LXIII.—*The Soluble Alkaline-Earth Aluminates.*

By HUBERT THOMAS STANLEY BRITTON.

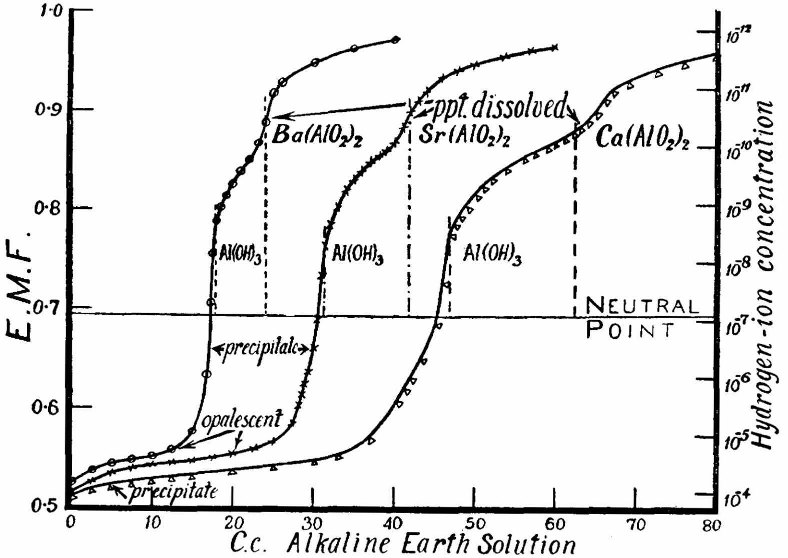
It is often stated that the aluminates of calcium, barium, and strontium are very sparingly soluble in water. Thus Marais (*Soil Science*, 1922, **13**, 368) asserts that lime removes alumina from a " soil solution " as a very sparingly soluble calcium aluminate, $Ca_3Al_2O_6$. Alumina, besides being present in soil solutions of which the hydrogen-ion concentrations are greater than that at which aluminium hydroxide begins to be precipitated, *viz.*, $10^{-4\cdot2}$ (compare Britton, J., 1925, **127**, 2121), is sometimes found in slightly alkaline soil solutions, of p_H about 9 (Magistad, *Soil Sci.*, 1925, **20**, 181). Pollard and Keast (private communication) found that it passed into the soil solution at p_H 7·7—8·6, as the result of treating soil with slaked lime, and, moreover, they observed that the aluminium content increased with the calcium content. It was suspected that the explanation lay in the formation of a soluble calcium aluminate. In order to test this supposition, the following titrations of dilute solutions of aluminium salts were carried out with solutions of each of the alkaline earths, the concentrations of which are given in Table I, and the changes in hydrogen-ion concentration were determined by means of the hydrogen and normal calomel electrodes, in the manner described in previous papers (J., 1924, **125**, 1572; 1925, **127**, 2110), the junction being a saturated solution of potassium chloride. The temperature was 20°.

The curves (see Fig. 1.) are similar to that obtained by using sodium hydroxide (J., 1925, **127**, 2121). The p_H's at which precipitation began in the three reactions are widely different, although those sections of the three curves which correspond to the formation of aluminium hydroxide cover approximately the same variation in hydrogen-ion concentration. Thus in the lime titration, in which the sulphate was employed, precipitation began when only

TABLE I.

Reactant.	Solution : 100 c.c. of	Precipitation began at		Precipitate dissolved at	
		p_H.	Equivs. alkali per atom Al.	p_H.	Equivs. alkali per atom Al.
0·0447N-$Ca(OH)_2$.	0·00349M-$Al_2(SO_4)_3$.	4·14	0·32	10·17	3·90
0·0558N-$Ba(OH)_2$.	0·00333M-$AlCl_3$.	Opalescent.			
		4·76	2·09		
		Coagulated.			
		6·50	2·71	10·43	4·02
0·0391N-$Sr(OH)_2$.	0·00408M-$AlCl_3$.	Opalescent.			
		4·69	1·92		
		Coagulated.			
		6·50	2·88	10·60	4·02

FIG. 1.



0·32 equiv. of alkali per atom of aluminium had been added, whereas in both the strontia and baryta titrations, in which aluminium chloride was used, the solutions remained clear until 2·09 equivs., p_H 4·76, and 1·92 equivs., p_H 4·69, respectively, of alkali had been added; only opalescence was then produced, coagulation of the precipitates not occurring until 2·71 and 2·88 equivs., respectively, had been added, and a considerably higher p_H attained, *viz.*, 6·5. This delay in precipitation, despite the fact that the requisite precipitation p_H, 4·14, had been exceeded, and that nearly the total stoicheiometrical quantity of alkali had been added, is due to the characteristic tendency of chlorides to promote the formation of colloidal solutions—the dispersed particles formed in the initial stage of the reactions being too small to affect the appearance of the solution to the unaided eye. A similar instance is that of the chloride and sulphate of zirconium (Britton, J., 1925, **127**, 2125).

The solutions became neutral when the alkaline earths had been added in amounts slightly less than those required for the formation of aluminium hydroxide owing to the retention by the precipitates of some of the acid radical present in the original salts. In each of the titrations, the precipitates redissolved completely when approximately another equivalent of alkaline earth had been added, the dissolutions being reflected in the characteristic aluminate inflexions of the titration curves extending over a p_H range from 8 to 10·5. Magistad's results (*loc. cit.*) on the solubility of alumina in sodium hydroxide solutions of varying p_H are important in that they show that the solubility first becomes perceptible at p_H 7·55, being then 2 parts per million; at p_H 8·35, the solubility is 8·4 parts, but thereafter it increases rapidly to 34·6 parts per million at p_H 8·95. In a natural soil solution it was 31·0 parts per million at p_H 9·01. Hence it appears probable that the formula $M^{\cdot\cdot}(AlO_2)_2$ represents the type of combination in which the alkaline earths and alumina exist in solution.

It should be mentioned that in the calcium titration a fine precipitate containing both calcium and aluminium began to separate at p_H 11·7 when 90 c.c. of lime water had been added. It follows, therefore, that the disappearance of alumina from " soil solutions " cannot be attributed, as Marais states, to the formation of an insoluble calcium aluminate, for the hydrogen-ion concentration of ordinary " soil solutions " never becomes so low as p_H 11·7. No precipitates were formed in the other two titrations, even although large excesses of the reactants were added. The conditions under which the solid aluminates of barium may exist have recently been investigated by Malquori (*Gazzetta*, 1926, **56**, 54).

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON.
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