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On the Cause of the Influence of Ions on the Rate of Diffusion of Water Through Collodion Membranes. I

Jacques Loeb

ON THE CAUSE OF THE INFLUENCE OF IONS ON THE RATE OF DIFFUSION OF WATER THROUGH COLLODION MEMBRANES. I.

BY JACQUES LOEB.

(*From the Laboratories of The Rockefeller Institute for Medical Research.*)

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I.

When we separate a watery solution from pure water by a collodion membrane water will diffuse into the solution and solute will diffuse out. We will call this diffusion free osmosis to distinguish it from osmosis due to an outside force; *e.g.*, electrical endosmose. The free diffusion of solute into pure water occurs at a rate proportional to the concentration of the solution[1] (with the possible exception of very low or very high concentrations) and need not occupy our interest in this paper. The diffusion of water into the solution has a different character when the solute is a non-electrolyte than when it is an electrolyte. When the solute is a non-electrolyte, the initial rate of diffusion of water into the solution is (within the limit of moderate concentrations) practically a linear function of the concentration of the solute, as it should be according to the law of van't Hoff. When the solution is an electrolyte, anomalies occur which are a characteristic function of the oppositely charged ions of the electrolyte and these anomalies were described for collodion membranes in a series of papers which have appeared recently.[1, 2, 3, 4] The anomalies seem to occur only in the lower concentrations of electrolytes, below M/8 or less; above these values the osmosis seems to occur in a way similar to that observed in solutions of non-electrolytes, though this point

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[1] Loeb, J., *J. Gen. Physiol.*, 1918–19, i, 717.
[2] Loeb, J., *J. Gen. Physiol.*, 1919–20, ii, 173.
[3] Loeb, J., *J. Gen. Physiol.*, 1919–20, ii, 255.
[4] Loeb, J., *Proc. Nat. Acad. Sc.*, 1919, v, 440.

needs further investigation. The present paper deals only with concentrations inside the anomalous range.

It was shown in the preceding papers that all the anomalies can be adequately described if we assume that the water in diffusing through the pores or interstices of the membrane is either positively or negatively charged and that the ions of the solution accelerate or retard the diffusion of the electrified water by their electrical charges. When we use collodion membranes which have been bathed for a short time in a 1 per cent solution of a protein (gelatin, casein, egg albumin, edestin, etc.) the effects of the two oppositely charged ions can be expressed in the following terms.

1. When we separate a neutral, alkaline, or faintly acid solution of an electrolyte with a monovalent or bivalent cation by a collodion membrane (treated with protein) from pure water, the latter diffuses into the solution as if its particles were positively charged and as if they were attracted by the anion and repelled by the cation of the solution with a force increasing with the valency of the ion and with a second constitutional quantity of the ion which we designated arbitrarily as the radius of the ion, but which needs another definition so as to include the strong effects of such monovalent ions as; *e.g.*, the aluminate or oleate anion.

2. When we separate solutions of electrolytes with a concentration of hydrogen ions of about 10^{-4} N or above, or with trivalent or tetravalent cations in sufficient concentration by a collodion membrane from pure water, water diffuses into the solution as if its particles were negatively charged and attracted by the cation and repelled by the anion of the electrolyte with a force increasing with the valency of the ion and with a second constitutional quantity of the ions still to be defined.

When we use collodion membranes *not* treated with protein one rule suffices to express all the phenomena; namely, water diffuses through the collodion membrane into the solution as if its particles were positively charged and as if it were attracted by the anion and repelled by the cation of the solution with a force increasing with the valency and a second quantity of the ion which is still to be defined.

What we designated in this statement as electrified particles of water is the watery phase or the mobile stratum of the electrical double layer (in the sense of Helmholtz) formed at the boundary of membrane and water or solution. The other stratum of this double layer, the membrane phase, must be considered as immobile in the experiments on osmosis. The influence of electrolytes on the double layer at the boundary of water and membrane will be assumed to be responsible for the phenomena of abnormal osmosis.

It follows from our previous publications that we must discriminate between two effects of electrolytes on the double layer. The one effect is the influence of certain ions on the sign of the electrification of the water or the solution phase of the double layer. Water in contact with a membrane is generally positively charged and only in the case of certain types of membranes, *e.g.* collodion membranes treated with proteins, can the sign of the charge be reversed by two kinds of ions; namely (*a*) hydrogen ions, or (*b*) simple (*i.e.* non-complex) cations whose valency is three or more.[3] All electrolytes which can lower the hydrogen ion concentration by a chemical action, *e.g.* alkalies, can restore the original positive electrification of the water stratum of the double layer. Some authors have drawn from this the conclusion that the OH ions act as directly as the H ions upon the sign of the electrification of the membrane (*e.g.* by transferring their negative charge to it). It seems to the writer that it is more in harmony with the facts to assume that the alkalies act merely by the diminution of the hydrogen ion concentration through neutralization of acid. The special effect of the two classes of positive ions—H ions and simple cations with a valency of three or above—on the sign of the electrification of the water stratum of the double layer will be discussed in another paper.

In addition to this *specific* influence of certain ions on the sign of the electrification of water at the boundary of the membrane there exists a second, more *general* effect of electrolytes on the *rate* of diffusion of water which was described in terms of electrostatic attraction and repulsion of the electrified stratum of water by the ions of the electrolyte in the previous papers, since this way of describing the results had the advantage of simplifying the presentation of the facts. It was not, however, intended to serve as a theoretical basis for the explanation of the phenomena of abnormal osmosis. For this latter purpose we must express the facts in the following form. When we separate a solution of an electrolyte from pure water by a collodion membrane the oppositely charged ions of the electrolyte influence the initial velocity of diffusion of water through the membrane into the solution in an opposite sense; the ion with the opposite sign of charge from that of the electrified water (or the watery phase of the double layer) increasing the velocity, the ion with the same sign of charge as the watery phase of the double layer diminishing the velocity. The accelerating and retarding effects of ions were found to increase with the valency and with that other constitutional quantity which was designated as the radius of the ion but which requires further definition.

In passing we may remark that the relative retarding and accelerating effect of oppositely charged ions of an electrolyte on the rate of osmosis of water into the solution was not found to be the same for all concentrations of a solution.[2] At the lowest concentrations the effect of that ion usually (and possibly always) prevails which has the opposite sign of charge from that of the watery phase of the double layer, at a higher concentration the effect of that ion prevails which has the same sign of charge as the watery phase. Hence in the lower concentrations the accelerating effect of the electrolyte prevails over the retarding effect and for the higher concentrations the reverse is true. For a number of solutions, *e.g.* salts of monovalent cations, the turning point lies at a concentration of about M/256. The anomalous osmosis ceases at that concentration of the solution where the retarding and accelerating effects of the oppositely charged ions become equal. From then on the solutions of electrolytes seem to behave like those of non-electrolytes. This group of facts has been described in a preceding paper[2] and will not be discussed here.

In our experiments on free osmosis the collodion membrane was bounded on one side by pure water and on the other by the solution. When both sides of the membrane are bounded by identical solutions the rate of diffusion of water and of electrolyte in opposite directions is equal, and no change occurs. When, however, an external difference of potential is produced on the two sides of the membrane, a transport of water or of liquid occurs through the membrane towards that electrode whose sign of charge is the opposite of that of the watery phase of the double layer in the pores or interstices of the membrane. This is the well known phenomenon of electrical endosmose which was first investigated experimentally by Quincke and Wiedemann and which was explained mathematically by Helmholtz. The earlier workers found that the watery phase of the double layer was generally positively electrified. Perrin[5] made the remarkable discovery that in the case of certain diaphragms, such as powdered charcoal, carborundum, gelatin, etc., the sign of charge can be reversed at will, chiefly with the aid of acid and of alkali. In a slightly acid medium the liquid moves to the anode, in a slightly alkaline medium it moves to the cathode. This has been confirmed by every observer, and his deductions have been generally accepted.

It has been suggested by Girard, Bernstein, Bartell and Hocker, and Freundlich[6] that the cases of so called negative osmosis where liquid diffuses from acid into pure water instead of in the opposite direction might be in reality manifestations of electrical endosmose. The only difference between the case of free osmosis and electrical endosmose being, according to these authors, the source of the potential difference, which is an external one in the case of electrical endosmose and an internal one—*e.g.* a diffusion or a boundary potential—in the case of free osmosis. But this is thus far merely an hypothesis which is not yet adequately supported by facts.

The possibility of correlating the phenomena of free and electrical osmosis meets at present with a difficulty. Our experiments on collodion membranes leave no doubt that in the case of *free osmosis* the influence of electrolytes on the velocity of diffusion of water from pure solvent to solution through the collodion membrane is an addi-

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[5] Perrin, J., *J. chim. physique*, 1904, ii, 601; 1905, iii, 50.

[6] Girard, P., *Compt. rend. Acad.*, 1908, cxlvi, 927; 1909, cxlviii, 1047, 1186; 1910, cl, 1446; 1911, cliii, 401; La pression osmotique et le mécanisme de l'osmose, Publications de la Société de Chimie-physique, Paris, 1912. Bernstein, J., Elektrobiologie, Braunschweig, 1912. Bartell, F. E., *J. Am. Chem. Soc.*, 1914, xxxvi, 646. Bartell, F. E., and Hocker, C. D., *J. Am. Chem. Soc.*, 1916, xxxviii, 1029, 1036. Freundlich, H., *Kolloid-Z.*, 1916, xviii, 11.

tive effect of the two oppositely charged ions. Perrin,[5] however, states that in the case of electrical endosmose only one of the oppositely charged ions of an electrolyte influences the transport of liquid through the membrane; namely, the one with the same sign of charge as that of the water (or with the opposite sign of charge from that of the membrane).

II.

Perrin's[5,7] view of the influence of electrolytes on the amount of liquid transported in electrical endosmose rests on the assumption that the sign of the electrification of the double layer is primarily determined by the H and OH ions. He assumes that the positive electrification of a membrane bounded by liquid containing a monovalent acid is due to the adsorption of a layer of hydrogen ions by the membrane. This membrane layer of adsorbed hydrogen ions is the fixed stratum of the double layer and the next stratum of the liquid—the watery phase—contains a corresponding excess of negative ions. The stratum of negative ions is sufficiently far removed from the fixed layer so as to be able to undergo the tangential displacement on which the phenomena of electrical osmosis are supposed to depend.

Perrin assumes that the negative electrification of a membrane under the influence of a monovalent base is due to the OH ions situated in that stratum of the liquid which is in immediate contact with the membrane, while a corresponding excess of positive ions exists in the opposite stratum of liquid (the watery phase, in our terminology). When another electrolyte is added to a weak acid or weak alkaline solution the charge of the membrane is, according to Perrin, *influenced only by one of the two ions* of the electrolyte added; namely, the one with the opposite sign of charge from that of the membrane.

> "When a liquid electrifies a membrane with a certain sign the addition to this liquid of a polyvalent ion of the same sign does not increase the electrification, while the addition of a polyvalent ion of the opposite sign diminishes this electrification considerably. The influence of bivalent ions is inferior to that of trivalent ions and that of trivalent ions is inferior to that of tetravalent ions. In the case of the ions with high valencies the diminution of the charge can result in the complete reversal of the sign of the charge."

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[7] Perrin, J., Notice sur les titres et travaux scientifiques de M. Jean Perrin, Paris, 1918, 36–37.

His theory which has revolutionized colloid chemistry is expressed in the following statement.

> "The primary factor of this electrification is always the action of the hydrogen or the hydroxyl ions, which are pressed against the membrane in the same way, no matter whether polyvalent ions are present or absent. But if polyvalent ions of the opposite sign are present they are attracted towards the membrane. To be more precise, let us suppose a liquid with a monovalent acid; hydrogen ions cover the membrane with a positive charge according to the degree of acidity. Behind them, at a distance which results from an equilibrium between the osmotic and the electric forces are found the monovalent negative ions forming the second stratum of the double layer. If we now add negative polyvalent ions, *e.g.* $Fe(CN)_6$, the osmotic forces acting on the tetravalent $Fe(CN)_6$ remain of the same order as before while the electric force is multiplied by four; the density of the double layer will therefore diminish and as a consequence the P.D. of contact and the amount of electrical endosmose. It only remains to explain in a precise manner reversion of the sign of charge due to the presence of the necessary amount of $Fe(CN)_6$ ions."[7]

Perrin's view on the effect of electrolytes on the double layer does not agree with our experiments with collodion membranes which show unequivocally that the influence of electrolytes on the rate of diffusion of water in the case of free osmosis is an additive effect of the two oppositely charged ions of an electrolyte, and not the effect of only one of the two ions.

If we assume that the influence of ions is the same in the case of free osmosis and in electrical endosmose an increase in the valency of the anion, according to Perrin, should not increase the rate of diffusion of positively electrified water in free osmosis, since in this case the membrane has the same sign of charge as the anion. A glance at Fig. 1 shows, however, that when we separate a solution from pure water by a collodion membrane the initial rate of diffusion of water into the solution increases in the lower concentrations of different potassium salts with increasing valency of the anion when the water is positively charged. In this case a watery solution of one of these salts was put into a collodion bag connected with a manometer and the bag was put into a beaker containing distilled water. The solutions of NaCl, $CaCl_2$, Na_2SO_4, and $Na_4Fe(CN)_6$ were rendered alkaline by dissolving the neutral salt in M/1,024 or M/1,000 KOH. The abscissæ are the logarithms of the concentration and the ordinates are the rise in the level of solution in the manometer after 20 minutes.

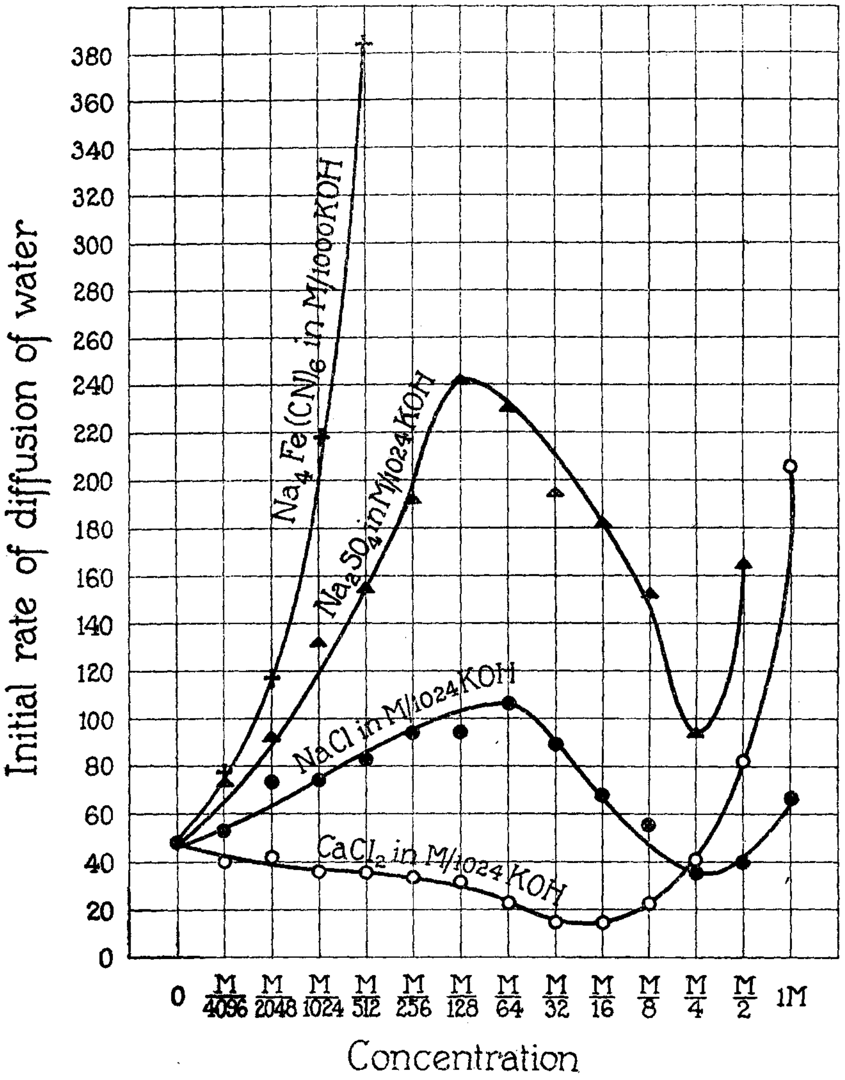

FIG. 1. Initial rate of diffusion of pure water through a collodion membrane into a solution containing an electrolyte. Abscissæ are the logarithms of concentration, ordinates rise of level of water in manometer connected with solution after 20 minutes. Solutions of salts were all rendered alkaline by enough KOH to make the solution about 10^{-3}N in regard to KOH. The water was positively electrified. The curves show that the initial rate of diffusion of water into the solution increases with increasing valency of the anion of the electrolyte, though the membrane has the same sign of charge as the anion. The cations have a depressing effect, increasing also with the valency. The drop in the curve beyond a concentration of M/128 or M/64 is due to the fact that beyond this concentration the effect of the cation begins to prevail over that of the anion, until at a concentration of M/8 or M/4 the gas pressure effect of the electrolyte begins to prevail over the electrical effect.[2, 3, 8]

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[8] Loeb, J., *J. Gen. Physiol.*, 1919–20, ii, 273.

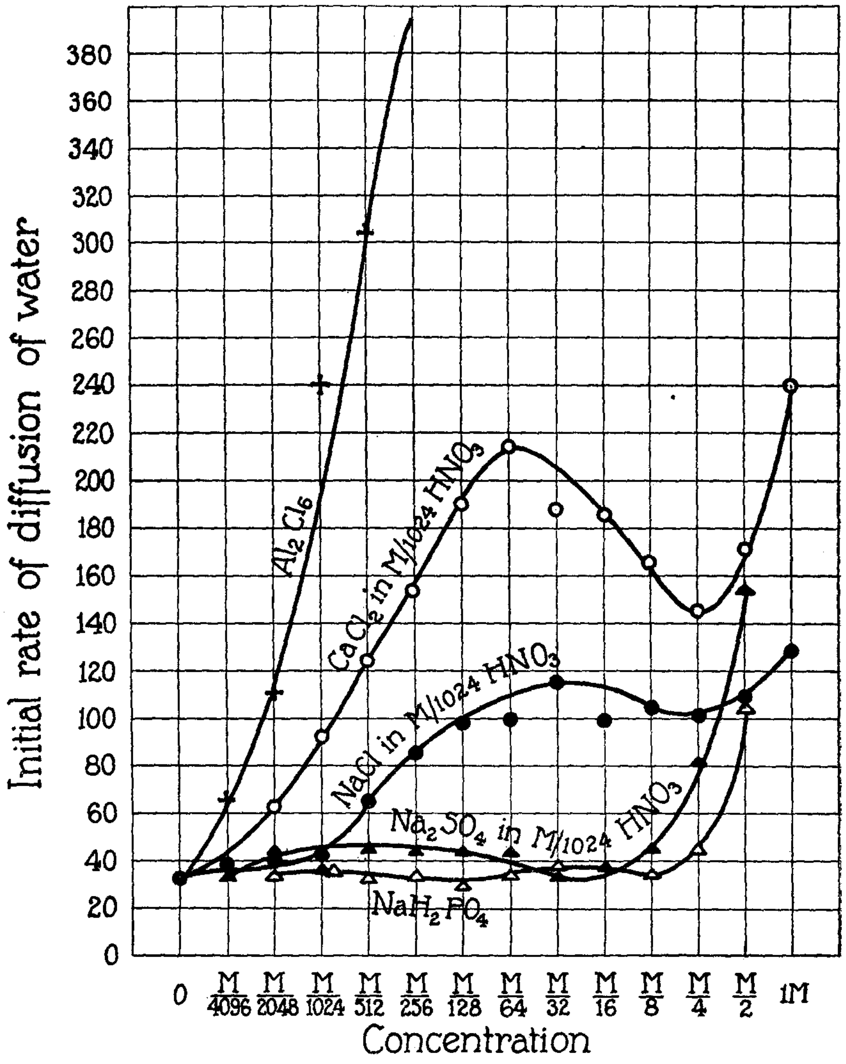

FIG. 2. Initial rate of diffusion of water from pure water through collodion membrane to solution of electrolytes rendered about 10^{-3} N acid through addition of HNO_3. Though the water is negatively (and the membrane positively) electrified the initial rate of diffusion of water into the solution increases with increasing valency of the cation and diminishes with increasing valency of the anion. The drop in the curves in concentrations beyond M/64 or M/32 is due to the fact that in concentrations higher than these the depressing effect of the anion prevails over the opposite effect of the cation. For explanation of second rise of curve see legend of Fig. 1.

Moreover, according to Perrin, an increase in the valency of the cation should not increase the rate of diffusion of water from pure water into a slightly acid solution of salts, yet a glance at Fig. 2 shows that the initial rate of diffusion of water through a collodion membrane into a slightly acid solution increases considerably with the increase in the valency of the cation of the salt added.

In former papers,[1, 2, 3] further proof of these statements can be found and in addition the writer has shown that in neutral solutions (where the water diffusing through the collodion membrane is positively electrified) the rate of diffusion of water into the solution increases with the valency of the anion of the electrolyte in the solution.

This discrepancy between the actual observations concerning the influence of electrolytes on the rate of diffusion of water through a collodion membrane in free osmosis on the one hand, and the theory of Perrin concerning the influence of electrolytes on the rate of diffusion of liquid in the case of electrical endosmose on the other indicates that either the influence of electrolytes is not the same in both cases or that the theory of Perrin is not the correct expression of the facts in the case of electrical endosmose, at least for collodion membranes. It seemed, therefore, necessary to test the influence of electrolytes on the rate of transport of water through collodion membranes by electrical endosmose as a first step towards a theory of the influence of electrolytes on free osmosis.

III.

In the experiments on electrical endosmose we used the collodion bags which served for the experiments on free osmosis. These collodion bags were cast inside an Erlenmeyer flask of a volume of about 50 cc. The collodion flask was closed with a rubber stopper which was perforated by a glass rod serving as a manometer. The bag was filled at the beginning of the experiment with the solution whose influence on the osmotic transport was to be investigated and was put into a beaker containing the identical solution. The bag was then so adjusted that the upper level of the rubber stopper was at the surface of the liquid in the beaker and that a column of liquid of about 30 mm. in the manometer was above the level of the liquid in the beaker. The manometer was a glass tube with a bore of about 2 mm. in diameter. One platinum electrode was put into this glass tube and one into the beaker. The distance between the electrodes was approximately the same in all experiments; namely, 6.7 cm. The electrode in the manometer was usually that pole towards which the transport of liquid occurred so that the rise of level in the manometer could serve as a measure for the volume of liquid transported. In this case the transport occurred against a hydrostatic pressure and it was necessary to compare the rise of level at about the same pressure head in different experiments.

The volume of liquid transported is a function of the external potential difference which was either 50 or 40 volts in our experiments. It turned out that in these experiments a disturbing variable entered inasmuch as with constant voltage the intensity of the current rose slowly and with the rise in intensity the amount of liquid flowing to one of the poles also rose gradually. The writer is inclined to interpret this gradual increase in intensity of current as being due to a gradual increase in the number of interstices through which the current can flow; and this means also an increase in the number of capillary spaces through which electrical endosmose can occur. Hence, for measurements of the transport of liquid only those changes in level could be used which occurred after the current had become approximately constant. In order to accelerate this process at the beginning of each experiment, a P.D. of 200 volts was used for 2 minutes or less until the intensity of the current was sufficiently high (above 1.0 or 2.0 milliamperes), and then the P.D. was lowered to the 40 or 50 volts desired. The voltage was then kept constant. As a measure of the effect of an electrolyte on the volume of liquid transported we used the rise in the level of liquid in the glass tube during the first 15 minutes after the current had become fairly constant. The following records will illustrate the way our figures were obtained. We omit the preliminary short treatment of the solution with a current of 200 volts, and give only the records for the 50 volt effects. The solutions used were M/512 KCl, M/512 K_2SO_4, M/512 and M/1,024 $K_4Fe(CN)_6$, M/512 $CaCl_2$, and M/512 $BaCl_2$. The solutions were almost neutral but slightly on the acid side of neutrality, the pH being about 6.2, and the transport of liquid occurred towards the cathode which was put into the glass tube. Table I gives the time in minutes, the in-

TABLE I.

Transport of Liquid in Electrical Endosmose in Approximately Neutral Solutions, pH = 6.2. 50 Volts. Cathode in Capillary.

Solution.	Time.	Milliampere.	Rise of level of liquid in manometer.
	min.		*mm.*
M/512 KCl	0	1.3	+1.0
	5	1.7	+2.0
	10	1.9	+2.5
	15	2.1	+3.5
	20	2.15	+5.0
	25	2.18	+6.0
	30	2.18	+7.0
M/512 K_2SO_4	0	1.0	+1.0
	5	1.4	+1.5
	10	1.9	+2.0
	15	2.4	+4.0
	20	2.3	+6.0
	25	2.3	+8.0
	30	2.25	+10.5
	35	2.25	+12.0
	40	2.26	+14.0
	45	2.2	+16.0
M/1,024 $K_4Fe(CN)_6$	0	1.0	+1.5
	5	1.45	+7.5
	10	2.0	+16.0
	15	2.35	+26.0
	20	2.45	+36.0
	25	2.45	+43.0
	30	2.6	+48.0
	35	2.7	+54.0
	40	2.76	+60.0
M/512 $K_4Fe(CN)_6$	0	1.4	+1.0
	5	2.4	+6.5
	10	3.4	+14.0
	15	3.85	+25.0
	20	4.0	+33.0
	25	4.2	+39.0
	30	4.2	+45.0
	35	4.2	+52.0
	40	4.4	+59.0

TABLE I—*Concluded.*

Solution.	Time.	Milliampere.	Rise of level of liquid in manometer.
	min.		*mm.*
	0	1.8	+3.0
	5	1.8	+3.0
	10	1.7	+3.0
M/512 $CaCl_2$	15	1.55	+2.0
	20	1.5	+1.5
	25	1.5	0
	30	1.5	−1.0
	0	2.3	0
	5	1.6	−1.5
	10	1.2	−3.0
M/512 $BaCl_2$	15	1.15	−4.5
	20	1.15	−5.5
	25	1.1	−6.5
	30	1.15	−7.5

tensity of the current in milliamperes, and the rise in the level of the liquid in the glass tube.

In the case of M/512 KCl the current became approximately constant after 15 minutes (2.1 to 2.2 milliamperes) and the rise in the level of liquid in the glass tube between 15 and 30 minutes, *i.e.* 7 − 3.5 mm. = 3.5 mm., was used as a measure for the relative influence of M/512 KCl (approximately neutral) upon the rate of endosmotic transport of liquid.

The figures for transport during 15 minutes were selected as follows: for M/512 $K_2SO_4 = 10.5 - 4 = 6.5$; for M/512 $K_4Fe(CN)_6 = 45 - 25 = 20$; etc.

Since in the case of M/512 $K_4Fe(CN)_6$ the intensity of the current was greater than in the experiments with KCl or K_2SO_4, an experiment with M/1,024 $K_4Fe(CN)_6$ is added in the table. It gave 48 − 26 = 22 mm. as the transport number though the intensity of current was almost as low as in the case of M/512 K_2SO_4 or M/512 KCl.

Experiments with neutral solutions of salts with bivalent cation, like $CaCl_2$, $BaCl_2$, gave no transport with electrical endosmose even with 100 volts and an intensity of current of 4.8 milliamperes. Table II gives the transport numbers for various approximately neutral solutions.

Table II shows that the rate of endosmotic transport increases in almost neutral solutions of salts with increasing valency of the anion and diminishes with increasing valency of the cation. Electrolytes influence, therefore, the osmotic transport in exactly the same sense in free and in electrical osmosis. This influence is in both cases an additive effect of the oppositely charged ions of the electrolyte. In the presence of the salt mentioned the watery phase of the double layer is positively charged. The slight fall of level in the case of $CaCl_2$ and of $BaCl_2$ must be ascribed to the pressure head of about 30 mm. solution existing at the beginning of the experiment; since the same or a slightly more rapid fall of level occurs if no current passes through the liquid.

TABLE II.

Relative Transport of Liquid by Electrical Endosmose in Approximately Neutral Solutions, pH = 6.2. 50 Volts.

	Rise of level of liquid in manometer in 15 min.
	mm.
M/512 KCl	3.5
M/512 K_2SO_4	6.5
M/512 $K_4Fe(CN)_6$	20.0
M/1,024 $K_4Fe(CN)_6$	22.0
M/512 $CaCl_2$	0
M/512 $BaCl_2$	0

We will now show that the statements made for neutral solutions are also true for alkaline solutions. In alkaline solutions the watery phase of the double layer is also positively charged and the liquid is transported to the cathode as in the case of neutral solutions. The cathode was put into the glass tube and the rise of level in the glass tube during the first 15 minutes after the current had become fairly constant was used as a measure for the transport. The solutions were brought to the same alkalinity as that of M/1,000 KOH and the pH varied between 10.9 and 11.0 (Table III).

The result is the same as before: the rate of endosmotic transport increases in alkaline solutions with increasing valency of the anion and diminishes with increasing valency of the cation. Electrolytes influence, therefore, the transport of liquid in alkaline solution in the same sense in electrical endosmose as in free osmosis. This influence is in both cases an additive effect of the oppositely charged ions of the electrolyte. In the alkaline solutions the watery phase of the double layer is positively charged as it is in neutral solutions. If Perrin's rule applied to these experiments, the increasing valency of the anion should have had no effect.

Table III contains also the transport numbers of solutions of Na acetate, Na aluminate, and K oleate which are all higher than those of NaCl, although the anion is monovalent in each case. Solutions of these salts also attract water more powerfully than solutions of NaCl in the case of free osmosis and the influence of these salts in electrical endosmose is parallel to their influence in free osmosis. These salts illustrate the statement that in addition to the valency another constitutional quantity of the ions determines their influence on the transport of liquid in free and electrical endosmose.

TABLE III.

Transport of Liquid by Electrical Endosmose to the Cathode in Alkaline Solutions, pH = 10.9 to 11.0. 40 Volts.

	Milliampere.	Rise of level of liquid in manometer in 15 min.
		mm.
M/512 NaCl	1.1	3.5
M/512 Na_2SO_4	1.6	10.0
M/512 $Na_4Fe(CN)_6$	2.1	22.0
M/512 $CaCl_2$	1.2	0
M/512 $BaCl_2$	1.15	0
M/512 Na acetate	1.35	7.0
M/512 $NaAlO_2$	1.15	7.0
M/512 K oleate (pH = 9.4)	1.15	22.5

We finally investigated the electrical transport of liquid in acid solutions. The salt solutions were made N/1,000 acid by the addition of HNO_3; the pH was in all cases exactly 3.0. Table IV gives the results. The anode was in the glass tube. In this case it was necessary to use membranes which had received a gelatin treatment.

If Perrin's rule applied to these cases, the increasing valency of the cation should not have influenced the result in these acid solutions.

We notice, however, that the rate of endosmotic transport to the anode increases in acid solutions with the increase in the valency of the cation and diminishes with the increase in the valency of the anion. Electrolytes influence, therefore, the transport of liquid in acid solutions in the same sense in the case of free and of electrical osmosis. The influence is in both cases an additive effect of the oppositely charged ions of the electrolyte. The watery phase of the electrical double layer is negatively charged in acid solutions of the hydrogen ion concentration used in this case; namely, 10^{-3} N.

TABLE IV.

Relative Transport of Liquid in Electrical Endosmose to the Anode in Acid Solutions, pH = 3.0. 40 Volts.

	Milliampere.	Rise of level of liquid in manometer in 15 min.
		mm.
M/512 NaCl	3.7	5.5
M/512 $CaCl_2$	2.6	11.5
M/512 $BaCl_2$	4.0	13.0
M/512 $CeCl_3$	3.5	16.5
M/512 $ThCl_4$	3.8	18.0
M/512 Na_2SO_4	3.4	0
M/512 Na_2 oxalate	3.2	0
M/512 NaH_2PO_4	1.8	2.0

If we summarize all three cases we may state that in both free and electrical osmosis, the transport of liquid is accelerated by that ion of an electrolyte which has the opposite sign of charge as the watery phase of the double layer (or the same sign of charge as the collodion membrane) and retarded by that ion which has the same sign of charge as the watery phase of the double layer (or the opposite sign of charge as the collodion membrane); and that both the accelerating and the retarding effect of ions increase with their valency and a second constitutional quantity of the ion which is still to be defined and for which the high transport number of several salts in Table III may serve as an example.

The writer has made a number of experiments on electrical endosmose with different concentrations of electrolytes. The curves representing this influence on the transport of liquid in electrical endosmose through collodion membranes seem to be similar to the curves, representing the influence of different concentrations of the same electrolytes on free osmosis, which were published in a preceding paper.[2]

In experiments with concentrations of electrolytes above M/512 or M/256 it is wiser to work with a lower voltage to avoid the excessive development of gas bubbles. Table V gives the numbers for the rise of liquid in the manometer for different concentrations of $K_4Fe(CN)_6$ during 15 minutes after the intensity of the current had become fairly constant. The P.D. applied was 20 volts.

TABLE V.

Influence of Concentration on Transport of Liquid by Electrical Endosmose to Cathode. 20 Volts.

	Milliampere.	Rise of level of liquid in manometer in 15 min.
		mm.
M/2,048 $K_4Fe(CN)_6$	0.1	1.5
M/1,024 $K_4Fe(CN)_6$	0.5	9.0
M/512 $K_4Fe(CN)_6$	0.9	10.5
M/256 $K_4Fe(CN)_6$	1.2	6.0
M/128 $K_4Fe(CN)_6$	1.8	3.0
M/64 $K_4Fe(CN)_6$	3.0	0

The maximum of transport of liquid in electrical endosmose was reached at a concentration of about M/512 $K_4Fe(CN)_6$ and then the electro-endosmotic transport fell rapidly to zero with increasing concentration, although the intensity of the current increased with concentration. The drop in the curves representing the initial rate of diffusion of water from pure water to solution through collodion membranes in the case of free osmosis is therefore paralleled in the case of electrical endosmose (Table V). A fuller account of these results will shortly be published.

Theoretical Remarks.

According to the formula of Helmholtz for the transport of liquid by a current through capillaries, modified by Perrin,[9] we have

$$v = \frac{q \cdot \epsilon \cdot E \cdot D}{4\,\pi .\,\eta .\,l}$$

where v is the quantity of liquid carried electro-osmotically, ϵ is the potential difference between the two strata of the double layer, E the external electromotive force, D the dielectric constant of the medium, η the coefficient of internal friction, and l the distance of the external electrodes. Since in our experiments all quantities occurring in this formula except v and ϵ were kept approximately constant, we must attribute the influence of electrolytes on the quantity of transport v to an influence of the ions on ϵ. We must therefore conclude that the influence of electrolytes on the rate of free osmosis is due to the effect of the ions of the electrolyte on the quantity of charge on the unit area of the Helmholtzian double layer. Our experiments on both free and electrical osmosis show that this influence is an additive effect of the two oppositely charged ions of the electrolyte at least in the case of collodion membranes. Since the quantity of transport v increases with the value of ϵ we must further conclude that the ion with the same sign of charge as the watery phase of the double layer diminishes the value of ϵ since this ion diminishes transport in both free and in electrical osmosis; while the ion with the opposite sign of charge as this watery phase increases the value of ϵ in both forms of osmosis. Both effects increase with the valency and with the second constitutional quantity of the ion (Table III). The total effect of the two oppositely charged ions of an electrolyte on the rate of diffusion of water through a collodion membrane is therefore the difference between the opposite effects of its ions on the value of ϵ. These statements give the theoretical basis of what we called in our former papers the apparent electrostatic action of the ions on the rate of diffusion of the electrified particles of water from pure water into solution through a collodion membrane (free osmosis).

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[9] Freundlich, H., Kapillarchemie, Leipsic, 1909, 226.

Positively charged particles of water in the pores or interstices of the membrane will be driven to that side of the membrane which is more negatively charged. Since this is usually the solution side, water will be driven from the side of pure water into the solution.

When the collodion membrane has been treated with a protein, it is also generally negatively charged when bounded by water except when the solution contains hydrogen ions or simple trivalent or tetravalent cations beyond a certain concentration (which for H is 10^{-4} N); in this case the membrane is positively and the watery phase is negatively charged. If we add in this case an electrolyte to the water, the charge on the membrane is increased by the cations and diminished by the anions of the electrolyte. Whenever the positive charge on the solution side of the membrane is greater than on the opposite side, the negatively charged particles of water will diffuse from the side of pure water to the side of solution.

When the charge on the solution side of the membrane is diminished by the electrolyte so that the charge is smaller than on the side of pure water, the liquid will flow through the membrane from solution side to the side of pure water (negative osmosis).

Our experiments were made with collodion membranes only and it is possible that Perrin's statement holds for other types of membranes. It seems, however, that in the case of the influence of electrolytes on the value of ϵ at the boundary of oil drops and water the effect is also an additive one of the oppositely charged ions. Powis[10] has measured this value from the velocity of the motion of oil drops through solutions on the basis of the Helmholtz-Perrin formula for five electrolytes, KCl, $BaCl_2$, $AlCl_3$, $ThCl_4$, and $K_4Fe(CN)_6$. The oil particles are negatively charged and their charge is increased more by $K_4Fe(CN)_6$ than by KCl. The charge is diminished with the increasing valency of the cation. This indicates that the influence of electrolytes on the value of the potential difference of the double layer is in this case also an additive effect of the two kinds of ions.

We have stated that in the case of free osmosis the rate of diffusion of water from pure solvent to solution through a collodion membrane increases at first with increasing concentration, reaches a maximum

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[10] Powis, F., *Z. physik. Chem.*, 1915, lxxxix, 91.

(which for many electrolytes lies at a concentration of about M/256) and then drops again with a further increase in concentration. It seems from the writer's experiments that the same phenomenon occurs in the case of electrical endosmose through collodion membranes and that the turning point lies near M/512. Powis reports a similar effect of concentration in his observation on the motion of oil drops in an electrical field, and recently published experiments of Kruyt[11] on "current potentials" demonstrate the same phenomenon.

It seems to follow from this that the density of the electrical double layer at the boundary of watery phase and membrane increases at first with increasing concentration of an electrolyte up to a certain point which for a number of electrolytes seems to lie at about M/512. If the concentration of the electrolyte rises beyond this point, the density of the charge on the double layer diminishes rapidly with a further increase in the concentration of the electrolyte.

SUMMARY.

1. In three previous publications it had been shown that electrolytes influence the rate of diffusion of pure water through a collodion membrane into a solution in three different ways, which can be understood on the assumption of an electrification of the water or the watery phase at the boundary of the membrane; namely,

(*a*) While the watery phase in contact with collodion is generally positively electrified, it happens that, when the membrane has received a treatment with a protein, the presence of hydrogen ions and of simple cations with a valency of three or above (beyond a certain concentration) causes the watery phase of the double layer at the boundary of membrane and solution to be negatively charged.

(*b*) When pure water is separated from a solution by a collodion membrane, the initial rate of diffusion of water into a solution is accelerated by the ion with the opposite sign of charge and retarded by the ion with the same sign of charge as that of the water, both effects increasing with the valency of the ion and a second constitutional quantity of the ion which is still to be defined.

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[11] Kruyt, H. R., *Kolloid-Z.*, 1918, xxii, 81.

(*c*) The relative influence of the oppositely charged ions, mentioned in (*b*), is not the same for all concentrations of electrolytes. For lower concentrations the influence of that ion usually prevails which has the opposite sign of charge from that of the watery phase of the double layer; while in higher concentrations the influence of that ion begins to prevail which has the same sign of charge as that of the watery phase of the double layer. For a number of solutions the turning point lies at a molecular concentration of about M/256 or M/512. In concentrations of M/8 or above the influence of the electrical charges of ions mentioned in (*b*) or (*c*) seems to become less noticeable or to disappear entirely.

2. It is shown in this paper that in electrical endosmose through a collodion membrane the influence of electrolytes on the rate of transport of liquids is the same as in free osmosis. Since the influence of electrolytes on the rate of transport in electrical endosmose must be ascribed to their influence on the quantity of electrical charge on the unit area of the membrane, we must conclude that the same explanation holds for the influence of electrolytes on the rate of transport of water into a solution through a collodion membrane in the case of free osmosis.

3. We may, therefore, conclude, that when pure water is separated from a solution of an electrolyte by a collodion membrane, the rate of diffusion of water into the solution by free osmosis is accelerated by the ion with the opposite sign of charge as that of the watery phase of the double layer, because this ion increases the quantity of charge on the unit area on the solution side of the membrane; and that the rate of diffusion of water is retarded by the ion with the same sign of charge as that of the watery phase for the reason that this ion diminishes the charge on the solution side of the membrane. When, therefore, the ions of an electrolyte raise the charge on the unit area of the membrane on the solution side above that on the side of pure water, a flow of the oppositely charged liquid must occur through the interstices of the membrane from the side of the water to the side of the solution (positive osmosis). When, however, the ions of an electrolyte lower the charge on the unit area of the solution side of the membrane below that on the pure water side of the membrane, liquid will diffuse from the solution into the pure water (negative osmosis).

4. We must, furthermore, conclude that in lower concentrations of many electrolytes the density of electrification of the double layer increases with an increase in concentration, while in higher concentrations of the same electrolytes it decreases with an increase in concentration. The turning point lies for a number of electrolytes at a molecular concentration of about M/512 or M/256. This explains why in lower concentrations of electrolytes the rate of diffusion of water through a collodion membrane from pure water into solution rises at first rapidly with an increase in concentration while beyond a certain concentration (which in a number of electrolytes is M/512 or M/256) the rate of diffusion of water diminishes with a further increase in concentration.