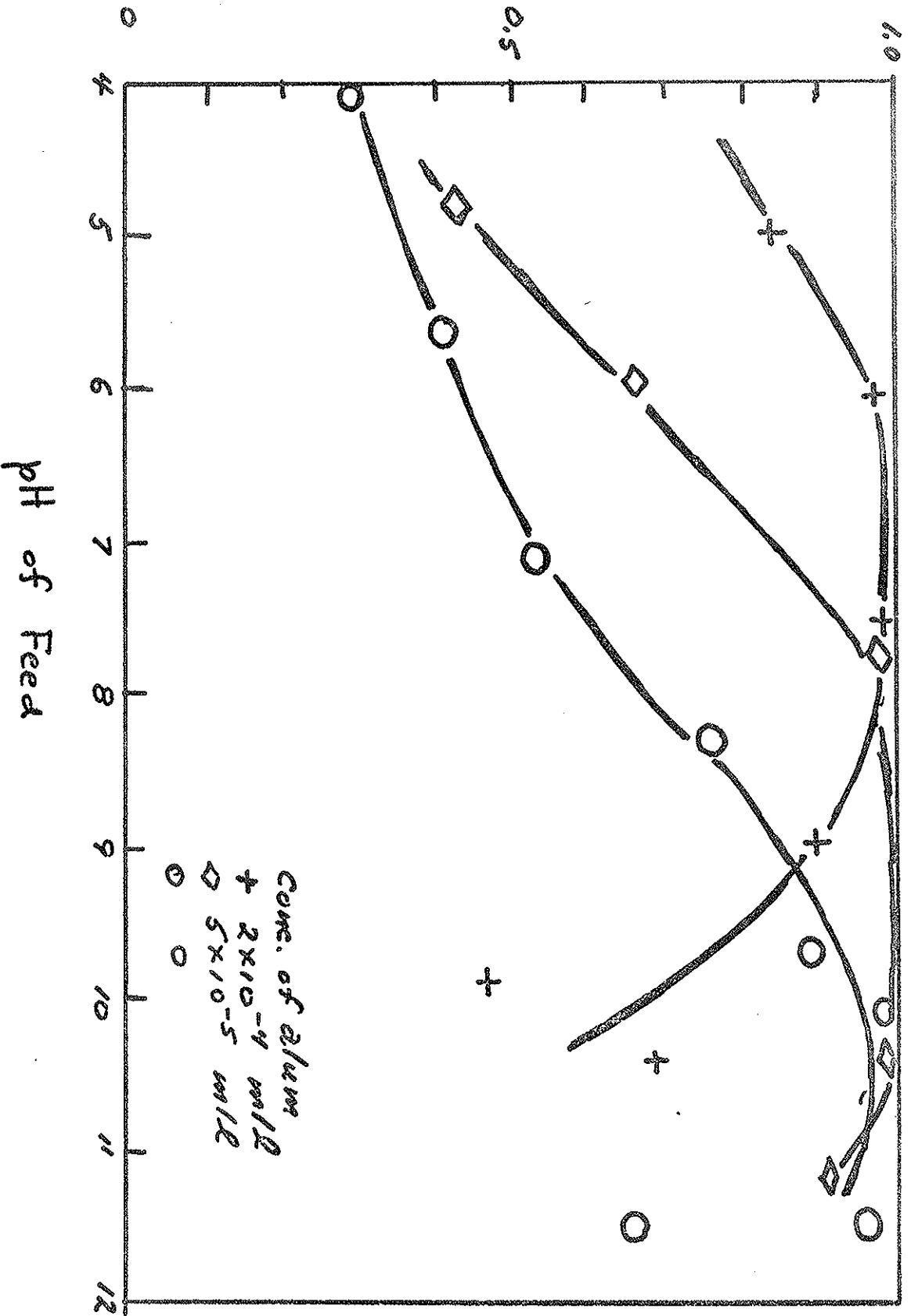


Fig. 3 Fraction of turbidity removed by flotation as a function of pH.

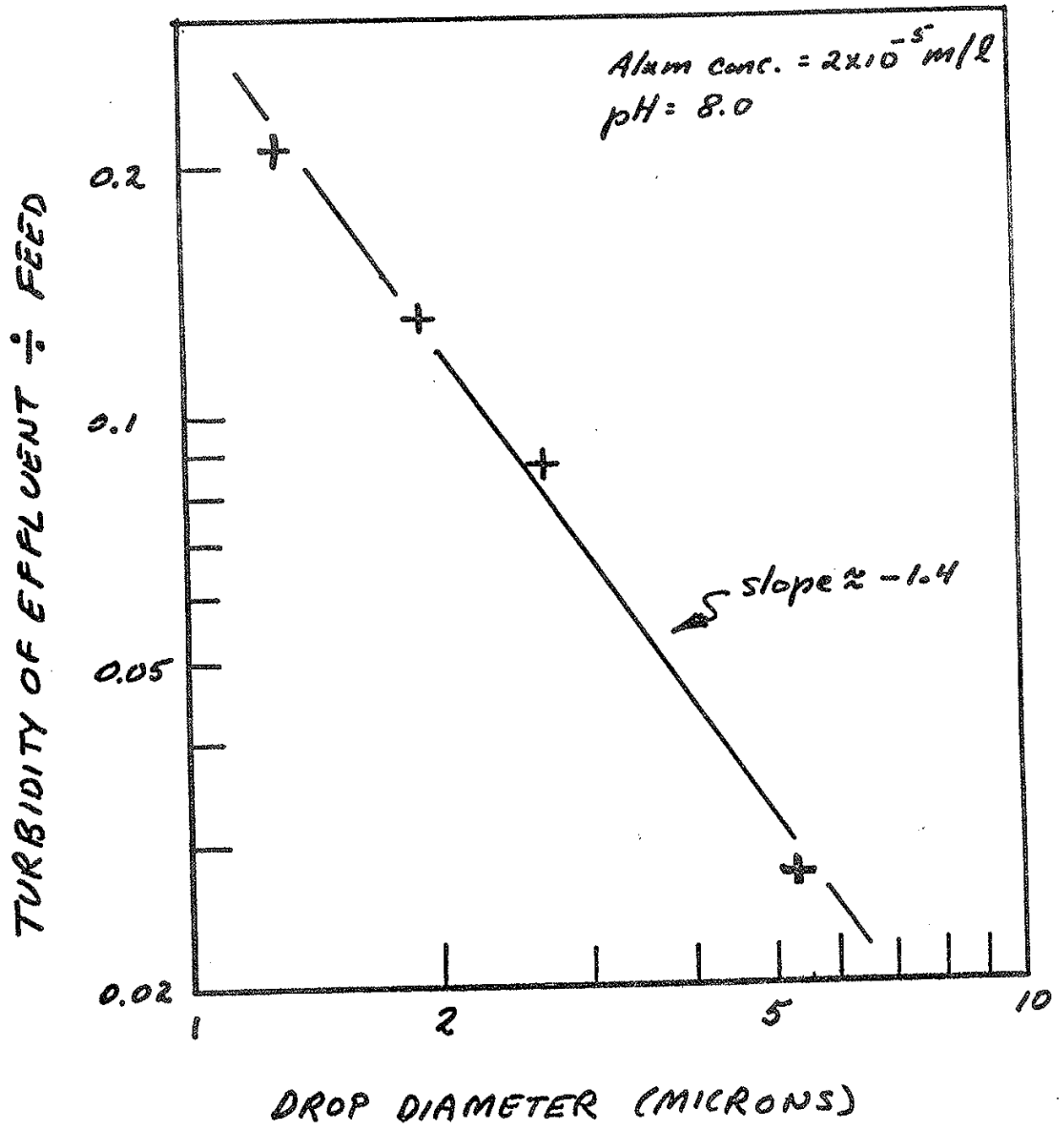


Fig. 4. Fraction of drops remaining after flotation as a function of drop diameter.