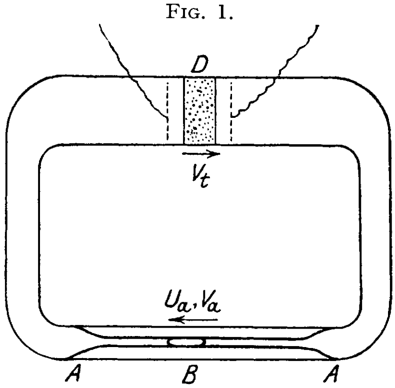
119. *Studies in Electro-endosmosis. Part VI. The "Bubble-tube" Method of Measurement.*

By Fred Fairbrother and Alfred E. Stubbs.

The principle of this method of measurement of electro-endosmosis, introduced by Briggs, Bennett, and Pierson (*J. Physical Chem.*, 1918, **22**, 256) and used subsequently by other workers, is illustrated in Fig. 1. The true electro-endosmotic speed, V_t, through the capillary or porous diaphragm, D, is measured by the apparent velocity of flow, V_a, of the liquid through the single capillary or narrow tube, AA, as indicated by the linear speed, U_a, of the bubble of air, B, which is contained in the capillary.

Fig. 1.



In using a bubble-flowmeter in this way, it is assumed in the first place that the hydrodynamic resistance of the flow-meter capillary and its associated connecting tubes is negligible compared with that of the electro-endosmosis diaphragm. If this is not so, the pressure difference between the ends of the diaphragm, which is necessarily present for any flow to take place through the capillary, will cause a "back-flow" through the diaphragm itself, and the flow observed by the flowmeter will represent only part of the total electro-endosmotic flow. This condition, to a close approximation, can be achieved in practice by careful attention to the design of the apparatus.

There are also other assumptions involved which are less obvious. It must be assumed that the liquid does not flow round the bubble in the direction of motion. It was found in the present work that the minimum length of bubble necessary to avoid this source of error was $1\frac{1}{2}$ times the diameter of the tube; with bubbles of length equal to the diameter of the tube, the effect can readily be observed, and with shorter bubbles, especially if the speed is slow and the bubble-tube slightly contaminated, the effect may be so pronounced as to leave the bubble stationary.

It is also assumed implicitly that the layer of liquid wetting the walls of the bubble-tube is of negligible thickness, *i.e.*, that the bubble moves along as a closely fitting piston. The bubble, however, is bounded not only by a liquid meniscus at each end, but also by the film of liquid on the walls of the tube. When the bubble is in motion, this film, which has been left behind by the liquid moving in front of the bubble, becomes part of the liquid behind the rear meniscus, as the bubble passes along. The effective cross-sectional area of the tube is therefore diminished by this layer of liquid. Hence, if the *volume* flow of the liquid per second is calculated from the *linear* velocity of the bubble and the total cross-sectional area of the tube, the value obtained will be too high. The discrepancy from the true value would be expected to depend upon the rate of flow and on other factors, such as the surface tension and viscosity of the liquid, which affect the rate of drainage from the wetted surface. When only dilute aqueous solutions are employed, together with slow movements of the bubble, this effect, as will be shown, does not introduce errors greater than a few units %. At higher speeds, on the other hand, or when organic liquids of widely differing physical properties are used, the errors introduced by this " wetting " or " drainage " effect may be large.

We have therefore examined experimentally the relationship between the true velocity of a liquid in a capillary tube and that indicated by the linear velocity of an entrained air bubble.

EXPERIMENTAL.

The experimental method consisted briefly in allowing the liquid under examination to flow at a constant rate through a long capillary tube which contained an air bubble whose velocity between two marks near the beginning and the end of the tube was observed by means of a stop-watch. The apparent velocity V_a of the liquid was calculated from the time of flow and the volume of the tube between the marks. A small correction was applied to the " volume " of the capillary tube when the bubble overshot the finishing mark, for it was not always easy to stop it exactly on the mark except at slow speeds. The liquid emerging from the capillary was caught in a small tared flask which was then stoppered. Capillary tubes of about 1 m. in length and 2·25 mm. in diameter were used. This bore was almost the same as that of the capillary tube used in the electro-endosmosis apparatus to be described in another paper. The present results could therefore be used to correct the apparent electro-endosmotic velocities obtained in this apparatus. The test of the expression given below with tubes of much greater or much smaller diameter is very difficult. With wider tubes the effect of gravity becomes noticeable, and the meniscuses are no longer symmetrical about the axis, whilst with narrower tubes the experimental error, caused largely by evaporation of the liquid during manipulation, becomes almost as large as the effect to be observed. It is reasonable to suppose, however, that the same expression holds for tubes of different diameters which are sufficiently small for the effect of gravity to be negligible in comparison to that of surface tension.

Experiments were carried out with a straight tube at room temperature (15—16°) and with loosely coiled tubes immersed in a thermostat at 20° : the results obtained in each case were very similar. A number of experiments carried out by Mr. H. P. Dakin with similar tubes and several aliphatic alcohols also confirm our results.

It was first established that, providing the bubble length was greater than about 1½ times the diameter of the tube, the difference between the apparent velocity of the liquid at a given rate of flow, as indicated by the bubble, and the true velocity was, within the experimental error, independent of the length of the bubble.

This difference between the velocities depends very greatly, however, on the rate at which the liquid and the bubble move through the capillary. The following table, which relates to the flow of water through a tube of 2·26 mm. diameter containing a bubble 1·5 cm. in length, illustrates this point. The last col. gives 100 W, the percentage error in the speed as estimated

U_a (cm./sec.).	V_a (c.c./sec.).	V_t (c.c./sec.).	$\frac{100(V_a - V_t)}{V_a}$.	U_a (cm./sec.).	V_a (c.c./sec.).	V_t (c.c./sec.).	$\frac{100(V_a - V_t)}{V_a}$.
0·79	0·0315	0·0312	1·1	8·5	0·3379	0·3253	3·7
1·4	0·0557	0·0548	1·5	9·1	0·3639	0·3496	3·9
3·1	0·1245	0·1216	2·3	12	0·4731	0·4531	4·2
3·6	0·1433	0·1397	2·5	16	0·631	0·598	5·1
4·4	0·1752	0·1704	2·7	22	0·860	0·810	5·9
4·7	0·1892	0·1836	3·0	30	1·182	1·097	7·1
5·9	0·2365	0·2289	3·2				

from the movement of the bubble. It will be observed that this " wetting " or " drainage " effect may give rise to errors of several units % in the estimated speeds of electro-endosmosis.

The difference between the true and the apparent speed is dependent upon the thickness, d, of the film of liquid adhering to the wall of the capillary. A simple calculation shows that if D is the internal diameter of the tube,

$$W = (V_a - V_t)/V_a = 4(D - d)d/D^2$$

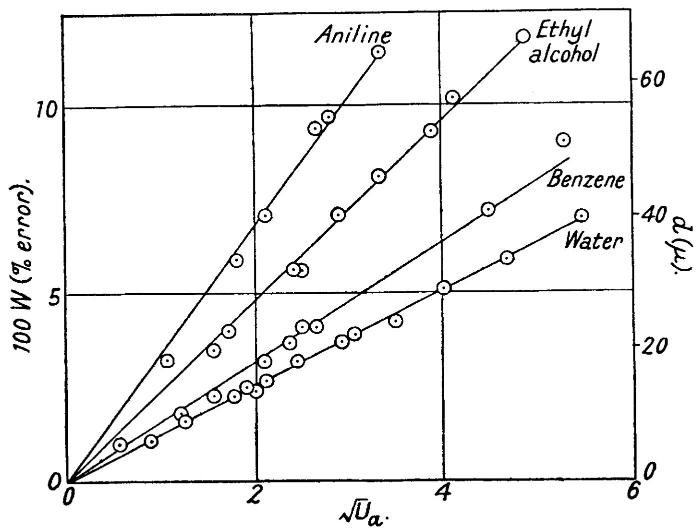
or, if d is small compared with D,

$$W = (V_a - V_t)/V_a = 4d/D.$$

Experiments carried out with various liquids showed that in each case, with a given capillary and liquid, W was proportional to the square root of the linear velocity of the bubble. This is illustrated for four liquids in Fig. 2, in which is also given the calculated thickness d (in μ) of the layer of liquid on the walls of the tube.

The effect here observed is somewhat similar to that discussed by the Research Staff of the General Electric Company, London (*Phil. Mag.*, 1922, **44**, 1002), who examined, theoretically and practically, the problem of the thickness of the liquid layer covering a solid body drawn out of a liquid, as in many industrial processes for the coating of solid surfaces. They found that, if the solid is a flat slab of infinite width, drawn vertically with velocity V through the surface

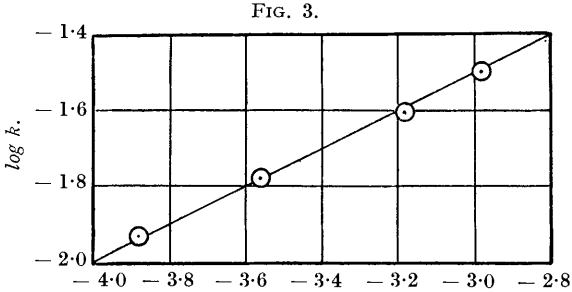
FIG. 2.



of a liquid of viscosity η and density ρ, the thickness t of the adherent film is approximately $t = \sqrt{2V\eta/g\rho}$. If the solid has a curved surface, the thickness of the adhering layer is also a function of the surface tension of the liquid, which, in the case of fine wires, becomes dominant.

In the case now under consideration, that of a horizontal capillary, the effect of gravity is negligible, and the chief factors concerned are the viscosity and surface tension of the liquid. It can be seen by qualitative inspection that these must act in opposite directions: the surface tension pulls the lagging film of liquid into the leading meniscus at a speed determined by the viscosity.

FIG. 3.



If we write $W = k\sqrt{U_a}$ and plot log k against log η/σ, where η and σ are respectively the viscosity and the surface tension of the liquid in question, both measured in C.G.S. units, we obtain a very close approximation to a straight line (Fig. 3) with a slope of 1/2, which on production passes through, or very close to, the origin. Hence it follows that we have to a first approximation the very simple empirical relation $W = 4d/D = \sqrt{U_a\eta/\sigma}$, which is also dimensionally correct.

The above results show that this effect is not by any means to be neglected in the measurement of electro-endosmosis by the bubble-tube method, except perhaps in the case of aqueous solutions over a small range of bubble speeds. Allowance may be made in any particular instance by carrying out a series of experiments as described here, or by use of the empirical relation given above. The effect is probably responsible for part, at least, of the non-linear relation between applied *E.M.F.* and electro-endosmosis observed by different workers.

THE UNIVERSITY, MANCHESTER. [*Received, February* 19*th*, 1935.]