

# Measurement of the Surface Ages of Water Jets

J. T. DAVIES

and

R. W. MAKEPEACE

Department of Chemical Engineering  
University of Birmingham  
Birmingham B15 2TT, England

Experimental values of the surface velocities  $v_s$  of water jets have been obtained by high speed flash ciné photography of talc particles on the surfaces of both laminar and turbulent jets. Values of the surface ages as defined variously by Defay and Hommelen (1958), Hansen (1964), and Harper (1973) have been obtained from our data for both pure water and for dilute solutions of surface active agents.

We find, by comparison with published entry length corrections for gas absorption, that  $x/v_s$  gives the most reasonable age of the surface at any distance  $x$  along a jet of pure water.

If a surface active agent is present in the water, the amount of adsorption of a few millimeters downstream from the nozzle is of the order ten times greater than calculated for laminar jets and five to six times greater than calculated for turbulent jets at  $Re_n = 18\,800$ . This we ascribe to liquid circulation in the jet adjacent to the nozzle, caused by the Marangoni surface flow, which also reduces  $v_s$  significantly.

## SCOPE

What is the age of the surface of a jet of water issuing from a nozzle? This age, often considerably greater than the time required for the bulk of the jet to reach a certain distance from the nozzle, is required in studies of gas absorption into jets of pure liquids and also in studies of the rates of adsorption to the surface of surface active substances in the jet liquid.

Previously theoretical work on surface ages of jets [particularly that of Hansen (1964) and of Harper (1973)] is contradictory, though apparently anomalously high

rates of adsorption of surface active substances from the jet liquid have often been reported.

By using a Fastax camera at 7 000 f.p.s., with a synchronized neon flash, we have been able to photograph the positions of talc particles dropped on to the surface of a water jet as close as 0.2 mm to the nozzle. From these studies, we could test experimentally the various theories of surface age and explain the rapid rates of adsorption of surface active substances.

## CONCLUSIONS AND SIGNIFICANCE

We find that of the variously defined surface ages,  $\bar{t}$  of Equation (1) gives the best agreement with the previously published entry lengths for gas adsorption into clean liquids. This age  $\bar{t}$  is greater than the mean time of passage of the jet liquid to any point downstream of the nozzle.

For solutions of surface active substances, the jet method of determining rates of adsorption is unreliable because of the complicated flow patterns induced by the reverse spreading tendency; that is, the surface film which has adsorbed on the surface several milli-

meters downstream of the nozzle tends to spread back to the clean surface being continually exposed at the nozzle. This Marangoni effect reduces the surface velocity noticeably near the nozzle and moreover induces some liquid circulation which accelerates the adsorption by as much as ten times.

We conclude that liquid jets are neither simple nor easy methods to use to obtain rates of adsorption of surface active substances. In industrial systems containing surface active materials, the Marangoni effect will result in the exposed liquid surface not being clean, even at short times of exposure.

When a jet of liquid emerges from a nozzle, it possesses a nonuniform velocity profile, the surface of the jet being at a velocity ( $v_s$ ) which is, in general, lower than the mean velocity of flow ( $v_m$ ) of the jet. When the jet is surrounded by an inviscid medium such as a gas, the velocity profile is free to relax. The surface velocity  $v_s$  thus increases from zero at the nozzle towards the mean velocity  $v_m$  as the surface moves downstream, though the possibility of the air drag preventing  $v_s$  from quite reaching  $v_m$  cannot be ignored.

Because  $v_s < v_m$ , the surface age of the liquid at any point  $x$  downstream is not simply  $(x/v_m)$  as was used by Defay and Hommelen (1958). Here  $x$  refers to the

distance along the liquid jet from the nozzle. This was pointed out by Scriven and Pigford (1959), who analyzed the surface flow in detail to calculate  $v_s/v_m$ . A more recent numerical analysis is that of Duda and Vrentas (1967).

Even when we know  $v_s/v_m$  as a function of  $x$ , however, we still need to interpret the age of the surface in terms of  $v_s$ .

Hansen's (1964) average surface age, based simply on the effective area of the surface of the jet as the velocity profile relaxes downstream of the nozzle, is

$$\bar{t} = x/v_s \quad (1)$$

It has been claimed by Harper (1973) that this surface age is approximately correct for surface active solutions in the region near the orifice if the surface aging is limited by a surface resistance [with the adsorption kinetics assumed by Tsonopoulos (1971)] and if there is

Correspondence concerning this paper should be addressed to J. T. Davies. R. W. Makepeace is with the Fire Research Station, Borehamwood, Herts, WD6 2BL, England.  
0001-1541/78-8562-0524-\$00.95. © The American Institute of Chemical Engineers, 1978.

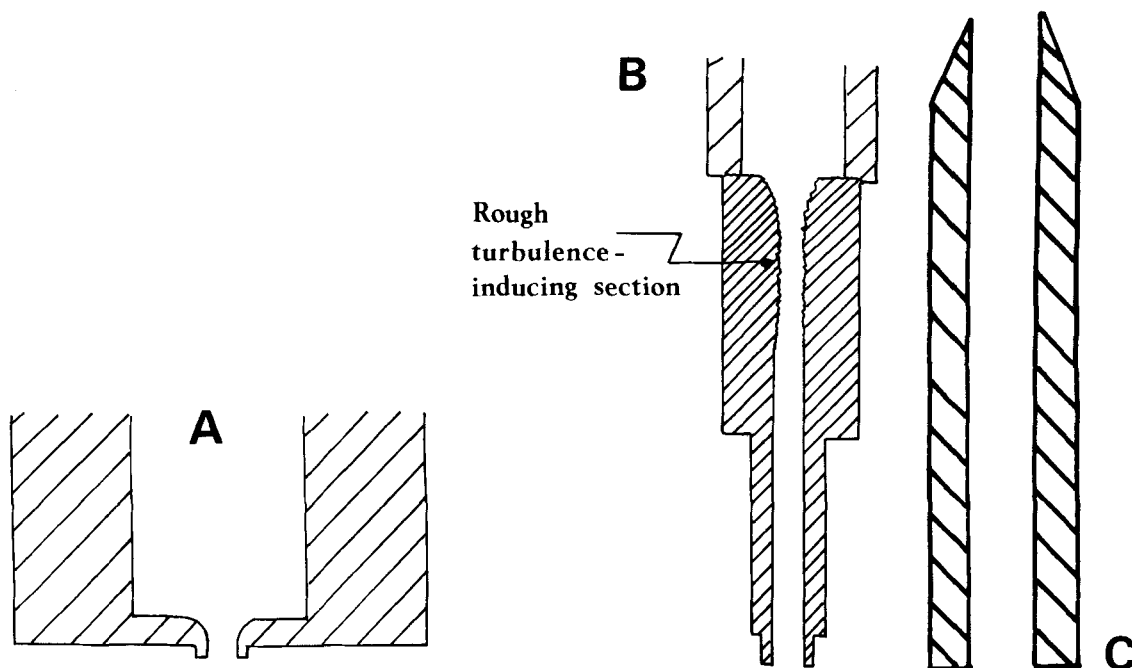


Fig. 1. a. S type of nozzle. b. R type of nozzle. c. Sharp edged nozzle.

no variation in jet diameter.

If diffusion to the surface is rate determining, however, Harper calculated that

$$T = (1/v_s^2) \int_0^x v_s dx \quad (2)$$

In both Equations (1) and (2),  $v_s$  is the surface velocity at any particular value of  $x$  downstream of the nozzle.

There is a further possible expression for the surface age; namely

$$\tau = \int_0^x dx/v_s \quad (3)$$

This is the time for a particle on the surface of the liquid to move from the orifice to a point  $x$  downstream.

We have carried out measurements on laminar and turbulent water jets in order to calculate the surface ages by the above expressions and to show the numerical differences between such ages. Both pure water and surface active solutions were used.

## EXPERIMENTAL

High speed photography was used to trace the motion of particles of talc (diameter  $<150 \mu\text{m}$ ) dropped on to the surface of horizontal jets of distilled water at  $25^\circ\text{C}$  close to the jet exit.

Three types of jet nozzles were used: flat edged, S type of nozzles (described below) of diameters 1.19 and 1.85 mm, at Reynolds numbers of 1 820 and 2 200, respectively; a sharp edged nozzle of diameter 1.85 mm at  $Re = 2 000$ ; and an R type of nozzle of diameter 2.04 mm at Reynolds numbers 9 200, 11 200, and 18 800. All these Reynolds numbers are based on the mean exit velocities and the nozzle diameters.

The S type of nozzles had a bell shaped orifice shaped according to Southwell's (1946) graphical method to favor a uniform velocity profile (Figure 1a). The R type was constructed to a design of Rupe (1962) with a length to diameter ratio of 1.20 and a rough turbulence inducing section. This and the sharp edged nozzle are shown in Figures 1b and c.

A Wollensak WR17 Fastax high speed camera synchronized with a neon flash was used to photograph the surfaces of the jets. The camera was positioned so that light reflected from the particles on the surface was recorded. The unit operated at speeds up to 7 000 frames/s, and the film was automatically marked at millisecond intervals.

The developed films were projected frame by frame (at a linear magnification of about thirty five times) on to a screen from which precise time and distance measurements of the talc particles were taken; the local velocities could thus be obtained. For such small particles as we used, any differences between the velocities of the talc and the water surface are negligible.

For measuring the rates of spreading on still clean water, we dipped a plate wetted with the appropriate solution into a trough of clean water on which a little talc was sprinkled. We observed the rate of spreading over the first 0.5 mm of travel, using the high speed camera.

As a surface active agent we used B.D.H. "Manoxol OT" (sodium dioctyl-sulphosuccinate). Also used were *n*-octanol and *n*-heptanol.

## RESULTS

Figures 2 and 3 show the observed variation of surface velocity  $v_s$  with the distance  $x$  from the orifice for jets of pure water at different velocities.

It was found (Figure 4) that the following empirical relationship between surface velocity and distance downstream applied over the first few millimeters:

$$v_s = Cx^\gamma \quad (4)$$

Typical values of  $C$  and  $\gamma$  are listed in Table 1.

With this power relationship, values of  $\bar{t}$ ,  $T$ , and  $\tau$  can be evaluated from

$$\bar{t} = x^{1-\gamma}C^{-1} \quad (5)$$

$$T = x^{1-\gamma}C^{-1}(1+\gamma)^{-1} \quad (6)$$

$$\tau = x^{1-\gamma}C^{-1}(1-\gamma)^{-1} \quad (7)$$

with the ranges of  $x$  as indicated in Table 1. These relations were applied to obtain the various surface ages as functions of  $x$  for small values of  $x$ . Graphical integration of the data was used for larger distances downstream.

For pure water, the velocities in Figure 3 show that for  $Re \geq 9 200$ , the surface velocities approach closely the mean exit velocities within about 7 mm (that is, about four orifice diameters) of the exit, whereas with an S type of nozzle (or a sharp edged nozzle), at  $Re$  about 2 000 the surface velocity approaches the mean exit velocity only at much greater distances (see Figure 2), for example, at 70 mm (32 diam) when  $Re = 2 200$ .

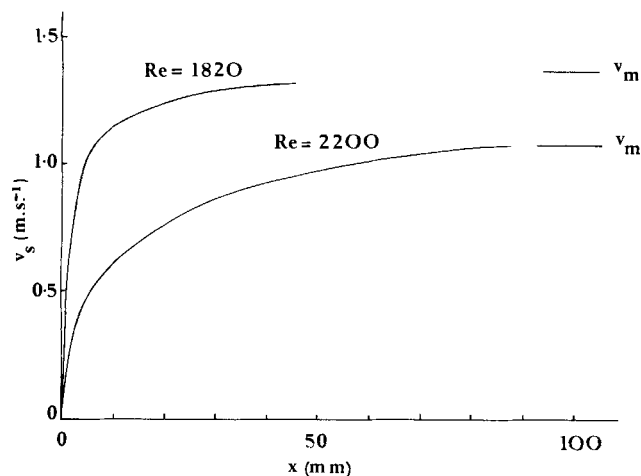


Fig. 2. Experimental data (from frame-by-frame analysis) of surface velocity  $v_s$  for pure water as function of distance  $x$  downstream of nozzle exit, for S type of nozzles and laminar flow.

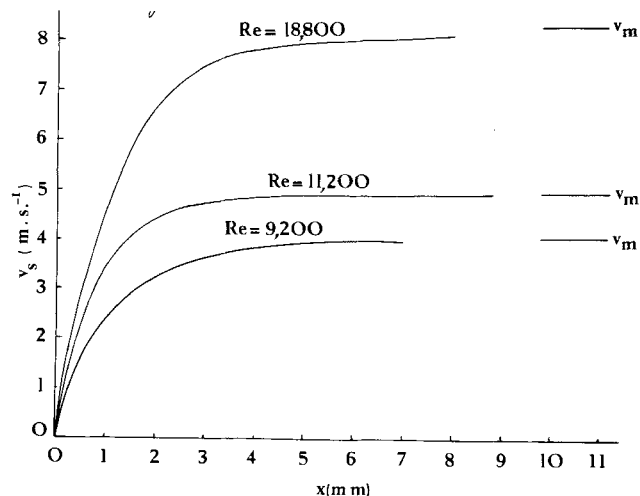


Fig. 3. Experimental data of  $v_s$  for pure water as function of  $x$ , for turbulent jets from the R type of nozzle.

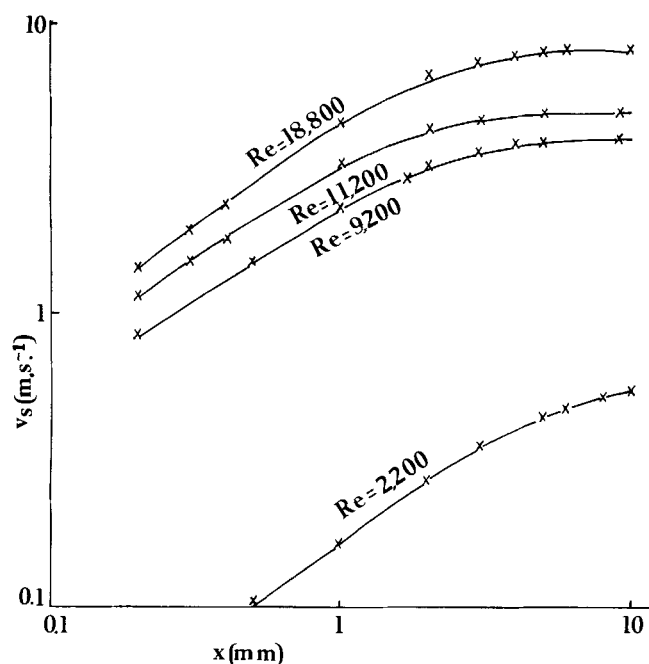


Fig. 4. Typical log-log plot of  $v_s$  vs.  $x$  for pure water, showing linearity for  $x < 1.5$  mm for turbulent flow, or  $x < 3$  mm for laminar flow.

The surface ages for jets of pure water, in Figures 5 and 6, show the increase in the values of  $\bar{t}$ ,  $T$ ,  $\tau$  [from Equations (5), (6), and (7)] and of  $(x/v_m)$  with distance  $x$  downstream from the nozzle at  $Re = 1820$  and  $18800$ . It is seen from these and other graphs that  $T$ ,  $\bar{t}$ , and  $\tau$  are all initially greater than  $(x/v_m)$ , but as  $v_s$  approaches  $v_m$  at large distances downstream,  $\bar{t}$  tends to  $(x/v_m)$  while  $T$  becomes less than  $(x/v_m)$  by a constant time interval.

The accuracy and reproducibility of the results can be judged by the typical points shown in Figures 4 and 7. Individual points through which the lines were drawn were consistent to  $\pm 4\%$  of these lines. Since we had many points, the accuracy of our mean lines was much better than this. We also measured  $\tau$  directly from the photographs at different distances  $x$  [see Equation (3)], and these values were usually in very close agreement with those obtained from Equation (7).

From the experimental points, we find a scatter of  $T$  of  $\pm 5\%$  and of  $\bar{t}$  of  $\pm 4\%$ . However, the lines drawn through many points to make up the graphs of this paper are, of course, more accurate than this ( $\pm 2\%$ ). The differences in the values of  $\bar{t}$ ,  $T$ ,  $\tau$  [and  $(x/v_m)$ ] are usually 8 to 100% and are therefore significant (and the same differences were found at other Reynolds numbers, not presented in the submitted paper for reasons of space).

TABLE 1. TYPICAL VALUES OF  $\gamma$  AND  $C$  IN EQUATION (4)

System	Nozzle	$v_m$ ( $\text{m s}^{-1}$ )	$Re$	$\gamma$	$C$	Limit of range of validity ( $\text{m} \times 10^3$ )
Clean water	S	1.08	2 200	0.72	26	3
Clean water	S	1.37	1 820	0.74	70	3
Clean water	S	4.05	9 200	0.7	240	1
Clean water	R	4.96	11 200	0.6	283	1
Clean water	R	8.30	18 800	0.7	440	1
Clean water	Sharp	0.98	2 000	0.7	20	2
0.01% octanol	S	0.98	2 000	1.1	276	1
0.02% octanol	S	0.98	2 000	1.9	915	1
0.02% octanol	Sharp	0.98	2 000	1.0	103	2
0.02% heptanol	S	0.98	2 000	1.3	915	1
0.9 ppm MOT	S	1.37	1 820	0.9	50	3
10.0 ppm MOT	S	1.37	1 820	1.1	164	3
0.9 ppm MOT	R	8.30	18 800	0.72	565	1.5
5.0 ppm MOT	R	8.30	18 800	0.70	478	1.5
10.0 ppm MOT	R	8.30	18 800	0.70	440	1.5

For jets of surface active solutions, results are shown in Figures 7 to 11. The surface active additive always reduces  $v_s$  below the value for clean water, though at higher values of  $x$  (for example, 10 to 15 mm) the surface velocities tend, with those for clean surfaces, towards  $v_m$  for the particular jet.

The spreading rates over the first 0.5 mm of travel for solutions of "Manoxol OT" on clean water are summarized in Table 2. Here  $\pi$  refers to the equilibrium surface pressure (that is, the equilibrium lowering of surface tension below the value for pure water). These results may be represented by

$$\text{Rate of spreading} = 0.064 \pi \quad (8)$$

The spreading rates decrease markedly as spreading proceeds because the local gradient of surface pressure falls.

## DISCUSSION

### Surface Velocities of Pure Water Jets

The point downstream at which the surface velocity  $v_s$  approaches closely the mean exit velocity of a laminar jet is a function of  $v_m$ , as Figure 2 shows. Jets with higher velocities  $v_m$  approach a uniform profile in shorter distances.

For laminar jets, Middleman (1964) predicted that with an initially parabolic profile,  $v_s$  should reach 99% of  $v_m$  within 1 jet diameter. This is in contrast with our experimental results for laminar jets.

Goren and Wronski (1966) used standard boundary-layer analysis, based on an initial parabolic profile, to derive

$$v_s/v_m = 5.07[x/(a_n Re)]^{1/3}$$

Clearly, the exponent of  $x$  of 0.33 is much less than we observe [Equation (4) and Table 1].

A more exact analysis by Duda and Vrentas (1967) for laminar jets gives results summarized in Table 3. Their calculated surface velocities are compared in that table with those of Goren and Wronski and also with our experimental data for the systems shown in Figure 2. It is seen that our experimental  $v_s$  values are generally lower than the calculated figures, particularly as the nozzle is approached. This is a reflection of the effective exponent of  $x$  being lower ( $\sim 0.3$ ) in these theories than is our measured exponent [ $\sim 0.7$ , that is,  $\gamma$  in Equation (4) and Table 1]. The difference may be due to a slight reverse swirl near the nozzle which in practice reduces  $v_s$  near the nozzle below the calculated values.

For turbulent jets, the data of Figure 3 show that  $v_s$  reaches 90% of  $v_m$  in about 3 mm, that is, in 1.5 jet diameters. This is much lower than the 25 diam reported by Rupe (1962) for his turbulent jets at  $Re = 30\,000$ .

### Surface Ages of Pure Water Jets

The various surface ages of a laminar jet at low exit velocities and low  $Re$  ( $v_s = 1.37 \text{ m s}^{-1}$ ,  $Re = 1\,820$ ) as calculated by Equations (1), (2), and (3) show differences between themselves of a few milliseconds (Figure 5).

Close to the orifice the surface age  $T$  as defined by Equation (2) exceeds the age  $(x/v_m)$ . However, at greater distances downstream,  $T$  falls below  $(x/v_m)$  as seen in Figures 5 and 6. This transition always occurs, as the following argument shows.

When  $T = (x/v_m)$ , Equation (2) gives

$$x = (v_m/v_s^2) \int_0^x v_s dx \quad (9)$$

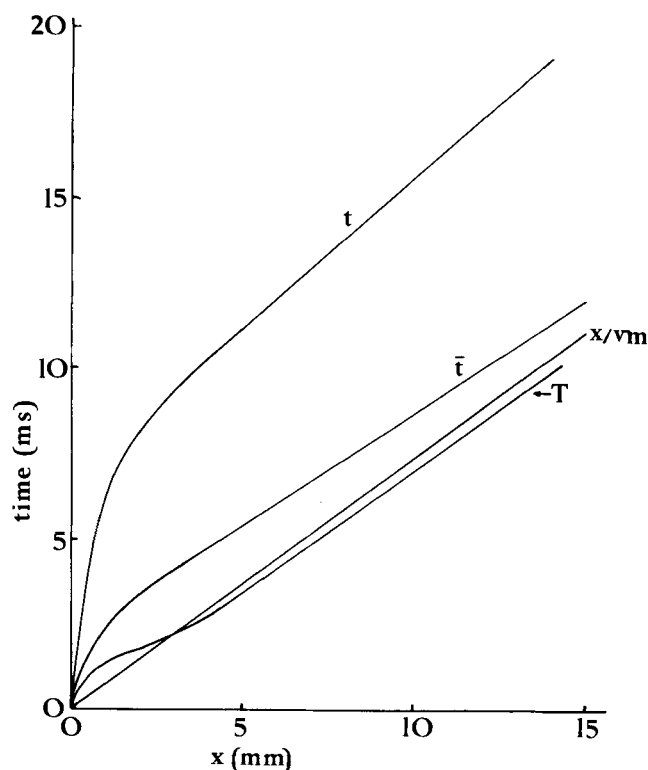


Fig. 5. Various surface ages derived from Equations (5), (6), and (7) for laminar jets from S type of nozzle of 1.19 mm diameter, for pure water ( $Re = 1\,820$ ,  $v_m = 1.37 \text{ m s}^{-1}$ ).

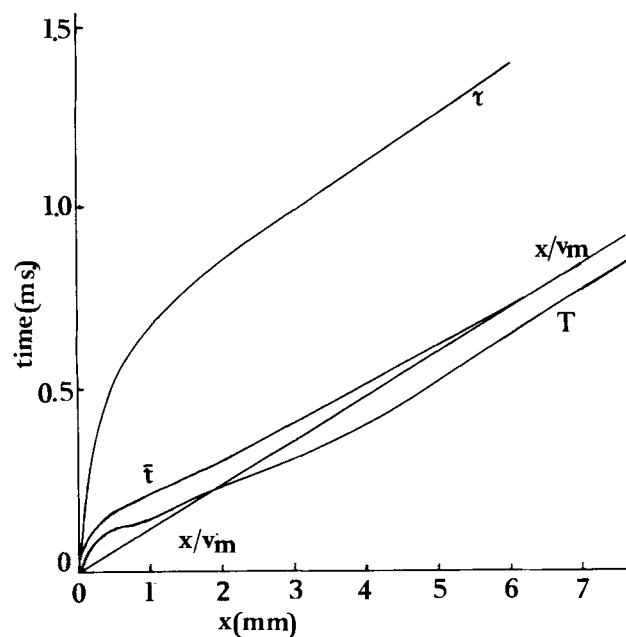


Fig. 6. Surface ages derived for turbulent jet of pure water from R type of nozzle ( $Re = 18\,800$ ,  $v_m = 8.3 \text{ m s}^{-1}$ ).

TABLE 2. VELOCITIES OF SPREAD FROM "MANOXOL OT" SOLUTIONS ON CLEAN WATER

Concentration, ppm	$\pi$ , mN m <sup>-1</sup>	Rate of spreading over first 0.5 mm, m s <sup>-1</sup>
0.9	2.8	0.18
5	5.5	0.32
10	9.0	0.60

TABLE 3. SURFACE VELOCITIES OF LAMINAR JETS OF WATER

 $Re = 1\,820$ ,  $v_m = 1.37\text{ m s}^{-1}$ ,  $d_n = 1.19\text{ mm}$ 

$x$ (in mm)	$v_s$ in $\text{m s}^{-1}$ (calc. by Goren and Wronski)	$v_s$ in $\text{m s}^{-1}$ (calc. by Duda and Vrentas)	$v_s$ in $\text{m s}^{-1}$ (present experiments)
21.65	—	1.37	1.26
10.84	1.48	1.17	1.17
5.42	1.17	0.99	1.04
2.71	0.93	0.84	0.84
1.36	0.74	0.63	0.52
0.54	0.54	0.51	0.27

 $Re = 2\,200$ ,  $v_m = 1.07\text{ m s}^{-1}$ ,  $d_n = 1.85\text{ mm}$ 

40.6	—	1.07	0.94
20.3	1.18	0.91	0.78
10.2	0.93	0.77	0.58
5.1	0.74	0.66	0.47
2.5	0.59	0.49	0.33
1.0	0.43	0.40	0.16

All quantities on the right-side of Equation (9) are positive, and thus there is always some value of  $x$  where the curve representing  $T$  crosses the line of  $(x/v_m)$ .

Thus, when we compare surface ages as defined by Harper (1973) and Defay (1958), a knowledge of the surface velocity at points along the jet is required before it can be determined which age is the greater at any point. However, the surface age  $\bar{t}$  as defined by Hansen (1964) is always greater than  $x/v_m$ .

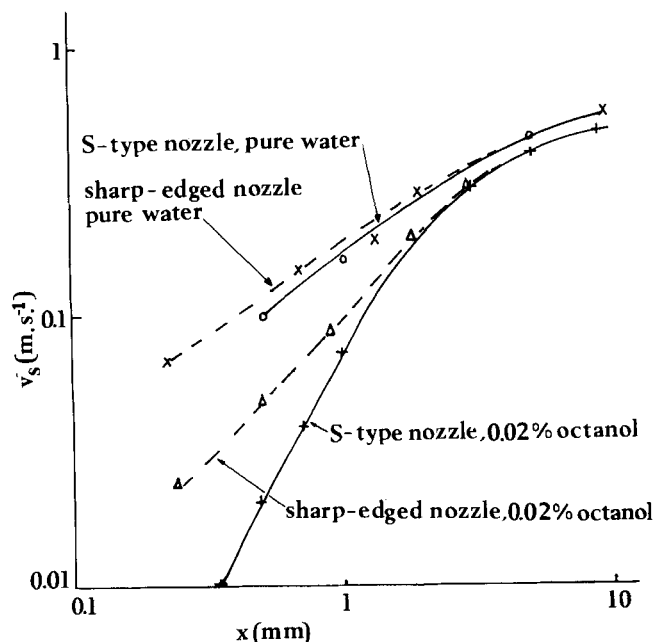
It can be seen from Figure 5 that apart from the initial regions near the orifice,  $[\bar{t} - (x/v_m)]$  is a few millimeters; that is, the surface lags by this distance behind the bulk flow which left the nozzle at the same time. For the sharp edged nozzle, the lag based on  $\bar{t}$  is 4 or 5 mm (Figure 8) for pure water.

The distance lag based on  $\tau$  is about 10 mm at  $Re = 1\,820$  (Figure 5), and about 9 mm for the sharp edged nozzle at  $Re = 2\,000$ .

The distance lag based on  $T$  is, as follows from the discussion above, slightly positive very close to the nozzle and thereafter negative (Figures 5, 6, and 9).

These distance lags can be compared with other experimental data from the rates of gas absorption into laminar jets of pure water. Because the surface of the jet may be exposed for a longer time than given by  $(x/v_m)$ , the rate of gas absorption is reduced (this rate depending on  $\text{time}^{-1/2}$ ). In practice, the so-called entry length of the laminar jet found from the gas absorption experiments is near zero in a few experiments (Cullen and Davidson, 1957; Manogue and Pigford, 1960; Clarke, 1964; Caskey and Barlage, 1972) ranging up to about 6 mm in others (Cullen and Davidson, 1957; Jeffreys and Bull, 1964), suggesting that Hansen's  $\bar{t}$  is the required age here. The variations between the results of different workers are presumably due to the different nozzles and orifices used. The sharpness of the edge of the nozzle may be particularly important.

It should be noted that in his theoretical treatment, Hansen calculated the age of the jet surface from considerations only of the increasing area of the surface (as  $v_s \rightarrow v_m$  along the jet). He did not assume any surface resistance to adsorption. However, Harper (1973) claimed from his calculations that Hansen's treatment was correct only if there was a surface resistance, and that otherwise one should use  $T$  as the relevant surface age. The experimental findings do not support Harper's

Fig. 7. Log-log plot of  $v_s$  vs.  $x$  for sharp edged nozzle and S type of nozzle, showing effect of 0.02% octanol in water ( $Re = 2\,000$ ).

contention, but they are consistent with Hansen's  $\bar{t}$  being appropriate for the published gas absorption experiments.

#### Surface Velocities of Jets of Surfactant Solutions

Experimentally, the surface velocity  $v_s$  is reduced by the presence of surfactants (Figures 7, 10, and 11). The relative reduction in  $v_s$  is greatest near the nozzle, as the log-log plot of Figure 7 indicates, and this is reflected in the exponent  $\gamma$  in Equation (4) increasing with the concentration of the surfactant. Under some conditions,  $\gamma$  can equal or even exceed unity for laminar jets, as indicated in Table 1.

The reduction of  $v_s$  when surfactant is adsorbing is, for example, as high as  $0.1\text{ m s}^{-1}$  at 1 mm downstream from the nozzle (Figure 10); thus,  $v_s$  can be reduced by 24% compared with  $v_s$  for the laminar jet of pure water, and the reduction in  $v_s$  is 7% of  $v_m$ . This latter observed reduction is greater than the 2% estimated theoretically by Hansen (1964).

The physical explanation of the reduction in  $v_s$  when a surfactant is present is as follows. Where the velocity profile is relaxing, the surface is expanding, that is, it is newly formed, and might even approach the composition (and surface tension) of pure water. A little further downstream, appreciable adsorption of the surfactant will have occurred, giving rise to a back spreading tendency from this part of the surface in the direction back towards the cleaner liquid on the surface immediately adjacent to the nozzle. The phenomenon is thus a form of the Marangoni effect.

Quantitatively, one can interpret the effect as follows. The reduction in  $v_s$  caused by 5 ppm of "Manoxol OT" is  $0.06\text{ m s}^{-1}$  at 0.5 mm downstream (Figure 10), and from Equation (8) this corresponds to  $\pi = 0.94\text{ mN m}^{-1}$ . The local surface tension gradient is thus  $-1.88\text{ N m}^{-2}$  (that is,  $-18.8\text{ dyne cm}^{-2}$ ). Hansen used a figure of  $-10\text{ dyne cm}^{-2}$  in his calculation that the back-spreading Marangoni velocity was of the order  $0.04\text{ m s}^{-1}$ , so that his theory is at least in general accord with our measurements.

#### Surface Ages of Jets of Surfactant Solutions

With the higher values of  $\gamma$  for the laminar jets of surfactant solutions (see Table 1), there are large changes

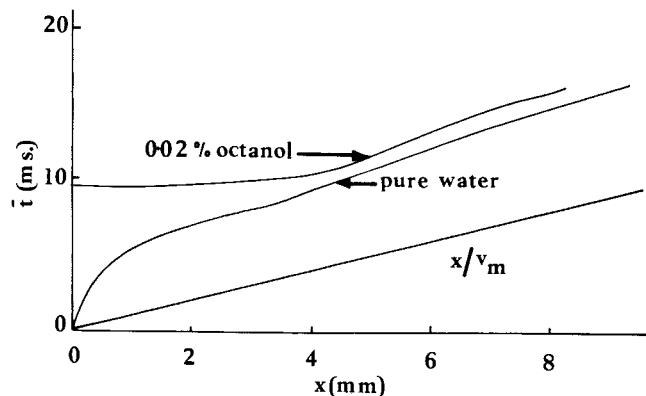


Fig. 8. Values of  $\bar{t}$  (in milliseconds) against  $x$  for the sharp edged nozzle ( $Re = 2000$ ,  $v_m = 0.98 \text{ m s}^{-1}$ ).

in the surface ages. Thus when  $\gamma = 1$ ,  $\bar{t}$  and  $T$  become constant [at the low values of  $x$  where Equations (5) and (6) apply], and  $\tau$  becomes very great. Figures 8 and 9 show the values of  $\bar{t}$  and  $T$  for laminar jets from the sharp edged nozzle for both pure water ( $\gamma = 0.7$ ) and for 0.02% octanol solutions ( $\gamma = 1.0$ ).

To test which (if any) of the definitions of surface age is to be used in practice, we considered the laminar jet at  $1.37 \text{ m s}^{-1}$  of 0.9 ppm "Manoxol OT" solution, for which  $\gamma = 0.9$ . The reduction in  $v_s$  (at  $x = 0.5 \text{ mm}$ ) caused by this surfactant is  $0.03 \text{ m s}^{-1}$  (Figure 10), which corresponds by Equation (8) to  $\pi = 0.47 \text{ mN m}^{-1}$ . From the properties of surface films, one can deduce that the corresponding surface concentration is  $0.05 \times 10^{18} \text{ molecules m}^{-2}$ . From simple diffusion theory for a noncirculating liquid, the time required to achieve this concentration would be 42 ms. The relevant values of  $(x/v_m)$ ,  $\bar{t}$ ,  $T$ , and  $\tau$  are, respectively, 0.36, 9, 5, and 93 ms for this surfactant solution. (The corresponding figures for pure water are 0.36, 2, 1, and 6 ms).

Though  $\tau$  gives the best agreement with the adsorption time, it is doubtful whether the simple diffusion theory applies, since the reverse Marangoni flow along the surface would be expected to enhance mass transfer to introducing some circulation normal to the surface of the jet.

When  $\gamma > 1$  (Figure 7 and Table 1), the surface ages all become extremely great in the region of low  $x$  ( $\sim 1 \text{ mm}$ ), where Equations (5), (6), and (7) apply. Indeed, the ages so defined increase as  $x$  decreases in this region, and only at  $x$  values great enough so that the relation  $v_s = Cx^\gamma$  no longer holds do the ages increase again downstream, having passed through a minimum a few millimeters downstream of the nozzle. Physically, this is the region of greatest expansion on the jet surface. Very close to the nozzle, the back spreading tendency of the surface film so reduces  $v_s$  that this slow moving surface is relatively old, and the surface film on it may be relatively concentrated. We observed on one ciné film (of a jet of water + 0.02% octanol) that within 1 mm of the nozzle the talc particles on the surface of the jet were stationary. In view of this effect, and the expected circulation normal to the surface where the Marangoni back spreading is fastest, we do not consider that any of the simple definitions of surface age can be adequate. The exact definition of surface age, our results suggest, must therefore be an operational one, based on the amount of adsorption actually measured at any point along the jet.

It is of interest that with laminar jets at the higher mean velocity of  $5 \text{ m s}^{-1}$ , Posner and Alexander (1953) found that 0.02% octanol solutions gave agreement with

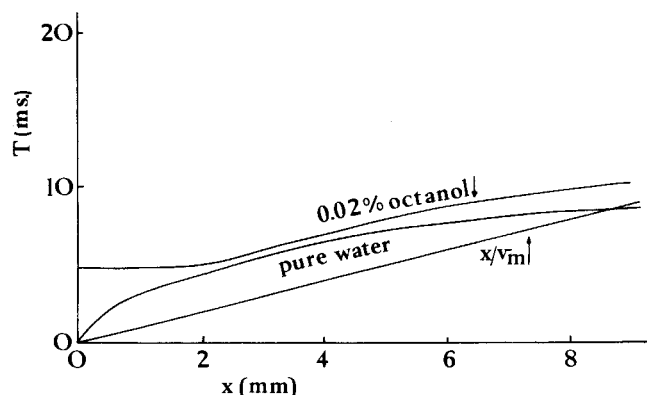


Fig. 9. As for Figure 8, but with  $T$  as a function of  $x$ .

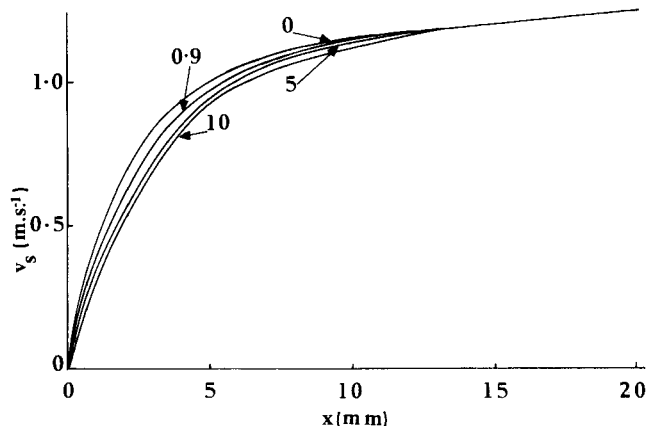


Fig. 10. Effect of "Manoxol OT" (in parts per million) on  $v_s$  for a laminar water jet from an S type of nozzle ( $Re = 1820$ ,  $v_m = 1.37 \text{ m s}^{-1}$ ).

simple adsorption theory at  $x/v_m = 1 \text{ ms}$ , though solutions of dioctyl-sodium sulfosuccinate ( $>300 \text{ ppm}$ ) or of cetyltrimethyl ammonium bromide ( $>10 \text{ ppm}$ ) gave adsorptions greater than calculated by factors of 4 or 5, suggesting that the effective adsorption time was really 16 to 25 ms. The greater lowering of surface

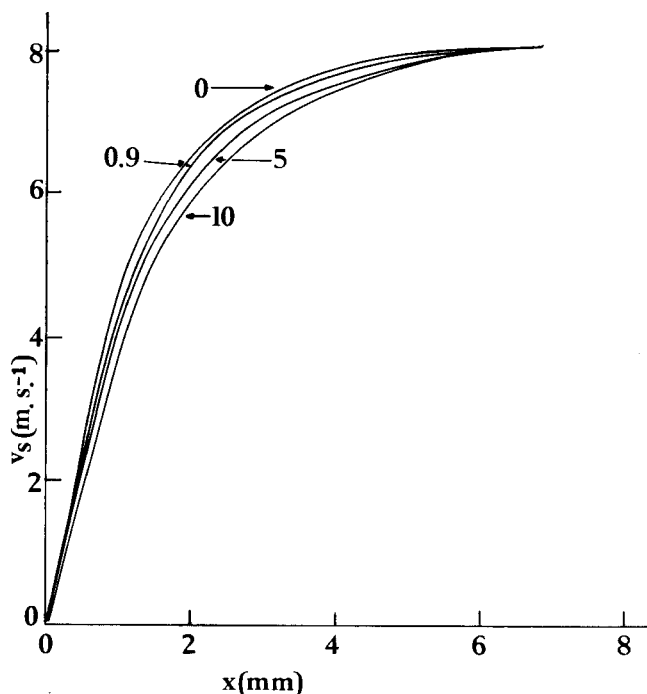


Fig. 11. Effect of "Manoxol OT" (in parts per million) on  $v_s$  for a turbulent water jet ( $Re = 18800$ ,  $v_m = 8.3 \text{ m s}^{-1}$ ).

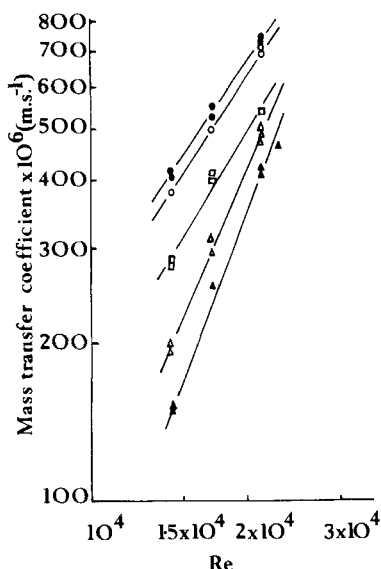


Fig. 12. Log-log plot showing effect of sodium dioctylsulfosuccinate in reducing the mass transfer coefficient of carbon dioxide absorbing into turbulent jets of water issuing from a nozzle of 2.04 mm diameter. Points as follows: ● pure water, ○ 0.1 ppm, □ 1 ppm, △ 5 ppm, ▲ 10 ppm.

tension for the latter solutions is presumably responsible for significant back spreading of the long-chain ions near the nozzle, even when  $v_m$  is as high as  $5 \text{ m s}^{-1}$ .

For the turbulent jets (from the R type of nozzle),  $\gamma$  remains close to 0.7 at  $Re = 9\,200$ ,  $11\,200$ , and  $18\,800$  when "Manoxol OT" is present (see Table 1). At  $Re = 18\,800$ , the distance lags (some millimeters downstream of the nozzle), for  $\bar{t}$ ,  $T$ , and  $\tau$  are zero,  $-1.2$ , and  $8 \text{ mm}$ , respectively, when the additive is at  $10 \text{ ppm}$ . These lags vary smoothly with concentration, as the latter is varied between 0 and  $10 \text{ ppm}$ .

For turbulent jets with  $v_m = 8.3 \text{ m s}^{-1}$ ,  $v_s$  is reduced (by  $10 \text{ ppm}$  of "Manoxol OT") from  $4.5$  to  $3.5 \text{ m s}^{-1}$  (Figure 11). This reduction by  $1 \text{ m s}^{-1}$  is at  $x = 1 \text{ mm}$  and represents the greatest reduction; the influence of the additive becomes negligible further than  $6 \text{ mm}$  from the nozzle.

Though this apparent back spreading velocity of  $1 \text{ m s}^{-1}$  may be too high because of experimental error, it is clear that the adsorption of the "Manoxol OT" is proceeding rapidly. Moreover, calculation from Equation (4.52) of Davies (1972) of the time required for  $0.5 \times 10^{18} \text{ molecules m}^{-2}$  to be adsorbed (one half of the equilibrium adsorption) gives a relatively great time of  $7.6 \text{ ms}$  ( $\bar{t} = 0.28 \text{ ms}$ ,  $T = 0.13 \text{ ms}$ ,  $\tau = 1.4 \text{ ms}$ , all at  $1 \text{ mm}$  from the nozzle, and in the presence of the additive).

It thus appears that for turbulent jets, as for laminar jets, some circulation associated with back spreading adjacent to the nozzle is hastening the adsorption. That a very rapid adsorption of the surface active agent is indeed occurring is confirmed by the finding (Young-Hoon, 1972) that there are considerable reductions in the mass transfer coefficient for the adsorption of carbon dioxide into a turbulent jet of water when a few parts per million of sodium dioctylsulfosuccinate are present (Figure 12). The adsorption of this additive is evidently particularly rapid in the first few milliseconds, thereafter being sufficient to damp quite strongly the surface eddy movement, as these latter are predicted to affect the rate of absorption of carbon dioxide (Davies, 1972, chapter 6). A study of gas absorption into thin turbulent films of water flowing down rough or smooth inclined

channels (at velocities up to  $1 \text{ m s}^{-1}$ ) (Davies, 1972) leads to a similar conclusion as to the very rapid adsorption of surface active additives.

#### ACKNOWLEDGMENT

The authors are grateful to the referees for helpful suggestions about the presentation of this paper.

#### NOTATION

- $a_n$  = radius of nozzle, m or mm
- $C$  = constant of Equation (4) for any given value of  $v_m$
- $d_n$  = diameter of nozzle, m or mm
- $Re$  = Reynolds number ( $= v_m d_n / \nu$ )
- $\bar{t}$  = ( $= x / v_s$ ), s or ms
- $T$  = surface age as defined by Equation (2), s or ms
- $v_m$  = mean velocity of liquid jet,  $\text{m s}^{-1}$
- $v_s$  = velocity of surface of jet,  $\text{m s}^{-1}$
- $x$  = distance along jet from nozzle, m or mm
- $\gamma$  = exponent in Equation (4)
- $\nu$  = kinematic viscosity of liquid,  $\text{m}^2 \text{ s}^{-1}$
- $\pi$  = surface tension lowering below value for clean water surface,  $\text{mN m}^{-1}$
- $\tau$  = surface age defined by Equation (3), s or ms

#### LITERATURE CITED

- Caskey, J. A., and W. B. Barlage, "A Study of the Effects of Soluble Surfactants on Gas Absorption Using Laminar Liquid Jets," *J. Colloid Interface Sci.*, **41**, 52 (1972).
- Clarke, J. K. A., "Kinetics of Absorption of Carbon Dioxide in Monoethanolamine Solutions at Short Contact Times," *Ind. Eng. Chem. Fundamentals*, **3**, 239 (1964).
- Cullen, E. J., and J. F. Davidson, "Absorption of Gases in Liquid Jets," *Trans. Faraday Soc.*, **53**, 113 (1957).
- Davies, J. T., *Turbulence Phenomena*, pp. 241, 260, 262, Academic Press, New York (1972).
- Defay, R., and J. R. Hommelen, "Measurements of Dynamic Surface Tensions of Aqueous Solutions by the Oscillating Jet Method," *J. Colloid Sci.*, **13**, 553 (1958).
- Duda, J. L., and J. S. Vrentas, "Fluid Mechanics in Laminar Liquid Jets," *Chem. Eng. Sci.*, **22**, 855 (1967).
- Goren, S. L., and S. Wronski, "The Shape of Low Speed Capillary Jets of Newtonian Liquids," *J. Fluid Mech.*, **25**, 185 (1966).
- Hansen, R. S., "The Calculation of Surface Age in Vibrating Jet Measurements," *J. Phys. Chem.*, **68**, 2012 (1964).
- Harper, J. F., "Surface Ages in Vibrating Jet Experiments," *Chem. Eng. Sci.*, **28**, 323 (1973).
- Jeffreys, G. V., and A. F. Bull, "The Effect of Glycine Additive on the Rate of Absorption of Carbon Dioxide in Sodium Carbonate Solutions," *Trans. Inst. Chem. Engrs.*, **42**, T118 (1964).
- Manogue, W. H., and R. L. Pigford, "The Kinetics of the Absorption of Phosgene into Water and Aqueous Solutions," *AIChE J.*, **6**, 494 (1960).
- Middleman, S., "Profile Relaxation in Newtonian Jets," *Ind. Eng. Chem. Fundamentals*, **3**, 118 (1964).
- Posner, A. M., and A. E. Alexander, "The Kinetics of Adsorption from Solution to the Air-Water Interface," *J. Colloid Sci.*, **8**, 575, 585 (1953).
- Rupe, J. H., "On the Dynamic Characteristics of Free Liquid Jets," *Jet Propulsion Lab. Tech. Rept. No. 32-207* (1962).
- Scriven, L. E., and R. L. Pigford, "Fluid Dynamics and Diffusion Calculations for Laminar Liquid Jets," *AIChE J.*, **5**, 397 (1959).
- Southwell, Sir R. V., *Relaxation Methods in Theoretical Physics*, p. 212, Clarendon Press, Oxford, England (1946).
- Tsonopoulos, C., J. Newman, and J. M. Prausnitz, "Rapid Aging and Dynamic Surface Tension of Dilute Aqueous Solutions," *Chem. Eng. Sci.*, **26**, 817 (1971).
- Young-Hoon, A. A., "Gas Absorption into Turbulent Jets," Ph.D. thesis, Univ. Birmingham, England (1972).

Manuscript received January 3, 1977; revision received January 3, and accepted January 5, 1978.