Flow-visualization by means of a time-reaction

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A continuous-flow system is fed with a liquid which turns blue a specified time θ after entering. A more or less stationary pattern is thus set up, those parts of the liquid which have spent times longer than θ in the system being blue while the rest is colourless. The value of θ can be changed at will, enabling details of the flow-pattern to be deduced. The interpretation of the finer points of the colour-pattern is made difficult by the effects of molecular interdiffusion of different parts of the liquid.

Denbigh, Dombrowski, Kisiel & Place (1962) have described the use of a time-reaction for flow-visualization. Two solutions are mixed, and the mixture turns blue quite suddenly a definite time after mixing. If the mixture is made up continuously and runs through a continuous-flow system a more or less stationary pattern is set up, only those parts of the liquid which at any instant have been in the system for more than a specified length of time being blue.

If a tracer such as a dye is injected uniformly into the fluid entering a continuous-flow system, only a momentary impression of the nature of the flow-pattern is obtained as the tracer spreads through the system. More can be discovered by injecting tracer at points in the interior of the system, but the injection tube itself disturbs the flow. On the other hand, if a time-reaction is used the pattern observed will be stationary, if the flow is steady. The boundary between blue and colourless liquid separates those parts of the system which are occupied by fluid 'older' and 'younger' than the reaction time θ, which can be varied at will. (The 'age' of the fluid here refers to the length of time for which it has been in the system.) The distribution of colour will reveal a good deal about the pattern of flow, regions of stagnation and recirculation, etc. If the flow is not steady, the fluctuations of the blue zones give a direct visual impression of the degree and nature of the unsteadiness, while a time-exposure photograph yields the time-average pattern.

Denbigh *et al.* used a reaction-mixture containing sulphite, iodate and starch. We have carried out experiments with a different reaction. In our case the mixture contained sodium persulphate, potassium iodide, sodium thiosulphate and starch. There is a slow reaction between persulphate and iodide ions, yielding iodine:

$$Na_2S_4O_8 + 2KI \rightarrow Na_2SO_4 + K_2SO_4 + I_2 \quad \text{(slow)}.$$

The iodine reacts instantaneously with the thiosulphate and is reduced back to iodide:

$$I_2 + Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI \quad \text{(instantaneous)}.$$

When all the thiosulphate has been used up in this way, free iodine is liberated and the solution immediately turns blue because of the well-known starch–iodine reaction. The intensity of the blue colour does not depend on the amount of iodine present. The rate of production of iodine and destruction of thiosulphate is proportional to the concentrations of both persulphate and iodide. Provided a substantial excess of persulphate is present the rate of destruction of thiosulphate is virtually constant up to the moment of turning blue because the concentration of iodide remains unchanged. The time θ required for the mixture to turn blue is thus $\theta = C_0/kC_1C_2$, where C_0, C_1, C_2 are the initial concentrations of thiosulphate, persulphate and iodide. The rate-constant k has the value $1{\cdot}52 \times 10^{-4}$ l/g mole sec at 20° C, according to our measurements. In our experiments the rate of production of iodine after the moment of turning blue could also be regarded as constant, because the fractional extent of reaction of iodide was small on the time-scale of the experiments.

Three solutions were mixed at the entrance to the flow-system under study: (*a*) 0·5 M sodium persulphate (151 g/l); (*b*) 0·1 M potassium iodide (16·6 g/l) with 1 g starch per litre; (*c*) 1 M sodium thiosulphate (142 g/l). The first two solutions were metered in with rotameters, and in all the experiments described here the flow-rate of each was 400 cm^3/min. The thiosulphate solution was added at a controlled rate (of the order of 1·5 cm^3/min) by displacing it from a container by means of the oxygen and hydrogen generated by the electrolysis of 5 N H_2SO_4 (50 % wt.) between platinum electrodes with a 12 V supply. The rate of addition was controlled by adjusting the current, without changing the total rate of flow through the system appreciably. The time θ required (at 20° C) for the resulting mixture to turn blue was $63i$ sec, where i is the current in amperes.

The flow-system consisted of a cylindrical vessel of 200 cm^3 capacity, about 5 cm diameter and 10 cm long. The mean residence-time of the liquid (i.e. volume divided by flow-rate) was 15 sec.

Figure 1 and figure 3, plate 1, illustrate an arrangement in which the liquid enters and leaves through radially directed tubes situated at opposite sides and ends of the vessel. Figures 3 (*a*), (*b*) and (*d*), plate 1, were taken with $\theta/\tau = 1{\cdot}0$ (τ being the mean residence-time). In these pictures, therefore, only fluid which has been in the system for a time longer than the mean residence-time is blue. Figures 3 (*a*) and (*b*) are instantaneous photographs, while figure 3 (*d*) is a time-exposure of duration 2τ. Figures 3 (*a*) and (*b*) show the degree of fluctuation in the spatial distribution of material of ages greater than the mean residence-time, while figure 3 (*d*) gives an idea of its time-average distribution. At first sight these pictures suggest that the flow-pattern is not far removed from 'piston-flow', in which all particles of fluid move along paths parallel to the axis and spend the same length of time in the system. In this case the time-reaction method would produce a piston-shaped blue region filling the outlet end of the cylinder and bounded by a plane perpendicular to its axis. However, in true piston-flow none of the liquid in the system would have an age greater than the mean residence-time. Figures 3 (*a*), (*b*) and (*d*) indicate that a substantial part of the system under discussion is occupied by liquid older than this, and as a corollary a substantial part of the liquid must spend times less than the mean residence-time in passage. Figure 3 (*c*), an instantaneous photograph with $\theta/\tau = 1{\cdot}25$, shows that an appreciable part of the liquid spends longer than $1{\cdot}25\tau$ in passage. Considerations concerning the spread of residence-times are important in the design of chemical reactors (for instance), where departures from piston flow may decrease output or affect the quality of the product.

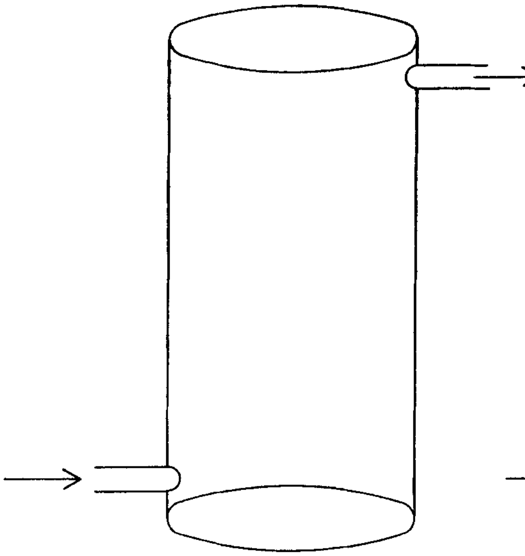

Figure 1. Inlet and outlet radially directed and at opposite sides and ends.

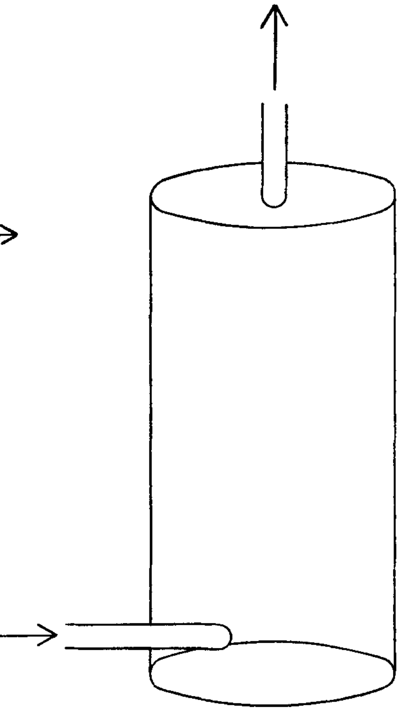

Figure 2. Tangential inlet and axial outlet.

Figure 2 and figure 4, plate 2, illustrate an arrangement in which the liquid is introduced tangentially at one end of the cylinder and leaves it via the centre of the other end. It is known that the flow in such systems is very complicated, with regions of reverse flow (Binnie 1957; Bradley & Pulling 1959; Place, Ridgway & Danckwerts 1959). Figures 4 (*a*) and (*c*) are instantaneous and time-exposure photographs, respectively, with $\theta/\tau = 1{\cdot}2$. They show that there is a region near the axis containing liquid which has spent more than the average length of time in the system, and the comparison between figures 4 (*a*) and (*c*) indicates considerable unsteadiness of flow in the region midway between the walls and the axis. Figures 4 (*b*) and (*d*) are instantaneous and time-exposure photographs, respectively, with $\theta/\tau = 1{\cdot}6$, and show that there is an annular region containing liquid which has entered the system more than $1{\cdot}6\tau$ before. It is known (Place *et al.* 1959) that in a flow-system of this kind there is upward flow near the cylindrical walls and through a narrow 'tube' surrounding the axis, and reverse flow through an annular region between these; there must therefore be two zones where the mean velocity is zero. The reverse flow probably originates somewhere near the surface of the top end of the cylinder. This behaviour is illustrated by figures 4 (*a*) and (*b*); some of the blue liquid is stationary and some flowing backwards. The time-reaction method is particularly suitable for the study of complicated, relatively steady flow-patterns of this kind, which can be observed at leisure and in detail without disturbing the flow.

The crudest way of interpreting such observations, employed above, is to say that only those parts of the fluid which have been in the system for a time exceeding θ will be blue. Although this interpretation will serve for a qualitative assessment of the results, the true significance of the pattern observed is subtler than this. To the extent that molecular diffusion plays a role in determining the spatial distribution of molecules of different ages it is not strictly possible to think in terms of elements of fluid which maintain their identity during passage through the system. Each element, in the sense understood in hydrodynamics, contains a constantly changing population of molecules. It will then not in general be possible to ascribe an age to a macroscopic, chemically homogeneous region of the liquid, as it may contain an intimate mixture of molecules of different ages. In an isolated portion of solution the thiosulphate has an initial concentration C_0, and at time t after reaction starts its concentration is $C = C_0(1-t/\theta)$. At times greater than θ free iodine is being formed at the same equivalent rate as that at which thiosulphate was formerly disappearing. If we regard the concentration of iodine as a negative concentration of thiosulphate, it is also governed by the above relationship. If we mix two portions of liquid which have been reacting for different lengths of time (have different ages), one greater and one smaller than θ, the free iodine in one portion will react instantaneously with the free thiosulphate in the other. The resulting mixture will be blue if the average age of the mixture (weighted by volume) is greater than θ (i.e. if $C < 0$) and colourless if the average age is less than θ ($C > 0$). If, in the flow-system, there is diffusional mixing of molecules of the liquid which have been in the system for different lengths of time the fraction of the liquid which is blue is not necessarily the same as the fraction which has been in the system for a time greater than θ. A small amount of very old liquid can turn a large amount of young liquid blue. Since some of the liquid may remain in the system for a very long time, while none can have an age less than zero, the fraction of the liquid which is blue is likely in general to be larger than the fraction older than θ. On the other hand, in figure 4 (*b*) the down-flowing old blue liquid is decolourized before it leaves the system by mixing and reaction with an excess of fresh incoming fluid.

The parts of the system which are blue are in fact those regions where the local average age of the molecules is greater than θ. A deeper analysis of this statement would lead to a discussion of concepts such as the composition at a point, which are beyond the scope of this communication. Some of the concepts involved have been discussed by Zwietering (1959).

These considerations indicate that caution should be exercised in interpreting the finer points of the observations made with the aid of the time-reaction. The broad picture, however, can generally be taken at its face value.

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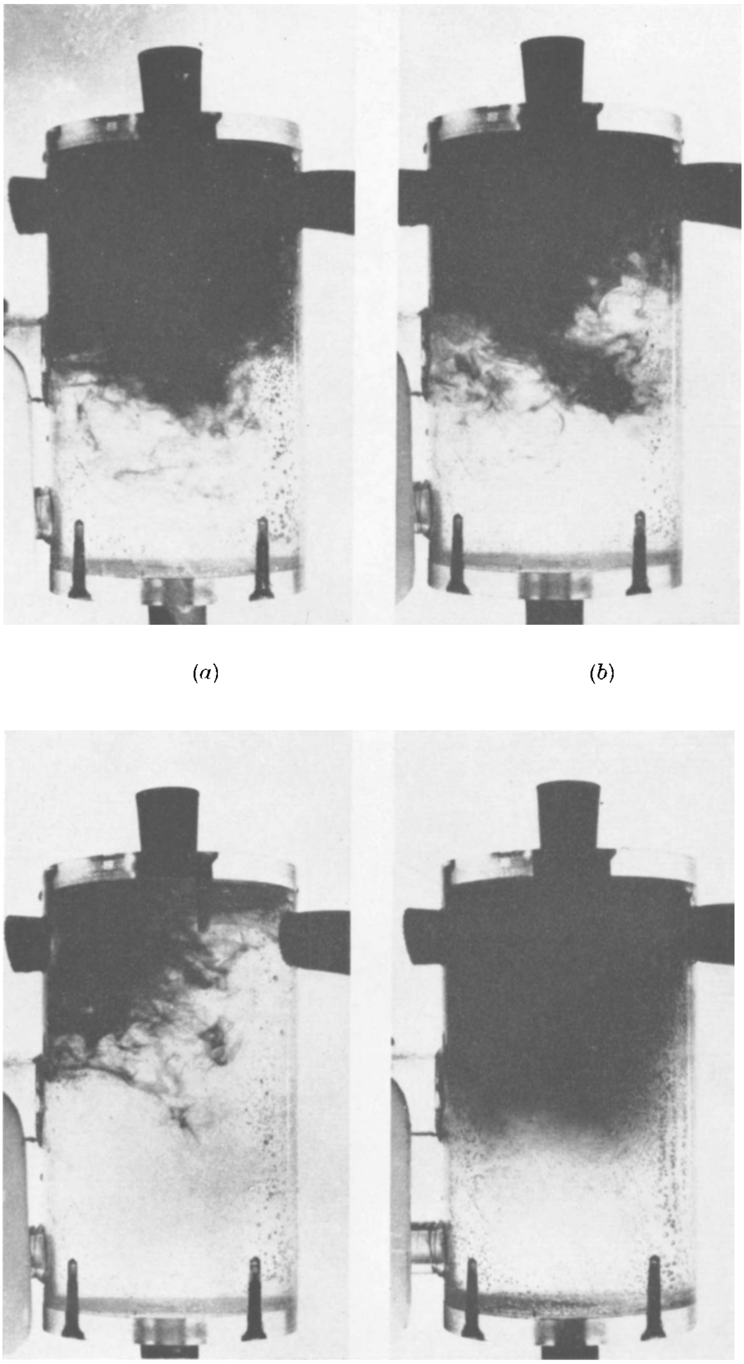
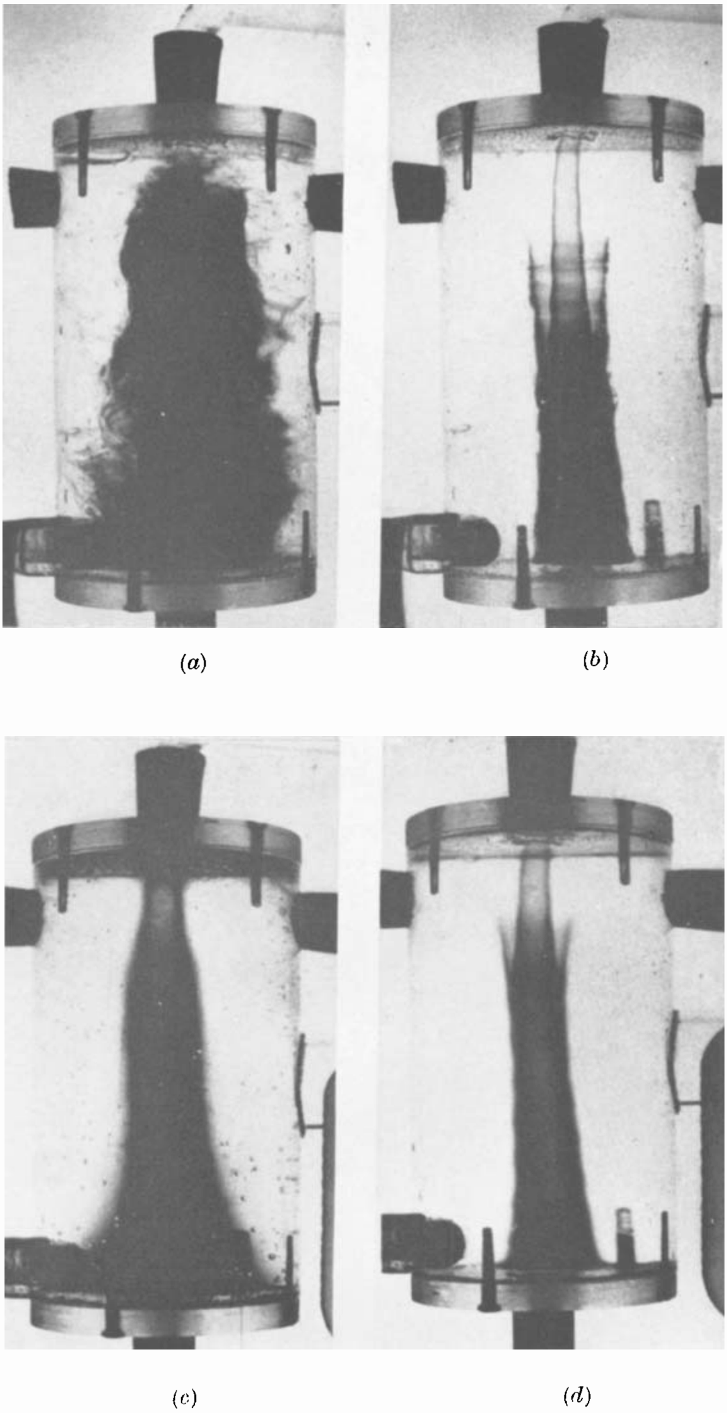


(*a*) (*b*)

(*c*) (*d*)

FIGURE 3. Inlet and outlet as shown in figure 1. (*a*) $\theta/\tau = 1{\cdot}0$, instantaneous; (*b*) $\theta/\tau = 1{\cdot}0$, instantaneous; (*c*) $\theta/\tau = 1{\cdot}25$, instantaneous; (*d*) $\theta/\tau = 1{\cdot}0$, time exposure.



(*a*) (*b*)

(*c*) (*d*)

FIGURE 4. Inlet and outlet as shown in figure 2. (*a*) $\theta/\tau = 1{\cdot}2$, instantaneous; (*b*) $\theta/\tau = 1{\cdot}6$, instantaneous; (*c*) $\theta/\tau = 1{\cdot}2$, time exposure; (*d*) $\theta/\tau = 1{\cdot}6$, time exposure.

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