The system appears to be one of the most satisfactory in the titration of weak base with strong acid. In the titration of weak acids or polybasic acids the system appears to be of little use.

PRINCETON, NEW JERSEY
RECEIVED JULY 9, 1932
PUBLISHED APRIL 6, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Dependence of the Ultrafiltrate from a Sol of "Ferric Hydroxide" upon Rate of Ultrafiltration; Donnan Equilibrium and *P*H of Sols

BY JAMES W. MCBAIN AND WINIFRED L. MCCLATCHIE

The unequal distribution of all mobile ions in any system involving a restraint upon certain electrical charges, now commonly known as the Donnan equilibrium,[1] was given quantitative formulation in the subject of electrokinetics by Gouy and Chapman for the diffuse double layer in the neighborhood of surfaces and colloidal particles, then by Donnan in 1911 for membrane equilibria, and very much later by Debye and Hückel in 1923–1924 for the interior of ordinary solutions. Further, although the classical nomenclature of colloids, still frequently employed, took no cognizance thereof, it is well known that all charged colloids in ionizing solvents partake of the nature of salts.[2]

Nevertheless, these matters have been overlooked in assigning to hydrogen ion, or any other ion, definite values of concentration in a sol, although these must vary greatly according to the distance from a colloidal particle. It is intriguing to reflect that the readings of electrode potential of the hydrogen electrode (or other reversible electrode) in different parts of a sol must be identical, although the actual concentrations of any ion yielding the constant electrode potential must vary even as a time average from point to point. A portion of the liquid near a positively charged particle such as that in a sol of "ferric hydroxide"[3] must be less acid than that further away, and although exhibiting the same hydrogen or chloride electrode potential, the actual *P*H and *P*Cl must be different in different parts of the sol. Serious discrepancies must, therefore, appear in the

---

(1) For references, including the classical work of Gibbs, see T. R. Bolam, "The Donnan Equilibria," G. Bell and Sons, Ltd., London, 1932.

(2) For the most comprehensive and authoritative monograph, see Wo. Pauli and E. Valkó, "Elektrochemie der Kolloide," Julius Springer, Vienna, 1929.

(3) It should be recalled that a sol of so-called "ferric hydroxide" prepared from ferric chloride is a colloidal complex salt. It contains as essential constituents particles consisting of heavily hydrated oxide or hydroxide with undissociated oxychloride and the positively charged ferric or ferroxy ion, compensated by an electrochemically equal amount of free chlorine ions in the surrounding liquid. There is also a trace of hydrochloric acid in hydrolytic equilibrium. These sols are by no means necessarily dilute, they possess a moderate proper conductivity and definite lowering of freezing point, and they diffuse as rapidly as sucrose.

treatment hitherto accorded the study of the constitution of colloidal sols and even in most of the published values for *P*H of colloids.

Ultrafiltration has frequently been employed as a tool in the study of colloids, yet there is only one paper, that of Greenberg and Greenberg,[4] in which the Donnan equilibrium is recognized and, even so, from the standpoint of membrane equilibrium rather than from the more general one outlined in these opening paragraphs, thus missing the main point of the present paper.

Most colloid chemists other than Pauli and his associates have assumed that an ultrafiltrate is identical with the solution in which the colloidal particles are suspended, quoting as evidence the observation of Duclaux,[5] Maffia,[6] and others (including Greenberg and Greenberg)[4] that the composition of the ultrafiltrate was independent of the amount filtered.

It has further been asserted by Kruyt, Roodvoets and van der Willigen[7] that the composition of the ultrafiltrate is independent of the density of the membrane, and in a recent paper by Duclaux and Titeica[8] that it is independent of the pressure applied. In other words, it is claimed that the composition of the ultrafiltrate is not affected by the rate of ultrafiltration. In neither case, however, are experimental data given for the composition of the sols or of the ultrafiltrates.

The series of ultrafiltrations to be described was incidental to the study of "sol 13" of "ferric hydroxide," the preparation and *P*H of which were given in a previous communication.[9] It was especially desired to observe the effect of changing the pressure on the composition of the ultrafiltrate, for we have utilized a far wider range of pressures than those in previous work, namely, from less than one atmosphere up to one hundred atmospheres. We find that the concentration of the ultrafiltrate may be varied four-fold by mere change in the pressure or the rate employed, a phenomenon which has not been suspected by previous workers in this field.

Experimental

Ultrafiltration.—A high pressure ultrafilter,[10] equipped with an electrically operated stirrer, was used. All portions of the apparatus coming in contact with solution were heavily silver plated or were replaced by parts of pure silver, except for a nickel gauze underneath the membrane. All portions not of solid silver were coated with a thin

---

[4] D. M. Greenberg and M. Greenberg, *J. Biol. Chem.*, **94**, 373 (1931). They found the concentration of salt in the ultrafiltrate to be greater than that in the original alkaline casein solution but independent of the amount filtered. Their reflection upon the interpretation of the ultrafiltration experiments of J. W. McBain and W. J. Jenkins [*J. Chem. Soc.*, **121**, 2325 (1922)] has been shown by subsequent work to be invalid.

[5] J. Duclaux, *Kolloid-Z.*, **3**, 126 (1908).

[6] P. Maffia, *Kolloidchem. Beihefte*, **3**, 85 (1911).

[7] H. R. Kruyt, A. C. W. Roodvoets, and P. C. van der Willigen, "Colloid Symposium Monograph," 1926, Vol. IV, p. 304.

[8] J. Duclaux and R. Titeica, *Compt. rend.*, **189**, 101 (1929).

[9] W. L. McClatchie, *J. Phys. Chem.*, **36**, 2087 (1932).

[10] Vereinigung Göttinger Werke, Göttingen.

film of boiled out medicinal vaseline. Cellophanes "No. 600," "450" or "1200" were used for the ultrafilter membranes and all washers likewise were cut from cellophane "No. 2400," three or four thicknesses being required. All membranes and washers were soaked for at least twenty-four hours in several changes of conductivity water before being used. Pressure was applied from a cylinder of compressed nitrogen.

To test the apparatus for freedom from conducting impurities, conductivity water was filtered. It showed an increase in specific conductivity only of 0.5 to 1.0 × 10^{-6}, which is well below the probable experimental error for the ultrafiltration of the sol.

The filter was rinsed with several portions of sol before the sample for ultrafiltration was introduced, and the first 10 to 15 cc. of ultrafiltrate was rejected, serving to saturate the membrane and to rinse the funnel below the filter. The sol was stirred at a moderate

TABLE I

THE EFFECT OF DIFFERENT PRESSURES USED IN ULTRAFILTRATION OF "FERRIC HYDROXIDE SOL 13" UPON THE COMPOSITION OF THE ULTRAFILTRATE

Expt.	Cellophane No.	Portion	Press. kg./sq. cm.	Total % filtered	Rate,[a] cc./min.	Ultrafiltrate $K \times 10^6$
1	600	2	40–50	20	0.21	6.97
		3	25–35	28	.32	6.42
		4	25–30	36	.28	6.42
		5	20–30	44	.24	6.64
		6	30–60	55	.38	5.38
2	600	2	45–55	14	.39	5.01
	Same as	3	40–60	22	.38	4.99
	for No. 1	4	10–14	31	.17	8.68
		5		38	.18	9.07
		6	45–60	45	.40	4.52
3	600	2	90–100	15	.45	4.62
	New mem-	3	90	23	.42	4.90
	brane	4	52–55	33	.30	6.52
		5	50–52	39	.30	6.34
		6	6–7	47	.12	11.3
		7	6	53	.13	11.1
		8	95	64	.49	3.56
4	600	2	1–2	17	.12	13.6
	Same as	3	>1	27	.086	14.8
	for No. 3	4	50	43	.46	5.26
		5		54	.56	3.76
5[b]	450	3	45–50	47	.51	5.15
		4	60–65	54	.61	4.38
6	1200	2	5	18	.082	13.9
		3	3	21	.073	14.1
		4	50	27	.19	7.16
7	1200	2	1	23	.065	12.3
	Same as	3	>1	36	.061	12.4
	for No. 6	4		53	.11	8.32
8	600	3	13	23	.20	8.65
		4	6	35	.15	9.88
		5	65	47	.38	4.31

[a] The membrane area was about 28 sq. cm.

[b] Sol came through when pressure was first applied.

rate, and a current of air on the apparatus prevented heating by the electromagnets. The ultrafiltrate was collected in stoppered Jena or Pyrex containers. The results of these experiments are collected in Table I. The last column gives the specific conductivity, at 25°, of the ultrafiltrate obtained.

It is obvious that the composition of the ultrafiltrate is by no means independent of the rate of ultrafiltration, and that it is the rate rather than the pressure that is the determining factor. This is shown by comparison of portion 2 of filtration 2 with portion 3 of filtration 3, where the pressures were different but the rates and conductivities were the same. The specific conductivities of the ultrafiltrates were, therefore, plotted against the rates of ultrafiltration, as shown in Fig. 1.

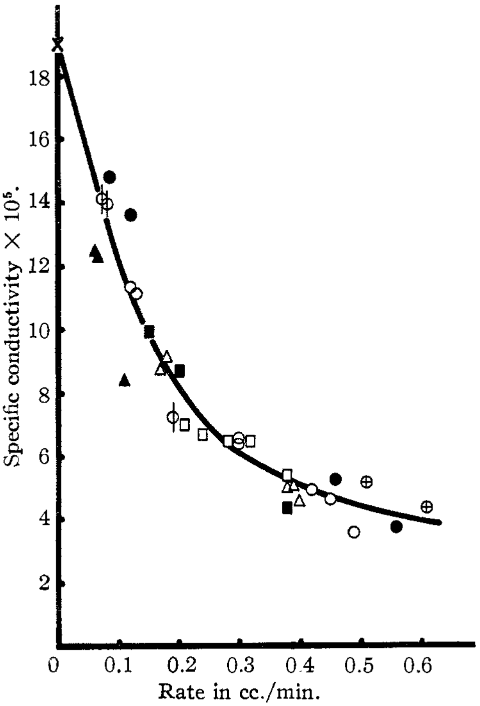


Fig. 1.—The effect of the rate of ultrafiltration of "ferric hydroxide" sol upon the composition of the ultrafiltrate: Expt. 1, □; Expt. 2, △; Expt. 3, ○; Expt. 4, ●; Expt. 5, ⊕; Expt. 6, ⌽; Expt. 7, ▲; Expt. 8, ■.

The general relationship between the rate of ultrafiltration and the conductivity is fairly well established by these experiments. The failure to obtain closer checks was probably due to temperature differences between the different samples that were ultrafiltered, as there is a tendency for all points from a single experiment to lie on the same side of the curve.

The main result cannot be attributed to any systematic influence of the amount filtered, or of the method of varying the pressure, or of temperature changes, for no routine method of varying the rates was followed. The frequently reported nearly constant composition of successive samples of ultrafiltrate is further confirmed by these experiments.

Dialysis.—It may be seen from Fig. 1 that the conductivity of the ultrafiltrate is still increasing rapidly at the lowest rates obtainable by ordinary ultrafiltration. It is of theoretical interest to know the limiting composition for zero rate or, in other words, after the residue and filtrate have come to an approximate equilibrium. Dialysis of the sol against its ultrafiltrate affords a means of evaluating approximately this equilibrium, although it is realized that the conditions obtained would not be quite identical with a zero rate ultrafiltration.

A 40-cc. sample of sol 13 was dialyzed at 25° against 50 cc. of ultrafiltrate with a specific conductivity of 6.4×10^{-5}. The sol was contained in a cellophane tube, and dialysis was carried out in a glass-stoppered conductivity cell of 150 cc. capacity.

TABLE II

Time in hours	0	$^3/_4$	$3^1/_2$	20	44	80
$K \times 10^5$ of dialyzate	6.4	11.8	16.4	17.7	19.0	19.0

The equilibrium concentration of the dialyzate, as shown in Table II, was plotted as point X in Fig. 1, and it fits fairly well on the curve for conductivity against rate of ultrafiltration.

Composition of the Ultrafiltrate.—The conductivity of the best conducting ultrafiltrate (lowest rate) is less than one-tenth of the total conductivity of the sol and it does not contain over one-twentieth of the total chloride. It contains the merest trace of iron, ammonium thiocyanate giving only a faint pink. Nessler's reagent indicated less than 10^{-5} *N* ammonia. Nevertheless, the conductivity of the ultrafiltrate was only partly due to free hydrochloric acid. This was shown by determining the concentration of hydrogen ion in the ultrafiltrate and in the dialyzate with a glass electrode[11] which had given concentrations of 1.2, 1.2 and 1.1×10^{-4} *N* with 1.0×10^{-4} *N* hydrochloric acid solution prepared by dilution of 1 *N* hydrochloric acid solution in two stages with boiled out conductivity water. The results are given in Table III. The next to the last column, headed C_{H^+} conductivity, is the concentration of hydrochloric acid that would be required to account for the total conductivity of the ultrafiltrate.

TABLE III

COMPARISON, USING GLASS ELECTRODE, OF CONDUCTIVITY OF ULTRAFILTRATE AND DIALYZATE WITH CONCENTRATION OF HYDROGEN ION PRESENT

Expt.	Portion	$t°$	"E"	"E_{KHP}"	$C_{H^+} \times 10^5$	C_{H^+} cond. $\times 10^5$	$\frac{C_{H^+}}{C_{H^+} \text{ cond.}}$
8	5	20	0.1175	0.0866	2.8	10.1	0.27
Not in Table I		24	.2260	.2335	7.9	18.0	.46
Not in Table I		24	.2280	.2335	8.7	18.0	
8	3	21	.1462	.1671	5.0	20.2	.25
8	4	20	.1512	.1671	5.8	23.2	.25
Dialyzate		19	.1675	.1627	16.0	46.3	.39
Dialyzate		19	.1718	.1625	20.0	46.3	

It is probable that there is a small concentration of some electrolyte derived from the glassware (or cellophane) to account for the greater portion of the conductivity of the ultrafiltrate. Fortunately, these concentrations are so low that they affect the total composition of the sol but little.

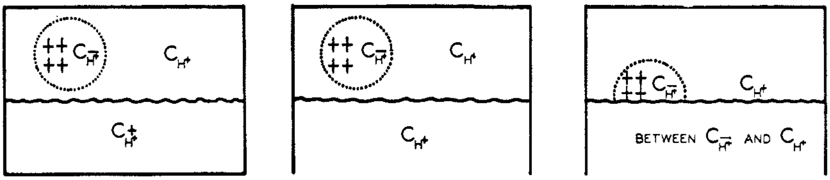
---

(11) For the technique and the reference electrodes and buffers, see W. L. McClatchie, *J. Phys. Chem.*, **36**, 2087 (1932).

If the extrapolated value of specific conductivity of ultrafiltrate for highest rate be taken as 3.0×10^{-5} and it is assumed that 25% of this conductivity is due to hydrochloric acid and the remainder to some other chloride, the total chloride ion in the ultrafiltrate would be only 1.7×10^{-4} *N*. The chloride present in the original sol is, however, 0.04405 *N*, and nearly all of this, namely, 0.0439 *N* chloride, is an integral part of the colloid particles and their compensating ions. Similarly, of the total specific conductivity of the sol, 5.70×10^{-4}, 5.40×10^{-4} would be the proper conductivity of the colloidal particles and their opposite chlorine ions. In one liter of sol there were 0.912 gram equivalent of iron and 0.04405 gram equivalent of chlorine.

Discussion of Results

The conceptions arising in the present work are illustrated diagrammatically in Fig. 2. Here the membrane, impermeable to one colloidal species only, is represented by a wavy line. Dialysis or Donnan membrane equilibrium is regarded as the limit of slow ultrafiltration. For the sake of clarity only one colloidal particle is indicated by an aggregation of four adjacent positive charges and only the distribution of a single diffusible ion, in this case hydrogen ion, is indicated. The positive particle is surrounded by a domain influenced by its concentration of charges. Although this domain has no definite boundary and the influence falls off with distance according to the well-known exponential formula of Gouy, Chapman, Debye and Hückel, it is indicated for diagrammatic purposes by a dotted enclosure. There are thus three regions distinguished: first, that within the domain of the colloidal charges; second, the intermicellar liquid; and third, the dialyzate or ultrafiltrate.



(a) Dialysis or osmotic (membrane) equilibrium; infinitely slow ultrafiltration.

(b) Moderately slow ultrafiltration.

(c) Rapid ultrafiltration.

Fig. 2.—The effects of Donnan equilibrium within a colloidal sol or electrolyte upon the distribution of *P*H (or other ion) and upon the results of ultrafiltration.

It is evident from Fig. 2a that all three regions are of different hydrogen-ion concentration, that of the dialyzate being calculable according to the usual Donnan formula for membrane equilibrium based on the average concentration of the other two. The three regions are, therefore, designated in order of decreasing concentration, $C_{H^+}+$, C_{H^+} and $C_{H^+}-$. It is obvious that the dialyzate has not the composition of the intermicellar liquid, contrary to the common assumption mentioned in the fourth paragraph of this paper. There is, however, one intermediate rate of ultrafiltration for which the concentration of the ultrafiltrate will be that of the intermicellar liquid, as shown in Fig. 2b. For slower ultrafiltration the results will lie between those of Figs. 2a and 2b.

For more rapid ultrafiltration the results will tend toward that illustrated in Fig. 2c. In other words, when ultrafiltration is pushed as rapidly as possible, it will encroach upon all regions of the solution and more nearly represent the average cross-sectional concentration of the filterable constituents within the sol. This well accounts for the low concentration of ultrafiltrate obtained in quick ultrafiltration and the relatively high concentrations obtained with slow ultrafiltration and dialysis.

Even in the most rapid ultrafiltration, owing to the enormous electrostatic forces otherwise involved, there must remain with the colloidal charges an equal number of oppositely charged free ions which cannot be filtered. This then does not affect the argument. The *P*H of a very rapidly obtained ultrafiltrate must be less than that of the original "ferric hydroxide" sol. In our work the *P*H of sol 13[9] corresponded to a hydrochloric acid concentration of 5.0×10^{-5} *N*, while from Table II it is seen that rapidly obtained ultrafiltrate contains only 2.8×10^{-5} *N*. At the other extreme the far higher concentration of 18×10^{-5} *N* was found for the dialyzate.

At first sight it might seem that even if the regions in the immediate neighborhood of colloidal particles were being encroached upon and robbed in rapid ultrafiltration, this might not greatly affect the total concentrations of ions passing through the filter, since the unequal distribution of positive ions in the domain of the positive colloid is offset by a similar unequal distribution of the same ions in the opposite direction in the neighborhood of the compensating negative ions such as the chloride ions in the present case. If the colloidal particles were monovalent, that is, each particle carried but one electrical charge, then indeed the effects of encroachment and the effects upon *P*H would disappear.

To produce the effects here uncovered two things are, therefore, necessary: first, that the particles are polyvalent; and, second, that the charges are close together.[12]

In the membrane equilibrium the hydrogen electrode gives the same potential for dialyzate and intermicellar liquid, the difference in concentration being offset by the membrane potential

$$E = \frac{RT}{F} \ln \frac{C_{H^+}+}{C_{H^+}}$$

---

[12] Compare J. W. McBain [THIS JOURNAL, **50**, 1636 (1928)] where it is shown that with the ionic micelle of soap solutions the ionic strength is essentially that only of a uni-univalent salt because of the very wide distance apart of the charges upon any one ionic micelle (20 Å.).

Similarly, the uniform electrode potential within a sol balances the difference of concentration near a colloidal particle as compared with that of the intermicellar liquid by that portion of the electrokinetic potential or potential of the ionic atmosphere embraced between the two points in question

$$\zeta = \frac{RT}{F} \ln \frac{C_{H^+}}{C_{H^+-}}$$

Of course, C_{H^+-} likewise varies from point to point within the domain of the colloidal particle.

It will be interesting to inquire whether these considerations account for the so-called Hammarsten effect. Hammarsten[13] in several instances found by electromotive force ionic concentrations that were not fully revealed in lowering of freezing point. We have just seen that the P_H in the neighborhood of positive charges is much less than that in the intermicellar liquid, although both give the same electrode potential, and that thus the concentrations as ordinarily obtained from e. m. f. measurements of colloids are partly fictitious. In this connection it should be pointed out that in our sols the domains of the colloidal charges almost or actually overlap. Thus in many colloidal sols there is no point at which there is true intermicellar liquid, and nowhere then will the real concentration equal the apparent P_H or C_{H^+}.

In conclusion, it should be mentioned that Maffia,[14] using a pressure of only a few millimeters, found 60 to 80% of the total conductivity in the ultrafiltrate for sols otherwise closely resembling sol 13. Wintgen and Biltz,[15] also working with sols similar to sol 13, used a pressure of one atmosphere, which gave fairly rapid rates with the membranes used. They found lower conductivities than did Maffia, but still about 30 to 60% of the total conductivity was found in the ultrafiltrate.

Variations in the concentration of the ultrafiltrate would be much less for sols with a higher ratio of simple electrolyte to colloidal electrolyte, for a Donnan equilibrium would then produce only a slight inequality in the distribution of the simple electrolyte. This may account for the failure of previous experimenters to observe such a variation, and for the assertions of Duclaux and Titeica[16] and of Kruyt, Roodvoets and van der Willigen[17] that the concentration of the ultrafiltrate is independent of the rate of ultrafiltration.

Additional Note

It has been very kindly pointed out to us that a graph of specific conductance against pressure is as satisfactory as that given against rate of ultrafiltration and that an alternative explanation might be that the

---

[13] E. Hammarsten, *Biochem. Z.*, **144**, 383 (1924); H. Hammersten, *ibid.*, **147**, 481 (1924).

[14] P. Maffia, *Kolloidchem. Beihefte*, **3**, 85 (1911).

[15] R. Wintgen and M. Biltz, *Z. physik. Chem.*, **107**, 403 (1923).

[16] J. Duclaux and R. Titeica, *Compt. rend.*, **189**, 101 (1929).

[17] H. R. Kruyt, A. C. W. Roodvoets and P. C. van der Willigen, "Colloid Symposium Monograph," 1926, Vol. IV, p. 304.

particles are carried down to the filter to form a highly hydrated gel-like mat which pressure might dehydrate, the process being continued by the arrival of new particles from the main body of the sol. This explanation is not, however, necessarily different from that which we have given, although we have stressed the electrical aspects which must exist. Every charged particle is surrounded by an ionic atmosphere, predominantly of opposite sign, and likewise by an atmosphere of polarized or loosely bound water. The two atmospheres in part coincide and overlap. When they are encroached upon through pressure or rapidity of filtration, the filtrate will be correspondingly diluted, as we have found. These atmospheres are spontaneously formed and will do work to maintain themselves. In the interionic attraction theory of electrolytes, about one-half of the lowering of equivalent conductivity as compared with that at infinite dilution is ascribed to this very effect. The forces involved are, therefore, enormous, being of the order of magnitude[18] of 10^5 kilograms per coulomb of charge for a linear movement of 0.02 cm. per minute as in the highest rate of ultrafiltration. Such reaction is evidently strong enough to push the charged particles away, and in fact the membrane does not become coated. Such movement (slippage or seepage) caused by relaxation of the ionic atmosphere would, of course, only take place when the particles became crowded in the immediate neighborhood of the ultrafilter. To discriminate further it will be necessary to carry out experiments with membranes differing greatly in degree of permeability, preferably using different kinds of membranes.

Summary

A series of ultrafiltrations was made with a fairly concentrated, very well dialyzed, ferric hydroxide sol. The concentration of the filtrate was found to vary many-fold with the rate of ultrafiltration, the most rapid rates yielding the lowest concentrations of ultrafiltrate, and a form of dialysis the highest concentration.

It is concluded that in slow ultrafiltration the ultrafiltrate approaches the Donnan membrane distribution due to the presence of charged colloids, whereas in very rapid ultrafiltration the regions immediately surrounding the colloidal particles are invaded and sampled. Thus the *P*H of a rapidly obtained ultrafiltrate is less than that of the sol of a positive colloid, whereas with very slow ultrafiltration it is much greater.

It is pointed out that neglect of these considerations necessitates a reinterpretation or recalculation of much of the existing data, not only of ultrafiltration but of the *P*H and C_{H^+} and ionic concentrations within all colloidal sols.

STANFORD UNIVERSITY, CALIFORNIA

RECEIVED AUGUST 13, 1932
PUBLISHED APRIL 6, 1933

---

[18] M. Le Blanc, "A Text-book of Electro-chemistry" (translation by W. R. Whitney and J. W. Brown), The Macmillan Co., New York, 1920, p. 124; seventh German edition (O. Leiner, Leipzig, 1920), p. 117.