LIII.—*Studies in Electro-endosmosis. Part IV. The Electro-endosmosis of Some Organic Liquids against a Glass Surface.*

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THE majority of investigations on electro-kinetic phenomena have been concerned with aqueous solutions of electrolytes. A displacement of liquid along a solid surface under the influence of a tangential electric field takes place, however, in many liquids which contain no ions in the ordinary sense. The study of electro-endosmosis in such liquids is necessary for the complete understanding of the mechanism underlying such phenomena.

The first contribution to the study of electro-endosmosis in organic liquids was that of Quincke (*Pogg. Ann.*, 1861, **113**, 513), who showed experimentally that a number of different solids, such as quartz, shellac, silk, clay, asbestos, animal membranes, etc., were negatively charged in water but acquired a positive charge in turpentine. Sulphur proved to be an exception, being negatively charged in both water and turpentine—weakly negative in the latter solvent, and the most strongly negative of all the solids examined in water.

Coehn (*Wied. Ann.*, 1898, **64**, 217) extended Quincke's work to a wider range of organic liquids, and formulated an empirical rule which bears his name and states that " substances of higher dielectric constant become positively charged by contact with substances of lower dielectric constant." Later, Coehn and Raydt (*Drude's Ann.*, [4], 1909, **30**, 777) carried out an investigation on the magnitude of the electrification at a glass–organic liquid interface, using a " capillary-rise " method, and extended Coehn's qualitative rule to include the quantitative statement that the electrical charge acquired is proportional to the difference between the dielectric constants of the phases in contact.

Strickler and Matthews (*J. Amer. Chem. Soc.*, 1922, **44**, 1647) have carried out electro-endosmosis experiments with a number of non-aqueous liquids and solutions, using a diaphragm composed of layers of filter paper. They used nine pure organic liquids and concluded that the magnitude but not the direction of electro-endosmosis was dependent on the dielectric-constant ratio.

Martin and Gortner (*J. Physical Chem.*, 1930, **34**, 1509) have recently investigated the electro-kinetic potential at a cellulose–organic liquid interface by means of a "streaming-potential" method, and have correlated their results with the structure of the molecules oriented at the interface.

The present work deals with the electro-endosmosis through a diaphragm of sintered glass powder, of fourteen carefully purified and dried organic liquids. Pure water has also been included for comparison. Considerable attention has been paid to purity of materials. Coehn (*loc. cit.*) observed that traces of impurities gave erroneous results, and during the present work this has been confirmed even in solvents of low ionising power.

EXPERIMENTAL.

Purification of Materials.—In some cases the starting material was a good commercial product which only required careful fractionation and drying. In other cases a more rigorous chemical method of purification was necessary. Distillations, except of the more volatile liquids, were carried out under reduced pressure, usually (and particularly when oxidation was likely) in an atmosphere of dry nitrogen.

Formamide. Formamide, obtained from Messrs. British Drug Houses Ltd., was stored over anhydrous sodium sulphate for 12 months and purified by a series of careful fractionations at very low pressure as described by Davis and Putnam (Jones, Carnegie Inst. Pub., 1915, **230**, 16). The course of the purification was followed by measurements of the electrical conductivity. The liquid distilled at 80—85°/1 mm. The original material on the first distillation yielded a distillate with a specific conductivity of $1{\cdot}19 \times 10^{-2}$ mho, but after four further fractionations the product had $\kappa = 1{\cdot}2 \times 10^{-5}$ mho. Formamide is very hygroscopic and is easily hydrolysed to ammonium formate, which is the chief impurity. This is ionised in the formamide, which is a solvent of high dielectric constant and high ionising power. For these experiments, therefore, it was necessary to remove both this salt and the water completely. The formamide actually used had $\kappa = 1{\cdot}2 \times 10^{-5}$ mho : liquid of lower conductivity could only be obtained in sufficient quantity at a prohibitive cost. Davis and Putnam (*loc. cit.*) obtained small quantities of formamide having $\kappa = 2{\cdot}8$—$4{\cdot}7 \times 10^{-6}$ mho, but their experiments were actually carried out with a liquid whose specific conductivity was above $1{\cdot}37 \times 10^{-5}$ mho.

Furfuraldehyde. This was fractionated at 10 mm. pressure, purified through the sodium bisulphite compound (Mains, *Chem. Met. Eng.*, 1922, **26**, 779), and dried over calcium chloride in the dark.

Nitrobenzene. A good commercial product, fractionated several times at atmospheric pressure, dried with phosphoric oxide, and fractionated five times at *ca.* 10 mm.

o-*Nitrotoluene.* A commercially pure product, dried over anhydrous sodium sulphate, and fractionated three times at *ca.* 10 mm.

Ether, chloroform, and acetone. Commercially pure materials, fractionated several times at atmospheric pressure and left over drying agents for several months—ether over sodium, chloroform and acetone over phosphoric oxide—and distilled. The chloroform was tested for absence of hydrogen chloride by silver nitrate solution.

n-*Propyl alcohol and* n-*butyl alcohol.* Commercially pure materials dried over barium oxide and fractionated twice.

Benzaldehyde. The commercially pure product was washed with sodium carbonate solution and with water, dried over fused calcium chloride, and fractionated at 10 mm., the constant-boiling fraction being retained for use. This purification was carried out immediately before the benzaldehyde was used, owing to its rapid oxidation in the air.

Aniline. A commercially pure sample was dried with solid caustic potash over which it was distilled three times, and then distilled twice from zinc dust. All distillations were carried out at reduced pressure in an atmosphere of dry nitrogen, the receiver being protected from the light. The final distillate was practically colourless and had a faint fluorescence.

Propionic acid. Kahlbaum's pure material was stored over anhydrous sodium sulphate for 4 months and fractionated twice at *ca.* 5 mm.

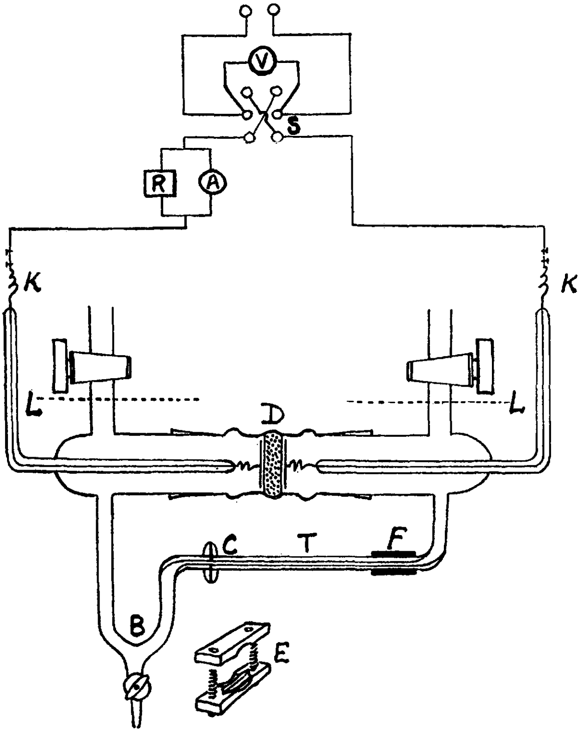
Benzene. Kahlbaum's " Cryst. thiophene free " was dried over phosphoric oxide and distilled twice. The absence of thiophen was confirmed by the isatin test.

Carbon tetrachloride. Kahlbaum's pure material was dried over anhydrous sodium sulphate and distilled twice.

Water. This was purified by a Bourdillon still (J., 1913, **103**, 791), no precautions being taken to avoid solution of carbon dioxide. It was then transferred to a large Jena-glass flask, boiled until free from carbon dioxide, and allowed to cool without admission of air. By means of a syphon tube previously fitted through the stopper of the flask, the water was transferred to the electro-endosmosis apparatus without exposure to the atmosphere. During this operation the open ends of the apparatus were protected by soda-lime tubes.

The organic liquids were well dried, but no attempt was made to attain that degree of dryness achieved by Baker. They were unavoidably exposed to the atmosphere during assembly and filling of the apparatus. These manipulations were therefore performed as rapidly as possible so that the exposure was of only a few seconds' duration. The electrical conductivity of the unexposed organic liquid showed no detectable change after it had been exposed to the atmosphere of the laboratory for several minutes.

Fig. 1.



The phosphoric oxide used for drying the liquids was purified by distillation in a stream of oxygen as described by Finch and Fraser (J., 1926, 117).

Apparatus. The electro-endosmosis apparatus is shown in Fig. 1. The glass portion consists essentially of three parts : the centre tube carrying the diaphragm *D*, and the two outer portions carrying the filling and connecting tubes, joined to the centre tube by ground joints. The centre tube was of Jena Geräte glass like the diaphragm, which was fused in position, whilst the outer portions were of soda-glass.

The actual electro-endosmosis was measured by the movement of a bubble in the graduated capillary tube *T*, a method originally used by Briggs, Bennett, and Pierson (*J. Physical Chem.*, 1918, **22**, 256). For accurate measurements by this method, it is essential that the hydrodynamic resistance of the "bubble tube" and associated connecting tubes should be negligible compared with that of the diaphragm, otherwise the return flow of the liquid will take place in part through the diaphragm along the centres of the capillary spaces contained in it. This point does not seem to have received much attention hitherto. Strickler and Matthews (*loc. cit.*) recognised this possibility and made measurements of electro-endosmosis with diaphragms of different porosity, but they appear to have confused two issues: the effect of porosity of the diaphragm on the relative hydrodynamic resistances of the diaphragm and "bubble-tube," affecting the *measurement*, and its effect on the electrical resistance and consequent potential gradient across the diaphragm, which determines the *actual* electro-endosmosis. Wiedemann's conclusion (*Pogg. Ann.*, 1852, **87**, 321; 1856, **99**, 177) that the flow was independent of the area or thickness of the porous wall, is misapplied by these authors, for it refers only to conditions of constant current.

It would seem that any measurement of electro-endosmosis by the present method is subject to some error, however slight, for the foregoing reason. Nevertheless, the method is exceedingly convenient and sensitive, and by suitable design of the apparatus, the error due to hydrodynamic resistance of the "bubble-tube" can be reduced to negligible proportions. In any case, with a given apparatus, in which the porosity of the diaphragm was constant as in the present one, the results would still be comparative, except perhaps with a very porous diaphragm and/or very high speeds of electro-endosmosis.

The actual bubble tube, of 2 mm. internal diameter, was therefore kept as short as was practicable—about 8 cm.—and the associated connecting tubes were of wide-bore tubing. No taps were included in the liquid circuit as in the original apparatus of Briggs, but the bubble was introduced through the tap on the bend *B*. The bubble itself was from 1·5 to 2 cm. long in all the experiments.

It was desirable, since organic liquids were to be used, to construct an apparatus having no rubber joints. By means of the ground glass butt-joint *C* and the clamp *E* (Fig. 1), the apparatus could be made into a completely closed glass system. This joint gave considerable trouble; it was necessary that its faces should meet in perfect alinement, since no lubricant or tap grease was used. This could be secured at the time of construction, with the rest of the apparatus assembled, but after dismantling and reassembling, it was difficult to attain alinement without unduly stressing the glass. This result was probably due to lack of symmetry of the main ground joints on the diaphragm tube. The U-bend *B* allowed a certain flexibility, but after a time the capillary fractured at *F*, and the use of an all-glass apparatus was abandoned for the present series of experiments. The measurements were continued with a short piece of rubber connecting tube at *F*; this was renewed for each liquid, and so arranged that the glass tubes within it were in close contact. The rubber tube was sufficiently remote from the diaphragm for the liquid in immediate contact with the latter to be unaffected by it. The measurements which had been made with the original all-glass apparatus were repeated with this arrangement and the results found to be quite reproducible.

The potential gradient across the diaphragm was applied by means of electrodes of disc form, consisting of a double layer of fine-mesh, bright platinum gauze, stretched across a ring of platinum wire; they almost completely covered the diaphragm faces and were kept in close contact with them by means of the stout platinum connecting wires, which were coiled for several turns, forming helical springs.

The experiments were carried out as follows. The two arms of the apparatus carrying the electrodes, taps, and capillary tube were thoroughly cleaned with chromic acid, washed with distilled water, and dried in an electrically heated oven; the diaphragm was specially cleaned and then impregnated with the organic liquid as described later. The apparatus was now quickly assembled, and the large ground joints on the central diaphragm tube were bound on the outside with pure strip rubber under tension, to prevent ingress of moisture on immersion in the thermostat. The apparatus was filled as quickly as possible with some 100 c.c. of the freshly distilled liquid under examination, which was poured down a funnel through either of the large vertical taps. The bubble was introduced into the horizontal capillary tube, and the whole apparatus immersed up to the level *LL* in a water thermostat at $20° \pm 0{\cdot}01°$, where it was left for about ½ hour to attain a constant temperature.

The electrical circuit was connected as shown, and the *E.M.F.* applied first in one direction and then in the other. The source of potential was, in part, the 200-volt direct-current supply mains, applied through a potentiometer for the lower voltages, and for the high-voltage measurements, small accumulators (510 volts) in series with the 400-volt mains. The mains voltage varied from time to time, but was sufficiently steady during the actual measurements. Immediately before application of the *E.M.F.*, the apparatus was adjusted so that the capillary tube was horizontal and no detectable gravitational movement of the bubble took place.

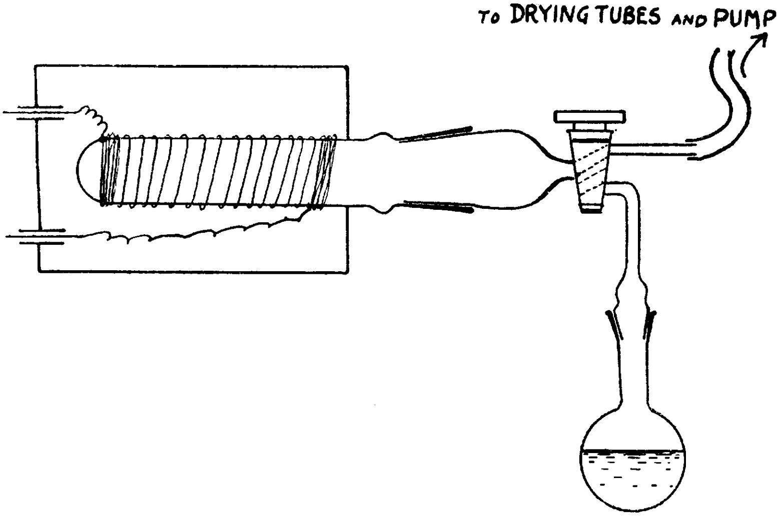
The movement of the bubble was observed at a distance by means of a telescope through a window in the side of the thermostat. About 20 runs in each direction were observed and timed by a stop-watch. The order of reproducibility was 1—2%. The bubble was allowed to move a short distance along the capillary tube to ensure the attainment of a steady velocity before an observation was made. It was necessary thoroughly to insulate the various portions of the electrical measuring apparatus by means of hard paraffin-wax blocks.

The particular diaphragm was made of Jena Geräte glass and was supplied fused in position by Messrs. Schott & Co. It was about 0·5 cm. thick and of 2 cm. diameter over-all; the porous area was slightly less than the over-all area : the region of the porous plate in immediate contact with the surrounding tube apparently becomes fused into a non-porous form during the fixing of the disc in the tube, since this region is more translucent than the rest of the disc. The diaphragm was first cleaned with alcohol and concentrated nitric acid. Between each series of observations the apparatus was dismantled, and the diaphragm cleaned and allowed to stand overnight in a bath of concentrated nitric acid. Chromic acid was not used in connexion with the diaphragm but only organic solvents, water, and nitric acid. The diaphragm was then rinsed with distilled water, steamed out for an hour, and dried at about 100° in an electrically heated oven. Final drying was effected in a vacuum at 100° in an electrically heated tube as shown in Fig. 2. This was provided with a two-way tap whereby the diaphragm could, after drying and cooling in a vacuum, be impregnated with the liquid under examination by distillation from the flask immediately prior to assembly of the apparatus. Preliminary experiments on drying in a vacuum at higher temperatures resulted in fracture of the tube round the porous disc.

Estimations were made of the ordinary bulk conductivity of the liquids as a means of detecting " surface conductivity " during electro-endosmosis, and, particularly in the case of water and formamide, as a control over their purity. With the last two liquids this was carried out in the usual manner with an alternating-current bridge at 1000 cycles, and in the other cases by direct current, using a small known *E.M.F.* of about 2 volts and a calibrated pointer galvanometer. Estimations of the conductivity after use in the electro-endosmosis apparatus showed in most cases a small increase, which is probably to be attributed to slight electrolytic decomposition.

Determinations of the conductivities of the liquids in the diaphragm during electro-endosmosis showed, in every case where electro-endosmosis occurred, the presence also of "surface conductivity." For this purpose and for the calculation of the "electrokinetic potential," the cell-constant, *i.e.*, the ratio of the effective length to the effective cross-section of the diaphragm, was ascertained by a slight modification of the method of Fairbrother and Mastin (J., 1924, **125**, 2319), by measuring the resistance of *N*/10-potassium chloride in the diaphragm; in this case the same gauze electrodes were used and the resistance was measured in an alternating-current bridge. The electrodes were not blackened, but the precision of the bridge setting was sufficient for the present purpose. Although surface conductivity may not be absent in *N*/10-potassium chloride, it is negligible compared with that in most of the liquids examined.

FIG. 2.



The specific conductivities (κ) of the liquids used are given in the fifth column of Table I. A value of $<1 \times 10^{-8}$ indicates that the conductivity of the liquid in question was too small to be measured with the apparatus in use at the time.

For the first eleven liquids in the table, measurements of electro-endosmosis were made with various *E.M.F.*'s, from about 30 to 200 volts, applied across the diaphragm. Up to about 150 volts, the relation between the voltage and the velocity of electro-endosmosis was linear within the accuracy of the determinations but at higher voltages, the velocity increased somewhat more rapidly than the voltage. The velocities and *E.M.F.*'s used for the calculations in Table I are taken from this linear region. In the case of ether, chloroform, benzene, and carbon tetrachloride, a voltage of 910 was applied across the diaphragm. Chloroform gave very irregular results which cannot be included in the quantitative discussion. It appears to be much more difficult to obtain reproducible results with liquids of low than with those of high dielectric constant.

Although some doubt (compare McBain, *J. Physical Chem.*, 1924, **28**, 706; *J. Amer. Chem. Soc.*, 1929, **51**, 3294) has been thrown on the meaning or reality of the electro-kinetic potential ζ as calculated from the Helmholtz–Smoluchowski formula $\zeta = 4\pi v l \eta / q E \varepsilon$—where l and q are respectively the effective length and cross-section of the diaphragm, E is the applied *E.M.F.*, ε the dielectric constant, η the viscosity, and v the velocity of electro-endosmosis—yet such calculations permit of a ready comparison between liquids and between the results of other workers. The values of v, in c.c./sec./volt, and those of ζ calculated in this way are given in Table I, in which μ represents the permanent dipole moment and f is defined later (p. 401).

The viscosities and the densities used in the later calculations were for the most part taken from Landolt–Börnstein and the International Critical Tables, and from the original publications. In the few cases where viscosity measurements at 20° were not available, these were measured in the usual manner in a viscometer of the Ostwald pattern.

TABLE I.

Liquid.	ϵ.	$v \times 10^5$.	ζ.	κ.	$\mu \times 10^{18}$.	$f \times 10^{18}$.
Formamide......	84	5·68	−0·0591	$1·2 \times 10^{-5}$	—	—
Water	81·1	16·16	−0·0554	$1·7 \times 10^{-6}$	1·7*	24·3
Furfuraldehyde	42	6·54	−0·0710	$1·8 \times 10^{-7}$	—	—
Nitrobenzene ...	36·4	5·53	−0·0834	$1·4 \times 10^{-8}$	3·89*	8·85
o-Nitrotoluene	27·7	4·41	−0·1013	$< 1 \times 10^{-8}$	3·75*	6·68
Acetone	21·5	14·76	−0·0620	$2·0 \times 10^{-7}$	2·70*	46·6
n-Propyl alcohol	22·2	1·95	−0·0535	$4·2 \times 10^{-8}$	1·75†	4·42
n-Butyl alcohol	19·2	1·10	−0·0469	$2·8 \times 10^{-8}$	1·74‡	2·86
Benzaldehyde	18·1	3·58	−0·0837	$1·8 \times 10^{-7}$	2·75*	8·18
Aniline	7·2	0·15	−0·0261	$1·4 \times 10^{-8}$	1·51§	1·67
Propionic acid	5·5	0·28	−0·0189	$< 1 \times 10^{-8}$	—	—
Chloroform ...	5·2	0·63	−0·0250	$< 1 \times 10^{-8}$	—	—
Ether	4·36	0·96	+0·0136	$< 1 \times 10^{-8}$	1·22*	1·48
Benzene	2·26	0	0·0	$< 1 \times 10^{-8}$	0·0	0·0
Carbon tetrachloride	2·23	0	0·0	$< 1 \times 10^{-8}$	0·0	0·0

* Williams, Collected values, *Chem. Rev.*, 1929, **6**, 589.
† Stranathan, *Physical Rev.*, 1928, **31**, 653.
‡ Smyth and Stoops, *J. Amer. Chem. Soc.*, 1929, **51**, 3312.
§ Højendahl, Diss., Copenhagen.

Discussion.

The following qualitative deductions may be made from these results. Carbon tetrachloride and benzene show no electro-endosmosis even when an *E.M.F.* of 910 volts is applied across the diaphragm. Coehn (*loc. cit.*) observed that it was extraordinarily difficult to obtain an unambiguous movement with pure benzene; he attributed this fact to lack of conduction in the liquid, and obviated the difficulty by dissolving a trace of hydrochloric acid therein. The sign, and later the magnitude, of the charge of such a solution against glass happened to coincide with that to be expected from the dielectric constants of benzene and glass: hence the surface charge was attributed to the benzene alone, the moisture and hydrogen chloride merely conferring conductivity on the system.

Strickler and Matthews (*loc. cit.*) state that pure benzene gives a small electro-endosmosis against a filter-paper diaphragm.

It was found in the present work that an artificially impure benzene, made by adding 0·5% of thiophen to the pure solvent, gave a very slight movement, which was too small to be measured with any precision, the glass being negatively charged.

Formamide gave very satisfactorily reproducible results. Strickler and Matthews were apparently unable to obtain quantitative measurements on account of the considerable electrolysis, which must be ascribed to lack of purity of the liquid. As has already been pointed out, formamide is very hygroscopic and easily hydrolysed to ammonium formate.

In every other case, excepting that of ether, the glass was negatively charged towards the liquid. Propionic acid, which Coehn found to confer a positive charge on the glass, did not show this anomaly in the present work. It should be added, however, that Coehn's statement refers to soft glass; he was unable to detect the sign of the charge on hard glass, which probably approximated in composition more nearly to the glass used here.

We may now consider certain quantitative deductions from the present work. The values of ζ are all of the same order of magnitude and a similar result follows, as Smoluchowski has shown (Graetz, Handb. d. Elek. u. Mag., **2**, 403), from the results of Coehn and Raydt if one uses for the calculation the modified Helmholtz formula, which takes account of the dielectric constant of the liquid medium.

The value of $\zeta = -0{\cdot}0554$ volt for water here given is in satisfactory agreement with the value of $\zeta = -0{\cdot}0557$ volt found by Fairbrother and Varley (J., 1927, 1584) for a different diaphragm of the same kind of glass. The present determinations were carried out during too short a period for any change of electro-endosmosis in water with time to be detected, as described by Fairbrother and Varley.

The quantitative relationship between the electro-endosmosis and the dielectric constants of the phases was first investigated by Coehn and Raydt (*loc. cit.*), who measured in effect, by a methyl alcohol manometer, the electro-endosmotic pressure developed when an *E.M.F.* was applied between the ends of a short glass capillary tube filled with the organic liquid under examination. They thus found an approximately constant ratio between the pressure developed and the difference between the dielectric constant of the liquid and of the glass. Their assumption that the potential between the phases was directly proportional to this pressure has been shown by Smoluchowski (*loc. cit.*) to be erroneous, in that it does not take into account the dielectric constant of the liquid.

The product of the velocity of electro-endosmosis (as found in the present work) and the viscosity of the liquid increases with the dielectric constant, but the relationship is not linear. Moreover, carbon tetrachloride and benzene, with very low dielectric constants, give no movement at all, whilst ether, with a higher dielectric constant, is charged negatively against the glass.

Consideration of the constitutive character of the dielectric constant, as pointed out by Debye (Marx, Handb. d. Radiologie, **6**; "Polar Molecules," 1929), suggests that a connexion may be found between the electro-endosmosis and the dipole moment of the individual molecules of the liquid.

Guyot (*Ann. Physique*, 1924, **2**, 501) and Frumkin (*Z. physikal. Chem.*, 1925, **116**, 485) have carried out experiments on the interfacial potential at an air–liquid interface in the presence of certain capillary-active organic compounds. From his results, Guyot has calculated the value of the effective dipole moment of the molecules in the interface, and Rideal ("Surface Chemistry," 1930, p. 335) has made further calculations from the data of Frumkin.

Frumkin and Williams (*Proc. Nat. Acad. Sci.*, 1929, **15**, 400) have pointed out that a close parallelism exists between the dipole moments of a number of capillary-active organic substances and the interfacial potential in air of solutions of such substances, but they regard this relationship as qualitative only.

According to the theory of Debye, the total electrical polarisability of a medium, of which the dielectric constant is a measure, is made up of three terms, *viz.*, the electron polarisability P_e, the atom polarisability P_a, and the orientation polarisability P_μ. In the case of substances with high dielectric constants, the molecules of which are always found to possess a comparatively large permanent dipole moment, the orientation polarisability may contribute by far the largest proportion towards the dielectric constant. The dielectric constant of the medium as a whole is a function of the mean polarisability (P_e, P_a, and P_μ) of the individual molecules and of the number of molecules in unit volume, *i.e.*, of the molecular volume.

The magnitude of the electrokinetic potential is probably a function of the mean polarisability of the individual molecules present in the interface, and of the number present per unit area of the interface.

It seems unlikely that the electron polarisation plays much part in the phenomenon, but rather that the electro-endosmosis is determined by the permanent dipole moment of the interfacial molecules and, to a much less degree, by the atom polarisability of the molecules.

Little is known, except in a few cases, as to the magnitude of the atom polarisability of a molecule, but it appears that ordinarily, in the kind of case we are considering, it is very small compared with the orientation polarisability, and by some authors it is regarded as negligible for the purpose of calculating the dipole moment from the total polarisability.

The space taken up by a molecule in the area of the interface will be intermediate between the cross-sectional area of the molecule (if the molecules are completely oriented normal to the interface, and close-packed) and an area proportional to the two-thirds power of the molecular volume (if the molecules are distributed at random). On account of thermal agitation and movement of the adsorbed molecules, the actual value, in the plane of slip, will more probably approximate to the latter figure.

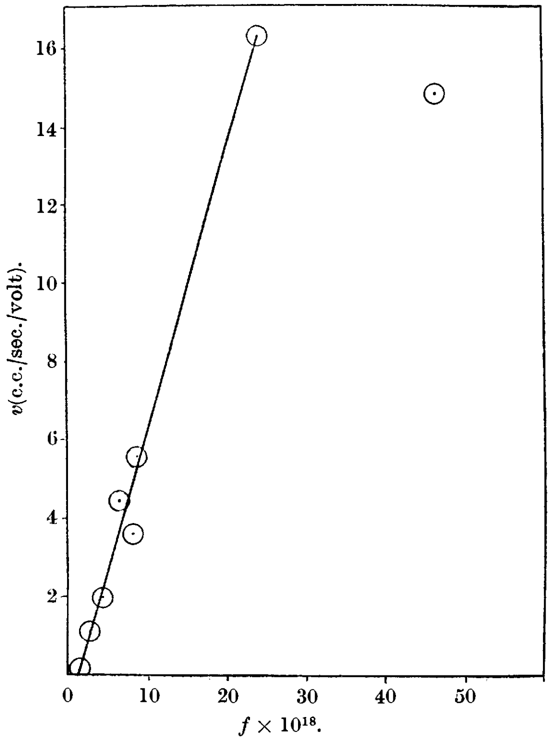
Rideal (*loc. cit.*), in discussing the value of the " vertical component of the integrated electric moment " of fatty acids adsorbed at a gas–liquid interface, as in the experiments of Frumkin, has pointed out that this will be less than the true moment on account of incomplete orientation and inclination of the dipole axis to the surface.

During electro-endosmosis, moreover, the tangential electrical field along the surface of the solid will cause an additional partial orientation of the molecules, in the direction of the field, and a small increase in effective moment due to the distortion of the molecule or " atom polarisation." This, and not electrolytic decomposition, may be the explanation of increased electro-endosmosis at higher voltages, observed by Strickler and Matthews (*loc. cit.*) and in the present work.

It must be remembered also that measurements of the true dipole moment are made essentially, either in dilute solution or in the gaseous state, under conditions such that the molecules are separated and uninfluenced by fields of force from other molecules. The interfacial molecules, on the other hand, are subjected to fields of force from one another, from the solid, and, in electro-endosmosis, from the applied *E.M.F.* also.

In the present experiments the same diaphragm was used throughout, so the hydrodynamic resistance offered to the various liquids by the diaphragm is simply proportional to their viscosities.

FIG. 3.



If, now, we take the reciprocal of the two-thirds power of the molecular volume as a measure of the number of molecules per unit area of the interface, and multiply this by the permanent dipole moment, and divide by the viscosity, we obtain $f \doteq (D/M)^{\frac{2}{3}} . \mu/\eta$ where D is the density and M the molecular weight of the liquid, and μ and η have the same significance as before.

This expression has been calculated where dipole moment data are available and is given in the last column of Table I. These values are plotted in Fig. 3 against the velocities of electro-endosmosis in c.c./sec./volt. The relationship is a linear one within the accuracy of the available data, which suggests a very close connexion between the true dipole moments and the electro-endosmosis. Unfortunately, our knowledge of the dipole moments of the substances in question is far from complete.

Acetone lies away from the curve, which may be due in part to experimental error and in part to the assumption of a too large dipole moment.

There are no measurements of the dipole moment of propionic acid : a value of $1 \cdot 54 \times 10^{-18}$ has been deduced by Smyth (*J. Amer. Chem. Soc.*, 1925, **47**, 1894) on theoretical grounds. This acid, however, is very strongly associated, and from the smallness of the electro-endosmosis it seems probable that the propionic acid molecules are oriented in the interface, at least in part, in the form of double molecules of very small moment. Smyth has concluded that acetic and butyric acids exist as single and double molecules, the latter of little or no electric moment (*J. Amer. Chem. Soc.*, 1930, **52**, 1824).

Benzene and carbon tetrachloride, which possess practically no moment, exhibit no electro-endosmosis, as would be expected.

The actual mechanism whereby a dipole oriented on a surface can bring about a relative displacement of the phases in a tangential electrical field, is another question. There are some molecules, like those of the fatty acids, which can be imagined as ionising in the interface, with adsorption of one ion on the solid. There are many liquids, however, which exhibit electro-endosmosis, any ionisation of which in the ordinary sense is difficult to conceive. In such cases it is possible that a limited mobility of electrons exists between the molecules in contact, and that the distribution of electrons in the interface, under influence of the oriented dipoles themselves and the field of force from the solid, is such as to produce a relative displacement of positive and negative charges under the potential gradient. This would also account for the surface conductivity shown by organic liquids, and for the conduction of the current in the very small distance between the electrodes and the ends of the capillaries.

It is perhaps unwise to deduce a general theory of electro-endosmosis on the basis of the information at present available—further experiments with other liquids and more accurate information as to the individual dipole moments are desirable. The present results, however, suggest that a very close connexion exists between the true dipole moment of a molecule and its electro-endosmotic behaviour. Further investigations along these lines are projected.

Summary.

1. Measurements have been made of the electro-endosmosis of fourteen pure organic liquids and water through a diaphragm of sintered Jena Geräte glass powder.

2. Pure benzene and carbon tetrachloride exhibit no measurable electro-endosmosis, ether is negatively charged towards the glass, and the rest of the organic liquids and water are positively charged.

3. The connexion between the dipole moment of the molecules and the electro-endosmosis is discussed.

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