291. *Studies in Electro-endosmosis. Part VII. Some Measurements with Non-aqueous Liquids and High Voltages.*

By HAROLD P. DAKIN, FRED FAIRBROTHER, and ALFRED E. STUBBS.

IN accordance with the well-known Helmholtz–Smoluchowski expression (*Wied. Ann.*, 1879, **7**, 337; *Krakau Anzeiger*, 1903, 182) $U = (E\xi\varepsilon/4\pi\eta).q/l$, the amount, U, of liquid transported in unit time by electro-endosmosis through a given capillary or porous diaphragm should be directly proportional to the *E.M.F.*, E, applied to the ends of the capillary or diaphragm, since the viscosity η, the dielectric constant ε, and (presumably) the interfacial potential ξ remain constant for a given system; q/l is the ratio of the effective cross-section to the effective length of the diaphragm.

Such a linear relation between U and E was shown by Tereschin (*Wied. Ann.*, 1887, **32**, 333) to obtain in the case of water and methyl and ethyl alcohols, in a glass capillary, over a range of 177—394 volts/cm. Quincke had previously (*Pogg. Ann.*, 1861, **113**, 513) found a similar connexion between U and E for lower potential gradients, and subsequent workers have also confirmed this relation for a similar range of voltage gradients.

On the other hand, several observers, working with non-aqueous liquids over a wider range of voltages, have reported that the relation between the applied *E.M.F.* and the amount of liquid transported is not linear; *e.g.*, Strickler and Matthews's curves (*J. Amer. Chem. Soc.*, 1922, **44**, 1647) for this relation in the case of a number of organic liquids and a filter-paper diaphragm show a marked deviation from linearity, and Fairbrother and Balkin, working with organic liquids and a glass surface (J., 1931, 389), found that, although the relation appeared to be linear when the applied voltage was below 200 (corresponding to about 400 volts/cm.), yet at higher voltages the velocity of the liquid increased somewhat more rapidly than the applied voltage.

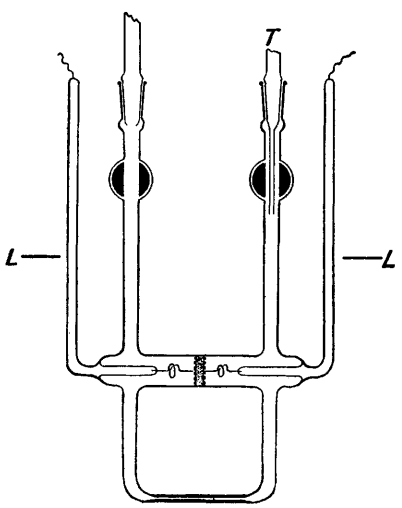
There is to some extent a corresponding uncertainty in the case of the converse phenomenon, that of streaming potentials. Ettisch and Zwanzig (*Z. physikal. Chem.*, 1930, *A*, **147**, 151) found that whereas a $10^{-5}N$-solution of sodium chloride, when forced through a Jena-glass capillary, gave a value of ξ which was independent of the velocity, yet the addition of methyl alcohol caused the value of ξ to increase with the applied pressure, the effect becoming more marked as the concentration of methyl alcohol was increased. These authors also report (*ibid.*, 1932, *A*, **160**, 385) that ξ depends upon the applied pressure in the case of dilute aqueous solutions alone, over a very small range of pressure and rate of flowing. On the other hand, Bull (*Kolloid-Z.*, 1934, **66**, 20), who repeated the experiments of Ettisch and Zwanzig with $10^{-5}N$-sodium chloride to which were added increasing amounts of methyl and *iso*propyl alcohols, found with a Pyrex capillary that ξ was independent of the applied pressure: he attributed Ettisch and Zwanzig's conclusions to an incorrect interpretation of their experimental results.

We have now examined the electro-endosmosis of several organic liquids through a sintered Jena Geräte-glass diaphragm, using applied voltages which correspond to potential gradients along the glass surface of about 400 to nearly 6000 volts/cm. It was originally intended to carry out experiments with a much wider range of liquids than was actually used, but this work has now been discontinued. The experimental results obtained so far, however, are sufficient to demonstrate the effects discussed here.

Experimental.

The electro-endosmosis apparatus is shown in Fig. 1. This was an improvement on that used by Fairbrother and Balkin (*loc. cit.*) in that it was wholly constructed of the same kind of glass (Jena Geräte), which permitted ground joints to be eliminated and the hydrodynamic resistance of the tubes associated with the bubble tube to be decreased. The diaphragm was approximately 2 cm. in diameter, 0·5 cm. thick, and of a porosity designated as G3 by the makers, who also give the average pore diameter as about 20—30 μ. The value of l/q was 4·94, as determined by measuring the resistance of the diaphragm when filled with $N/10$-potassium chloride. The bubble tube was of 2·25 mm. internal diameter and about 7 cm. long: its hydrodynamic resistance, together with that of its connecting tubes (measured before assembly of the apparatus), was less than 0·5% of that of the diaphragm. Platinum-gauze electrodes, similar to those described by Fairbrother and Balkin, were used.

Fig. 1.



Transformed, rectified, and smoothed 50-cycle alternating current was used as a source of applied *E.M.F.* The circuit was operated by relays, one of which inserted a high-resistance load in the "off" position, equal to the resistance of the electro-endosmosis apparatus, so that the voltmeter reading remained constant when the circuit to the latter was closed.

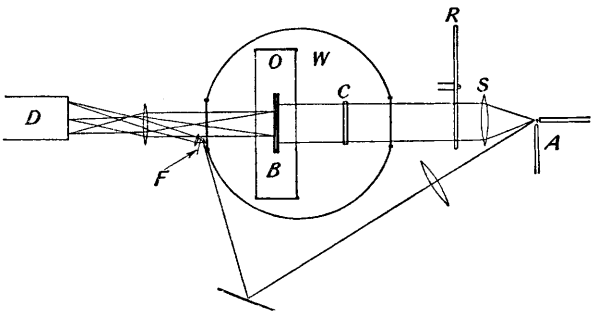
The liquids used were a number of alcohols and ethers. These were chosen because the variation in dipole moment is small, whilst the molecular volumes and viscosities vary over a wide range, resulting in widely different rates of electro-endosmosis with a given applied voltage. They are also typical of associated and non-associated liquids respectively. The liquids, purified and dried by appropriate methods, were distilled from an all-glass apparatus into the electro-endosmosis apparatus through the tube T, thus avoiding contact with the taps. As an additional precaution the taps on the apparatus were greased only at the ends. The apparatus was completely filled with the liquid, and set aside over-night. A small amount of liquid was then removed by a fine pipette, and the resulting air bubble manœuvred into the bubble tube by inverting the apparatus.

Before each series of experiments, the diaphragm was cleaned in the following way. The apparatus, from which the previous liquid had been drained, was washed out with ethyl alcohol or a mixture of this with ethyl ether followed by alcohol alone. Most of the alcohol was then

removed by distilled water, and the apparatus filled with concentrated nitric acid, with which the remaining alcohol reacted vigorously. The apparatus was then rinsed well with distilled water, and evacuated by a mercury-vapour pump. The part of the apparatus below the line *LL* was slowly heated in an electric oven to about 200°, and kept at this temperature for about 2 hours after the pressure in the apparatus had fallen below 0·001 mm. It was then allowed to cool slowly, and air was admitted through a phosphoric oxide tube just before the distillation of the liquid into the apparatus.

In order to measure the higher speeds of electro-endosmosis, a new photographic method of recording the speed of the air bubble was developed. This method, shown diagrammatically in Fig. 2, permitted an accurate estimate to be made of the speed of the bubble over runs as short as 1 sec. or less, thus enabling high speeds to be measured with the passage of little current through the diaphragm, and also rendered possible the detection of any variation in speed during a run, such as would be unobserved by the usual stop-watch method of timing. In this method, the bubble-tube, *B*, was brightly illuminated by the arc-lamp *A*, through the spherical condenser *S* and the cylindrical lens *C*, and an image of the bubble (which was usually 1—2 cm. long) was projected on to a strip of Ciné-Kodak bromide paper, wound on the periphery of a drum *D*, which was 1 m. in circumference and 10 cm. wide. This drum could be rotated uniformly at any desired speed by suitable gearing. Blurring of the image as the drum rotated was prevented by a narrow slit, parallel to and near the surface of the paper. On one end of this slit was also projected the image of a stylus *F* fixed to one leg of a valve-maintained tuning

FIG. 2.



fork, with a frequency of 100 cycles/sec. The time and the movement of the bubble were therefore recorded simultaneously. An electro-magnetic shutter, close to the slit, working in conjunction with the relay which closed the high-voltage circuit, prevented fogging or premature exposure of the paper. The latter relay worked somewhat more slowly (about 0·25 sec.) than the shutter, so that the shutter was fully opened when the *E.M.F.* was applied. A contact arm on the drum shaft, moving over a ring of contacts, enabled exposure to be made at any position and over any length of the recording paper, and also allowed several exposures to be made on one strip. The corresponding positions of the front and the rear meniscus were recorded on the photograph by rapidly (about 50 times/sec.) interrupting the light which illuminated the bubble, by a revolving bar *R*, giving rise to a series of instantaneous exposures in the form of very narrow shadows across the photograph : in this way a correction could be made for a slight inclination of the capillary tube to the axis of the drum.

Fig. 3 is reproduced from a line tracing of a portion of one of these photographs : *A* is the image of the tuning-fork stylus, *BB* of the bubble meniscuses, and *CC* of the edges of two metal reference strips, of known distance apart, attached to the metal **V** supports in which the bubble tube was located.

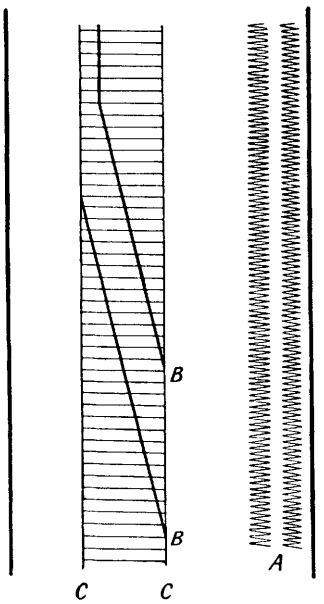
Experiments in the lower range of speeds, requiring more than about 10 secs. (corresponding to a speed of 0·013 c.c./sec.) were difficult to time by the tuning-fork, on account of the necessary slowness of rotation of the drum and the consequent closeness of the time markings. These speeds were therefore measured visually with a stop watch (3-seconds dial) : measurements by both methods over a common range gave good agreement.

The photographic records showed, in all cases where the actual start was recorded, that the electro-endosmosis started with great suddenness, and thereafter, except in a few unexplained cases, maintained a constant velocity during the run. This steady velocity was attained, so far as could be ascertained, in less than 0·002 sec. In some cases, at the higher end of the voltage range used, the image of a small, quickly damped, compressional wave could be seen

at the start of the track of the front meniscus. When it is remembered that the electro-endosmosis has to overcome the inertia of the liquid in the apparatus before a steady speed can be attained, this sudden start is very striking.

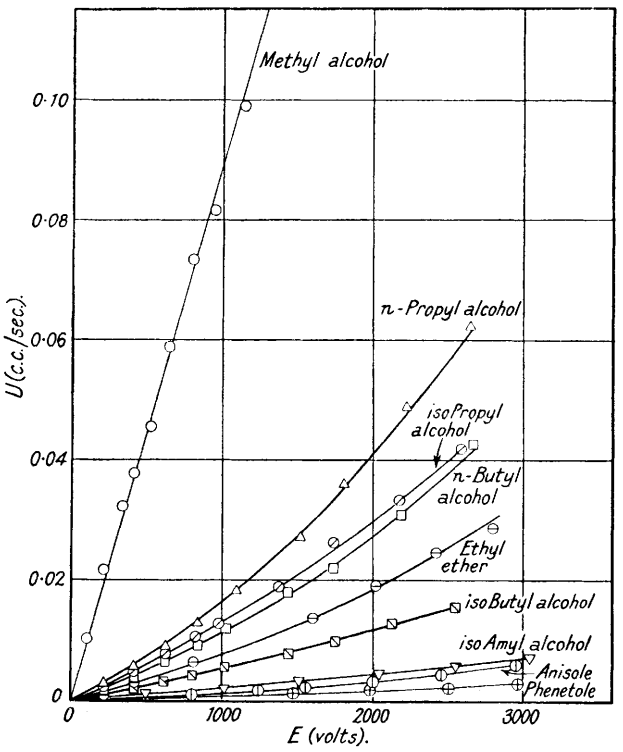
All the experiments were carried out at 20·00°, the apparatus being immersed in a thermostat *O* (Fig. 2), filled with paraffin oil, and surrounded by one, *W*, filled with water, each having plate-glass windows.

FIG. 3.



Methyl alcohol : applied E.M.F., 2320 volts.

FIG. 4.



The results are given in the table (where E is in volts, and U in c.c./sec.), and are shown graphically in Fig. 4, in which the abscissæ are the actual voltages applied across the diaphragm. The velocities given as ordinates have been corrected for the " wetting effect " of the bubble in the capillary tube (Fairbrother and Stubbs, this vol., p. 527); the greatest value of this

Methyl alcohol.			*n*-Propyl alcohol.			*iso*Propyl alcohol.			*iso*Amyl alcohol.		
E.	U.	$10^5U/E$.	E.	U.	$10^5U/E$.	E.	U.	$10^5U/E$.	E.	U.	$10^5U/E$.
106	0·0101	9·5	231	0·00266	1·15	222	0·00249	1·12	504	0·00112	0·22
222	0·0217	9·9	424	0·00577	1·36	420	0·00494	1·18	1020	0·00224	0·22
343	0·0322	9·4	631	0·00909	1·44	623	0·00768	1·23	1530	0·00334	0·22
419	0·0376	9·0	840	0·0130	1·55	833	0·0104	1·25	2050	0·00453	0·22
527	0·0455	8·6	1100	0·0181	1·65	984	0·0127	1·29	2560	0·00572	0·22
651	0·0587	9·0	1460	0·0272	1·86	1400	0·0189	1·35	3050	0·00685	0·23
803	0·0734	9·1	1810	0·0362	2·00	1750	0·0263	1·50			
949	0·0815	8·6	2250	0·0489	2·17	2180	0·0334	1·53	Ethyl ether.		
1170	0·0991	8·5	2650	0·0623	2·35	2590	0·0419	1·62	214	0·00131	0·61
1560	0·1223	7·9							428	0·00305	0·71
1970	0·1560	7·9	*n*-Butyl alcohol.			*iso*Butyl alcohol.			817	0·00631	0·77
2320	0·2185	9·4	231	0·00199	0·86	222	0·00097	0·44	1620	0·0137	0·85
			423	0·00399	0·94	426	0·00192	0·45	2030	0·0192	0·95
Phenyl methyl ether.			625	0·00648	1·04	618	0·00299	0·48	2430	0·0247	1·02
813	0·00096	0·12	837	0·00932	1·11	809	0·00407	0·50	2800	0·0285	1·02
1250	0·00163	0·13	1030	0·0122	1·18	1020	0·00529	0·52			
1560	0·00219	0·14	1440	0·0178	1·24	1450	0·00765	0·53	Phenyl ethyl ether.		
2010	0·00310	0·15	1750	0·0221	1·26	1760	0·00982	0·56	1480	0·00115	0·78
2460	0·00425	0·17	2190	0·0309	1·41	2150	0·0126	0·59	1990	0·00155	0·78
2960	0·00557	0·19	2660	0·0426	1·60	2560	0·0155	0·61	2510	0·00202	0·80
									2970	0·00264	0·89

correction in the present work was about 4%. In computing these velocities, the average (corrected) velocity in a pair of runs, backwards and forwards, has been taken : these individual runs generally agreed to within about 1—5%.

All the liquids examined were found to be positively charged relative to the glass, although this is contrary to Fairbrother and Balkin's results (*loc. cit.*) for ethyl ether.

It was concluded, from an extrapolation of the curves to the origin, that the divergence of the U–E relation from linearity is small if the applied voltage is small. With many liquids, over a range of a few hundred volts per cm., this divergence may be no greater than the average experimental error. The results for methyl alcohol, which are somewhat irregular, fall about a straight line over the whole range examined. Since many of the present measurements were made over definitely non-linear portions of the curves, no calculations of the interfacial potential are given.

A review of published and some of our own unpublished work on the electro-endosmosis of organic liquids against a glass surface leads us to conclude that " absolute " results are very difficult to obtain. Different observers, using different diaphragms of the same kind of glass, and a given organic liquid carefully purified in each case, have obtained results which, though self-consistent and very reproducible after cleaning of the diaphragm and re-filling with the same sample of organic liquid, yet have differed among themselves by as much as or even more than 40 or 50%. To some extent this divergence may be due to individual diaphragms, for even with diaphragms of the same value of l/q, the actual potential gradient with a given voltage may vary greatly and may be different at different parts of the diaphragm. The major cause of the variations, however, probably lies in the extreme difficulty of removing every trace of capillary active material from an organic liquid. The regularities discussed by Fairbrother and Balkin (*loc. cit.*) may therefore be fortuitous, though the present results with the alcohols show the same kind of regularity, in a qualitative way : the ethers, however, move less rapidly than would be expected on this basis. In the present work we are chiefly concerned with the behaviour of a given sample of liquid in a given diaphragm. Most of the experiments recorded here relate to measurements made with a single filling of the electro-endosmosis apparatus with the liquid in question. In the case of *iso*propyl alcohol, however, two separate fillings and series of experiments were made at an interval of about 2 weeks, during which the apparatus was cleaned and dried in the manner described above : the results of the two series were indistinguishable.

The cause of the increase of the U/E ratio at high voltages is most probably to be found in a deformation of the double layer in these circumstances. It may be recalled that the conductivity of aqueous electrolytes has been shown to be greater at high voltages (Wien, *Ann. Physik*, 1927, **83**, 327; 1928, **85**, 795; *Physikal. Z.*, 1928, **29**, 751; Gyemant, *ibid.*, p. 289). This effect has been attributed to the deformation of the ionic envelopes. If we postulate the existence of a diffuse double layer in the case of an organic liquid–glass system (deferring a discussion of the mechanism whereby this is produced in a poor conductor), then we may visualise a similar cause of the increased electro-endosmosis at high voltages. The extremely short time necessary for the development of a uniform movement in a capillary of some 20—30 μ diameter also suggests that the double layer is of more than unimolecular thickness.

SUMMARY.

1. Measurements have been made of the electro-endosmosis of a number of organic alcohols and ethers through a diaphragm of sintered Jena Geräte glass powder, applied voltages up to nearly 6000 volts per cm. being used.

2. At low voltages, the relation between the voltage applied to the diaphragm and the velocity of flow of the liquid is linear, or nearly so, but departs to an increasing degree at high voltages.

3. A continuous photographic method of recording the rate of electro-endosmosis is described, which permits observations to be made of high speeds over a short time and of any change of speed during a run.

4. The electro-endosmotic flow attains a constant speed within a very small fraction of a second after the application of the $E.M.F.$

We acknowledge with thanks assistance from grants made by Messrs. Imperial Chemical Industries Ltd., and from the Research Fund of the Chemical Society.

THE UNIVERSITY, MANCHESTER. [*Received, June 22nd,* 1935.]