θ = time, hr.
π = total pressure, atm.

Subscripts

o = initial conditions
s = designation of an empty active site

LITERATURE CITED

1. Armour Research Foundation, Report No. 8, *ARF Project No. C711* (February, 1957).
2. Bachman, P. W., and G. B. Taylor, *J. Phys. Chem.*, **33**, 447 (1929).
3. Briner, E., and N. Bouboff, *Compt. Rend.*, **156**, 228 (1913).
4. ——————, *J. Chim. Phys.*, **11**, 597 (1914).
5. Briner, E., and A. Wroczynski, *Compt. Rend.*, **149**, 1372 (1910).
6. Fraser, J. M., and F. Daniels, *J. Phys. Chem.*, **62**, 215 (1958).
7. Granier-Mayence, J., J. Robin, and S. Robin, *Compt. Rend.*, **236**, 1011 (1953).
8. Green, T. E., and C. N. Hinshelwood, *J. Chem. Soc.*, **129**, 1709 (1926).
9. Hougen, O. A., and K. M. Watson, "Chemical Process Principles, Part Three. Kinetics and Catalysis," p. 923, Wiley, New York (1947).
10. *Ibid.*, p. 938.
11. Muller E., and H. Barck, *Z. Anorg. Allgem. Chem.*, **129**, 309 (1923).
12. Porter, P. E., C. H. Deal, and F. H. Stross, *J. Am. Chem. Soc.*, **78**, 2999 (1956).
13. Sakaida, R. R., Ph.D. thesis, Calif. Inst. Technol., Pasadena, California (1960).
14. Sakaida, R. R., Y. I. Wang, R. G. Rinker, and W. H. Corcoran, Am. Doc. Inst., Washington 25, D. C., Document 6891 (1961). A copy of this document may be secured by citing the document number and by remitting $2.50 for photoprints or $1.75 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress, Washington 25, D. C.
15. Sakaida, R. R., R. G. Rinker, R. F. Cuffel, and W. H. Corcoran, *Anal. Chem.*, 33, 32 (1961).
16. Scheuer, O., *Wien. Ber.* (11a), **123**, 931 (1914).
17. Schwab, G., R. Staeger, and H. H. Baumbach, *Z. Physik. Chem.*, **B21**, 65 (1933).
18. Smith, J. M., "Chemical Engineering Kinetics," p. 234, McGraw-Hill, New York (1956).
19. Thiele, E. W., *Ind. Eng. Chem.*, **31**, 916 (1939).
20. Wheeler, A., "Catalysis," Vol. 2, P. H. Emmett, ed., p. 138, Reinhold, New York (1955).
21. Yost, D. M., and H. Russell, Jr., "Systematic Inorganic Chemistry," p. 25, Prentice-Hall, New York (1946).
22. Zawadski, J., and T. Badzynski, *Roczniki Chem.*, **11**, 158 (1931).
23. Zawadski, J., and G. Perlinsky, *Compt. Rend.*, **198**, 260 (1934).

Manuscript received January 4, 1961; revision received May 23, 1961; paper accepted May 26, 1961.

Interfacial Area in Liquid-Liquid Mixing

FERDINAND RODRIGUEZ, L.C. GROTZ, and D. L. ENGLE

Union Carbide Chemicals Company, South Charleston, West Virginia

In predicting interfacial area in liquid-liquid systems there are several published reports which give different results. Differences in methods of measurement of interfacial area and impeller design and location account for some of these discrepancies.

For one pair of liquids, 40 parts by volume of ethylhexanol and 60 parts water, it was found that over wide ranges of impeller size to tank size ratio (0.27 to 0.67) that equal power per unit volume gave equal interfacial area per unit volume.

A familiar rule-of-thumb for scaling up a mixing operation is to hold constant the energy input per unit volume. When mixing involves the creation and maintenance of interfacial area between two immiscible liquids, the rule has been supplanted by dimensionless correlations of interfacial area, impeller diameter, and Weber number (*2, 3, 5, 6*). In the model system reported here energy input per unit volume appears to be a more valid criterion than the dimensionless grouping. Specifically it has been found that the average interfacial area per unit volume is proportional to the 0.4 power of energy input per unit volume for a number of geometric variations.

EXPERIMENTAL

The system used for the correlation of interfacial area with power input consisted of 40 parts by volume of 2-ethylhexanol and 60 parts of water. The alcohol was commercial grade (interfacial tension, 13.9 dynes/cm.; density 0.834 g./cc.; refractive index, 1.431 at 20°C.).

As in previous studies (*1* to *5*, *7*, *8*) light transmission was used as a measure of particle size. The apparatus is patterned after that of Trice and Rodger (*7*). Essentially a beam of light is led through a glass probe into the suspension. Another probe transfers light transmitted by the suspension to a photocell (Figure 1). The signal from the photocell is amplified, compared with the initial beam, and recorded.

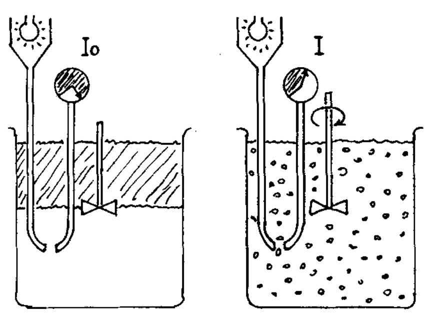

Fig. 1. The light beam transmitted by the glass probe is interrupted by a 0.9 cm long path through the continuous phase (I_o) or by the agitated suspension (I).

For measurement of power input a Chemineer ELB kit was used. The basic kit (*9*) consists of a ball-bearing mounted motor and variable speed reducer, various impellers and baffles, an 8- and a 16-gal. tank. The maximum of three baffles, symmetrically located, was used in the above tanks and also in a 1-gal. tank. The dynamometer is simply a two-pan balance, one pan of which is connected by a wire to an arm from the speed reducer mounting.

LIGHT TRANSMISSION AS A MEASURE OF INTERFACIAL AREA

Three groups of workers have reported the measurement of interfacial area of liquid-liquid dispersions (*1, 4,*

Ferdinand Rodriguez is at Cornell University, Ithaca, New York; L. C. Grotz is at the University of Wisconsin, Milwaukee, Wisconsin.

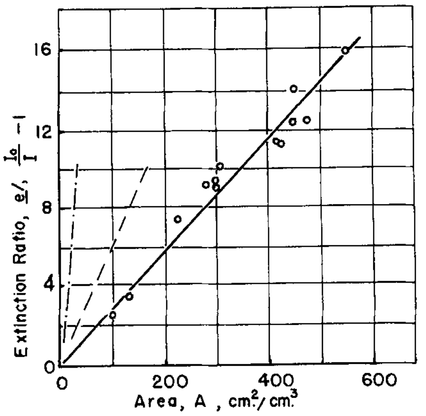

Fig. 2. Correlation of extinction ratio with interfacial area measured microscopically for 2-ethylhexanol and water stabilized by polyvinyl alcohol. Dashed line is prediction of Langlois (1) while dash-dot line is based on calibration work of Rodger (7).

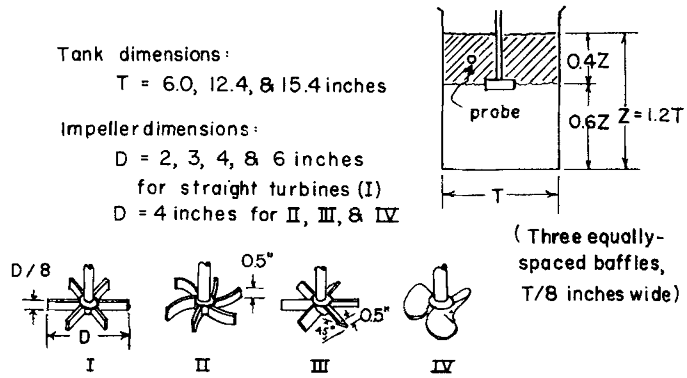

Fig. 3. Impellers used included straight, curved, and pitched-blade turbines as well as a 3-bladed, square-pitch propeller.

7). All took high-speed photomicrographs of agitated, unstable systems to calibrate particle size as a function of light transmission. Their calibrations are peculiar to their individual instruments. Two groups reported (*1*, *4*):
$e|$ (extinction ratio)

$$= \left(\frac{I_o}{I} - 1\right) = \beta A \qquad (1)$$

Also

$$A = 6\phi \frac{\Sigma n_i d_i^2}{\Sigma n_i d_i^3} \qquad (2)$$

The second group (*7*) presented their data as a plot of $\log_e(I_o/I)$ against $\alpha A L^{0.8}$, where α, like β, depends on refractive indices. However most of their data can be represented by the equation

$$e| = (\alpha A)^{1.6} \qquad (3)$$

where $L = 1$ cm. and $\alpha = 2\beta$.

In the present work interfacial area was measured for the system 2-ethylhexanol-water. This is a rapidly settling system in that the layers re-form on cessation of stirring in less than a minute. However concurrent work with stabilized systems was carried out. Although correlations are not reported here for such stabilized systems, one of them led to a means of calibration of the light transmittance apparatus.

Presumably because of the quantitative insolubility of polyvinyl alcohol in 2-ethylhexanol, suspensions stabilized with this agent appear to exhibit no unusual light absorbance. At low concentrations of this agent (0.03% of oil phase) particle size remains constant despite cessation of stirring for up to an hour. This stability permits microscopic measurement of n_i and d_i and therefore A. While it was stirred, the suspension was taken up in a medicine dropper and a few drops placed in a beaker of 4.7% polyvinyl alcohol in water. This treatment did not appear to disturb the individual particles. The droplets could then be seen as distinct spheres rather than as the mass of confusing boundaries in the original 40% oil-in-water suspension. Placed under a microscope at 90X the particles could be counted and classified as they passed a scale. Thirty to fifty particles were counted in each sample. With a volume fraction (ϕ) of 0.40 the correlation obtained in Figure 2 is

$$e| = 0.028\,A \qquad (4)$$

Despite the fact that the apparatus used here is more like that of Trice (*7*) than it is like that of Langlois (*1*), the prediction of the former is much farther from the data. Since most of the conclusions in this report are on a relative basis, the exact value of β is of less importance than the basic assumption of linearity between $e|$ and A.

CHANGES IN INTERFACIAL AREA WITH SPEED ROTATION (N, REV./MIN.)

Previous workers have found that

$$A = kN^a \qquad (5)$$

where a is 1.0 (*2*), 1.2 (*8*), or 0.72 (*5*). If the relationship between $e|$ and A is inserted [Equations (1) and (3), respectively], both of the last two groups agree that $e|$ is proportional to $N^{1.2}$. All the data in the present work have been correlated by assuming an exponent of 1.2; that is

$$e| = \delta \left(\frac{N}{1{,}000}\right)^{1.2} \qquad (6)$$

This assumption does violence to very little of the data, including results with four impeller designs and four diameters in three tank sizes (Figure 3).

CHANGES IN PARTICLE SIZE WITH IMPELLER DESIGN

One of the paramount goals of this study is to establish a basis for scaling up agitation requirements for dispersing immiscible liquid systems. Previous workers have not been able to present a satisfactory basis. One group (*8*) used but one agitator-to-tank diameter ratio in two tanks. The fragmentary results in the large tank did not correlate with those in the smaller. Another group (*2*) included in their presentation two factors; k which varies with Weber number, and ϕ which is a scale-up function, also variable. Both groups dealt only with straight-blade turbine impellers.

Because of the particular probe unit available the most complete set of data obtained gives an average interfacial area. For each run in which im-

TABLE 1. LIGHT TRANSMISSION AND POWER COEFFICIENTS

Run no.	Impeller	N, rev./min.	Tank volume, gal.	δ for Equation (6)	γ/V for Equation (7)
2S-6	straight, flat-blade	500-1,100	0.85	1.9	0.0031
3S-6		350-600		5.0	0.039
4S-6		200-400		8.0	0.16
4S-12		400-1,100	7.5	3.1	0.018
6S-12		150-500		10.0	0.18
4C-12	curved, flat	400-1,000		3.2	0.021
4A-12	pitched-blade	400-1,000		2.1	0.011
4P-12	propeller	500-1,000		1.5	0.0031
4S-15	straight, flat-blade	400-800	14.4	2.5	0.0094
6S-15		200-400		6.0	0.093

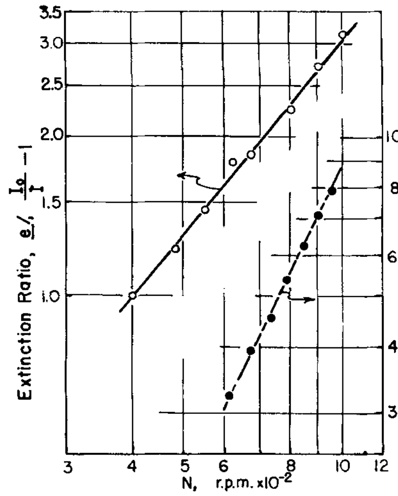

Fig. 4. Correlations corresponding to Equations 8 and 9 for a 4-inch straight turbine in a 12.4-inch diameter tank.

peller design, impeller diameter, and tank size were varied values of δ and γ were obtained by graphical estimation (Table 1). The quantity γ is a measure of power input

$$P = \gamma \left(\frac{N}{1{,}000}\right)^3 \qquad (7)$$

The values of δ and γ are for single impellers rotating at the interface with light transmission measured halfway between interface and surface. Figure 4 shows the type of original data from which these values were derived.* A plot of δ vs. γ/V relates the two (Figure 5) by the equation

$$\delta = 16\,(\gamma/V)^{0.4} \qquad (8)$$

Combining Equations (6), (7), and (8) together with the results of calibration [Equation (4)] one gets

$$e| = 16(P/V)^{0.4} = 0.028\,A \qquad (9)$$

* Tabular material has been deposited as document 6885 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

Table 2. Published Correlations of Interfacial Area in Terms of Impeller Diameter and Speed

Langlois (8)	$A = C_1 N^{1.2}$
Pavlushenko (2)	$A = C_2 N\, T^{-1.2} D^{1.65}$
Rodgers (5) (original)	$A = C_3 N^{0.72}\, T^{-0.4} D^{1.1}$
Rodgers (5) (assuming linear calibration)	$A = C_4 N^{1.15} T^{-0.6} D^{1.8}$

C_1, C_2, C_3, and C_4 are lumped constants.

Thus the interfacial area varies as the energy input rate per unit volume raised to the 0.4 power.

Since the time-honored rule-of-thumb for scaling up is to use constant power per unit volume, the result is not overwhelming. Logically the rate at which surface energy of a system tends to a minimum is counterbalanced by the rate of energy input. Also the unstable particles may be looked upon as a measure of turbulence in the system. The smaller the particle the greater the scale of turbulence. Shinnar and Church (6) recently presented an elegant discussion of these ideas.

In these experiments it appeared that power for straight, six-bladed, turbine agitators varied with $N^3 D^5$. Since the depth of liquid was always 1.2*T* (the tank diameter), the volume is proportional to T^3. Therefore one can rewrite Equation (9):

$$A = C_5\, N^{1.2}\, T^{-1.2}\, D^2 \qquad (10)$$

where C_5 is a lumped constant. This is in reasonable agreement with work by Langlois and Pavlushenko (Table 1). To write Rodgers' correlation in the same form it is necessary to assume the factors $\phi = (T/T_o)^{0.6}$ and $k = 1$. This gives the equation listed in Table 2. Furthermore if one assumes a linear relationship between area and e| instead of Equation (4), one gets the second equation listed to Rodgers in the table. However the exponent on *T* can vary from −0.2 to −1.5 and on *D* from 1.2 to 2.5, depending on the Weber number. When one takes into account differences in baffling and in kettle geometry, the agreement is poor only in terms of the exponent for *D*, which is the parameter least likely to be duplicated by separate experimenters.

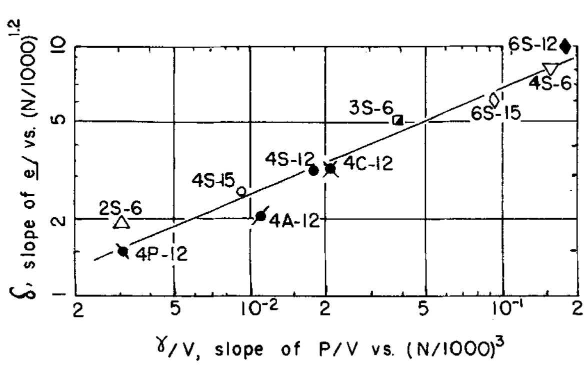

Fig. 5. Parameters measuring area (δ) and power per unit volume (γ/V) are simple related for the 2-ethylhexanol-water system investigated. Code numbers identify impeller diameter in type, straight (S), pitched-blade (A), or curved (C), turbine or propeller (P); and tank diameter in inches (approximately).

NOTATION

- *a* = exponent of *N* in Equation (5)
- *A* = interfacial area, sq.cm./cc.
- d_i = individual particle diameter, cm.
- *D* = impeller diameter, in.
- e| = extinction ratio defined by Equation (1)
- I_o, *I* = intensity of standard light beam transmitted by pure continuous phase and by suspension, respectively
- *k* = constant in Equation (5), also constant in reference (4)
- *L* = optical path length, cm.
- *N* = impeller speed, rev./min.
- n_i = number of particles of diameter d_i
- *P* = power, hp.
- *T* = tank diameter, in.
- *V* = volume, gal.

Greek Letters

- α = constant in Equation (3), $(\text{cc./cc.})^{0.2}$
- β = constant in Equation (1), (cc./sq.cm.)
- γ = constant in Equation (7), $(\text{rev./min.})^{-3}$
- δ = constant in Equation (6), $(\text{rev./min.})^{-1.2}$
- φ = volume fraction of dispersed phase, also scale-up factor in reference (4)

LITERATURE CITED

1. Langlois, G. E., J. E. Gullberg, and Theodore Vermeulen, *Rev. Sci. Inst.*, **25**, 360-3 (1954).
2. Pavlushenko, I. S., and A. V. Yanishevskii, *Zhur. Priklad. Khim.*, **32**, 1496 (1959); *Chem. Abs.*, **53**, 19, p. 479 f (1959).
3. *Ibid.*, **31**, 1348 (1958); *Chem. Abs.*, **53**, 777d (1959).
4. *Ibid.*, **31**, 1215 (1958); *Chem. Abs.*, **52**, 19, p. 342 g (1959).
5. Rodger, W. A., V. G. Trice, Jr., and J. H. Rushton, *Chem. Eng. Progr.*, **52**, No. 12, p. 515-520 (1956).
6. Shinnar, R., and J. M. Church, *Ind. Eng. Chem.*, **52**, 253 (1960).
7. Trice, V. G., Jr., and W. A. Rodger, *A.I.Ch.E. Journal*, **2**, 205-10 (1956).
8. Vermeulen, Theodore, G. M. Williams, and G. E. Langlois, *Chem. Eng. Progr.*, **51**, No. 2, p. 85F-94F (1955).
9. ELB Experimental Agitator is made by Chemineer, Inc., 1044 East First Street, Dayton 3, Ohio. See especially Bulletin 109.

Manuscript received April 10, 1961; revision received June 19, 1961; paper accepted June 21, 1961.