

to the Director of the Ryerson Physical Laboratory of the University of Chicago for the use of indispensable apparatus and instruments; and especially to E. I. DuPont de Nemours and Co. for the establishment of a research fellowship under the tenancy of which by one of us much of this work was done.

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## CLAY AS AN AMPHOLYTE

BY OLOF ARRHENIUS

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Most soil scientists know that alkali soils during filtration cause serious troubles, because the extract is grayish or turbid. Furthermore, it is a well known fact that alkali stabilizes, whereas acid peptizes the soil suspensions.

The rate of settling of soil suspensions plays a great role in mechanical soil analysis, and there has been much discussion on this subject, such as that between Rohland<sup>1</sup> and Maschhaupt,<sup>2</sup> in which the divergences were great and both were right. Rohland points out that the same addition of alkali or acid does not cause the same effect in suspensions of different soils and Maschhaupt finds that alkali first stabilizes and then suddenly peptizes the suspensions.

It is very probable that the actual acidity of the suspension, the hydrogen-ion concentration, plays the greatest role, rather than the amount of acid or alkali added. From this point of view it is not astonishing that the authors mentioned above and several others have not been able to find a satisfactory explanation. The conception of the soil as a buffer is a rather recent one,<sup>3,4</sup> but only when one assumes this buffer action is one able to understand why some soils change their reaction markedly and others not at all when the same amount of acid is added to each.

In order to ascertain the influence of the hydrogen-ion concentration and compare it with that of the amounts of alkali and acid added, the following experiment was carried out.

Two clay soils, one used for brick-making, with a Sørensen value ( $P_H$ ) of 7.5 and another, a peaty clay with a Sørensen value of 5.0, were used for making up the suspensions. Two hundred and fifty cc. portions of each suspension (100 g. of clay in 5 liters of water) were placed in glass cylinders; alkali or acid was then added and the different lots filled up to the same volume, 350 cc. The suspensions were then shaken and left

<sup>1</sup> Rohland, *Landw. Vers. Sta.*, 1914, 85.

<sup>2</sup> Maschhaupt, *ibid.*, 1914, 83.

<sup>3</sup> Bjerrum, *Landbo og Veterinaerhøisk. Aarskr.*, 1917.

<sup>4</sup> Arrhenius, *Soil Science*, 1922.

to settle. After definite intervals of time, the heights of the clear columns were measured. The data thus obtained are shown in the table below.

TABLE I

		Brick Clay		Peaty Clay	
Ce. of acid	Ce. of alkali	Sørensen value	Settling rate cc./hour	Sørensen value	Settling rate cc./hour
100 (HCl)	...	...	...	0.5	3.0
20	...	2.5	38	...	..
10	...	...	...	2.5	2.5
9	...	...	...	2.7	2.0
8	...	...	...	3.1	1.5
7	...	...	...	3.4	0.5
6	...	3.8	25	3.8	0.5
5.5	...	4.0	33	...	...
5	...	4.2	38	4.0	0.5
4.5	...	4.3	48	...	...
4	...	4.5	39	...	...
3.5	...	4.9	36	...	...
2	...	6.2	13	4.2	1.0
1	...	...	...	4.3	2.0
0.5	...	...	...	4.5	1.0
0	0	7.5	0.3	5.0	0.1
...	4.5	8.4	0.1	6.7	0.05
...	9	10	0.001	7.5	0.01
...	11	11	0.1	...	...
...	13.5	12	1.4	...	...
...	18	...	...	8.4	0.001
...	27	12.5	25	...	...
...	40	...	...	9	0
...	90	...	...	11	0.5
...	140	...	...	12	2.0

With the data given in this table the curves have been constructed. It is easily seen that the curves are very similar. Beginning on the acid side there is a decrease in the rate of settling and the curve sharply bends over into an increasing branch till the iso-electric point is reached (the maximum rate). Then, with lower hydrogen-ion concentration the suspension is more and more stabilized and thus the settling rate reaches a minimum, after which at high alkalinity the rate increases decidedly again.

Wilson and Heisig<sup>5</sup> found the same type of curve as far as their experiments went for sewage sludge when measuring the influence of hydrogen-ion concentration on the rate of filtration.

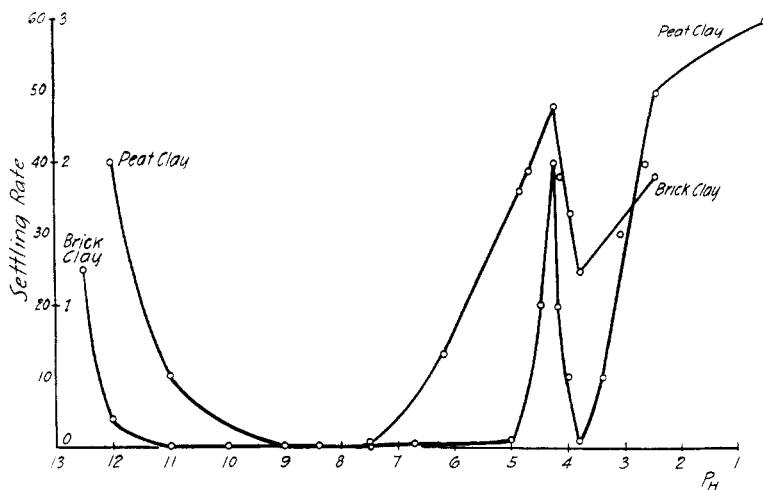
It is interesting that this curve is almost the same as that for the swelling of gelatin, showing that the clay acts as an ampholyte just as does gelatin.

<sup>5</sup> Wilson and Heisig, *J. Ind. Eng. Chem.*, **13**, 406 (1921).

and therefore the course of the curve may be explained by the help of the Donnan equilibrium as shown in Loeb's interesting experiments.<sup>6</sup>

If the clay indeed acts as an ampholyte, it should combine stoichiometrically with acids and bases as shown by Loeb. This is actually the case. When using sulfuric acid the rate of settling is double that when using phosphoric acid, hydrochloric or oxalic acid, which is in full agreement with Loeb's investigations.

Another proof of this theory is drawn from Rohland's<sup>1</sup> paper. He mentions that it is impossible to compare the adsorption of different dyes caused by soils, because they are adsorbed to different extents. He points



out that Vesuvium solution is decolorized by about 15 g. of clay, three times as much as required by an equal amount of Victoria blue. Beilstein's "Handbuch" gives the molecular weight of Vesuvium as 227, whereas Victoria blue has that of 505. The ratio between these two is 2.0, which is quite near the ratio given above, considering the big errors involved in these experiments. The author has found in some preliminary experiments that indicators are "adsorbed" by the same clay in proportion to their molecular weight. Whitney and Ober<sup>7</sup> found that colloidal arsenic trioxide when precipitated with calcium, strontium or barium chloride "adsorbed" 39, 77 and 152 parts of the cations as compared with the atomic weights 40, 88 and 137.

Thus Loeb's assumption that ampholytes combine with acids or bases in stoichiometrical proportions holds also for the mineral ampholytes of the soil. The facts here shown may have a revolutionary effect on our conception of the soil and the soil conditions. We may dispense with such

<sup>6</sup> Loeb, *J. Gen. Physiol.*, 1920, 1921.

<sup>7</sup> Whitney and Ober, *Z. physik. Chem.*, 41, 379 (1902).

convenient words as adsorption used by the colloid chemists, since we see that purely physico-chemical laws find application to mineral colloids also, in this case the soil. The word colloid will then mean only a particle of special dimensions and not of special properties.

### Summary

It has been shown that clays of different origin and different reaction have the same iso-electric point and the curve obtained by plotting rate of settling against the hydrogen-ion concentration has the same course as that of gelatin. The clay acts as an amphoteric electrolyte and can therefore combine with either acid or base. This is also shown by the buffer action of the clays. The result is important theoretically, as well as practically.

The work has been carried out in the Laboratory of Plant Physiology of Harvard University. To Professor Osterhout I express my warmest thanks for his kind help and suggestions.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

## SOLID THALLIUM AMALGAMS AND THE ELECTRODE POTENTIAL OF PURE THALLIUM

By THEODORE W. RICHARDS AND CHARLES P. SMYTH

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This investigation was undertaken for the purpose of ascertaining the cause of the potential difference recently found to exist between pure thallium and saturated thallium amalgam. Several earlier investigators concluded that, as in the case of zinc, the solid phase in equilibrium with the liquid in the 2-phase amalgam consists of pure solid metal,—the solubility of mercury in solid thallium being regarded as practically zero, when, of course, the potential of the 2-phase amalgam would be identical with that of pure thallium. Lewis and von Ende,<sup>1</sup> in their excellent determination of the potential of the thallium electrode, assumed this to be the case, and used, in place of a pure thallium electrode, a 55% amalgam consisting of 2 phases. The basis for their assumption was the thermal analysis of Kurnakov and Puschin,<sup>2</sup> the electromotive force measurements of Sucheni,<sup>3</sup> and experiments of their own.

The experimental precautions employed, however, were evidently not adequate to prove the point, for the work of recent Harvard investigators

<sup>1</sup> Lewis and von Ende, *THIS JOURNAL*, **32**, 732 (1910).

<sup>2</sup> Kurnakov and Puschin, *Z. anorg. Chem.*, **30**, 86 (1902).

<sup>3</sup> Sucheni, *Z. Elektrochem.*, **12**, 726 (1906). See also Spencer, *ibid.*, **11**, 681 (1905).