CCCXCII.—*The Amphoteric Nature of Aluminium Hydroxide.*

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THE amphoteric nature of aluminium hydroxide has been established by measurements of the hydrogen-ion concentrations prevailing during the precipitation of the hydroxide and its subsequent dissolution in excess alkali (Hildebrand, *J. Amer. Chem. Soc.*, 1913, **35**, 847; Blum, *ibid.*, p. 1499; Britton, J., 1925, **127**, 2120). However, other experiments, and especially the somewhat scanty conductivity data, have not always supported this view. Thus, Chatterji and Dhar (*Trans. Faraday Soc.*, Colloid Symposium, 1920, 122) state that the addition of aluminium hydroxide to sodium hydroxide solution causes no "appreciable change" in the conductivity, a statement with which we do not agree, and conclude that the solution of aluminium hydroxide in alkalis is a case of true peptisation. On the other hand, Hantzsch (*Z. anorg. Chem.*, 1902, **30**, 289), also as a result of conductivity measurements, concludes that an aluminate, $NaAlO_2$, is formed which is afterwards hydrolysed to a hydrosol and is ultimately precipitated as crystalline aluminium hydroxide. Slade and Polack (*Trans. Faraday Soc.*, 1914, **10**, 150) hold the view that the hydrolysis of sodium aluminate produces crystalline aluminium hydroxide directly, without the intermediate colloidal phase, but that the crystals do not separate until nuclei are provided. Recently, Prasad, Mehta, and Joshi (*J. Indian Chem. Soc.*, 1930, **7**, 973) found that the conductivity of dilute solutions of sodium hydroxide is considerably depressed by the addition of aluminium hydroxide, and they concluded that no definite aluminate exists in dilute solutions. In more concentrated solutions, however, they interpret their results as indicating the formation of Na_3AlO_3. In some of these experiments the aluminium hydroxide was prepared by precipitation and subsequent washing until the filtrate gave no test for chloride or sulphate, but since aluminium hydroxide is known to exhibit strong adsorption of electrolytes, it is very doubtful whether this is a satisfactory process.

There is no record of any investigation of this problem by means of a conductometric titration; as this has given valuable information in other problems, such a titration was therefore carried out.

EXPERIMENTAL.

100 C.c. of a solution of 0·003125M-$Al_2(SO_4)_3$ were titrated with 0·2N-sodium hydroxide, the specific conductivity, κ, at 25° being measured at frequent intervals during the titration. The apparatus was that used in previous work (J., 1930, 1249, 1261, 2154). The following table contains a representative selection of the conductivities measured at different titres.

NaOH, c.c.	0	0·5	1·0	1·5	2·0	4·0	7·0	7·5	8·0	8·5	9·0	9·5	10·0	11·0	12·0	12·5	13·0	15·0	20·0
$\kappa \times 10^{-3}$	0·96	0·98	1·00	1·03	1·07	1·23	1·47	1·52	1·59	1·69	1·76	1·82	1·88	2·00	2·11	2·16	2·28	2·94	4·69

Sufficient alkali was added to give an excess over that required to form $Al(ONa)_3$, and then the solution was back-titrated with 0·2N-hydrochloric acid. The two titration curves so obtained are shown in Fig. 1, the alkaline titration of aluminium sulphate being represented by the lower curve B proceeding from left to right, and the acid back-titration by the curve A proceeding from right to left. During the precipitation of aluminium hydroxide with alkali, sodium sulphate is formed, and the calculated specific conductivity due to this salt at different titres is shown by the curve D. The difference between curves B and D, represented by C, therefore gives the conductivity at different titres due to the aluminium salts in solution. These curves show that at 9·0 c.c. the conductivity of the solution is accounted for solely by sodium sulphate. This is the end-point of the precipitation, and further addition of alkali results in redissolution of the aluminium hydroxide.

The foregoing results are reproducible.

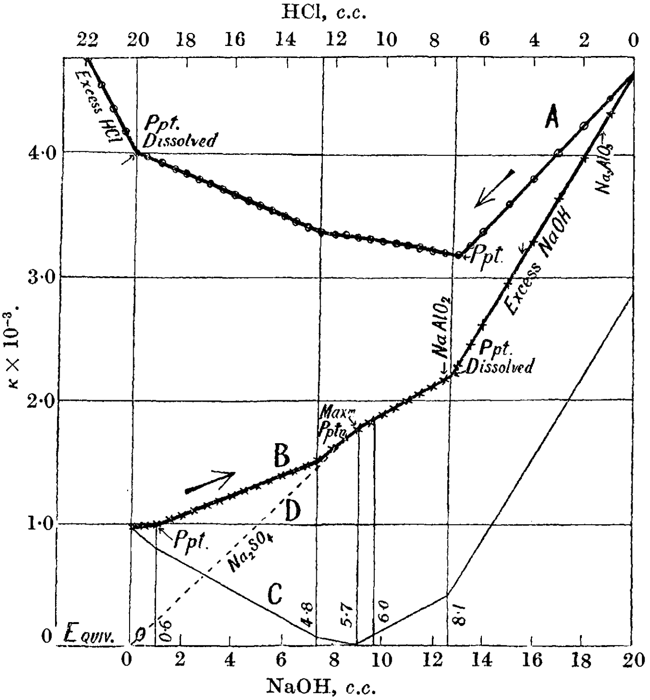
Discussion.

An examination of curves B or C reveals five distinct processes, three of which are concerned with precipitation, one with redissolution, and one with the addition of excess alkali, *viz.*:

(I*a*) Up to the addition of 1 c.c. of alkali [= 0·64 equiv. of alkali per mol. of $Al_2(SO_4)_3$], no precipitation occurs. A soluble basic sulphate having the composition $Al_2O_3,2{\cdot}68SO_3$ is therefore formed whose equivalent conductivity must be lower than that of the normal sulphate. Britton (*loc. cit.*) found that precipitation began when the solution corresponded to $Al_2O_3,2{\cdot}65SO_3$.

(I*b*) Between 1 and 7·5 c.c. there is precipitation of a basic sulphate, this process being complete at 4·80 equivs. of alkali, corresponding to a precipitate of composition $Al_2O_3,0{\cdot}60SO_3$. Williamson (*J. Physical Chem.*, 1923, **27**, 284) found that precipitates formed by the addition of 2—4 equivs. of alkali had the composition $Al_2O_3,0{\cdot}6SO_3,3H_2O$, and Miller (*U.S. Public Health Reports*, 1923, **38**, 1995) found that even up to 5 equivs. of alkali the precipitate was of this composition.

FIG. 1.



(I*c*) A change in direction occurs in the curves at 7·5 c.c., the conductivity due to the aluminium salts decreasing to zero at 9·0 c.c. (= 5·76 equivs.) of alkali, the precipitate then having the composition $Al_2O_3,0{\cdot}12SO_3$. Britton found that the final precipitate had the composition $Al_2O_3,0{\cdot}15SO_3$, and Miller showed that maximum insolubility occurred at 5·5 equivs., corresponding to $Al_2O_3,0{\cdot}25SO_3$.

(II) Redissolution of aluminium hydroxide begins at 9·0 c.c. and is complete at 12·7 c.c. (= 8·12 equivs.) of alkali. Therefore, little doubt can be entertained but that a sodium aluminate is formed of composition $NaAlO_2$. The specific conductivity of the solution at the point of complete dissolution, after allowance is made for the conductivity of the sodium sulphate, leads to a value for the equivalent conductivity of sodium aluminate of approximately 60. Slade and Polack (*loc. cit.*) found an equivalent conductivity of about 54 at 16° with a solution 0·1383N with respect to sodium.

(III) Beyond 12·7 c.c. of alkali, a rapid increase in conductivity occurs which is characteristic of free sodium hydroxide. The observed conductivity at 20 c.c. is 0·00469 mho, that calculated on the assumption that 7·3 c.c. of alkali are present along with sodium aluminate and sodium sulphate being 0·00480 mho; the difference is certainly to be accounted for by a repression of the hydrolysis of the aluminate and of the ionisation of the unhydrolysed aluminate. There is no discontinuity in the curve at the points corresponding to Na_2HAlO_3 or Na_3AlO_3, although according to Prasad, Mehta, and Joshi (*loc. cit.*), a minimum equivalent conductivity is observed in concentrated solutions in which the Na/Al ratio is 3 : 1. These investigators, however, used solutions prepared by boiling aluminium hydroxide with sodium hydroxide solutions; moreover, since the former was prepared by precipitation, it is doubtful whether it was completely free from adsorbed electrolytes.

The back-titration with hydrochloric acid leads to the conclusion that these reactions are reversible, since the difference in conductivity between the curves A and B at any titre agrees at all points with that calculated for the requisite amount of sodium chloride. Owing to the fact that higher conductivities are being measured, however, some of the finer details in the direct titration curve of aluminium sulphate are lost.

The reactions between aluminium sulphate and sodium hydroxide may be summarised thus :

$$Al_2O_3,3SO_3 \longrightarrow \underset{\text{(soluble)}}{Al_2O_3,2{\cdot}68SO_3} \longrightarrow \underset{\text{(insoluble)}}{Al_2O_3,0{\cdot}6SO_3} \longrightarrow$$

$$\underset{\text{(maximum insolubility)}}{Al_2O_3,0{\cdot}12SO_3} \longrightarrow NaAlO_2.$$

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