

by reduction of the oxide in hydrogen at 150–200°), in the temperature range 100–200°, using gaseous mixtures containing up to 5% oxygen.

1. Combination is practically complete at 200° and is just measurable at 100°.

2. In nearly all cases copper oxide is formed simultaneously with water. After the oxygen is shut off and pure hydrogen alone passed over the catalyst, the oxide so formed is reduced at a greater rate than that of the formation of water while the oxygen is on.

3. Between 130° and 100°, the rate of oxidation of the copper and the rate of reduction of the oxide so formed, as well as the catalytic activity, suffer a marked reduction.

4. At 130° with oxygen equivalent to 10 mg. of water in 5 minutes, the rate of water formation passes through a maximum to a steady minimum value.

These results are believed to be satisfactorily explained by assuming that the combination takes place mainly as a result of the alternate oxidation and reduction of the catalyst, the reduction reaction being complicated by the known inhibitory influence of free oxygen on that reaction.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

STUDIES IN ELECTRIC-ENDOSMOSE¹

BY ALVIN STRICKLER AND J. HOWARD MATHEWS

Received May 3, 1922

Practically all of the previous work on electric-endosmose has been with water and aqueous solutions. The work to be described was extended to 9 typical organic solvents, and it will be shown that some of the general conclusions based on a study of aqueous solutions are quite erroneous.

Since the publication of Briggs'² bibliography in 1917 and his experimental results in 1918 but little has been reported. Loeb³ has carried out experiments to determine the influence of electrolytes on the electrification and the rate of flow of water through colloidal membranes, and the cause of this influence. Articles by Girard and Morax,⁴ and by Frank and Withrow⁵ have appeared but have no bearing on our work.

¹ Submitted by Alvin Strickler in partial fulfilment of the requirements for the Degree of Doctor of Philosophy at the University of Wisconsin.

² Briggs, *J. Phys. Chem.*, **21**, 198 (1917); **22**, 256 (1918).

³ Loeb, *J. Gen. Physiol.*, **1**, 717 (1919); **2**, 577 (1920).

⁴ Girard and Morax, *Compt. rend.*, **170**, 821 (1920).

⁵ Frank and Withrow, *THIS JOURNAL*, **42**, 671 (1920).

Apparatus.—The Briggs type of apparatus,² slightly modified, was used. These modifications, as shown in Fig. 1, greatly facilitated cleaning, filling and the renewal of membranes.

Constant temperature was maintained by a thermostat regulated to $\pm 0.01^\circ$. The water from this was pumped through an oblong tank in which the apparatus was clamped and which was provided with a window for viewing the bubble.

In order to determine the permeability of the membranes, the apparatus was clamped in a vertical position and the solution maintained at a constant head. The rate of flow through the membrane was measured in a capillary tube equal in size to D, the bubble tube.

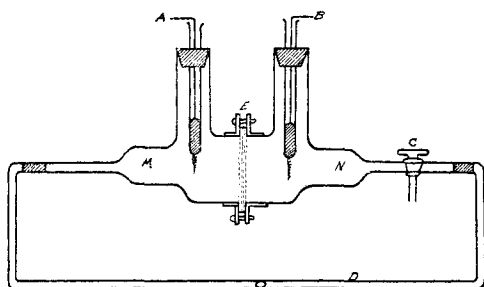


Fig. 1.—Apparatus.

As a source of direct current, 690 flash-light batteries were soldered together in series. These were arranged in wooden trays and insulated by casting in beeswax.

Preliminary Work.—While testing the apparatus with water, the idea was suggested that the porosity of the membrane might be a disturbing factor. No success resulted when using Briggs'² procedure and that of previous investigators for building up membranes. After trying various materials, filter paper (of good quantitative grade), cut into circles a little larger than the opening, was chosen as the most satisfactory. The circles were soaked in the solution for about 12 hours before making the run and then pressed firmly together to remove air bubbles. The duplication was very good and it was possible to make a large number of runs in a comparatively short time. The permeability was changed by varying the number of thicknesses of paper. No single membrane was used more than once.

The Effect of the Permeability of the Membrane on the Rate of Endosmose.—This phenomenon arises from the fact that, as the solution is forced through the membrane, there is a certain amount of friction in the bubble tube, and thus a tendency to pile up in one of the electrode chambers. Before the bubble can move, this friction must be overcome. As this must result in a slight difference in level in the two electrode chambers, the pressure naturally tends to force some of the liquid back through the membrane. The extent of this effect depends on the porosity or permeability of the membrane. This would suggest a steady increase in endosmose with decrease in permeability. The curves show such an increase, in every case, up to a maximum, and then a decrease tending toward zero. The membrane permeability was changed by varying the number of

thicknesses of filter paper. Rate of endosmose is plotted against rate of permeability.

Preparation of Materials.—The following solvents were used: acetone; amyl alcohol, nitrobenzene, pyridine, benzaldehyde, *n*-butyl alcohol; furfural, *isopropyl* alcohol and *o*-nitrotoluene. They were of the highest purity obtainable and were further purified and dried by the most approved methods. The solutes were commercial products of high quality and were in some cases merely dried, in others recrystallized and dried.

Reproducibility.—Former workers on membranes⁶ have found reproducibility one of their greatest problems. We have found comparatively good duplication when filter paper is used as a membrane for measurements with non-aqueous solvents. With constant voltage, temperature, current and the same thickness of membrane, furfural gave for the rate of endosmose in centimeters per second: 0.201, 0.202, 0.204, 0.204; *isopropyl* alcohol gave 0.630, 0.707, 0.717, 0.720; nitrobenzene gave 0.660, 0.654, 0.654, 0.649, 0.655. All the solvents used gave about this same degree of reproducibility.

Continuous Runs.—A long continuous run was made with each solvent. This was carried out by causing the bubble to move for a certain number of centimeters to the right and then reversing the current so the flow was to the left for the same distance. The flow was then reversed again, and so on, timing the movement over this distance. This was continued for from 20 to 50 reversals to the right and left. The number of the run was plotted as the abscissa, and the corresponding time required to flow a certain number of centimeters as the ordinate, but no quantitative relationship was discovered.

Effect of Varying the Applied Potential.—Earlier work on electric endosmose indicated that the endosmose was a linear function of the applied voltage. The accompanying curves show the effect of varying the potential through a wide range.

Effect of the Addition of Acid and Alkali.—Work with water solutions has in most cases shown a reversal of flow in acid solutions when the original charge on the membrane was negative. With non-aqueous solvents variations are common, due doubtless to chemical action.

Succinic acid and sodium hydroxide were chosen as the acid and base to be studied. Solutions of 0.01 *N* concentration were made and diluted to 0.001 *N*, 0.0001 *N*, 0.00001 *N*, and 0.000001 *N*. The least concentrated was run first. The accompanying curves, where the rate of endosmose is plotted against the acid and alkali concentration, show the results obtained.

Effect of Temperature Change.—The temperature of the bath was

⁶ Bartell and co-workers, *J. Phys. Chem.*, 16, 318 (1912); *THIS JOURNAL*, 36, 646 (1914); 38, 1036, 1039 (1916).

varied and 4 or 5 runs were made with each solvent. The curves are of the same general shape as that found by Briggs² when using water. The acetone curve, however, shows a decided maximum. This is attributed to its high vapor pressure and the formation of vapor bubbles in the apparatus.

The Effect of the Addition of Certain Salts.—Very early in his work, Perrin⁷ stated his valence rule which has been accepted by most investigators and found to hold very well in aqueous solutions and in the lower alcohols. Experiments were carried out to determine whether such a relationship exists in the case of the solvents under investigation. For what would be called "cation effect" in water solutions, the following salts were used: NaNO_3 , KNO_3 , $\text{Ca}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, $\text{Cr}(\text{Ac})_3$, $\text{U}(\text{Ac})_4$. Again using the nomenclature for water solutions, the salts for "anion effect" were KCNS , $\text{Cu}(\text{Ac})_2$, K_2SO_4 , $\text{K}_2\text{C}_2\text{O}_4$, K_3PO_4 , $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ (citrate) $\text{K}_4\text{Fe}(\text{CN})_6$. Solutions of 0.0001 *N* concentration were used. The voltage, temperature, and number of thicknesses of filter paper membrane were kept constant for each solvent. Tables for two solvents only are listed here.

TABLE I
ACETONE ("CATION EFFECT")

Solute	Direction	Cm./sec. Permeability	Cm./sec. Endosmose	Cm./sec./volt Endosmose $\times 10^{-4}$
$\text{Cr}(\text{Ac})_3$	+	0.64	1.796	62.1
$\text{U}(\text{Ac})_4$	+	0.74	1.082	37.3
Pure solvent	+	0.78	0.510	17.6
KNO_3	+	0.59	0.492	17.0
$\text{Al}(\text{NO}_3)_3$	+	0.61	0.430	14.8
NaNO_3	+	0.80	0.409	14.1
$\text{Ca}(\text{NO}_3)_2$	+	0.62	0.198	6.8
$\text{Ba}(\text{NO}_3)_2$	+	0.73	0.123	4.2

TABLE II
ACETONE ("ANION EFFECT")

$\text{Cu}(\text{Ac})_2$	+	1.70	1.293	42.8
K_3PO_4	+	0.64	1.203	41.6
K_2SO_4	+	1.29	1.123	38.8
$\text{K}_2\text{C}_2\text{O}_4$	+	0.94	0.919	31.8
$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$	+	0.74	0.843	29.1
$\text{K}_4\text{Fe}(\text{CN})_6$	+	0.78	0.703	24.3
Pure Solvent	+	0.78	0.509	17.6
KCNS	+	1.70	0.353	12.2

⁷ Perrin, *J. Phys. Chem.*, **2**, 601 (1904); **3**, 50 (1905); *Compt. rend.*, **136**, 1388 (1903).

TABLE III
 PYRIDINE ("CATION EFFECT")

				× 10 ⁻⁵
NaNO ₃	—	2.00	0.481	57.1
Al(NO ₃) ₃	—	1.76	0.352	41.8
U(Ac) ₄	+	1.36	0.212	25.2
Ca(NO ₃) ₂	—	1.87	0.192	22.8
KNO ₃	—	1.81	0.087	10.4
Pure Solvent	+	1.50	0.083	9.8
Cr(Ac) ₃	+	1.42	0.081	9.6
Ba(NO ₃) ₂	+	1.66	0.061	7.2

 TABLE IV
 PYRIDINE ("ANION EFFECT")

				× 10 ⁻⁵
KCNS	—	1.50	0.973	115.5
Cu(Ac) ₂	—	1.87	0.684	81.3
K ₂ C ₂ O ₄	+	1.66	0.169	20.0
K ₂ SO ₄	+	1.42	0.120	14.2
K ₄ Fe(CN) ₆	+	1.57	0.099	11.7
K ₃ PO ₄	+	1.57	0.095	11.2
Na ₃ C ₆ H ₅ O ₇	+	1.87	0.081	9.6
Pure Solvent	+	1.50	0.083	9.8

No generalization can explain the effect on the rate of endosmose of the various salts in the same solvent or of the same salt in different solvents.

Effect of Varying the Concentration of the Salts in Solution.—Most workers with water solutions found a maximum endosmotic effect at a definite concentration of the dissolved salt. This has been noted: that any solution if sufficiently dilute will flow, under a potential gradient, in the direction exhibited by the pure solvent. The salt having the greatest solubility was selected, and a 0.01 *N* solution was prepared and diluted to 0.001 *N*, 0.0001 *N*, 0.00001 *N* and 0.000001 *N*. The curves show a striking similarity of shape. The maximum comes at about the same concentration in each case. The benzaldehyde irregularity is attributed to oxidation effects.

Effect of Adding Water.—A series of runs was made with varying percentages of water added to the solvent and also to the solvent containing a dissolved salt, where this was possible. In the curves, rate of endosmose is plotted against percentage of water added.

Effect of Varying the Dielectric Constant.—The accompanying table shows the rate of endosmose of 19 different solvents of various dielectric constants. Coehn's rule⁸ does not seem to hold in every case. The dielectric-constant ratio appears to affect the magnitude, but not necessarily the direction of endosmotic flow.

Studies on the Hofmeister Series.—There seems to be manifest in electric-endosmose, beside the factor of selective adsorption, an additional

⁸ Coehn, *Wied. Ann.*, **64**, 227 (1898).

TABLE V
RATE OF ENDOSMOSE WITH VARIOUS ORGANIC SOLVENTS

Solvent	Direct ion	Dielectric constant	Cm./sec. Permeability	Cm./sec. Endosmose
Amylene	+	2.2	..	very slight
Toluene	-	2.335	2.40	0.0012
Benzene	-	2.3	1.92	0.0009
Xylene	-	2.37	1.92	0.0006
Carbon disulfide	+	2.6	5.0	0.0007
Propionic acid	+	3 to 5	..	very slight
Ether	+	4.4	1.92	0.0011
Chloroform	+	5.0	3.33	0.0038
Ethyl <i>Isobutyrate</i>	+	5.08	2.06	0.012
<i>Isobutyl Acetate</i>	+	5.26	1.25	0.034
<i>Iso-amyl Formate</i>	-	5.61	1.50	0.053
Ethyl Propionate	+	5.64	2.14	0.483
Aniline	+	7.2	0.25	0.074
<i>Isobutyl Formate</i>	-	7.28	1.36	0.122
Propyl Alcohol	+	11 to 22	0.57	0.077
Allyl Alcohol	-	20.6	..	0.00068
Formamide	-	84.0	..	too much current
Diethyl Aniline	+	..	0.40	0.0067
Propyl Propionate	+	..	1.25	0.129

specificity which is determined by the nature of the solvent used. A series of runs was made using the salts ordinarily employed in studies on the Hofmeister series. Bethe and Toropoff⁹ found that the Hofmeister order apparently held in water. Acetone, furfural and *n*-butyl alcohol were selected as solvents. The salts used for the anion series were: $K_3C_6H_5O_7$, $K_2C_4H_4O_6$, K_2SO_4 , KAc , KCl , KNO_3 , $KClO_3$, KI , $KCNS$, K_2CO_3 , KBr , and K_2HPO_4 . Those for the cation series were: NH_4NO_3 , $LiNO_3$, $NaNO_3$, KNO_3 and $Mg(NO_3)_2$; 0.0001 *N* solutions were used. Tables VI and VII give the results.

While it was formerly assumed that the potassium ion must have the same effect in every case, it is probably the particular combination of ions which produces the final result. K^+ combined with NO_3^- may not have the same effect as K^+ combined with Cl^- because the adsorption may be modified by the presence of other ions.

Accepting, for the present, the assumption that the potassium ion effect is constant, the order of the anions in acetone is $C_2H_3O_2 > Cl > CO_3 > HPO_4 > C_4H_4O_6 > Br > SO_4 > C_6H_5O_7 > NO_3 > ClO_3 > I > CNS$. In furfural the order is $Cl > CO_3 > C_4H_4O_6 > C_6H_5O_7 > C_2H_3O_2 > Br > SO_4 > HPO_4 > I > ClO_3 > CNS > NO_3$; in *n*-butyl alcohol it is $SO_4 > C_4H_4O_6 > CO_3 > HPO_4 > C_2H_3O_2 > C_6H_5O_7 > ClO_3 > Cl > CNS > I > NO_3 > Br$.

⁹ Bethe and Toropoff, *Z. physik. Chem.*, **89**, 637 (1915).

TABLE VI
ENDOSMOSE OF SALTS; ANION SERIES AND ACETONE

Solute	Direction	Cm./sec. Perme- ability	Cm./sec. Endosmose	Cm./sec./volt
				Endosmose
KAc	+	4.76	7.692	211.3
KCl	+	4.34	6.607	126.3
K ₂ CO ₃	+	5.00	3.597	98.8
K ₂ HPO ₄	+	4.54	3.086	84.7
K ₂ C ₄ H ₄ O ₆	+	4.54	3.073	84.4
KBr	+	4.76	2.276	62.5
K ₂ SO ₄	+	4.76	2.186	60.0
K ₃ C ₆ H ₅ O ₇	+	4.76	2.161	59.3
KNO ₃	+	4.16	0.474	13.0
KClO ₃	+	4.54	0.202	5.5
KI	+	3.84	0.175	4.8
KCNS	-	4.00	0.176	4.8

TABLE VII
ENDOSMOSE OF SALTS; CATION SERIES AND ACETONE

Mg(NO ₃) ₂	-	4.16	0.897	24.6
KNO ₃	+	4.00	0.414	11.3
NaNO ₃	+	4.34	0.259	7.1
LiNO ₃	+	4.16	0.203	5.5
NH ₄ NO ₃	+	4.00	0.106	2.9

TABLE VIII
ENDOSMOSE OF SALTS; ANION SERIES AND FURFURAL

Solute	Direction	Cm./sec. Perme- ability	Cm./sec. Endosmose	Cm./sec./volt
				Endosmose
KCl	+	1.00	0.616	9.7
K ₂ CO ₃	+	1.00	0.381	6.0
K ₂ C ₄ H ₄ O ₆	+	1.06	0.344	5.4
K ₃ C ₆ H ₅ O ₇	+	1.03	0.340	5.3
KAc	+	0.93	0.333	5.2
KBr	+	0.90	0.330	5.2
K ₂ SO ₄	+	0.93	0.321	5.0
K ₂ HPO ₄	+	0.92	0.311	4.9
KI	+	1.11	0.196	3.1
KClO ₃	+	0.88	0.146	2.3
KCNS	+	1.08	0.098	1.5
KNO ₃	+	0.96	0.092	1.4

TABLE IX
ENDOSMOSE OF SALTS; CATION SERIES AND FURFURAL

LiNO ₃	-	0.96	0.361	5.7
Mg(NO ₃) ₂	-	1.00	0.269	4.2
NaNO ₃	-	0.89	0.056	0.8
NH ₄ NO ₃	+	0.93	0.062	0.9
KNO ₃	+	1.01	0.110	1.7

TABLE X
ENDOSMOSE OF SALTS; ANION SERIES AND *n*-BUTYL ALCOHOL

Solute	Direction	Cm./sec.	Cm./sec. Endosmose	Cm./sec./volt
		Perme- ability		Endosmose
K ₂ SO ₄	—	0.53	0.163	1.9
K ₂ C ₄ H ₄ O ₆	—	0.50	0.207	2.4
K ₂ CO ₃	—	0.50	0.216	2.5
K ₂ HPO ₄	—	0.55	0.221	2.59
KAc	—	0.54	0.262	3.0
K ₃ C ₆ H ₅ O ₇	—	0.54	0.302	3.5
KClO ₃	—	0.50	0.418	4.9
KCl	—	0.50	0.427	5.0
KCNS	—	0.57	0.485	5.7
KI	—	0.50	0.535	6.2
KNO ₃	—	0.50	0.538	6.3
KBr	—	0.51	0.564	6.6

TABLE XI
ENDOSMOSE OF SALTS; CATION SERIES AND *n*-BUTYL ALCOHOL

KNO ₃	—	0.57	0.527	6.2
NaNO ₃	—	0.50	0.289	3.4
Mg(NO ₃) ₂	—	0.55	0.210	2.4
NH ₄ NO ₃	—	0.52	0.115	1.3
LiNO ₃	—	0.56	0.017	0.2

These variations of order can be explained only by assuming a specific effect due to the nature of the solvent. The order of the cations is in acetone, Mg > K > Na > Li > NH₄; in furfural, Li > Mg > Na > NH₄ > K; and in *n*-butyl alcohol, K > Na > Mg > NH₄ > Li.

Theoretical Discussion

Any solid medium in contact with a liquid medium was found by Quincke¹⁰ and Helmholtz¹¹ to possess at the surface an electric double layer, established by contact. Coehn⁸ noted that this charge seemed to be directly related to the dielectric-constant ratio. The exceptions found when electrolytes were present were explained rightly by Freundlich¹² and Bancroft¹³ as due to the selective adsorption of ions by the membrane material.

This did not, however, adequately explain the source of the original charge on the membrane. Briggs² says it is purely an adsorption phenomenon, the charge being produced by ionization with subsequent preferential adsorption of the hydroxyl ions. But this does not include the non-aqueous solvent.

¹⁰ Quincke, *Wied. Ann.*, **7**, 351 (1879); *Pogg. Ann.*, **107**, 1 (1859); **110**, 38 (1860).

¹¹ Helmholtz, *ibid.*, **7**, 337 (1879).

¹² Freundlich, "Kapillarchemie," Akad. Verlag. m. b. H., 1909.

¹³ Bancroft, *J. Phys. Chem.*, **16**, 312 (1912).

In 1916 and 1917 Langmuir¹⁴ found that many of the conditions existing at the surface of a liquid might be accounted for by assuming an orientation of the molecules at this surface. Harkins and his co-workers,¹⁵ following an illuminating mathematical theory by Frenkel,¹⁶ made an elaborate study of the "thermodynamic environment" of liquid surfaces and reached like conclusions. In the light of this work it is suggested that it is the orientation of the solvent molecules at the surface and within

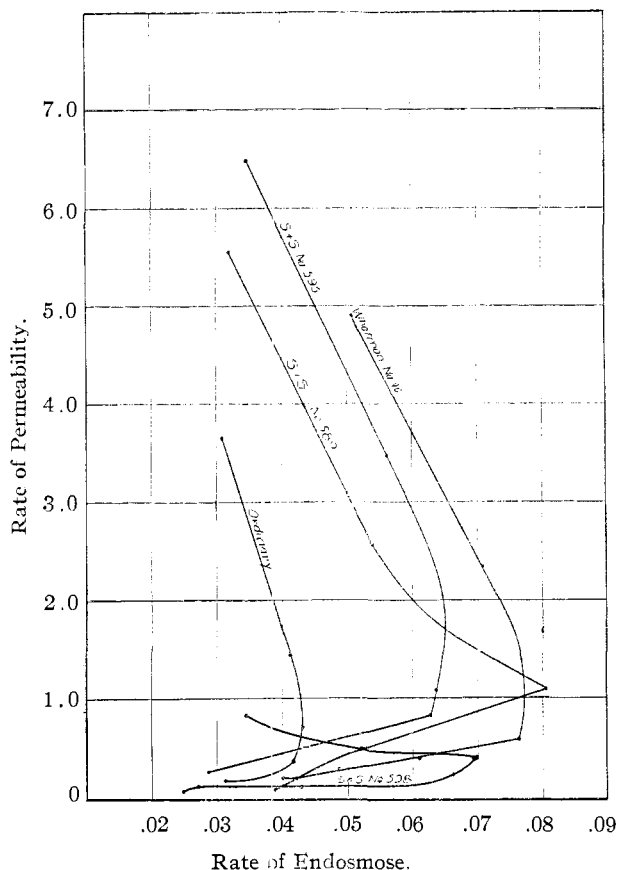


Fig. 2.—Curve for water vs. filter paper.

the pores of the membrane which produces the charge. The orientation depends upon both the solvent and the membrane. The nature of the charge can generally be predicted by Coehn's rule, but not always. Thus the lower alcohols would be oriented with the hydroxyl group toward the membrane, while the higher ones (*n*-butyl and amyl) would either be

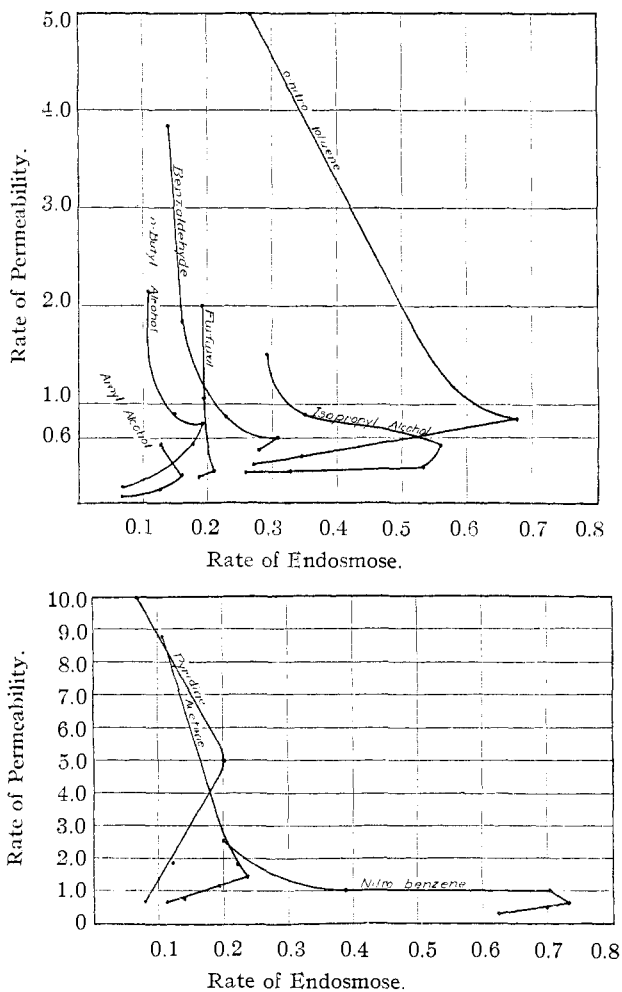
¹⁴ Langmuir, *Met. Chem. Eng.*, 15, 468 (1916); *THIS JOURNAL*, 39, 1848 (1917).

¹⁵ Harkins, *et al.*, *THIS JOURNAL*, 39, 354 (1917).

¹⁶ Frenkel, *Phil. Mag.*, 33, 297 (1917).

reversed or have their hydroxyl effect reduced by the large and unwieldy remainder of the molecule.

A salt dissolved in the solvent would add to or deduct from this charge through selective adsorption. The order of this latter effect seems to be



For Acetone—multiply Endosmose by 10.

Fig. 3.

Above: Non-aqueous Solvents vs. S. & S. No. 589 Filter Paper.

Below: Non-aqueous Solvents vs. S. & S. No. 589 Filter Paper.

specific for the ion combination and the solvent employed and is apparently not determined by the valence of the ions in non-aqueous solvents.

The nature of the continuous run curves (not shown) might be largely

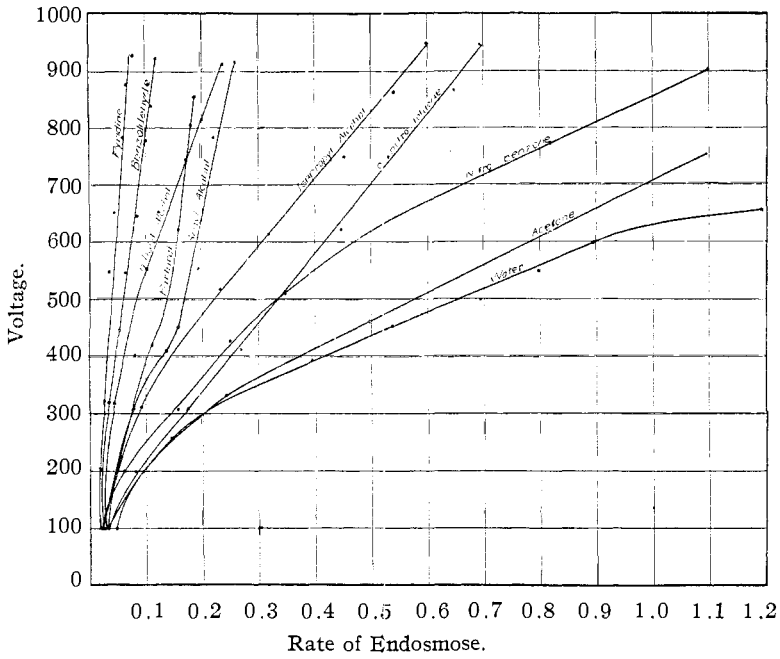


Fig. 4.

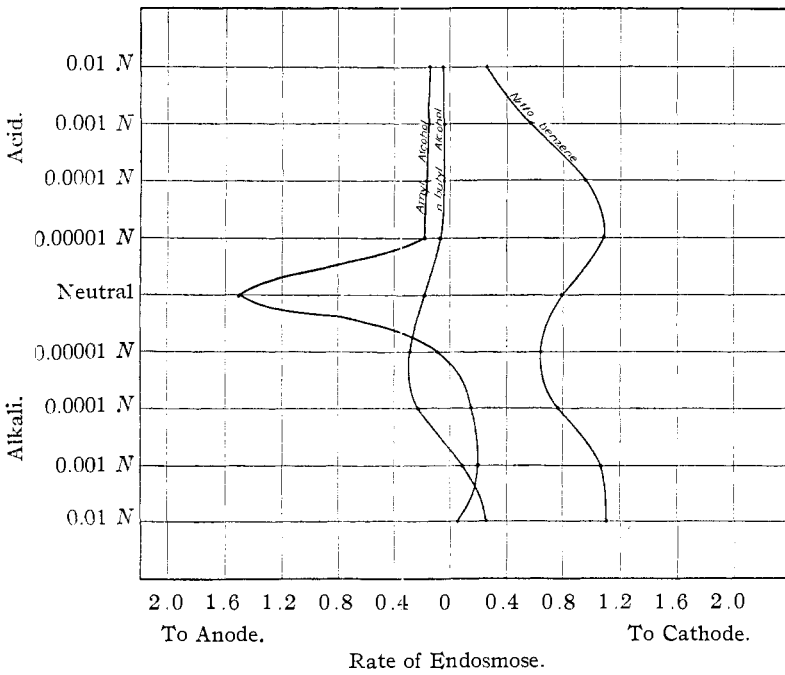


Fig. 5.

explained by the formation of products directly adsorbed and affecting the rate of flow.

Wiedemann¹⁷ concluded that the "flow was independent of the area or thickness of the porous wall." Our work has shown (Figs. 2 and 3) that the permeability of the membrane is a very important factor with the apparatus used. Some such relationship might also account for some of the phenomena of "free osmosis."

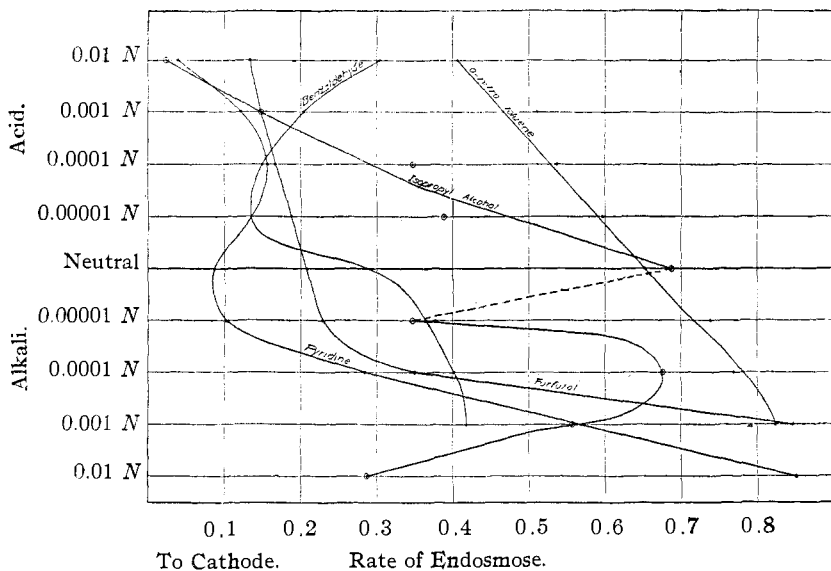


Fig. 6.

The fact that duplication has been made possible is important. Water materially altered the texture of the paper, changing the nature of the surface and hence its adsorbing power. This explains the lack of uniformity when using water as the solvent.

The curves of endosmose against voltage cannot in most cases be considered straight lines (Fig. 4). This may be partially explained by electrolysis effects at high voltage.

Most of the acid-alkali curves (Figs. 5 and 6) exhibit maxima at a definite concentration, evidently due to complete dissociation. Though the preferential adsorption of the hydrogen and hydroxyl ions will explain most of the curves, specificity of the solvent is found to be a large factor.

The increase of temperature decreases viscosity and increases mobility, thus favoring orientation and increased rate of endosmose. The function is not quite linear (Fig. 7).

¹⁷ Wiedemann, *Pogg. Ann.*, **87**, 321 (1852); **99**, 177 (1856).

The results obtained by the addition of certain salts (Tables I, II, III, IV) were doubtless in many cases purely molecular, with the additional factor of solvation. Most of the results can be explained on the theory

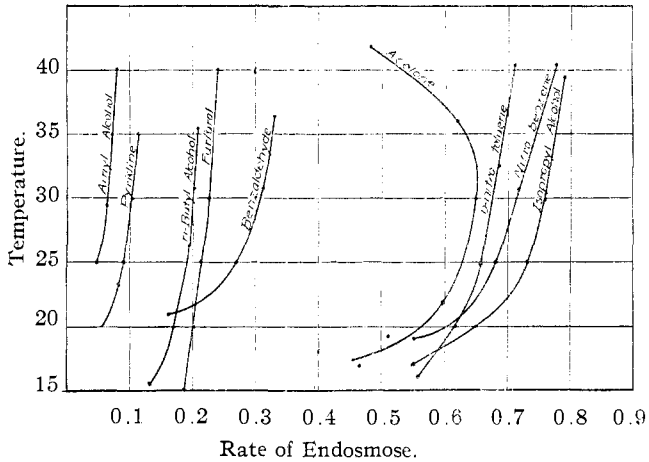


Fig. 7.

of selective adsorption if we note that the relative adsorption varies with the medium in which the salt is dissolved. In acetone aluminum is less adsorbed than is calcium, and in amyl alcohol the reverse is true. In pyridine sodium shows a greater effect than does calcium. The tables are full of irregularities.

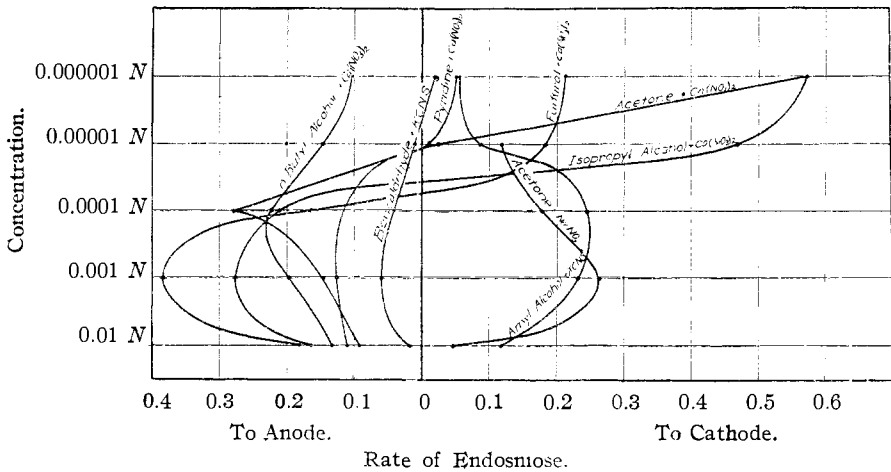


Fig. 8.

The maxiam exhibited by the concentration curves (Fig. 8) are due to a change from the molecular to the ionic condition and then to a state of dilution where the charge on the membrane is that produced merely

by contact. This accounts for the reversals of the curves of acetone plus calcium acetate, pyridine plus calcium nitrate and benzaldehyde plus potassium thiocyanate.

When water is added to the solvent (Fig. 9) the water molecules are oriented at the membrane, adding to or subtracting from the charge, depending upon the nature of the solvent and the selective adsorption of the membrane for water. Change in viscosity is also a factor. When a salt is present the problem is complicated by specificity of ion adsorption

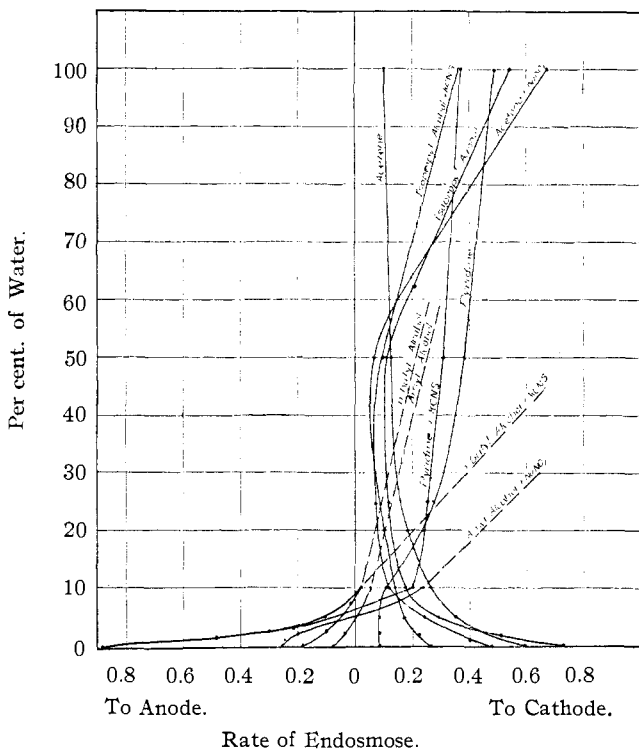


Fig. 9.

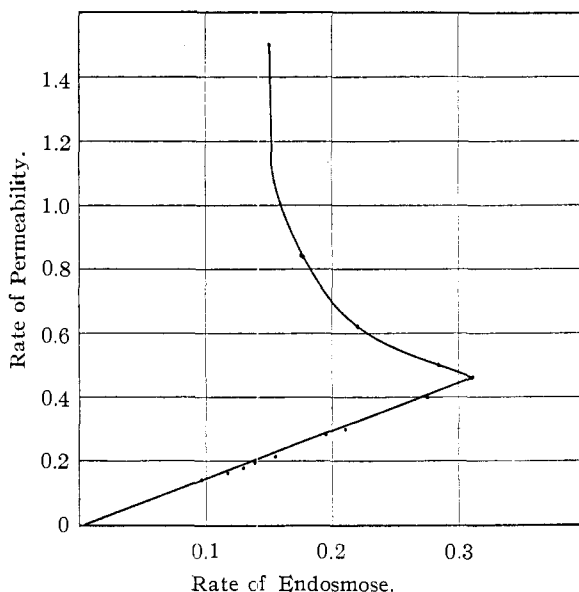
which depends not only upon the salt used but also upon the solvent. Finally, as dissociation is largely a phenomenon of aqueous solution, we might find the differences are partly due to the fact that the dissolved substance is chiefly in the molecular condition in the non-aqueous solvent.

Endosmotic flow may then be considered as dependent on the algebraic sum of the factors of orientation and ion adsorption.

The questions of ion mobility as suggested by Bartell⁶ and Loeb³ and solvation as studied by Remy¹⁸ are left for later consideration.

¹⁸ Remy, *Z. physik. Chem.*, **89**, 467 (1915).

The accompanying curve (Fig. 10) is the result of a study of *isopropyl* alcohol with membranes of wide porosity variations. It shows that the maximum is sharp and definite and that the curve for decreasing rate is apparently a straight line through the origin.



Isopropyl Alcohol vs. S. & S. 589 Filter Paper.

Fig. 10.

Summary and Conclusions

1. Experiments measuring endosmotic flow have been extended to 9 typical organic solvents using a modified Briggs apparatus.

2. An adsorption orientation theory has been suggested to explain the establishment of the original charge at the surface of contact of the membrane and solvent. This states that the molecules of the solvent, upon adsorption, are oriented upon the membrane surface producing a charge by their polarity. If dissociated molecules are present they affect the membrane charge by specific adsorption of the ions produced. This does not eliminate adsorption but suggests a more comprehensive view of the mechanism for the establishment of the original charge.

The following conclusions were reached.

1. The permeability of the membrane is an important factor in determining endosmotic flow.

2. It is possible to duplicate membranes of filter paper when using non-aqueous solvents.

3. The endosmose rate (as measured) is not quite a linear function of the voltage when varied over a wide range.

4. The effect of acid and alkali can be explained on the assumption of adsorption, making due allowance for concentration and chemical change.

5. Briggs' results as to temperature effects with water have been confirmed with non-aqueous solvents.

6. The valence rule does not hold with the non-aqueous solvents studied.

7. The order of adsorption of ions and their relative adsorption varies with the solvent employed.

8. The concentration curve exhibits a maximum with non-aqueous solvents and the flow at low concentration is in the same direction as that of the pure solvent.

9. The addition of water to non-aqueous solutions changes the endosmose in the direction it would manifest in pure water, the first additions showing the greatest effects.

10. The direction of endosmose (as here measured) is not determined by the dielectric constant ratio, although this probably does measure the magnitude of flow.

11. The Hofmeister series is not consistent when considering endosmotic effects in non-aqueous solvents.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF CINCINNATI]

A COLORIMETRIC DETERMINATION OF HYDROGEN PEROXIDE

By M. L. ISAACS

Received May 19, 1922

The yellow color produced by the action of hydrogen peroxide on a molybdate in acid solution was first observed by Schön¹ in 1870. In 1890 Denigès² described the reaction, but immediately M. L. Crismer³ called attention to Schön's work and to his own discovery of the reaction in 1888.⁴ He also pointed out that the yellow substance had been isolated by Baerwald,⁵ who assigned to it the formula $18\text{MoO}_3 \cdot 14\text{NH}_3 \cdot 3\text{H}_2\text{O}_2 \cdot 18\text{H}_2\text{O}$. Nagel and Muthman⁶ have studied the action of conc. hydrogen peroxide on molybdic oxide and picture the formation of ozomolybdates, that is, a molybdate compound containing an oxygen atom of a peroxide nature.

¹ Schön, *Z. anal. Chem.*, [9] **41**, 330 (1870).

² Denigès, *Compt. rend.*, **110**, 1007 (1890).

³ Crismer, *Bull. soc. chim.*, [3] **6**, 22 (1891).

⁴ Crismer, *Gaz. med. Liège*, **7**, 77 (1888).

⁵ Baerwald, *Ber.*, **17**, 1206 (1884).

⁶ Nagel and Muthman, *ibid.*, **31**, 1836 (1898).