and predicted velocities is probably due to oversimplifications in the theoretical model. Inconsistencies in the experimental data for the lowest pressures and richest mixtures are probably due to insufficient distance for wave development.

At higher pressures the slight disagreement can be rationalized in terms of the idealized properties necessarily used in the computations. The effects of errors in the different properties tend to cancel, leaving a small net error in the predicted velocity.

An important consideration for design purposes is the pressure realized when a detonation occurs. The computed ratios of the detonation and impact pressures to the initial pressure are about 20 and 50, respectively, for the conditions investigated.

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A Scintillation Method for Determining Liquid - Liquid Interfacial Areas

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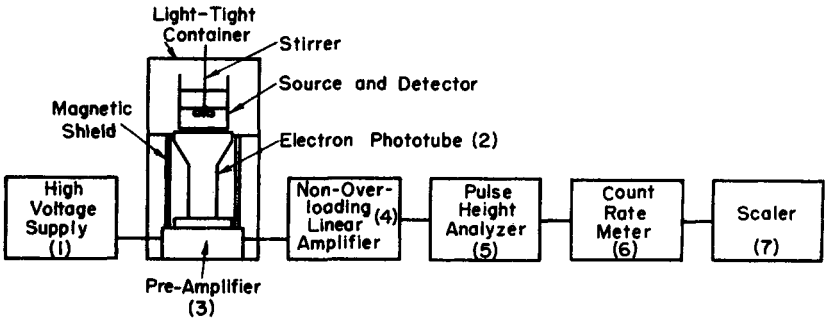
In stirred beakers the interfacial area between xylene containing a scintillator and tritiated water was measured as a function of stirrer speed by a scintillation counting technique. Because of the 6 μ average range of the tritium betas the rate at which flashes are detected by a phototube is a function of the interfacial area. A calibration curve of count rate against known interfacial area for unstirred phases in containers of various diameters gave a numerical estimate of the interfacial area for ten configurations.

Data for mass transfer between dispersed phases in equipment such as extractors, distillation columns, and sprayers can be correlated on the basis of equations of the form

$$W = k'a(f_s - f_w) = ka(c_s - mc_w) \quad (1)$$

Because of the difficulty of obtaining interfacial areas it is usual not to attempt to separate k and a, obtaining values for each, but rather to correlate ka. Measurements of the interfacial area should contribute to a further understanding of mass transfer.

Interfacial areas have been measured



(1) Nuclear Instrument & Chemical Corp. Model 172

(2) Dumont 6363

(3) Modified A-1-A

(4) Baird Atomic's D-D-1 Model 215

(5) Radiation Control Lab, Model 2204

(6) Radiation Control Lab, Model 15

(7) Radiation Control Lab, Model 2006

Fig. 1. Detection and counting system.

previously by light-transmittance techniques (*7, 8*). The absorptivity of light in a highly agitated two-phase system was calibrated with the volumetric interfacial area by estimating the number and size of drops in photographs. Light transmittance has also been used to measure froth densities on a bubble-cap plate (*3*).

The possibility of using short range radioactive particles for measuring interfacial areas was first investigated at the Oak Ridge National Laboratory (*6*). Here a radioisotope emitting short-range particles was contacted with an immiscible phase capable of interacting with the particles. Because of the short range of the particles interaction was restricted to the region close to the interface. Thus the product of the interaction (such as new chemical species or radiation) will be approximately proportional to the interfacial area. Preliminary investigations with tetrachloroethylene and alpha particles from polonium-210 gave inconclusive results due to low yields of chlorine. Considerable improvement resulted at Oak Ridge when a fluorocarbon was substituted as the target phase and the neutrons produced from the nuclear interaction between the alpha particles and fluorine were detected (*2*). This general technique for measuring interfacial areas is limited by the necessity of high immiscibility between the phases as well as the availability of suitable isotope and target materials. The system used in the present study was tritiated water and xylene with scintillator. It satisfies both the requirement of immiscibility between the phases and of having a short particle range. In contrast to previous techniques it has a negligible health hazard. A good introduction to recent scintillation techniques may be found in a collection of papers edited by Bell and Hayes (*1*).

The scintillator consisted of 4 g./liter of 2, 5-diphenyloxazole with 0.05 g./liter of POPOP; 1, 4 bis-2-(5-phenyloxozolyl)-benzene, as wave length shifter, to bring the photon spectrum closer to the maximum photo tube response, and 0.01 g./liter of NPO; 2-(1-naphthyl)-5-phenyloxazole for a light restorer.

EQUIPMENT

Vessels and Stirrers

For the stirring studies and the calibration of count rate against interfacial area five beakers were used with nominal diameters of 1, 2, 3, 5, and 7 in. The beakers were 7 in. high except for the 7-in. diameter one which was 6 in. high. Shell vials 8 to 36 mm. in diameter were also used. The floors of the beakers were ground flat, and the walls were given a reflective coating of alpha-alumina while the vials were untreated. The 7-in. diameter beaker had four removable brass baffles each of beaker height and of width equal to one tenth of that of the beaker.

Detection and Counting Systems

Detection and counting of scintillations were accomplished by the single channel analyzer arrangement shown as a block diagram in Figure 1. A complete description of each component and its method of use as well as the precautions that were taken is given elsewhere (*4*). The phototube had a photo-sensitive surface of a 2.5-in. diameter circle. The calibration of the detection equipment indicated that a high voltage setting of 1,110 v. and a pulse height of 60 on the E Dial of the single-channel analyzer gave the maximum ratio of tritium count rate to background. The setting was used up to a count rate of 37,000 c.p.s. Above this the E dial setting was changed to a pulse height of 150 reducing the count rate by more than an order of magnitude preventing counting difficulties. The relationship between the two dial settings was established by direct calibration. While improvements could be made, such as reducing the noise by cooling the circuit and using a coincidence counter, the present method was quite adequate to demonstrate the technique.

EXPERIMENTAL

To test the equipment and settings the count rate as a function of the specific activity of the tritiated water was determined in a shell vial. When plotted on log-log paper the points fell within 10% of a straight line of unit slope from 118 counts/sec. at 0.01 mc./ml. and 11,800 counts/sec. at 1 mc./ml. The background plus noise count rate was 47 to 120 counts/sec. giving deviating points below 0.01 mc./ml. The specific activity used for the stirring results was 0.1 mc./ml. where the background and noise correction was relatively low.

Calibration of Interfacial Area

A calibration curve of the count rate in beakers as a function of interfacial area was obtained by contacting the tritium and scintillator in beakers of various cross sections. They had walls coated with alpha-alumina polishing powder as a diffuse reflector and flat ground bottoms which were optically coupled to the photocathode with silicone. The interface was a constant distance of 2 in. from the bottom in order to eliminate the effect of liquid level. Background measurements, with pure water substituted for tritiated water, were made before and after each run. The count rate increases to a maximum as the scintillator and tritium equilibrate between the phases. To insure that only counts originating at the interface were measured the count rates were taken immediately after the two liquids were contacted.

In Figure 2 it is seen that the count rate results for the two beakers smaller and one slightly larger than the photo-

Table 1. Propeller Dimensions

Number	Type	Blade dimensions (in.)	Shaft dimensions (in.)
1	Horizontal blade	2 × 0.5 × 0.025	0.25 × 14
2	Horizontal blade	3.1 × 0.75 × 0.065	0.375 × 14
3	Horizontal blade	1.15 × 0.286 × 0.020	0.130 × 14
4	Vertical blade	3.1 × 0.065 × 0.75	0.375 × 14
5	Vertical blade	1.15 × 0.020 × 0.286	0.130 × 14

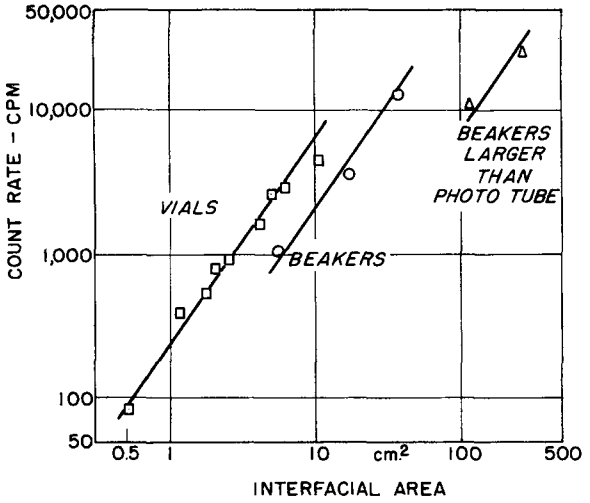


Fig. 2. Variation of count rate with interfacial area.

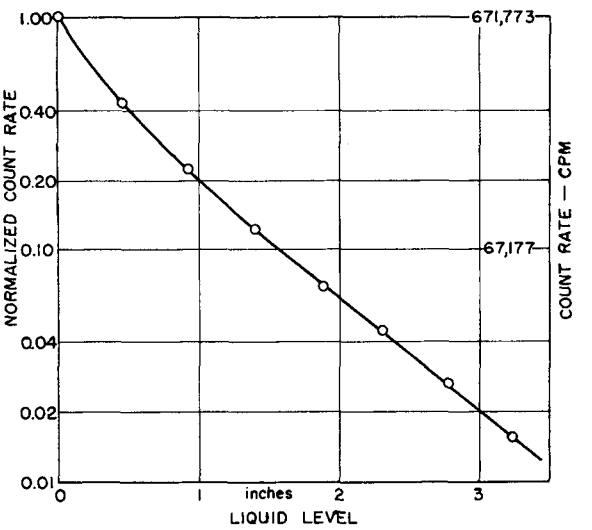


Fig. 3. Effect of interface level on count rate.

cathode fall on a straight line on log-log paper, while there is a definite effect of the geometry of the two beakers which were much larger than the photocathode. To establish conclusively that there was a direct dependence of counting rate on interfacial area a series of runs was made in uncoated vials with unground bottoms with the interface ½ in. above the bottom of the vials. Because of the effect of height of interface on the count rate, the rate for the vials has been put on the basis of that for the beakers with an interface at 2 in., as discussed below. The results are then plotted in Figure 2.

It is to be expected that the two beakers larger than the photocathode would give a lower number of counts per unit area than the smaller beakers. In the case of the large beakers the fraction of photons detected by the photocathode is reduced because of its smaller relative size. The result is that a smaller number of pulses are counted.

The effect of contamination of each phase by the other was determined by observing the difference between the initial count rate and that after steady state had been obtained as the scintillator and tritium equilibrate between the phases. The differences were within 5% of a straight line on log-log paper between 38.3 counts/sec. at 5.5 sq. cm. interfacial area and 1,210 counts/sec. at 112 sq. cm., with that for the largest beaker, 270 sq. cm., falling well below the line.

To determine the effect of liquid height a sample of used xylene and scintillator, contaminated with tritium, was placed in a 3-in. beaker and the count rate taken. Successive portions of pure water were added to raise the interface, and the count rate was measured after each addition. The ratio of count rate to that with the interface at the floor of the beaker is given in Figure 3. The count rate fell off approximately exponentially with increasing distance between the interface and the beaker floor. These results allowed a direct comparison of the calibration from the shell vials at a ½-in. level with the beakers at a 2-in. level interface as shown in Figure 2, where the data are all on the basis of a 2-in. level. The count rate for the ½-in. level was multiplied by the ratio of the normalized count rates for 2-in. and ½-in. levels, 0.055/0.432.

Because of the need for conserving tritium the more direct method of calibration with tritium and fresh scintillator was not used. In this determination some scintillations originated in the scintillator phase as well as at the interface, but as can be shown the normalized exponential curve will be the same as when all the scintillations originate at the interface. This is because below the xylene-water interface all photons will behave in the same manner independently of their place of origin.

Mixing Results

In the various combinations of beakers, propellers, and baffles the count rate was obtained as a function of stirrer speed yielding results such as those given in Figure 4. Tables 1 and 2 give the dimensions and combinations of stirrers and beakers used. Reproducibility was good with count rates obtained by increasing the stirrer speed agreeing well with those obtained by decreasing the speed.

Each plot obtained may be divided into three distinct regions. Initially there is a gradual increase in surface area as the slowly rotating propeller caused waves. As the interface is broken the area and count rate increases rapidly over a narrow range of stirrer speed. In the third region the dispersion is relatively homogeneous with the main effect being a decrease in droplet size with possibly some distortion.

CALCULATION

The effects of liquid height, insertion of propeller, and mutual contamination of the phases were observed to change the count rate considerably, and appropriate corrections were required.

Because the detected count rate is a strong function of the height from where the counts are originating, allowance must be made for the variation of efficiency of detection with position in beaker. The data of Figure 3 are used under the assumption that in the experiment the true time-average interaction or scintillation rate per unit volume of stirred beaker is constant; that is the system is homogenous. From the figure it is seen that for a given interaction rate the interactions arising near the floor of the beaker will contribute a unit count rate, while those 2 in. up will contribute a count rate of only 0.055 on the same scale. Integrating the data of Figure 3 over

Table 2. Identification of Runs

	Unbaffled							Baffled		
Run number	1	2	3	4	5	6	7	8	9	10
Beaker diam., in.	2.73	2.73	2.73	2.9	4.7	7.3	7.3	7.3	7.3	7.3
Propeller number	1	3	5	1	1	1	2	4	2	4

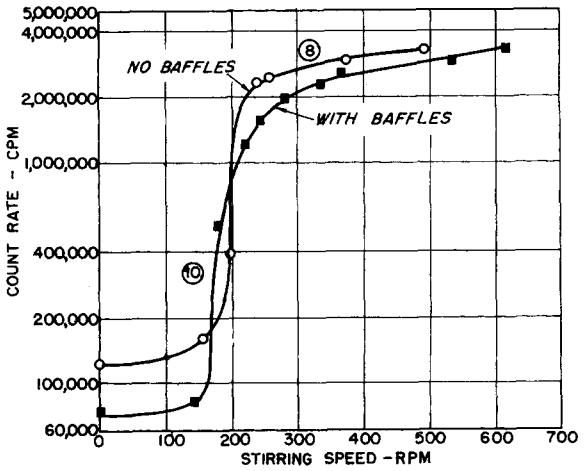


Fig. 4. Typical stirring curve.

the whole volume one can make an allowance for the detection efficiency.

The mean normalized count rate is the ratio of the count rate actually observed to that which would be observed if there were no attenuation of the scintillations between the height where they originate and the beaker floor. It is given by

$$\frac{\overline{C}}{C_o} = \left(\frac{C}{C_o}\right)_{ave} = \frac{\int_0^v C/C_o\, dv}{\int_0^v dv}$$

$$= \frac{\int_0^h C/C_o\, A dh}{Ah}$$

$$= \frac{\int_0^{h=4\text{ in.}} C/C_o\, dh}{h} = 0.153 \quad (2)$$

For the liquid levels of ½ or 2 in. used in the count rates vs. interfacial area calibration the product of the detection efficiency at the floor of the beaker and the true interaction or scintillation rate through the entire volume can be obtained from the observed interaction rate. It will be noted that $EN = C_o$:

$$C_o = EN = \frac{C_{2\text{ in.}}}{(C/C_o)_{2\text{ in.}}} = \frac{C_{1/2\text{ in.}}}{(C/C_o)_{1/2\text{ in.}}} \quad (3)$$

Calibration curves at both levels can then be placed on the same basis, say 2 in., as in Figure 3. When the system is stirred so as to be homogeneous and there is no blocking by the propeller being between a scintillation and the phototube, the count rate for the whole beaker is given by

$$C_o = EN = \frac{\overline{C}}{\overline{C}/C_o} \quad (4)$$

Not all of the count rate was due to scintillations rising at the interface. Some scintillations arose in the bulk phases because of equilibration of the tritium and the scintillator between the phases. An allowance for these two effects had to be made. The allowance was obtained by subtracting the count rate at 0 rev./min., with the propeller present and after operation and contamination, from the value obtained during calibration with fresh samples of scintillator and tritiated water where there was neither contamination nor propeller present. This correction was 38 to 69% at 0 rev./min. decreasing with increasing stirrer speed and count rate to only 0.5% at higher stirrer speeds, thus becoming negligible in the main region of interest.

At low stirrer speeds where the interface is wavy but yet essentially at a level of 2 in. the count rate yields the interfacial area directly from Figure 2, after first correcting for contamination of the phases and blocking due to the propeller, by subtracting a constant from the observed count rates.

With a high stirrer speed the contents of the beaker were homogeneous. The interfacial area was calculated by first subtracting the constant from the count rate to correct for contamination and blocking. This correction of about 0.5% is not of high accuracy because of the differing effect of the propeller yet is quite satisfactory having no appreciable effect on the results. The resulting count rate is that observed from scintillations arising throughout the whole beaker; yet the calibration curve, Figure 2, is for those arising at

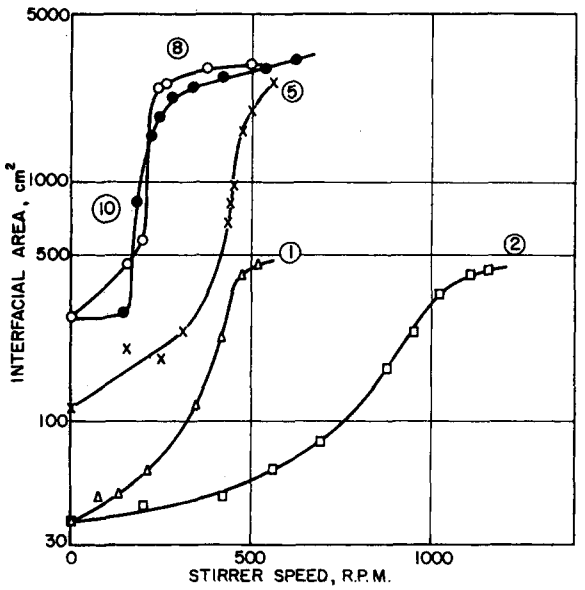


Fig 5a. Experimental values for interfacial area in stirred beaker.

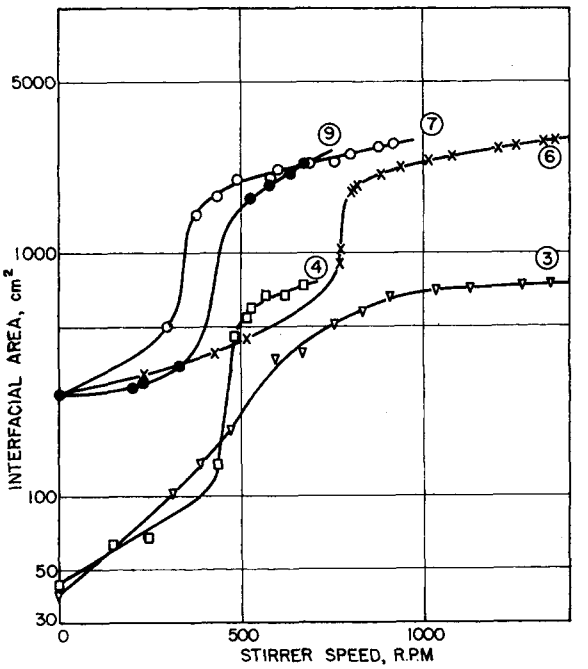


Fig. 5b. Experimental values for interfacial area in stirred beaker.

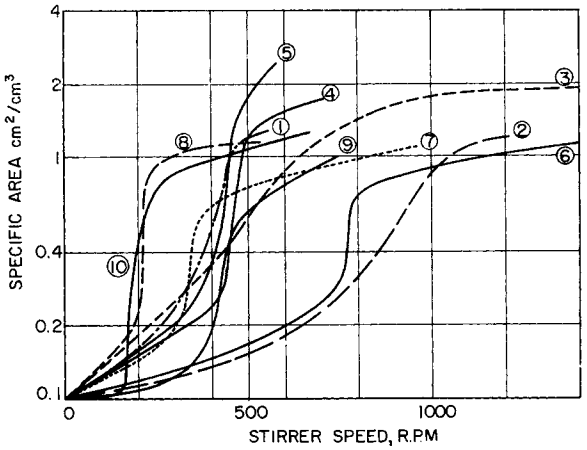


Fig. 6. Interfacial area per unit volume in stirred beakers.

a 2-in. level, $C_{2in.}$. Equation (2) gives the rate if there were no attenuation C_o by division by 0.153. The count rate must now be put on the basis of that which would be detected if the scintillations had all originated at 2 in., the height of the interface for the calibration curve. This is done by multiplying by $(C/C_o)_{2in.}$ which is 0.055 from Figure 3. The interfacial area can be read directly from Figure 2 with the resulting count rate used. This assumes that the attenuation through the xylene mixture is the same as that through water, a matter on which we do not have any information.

The interfacial area for high and low speeds is readily calculated as described above. To obtain the interfacial area at intermediate speeds it is noted that in the region of intermediate stirrer speeds the plot of count rate against stirrer speed is smooth on semi-log paper. As the interfacial area is approximately proportional to the count rate, the interfacial area for the region was drawn as a smooth line between the curves calculated for high and low stirrer speeds.

From the curves for the ten runs shown in Figure 5 it can be seen that the interfacial area is increased fifteen to fortyfold by stirring. From the identifying run number in Figures 5*a* and 5*b* and Table 2 the effect of various combinations of propellors, baffles, and beakers can be seen. While baffles may affect the critical speed where the interface breaks up, it does not seem to affect the final area greatly. The breakup of the interface could just as well be determined visually, for the speed at which it was observed to occur coincided with the rapid increase in count rate. Increasing the size of the stirrer does not seem to affect the beginning of the critical or intermediate region, but it does decrease the speed range it covers without changing the final interfacial area greatly.

From a mass transfer viewpoint the interfacial area per unit volume is of more interest than the interfacial area alone, for it relates to the efficiency of utilization of the beaker volume. This is shown in Figure 6, where it is seen that, stirring increases interfacial area per unit volume fifteen to fortyfold. For the combination of beakers, baffles, and stirrers employed, the plateauing of the interfacial area occurred over a fivefold range of speed. As would be expected the vertical blades are better than horizontal ones. It is to be remembered that all the stirring results are for beakers filled to the same depth, 2 in. of water and 2 in. of xylene. No attempt was made to optimize the stirrer and baffles, for the sole aim was to demonstrate a new technique. Further work might include the determination of the attenuation, Figures 3, for mixed phases, various beakers, and a confirmation of the resulting experimental area by other techniques.

CONCLUSIONS

Interfacial areas in stirred vessels can be estimated by a scintillation technique without undue radiation hazards. The method is not expensive in expended materials, but the capital cost of the photodetection and counting circuits is high.

It is hoped that this method might prove to be a useful tool for the measurement of interfacial areas. This technique could be used in certain systems in which mass is being transferred.

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A preliminary portion of this investigation, which was taken from the thesis submitted in partial fulfillment of the requirements for the Master's degree in Nuclear Engineering, was the subject of a thirty-five line note (5).

NOTATION

A = cross-sectional area of beaker
a = interfacial area per unit volume
C = observed count rate due to volume or interfacial area element at height h above beaker floor
C_o = count rate that would be observed if volume or interfacial area element were at beaker floor
$\overline{C}$ = observed count rate due to interactions throughout the whole beaker
c = concentration
E = detection efficiency for scintillations arising on floor of beaker
f = fugacity
h = height above beaker floor
k' = mass transfer coefficient based on fugacity driving force
k = mass transfer coefficient based on concentration driving force
m = distribution coefficient
N = number of interactions occurring per unit time throughout the entire beaker volume
n = number of interactions occurring per unit time per unit thickness of contaminated scintillator
v = volume of liquid phases in beaker
W = mass transfer rate

Subscripts

s = solvent or xylene phase
w = water phase

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