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Turbulence and Surface Renewal at the Clean Surface of a Stirred Vessel

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INTRODUCTION

Whether the clean free surface of an agitated liquid is truly turbulent (i.e., undergoing random fluctuations) is of considerable importance (Davies, 1971); in particular, the distribution of residence times of elements of liquid at the surface has been widely discussed. Higbie (1935) proposed a single residence time, while the theory of Danckwerts (1951) was based on an exponential distribution of residence times.

Direct experimental tests of the residence time distribution have been lacking, though indirect gas absorption studies (Springer and Pigford, 1970) and experiments using radioactive tracers in a liquid stream projected towards a free surface (Davies, 1980) have suggested that the Danckwerts distribution function is indeed physically realistic.

The present work involves direct meaurements of the turbulence parameters of the liquid in the plane of the surface at the surface of a stirred vessel. The distribution of the residence times of eddies is obtained from these experimental results by use of the appropriate autocorrelation functions. The latter describes the turbulence by correlations between the flows (at a given point) after various delay times Δt. For a random process, the correlation will be a maximum at $\Delta t = 0$, decreasing monotonically to zero at large times. This is the general pattern we have observed (Figure 1). We now proceed to derive the distribution of eddy residence times from these measured autocorrelations.

THEORY

The autocorrelation coefficient of velocity with respect to time, $Q(\Delta t)$, is defined as:

$$Q(\Delta t) = \overline{v_x'(t) \cdot v_x'(t + \Delta t)} \qquad (1)$$

where the overbar refers to the mean value, the prime to fluctuations, and subscript x to flow in the plane of the surface. It is convenient to normalize $Q(\Delta t)$ by dividing by the mean square of the fluctuation velocity:

$$Q^*(\Delta t) = Q(\Delta t)/\overline{(v_x')^2} \qquad (2)$$

The time macroscale t_L is the mean time over which an observed fluctuation is correlated with itself, and in the mean time of persistence of the larger (energy containing) eddies, before they are replaced by another large eddy. The time t_L is defined by:

$$t_L = \int_0^\infty Q^*(\Delta t) d(\Delta t) \qquad (3)$$

and is a measure of the average time for which each eddy persists in the surface region under study.

The fractional disappearance of the original eddies after time t is then given by:

$$\text{fractional disappearance of original eddies} = (1/t_L) \int_0^t Q^*(\Delta t) d(\Delta t) \qquad (4)$$

This is our model (assuming turbulence theory) for the nonpersistence of eddies in the immediate vicinity of the surface. We now compare this model with the well-known model of Danckwerts.

In the theory of Danckwerts (1951) the fraction of free surface of a turbulent liquid having ages between times t and $(t + dt)$ is designated ϕdt, where ϕ is the surface age distribution function. Assuming that the fractional rate of replacement of the "elements of liquid" in the surface, of any age group, is constant at a value s (stirring being at a steady shaft speed), Danckwerts showed that

$$\phi = se^{-st}$$

where s has the dimension of $(\text{time})^{-1}$.

Hence one derives that the fraction of surface having an age less than t is given by $\int_0^t \phi dt$, i.e.

$$\text{Fraction of surface renewed by fresh eddies within time } t = \int_0^t se^{-st} dt = 1 - e^{-st} \qquad (5)$$

In this paper we test experimentally the assumption of Danckwerts that the replacement of "elements of liquid" in the surface is independent of the time they have been there. We also try to check from turbulence measurements the value of s^{-1}, i.e., of the mean time of persistence of an eddy in the surface. We proceed

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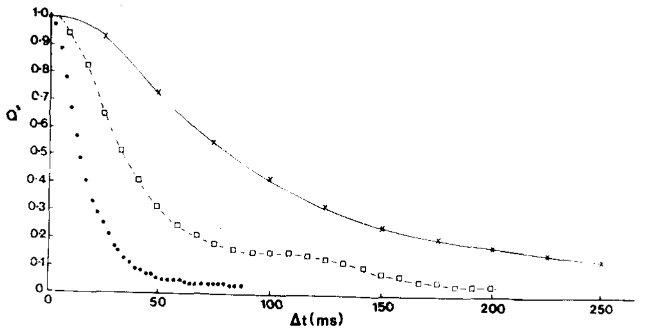

Figure 1. Experimental normalized autocorrelation functions for stirred cell. X *Re* = 2,530; □ *Re* = 4,740; ● *Re* = 9,470. The times shown here are uncorrected for the effect of the overall rotational flow in the surface.

by setting s^{-1} equal to t_L, and, then comparing numerically our model (Eq. 4) with the Danckwerts model (Eq. 5). In this way we check whether the energy-containing eddies studied in our experiments are the "elements of liquid" referred to by Danckwerts, i.e., that cause surface renewal by their internal circulation.

We also relate t_L to the shaft speed (N) and to our measured rates of mass transfer of gas into the stirred liquid.

EXPERIMENTAL

Details of the stirred cell, of the hot wire probes and of the method of recording and processing the velocity fluctuation signals have already been described (Davies and Lozano, 1979). The stirrer blade length L was 31.9 mm. The hot wire probe was immersed at 0.5 mm below the free surface of the water at Re = 2,530 and Re = 4,740, and 1 mm below at Re = 9,470, these bring the the three Reynolds numbers for which we derived autocorrelations.

RESULTS

Figure 1 shows the three autocorrelations. They are typical of truly turbulent flow. Numerical integration of Eq. 3 based on these data gives for the apparent times (t_L) 0.131 s at Re = 2,530; 0.056 s at Re = 4,740; and 0.022 s at Re = 9,470. These times, however, refer to the passage of an eddy across the hot wire in an overall flow of velocity $\bar{v}_x$, i.e., when the eddies are being carried away from the wire by the overall flow. Thus these measured persistence times in the overall flow $\bar{v}_x$ are too small: the times we require to compare Eq. 4 with Eq. 5 are those relating only to the turbulent fluctuations $\tilde{v}_x'$. If there were no overall flow, the eddy frequency would be simply $\tilde{v}_x'/l_L$, which is what is required. Here l_L is the integral eddy length scale. But with an overall flow $\bar{v}_x$, we measure a higher eddy frequency $(\tilde{v}_x' + \bar{v}_x)/l_L$. Thus our measured frequencies are too high by $(\tilde{v}_x' + \bar{x}_x)/\tilde{v}_x'$, i.e., our apparent times quoted above must be increased by multiplying them by this factor. With these correction factors (Davies and Lozano, 1979) the values of t_L in column 3 on Table 1 are obtained.

Figure 2 compares Eq. 4 interpreted numerically using our experimental data (on the corrected time scales) with the Danckwerts Eq. 5 with $s = t_L^{-1}$, for Re = 4,740. The results at the other Reynolds numbers are essentially similar.

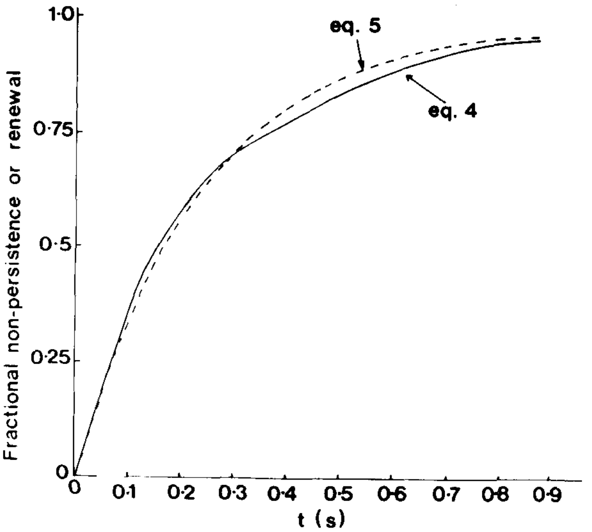

Figure 2. Plot of Eq. 4 (full line) against corrected time intervals *t*, at *Re* = 4,740. Also shown (broken line) is Eq. 5 with $s = t_L^{-1} = 4.22\ s^{-1}$.

DISCUSSION

The fairly close fit between curves of Eqs. 4 and 5 as shown in Figure 2 confirms in general terms the turbulent nature of the surface and the model of Danckwerts. It is also found that $t_L^{-1} = 0.8N^{1.3}$, where N is the shaft speed.

To relate t_L (or s^{-1}) to our measured mass transfer rates for the absorption of oxygen into the stirred vessel, we use the equation (Danckwerts, 1951):

$$k_L = D^{1/2}s^{1/2} \tag{6}$$

However, with $D = 2.4 \times 10^{-9} m^2 \cdot s^{-1}$ and $s = t_L^{-1}$, the calculated k_L values are much higher than the experimental figures (Table 1, columns 6 and 8).

Clearly our $s^{1/2} (= t_L^{-1/2})$ values are too large, particularly at the lowest value of Re. Thus the t_L times are too small to correlate with mass transfer, implying that slower (larger) eddies than those averaged in the integral time-scale play the dominant part in mass transfer.

Indeed, the integral eddy length scales l_L (Davies and Lozano, 1979) increase with Re from 5.5 to 6.6 mm to 8.1 mm respectively, below the value of 9.6 mm for the Prandtl eddies. The latter figure is obtained from $l = 0.3\ L$, where L is the length of the stirrer blades (Davies, 1972). It is clear that mass transfer rates are determined by the large eddies, of size 10 mm or more. Nevertheless these are turbulence eddies, and not roll cells, though there are some measurable swirl effects at the free surface of our stirred cell. (See Figure 4 of Davies and Lozano, 1979).

The frequencies f of the large eddies in a stirred cell can be obtained (Davies, 1972) from the relationships $f = (\tilde{v}'/l)$, $\tilde{v}' = 0.5\bar{v}$, $\bar{v} = 0.8NL$, and $l = 0.3L$. This gives $f = 1.33N$, which may be compared with the macroscale eddy frequencies t_L^{-1} (Table 1, columns 4 and 5).

Direct observation of the rates of the larger (10 mm) surface renewals (rendered visible with a fine dusting of talc on the surface of the stirred cell) led Davies and Khan (1965) to the following empirical relation for s

TABLE 1. EDDY FREQUENCY

N (Revs. s^{-1})	Re	t_L (s)	t_L^{-1} (s^{-1})	$1.33N$ (s^{-1})	k_L ($m \cdot s^{-1} \times 10^6$) Calc. from Eq. 6 with $s = t_L^{-1}$	k_L ($m \cdot s^{-1} \times 10^6$) Using s from Eq. 7 in Eq. 6	k_L ($m \cdot s^{-1} \times 10^6$) (Experimental) (Davies & Lozano, 1979)
2.22	2530	0.45	2.22	2.9	73	21	26
4.17	4740	0.24	4.22	5.5	101	34	54
8.33	9470	0.078	12.9	11	176	97	133

$$\ln s = 0.50\,N - 2.8 \tag{7}$$

where N is expressed in revolutions per second. Using this relation and Eq. 6 one obtains the calculated k_L values in column 7 of Table 1, in somewhat better agreement with the experimental data in column 8.

Our conclusions are as follows:

(i) The surface region of the stirred cell is turbulent.

(ii) The distsribution of the large (integral scale) eddies near the surface agrees well with the Danckwerts distribution function (Eq. 5), though there is a tendency for the larger eddies to be replaced more slowly than this equation predicts.

(iii) The eddies responsible for most of the mass transfer are larger and of lower frequency than the integral scale or Prandtl eddies, i.e., the small x-directional movements in the surface are less important in mass transfer than are the larger movements which relate to "surface renewal."

NOTATION

D = molecular diffusivity, $m^2 \cdot s^{-1}$
f = frequency of eddies., s^{-1}
k_L = mass transfer coefficient on liquid side of surface $m \cdot s^{-1}$
l = eddy length, mm
l_L = macroscale of eddies, mm
L = tip-to-tip length of stirrer blade, mm
N = shaft speed, revolutions per second
$Q(\Delta t)$ = velocity autocorrelation coefficient with respect to time $m^2 \cdot s^{-2}$
$Q^*(\Delta t)$ = $Q(\Delta t)/(\tilde{v}_x')^2$, dimensionless
Re = Reynolds number ($= NL^2/\nu$), dimensionless
s = frequency of surface renewal, s^{-1}
t = time, s or ms
t_L = eddy macro-timescale, s
$\bar{v}_x$ = mean overall velocity of flow in the x-direction (along the surface), $m \cdot s^{-1}$
v_x' = fluctuation velocity, $m \cdot s^{-1}$
$\tilde{v}_x'$ = root mean square value of v_x', $m \cdot s^{-1}$
ν = kinematic viscosity, $m^2 s^{-1}$
ϕ = surface age distribution function of Danckwerts theory, s^{-1}

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Observations on Catalytic Dissociation of Ammonia at High Temperatures and Pressures

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INTRODUCTION

There has been relatively little work done on ammonia dissociation under high temperature and pressure conditions. Conventional promoted iron catalyst used effectively for synthesis of ammonia cannot be used for the dissociation reaction at high pressures since at temperatures greater than 550°C this catalyst sinters. Hence, we undertook a study of this dissociation reaction, at substantial pressures using other catalyst materials.

EXPERIMENTAL

Our experimental studies were performed in a plug flow reactor, where the pressure was maintained between 6.9 and 10 MPa (68 and 100 atm), the temperature between 875 and 1,050 K, the ammonia flow rate between 0.12 and 0.60 kg/h and the weight of the catalyst between 0.006 and 0.01 kg.

A schematic diagram of the experimental apparatus is shown in Figure 1. A detailed description of this apparatus is given elsewhere (Nandy et al., 1981). Basically, the system comprises a plug flow reactor, which is heated electrically. Ammonia is pumped into the reactor and the degree of dissociation is measured from the flow rate of exiting nitrogen and hydrogen.

The dissociation reaction conditions are similar to the reaction conditions

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