CCXV.—*Studies in Electro-endosmosis. Part V. The Electro-endosmosis and Surface Conductivity against a Glass Surface of Solutions of Hydrogen Chloride in Benzene and Other Solvents.*

By FRED FAIRBROTHER and MARK BALKIN.

IN his research on the connexion between electro-endosmosis and dielectric constant, Coehn (*Wied. Ann.*, 1898, **64**, 217) found that pure benzene in a glass capillary tube showed no electro-endosmosis. He then dissolved in the benzene a trace of hydrochloric acid and obtained a small electro-endosmosis, the glass being positively charged. This result Coehn ascribed to the fact that the dielectric constant of benzene was less than that of the glass used by him, and stated that the addition of hydrochloric acid simply increased the conductivity, whilst the dielectric constant remained approximately the same. The experiment was repeated later by Coehn and Raydt (*Ann. Physik*, 1909, **30**, 777), who found that the magnitude of the electro-endosmotic pressure developed was such as would be expected from the dielectric constant of pure benzene.

This result is unsatisfactory in several respects. It seems much more likely that the electro-endosmosis was caused, not by the benzene, but by hydrogen chloride adsorbed in the interface. Moreover, dry hydrogen chloride does not confer any appreciable bulk conductivity on benzene. From the statement of Coehn and Raydt that the benzene was " geschüttelte " with the hydrochloric acid, it would appear that the aqueous acid was used, which would give a solution in moist benzene of a single and unknown concentration of hydrogen chloride.

If we assume that Coehn and Raydt used the ordinary concen-

trated aqueous acid, which is rarely much more than $10N$, we can estimate from the partition coefficients given by Knight and Hinshelwood (J., 1927, 466) that the concentration of hydrogen chloride in the benzene could at the most have been 1—1·5 g. per litre, and was probably very much less, depending on the relative amounts of benzene and acid used.

The electro-endosmosis of solutions of dry hydrogen chloride in dry benzene and other solvents, through a diaphragm of sintered glass powder, has now been examined, from low concentrations of hydrogen chloride to saturation.

Surface Conductivity.—Closely associated with the phenomenon of electro-endosmosis is that of surface conductivity, where a liquid in a capillary tube or enclosed between the grains of a powder, exhibits a conductivity greater than that to be expected from its specific conductivity in bulk and the dimensions of its environment. Smoluchowski (*Physikal. Z.*, 1905, **6**, 529) first predicted mathematically that such an augmentation of conductivity would result from the operation of electro-endosmosis. The phenomenon was first observed experimentally by Stock (*Anzeiger Akad. Wiss. Krakau*, 1912, *A*, 635) in the case of several organic liquids in quartz powder, and later by other observers in solutions of electrolytes.

The equation of Smoluchowski connected the surface conductivity with the ζ potential and the thickness of the double layer visualised by Helmholtz; according to this equation, the surface conductivity should vary in the same manner as the ζ potential and become zero when there is no electro-endosmosis.

The results of later observers, however, seem to show that surface conductivity may be observed in comparatively well-conducting solutions and other solutions which show very little or no electro-endosmosis. For instance, McBain and his collaborators (*J. Amer. Chem. Soc.*, 1929, **51**, 3294) have examined the surface conductivity shown by dilute solutions of potassium chloride in the neighbourhood of surfaces of fused silica, polished quartz, and polished glass; they found that the specific surface conductivity remained of the same order of magnitude in solutions varying from $N/1000$ to N, whilst a 1000-fold change in the bulk conductivity took place; other observers have shown that the electro-endosmosis decreases with increasing concentration of potassium chloride. Also, Briggs (*Colloid Symposium Monograph*, 1928, **6**, 41) has shown clearly that the surface conductivity of aqueous solutions in a mass of cellulose fibres is not a function of the ζ potential as measured by the streaming-potential method, the surface conductivity having a finite value even when the ζ potential is zero.

It seems, therefore, that whilst surface conductivity is a necessary

concomitant of electro-endosmosis, the converse is not the case in aqueous solutions.

The present results with some non-aqueous solutions likewise show that surface conductivity is not dependent upon electro-endosmosis. Solutions of hydrogen chloride in non-polar solvents are well adapted for the observance of surface conductivity, since the conductivity in bulk is very small whilst the hydrogen chloride provides suitable material for the production of ions by the forces operating at the interface.

EXPERIMENTAL.

1. *Electro-endosmosis.*

The arrangement of the apparatus is shown diagrammatically in Fig. 1. The apparatus was made in three parts, (i) the electro-

FIG. 1.
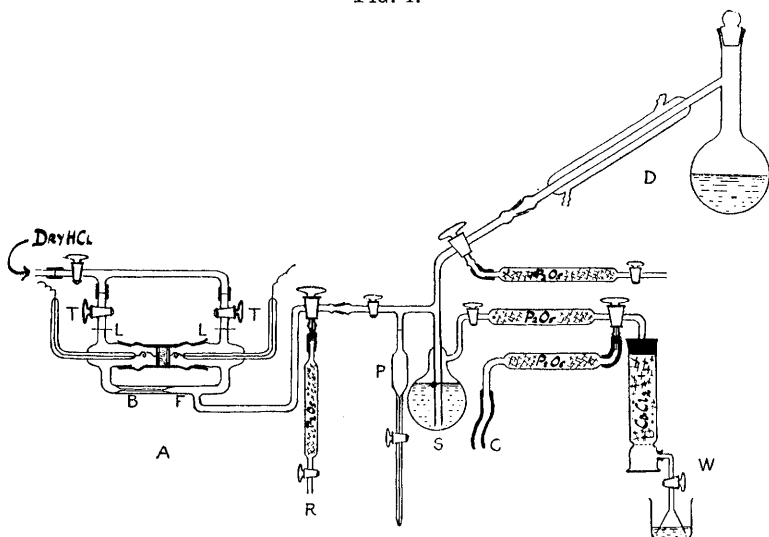
endosmosis apparatus A, (ii) the absorption vessel S and measuring pipette P, and (iii) the distillation flask D with attached condenser. The three parts were connected by ground-glass joints, which permitted of their being detached from one another and avoided any contact of the liquids with rubber tubing.

The electro-endosmosis apparatus and method of measurement were essentially as previously described (this vol., p. 389). The same diaphragm and electrodes were used, but the " bubble-tube " was improved in that the actual capillary tube and the connecting tubes were made shorter and no detachable joint was used, the tubes,

after assembly of the apparatus, being sealed together at F. This joint required to be cut and re-made each time the apparatus was dismantled for cleaning; but the inconvenience thus caused was not great.

The apparatus, with the exception of the diaphragm, was cleaned with chromic acid, washed, and dried. The diaphragm was cleaned and dried as previously described (loc. cit.). The electro-endosmosis apparatus and absorption vessel were further dried, after assembly, by the slow passage through them of heated air dried by phosphoric oxide. Throughout the experiments great care was taken to ensure the absence of moisture : taps were lubricated with a minimum of metaphosphoric acid, and all connexions to the atmosphere were provided with phosphoric oxide guard tubes.

The solvents, previously purified and dried by long contact with phosphoric oxide, were distilled from phosphoric oxide in the flask D into the absorption vessel S. The distillation was usually carried out under slightly reduced pressure, which assisted in the removal of dissolved air from the solvents. The benzene (Kahlbaum's " cryst. thiophene free ") gave no indication of thiophen by the isatin test, and after repeated distillation and contact with phosphoric oxide, did not colour the latter on standing in contact with it for many months (compare Greer, J. Amer. Chem. Soc., 1930, 52, 4191). The cyclohexane was shaken vigorously for 8 hours with 100% sulphuric acid, washed, dried, and fractionated; an ultra-violet spectro-photograph showed an almost complete absence of benzene.

The phosphoric oxide used for the drying of the solvents was purified by volatilisation in a stream of oxygen.

The hydrogen chloride was ·prepared from pure sulphuric and hydrochloric acids and A.R. sodium chloride, and was dried, first by sulphuric acid and then by phosphoric oxide, being passed through a tube tightly packed with glass wool, after leaving the sulphuric acid, in order to catch any spray. The gas was then passed into the vessel S, for periods varying from a few minutes to several hours, according to the concentration required. The unabsorbed gas was passed into water as shown in Fig. 1, the drying agents serving to protect the absorption vessel and solution from the diffusion of moisture against the hydrogen chloride stream.

The solution was transferred from S, by the application of pressure at C, into the electro-endosmosis apparatus and the pipette P. To permit of the emptying of the latter, air was admitted at R.

Estimations of the hydrogen chloride content were made by running a measured volume of the solution from P into an excess of standard alkali contained in a conical flask, with the end of the

pipette nearly touching the surface of the alkali. Immediately after the delivery of the last drop of the solution the tap was closed and the flask withdrawn and closed by a ground-glass stopper. The flask was shaken carefully for some minutes to ensure complete neutralisation of the hydrogen chloride and the excess of alkali estimated with standard hydrochloric acid. The neutralisation was not instantaneous, but by this procedure the loss of hydrogen chloride was reduced to a minimum even in the case of the lighter solvents which floated on the aqueous alkali. The pipette P was calibrated by weighing with water to deliver a fixed amount of solution, about 10 c.c.

Some doubt having been felt at one stage as to the completeness of extraction of the hydrogen chloride from the solvent in the above method, an alternative procedure was also used in the case of solutions in benzene and carbon tetrachloride. In this second method a measured amount of the solution was run into excess of a 0·4% solution of sodium in ethyl alcohol, water being added in sufficient quantity to keep the solution clear and homogeneous. The organic solvents were then evaporated off on the water-bath, and after acidification, the sodium chloride was estimated volumetrically by Volhard's method. The results were quite reproducible and almost identical with those obtained by the first method with the same solution of hydrogen chloride. In all subsequent estimations the neutralisation with aqueous alkali was used, as being more convenient.

The electro-endosmosis apparatus, from which the air had been swept by the hydrogen chloride gas during the preparation of the solution, was filled with the solution up to the taps TT, a small bubble being left, which by inversion and manipulation of the apparatus could be brought into the tube B to serve for the measurements : after being detached from the other parts of the apparatus, it was immersed in a water thermostat at $20° \pm 0·01°$ up to the level L, the attached phosphoric oxide tube being outside the thermostat. The large ground joints on the diaphragm tube, as before, were wound with strip rubber under tension, to prevent ingress of moisture. The applied voltage was 710 in each experiment; this was obtained in part from the 400-volt D.C. supply mains and in part from small accumulators. The electro-endosmosis was observed by a telescope through a window in the side of the thermostat.

After a series of measurements at one particular concentration, the electro-endosmosis apparatus was again connected to the rest of the apparatus and the solution forced back into the vessel S. The concentration of hydrogen chloride was then either increased

by the passage of more gas, or reduced by drawing purified and dried air through the solution. The new solution was then used as before.

After the completion of measurements with one solvent, the liquid was drained from the apparatus as far as possible, care being taken to prevent the entry of atmospheric moisture. The remainder of the solvent was then removed by a slow current of dry air drawn through the apparatus for several hours by a water pump attached at W. A small quantity of the new solvent was then distilled into the apparatus, which was rinsed out with the liquid. This washing was applied particularly to the diaphragm through which the new solvent was allowed to drain, the electro-endosmosis apparatus being detached for this purpose. The apparatus was then again emptied, re-assembled, and dry air drawn through as before. It was then ready for use with the new solvent.

The sulphuric acid and phosphoric oxide used for drying the hydrogen chloride and in the guard tubes, were changed from time to time, and always before experiments with a fresh solvent were commenced. Three pure solvents and their hydrogen chloride solutions were used in turn, *viz.*, benzene, carbon tetrachloride, and *cyclo*hexane. The apparatus was then dismantled, cleaned, and re-assembled for experiments with *cyclo*hexene.

The results with benzene and *cyclo*hexene are summarised in Table I, in which c is the concentration of hydrogen chloride (in g. per litre of solution), and v is the velocity of electro-endosmosis (in c.c./sec./volt $\times 10^7$). The experiments are given in the order in which they were performed.

TABLE I.

Solvent.	c.	v.	Solvent.	c.	v.
Benzene	0·00	0·00	Benzene	16·33	9·35
,, ...	17·12	8·91	,, ...	1·18	1·89
,, ...	6·02	7·93	*cyclo*Hexene	0·00	very slight
,, ...	3·06	5·27	,,	saturated	*ca.* 1·0
,, ...	2·71	5·04			

Only in the case of solutions of hydrogen chloride in benzene was there any appreciable electro-endosmosis; the values with a particular solution could be reproduced to within 1%. The variation of electro-endosmosis with concentration is shown graphically in Fig. 2. The first solution examined, owing to saturation at a lower temperature, was slightly supersaturated at the temperature of the experiment.

Pure carbon tetrachloride and *cyclo*hexane or their solutions gave no indication of any electro-endosmosis. Pure *cyclo*hexene gave an extremely small movement which was too slow and irregular to be

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measured with any accuracy : the movement of the saturated
solution was more definite and of the order given.

In every case where electro-endosmosis was observed, the glass
was positively charged with respect to the liquid.

Even with a saturated solution in benzene, the velocity of electro-
endosmosis was much smaller than that of many pure organic

FIG. 2.

Conc. of HCl, *g./litre*.
- - - - *Electro-endosmosis curve for benzene.*
——— *Surface conductivity curves.*
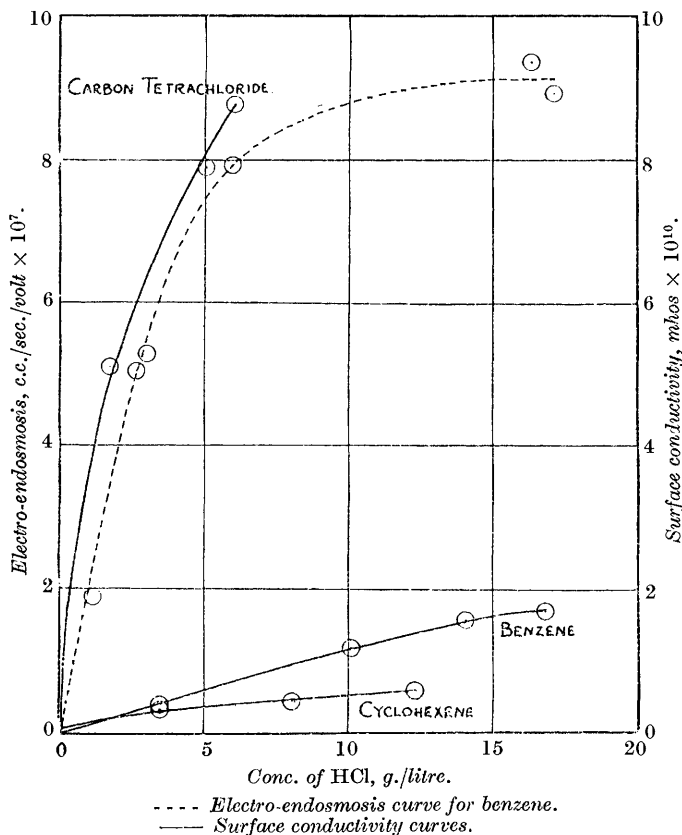
solvents through the same diaphragm (Fairbrother and Balkin,
loc. cit.). Its dependence on the concentration of hydrogen chloride
shows that it is the latter, and not the relative dielectric constants
of benzene and the glass, which determines the effect. The fact that
Coehn and Raydt's results with a moist benzene solution of hydrogen
chloride agreed with their theory, must be regarded as accidental.

A strict comparison between the electro-endosmosis and the
dielectric constants of the solutions used in the present work is not

possible, since no data are available for the latter. On the other hand, however, the molecules of hydrogen chloride in the gaseous form possess an appreciable permanent dipole moment (1.034×10^{-18} e.s.u., according to Zahn, *Physical Rev.*, 1924, **24**, 400), whilst the molecules of benzene have hardly any moment : also the dielectric constant of liquid hydrogen chloride is 4.60 at 27.7° (Schaefer and Schlundt, *J. Physical Chem.*, 1909, **13**, 669), whilst that of benzene is 2.282 at 20° (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 664). It is probable, therefore, that the solutions used in the present work had dielectric constants greater than that of the pure solvent. Hence, according to the theory of Coehn and Raydt, the glass should become decreasingly positive with increasing concentration of hydrogen chloride, whereas, as is shown, the reverse takes place.

Measurements of the current flowing through the diaphragm during electro-endosmosis, showed in each case the presence of surface conductivity, the magnitude of which agreed well with the results obtained by the method described in the latter part of this paper.

Solubilities of Hydrogen Chloride.—During the course of this work, estimations were made of the solubilities of dry hydrogen chloride in the various solvents; the results are given below, S denoting the solubility as g. per litre of solution. The saturated solutions in benzene and carbon tetrachloride were made in a manner similar to that described above, but in a separate absorption vessel which was immersed in the thermostat at 20.00°. The measuring pipette delivered 12.20 c.c. Saturation was generally carried out for about 48 hours, the gas escaping at atmospheric pressure.

Solubility of dry hydrogen chloride in benzene at 20.00°.

Pressure, mm. ...	753	747	753	745	758	745	752	761	747	753
S	16.83	16.67	16.83	16.63	16.80	16.67	16.70	16.82	16.58	16.67

Mean at 760 mm., $S = 16.91$.

[In the first five experiments, the estimation of hydrogen chloride was done by the first method (p. 1567), and in the last five by the second method.]

The pressures given are those at the conclusion of the saturation. Knight and Hinshelwood (*loc. cit.*) found the solubility of hydrogen chloride in dry benzene at 20.00° and 760 mm. to be 16.80 g. per litre.

Solubility of dry hydrogen chloride in carbon tetrachloride at 20.00°.

Pressure, mm.	751	751	743	756	756	756	743	760
S	6.08	6.08	6.03	6.19	6.19	6.19	6.03	6.20

Mean at 760 mm., $S = 6.19$.

[In the first four experiments, the estimation of hydrogen chloride was done by the first method (p. 1567), and in the last four by the second method.]

Solubility measurements in *cyclo*hexane and *cyclo*hexene were carried out at room temperature; the solutions were neutralised with sodium hydroxide (see p. 1567).

| | *cyclo*Hexane. | | | *cyclo*Hexene. | |
Temp.	Press., mm.	S.	Temp.	Press., mm.	S.
17·0°	751	4·98	18·6°	765	12·29
17·0	751	·5·08	18·6	765	12·29
18·0	752	4·79	17·1	765	12·29
18·0	752	4·93	16·0	761	12·44

2. *Surface Conductivity.*

The materials and the preparation and estimation of the solutions were as already described. The apparatus was essentially the same as that shown in Fig. 1, but with the replacement of the electro-endosmosis apparatus and the absorption vessel and pipette (A, S, and P) by the apparatus shown in Fig. 3, consisting of the conductivity cell, absorption vessel, and pipette. These were rigidly clamped together by two parallel wooden strips, as shown by the broken line, to facilitate the subsequent manipulation of this unit as a whole without fracture. The conductivity cell was made of Jena 16^{III} (normal) glass; the platinum electrodes were about 2·25 sq. cm. in area, about 0·5 mm. thick, and were very rigid. They were separated by about 5 mm. and were rigidly held relative to one another by glass bridges sealed to the platinum at the edges. After being cleaned, steamed, and dried, the cell was partly filled with powdered Jena Geräte glass, " grade 5—7," supplied by Schott u. Gen. This was a sample of the same material used in the manufacture of sintered discs as used in the electro-endosmosis experiments. The powder was cleaned by repeated extraction with pure concentrated hydrochloric acid, washed, dried, and filled into the cell until the surface of the powder was about 2 cm. above the top edge of the electrodes. The cell was then attached to the rest of the apparatus by its hollow stopper, to which a trace of metaphosphoric acid was applied, the joint then being covered on the outside with wax to prevent the ingress of moisture. The tubes through which contact was made with the electrodes were filled completely with mercury and closed by small corks through which wires passed; the corks were coated on the outside with sealing wax. This was done in order to ensure that the lack of bulk conductivity shown by the solutions was not due to a break in the circuit on inverting the cell as described below.

The cell was evacuated through the tap T_1 (Fig. 3) and then allowed to fill completely with the solution from the absorption vessel S, dry air being admitted through T_2. The conductivity measurements were made with direct current and an Einthoven

string galvanometer, the latter being calibrated each time immediately before the measurement. The particular $E.M.F.$ used (up to a maximum of 120 volts) was chosen to give a suitable deflexion of the galvanometer fibre.

The cell was then inverted, the powder well shaken, and then (with the cell in an upright position) allowed to settle with occasional tapping for about 2 mins., by which time all the grains of the powder had settled below the bulk of the solution, and the resistance was again measured. This was repeated several times, and measurements were also made after long settling (over-night). The resistances were reproducible to about 3—4%.

FIG. 3.
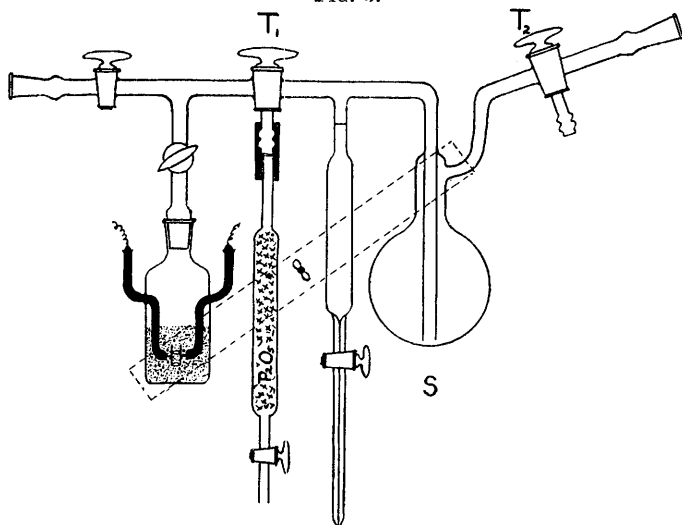
The bulk conductivity of the solution was measured by keeping the cell inverted. The capacity of the cell and the volume of powder were so proportioned that when the cell was inverted the powder fell to the stopper end, leaving the electrodes in the clear solution, about 2 cm. above the powder. In this position the ordinary bulk conductivity of the solution could be measured. Thus the surface conductivity and bulk conductivity were measured with the same solution in the same apparatus, obviating any errors due to transference from one vessel to another or to the use of two vessels.

The conductivity cell containing the dry glass powder was tested for electrical leaks before the introduction of the solvent into the apparatus.

The " cell constant " of the glass powder and of the electrodes in the free liquid were measured at $20{\cdot}00°$ with $N/10$-aqueous potassium

chloride solution.   The ratio of surface conductivity to bulk con-
ductivity in this solution is negligble compared with the same ratio
in the other solutions.

After measurements with a hydrogen chloride solution of a parti-
cular concentration, the apparatus (Fig. 3) was evacuated through
the tap T_2, and the solvent distilled from the conductivity cell into
S by surrounding these with rags dipped in hot and cold water
respectively.

In addition to the measurements with hydrogen chloride solutions,
observations were made with the pure solvents.   These were made
first in each series to ensure the absence of hydrogen chloride.   The
whole apparatus was dismantled and cleaned before use with a new
solvent.

In order to compare the results with those previously obtained
with pure organic liquids measured in the pores of a glass diaphragm
during electro-endosmosis and with Stock's (loc. cit.) results, an
additional measurement was made with pure, dry, freshly distilled
nitrobenzene.

The conductivity measurements were carried out at room
temperature which averaged about 17°.   The results are summarised
in Table II, in which "$\kappa \times 10^{10}$, in glass powder" refers to the
apparent specific conductivity of the liquid in the powder, and may
be called the "surface conductivity."   Since the bulk conductivity
was negligible, the observed conductivity could be regarded as
wholly due to surface conductivity.   We were unable to obtain an
unambiguous estimate of the extent of the surface of the glass powder
owing to the irregularity in shape of the particles.

No bulk conductivity could be detected even in saturated solutions
of dry hydrogen chloride in the solvents used, with the single excep-
tion of the carbon tetrachloride solution noted below, and in this
case it was probably due to moisture.   The various factors involved
were such that, when the maximum voltage of 120 was used, 0·5 div.
of the eyepiece scale of the galvanometer corresponded, in the
measurements of the bulk conductivity, to a specfic conductivity
of $6·7 \times 10^{-13}$.   This was the lowest conductivity that could con-
veniently be measured, and where no conductivity could be detected,
the value is given as below this figure : in such cases the actual
conductivity may be very much less.

The experiments are given in the order in which they were carried
out.   Each of the series A, B, and C refers to a set of measurements
with the same sample of solvent.   In the case of benzene, three
separate series of estimations were made, each with a fresh amount
of solvent, and between each of which the apparatus, including the
cell and glass powder, was dismantled, cleaned, and dried.   It was

TABLE II.

(All conductivities are expressed in reciprocal ohms.)

Expt. No.	Series.	HCl, g./litre.	$\kappa \times 10^{10}$, in glass powder.	Expt. No.	Series.	HCl, g./litre.	$\kappa \times 10^{10}$, in glass powder.
		Benzene				*cycloHexene*	
1	A	10·70	(9·72)	1	A	0·0	0·097
2		14·09	1·55	2		3·48	0·31
3	B	0·0	<0·0067	3		8·02	0·44
4		2·31	(0·98)	4		12·30	0·58
5		3·50	0·37				
6	C	11·16	(14·6)			*Carbon tetrachloride*	
7		12·99	(4·17)	1	A	0·0	<0·0067
8		10·11	1·17	2		3·08	(333·4)*
9		16·83	1·64	3		5·12	7·9
				4		6·07	8·8
		cycloHexane		5		1·76	5·1
1	A	0·0	<0·0067				
2		4·97	0·097				

Nitrobenzene (κ in bulk, 147×10^{-10})

1	A	0·0	250

* For this solution, κ in bulk $= 2.30 \times 10^{-10}$: for all other solutions, κ in bulk $< 6.7 \times 10^{-13}$ mho.

observed that the first measurement of a series, particularly in benzene and carbon tetrachloride, showed a very large surface conductivity, which in a continuous series of estimations with the same sample of solvent, was not reproducible. For example, in benzene, Expt. 6, which was the first experiment in Series C, gave a value for the surface conductivity of 14.6×10^{-10} mho; when the solution had been distilled completely out from the cell under reduced pressure, whereby a considerable quantity of hydrogen chloride gas passed out to the pump and was absorbed, and the solution was re-made to a slightly higher concentration, a value of 4.17×10^{-10} was obtained; this fell subsequently to 1.64×10^{-10} mho in a still stronger solution (Expt. 9).

These anomalies could not be attributed to differences in concentration of the solution, since they disappeared after one or two fillings of the cell. The phenomenon was particularly marked in the case of the first experiment with a solution of hydrogen chloride in carbon tetrachloride (Expt. 2) where, not only was the initial surface conductivity very large, but the bulk conductivity was appreciable. It is suggested that the large values for the surface conductivity in the first, and sometimes the second, measurement in a series is due to the presence of traces of moisture still present in the glass powder which are removed by the hydrogen chloride, eventually passing away with the, otherwise dry, hydrogen chloride from the absorption vessel. The glass powder ultimately reached an equilibrium condition when no more moisture was removed. That a similar effect was not observed in the electro-endosmosis experi-

ments, must be ascribed to the more efficient preliminary drying of
the diaphragm in the latter case, by the stream of warm, dry air and
the hydrogen chloride gas. The glass powder in the conductivity
cell was dried *in situ* to some extent by evacuation, and by leaving
open for several days, prior to a measurement, the taps between
the conductivity cell and the phosphoric oxide tubes, but this was
not so efficient as the long passage of a current of dry air and
hydrogen chloride gas used in the electro-endosmosis experiments.

The results of Francis and Burt (*Proc. Roy. Soc.*, 1927, *A*, **116**,
586) are interesting in this connexion. These authors showed that
the shape of the sorption-rate curve of ammonia on glass depends
on the dryness of the glass. The glass wool was heated in the
presence of dry ammonia, and early experiments indicated higher
values for the sorption of the ammonia than the later ones, which
tended towards uniformity. The progressive change was ascribed
to the gradual removal of moisture by the dry ammonia, which
appeared to be more effective in reducing the water content of the
glass than heating in a vacuum.

Neglecting the obviously anomalous values, which are indicated by
parentheses in Table II, the surface conductivity is plotted against
the concentration of hydrogen chloride in Fig. 2 (full line). In
*cyclo*hexane the surface conductivity was very small even in saturated
solution.

Discussion.

A consideration of these results shows that the surface con-
ductivity is not caused by electro-endosmosis : its source must be
sought in the changed properties of the hydrogen chloride molecules
present in the interface.

McBain (*J. Amer. Chem. Soc.*, 1929, **51**, 3294) has suggested that
surface conductivity in electrolytic solutions is due to the presence
in the interface of an increased number of mobile ions, not neces-
sarily all of one sign, corresponding to sessile ions on the fixed portion
of the " double layer." This, however, is an augmentation of a
condition of affairs already existing in the *bulk* of the solution,
namely, ionisation : in the present instance we are not dealing with
an ionising solvent ; moreover, in carbon tetrachloride, in which
the surface conductivity was considerable, we were unable to obtain
any evidence of a " double layer." We must assume, on account of
the absence of appreciable bulk conductivity in these solutions, that
the hydrogen chloride molecules are present as un-ionised dipoles,
as in the gaseous state.

On the other hand, in the interface, the hydrogen chloride becomes
conducting. The figures given are calculated for comparison pur-
poses from the *whole* effective cross section of the pores, in the

absence of precise knowledge as to the dimensions of the conducting layer. The actual surface conduction takes place in a very thin layer on the solid, and is therefore enormously greater in that region than the apparent surface conductivity given in Table II.

There are two possibilities which may account for this increase of conductivity. (1) When a dipole is adsorbed on a heteropolar solid surface, it may, if deformable, suffer a considerable distortion. This aspect of adsorption has been considered by several authors (see Rideal, " Surface Chemistry," 1930, p. 208). In particular, we may cite the work of Boer (*Proc. K. Akad. Wetensch. Amsterdam*, 1928, **31**, 906) on the adsorption of iodine on calcium fluoride, who has calculated the moment induced by polarisation of iodine adsorbed on calcium fluoride to be $2 \cdot 3 \times 10^{-18}$ *e.s.u.*, which is of the same order of magnitude as the dipole moment of water. He also observed that the light-absorption band of the adsorbed iodine was shifted in the direction of shorter wave-lengths. The effect of adsorption of the iodine is therefore comparable with the effect of dissolution in a highly polar solvent. Now glass is not so obviously a heteropolar solid as calcium fluoride; but the polar nature of a glass surface has been demonstrated by Norrish (J., 1923, **123**, 3006; 1926, 56) by its catalytic effect on the halogenation of ethylene. In the present instance, therefore, it may be that the adsorbed hydrogen chloride molecules have undergone a distortion amounting to separation of the ions.

(2) Although the glass surface was " dry " in the ordinary sense and in equilibrium with the dry hydrogen chloride solution, yet it does not follow that the whole of the adsorbed moisture had been removed from the surface. The tenacity with which glass retains traces of moisture even after being strongly heated in a vacuum is well known, and in the present experiments it is possible that part of the glass surface was covered with a layer of adsorbed water. Such strongly adsorbed water, however, must be regarded for the present argument as part of the solid, and not as a solvent in which the hydrogen chloride was dissolved and ionised. A hydrogen chloride molecule superimposed on the top of an adsorbed water molecule would tend to ionise according to the scheme Solid $\cdot$ H_2O + HCl $\rightleftharpoons$ Solid $\cdot$ $H_3O^{\cdot}$ + Cl′, which is similar to the scheme proposed by Brönsted for ionisation in aqueous solution. Such a scheme, moreover, would serve to explain the positive electrokinetic charge in benzene and *cyclo*hexane, and is almost certainly the explanation of the large surface conductivity shown in the initial experiments of a series when the system was incompletely dried.

The solvent also clearly exercises an important influence on both the electro-endosmosis and the surface conductivity; but there is

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little evidence here to guide us towards an explanation of the mechanism. The influence of the solvent on the surface conductivity may be due to differences in adsorption of hydrogen chloride or to differences in surface ionisation, or to both.

Summary.

1. Measurements have been made of the electro-endosmosis through a diaphragm of sintered glass powder, and of the surface conductivity in glass powder of the same kind, of solutions of dry hydrogen chloride in benzene, carbon tetrachloride, *cyclo*hexane, and *cyclo*hexene.

2. Solutions in benzene show the greatest electro-endosmosis, which increases with concentration of hydrogen chloride, the glass being positively charged throughout.

3. Solutions in *cyclo*hexene show a very small electro-endosmosis, the glass being positively charged.

4. Solutions in carbon tetrachloride and *cyclo*hexane gave no measurable electro-endosmosis.

5. Solutions in all four solvents show surface conductivity, that in *cyclo*hexane being much smaller than in the other solvents.

6. It is shown that the surface conductivity is not caused by the electro-endosmosis.

7. A mechanism is suggested to account for the surface conductivity by surface ionisation of the hydrogen chloride.

8. Measurements have been made of the solubilities of dry hydrogen chloride in the four solvents used.