On the behaviour of liquid dispersions in mixing vessels

By **REUEL SHINNAR**

Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa

(Received 8 March 1960 and in revised form 26 November 1960)

The present paper is concerned with the conditions of flow in tanks containing stirred fluids. An attempt is made to apply the theoretical concepts of local isotropy to explain the behaviour of liquid in liquid dispersions, subjected to turbulent agitation. Relations describing quantitatively the influence of turbulence on both break-up and coalescence of individual droplets are derived and are compared with experimental evidence. A special type of dispersion is described in which droplet size is controlled by the prevention of coalescence due to turbulence. The dependence of droplet size on energy dissipation per unit mass, as predicted by the theory of local isotropy, is put to an experimental test using geometrically similar vessels of different sizes.

Though the results are not entirely conclusive, experimental evidence suggests that the hypothesis of locally isotropic flow may be applicable to the flow conditions described in the paper, and that statistical theories of turbulence can be of practical value in estimating droplet sizes in agitated dispersions.

Introduction

The mixing or agitation of fluids in cylindrical tanks is a common operation in chemical industry, and as such has been studied extensively. A wide variety of agitator designs is used, while conditions of flow may vary from laminar flow to fully-developed turbulence. The following discussion is limited to turbine agitators and conditions of turbulent flow only.

The behaviour of liquid-liquid dispersions in such tanks is of special interest. If two immiscible liquids are agitated, a dispersion is formed, in which continuous break-up and coalescence of droplets occur simultaneously. If the agitation is continued over a sufficiently long time, a local dynamical balance between break-up and coalescence is established. The average size of the droplets at equilibrium will then depend on the conditions of agitation, which affect the dispersion in several ways:

(*a*) droplets will be broken up in regions of high shear stress near the agitator blades;

(*b*) turbulent velocity and pressure variations along the surface of a single droplet may cause break-up;

(*c*) the turbulent flow may accelerate or slow down the coalescence of the droplets.

In an actual dispersion all three processes occur simultaneously. Break-up in regions of high shear stress should be important in very dilute dispersions, and in cases where coalescence is negligible. In cases in which coalescence is important, the influence of the local turbulent flow on the equilibrium state of the dispersion should predominate.

The phenomena mentioned under (*b*) and (*c*) are on a microscale, and the average droplet size of the dispersion is determined by what happens in a very small volume of fluid around the individual droplet. Thus the direct influence of the large-scale flow may be comparatively small. Now, a hypothesis put forward by Kolmogoroff is that, if the Reynolds number of the flow is high, the statistical properties of the flow-field in a very small volume of liquid can be estimated from a concept of local isotropy. The possibility of applying Kolmogoroff's theory to predict the droplet sizes in such dispersions is investigated here. This investigation should be of wider interest for the study of locally isotropic turbulence in general, especially as conditions of flow in stirred tanks allow the realization of very high degrees of turbulence. Such conditions are hard to obtain in wind tunnels.

A rule for the scaling-up of mixing plants from experimental results on the basis of a criterion of specific power input has been used empirically for a long time by chemical engineers. The theory of local isotropy is qualitatively closely related to such a criterion. Thus it should be expected that this theory, by putting the criterion on a more solid analytical basis, would shed new light on the range of its applicability.

For completeness, a short review of the basic concepts of local isotropy will be given, before the possibility of locally isotropic flow in a stirred tank is considered.

Kolmogoroff's theory of local isotropy

The theory of local isotropy (Kolmogoroff 1941) has been reviewed extensively (Batchelor 1947, 1953). Therefore only a short summary will be given in what follows.

Kolmogoroff has put forward the hypothesis that in any turbulent flow at sufficiently high Reynolds numbers the small-scale components of the turbulent velocity fluctuations are statistically independent of the main flow and of the turbulence-generating mechanism. The small-scale velocity fluctuations are determined by the local rate of energy dissipation per unit mass of fluid ϵ and the kinematic viscosity ν. Otherwise put, the spectrum of turbulent velocity fluctuations includes a range of high wave-numbers called the 'universal equilibrium range', which is uniquely determined by ϵ and ν. Kolmogoroff defines a length scale by

$$\eta = (\nu^3/\epsilon)^{\frac{1}{4}}, \qquad (1)$$

and a velocity scale by

$$v = (\nu\epsilon)^{\frac{1}{4}}. \qquad (2)$$

These parameters can be used to define conditions of flow in the equilibrium range instead of ϵ and ν.

For local isotropy to exist, the linear scale L of the energy-containing eddies must be large compared to the scale of the small energy-dissipating eddies η.

This implies that the Reynolds number of the flow must be high, or alternatively (cf. Batchelor 1953) that $(Lu'/\nu)^{\frac{3}{4}} \gg 1$, where u' is the root-mean-square of one component of the turbulent velocity fluctuation. If the conditions mentioned above for the existence of local isotropy are met, then in any small volume of characteristic dimension r ($\ll L$) all velocity correlations must be functions of v and η, or of ϵ and ν, only. Thus the mean-square of relative velocity $u(r)$ between any two points distance r apart† is a universal function of v and η. Furthermore, if $L \gg r \gg \eta$, then $\overline{u^2(r)}$ is independent of viscosity, and is a function of ϵ only.

In this case, and for very small values of r as well, the form of the universal function can be obtained from dimensional analysis.

$$\overline{u^2(r)} = C_1 \epsilon^{\frac{2}{3}} r^{\frac{2}{3}} \qquad \text{for} \quad L \gg r \gg \eta, \tag{3}$$

$$\overline{u^2(r)} = C_2 \epsilon r^2/\nu \qquad \text{for} \quad L \gg \eta \gg r. \tag{4}$$

The range of values of r for which (3) applies is called the 'inertial subrange'. In order for an inertial subrange to exist, $(Lu'/\nu)^{\frac{3}{8}}$ must be large compared to unity. Under the experimental conditions generally used for the study of turbulence in the laboratory, it is very difficult to satisfy the above conditions, and therefore few data proving the existence of local isotropy in the inertial subrange are available. The possibility of obtaining very high values of ϵ and of $u'L/\nu$ in a mixing tank should therefore be of interest for the study of locally isotropic turbulence.

Conditions of flow in stirred tanks

Local isotropy is possible with different types of agitators. However, the discussion will be limited to paddle and turbine agitators, because of their simple design and wide application. A typical agitator of this type is shown in figure 1. The mixing vessel is equipped with flow baffles to prevent the establishment of a vortex around the agitator shaft (avoidance of the influence of Froude number). The same effect can be obtained by excluding air from the vessel and filling it completely with liquid. The conditions of turbulence in such a mixing vessel can be predicted from a modified Reynolds number ND^2/ν, where D is the diameter of the agitator and N is its speed in revolutions per second. Fully developed turbulence (in the region of the agitator) exists with such agitators if this modified Reynolds number is higher than 10^4. It has been shown experimentally that for high Reynolds numbers the energy input of the mixing impellor per unit mass of liquid in the vessel is independent of the properties of the liquid, and a function only of the geometrical design of the agitator and its speed (Rushton *et al.* 1950). In geometrically similar vessels the average energy dissipation $\bar{\epsilon}$ in the liquid must therefore be a function of N and D only, and by dimensional analysis one can derive

$$\bar{\epsilon} = KN^3D^2. \tag{5}$$

Here K is a dimensionless constant dependent on the geometry of the vessel and the agitator only.

---

† u can be taken as the component of relative velocity parallel to the line joining the two points; similar results can be stated for other components of the relative velocity.

The knowledge of the average energy dissipation is not sufficient to determine the dependence of local values of ϵ on N and D, unless the distribution of the main flow velocity in the tank is universal. That means that the ratio of the average flow velocities at any two points is constant, and independent of Reynolds number and fluid properties. In this case only can it be assumed that the distribution in space of ϵ is universal also, and all local values of ϵ are then directly proportional to $\bar{\epsilon}$. Thus

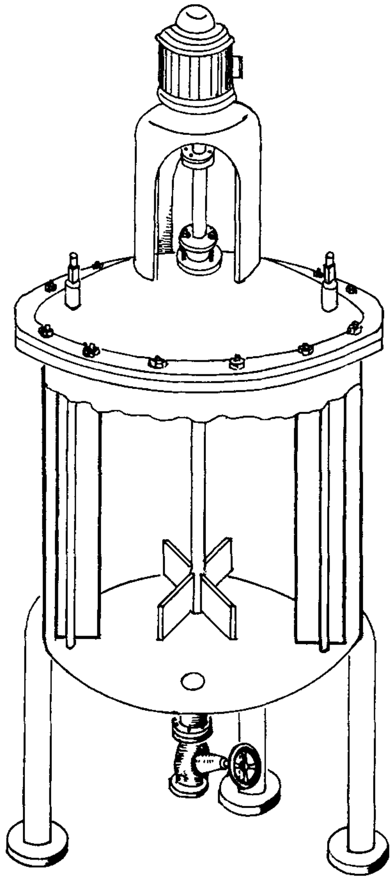


FIGURE 1. Sketch of a turbine mixer.

$$\epsilon(x,y,z) = K'(x,y,z)\,N^3D^2. \tag{6}$$

The dimensionless factor K' is an experimentally determinable function of the co-ordinates of any point in the vessel.

The velocity distribution in mixing tanks of this type has been experimentally investigated by Rushton & Sachs (1954) and by Aiba Schuichi (1958), and was found to be universal at Reynolds numbers above 10^4 with the equipment used. It is of particular interest to note that the velocity distribution in the liquid jets leaving the agitator blades was also found to be universal, whereas in a free jet the distribution becomes universal only at large distances from the origin.

Though the mixing action of a turbine agitator has often been compared to that of a free jet in stagnant surroundings, there is a basic difference between the two cases. While liquid entering the agitator is already highly turbulent, in a jet fully developed turbulence exists only at a comparatively large distance from the origin.

Taking into consideration the above discussion, it is permissible to conclude that, in an agitated fluid, statistical equilibrium is possible at any location in the liquid.

The requirements for the existence of local isotropy in a mixing tank can be fulfilled, though the flow is definitely non-isotropic. Experimentally, the realization of Reynolds numbers of several millions and local values of ϵ above 10^6 are feasible. Thus, for $\bar{\epsilon} = 10^6\,\mathrm{cm}^3/\mathrm{sec}^2$ and $\nu = 1$ centistoke, η becomes equal to 10 microns. The Reynolds number of turbulence (Lu'/ν) in this case will be approximately 8500 for $L = 5\,\mathrm{cm}$, and 75,000 for $L = 25\,\mathrm{cm}$. Thus even for relatively small L, L/η will be very large.†

The flow around a turbine agitator should therefore furnish experimental evidence as to the validity of the concepts of local isotropy. However, one practical difficulty is that a reliable instrument for the detection and measurement of turbulent velocity fluctuations is not yet available for use with liquids.

Some indirect experimental evidence, however, can be obtained by measuring the droplet size distribution of agitated dilute dispersions of two immiscible liquids.

Break-up and coalescence of liquid dispersions in turbulent flow

If a dilute liquid-liquid dispersion is exposed to turbulent flow conditions, simultaneous coalescence and break-up occur. If the dispersion remains in a quasi-stationary flow-field for a sufficient duration, a dynamical equilibrium between coalescence and break-up is established. It is possible to predict from simple theoretical considerations the influence of the turbulent velocity fluctuations on both break-up and coalescence. The case of break-up has been treated previously by Kolmogoroff (1949) and Hinze (1955). The equations for prevention of coalescence were derived by Shinnar & Church (1960).

(a) *Break-up of droplets*

Consider a small volume of fluid in which turbulence is locally isotropic. Any of the droplets in this volume will be exposed to both inertial forces due to velocity fluctuations and to viscous shear forces. If the droplet is much larger than the microscale η, viscous forces can be neglected. In this case the droplet will oscillate about its spherical equilibrium shape concurrently with the surrounding fluid, provided the densities and viscosities of both liquids are not much different. If the deformations are large, the droplets become unstable and break up into two or more smaller fragments. But in order to become unstable, the kinetic energy of the oscillations must be sufficient to provide the gain in surface energy

---

† In order to calculate the Reynolds number of turbulence defined above, the macroscale of turbulence L must be known. Though L has not been determined, its order of magnitude should be comparable to the width of the agitator blades.

due to the break-up. The kinetic energy of the oscillating droplet may be assumed proportional to $\rho \overline{u^2(d)}\, d^3$, where $\overline{u^2(d)}$ is the mean-square of the relative velocity fluctuations between two diametrically opposite points on the surface of the droplet. The minimum gain in surface energy is approximately proportional to σd^2. The value of the ratio between these two energies $(\rho \overline{u^2(d)}\, d/\sigma)$ is called the Weber number. The critical value of this ratio at which break-up occurs is dependent on the number of droplets formed as a result of the break-up. This critical value should be constant for any given system, though it may vary for different liquids.

In locally isotropic flow the average mean-squared velocity between two points is given by equations (3) and (4), and therefore the Weber number of a droplet, the diameter of which is much larger than η, becomes

$$We = \frac{\rho \overline{u^2(d)}\, d}{\sigma} = \frac{\rho C_1 \bar{\epsilon}^{\frac{2}{3}} d^{\frac{5}{3}}}{\sigma}. \tag{7}$$

The relation $\bar{\epsilon} = KN^3D^2$, which was obtained from other evidence, has been discussed in connexion with equation (5). Thus the value of the maximum stable droplet diameter can be obtained from the relation

$$\rho C_1 K^{\frac{2}{3}} N^2 D^{\frac{4}{3}} d^{\frac{5}{3}} \sigma^{-1} = \text{constant}. \tag{8}$$

Equation (8) should apply only to cases in which the maximum diameter obtained is larger than η.

In contrast to the above, if σ is very small or ν is rather large, as for instance for some emulsions, the maximum stable droplet diameter will be smaller than the microscale η. In this case the viscous shear forces cannot be neglected any longer, as the stresses due to viscous shear will be much larger than those due to inertial effects. The corresponding equation for the break-up of a droplet, due to viscous shear only, was derived by Taylor (1932):

$$\mu_c \frac{\partial u}{\partial r} \frac{d}{\sigma} = \Phi\left(\frac{\mu_d}{\mu_c}\right), \tag{9}$$

where Φ is a certain function, and the suffices c and d refer to the continuous and dispersed phases. In locally isotropic flow $(\partial u/\partial r)^2 = 2\epsilon/15\nu$. Therefore equation (9) now becomes

$$\frac{\mu_c \bar{\epsilon}^{\frac{1}{2}} d}{\nu_c^{\frac{1}{2}} \sigma} = \frac{\mu_c K^{\frac{1}{2}} N^{\frac{3}{2}} D d}{\nu_c^{\frac{1}{2}} \sigma} = \Phi\left(\frac{\mu_d}{\mu_c}\right). \tag{10}$$

This equation should describe the breakup of droplets in emulsions, whenever $d < \eta$.[†]

[†] Kolmogoroff has suggested for this case, in analogy with equation (7), that

$$\frac{\rho \overline{u^2(d)}\, d}{\sigma} = \frac{\rho C_2 \bar{\epsilon} d^3}{\nu \sigma} = \phi\left(\frac{\mu_d}{\mu_c}\right),$$

where ϕ is an unknown function. It should be pointed out, however, that, if $d \ll \eta$, then the viscous shear forces should be *much* larger than the inertial forces, which are given by $\rho \overline{u^2(d)}$.

(*b*) *Coalescence of droplets*

In an agitated dispersion, the rate of coalescence of droplets may be accelerated or slowed down by turbulence, depending on the physical properties of the constituents of the system.

Local velocity fluctuations will increase the rate of collisions between droplets and thereby increase the chance of coalescence. However, it is well known that only a small number of collisions result in immediate coalescence. This is so because a thin film of liquid, trapped between two colliding droplets, acts as an elastic cushion and may cause the droplets to recoil. If the two droplets adhere to each other, the thickness of the film separating them will gradually decrease due to diffusion. When the film has thinned down sufficiently, the boundary between the two droplets may collapse. However, turbulent velocity fluctuations may meanwhile communicate sufficient energy to the two droplets to cause re-separation, before coalescence has occurred. This effect will be enhanced if the time needed for the thinning down of the film is artificially increased, for instance by adding a protective colloid to the dispersion. This may be pushed to the point of complete prevention of coalescence in turbulent flow. Coalescence of such a dispersion will, of course, take place rapidly if agitation is stopped.

The effectiveness of the prevention of coalescence as described above is found to be a function of individual droplet diameters, since the forces of adhesion and those of inertia are different functions of droplet diameter. Hence, for very small droplets, turbulent energy input into a droplet pair may be insufficient to overcome the adhesion energy barrier.

The droplet diameter $d_{\min}$, for which the energy due to turbulent velocity fluctuations is equal to the energy of adhesion, depends on the intensity of agitation defined by $\bar{\epsilon}$, and also, naturally, on the physical properties of the constituents. This droplet diameter can be estimated as follows.

The force of adhesion between any two droplets of respective diameters d_1 and d_2 is given by

$$F(h_0) = \frac{\pi d_1 d_2}{d_1+d_2}\int_{h_0}^{\infty} f(h)\,dh. \tag{11}$$

Here h_0 is the smallest distance between the two droplets, i.e. h_0 is actually the thickness of the 'films' separating them; h_0 is zero when the droplets touch each other; $f(h)$ is the force of attraction per square centimetre between two infinite parallel surfaces separated by a distance h (Bradley 1932; Deryaguin *et al.* 1934). The energy of adhesion E_a can be calculated from equation (11) by

$$E_a = \int_{h_0}^{\infty} F(h')\,dh' = \pi\int_{h_0}^{\infty}\int_{h}^{\infty}\frac{d_1 d_2}{d_1+d_2} f(h)\,dh\,dh', \tag{12}$$

$$= 2\frac{d_1 d_2}{d_1+d_2}A(h_0), \tag{12a}$$

where $A(h_0)$ is defined by

$$\tfrac{1}{2}\pi\int_{h_0}^{\infty}\int_{h}^{\infty} f(h)\,dh\,dh'$$

and is the energy necessary to separate completely two droplets of unit diameter initially separated by the minimum distance h_0. If the two droplets are of equal diameter, equation (12*a*) simplifies to

$$E_a = A(h_0)\,d. \tag{13}$$

The kinetic energy of two droplets of diameter d in movement relative to each other is proportional to $\rho\,\overline{u^2(d)}\,d^3$. As already stated, this must be larger than the energy of adhesion in order to prevent coalescence. The drop diameter for which separation is still possible in a given fluid is therefore given implicitly by

$$\frac{\rho\,\overline{u^2(d)}\,d^2}{A(h_0)} = \text{constant.} \tag{14}$$

In locally isotropic flow $\overline{u^2(d)} = C(\epsilon d)^{\frac{2}{3}}$ [see equation (3)], and so (14) may be written as

$$C_1 \rho \epsilon^{\frac{2}{3}} d^{\frac{8}{3}} / A(h_0) = \text{constant.} \tag{15}$$

For fluid stirred in a tank at constant power number, this is equivalent to

$$C_1 \rho K^{\frac{2}{3}} N^2 D^{\frac{4}{3}} d^{\frac{8}{3}} / A(h_0) = \text{constant.} \tag{16}$$

Both $A(h_0)$ and h_0 are constant and independent of the droplet diameter d in any given dispersion as long as h_0/d is small. However, the numerical values of these constants are difficult to estimate from the properties of the system. For a given pair of fluids, $A(h_0)$ is constant, and equations (15) and (16) may be applied to predict the dependence of $d_{\min}$ on $\bar{\epsilon}$.

The considerations set out above do not apply if the maximum diameter defined by equation (8) is *smaller* than the diameter as given by equation (16), for then separation of adhering droplets by turbulent agitation becomes insignificant. Thus droplets in the dispersion fuse rapidly until the diameter of the drop formed reaches the unstable size for *break-up*, and then fragmentation into several smaller droplets becomes probable. The process restarts with coalescence. The size distribution is determined by the state of dynamical equilibrium reached.

In figure 2 the maximum stable droplet diameter as determined by the process of break-up, and the minimum stable droplet diameter as determined by the process of coalescence, are plotted against agitator speed. This latter quantity is proportional to $\epsilon^{\frac{1}{3}}$.

From this figure it is apparent that prevention of coalescence due to turbulent velocity fluctuations in the bulk liquid is of importance in the region to the left of the point of intersection between the two lines plotted on the graph, while being relatively unimportant to the right of this point. The value of $\bar{\epsilon}$ at which the two lines intersect depends on the physical properties of the constituents. The existence of such a critical value has been confirmed experimentally as will be seen later.

(*c*) *Simultaneous break-up and coalescence*

In practice, the size distribution of droplets in an agitated dispersion is determined by both break-up and coalescence occurring simultaneously. The diameters defined in equations (8) and (16) are in reality statistical averages; in the case of

(8), of the droplet size for which break-up most probably occurs, and in the case of (16), of the droplet size above which prevention of coalescence becomes effective. From the plots of the dependence of d on ϵ some conclusions as to which of the two processes predominates in the dispersion can be drawn. In addition, it is possible to conclude that in cases where locally isotropic flow may be assumed to exist, droplet size distribution is a function of energy dissipation and the physical properties of the constituents only.

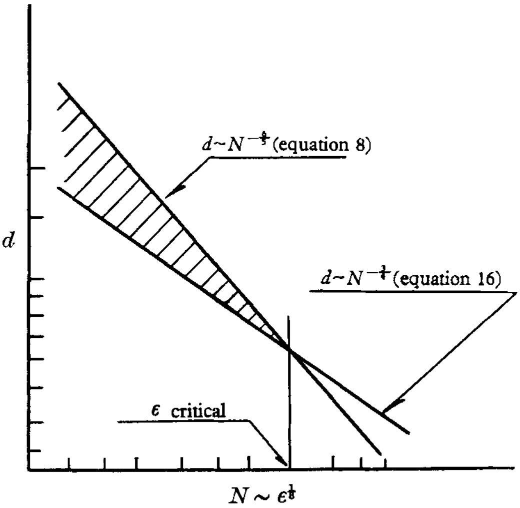


FIGURE 2. Logarithmic plot of droplet diameter as a function of agitator speed. Equation (8): d controlled by breakup; equation (16): d controlled by prevention of coalescence.

The reasoning set out above provides the limitations to the empirical engineering rule of scaling-up mixing plants. As already mentioned above, this rule is based on a specific energy input per unit mass criterion. Thus this criterion, which of course applies only approximately, can safely be applied to all those cases where (*a*) local isotropy is expected to exist, (*b*) the main influence of turbulent agitation is confined to the vicinity of a small particle or droplet, and (*c*) the influence of the large-scale flow (gross mixing) may be neglected.

There exist some special dispersions in which prevention of coalescence is the factor determining droplet size; this can be shown by experimental evidence unrelated to the above. As already mentioned, the addition of a protective colloid to the dispersion may slow down coalescence. Dispersions can be prepared in which no break-up or coalescence will occur as long as constant agitation is maintained, and individual droplets are completely stable for many hours of agitation. This effect can be shown very convincingly by colouring part of the droplets: it will be found that under these special conditions the coloured droplets will retain their original colour without sharing this with other droplets. Also, droplet sizes will be distributed in a relatively narrow band. The sizes will again depend on agitation, and a reduction in agitator speed will lead to a different size distribution in equilibrium. If a stable equilibrium is again attained at the reduced agitator speed, the colour tracer method may again be used to show that no further intermixing does occur.

For these special dispersions, the term 'turbulence-stabilized dispersions' has been suggested by the author, and a detailed discussion of the properties of such dispersions has been given (Shinnar & Church 1961).

Experimental evidence

Several authors have studied experimentally the behaviour of two immiscible liquids when agitated together (Magnusson 1954; Vermeulen, Williams & Langlois 1955; Shinnar 1957; Shinnar & Church 1961). Their results will be discussed below. In addition, some new experimental evidence obtained by the author is given.

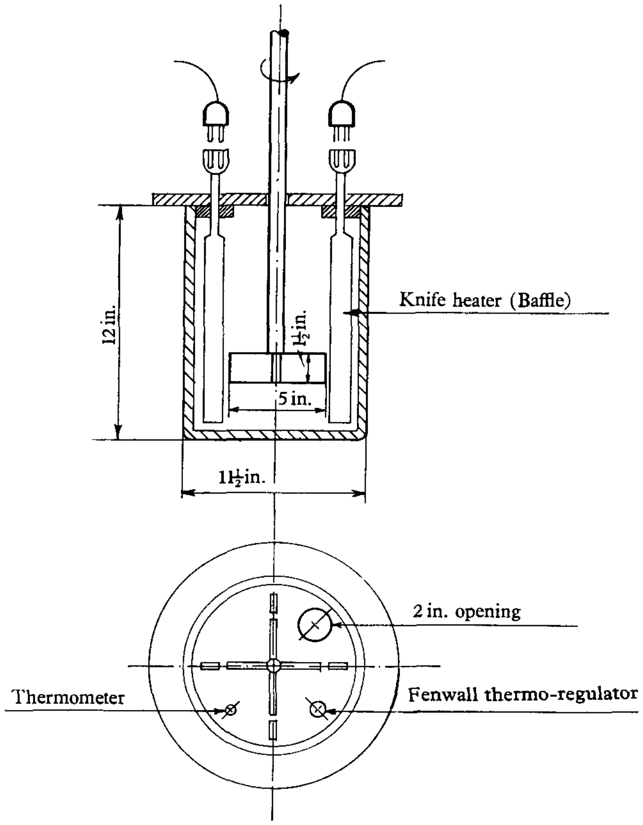


FIGURE 3. Schematic diagram of the mixing-tank used by Shinnar & Church in their experiments.

Shinnar & Church dispersed a molten microcrystalline wax in hot water to which polyvinylalcohol had been added as a protective colloid. By syphoning off small samples and freezing these rapidly, droplet size distributions could be obtained by microscopic inspection. The experimental arrangement used is shown in figure 3. The behaviour of single droplets was studied by adding small quantities of coloured wax to the dispersion as a tracer. It was found that under certain conditions the agitated dispersion was stable to such a degree that no intermixing occurred even after 12 hr of continuous operation of the agitator.

However, whenever agitator speed was reduced, coalescence took place at once, and proceeded until after about 2 hr a new stable equilibrium was established, and no further intermixing and coalescence occurred. This was taken to indicate that droplet size in such dispersions is determined by the prevention of coalescence by turbulence; thus (16) should apply to these dispersions. Figure 4 shows the appearance of samples of dispersions stabilized at different agitator speeds. Samples were taken from various points in the mixing tank, and no variation of droplet size with location could be detected.

In figures 5 and 6 average droplet sizes are plotted against agitator speed for some typical experiments with two different protective colloids. The droplet diameter given in these figures is the Sauter mean diameter defined by $d_{32} = \Sigma nd^3/\Sigma nd^2$, where d is the diameter of each droplet and n is the number of droplets in each size group. The use of a mean diameter instead of a maximum or minimum diameter as employed above appears permissible, as the spread of the size distribution curves is small and the curves are all of similar shape. Table 1 lists all size distributions for the experimental points plotted in figure 6. The ratio of $d_{\max}$ and $d_{\min}$, which are defined so that 90 % of the cumulative volume of all droplets have a diameter smaller than $d_{\max}$ and 10 % are smaller than $d_{\min}$, is fairly constant and its value is about two. It is only at 627 r.p.m. that this ratio increases slightly to a value of about three, but as will be explained later the dispersion was not 'stable' at this agitator speed.

All points plotted on figures 5 and 6 were tested for stability by the tracer method and the results are indicated in the figure. The assumption that prevention of coalescence by turbulence controls droplet size is of course justified only for those points for which no intermixing of the tracer wax occurred. For these points the results are in reasonable agreement with (16). One of the stabilizers tested (figure 6) gave rise to dispersions in which the existence of a critical agitator speed could be experimentally checked. Thus at 627 r.p.m. the dispersion behaved as if no protective colloid were present and the tracer wax became completely dispersed after only 10 min of agitation, even though at lower agitator speeds no intermixing could be detected after as long as 12 hr of continuous agitation. When the concentration of the protective colloid was increased by as much as fivefold, rapid intermixing was not prevented, though analysis of the water phase showed that a large excess of free colloid was present. It may therefore be assumed that 627 r.p.m. was above the critical agitator speed in these dispersions and for the experimental arrangement used.

All experimental results given by Shinnar & Church were obtained from tests carried out with the same equipment. To test the validity of (16) for scaling-up purposes another series of experiments with turbulence-stabilized dispersions was carried out by the author. Two sets of similar tanks and impellors were employed, the dimensions of which are given in figure 7. A Pfaudler type turbine-agitator was used instead of the flat-blade turbine shown in figure 3 as two sets of such agitators were available. Test results are plotted in figure 8 where droplet sizes are given as functions of N^3D^2. The agreement with theory is seen to be quite good.

It should be pointed out that in the experiments described above the agitator chosen was large in comparison with the mixing vessel. Thus the influence of agitation extended to all parts of the mixing tank. Smaller agitators may be expected to give much less uniform agitation, and in such cases droplet sizes

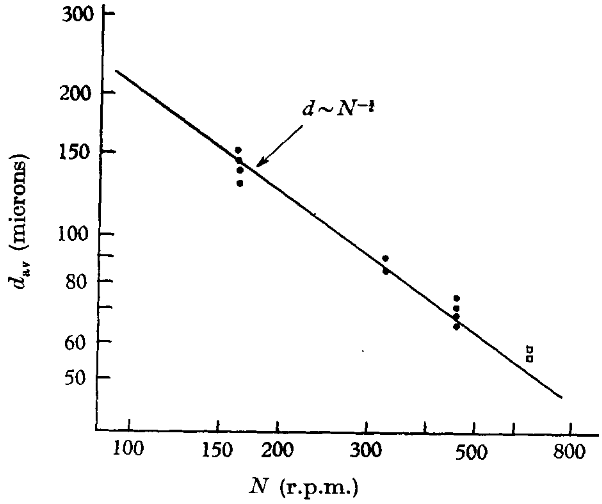


FIGURE 5. Average droplet size as a function of agitator speed in a turbulence-stabilized dispersion (droplet size controlled by prevention of coalescence). Experimental arrangement shown in figure 3. Dispersion used: 5 % molten wax (Shellwax 700) in hot water containing 0·1 % polyvinylalcohol (Du Pont Elvanol 51–05 low molecular weight). Viscosity $\nu_c = 0{\cdot}35$ centistokes; $\nu_d = 22{\cdot}5$ centistokes. Results of colour tracer test indicated on plot as follows: ●, no visible intermixing after 2 hr; ☐, partial intermixing after 2 hr.

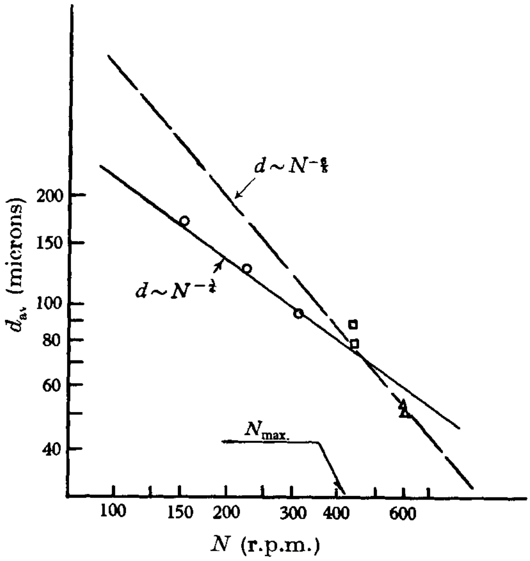


FIGURE 6. As in figure 5. Dispersion used: 5 % molten wax (Shellwax 700) in hot water containing 0·1 % polyvinylalcohol (Du Pont Elvanol 50–42 high molecular weight). Viscosity $\nu_c = 0{\cdot}4$ centistokes, $\nu_d = 22{\cdot}5$ centistokes. Results of colour tracer test indicated on plot as follows: ○, no visible intermixing after 2 hr; ☐, partial intermixing after 2 hr; △, rapid intermixing.

r.p.m. ...	156		220		312		440		440		627		627	
d_{av} (microns)	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
15	—	—	10	0·002	14	0·005	65	0·035	95	0·10	410	1·90	334	1·6
30	61	0·07	25	0·038	75	0·205	135	0·605	183	1·55	297	11·30	310	12·0
45	—	—	47	0·240	87	0·81	175	2·51	179	5·15	210	27·0	199	26·0
60	67	0·81	79	0·97	171	3·83	195	6·9	255	17·40	95	29·2	98	30·4
75	—	—	115	2·77	258	11·35	164	11·2	121	16·05	21	12·6	24	14·5
90	83	2·43	165	6·85	281	21·2	211	25·2	114	26·1	7	7·2	11	11·5
105	—	—	201	13·1	293	35·1	141	26·6	55	20·0	3	4·9	1	1·6
120	127	8·80	177	17·3	101	18·1	65	18·4	18	9·75	1	2·44	1	2·4
135	—	—	127	17·7	21	5·3	15	6·2	1	0·78	1	3·46	—	—
150	171	23·1	113	21·6	8	2·8	3	1·65	3	3·12	—	—	—	—
165	—	—	35	8·9	3	1·3	1	0·70	—	—	—	—	—	—
180	111	26·0	20	6·6	—	—	—	—	—	—	—	—	—	—
195	—	—	8	3·4	—	—	—	—	—	—	—	—	—	—
210	34	12·6	1	0·53	—	—	—	—	—	—	—	—	—	—
225	—	—	—	—	—	—	—	—	—	—	—	—	—	—
240	23	12·7	—	—	—	—	—	—	—	—	—	—	—	—
255	—	—	—	—	—	—	—	—	—	—	—	—	—	—
270	16	12·4	—	—	—	—	—	—	—	—	—	—	—	—
285	—	—	—	—	—	—	—	—	—	—	—	—	—	—
300	1	1·09	—	—	—	—	—	—	—	—	—	—	—	—
$d_{3,2}$	177		127		97		91		79		53		51	
d_{max}	265		174		135		130		115		98		92	
d_{min}	128		96		75		68		57		34		35	
d_{max}/d_{min}	2·07		1·82		1·80		1·91		2·02		2·88		2·63	

TABLE 1. Size distribution of dispersion of figure 6

A, number of particles in size group; *B*, volume percentage of particle class; d_{av}, average diameter in size group.

may not be independent of location in the tank. Furthermore, complete prevention of coalescence due to turbulence may no longer be possible. No quantitative criteria for a minimum agitator size (compared with tank size) have as yet been established. The problem is currently under investigation.

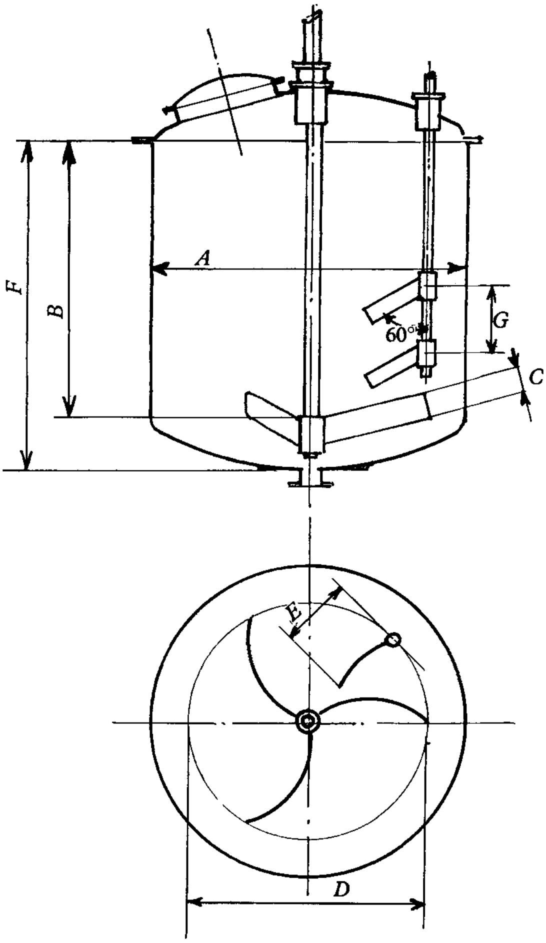


FIGURE 7. Experimental arrangement used for testing scaling-up relations in author's experiments. Dimensions in mm.

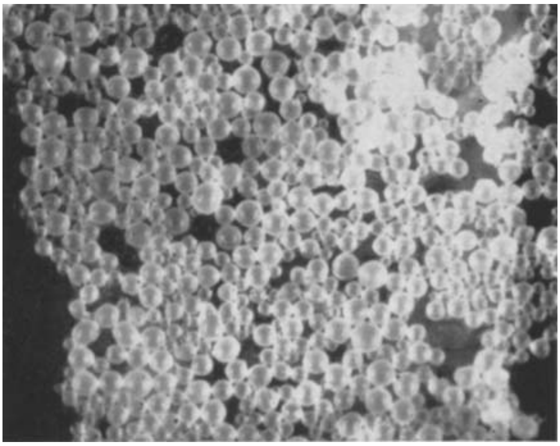
	A	*B*	*C*	*D*	*E*	*F*	*G*
Large vessel	1220	1064	102	914	274	1270	254
Small vessel	305	266	25·5	228·5	68·5	317·5	83·5

Vermeulen determined average droplet sizes in agitated dispersions indirectly by measuring the amount of light scattered. A wide range of different combinations of two liquids was studied. The concentration of the dispersed liquid was varied from 10 to 40 %.

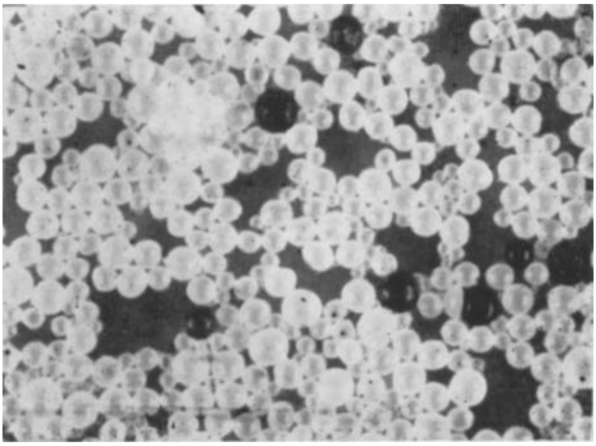
Vermeulen's results were correlated by the following empirically derived equation

$$\rho N^2 D^{\frac{4}{3}} d^{\frac{5}{3}} \sigma^{-1} = 0{\cdot}016, \tag{17}$$

which is identical to equation (8) derived in the present paper analytically. The deviation of Vermeulen's experimental data from (17) was about ±40 %.



(*a*)



(*b*)

FIGURE 4. Photomicrograph of frozen samples of turbulence-stabilized dispersions; results of colour tracer tests (experimental conditions and results given in figure 6). Magnification × 20. (*a*) Dispersion agitated at 220 r.p.m. 4 hr. after addition of red-coloured wax. (*b*) Same dispersion as in (*a*), agitated at 156 r.p.m. 4 hr after addition of red-coloured wax.

However, the comparatively large scatter could be explained if it is borne in mind that a number of these tests were carried out at conditions where the above theory does not apply (relatively low Reynolds numbers, high concentration of the dispersed phase, etc.). If only dilute dispersions of liquids of low viscosity are considered, the scatter of the experimental results is found to be much reduced. Some typical results are given in figure 9. The curve of d *vs* N on the log-log plot is seen to be concave upwards at low agitator speeds. For all liquids agreement with (17) is better at higher speeds. The extension of Vermeulen's tests to cover a large range of mixing-vessel dimensions and the measurement of droplet size distributions (instead of average droplet sizes only) should be of great interest. Rodger, Trice & Rushton (1956) measured droplet sizes in agitated liquid-liquid dispersions, using equal volumes of both liquids. Technique and experimental conditions were similar to Vermeulen's, but both agitator and mixing-vessel dimensions were varied. A complicated equation relating droplet size to agitator speed, liquid properties and the dimensions of both agitator and vessel was empirically derived from these tests. This equation is quite different from the correlation proposed by Vermeulen. For any one pair of liquids and geometrically similar agitators this equation reverts practically to (16). Rodger's formula predicts droplet sizes to be a function of $N^{-\frac{19}{25}}$ as compared to $N^{-\frac{3}{4}}$ in (16). In

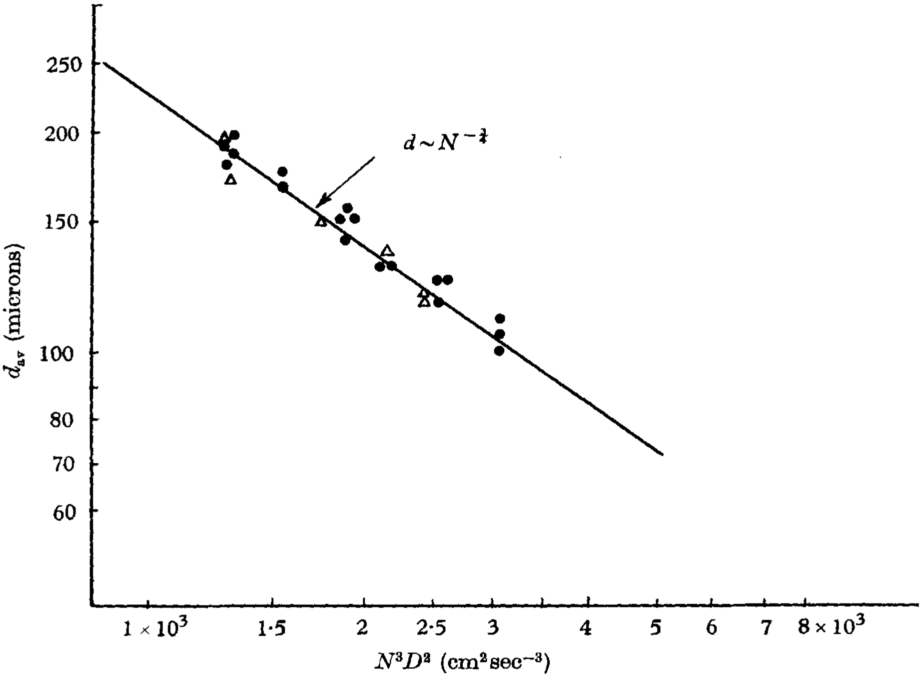


FIGURE 8. Average droplet size in mixing vessels of various sizes for a turbulence-stabilized dispersion. Dimensions of both vessels and agitators given in figure 7. Dispersion used: 5 % molten wax (Shellwax 700) in water containing 3 % polyvinylalcohol (Du Pont Elvanol 50–42 high molecular weight). All points were tested by colour tracer method and no visible intermixing could be detected after 2 hr. ●, Small vessel; △, large vessel.

geometrically similar vessels of different dimensions, equal droplet sizes are predicted approximately at equal energy input per unit mass; this applies only to the range over which experiments were actually performed.

A possible explanation for the difference in the experimental results obtained by Vermeulen and Rodger could be that, in the first set of experiments, break-up of droplets is the determining factor, whereas in the second set slowing up of coalescence due to turbulence controls droplet size. Though it is questionable whether (16) is applicable to concentrated dispersions, as used by Rodger, the agreement with (16) is interesting to note.

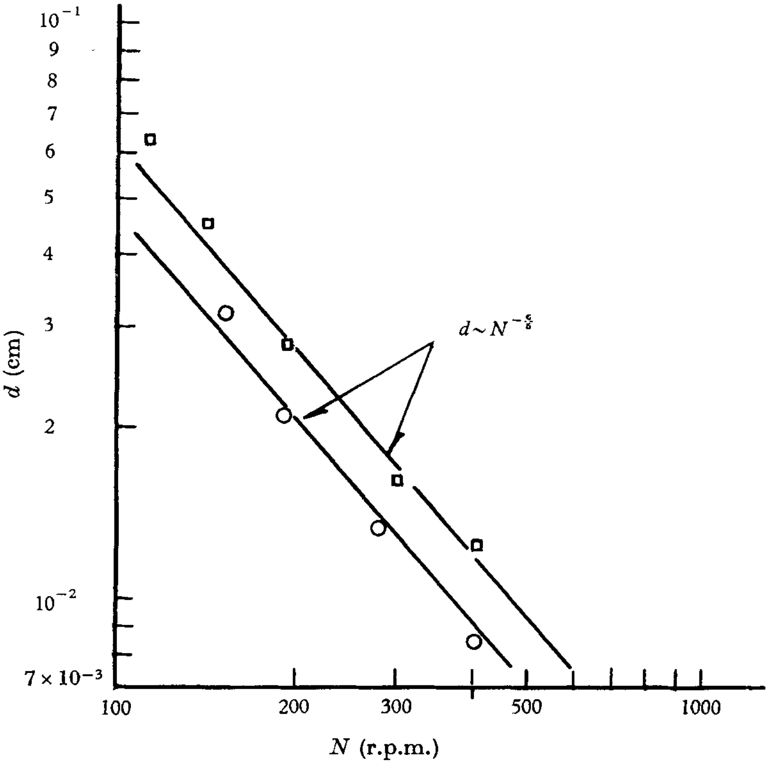


FIGURE 9. Droplet size as a function of agitator speed, d controlled by break-up. Data from Vermeulen *et al.* □, 10 % dispersion of kerosene in water; ○, 10 % dispersion of an iso-octanol carbon tetrachloride mixture in water.

Magnusson (1954) studied agitation power requirements for oil-in-water dispersions in mixing vessels of various sizes and found the energy per unit mass needed to be approximately constant. However, droplet sizes were not determined directly. The time needed for coalescence of a sample of each dispersion was used as a criterion for the state of mixing. Comparison with other data is therefore difficult.

Equation (7) for break-up was applied by Kolmogoroff (1949) to droplet sizes in a pipe in order to provide experimental evidence for his theory of local isotropy. The data were obtained at relatively low Reynolds numbers and were found to be non-conclusive, as droplet diameter was found to be proportional to U^{-1}

and not to $U^{-\frac{6}{5}}$ (here U is the mean bulk velocity). Hinze (1955) applied equation (7) to Clay's data (1940) on dispersions agitated between rotating cylinders, but again the scatter is much larger than in Vermeulen's tests.

There is as yet no experimental evidence justifying the application of equation (10) to dispersions in which $d \ll \eta$. It is therefore interesting to note that (10) describes to a good approximation the equilibrium size distribution of gas bubbles in a liquid agitated by a turbine agitator. In such a case the size distribution of the gas bubbles reaches an equilibrium value which depends on the intensity of the agitation and the physical properties of the system. Vermeulen *et al.* (1955) measured bubble sizes of different gases in water and other liquids with the same experimental arrangement used to measure droplet sizes in agitated liquid-liquid dispersions, and obtained the following dimensionless correlation

$$\frac{N^{\frac{3}{2}} D d \rho_c^{\frac{1}{2}} \mu_d^{\frac{3}{4}}}{\sigma \mu_c^{\frac{1}{4}}} = \text{constant}. \tag{18}$$

This may be rewritten as

$$\frac{N^{\frac{3}{2}} D d \mu_c}{\nu_c^{\frac{1}{2}} \sigma} \propto \left(\frac{\mu_c}{\mu_d}\right)^{\frac{3}{4}}. \tag{18}$$

Equation (18) is identical with (10). However, this problem is of much greater complexity, because of the large difference in densities of the two fluids, and no definite conclusions can be drawn at the present stage.

The author is indebted to Mr Z. Rotem for reading the manuscript and for some useful suggestions.

REFERENCES

Batchelor, G. K. 1947 *Proc. Camb. Phil. Soc.* **43**, 533; **47**, 359.

Batchelor, G. K. 1953 *The Theory of Homogeneous Turbulence.* Cambridge University Press.

Bradley, R. S. 1932 *Phil. Mag.* **13**, 853.

Clay, P. H. 1940 *Proc. K. Akad. Wet. Amst.* **43**, 852 and 979.

Deryaguin, B. *et al.* 1934 *Kolloidzschr.* **69**, 135.

Hinze, J. O. 1955 *Amer. Inst. Chem. Eng. J.* **1**, 289.

Kolmogoroff, A. M. 1941 *C.R. Acad. Sci. U.R.S.S.* **30**, 301 and **32**, 16.

Kolmogoroff, A. M. 1949 *Dokl. Akad. Nauk, S.S.S.R.* **66**, 825.

Magnusson, K. 1954 *Chem. Proc. Engng,* **35**, 276.

Rodger, W. A., Trice, V. G. & Rushton, J. H. 1956 *Chem. Engng Progr.* **52**, 515.

Rushton, J. H. & Sachs, J. P. 1954 *Chem. Engng Progr.* **50**, 597.

Rushton, J. H. *et al.* 1950 *Chem. Engng Progr.* **46**, 395–497.

Schuichi, Aiba 1958 *Amer. Inst. Chem. Eng. J.* **4**, 485.

Shinnar, R. & Church, J. M. 1960 *Ind. Engng Chem.* **52**, 253.

Shinnar, R. & Church, J. M. 1961 (To be published.)

Shinnar, R. 1957 Doctoral thesis, Columbia University.

Taylor, G. I. 1932 *Proc. Roy. Soc.* A, **138**, 41.

Vermeulen, Th., Williams, G. M. & Langlois, G. E. 1955 *Chem. Engng Progr.* **51**, 85F.