ELECTROLYTIC ENDOSMOSE.

By Horace G. Byers and Carl H. Walter.

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In 1901, F. J. Parker presented a thesis "In Partial Fulfilment of the Requirements for the Doctor's Degree," which has not otherwise found publication, in which he details the results of certain experiments with a tripartite cell involving electrical endosmose. These results are of a character which held a high degree of interest for one of the present writers and have led to the present investigation. The experiments here detailed represent the beginning of what we hope may develop into a much more extended series which may be of value. We shall, therefore, attempt to present first an historical résumé of the subject with a bibliography which, if incomplete, may be extended in subsequent papers.

Historical.

Apparently the first observation of electrical endosmose was by Reuss,[1] who observed the transfer of liquid from one side of a porous clay membrane to the other during the process of electrolysis. Similar observations were made by Poiret, Becquerel, Armstrong and Daniels with other membranes. The first careful study of this transfer of water during electrolysis was made by Wiedman[2] and by Quincke.[3] The general results of these observations may be summarized as follows:

When a liquid, separated into two portions by a porous septum, is subjected to electrolysis, the flow of liquid through the septum is proportional to the intensity of the current, the specific resistance of the liquid and the thickness of the membrane, and inversely proportional to the porosity of the membrane. The direction of the flow with electrolytes is generally with the current, *i. e.*, toward the cathode, but under certain circumstances the flow is contrary to the current. No further contribution to the experimental side of the subject appears to have been made until 1898, when Alfred Coehn[4] showed that during the progress of endosmose the liquids and the diaphragm became electrically charged and in different liquids with charges of opposite sign.

In 1900, J. C. Olson[5] accidentally encountered electrical endosmose in the preparation of permanganic acid from potassium permanganate by electrolysis, using a porous clay cup as a means of separation between anode and cathode. In attempting to improve upon his method, F. J. Parker[6] made use of two cups, one containing the anode and the other the

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[1] *Mem. de la Soc. imp. des Nat. de Moscow*, 11, 332 (1808).

[2] *Pogg. Ann.*, 87, 321 (1852).

[3] *Ibid.*, 107, 1 (1859); 110, 38 (1860); 113, 513 (1861).

[4] *Wied. Ann.*, 64, 217 (1898); 66, 1191 (1898).

[5] *Am. Chem. J.*, 23, 431 (1900).

[6] Johns Hopkins Dissertations, 1901.

cathode. He says: "Electrical endosmose in these experiments proceeded simultaneously in both cups in *opposite* directions."

In 1903-4, Jean Perrin[1] published an exhaustive account of many experiments. In these he used very thick membranes, 10-12 cc., made of a large variety of substances. He found, in general, that all membranes behaved alike in respect to the charge assumed by it and that, in general, the direction of flow of water during electrolysis was with or against the current according to the charge assumed by the membrane. Apparently this charge was positive or negative according as hydrogen or hydroxyl ions were in excess in contact with the membrane.

In 1902, Reed,[2] in a paper designed to point out errors in the determination of migration ratios, called attention to a case of endosmose in which the solvent migrated toward neither electrode but apparently away from both. Certain experiments with the apparatus designed by him are described in this paper.

Bancroft[3] advances, in a discussion of the work of both Perrin and Reed, an explanation of endosmose which is essentially that the direction of flow is determined by the relative adsorption of the ions of greatest concentration.

It will be observed that in the explanations offered by Wiedeman, Perrin and Bancroft, note is taken of the electrical charges on the porous septa. No explanation is furnished for the transfer of water through the septa. It does not appear to have been realized that water may be transmitted through septa, under varied conditions, either with or against the direction of the current, in both directions at the same time, or away from both electrodes. In this paper instances of all these kinds are described and also an instance where it is apparent that water not only migrates with the current but flows more rapidly away from the anode than to the cathode.

Before presenting the experiments, we also desire to call attention to the work of Washburn, which itself presents a summary of previous work on the hydration of ions. In his paper Washburn[4] demonstrates that water is carried with the cathions of hydrogen and the alkali metals into the cathode chamber of a migration ratio apparatus specially designed for the investigation. This Washburn takes to be a demonstration that these ions are hydrated. The work of Washburn was repeated in this laboratory and the observations extended to the chlorides of the alkaline earth metals.[5]

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[1] *Compt. rend.*, 137, 513 (1903); *J. chim. phys.*, 2, 601 (1904).

[2] *Trans. Am. Electrochem. Soc.*, 2, 238 (1902).

[3] *Ibid.*, 21, 233 (1912).

[4] THIS JOURNAL, 31, 322 (1909).

[5] The work has not been published except as a Master's thesis by J. M. McGee.

Bartell[1] in an article on negative osmose, describes a series of experiments in which he obtains *concentration* of solutions by transfer of water through clay membranes into the pure solvent. The bearing of these papers on the subject of the paper will be pointed out in our conclusions.

Before passing by the literature of the subject, attention may be called to the fact that industrial application of endosmose is being attempted and the various plans are covered by patents among which are German patents 124,509, 128,085, 239,649, and English patents 3,364 and 11,626.

Experimental.

In the experiments described below, the apparatus first used was a simple tripartite cell, consisting of two battery cups of ordinary type, set in a battery jar, and kept about a quarter of an inch apart (Fig. 1). In each cup was placed a platinum electrode 100 × 50 mm. and an intermittent syphon, so that any rise in the level of the liquid would cause an overflow into a suitable graduated vessel. Before beginning an experiment, the whole apparatus was filled with the solution to be examined and when in the course of an experiment the level of liquid in the battery jar tended to fall materially, its level was maintained by addition of the original solution from a reservoir through a dropping siphon. In this apparatus nine solutions and a total of twenty-two experiments were performed. The results are given in Table I.

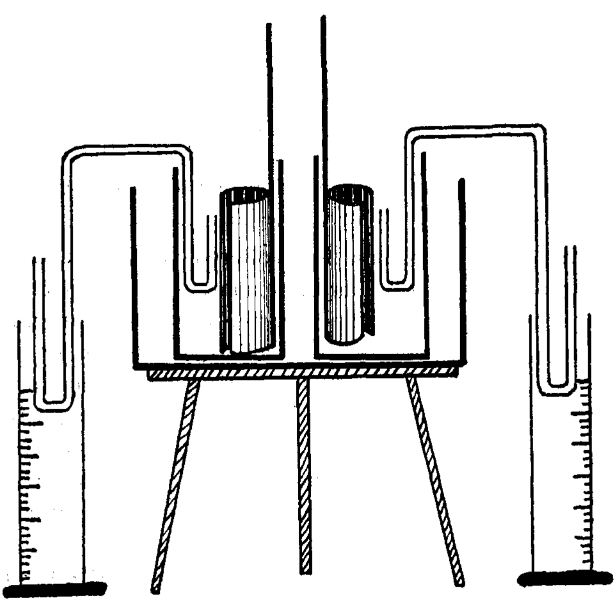

Fig 1.

Attention is directed to the following points illustrated by the table:

The first four experiments show the verification of Parker's work, and that both anode and cathode flow takes place at various dilutions. The walls of both cups become more or less clogged with reduction products of the permanganate. Similarly, flow in both directions occurs with

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[1] This Journal, 36, 646 (1914).

TABLE I.

	Solute.	Solvent.	Solution.	Amperes.	Volts.	Kathode flow. Cc.	Anode flow. Cc.	Time in hrs.	Temperature Initial-Final
1	$KMnO_4$	Water	Saturated	2 −1.4	26–52	212	40	5:30	22–55
2	$MKnO_4$	"	20 g.-L.	2 −1.3	32–54	560	103	5:30	20–57.5
3	$KMnO_4$	"	10 g.-L.	2 −2.0	68–42	1565	265	5:10	21–56
4	$KMnO_4$	"	1 g.-L.	0.4 −1.2	106–108	3000	210	5	18–60
5	$KClO_4$	"	20 g.-L.	2 −1.2	13–35	265	62	8:10	28–48
6	$KClO_4$	"	20 g.-L.	2 −1.3	87–70	295	58	5	21–59
7	$KClO_4$	"	10 g.-L.	2 −1	33–72	900	160	7:30	26–54
8	NaCl	"	20 g.-L.	2 −2.2	20–9.5	125	100	8:10	24–38
9	$CuSO_4$	"	....	....	.....	..	...	0:15	.....
10	$CuNO_3$	"	Normal	2 −0.5	86–102	..	...	2	10–34
11	$Na_2SO_4.10H_2O$	"	$^1/_2$ *N*	2 −2.0	42–10	55	0	6	9–17
12	$Na_2SO_4.10H_2O$	"	$^1/_2$ *N*	2 −2.0	.....	60	0	6	45–50
13	Borax	"	Saturated	2 −	34–	10	0	0:08	20–32
14	Borax	"	Saturated	2 −1	32–78	500	0	3:18	20–58
15	K, alum	"	Saturated	2 −0.2	48–120	0	0	7:20	21–36
16	K, alum	"	1/1000 sat.	0.025–0.005	108–110	85	75	8:30	19–24
17	K, alum	"	1/1000 sat.	0.050–0.006	101–110	425	0	9:00	21–23
18	K, alum	"	9/1000 sat.	0.023–0.006	110–110	500	16	6:30	19–24
19	$FeCl_3$	"	Sp. gr. 1.070	2 −0.4	12–0	0	20	2:40	18–34
20	$FeCl_3$	"	Sp. gr. 1.070	2 −0.4	0.6–120	0	22	6:45	20–60
21	$FeCl_3$	"	Sp. gr. 1.070	0.09 −0.09	.....	0	0	8:30	17–21
22	$FeCl_3$	"	1/1000	22.6 −0	100–0	0	45	4:00	16–17

potassium perchlorate. When sodium chloride is used no anode flow takes place at first, and indeed, in one experiment for three hours, while at the end of the experiment the anode flow is approximately five drops to one at the cathode. It is probable that perchloric acid, formed at the anode, is the cause of the flow but no attempt was made to determine its quantity.

Copper sulfate shows no tendency toward flow toward either cathode or anode, but at the end of fifteen minutes the current automatically disconnected itself, due to recession of liquid from *both* cups. Copper nitrate shows lowering of level in the cathode compartment alone.

Since in all the previous cases the electrolysis caused considerable rise of temperature, in the next case (11) the solution of sodium sulfate, hydrated, was kept in a cold water bath to prevent decomposition of the hydrate. Yet under these circumstances, as well as where the temperature was allowed to rise, only slight cathodic flow is to be observed. In Expt. 13, with a saturated borax solution, within eight minutes, the solutions had receded from the anode cup so rapidly as to break the circuit, indicating a flow of about 100 cc., while an increase of only 10 cc. had taken place in the cathode cup. This seemed a good case with which to ascertain whether acidity causes anodic, and alkalinity, cathodic flow. Expt. 14 was conducted exactly as thirteen except that in the anode cup was placed a mixture of borax solution and concentrated sulfuric acid. No change in the level of the anode cup was observed, though 500 cc. passed from the battery jar into the cathode cup.

Experiments with potassium alum (15, 16, 17, 18) show very interesting variations. In a saturated solution there occurred a very slight cathodic flow and then a fall in both cups, though in neither to an extent to disconnect the current. The cathode cup became coated on the *outside* with a deposit of aluminium hydroxide and finally showed a static charge of sufficient intensity to give sparks when touched above and below the liquid surface. This is evidently a marked case of stenolysis. With the formation of the hydroxide the resistance rises markedly with consequent fall of current.

With 0.001 N alum solution, the solution fell at first in both cups and then began to rise, but while the anode cup slowly overflowed no rise took place in the cathode cup for six hours, after which it flowed so rapidly that in two and a half hours more the total flow exceeded that of the anode. Seventeen and eighteen are attempted duplicates of sixteen.

In several experiments not included in the table, the acidification of the cathode cup with dilute sulfuric acid, stopped the flow, while making it alkaline increased it. Acidification of the anode cup had the opposite result.

In the experiments with ferric chloride, uniform results are secured and only anodic flow is noted. Yet the flow *from* the cathode cup is so marked that to keep from disconnecting the current solution must be continually added. In Expt. 19, 220 cc. were added to the cathode while only 20 cc. passed into the anode cup. The iron deposited at the cathode was apparently pyrophoric. In Expt. 21, with only 90 m. amp. current, no flow occurs in either cup. In Expt. 22, while only 45 cc. overflow occurs in the anode cup, 280 cc. had to be added to the cathode.

Manganese chloride and magnesium chloride also show only negative flow, and *from* the cathode cup in excess of that *into* the anode cup. The results due to formation of oxides were variable and no definite figures are given.

In order to study these phenomena more closely, two pieces of apparatus[1] were prepared as illustrated in Fig. 2. The membranes were made of ordinary unglazed plates and were ground to a thickness of 2 mm. Each compartment was provided with an automatic overflow by tubes held in position by rubber tubing. The whole apparatus was placed in a trough through which tap water was continually running. The electrodes

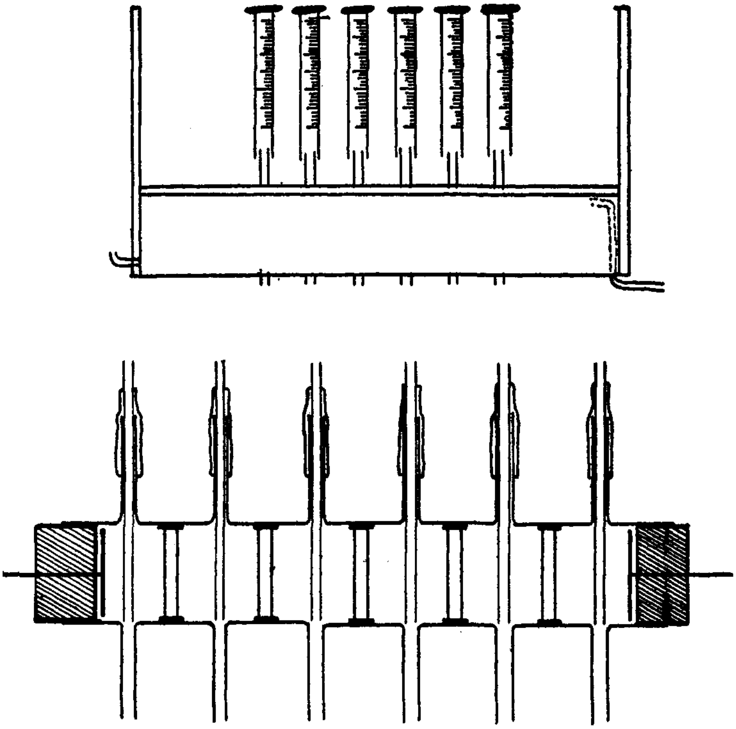

Fig 2.

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[1] After Reed, *Loc. cit.*

were either coiled platinum wires or platinum plates inserted in rubber stoppers. In running this apparatus the chief difficulty is caused by stenolytic deposits in the plates, the removal of which, with assured completeness, is nearly impossible. In detailing experiments, the compartments are numbered from the anode end.

One experiment, which could not be duplicated, has special interest. The apparatus was filled with a saturated alum solution and electrolysis begun with a current of 30 m. amp. and 120 volts. A miniature tidal wave moved from compartment one through two until six was reached, a small overflow taking place in each. The tide then turned, and starting from six, the wave flowed back, filling each partly emptied compartment, until "one" was again full. The wave then started on the reverse path, but the double turn had consumed about ten hours and, due to stenolytic deposit, the current had fallen to 5 m. amps. and the transfer of liquid was very slow. The experiment was discontinued and, when repeated, similar results were not obtained.

The results obtained with this apparatus verified in general those obtained in the tripartite cell. A careful study was made of the behavior of ferric chloride. Overflow took place as indicated in Table II, in four series of experiments. In Series 1, 2 and 3, the solution was ferric chloride of specific gravity 1.070 and in 4 the same solution diluted ten fold.

TABLE II.

Expt.	Time. Hours.	1. Cc.	2. Cc.	3. Cc.	4. Cc.	5. Cc.	6.	Current. M. a.
1	7	5.0	1	0.6	1.8	15.0	0	325
2	5$^1/_4$	9.0	0	0.4	1.3	7.0	0	325
3	7	6.0	0	0	0.8	20.0	0	325
4	5	10.0	1	2.0	1.5	16.0	0	150

The plate between compartments 5 and 6 showed granular nodules of metallic iron on the side toward the anode pole. There was also liberation of chlorine from compartments 5 and 6 as well as from 1. These results are clearly due to stenolytic decomposition. Considerable color change also accompanied the process of electrolysis as is to be expected, but apparently no connection exists between the color and iron content. No attempt was made to determine the relative quantities of ferrous and ferric iron. At the end of each run the contents of each compartment were withdrawn and added to the overflow, if any. The iron from compartments 5 and 6 was dissolved, except as noted in the table, and also added. The total quantity of iron in each compartment liquid was then determined, after reduction with stannous chloride, by titration with permanganate. The results are indicated in Table III, calculated per cc. of solution. The value of the original solution in iron is 0.03498 gram per cc. for 1, 2 and 3 and 0.003498 for No. 4.

Comp.	Run 1.	Run 2.	Run 3.	Run 4.
1	0.0187488	0.016202	0.0169632	0.0024552
2	0.031649	0.045756	0.0308016	0.0035712
3	0.0316154	0.0310248	0.0319396	0.0036828
4	0.0305226	0.0325314	0.0319396	0.003906
5	0.023591[1]	0.0275652	0.0325872	0.0040176
6	0.040979	0.0479322	0.0465372	0.0074772

A set of readings of galvanometer deflections produced when the instrument was connected with wires leading from opposite sides of each of the plates was also taken, for experiment marked above, Run 1, but aside from indicating that the opposite sides of each plate had different potentials at the end of the experiment, no value is to be attached to the same and the data obtained are omitted.

Summary and Conclusions.

The following facts are illustrated by the foregoing experiments:

1. Endosmose is capable of producing flow of electrolytes in the direction of the current, in the opposite direction and in both directions at the same time.

2. In certain cases the flow of electrolyte is away from both electrodes and also may be more rapid away from one than to the other; in either case the content of the middle compartment of a tripartite cell is increased.

3. In the six-compartment cell the change in volume is not confined to the anode and cathode compartments, but varies in the other compartments in an apparently erratic manner.

4. The quantity of water transported is clearly affected by the dilution of the electrolyte.

5. When clay membranes are used, the endosmose is complicated by stenolysis.

Far-reaching conclusions of a theoretical nature are not to be drawn from the meager data submitted in this paper and, since there seems to be a more or less intimate connection between these observations and the questions of molecular and ionic hydration in solution, negative osmosis and migration ratios, as well as the question of endosmose itself, the work will be continued in the hope that more accurate and valuable results may be obtained.

In the meantime it does not appear clear to the writers how electrical charges upon the plates induced by varying degrees of ion adsorption or otherwise accounts for the *traversal* of the plates by water.

UNIVERSITY OF WASHINGTON.
SEATTLE, WASH.

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[1] Iron on electrode not dissolved.