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The preparation of water for surface-clean fluid mechanics

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This paper describes the development of a new technique for removing surface-active contaminants from water so that it may be used for surface-clean experiments in fluid mechanics. The removal of contamination from concentrated aqueous solutions of non-surface-active materials is also possible, allowing considerable variation of density and viscosity in these experiments. Instead of using the conventional distillation processes necessary for most work involving surface chemical phenomena, surface-active substances are removed by adsorption onto a dense current of small nitrogen gas bubbles rising in a long vertical column of the water. The efficiency of the technique was found to increase to a great extent when common salt was dissolved in the water, up to concentrations around 40 g/l, and experiments are described which allow the identification of several physical processes which aid the operation of the method. The adequate performance of the cleaning technique in the removal both of an ionic surface-active material and also of Gentian Violet dye is demonstrated. The method should permit the design of surface-clean experiments using much larger volumes of water than are possible when the water has to be distilled using conventional surface chemical techniques. A simple apparatus for the measurement of surface tension is also described.

1. Introduction

1.1. *The preparation of surface-clean water*

The need for special techniques for the performance of fluid-mechanical experiments with film-free surfaces is becoming increasingly recognized. It has been known for a very long time (Lamb 1932) that surface films greatly increase the damping of surface waves on water, but the lengths to which one must go in order to remove significant surface films are still not widely appreciated. The absence of a visible film is not a sufficient guarantee, since an organic film may have a significant elastic effect when its thickness is less than 10 nm, much less than the optical wavelengths used for visual observation. Accurate measurements of the damping of progressive waves on film-free water have been performed with capillary ripples only comparatively recently (Davies & Vose 1965), while similar measurements on gravity waves have apparently so far not been reported.

There are two aspects of the preparation of clean-surface fluid-mechanical experiments which present considerable experimental difficulties and often limit the scale of experiments. One is the preparation of water with a sufficiently low bulk concentration of organic materials which reduce surface tension and the other is the maintenance of a clean surface on this water once it is in the apparatus. There are established means of dealing with both types of problem on a small scale, and much work has been done using clean-surface techniques in investigations of the effects of surface-active materials on capillary-wave damping (Lucassen-Reynders & Lucassen 1969). The second problem, that of keeping the water clean, is tackled by restricting the design to the few acceptable constructional materials, employing rigorous cleaning techniques and avoiding touching the surface with anything not sufficiently clean. Should slight accidental contamination occur, there is a remedy described by Davies & Vose (1965) in which clean powdered talc is sucked from the surface, removing the surface layer of water together with adsorbed contamination. These techniques are readily mastered with practice.

It is the process of preparation of the water which severely limits the design of fluid-mechanical experiments such as those involving measurements of the damping of gravity waves. One of the most used techniques involves a final distillation of the water from dilute alkaline potassium permanganate solution, whose purpose is to oxidize and remove the offending organic materials which usually occur in tap water. Limits are imposed both on the rate of production of clean water and also on the total volume available for a given experiment. The total volume is limited because it is often found that the distillation cannot be made a continuous process, a small fraction of offending organics being present which is sufficiently volatile to be boiled away at the beginning of the distillation. In a continuous process this small fraction would accumulate in the distillate. Because storage is made difficult by the severe risks of contamination, batch production limits an experiment to the volume given by the distillation apparatus, and volumes in excess of 10 l require very expensive apparatus. A 10 l capacity denotes an experiment on a relatively small scale, and the distillation cleaning process is therefore found to limit the design of experiments to a very large extent.

A second cleaning technique which is often used passes the water through a bed of activated charcoal, upon which the undesired organic materials become adsorbed. Although this technique avoids the disadvantages of the distillation process, the contamination unavoidably builds up in the charcoal bed, necessitating either complete replacement of the bed or its regeneration using steam.

The cleaning technique to be described here uses an entirely different approach to the preparation of clean water, and it is believed that it will allow the execution of experiments using much greater water volumes than are possible with the established distillation processes. Because the present technique avoids the distillation of the water, it also has the advantage of allowing a certain amount of variation in the physical properties of the resulting liquid, while retaining its intrinsically aqueous surface chemical behaviour. Moderate increases in density and in viscosity are possible, using the same cleaning technique with solutions of ionic salts and of sucrose, respectively. While modification of one physical property necessarily affects the others, including surface tension, and the range of properties possible without losing the distinctive surface chemical behaviour of water is limited, the possibility of removal of the highly surface-active contamination which tends to accompany soluble additives considerably extends the range of possible experiments. Solutions of both inorganic salts and sucrose (commercial grades) have been stripped of surface-active material using the present technique, and substantial modifications of the density and viscosity have been produced. Salts such as potassium iodide can increase the density of the liquid by as much as 50 %, and surface-clean experiments have been performed on sucrose solutions with viscosities up to $5\,\mathrm{mN\,s\,m^{-2}}$ (cf. that of water at the same temperature: $1\,\mathrm{mN\,s\,m^{-2}}$). The cleaning process remains substantially the same, and it is possible that even higher viscosities may be feasible using more concentrated sucrose solutions.

1.2. *The use of adsorptive bubble separation techniques*

The method for cleaning water described here removes contaminants using precisely those qualities they possess which are found to upset clean-surface experiments. Since the contaminants find it energetically favourable to become adsorbed on water/air surfaces, reducing the surface tension and giving an unwanted elasticity to the surface, they will tend to become attached to small air bubbles rising through the contaminated water. Even though the adsorbed molecules may be in a state of dynamic equilibrium with the bulk liquid, adsorption and desorption processes occurring simultaneously, there will be a net flow of surface-active material upwards through the water. At the surface of the water, the bubbles will break, sometimes after going through a foam phase, and the adsorbed material will become concentrated at the top. If it is arranged that this more highly concentrated material is flushed away, the water remaining at the lower levels will have been to some extent cleansed.

Sebba (1960) demonstrated the use of bubbles and foams to separate mixtures of dyes dissolved in water, and Lemlich (1972) gives a review of the work done on a wide variety of bubble/foam systems, together with an examination of the physical principles involved. These techniques, many of which are commercially significant in mineral separation and associated processes, are related to the technique used here, although the present process is designed for the recovery of the solvent rather than of the dissolved or dispersed material it contains. The process is selective, since only surface-active materials are removed, the other components of tap water, such as its inorganic salts, being allowed to remain in the water. According to Lemlich such salts may actually aid the removal of the organic substances, since, especially for ionic surface-active materials, the presence of ionized salts may make the adsorption processes more favourable. While the presence of inorganic salts in the water would make it unsuitable for precision surface chemistry work, their effects on fluid-mechanical experiments are likely to be very small, being essentially only small modifications to the specific gravity, viscosity and static surface tension of the water.

Experiments have been carried out to assess the possibility of using the bubble cleaning principle to reduce the contamination level in tap water sufficiently for surface-clean fluid-mechanical experiments to be carried out in a reasonable time without significant degradation of surface cleanliness caused by diffusion of surface-active material from the bulk to the surface.

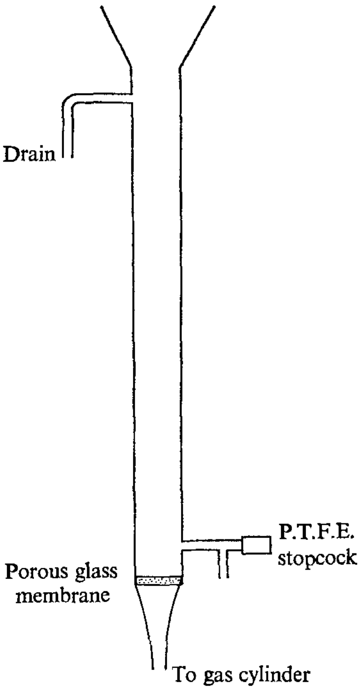

FIGURE 1. The bubble column (not to scale). The conical bell aids the breaking of foam in highly contaminated systems. The sintered glass membrane has pore sizes in the range 5–15 μm.

2. Experimental techniques

2.1. *The bubble column*

Experiments were performed using an all silica glass/P.T.F.E. apparatus consisting of a 1·9 m length of 30 mm Pyrex tubing mounted vertically with a short conical bell at its upper end (figure 1). A short tube was attached near the top end, and contaminated water from collapsing foam was allowed to drain away through this tube. The lower end of the column was sealed with a porous glass membrane, through which oxygen-free nitrogen gas was forced. The gas was taken from a cylinder via a flowmeter calibrated for the 0–0·6 l/min range. Control of the gas flow rate to within 10 % required only occasional adjustment of the needle valve on the cylinder. Water was withdrawn from the tube, at a point about 15 mm above the glass membrane, through a Pyrex/P.T.F.E. stopcock (Quickfit Rotaflo) which allowed the slow trickle of liquid to be sensitively controlled. In the experiments to be described, water was added to the top of the column using a beaker, but automation of the feed to compensate for the withdrawn volume and also to flush out the upper concentrated layers should present few problems. The gas was not humidified before it passed into the column, and this had the effect of cooling the water.

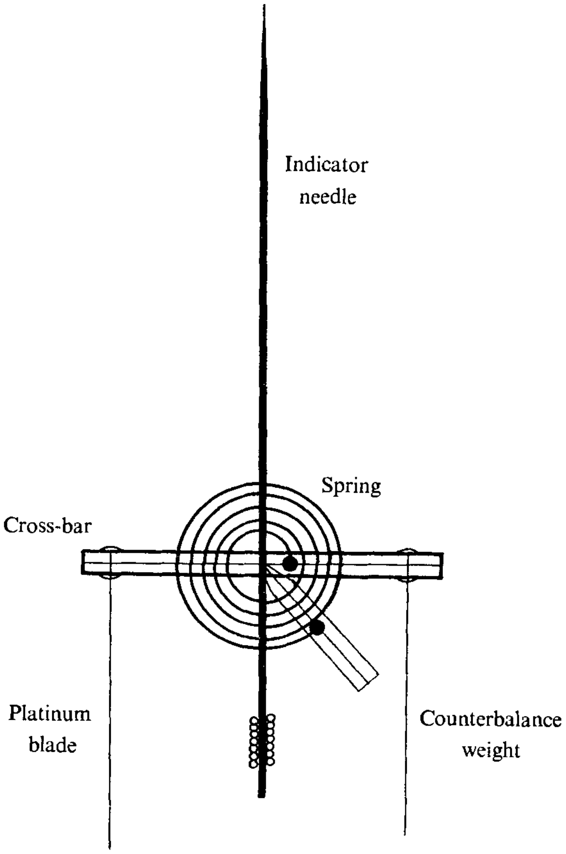

FIGURE 2. The moving-coil electrical surface-tension balance. The platinum plate is suspended in the surface from a length of hair attached to the cross-bar on the moving coil. The counterbalance weight is sufficient to balance the dry plate with the needle in the null position, and surface-tension force is counterbalanced by the passage of current through the coil.

2.2. *The surface-tension measurement apparatus*

The measurement of surface tension and of its variations (such as those caused by deliberately added surface-active material) is very important in clean-surface fluid mechanics. The most reliable method of measurement appears to be that which measures the force exerted by the surface on a wetted rectangular plate with zero contact angle when its lower horizontal edge just reaches the level of the undisturbed surface (Padday 1969). The apparatus used for this work is a simplification of an electrical balance described by Padday (1957). As may be seen from figure 2, the present instrument measures the pull of the surface on the plate by opposing the force with a known electrical current applied to a simple moving-coil ammeter movement such that the indicating needle attached to the movement registers an arbitrary null displacement condition. One advantage of this simple system is that the linearity of the meter movement may be ignored, measurements being always made with the coil in the same position. In this case current was supplied to the coil from a constant-voltage power supply using a

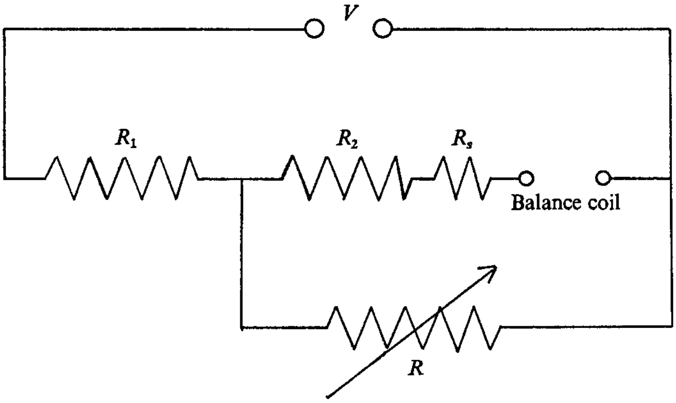

FIGURE 3. Circuit of the surface-tension balance. R is a 500 ohm, linear, 10 turn potentiometer with a 1–999 digital indicator; R_1 = 560 ohm; R_2 = 510 ohm; R_s = 10 ohm standard resistor; V = 26·5 V, from a constant-voltage power supply. The current through the balance coil is not linearly dependent on R but varies in a way which gives greater force resolution for high surface-tension forces.

circuit which allows continuous variation, controlled by a 10 turn digitally indicating potentiometer (figure 3). Accurate current measurements could be made by connecting a digital millivoltmeter to a laboratory standard 10 ohm resistor left permanently in the circuit. More routine measurements, to within 0·1 mN m^{-1}, could be made by calibrating the current source with its 1–999 indicator, and consulting the calibration table to find the current. The rectangular plate used to measure the surface-tension force in this case was a roughened platinum plate, the whole meter being lowered with its indicating needle balanced at null until the plate just touched the water surface. Measurement of the current required to return the needle to null allowed the surface tension to be deduced. One of the advantages of the hanging-plate system over plate-detachment techniques is that the monitoring of surface tension is continuous as long as the plate is correctly positioned in the surface.

3. Assessment of the efficiency of bubble cleaning

3.1. *Methods of assessment*

Routine surface-tension measurements to within 0·1 mN m^{-1} give a reasonable idea of how much contamination is present on a surface, but it is usually necessary to combine these measurements with an extremely sensitive empirical test described by Kitchener (1964). The water is violently agitated, and if any bubble persists at the surface for longer than 1 s, then the water should be rejected for clean-surface experiments. This test uses the fact that surface-active materials, in changing the surface tension, impart a certain degree of elasticity to the surface. Expansion and contraction of the surface is resisted by the consequent changes in surface tension, and this effect gives stability to thin films such as those which enclose surface bubbles and those which occur during the close approach of bubbles in the bulk liquid. It is found in practice that the time of surface-bubble persistence on a clean water surface is considerably below 0·5 s, and that the presence of surface-active material in a quantity barely detectable by surface-tension measurement gives a marked increase in this persistence time. Tap water usually contains calcium and magnesium salts as its principal impurities, and, although in general the effect of inorganic salts on bubble persistence time is not yet completely certain (Kitchener 1964), it can be said that, at the concentrations of these compounds which are usually found in tap water, the effect on persistence time is negligible. At higher concentrations, such as those used in the experiments described here, there is disagreement over the persistence-time effect.

Gleim, Shelomov & Shidlovskii (1959) found that some high concentrations of magnesium and sodium salts tended to stabilize surface bubbles, and they found that bubbles persisted on clean surfaces of salt solutions for as long as 1·5 s. Kitchener considers that this stabilization may be due to small quantities of organic surface-active materials carried into the water along with the salt, and in view of the importance of this point regarding both the use of the persistence test for salt solutions and the mechanisms underlying the bubble coalescence phenomena described in the following section, careful experiments were performed in order to clarify the situation. Sodium chloride was heated to red heat in a clean porcelain crucible for 20 min to remove organic material, and, when cool, the fused salt was added to clean distilled water in a Pyrex flask, up to a concentration of 20 g/l. The water initially passed the shaking test, no bubble existing at the surface for as long as 0·5 s, and no definite effect was perceived visually at concentrations up to 5 g/l. However, by 20 g/l the vigorous shaking of the flask produced bubbles persisting at the surface for between 1·0 and 1·5 s. As well as the effect on the bubbles after reaching the surface, it was also observed that the shaking process resulted in larger numbers of small bubbles (around 1 mm) being seen rising to the surface than was the case with the water alone. It is believed that this observation is associated with the effect of the salt on bubble coalescence illustrated by the experiments described in §3.2.

The experiment agrees well with the work of Gleim *et al.* using apparently clean conditions, and also with the results of Marrucci, Nicodemo & Acierno (1969), although the conditions under which the experiments were performed are less well specified in this case. It is therefore concluded that high concentrations of inorganic salts can lead to elastic effects in situations involving the rupture of thin liquid films. The observations discussed in §3.2 give further evidence of this elastic effect.

3.2. *The effects on tap water*

Using both surface-tension measurements and the shaking test, bubble cleaning experiments were performed on fresh tap water. A definite cleaning effect was observed on water withdrawn from the column after 30 min bubbling at 0·4 l/min, but it was found that under conditions of steady withdrawal the improvement could be maintained only at withdrawal rates less than 0·5 l/h. Following the indication of Lemlich (1972) that the presence of inorganic salts may increase the removal of surface-active substances, the effect of addition of sodium chloride was investigated. It was found that additions of quantities a pure vacuum-dried grade of salt up to about 20 g/l had remarkable effects bo on the cleaning properties of the column and on the observed distribution bubble sizes within the system. The large extent of the observed improveme was not expected on the basis of the results shown by Lemlich, however, and it thought that a large part of the improvement in this case is probably due to th accompanying marked reduction in bubble sizes, apart from any effect relate to the ionic properties of the contaminants. It is obvious that the cleanin properties should be related to the size of the bubbles produced at a given flo rate, since smaller bubbles both have a greater specific surface area and also ris at a lower velocity, giving more prolonged contact with the contaminated water

Figure 4 (plates 1–3) shows a series of photographs which are representativ of the stable bubble sizes and distributions produced by the same gas flow rat and the same porous glass membrane for a series of salt concentrations. The static pressure in the observed region was almost constant through the series of photographs, since, although the density of the bubbly liquid varied as the bubble size changed, the total mass of water in the tube was kept constant and decreasing density was almost completely compensated at this depth by increasing column height. The photographs were taken 430 mm above the membrane, well away from the confused region which occurs immediately above the membrane, within which the bubbles are observed to coalesce to some extent. It is in this region that the ultimate size of the bubbles appears to be determined, and it is apparent that the action of the salt is probably on the coalescence process in this region rather than on the processes of small-bubble formation immediately adjacent to the glass membrane.

This reduction in bubble size is in itself an indication that the dissolved salt imparts some stability to the water/air surface, and it supports the conclusions of §3.1. The criticism voiced by Kitchener (1964), that examinations of thin-film stability are prone to interference from small concentrations of organic materials, applies equally to bubbles at the free surface and to bubbles in the bulk liquid. However, at the free surface, a bubble enters a region in which any surface-active material is being continuously concentrated by diffusion and adsorption, and this concentration is being reinforced by the transport of extra active material from the bulk via rising bubbles. A contamination effect at the surface would therefore be expected to be more apparent than an effect in the bulk concerning the coalescence of colliding, freshly formed bubbles. With a flow rate of 0·4 l/min and a constant bubble diameter of 1 mm, the rate of creation of fresh surface in the tube would be about $0{\cdot}04\,\mathrm{m^2\,s^{-1}}$, and, although bubble diameters in the practical case are distributed over a range, this simple example does serve to indicate that surface is being created at a considerable rate. Contamination present in small quantities would require some time to diffuse to this freshly formed surface, and an effect would not be expected in the bulk in a situation where the accumulated contamination at the free surface has such little effect. The coalescence of bubbles is therefore much less likely to be affected than is surface-bubble persistence, and the observed retardation of the coalescence process is a more reliable indicator of the elastic effects due to the presence of the salt.

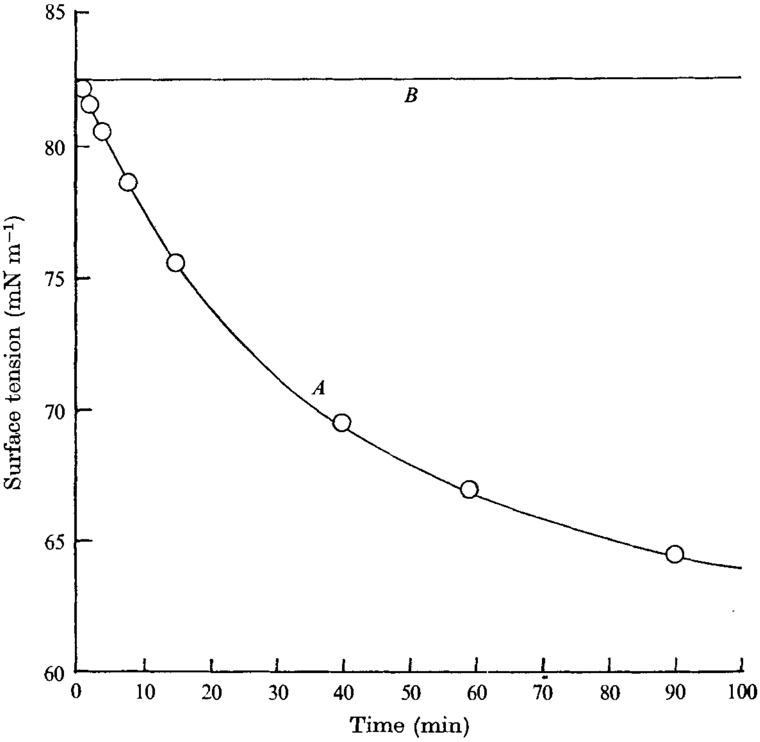

FIGURE 5. Measurements of the surface tension of a contaminated salt-water system: salt concentration = 250 g/l. The salt used was a vacuum-dried commercial grade. *A*, decrease of surface tension with time following the suction of talc from the surface; *B*, surface tension (82·5 mN m^{-1}) of the bubble-treated solution, which remained constant over a 2h period.

A further effect of the salt was observed to be that a short length of draining foam was often produced at the surface of the bubbly solution. This foam may have been due to a combination of the effects of there being smaller bubbles, draining more slowly, more efficient scavenging of bubble-stabilizing surface-active material, and perhaps stronger adsorption processes in the presence of the salt. This foam had the ability to trap surface-active material, carrying it away from the bulk liquid phase, and reducing the effect of molecular diffusion processes, which tend to oppose the cleaning action of the bubbles.

The performance of the bubble cleaning process is amply illustrated by the surface-tension measurements shown in figure 5. A vacuum-dried commercial grade of salt was dissolved in tap water to 250 g/l, taking precautions against contamination. The variation of the surface tension of this solution as a function of time after talc cleaning is shown by curve *A*. The fairly rapid fall observed is believed to be due to a small concentration of soapy material introduced along with the salt, since this sort of contamination is quite common with commercial grades of salt and no attempt had been made to remove it. Following cleaning in the bubble column, working continuously with a gas flow of 0·4 l/min and a water withdrawal rate of 1·0 l/h, the surface tension was found to maintain a steady value of 82·5 mN m^{-1} after talc cleaning, represented by the straight line *B*. No decrease in surface tension was observed over a 2 h period, and the water was of adequate quality for surface-clean fluid mechanics, both normal tap-water contamination and the salt-borne contamination having apparently been removed.

3.3. *The effects on solutions of sodium lauryl sulphate*

An extreme case of contamination was contrived in distilled water by adding 500 mg of sodium lauryl sulphate, a highly surface-active ionic material, to 1·0 l of water. The surface tension of this solution at room temperature was found to be 41·6 mN m^{-1}. Talc cleaning was performed, and understandably, in view of the extremely high concentration of surface-active material in this case, immediate remeasurement of the surface tension indicated no increase following the cleaning process. When the solution was placed in the bubble column and air passed through it, a stable foam was continuously generated until all the solution had been foamed away. It is obviously too much to expect the bubble cleaning process to operate in the presence of such a large quantity of strongly foaming material, but this system does give a good illustration of the remarkable improvement which may be produced by the addition of salt. On adding salt to a concentration of 40 g/l, it was found that after the column had been operated at the usual flow rate of 0·4 l/min for less than 20 min, the foam had almost completely disappeared from the top of the bubbly solution via the drain tube, leaving nearly three-quarters of the original volume of liquid behind in the tube. The water withdrawn from the stopcock had a surface tension identical to that expected of surface-clean salt solution at this concentration, showing no deterioration over 2 h.

3.4. *The effects on solutions of Gentian Violet dye*

A similar though more spectacular experiment was performed using the surface-active dye Gentian Violet dissolved in distilled water. With sodium chloride added to the 1 g/l dye solution to a concentration of 40 g/l, and a gas flow of 0·4 l/min, the intensity of the dye was observed gradually to decrease at the bottom of the column, increasing at the top and allowing quite a concentrated solution to drain away from the upper drain tube. After some 15 min, the dye left the bottom region completely, and the resulting clear-water zone gradually extended through the whole of the bubbly phase. Such observations as this were found to give a good indication of the role of the various parameters involved in the bubble cleaning method, and a series of experiments was performed to investigate the effects of different gas flow rates and of different salt concentrations. A range of salt concentrations up to 40 g/l was investigated using distilled water, and an interesting competition was observed between the effects of the dye and of the salt on the size of bubbles emerging from the coalescing zone. In pure water, surface-active materials decrease the size of bubbles (this was observed with both the sodium lauryl sulphate solution and the dye solution), and, as was seen in the photographs in figure 4, salt also has the effect of decreasing the size of bubbles. The action of large concentrations of surface-active materials on salt solutions however appears to be to increase the size of bubbles. Thus, as the relative con-

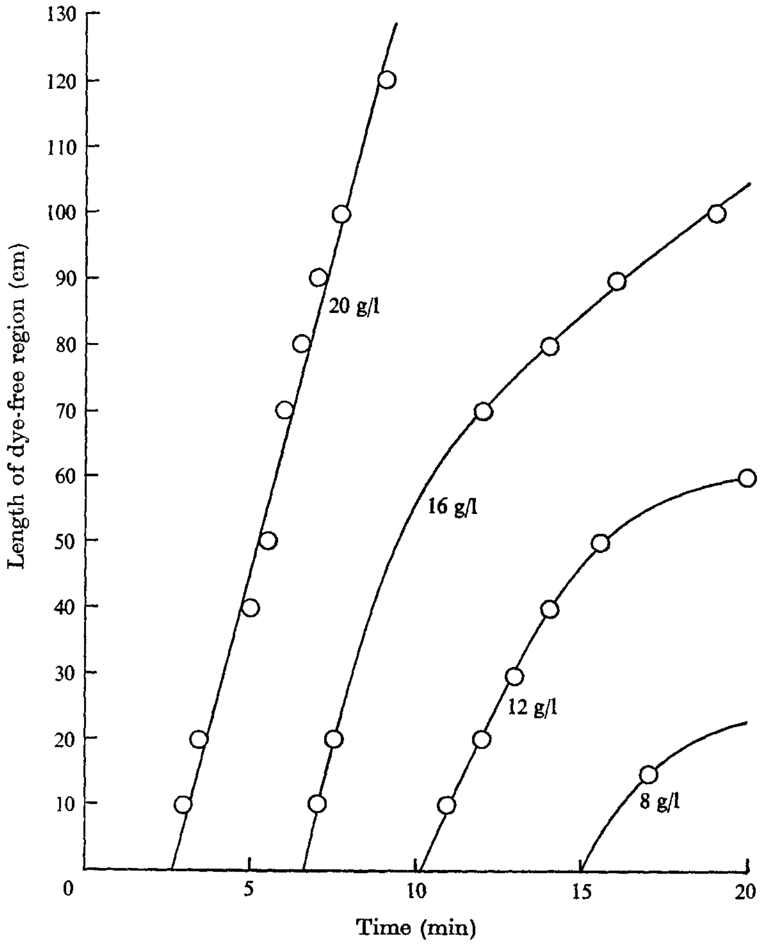

FIGURE 6. The effect of sodium chloride concentration on the removal of Gentian Violet dye from water by bubbling. The gas flow was held constant at 0·4 l/min, the same rate as in the photographs in figure 4.

centrations of dye and salt are changed, the bubble size is observed to vary in a complicated way which is very likely to affect the cleaning process to a large extent.

Figure 6 shows the effect of varying the salt concentration on the time taken for the clear-water region at the bottom of the column to extend upwards through the tube. The measurements are necessarily imprecise, because of the judgement used in deciding the position of the end of the dyed region, and an uncertainty of some 50 mm is estimated for this measurement. It is apparent that the critical concentration of salt for the process to begin working efficiently is around 10 g/l, the beneficial effect increasing rapidly up to concentrations around 20 g/l. It should be noticed that the salt concentrations examined here are about a thousand times greater than those reported in the experiments of Lemlich (1972). At the lower concentrations investigated here, the progress of the cleaning process was found to be accompanied by increasing bubble size, a change which is likely to degrade the process, as explained in § 1.2. At the higher concentrations however, this increase in bubble size did not occur, and this is thought to be a contributory factor in the improvement of the technique around a salt concentration of 10 g/l.

A further effect which was noted at about this concentration was that a foam began to be produced on top of the bubbly liquid, and, as the salt concentration increased, the length of this foam section increased, initiating a further mechanism which aided the cleaning process. After a short time, the constant supply of dye-contaminated bubbles to this continuously collapsing foam produced a visible concentration of dye in the upper layers. This effect was so marked at the higher concentrations that it was possible for all the visible dye to become concentrated at the upper end of the foam, allowing the whole of the liquid region to be cleared of dye.

In order to clarify whether the beneficial effect of the salt is simply due to its reduction of the mean bubble size, another way of generating small bubbles was tried. In this experiment, 1 g/l of a water-soluble, mildly surface-active polymer, polyethylene glycol (molecular weight about 200), was added to distilled water containing dye. The bubbles produced with this solution in the column were similar in size and distribution to those found at salt concentrations in the range 20–40 g/l. The dye was observed to be swept up the column more slowly, but in much the same way as with the added salt, indicating that the decrease in bubble size with salt solutions is one of the major factors determining the greater efficiency of small bubbles.

In summary, the experiments with Gentian Violet dye indicated that the decrease in mean size of the bubbles which emerge from the coalescing region of the bubble column is a major factor in the improvement of the cleaning properties of the column produced by the addition of the salt. This appears to be due to the large increase in freshly formed water/gas surface area for a given gas flow rate as the mean diameter of the bubble decreases. A second factor appears to be the production of a foam region, above the bubbly liquid, which is capable of isolating a large quantity of surface-active contamination. If this foam is adequately removed from the top of the liquid, the isolation effect makes it possible to improve the operation of the process by reducing the likelihood of diffusion of contaminants back down the tube.

4. Discussion

The present experiments have shown that, with bubble flow rates of around 0·4 l/min in a tube 2 m long and 30 mm in diameter, continuous withdrawal of clean water may take place at rates of 1·0 l/h or more when sodium chloride is dissolved in the water. The technique is very flexible, and for a particular application it may be found by experiment that adequate quality may be obtained at greater withdrawal rates. However, even at the rate found here to be sufficient, the simplicity and low cost of the necessary apparatus make the operation of a set of parallel bubble columns a reasonable proposition. The most expensive item in the system, the flowmeter, may be replaced by a cruder instrument, reducing the cost of increasing the number of columns.

The use of cylinder nitrogen gas is thought to be unnecessary, compressed air being adequate. This could be very cheaply provided using a small compressor, as long as a filter is included in the gas flow to ensure removal of foreign matter such as dust and traces of lubricant from the compressor.

The observations on the effect of salt on the distribution of bubble sizes are interesting from the point of view of oceanography. The salinity of sea water is typically in the region of 35 g/l and the present results indicate that at this concentration small bubbles are likely to resist coalescence to a greater degree than they would in fresh water. This would both favour the persistence of whitecaps on the oceans and also aid the transport of naturally occurring surface-active substances to the ocean surface. Monahan & Zeitlow (1969) found that the bubbles formed by breaking waves had a higher proportion of smaller bubbles in salt water than in fresh water, and the present results indicate that this may be an effect of the salt itself rather than of incidental surface-active contamination.

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REFERENCES

DAVIES, J. T. & VOSE, R. W. 1965 *Proc. Roy. Soc.* A **286**, 218–234.

GLEIM, V. G., SHELOMOV, I. K. & SHIDLOVSKII, B. R. 1959 *J. Appl. Chem. U.S.S.R.* **32**, 1069–1072.

KITCHENER, J. A. 1964 In *Recent Progress in Surface Science*, vol. 1, pp. 51–93. Academic.

LAMB, H. 1932 *Hydrodynamics*, 6th edn, pp. 631–632. Cambridge University Press.

LEMLICH, R. 1972 *Adsorptive Bubble Separation Techniques*, pp. 1–5, 133–143. Academic.

LUCASSEN-REYNDERS, E. H. & LUCASSEN, J. 1969 *Adv. Colloid Int. Sci.* **2**, 347–395.

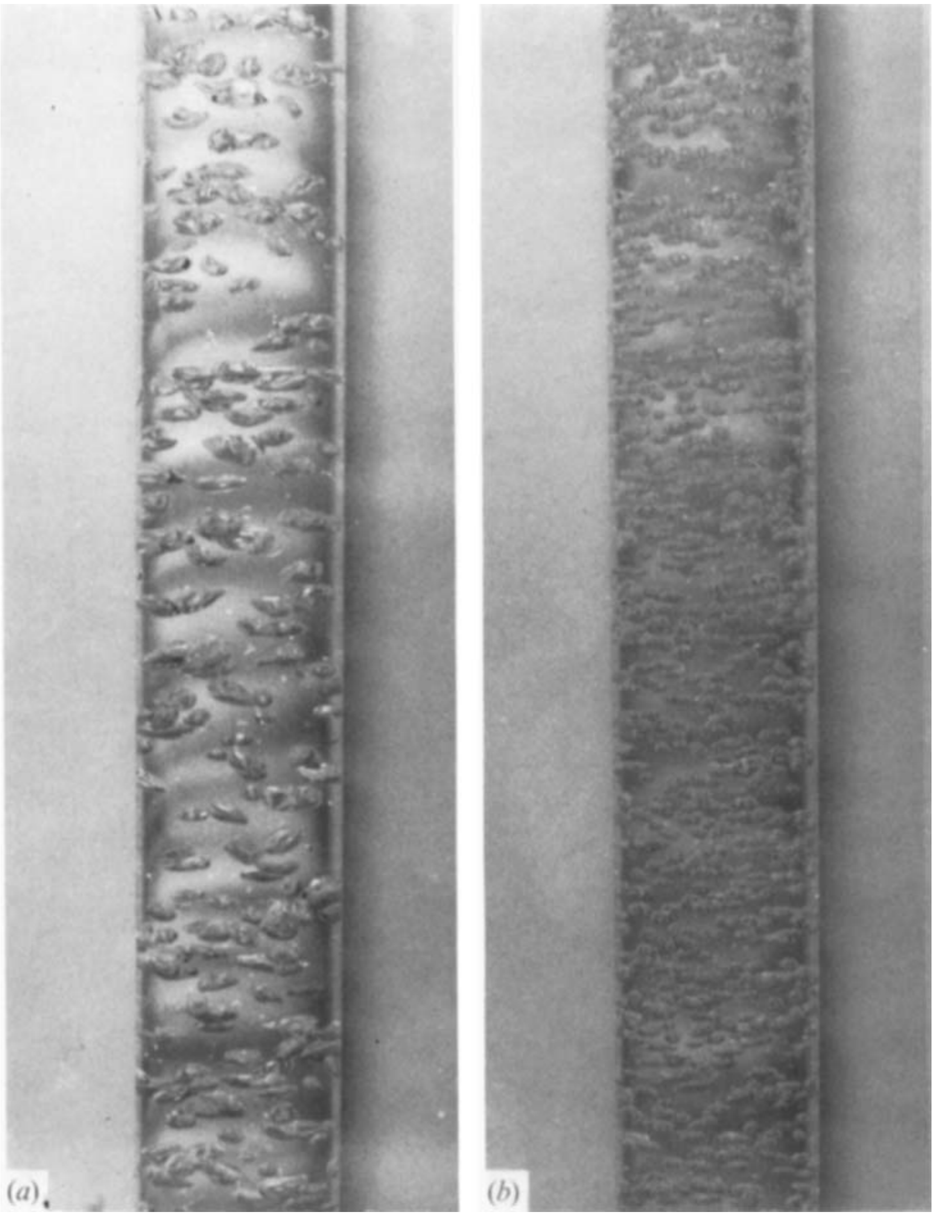
MARRUCCI, G., NICODEMO, L. & ACIERNO, D. 1969 In *Co-Current Gas Liquid Flow*, pp. 95–108. Plenum.

MONAHAN, E. C. & ZEITLOW, C. R. 1969 *J. Geophys. Res.* **74**, 6961–6966.

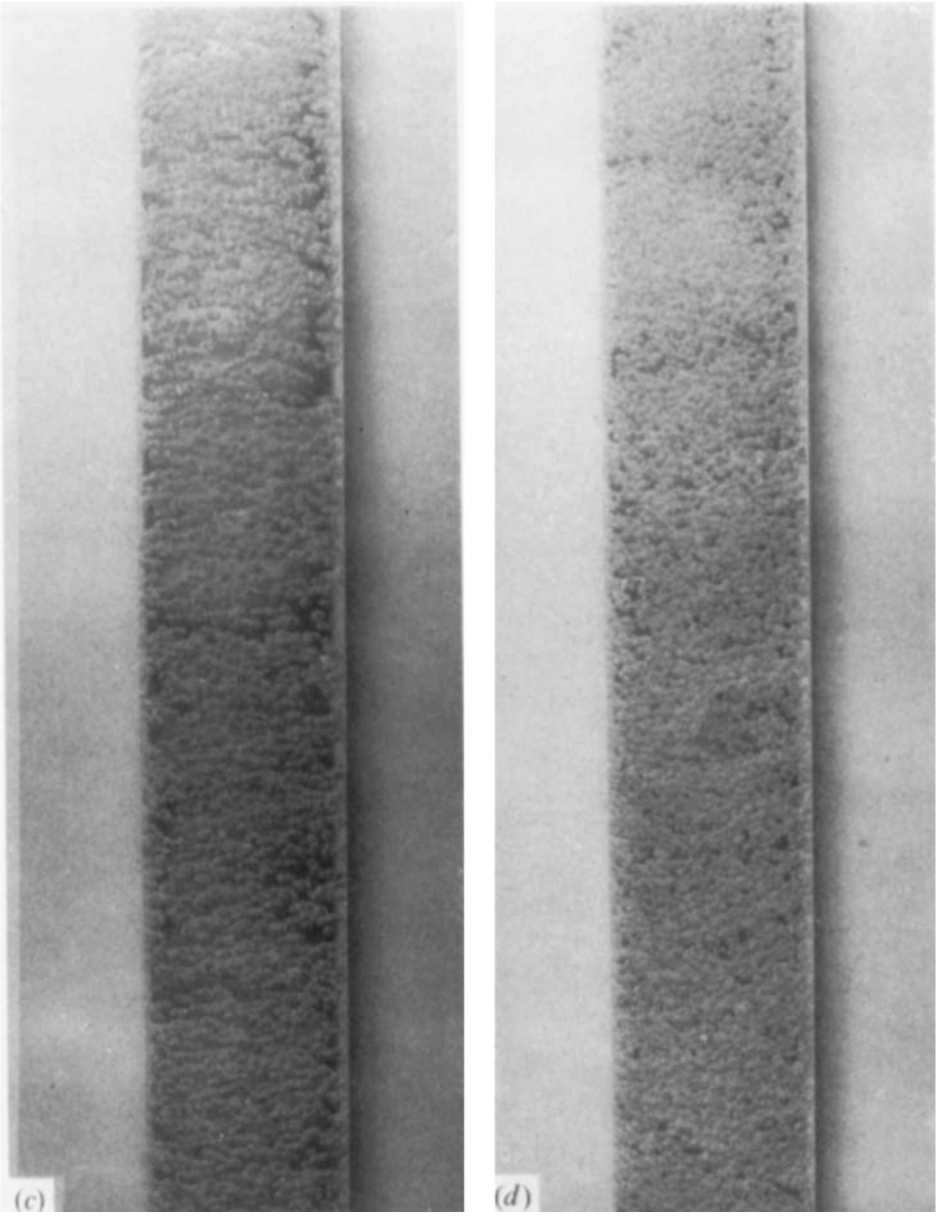
PADDAY, J. F. 1957 In *Proc. 2nd Int. Cong. Surface Activity*, vol. 1, pp. 1–6. Butterworths.

PADDAY, J. F. 1969 *Surface Colloid Sci.* **1**, 101–149.

SEBBA, F. 1960 *Nature*, **188**, 736–737.



FIGURES 4(a) and (b). For legend see plate 3.



FIGURES 4(*c*) and (*d*). For legend see plate 3.

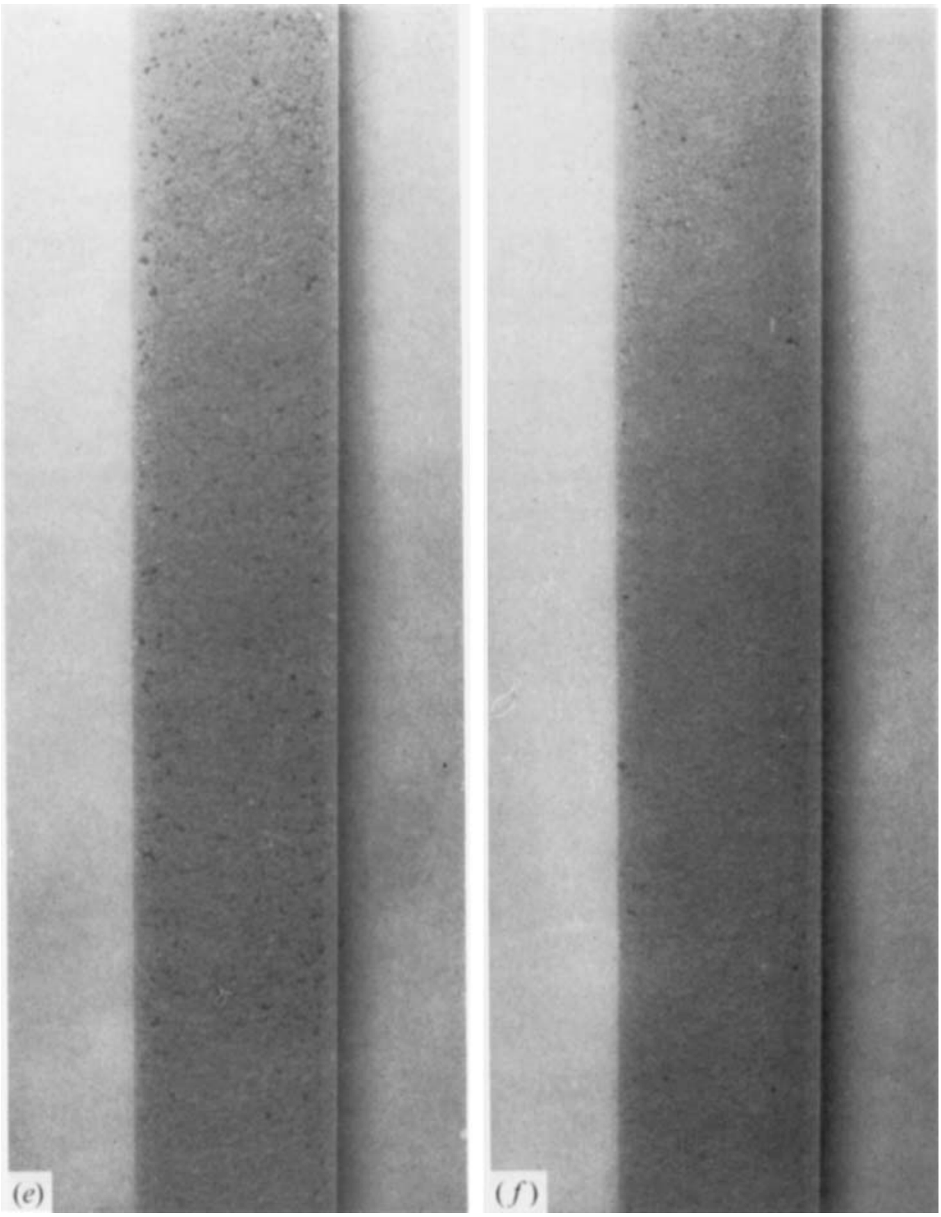


FIGURE 4. The effect of increasing sodium chloride concentration on the size of gas bubbles in the column. Salt concentrations: (*a*) 0; (*b*) 6 g/l; (*c*) 10 g/l; (*d*) 12 g/l; (*e*) 14 g/l; (*f*) 18g/l. The external diameter of the column is 34 mm.