On soil genesis in temperate humid climate. V. The formation of the "albic" and "spodic" horizon

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Summary

With the aid of parahydroxybenzoic acid as a model substance some suggestions are reported on the formation of the albic and spodic horizon. The acid forms soluble complexes with iron whereas insoluble compounds are formed with aluminium. The stability constants of the iron complexes and the solubility product of the aluminium complex has been determined. Hydrolysis of the iron complexes (formed in the A-horizon) and the formation of an insoluble aluminium complex are considered as the most important mechanisms in the formation of the B_{2ir}- and B_{2h}- horizon respectively.

1. Introduction

It was concluded from many analyses, some of which were published in part I of these series (1962), that soils with an albic and spodic horizon were formed under Dutch climatic and well-aerated conditions in very poor, acid parent materials (silt content of 12 % or less; clay content of 2 % or less; the sand fraction is predominantly composed of quartz). The characteristics of these soils can be summarized as follows: 1. the albic horizon has been deprived of iron and aluminium, but more of the former than of the latter; 2. the horizon of maximum organic-matter accumulation (B_{2h}) is generally also the horizon of maximum Al-accumulation, while its Fe_2O_3-content is lower than that of the C-material; 3. the horizon of maximum iron accumulation (B_{2ir}) immediately below the B_{2h}-horizon has a much lower organic-matter content; 4. the high organic-matter content of the B_{2h}-horizon is not only caused by an accumulation of organic matter dispersed in the A-horizon, but also by the sometimes dense root growth in this horizon (see prof. V, part I, 1962); 5. soil-animal activity is very low; 6. below the B-horizon several narrow bands can be observed. The upper bands are micro B-horizons, the upper half millimetre having the colour of the B_{2h}- horizon and the lower half millimetre that of the B_{2ir}- horizon. The lower bands have only one colour, *i.e.* that similar to the B_{ir}- horizon; 7. as a whole can be stated that in podzol formation Fe moves to greater depths than Al; this is in contradiction to a statement of WRIGHT and SCHNITZER, 1963.

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It is the purpose of this paper to throw some light on the formation of these horizons with the aid of results published by several authors and the results of own experiments.

2. The formation of the albic horizon

A priori, three mechanisms can be responsible for the transport of Fe and Al, the merits of which were discussed by STOBBE and WRIGHT (1959), *viz.* 1. transport in ionic form; 2. transport in colloidal form (AARNIO, 1913; MATTSON and GUSTAVSON, 1937; BARBIER, 1938; MATTSON and KOUTLER–ANDERSSON, 1942; REIFENBERG, 1947; RODE, cited by JOFFE, 1949; DEB, 1950; HERBILLON and GASTUCHE, 1962a and b); 3. transport as metallo-organic complexes (for references, see STOBBE and WRIGHT, 1959; WRIGHT and SCHNITZER, 1963).

In this paper the authors only consider the processes 1. and 3., not because they deny the existence of process 2., but because they want to examine whether the characteristics, found in podzol soils, can be explained when processes 1. and/or 3. are proceeding.

2.1. Transport in ionic form

To answer the question whether the removal of sesquioxides from the A-horizon in well-aerated parent materials can be the result of the transport of the metals in ionic form, the systems iron-hydroxide (s) — water and aluminium-hydroxide (s) — water have to be studied. In the first system the following equilibria occur (using for convenience a notation neglecting the hydration of the ions and the possible occurrence of polymers):

$$Fe(OH)_3\ (s) \rightleftharpoons Fe^{3+} + 3\ OH^- \text{ with } pK_{so} = pFe + 3\ pOH = -38.20\ (20°\ C)$$

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \text{ with } p^*K_1 = pFeOH + pH - pFe = -2.14$$

$$FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^+ + H^+ \text{ with } p^*K_2 = pFe(OH)_2 + pH - pFeOH = -4.70$$

(The constants were taken from BJERRUM, SCHWARZENBACH and SILLÉN, 1958).

From these relations the total ferric-ion concentration can be calculated at different pH-values. TABLE 1 shows the results (the activity coefficients are calculated with the DEBYE-HÜCKEL formula, as effective ionic radii using those reported by KIELLAND, 1937; *ionic strength of the systems was assumed to be* 5×10^{-4} M/l).

TABLE 1. Total ferric-ion concentration (as mol/l and g/l) of the system $Fe(OH)_3(s)$ aqueous-dilute acid solution

pH	$c_{Fe(tot.)}$ mol/l	$c_{Fe(tot.)}$ g/l
4.0	6.98×10^{-7}	3.91×10^{-5}
4.5	9.41×10^{-8}	5.27×10^{-6}
5.0	1.72×10^{-8}	0.96×10^{-6}
5.5	4.21×10^{-9}	2.36×10^{-7}
6.0	1.21×10^{-9}	6.78×10^{-8}

The question whether this process is responsible for the removal of iron from the A-horizon of podzols, can only be answered provided something is known about the losses that generally occur under Dutch climatic and well-aerated conditions. It can be stated that the A-horizon (with a mean pH-value of 4) has lost roughly 1 % and 3 % by weight of Fe_2O_3 and Al_2O_3 respectively. The A-horizon has generally a thickness of 40 cm and a porosity of 40 %. The pH-value of the B-horizon is roughly 4.5 and of the C-horizon 5 to 5.5. The maximum age of the soils is about 15,000 years for those formed in old aeolian sands and 9,000 years for those developed in young aeolian sands (see: Edelman and Maarleveld, 1958).

As no changes in volume are likely to occur during the formation of these soils because the sands are closely packed and animal activity is extremely low, it can be calculated that 1 dm^2 of the A-horizon has lost: 3/5 (volume of the solid phase) × 4 (volume in litres of 1 dm^2 A-horizon with 40 cm thickness) × 2.5 (specific weight) × 0.01 (1 % Fe_2O_3) = 0.060 kg of Fe_2O_3. This is 42.0 g Fe/dm^2. In cases of sandy soils and forest vegetation about 1/3 of the rainfall (750 mm a year) percolates through the soil. Hence, 2.5 l of water drains through 1 dm^2 and can dissolve every year (see table 1) $2.5 \times 3.91 \times 10^{-5}$ g of Fe at pH 4 and $2.5 \times 0.96 \times 10^{-6}$ g of Fe at pH 5, if equilibrium is established between the solid material and the draining water. Consequently, $\frac{42.0}{9.78 \times 10^{-5}}$ and $\frac{42.0}{2.40 \times 10^{-6}}$ years are needed to remove 42.0 g of Fe/dm^2 from the A-horizon at pH 4 and 5 respectively. This is roughly 430,000 years at pH 4 and 17,400,000 years at pH 5. It can easily be concluded that this mechanism can not explain the removal of iron oxide from the A-horizon in podzols, as these soils have a maximum age of 15,000 years in the Netherlands.

It is possible to set up the same calculation for Al_2O_3. The system $Al(OH)_3$ (s) — water is governed by the following equilibria (again using a notation neglecting hydration and neglecting the occurrence of polymers):

$$Al(OH)_3\,(s) \rightleftharpoons Al^{3+} + 3\,OH^- \text{ with } pK_{so} = pAl + 3\,pOH = -32.30\ (25^\circ\,C)$$

$$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+ \text{ with } p^*K_1 = pAlOH + pH - pAl = -5.05$$

$$AlOH^{2+} + N_2O \rightleftharpoons Al(OH)_2^+ + H^+ \text{ with } p^*K_2 = pAl(OH)_2 + pH - pAlOH = -4.71$$

$$Al(OH)_3\,(s) + H_2O \rightleftharpoons Al(OH)_4^- + H^+ \text{ with } p^*K_{s4} = pAl(OH)_4 + pH = -12.70$$

The constants were taken from Raupach (1962a and b) and Bjerrum, Schwarzenbach and Sillén (1958).

From these relations the total Al-ion concentrations can be calculated at different pH-levels. The results are given in table 2.

Table 2. Total Al-ion concentration (in mol/l and g/l of the system $Al(OH)_3$ aqueous-dilute acid solution

pH	$c_{Al(tot.)}$ mol/l	$c_{Al(tot.)}$ g/l
4.0	6.92×10^{-3}	1.87×10^{-1}
4.5	2.54×10^{-4}	6.86×10^{-3}
5.0	2.10×10^{-5}	5.67×10^{-4}
5.5	3.80×10^{-6}	1.03×10^{-4}
6.0	1.21×10^{-6}	3.27×10^{-5}

In the same way as shown for iron, it can be calculated that for the removal of 3 % Al_2O_3 (= 95.3 g Al/dm^2) the time required is 204 years at pH 4 and 67,200 years at pH 5. It seems that the solubility of aluminium hydroxide is large enough to explain the removal of Al_2O_3 from the A-horizon. However, it is rather unlikely that it then accumulates in the B-horizon with a pH-value of 4.5. Hence, other factors are acting to allow alumina to accumulate. One of these factors may be the silicate ions which form insoluble alumino silicates with Al-ions.

Another factor may be the organic matter as it is possible that it forms an insoluble complex with aluminium. Point 2 of the introduction supports this possibility. It is therefore quite possible that another mechanism than the solubility of Al-hydroxide is responsible for the translocation of aluminium in the podzol profile.

2.2. Transport as metallo-organic complex

In recent years an ever increasing attention has been paid in soil science to the formation of complexes of metal ions and organic ligands. A review was given by MORTENSEN (1963), who concluded that more research has to be done on the identification of the organic-matter components to obtain full understanding of the chemistry of complexing of metals by organic matter. With respect to soil formation several authors have paid attention to this problem (for reviews see: STOBBE and WRIGHT, 1959; WRIGHT and SCHNITZER, 1963).

Very recently SCHNITZER and DESJARDIN (1962) succeeded to identify the organic matter extracted from the A_o- and B_h-horizon of a podzol. SCHNITZER and SKINNER (1963, a and b) studied the organic material of the B_h-horizon in particular and found that at pH 3 1 : 1 complexes were formed with iron and aluminium, whereas at pH 5 a 2 : 1 complex was formed with iron. They also obtained indications on the formation of 6 : 1 complexes, which were insoluble in water and suggest the formation of a range of molar complexes, varying from 1 : 1 to 6 : 1, and becoming increasingly water-insoluble as more metal is complexed. This is an extremely important observation as will be seen later. The present authors are of the opinion, although they cannot prove it, that the translocation of iron in particular is due to the presence of simple organic acids which are formed in the coarse of plant decomposition and can be expected to have but a transient independent existence in the soil. This idea was already put forward by GALLAGHER (1942/43) and GALLAGHER and WALSH (1943/44). The translocation of aluminium is, in the authors opinion, related to the formation of insoluble organic complexes and/or the solubility of alumino silicates (see later). Elaborating on this idea, the complexing properties of p-hydroxy-benzoic acid (pHBA) were studied. This acid can occur in the soil, as HENDERSON (1963) showed that it is a decomposition product of lignin. Although this acid is not stable, it may be important for soil formation because of the continual abundant supply of the soil with lignin.

The dissociation constants (K_1 and K_2) of this acid (pHBA $= H_2Z$) and the stability constant of the Fe- and the solubility product of the Al-complex were determined (see APPENDIX). The dissociation constants are: 0.37×10^{-4} and 0.45×10^{-9} respectively. The formation constants of the complexes FeZ^+ and $FeOHZ$ are: 0.26×10^{13} and 0.27×10^{12} respectively. The acid appeared to form an insoluble complex with Al-ions under the conditions of the experiments. The solubility product of the complex, AlOHZ, was: 0.15×10^{-20}. From these data the complex-ion concentrations of the system $Fe(OH)_3$ (s) — *e.g.* 10^{-4} M pHBA-solution can be calculated at different pH-values. Here it is assumed that the overall effect of organic matter on leaching of iron can be compared with the leaching effect of a 10^{-4} molar solution of pHBA. If we put activity coefficients in these dilute solutions equal to 1, the complex-ion concentration $c_{FeZ} + c_{FeOHZ}$ can be computed from:

$$K_{FeZ} = \frac{c_{FeZ}}{c_{Fe}\,c_Z} = 0.26 \times 10^{13} \text{ and } K_{FeOHZ} = \frac{c_{FeOHZ}}{c_{FeOH}\,c_Z} = 0.27 \times 10^{12}$$

$$\text{where: } c_{Fe} = c_H^3 \times 10^{3.8};\ c_{FeOH} = 10^{1.66} \times c_H^2;\ c_Z = \frac{10^{-4} - c_{FeZ} - c_{FeOHZ}}{\beta_H}$$

$$\text{and } \beta_H = 1 + \frac{c_H}{K_2} + \frac{c_H^2}{K_1 K_2}$$

The results are given in TABLE 3.

TABLE 3. Ferric-ion concentrations (M/l) in 10^{-4} M pHBA-solution in equilibrium with ferric hydroxide

pH	c_{Fe}	c_{FeOH}	$c_{FeZ} + c_{FeOHZ}$
4	0.63×10^{-8}	0.46×10^{-6}	0.15×10^{-4}
4.5	0.20×10^{-9}	0.46×10^{-7}	0.90×10^{-5}
5	0.63×10^{-11}	0.46×10^{-8}	0.43×10^{-5}

This TABLE clearly shows that the total-iron concentration in the system is greatly enhanced by the presence of pHBA. Furthermore it appears that the pH does not affect the complex-iron concentration so much as the ferric-ion concentration.

TABLE 3 shows furthermore that pHBA dissolves $0.15 \times 10^{-4} \times 56$ g Fe/l at pH 4 and $0.43 \times 10^{-5} \times 56$ g Fe/l at pH 5. Applying this to the podzol profile page 268/269, it appears that it would take $\frac{42.0}{21.0 \times 10^{-4}}$ years at pH 4 and $\frac{42.0}{6.02 \times 10^{-4}}$ years at pH 5 to remove 1 % Fe_2O_3 from the A-horizon. This is roughly 20,000 and 70,000 years respectively. At pH 4 a number of years is obtained that is close to reality. Of course a higher concentration of pHBA or other acids with larger formation constants will dissolve more iron and, consequently, a shorter time will be needed to bring about podzolization of the above-mentioned intensity.

The same calculations cannot be given for the Al-systems. It depends on the concentration of the acid and the pH-value whether the solubility of AlOHZ determines the Al-ion concentration in solution or that of $Al(OH)_3$. If the acid concentration is 10^{-4} M/l or smaller, then the Al-ion concentrations are controlled by the solubility product of $Al(OH)_3$. If the concentration of the acid is higher (*e.g.* 10^{-3} M/l), the solubility product of AlOHZ regulates the Al-ion concentrations. However, it is questionable whether free $Al(OH)_3$ can exist under conditions of high acidity and low organic-acid content. The authors are inclined to deny this possibility and they think it better to study the properties of the system of some Al-silicates (*e.g.* clay mineral) — water.

Summarizing, it can be stated that the leaching of iron can be readily understood by assuming the formation of soluble complexes with final, simple decomposition products of fresh organic material. The leaching of aluminium can be sufficiently explained by the solubility of the hydroxide. In this way the first part of point 1 of the introduction has been explained. The second part could be realised by assuming the formation of slightly soluble complex Al-compounds (such as occurs in the acid investigated), if conditions (moderate high concentration of the acid and not too acid a medium) are favourable.

3. The formation of the spodic horizon

From a physico-chemical point of view the accumulation of sesquioxides in the B-horizon can easily be understood. The soil solution loaded with the complexes formed in the A-horizon descends in the profile where pH-values are higher than in the A-horizon. A mere hydrolysis of the complex takes place and Fe- and Al-hydroxide is deposited, according to the overall reaction: –

$$MZ^{+} + 3\ OH^{-} \rightleftharpoons M(OH)_3 + Z^{2-},$$

where M represents Al or Fe. The extent of the hydrolysis depends on the formation constants of the complexes, the solubility of the hydroxides and the pH-level. It can easily be formulated that

$$K_h = \frac{1}{K_{MZ}\,K_{so}} \text{ or } (K_h)_H = \frac{1}{(K_{MZ})_H\,K_{so}},$$

where K_h and $(K_h)_H$ are the hydrolysis constant and apparent hydrolysis constant respectively, K_{MZ} and $(K_{MZ})_H$ are the formation and apparent formation constant respectively, and K_{so} is the solubility product of the hydroxide. The higher this constant is, the lower the pH at which the complex is hydrolyzed. In the case of our pHBA-complexes the logarithms of the hydrolysis constants are 24.8 and 26.8 for FeZ^{+} and FeOHZ respectively. This means that the complexes are easily hydrolysable and that a slight change in the pH is sufficient to cause a partial splitting off of iron hydroxide. With respect to this, an interesting point is the following. It is possible to calculate the amount of complex that has been percolated through the B-horizon. The pH at the lower boundary of the B-horizon is 5; in 20,000 years (that were needed to remove 1 % of Fe_2O_3 from the A-horizon at pH 4) there has been percolated (see TABLE 3): $20{,}000 \times 0.43 \times 10^{-5} \times 2.5 \times 56$ g Fe/dm^2 = 12.0 g Fe/dm^2. To this must be added the amount that dissolves from the precipitated Fe-hydroxide and equals to: $20{,}000 \times 0.20 \times 10^{-9} \times 2.5 \times 56 = 0.0006$ g Fe/dm^2, which is negligible. It can be concluded that 42.0 — 12.0 = 30.0 g of iron has been accumulated in the B-horizon as the result of a pH-gradient of only one unit.

Another interesting point is that there is still a certain amount of complex (amounting to the equivalent of 6.02×10^{-4} g of Fe/dm^2/year) present at pH 5 and this will percolate through the C-material unchanged if there is no pH-gradient in this material. However, as soon as some discontinuity occurs in the C-material (which is quite common in the wind-blown sands where the podzols in the Netherlands predominantly occur) with a higher pH-level, precipitation of iron hydroxide takes place. Again it is possible that not all of the complex is hydrolyzed; a part will then percolate further down in the profile and even some of the acid set free during the hydrolysis can complex some Fe and Al of the underlying material if the pH of this material is lower. At another discontinuity with a higher pH, hydrolysis takes place with the formation of a second micro B-horizon. It is evident, that in this way we support the viewpoint of ROBINSON and RICH (1960) that the formation of the micro B-horizons (point 6 of the introduction) is primarily determined by discontinuities in the parent material, which is the result of geological deposition. It is possible that in other parent materials the formation of bands in the subsoil and in the B-horizon of grey-brown podsolic soils are purely pedogenetic, as suggested by SMITH *et al.* (1950), FOLKS and RIECKEN (1956), TAVERNIER and SMITH (1957) and WURMAN *et al.* (1959), but this will be discussed in another paper.

The mechanism of accumulation proposed above cannot explain the accumulation of organic material in the B_h-horizon, as the organic acid set free by the hydrolysis moves downwards with the percolating water. It can be applied to the accumulation of iron in the B_{2ir}-horizon, because there is hardly any accumulation of organic matter in that horizon (the rather high values are undoubtedly also due to the many fine rootlets often present). The accumulation of Al_2O_3 in the B_h-horizon can only be explained by assuming that the Al-complexes are insoluble, as demonstrated to happen with pHBA. The observation mentioned in point 4 of the introduction suggests a high concentration of simple organic acids in the B-horizon with the subsequent precipitation of insoluble Al-complexes. It is also quite understandable that under certain conditions precipitation of the Al-complexes and hydrolysis of the Fe-complexes take place at the same depth, thus giving rise to the formation of B_h-horizons which are at the same time horizons of maximum Al- and Fe-oxide accumulation. In this respect it is important to mention the observations of SCHNITZER and SKINNER (1963, a and b) on the formation of insoluble poly-nuclear Fe- and Al-complexes.

The authors are fully aware of the fact that they have discussed the problem in too simple a way. They have not mentioned the possibility of reduction of iron when complexed to polyphenolic substances, as was, to the authors' knowledge, first proposed by MAYER (1903), nor have they pointed to microbial intervention, *e.g.* the deposition of sesquioxides by microbial attack of the organic ligand (*e.g.* HALVERSON and STARKEY, 1927; GALLAGHER, 1942/43; ARISTOVSKAYA, 1963). However, the soils studied have a very poor animal activity and it was for this reason that the authors tried to explain the phenomena in a simple, purely physico-chemical manner.

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APPENDIX. The determination of the dissociation constants of p-hydroxybenzoic acid and stability and solubility constants of its Fe- and Al-complexes respectively.

a. The determination of the dissociation constants

The constants were calculated from a titration curve of 100 ml of a solution, that was 0.002 M in pHBA and 0.1 M in KCl with a solution of 0.1 M NaOH and 0.1 M KCl. In this way ionic strength was kept nearly constant, while the Ag/AgCl-electrode could be used as reference electrode, thus avoiding diffusion potentials. A wide-range glass electrode of Metrohm was used as hydrogen electrode. This glass electrode was carefully checked against different buffers and over the pH-range 3 to 11 gave a potential difference of 58.0 mV/unit pH at a temperature of 23.5° C. This temperature was kept constant during the titration. The titration and electrode vessel was an all-glass assembly designed by the Metrohm factory. The curve was made with the aid of the Metrohm potentiograph E 336. Oxygen-free nitrogen gas was led through the solution for some time before the titration and during the titration. Also the first derivative curve was made with the potentiograph, obtaining in this way the exact inflexion point of the titration curve. They are represented in FIG. 1.

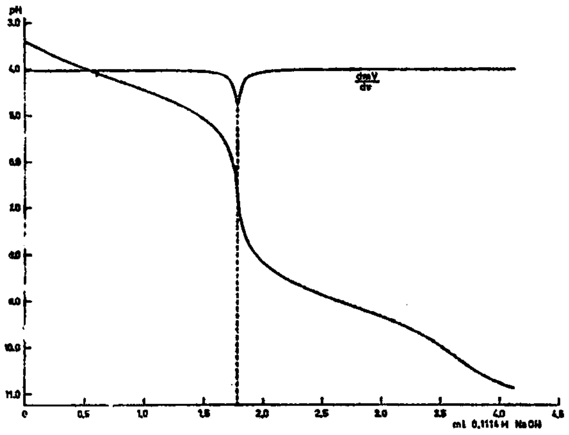

FIG. 1
Titration curve with first derivative of 100 ml 0.002 M p-hydroxybenzoic acid with 0.1 M NaOH

The FIGURE shows two well-separated buffer regions which simplified the calculation of the dissociation constants to such an extent that this could be done in the usual way. The activity coefficients were calculated with the DEBYE-HÜCKEL formula, using as ionic strength 0.1 M/l and as a_i (effective ionic radii) those reported in the paper of KIELLAND (1937). The activity coefficient of the non-dissociated acid was assumed to be 1. The results were:

$$K_1 = (0.369 \pm 0.028) \times 10^{-4}; \; K_2 = (0.451 \pm 0.036) \times 10^{-9}$$

For the calculations of the stability constants, the values 0.37×10^{-4} and 0.45×10^{-9} were used.

b. The determination of the stability constants and the solubility product

BERTIN-BATSCH (1952) found that iron and pHBA formed a 1 : 1-complex, FeZ^+, with the stability constant of 0.16×10^{16}. When repeating the experiments of BERTIN-BATSCH, we found an indication of another 1 : 1-complex, *viz.* FeOHZ. The experiments were conducted in the following way: solutions were prepared containing either 10^{-2} M $FeCl_3$ (or $AlCl_3$) + 10^{-2} M NapHBA, or 10^{-2} M $FeCl_3$ (or $AlCl_3$) + 3×10^{-2} M NapHBA, or 10^{-2} M $FeCl_3$ (or $AlCl_3$) + 5×10^{-2} M NapHBA. Of each of these solutions, which were made 0.01 M with respect to HCl, series were prepared with increasing concentrations of NaOH. The final volume was 50 ml. After being agitated for one night the solutions were centrifuged; the supernatant liquid was siphoned off and its pH-value and total Fe- or Al-concentration determined. The titration curves are represented in FIG. 2 and 3, the Fe- or Al-concentrations in dependence of pH in FIG. 4 and 5. As soon as a precipitate of iron hydroxide has been formed, the following relations can be formulated:

$$c_{\mathrm{FeZ}} + c_{\mathrm{FeOHZ}} = c_{\mathrm{Fe\ in\ solution}} - c_{\mathrm{Fe}} - c_{\mathrm{FeOH}} - c_{\mathrm{Fe(OH)_2}} - c_{\mathrm{FeCl}} \qquad (1)$$

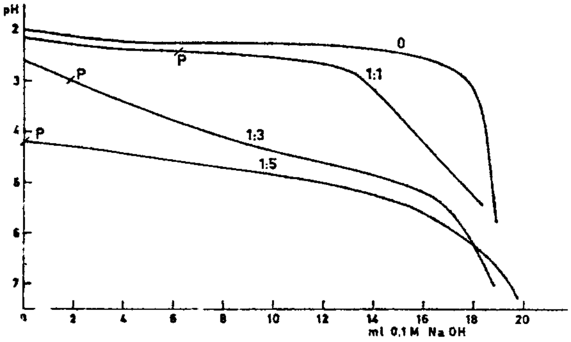

FIG. 2
Titration curves of $FeCl_3$-solution and of mixed solutions of $FeCl_3$ and p-hydroxybenzoic acid with 0.1 M NaOH. 0, 0.01 M $FeCl_3$ (0.01 M HCl); 1 : 1, 0.01 M $FeCl_3$ (0.01 M HCl) + 0.01 M pHBA-Na salt; 1 : 3, 0.01 M $FeCl_3$ (0.01 M HCl) + 0.03 M pHBA-Na salt; 1 : 5, 0.01 M $FeCl_3$ (0.01 M HCl) + 0.05 M pHBA-Na salt. All solutions had a final volume of 50 ml. P gives the position of beginning precipitation

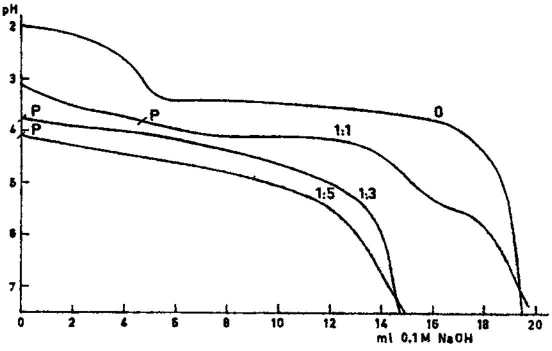

FIG. 3
Titration curves of $AlCl_3$ solution and of mixed solution of $AlCl_3$ and p-hydroxybenzoic acid with 0.1 M NaOH. 0, 0.01 M $AlCl_3$ (0.01 M HCl); 1 : 1, 0.01 M $AlCl_3$ (0.01 M HCl) + 0.01 M pHBA-Na salt; 1 : 3, 0.01 M $AlCl_3$ (0.01 M HCl) + 0.03 M pHBA-Na salt; 1 : 5, 0.01 M $AlCl_3$ (0.01 M HCl) + 0.05 M pHBA-Na salt. All solutions had a final volume of 50 ml. P gives the position of beginning precipitation

$c_{\mathrm{Fe\ in\ solution}}$ was determined experimentally and the other concentrations can be calculated from the known ionic product of water (k_w), the solubility product of ferric hydroxide, the hydrolysis constants of the ferric ions and the stability constant of $FeCl^{2+}$:

$$k_w = a_H a_{OH} = 10^{-14.00}$$

$$a_{Fe} = \frac{K_{so}}{a^3_{OH}} = \frac{10^{-38,20}}{a^3_{OH}} = 10^{3,80} \times a^3_H \qquad (2)$$

$$a_{FeOH} = \frac{{}^*K_1 a_{Fe}}{a_H} = 10^{1,66} \times a^2_H \qquad (3)$$

$$a_{Fe(OH)_2} = \frac{{}^*K_2 a_{FeOH}}{a_H} = 10^{3,04} \times a_H \qquad (4)$$

$$a_{FeCl} = K_{FeCl}\, a_{Fe}\, a_{Cl} = \frac{10^{5,21}\, a_H^3\, f_{Cl}\, c_{Cl\ tot.}\, f_{FeCl}}{f_{FeCl} + 10^{5,21}\, a_H^3\, f_{Cl}} \qquad (5)$$

Furthermore we have:

$$c_{acid\ total} = c_{FeZ} + c_{FeOHZ} + c_{H_2Z} + c_{HZ} + c_Z \qquad (6)$$

$$K_1 = \frac{a_H\, a_{HZ}}{a_{H_2Z}} \quad (7) \quad \text{and} \quad K_2 = \frac{a_H\, a_Z}{a_{HZ}} \quad (8)$$

Equations (6), (7) and (8) can be dissolved for a_{HZ} and a_Z:

$$a_Z = \frac{c_{acid\ total} - c_{FeZ} - c_{FeOHZ}}{\beta_H} \qquad (9)$$

$$a_{HZ} = \frac{a_H}{K_2} \times \frac{c_{acid\ total} - c_{FeZ} - c_{FeOHZ}}{\beta_H} \qquad (10)$$

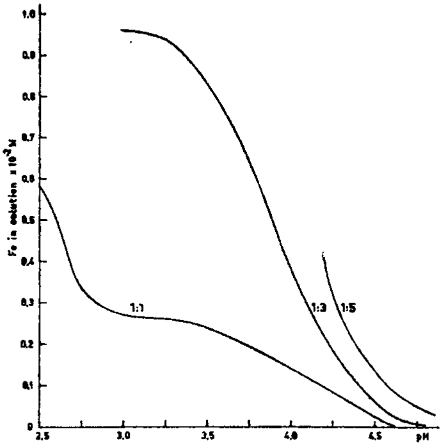

FIG. 4
Relation between total iron in solution and pH (the notation at the curves have the same meaning as in FIG. 2 and 3)

$$\text{Where } \beta_H = \frac{1}{f_Z} + \frac{a_H}{f_{HZ}\, K_2} + \frac{a_H^2}{K_1\, K_2} \qquad (11)$$

Combination of (9) and (10) with (1) gives a_Z and a_{HZ}.

Finally c_{FeZ} can be calculated from the equation indicating the electro-neutrality of the system:

$$c_{FeZ} + 3c_{Fe} + 2c_{FeOH} + c_{Fe(OH)_2} + c_{Na} + c_H + 2c_{FeCl} = 2c_Z + c_{HZ} + (c_{Cl\ total} - c_{FeCl}) + c_{OH} \qquad (12)$$

From the concentrations, of which c_{FeZ}, c_{Cl}, c_{Na} and c_H contribute most to the ionic strength, the latter could be roughly calculated. After that, the activity coefficients could be calculated as reported earlier in this paper.

All the quantities required for computing K_{FeZ} and K_{FeOHZ} are now known:

$$K_{FeZ} = \frac{a_{FeZ}}{a_{Fe}\, a_Z} \quad \text{and} \quad K_{FeOHZ} = \frac{a_{FeOHZ}}{a_{FeOH}\, a_Z}$$

The results are given in TABLE 4. It shows that the calculated values of the stability constants are essentially constant, which is another indication that 1 : 1 complexes of the described composition were actually formed. The values are:

$$K_{FeZ} = (0.259 \pm 0.039) \times 10^{13} \approx 0.26 \times 10^{13}$$
$$K_{FeOHZ} = (0.271 \pm 0.025) \times 10^{12} \approx 0.27 \times 10^{12}$$

TABLE 4. Ion activities and stability constants of the complexes FeZ+ and FeOHZ (for convenience expressed in logarithmic terms)

pH	pFe	pFeOH	pZ	pFeZ	pFeOHZ	log K_{FeZ}	log K_{FeOHZ}	Series
2.50	3.70	3.34	11.17	2.41	2.89	12.46	11.57	1 : 1
2.70	4.30	3.74	10.60	2.65	2.96	12.25	11.38	1 : 1
3.00	5.20	4.34	9.94	2.78	3.10	12.36	11.18	1 : 1
3.50	6.70	5.34	9.00	2.95	2.96	12.75	11.38	1 : 1
3.00	5.20	4.34	9.47	2.31	2.40	12.37	11.41	1 : 3
3.25	5.95	4.84	8.99	2.40	2.32	12.54	11.51	1 : 3
3.50	6.70	5.34	8.50	2.52	2.32	12.68	11.52	1 : 3
3.70	7.30	5.74	8.08	2.58	2.41	12.80	11.42	1 : 3
4.50	9.70	7.34	6.69	3.29	—	12.10	—	1 : 3
5.00	11.20	8.34	5.04	4.22	—	12.02	—	1 : 3
4.20	8.80	6.74	5.94	2.44	—	12.30	—	1 : 5
4.45	9.55	7.24	5.55	2.86	—	12.24	—	1 : 5
4.75	10.45	7.84	5.13	3.37	—	12.21	—	1 : 5
5.00	11.20	8.34	4.90	3.89	—	12.21	—	1 : 5
5.25	11.95	8.84	4.34	4.16	—	12.13	—	1 : 5
5.50	12.70	9.34	4.26	4.77	—	12.19	—	1 : 5

The same procedure could not be followed in the case of the Al-systems. FIG. 5 shows that, contrary to the curves of the Fe-systems, the 1 : 3 and 1 : 5 curves are on the left hand side of the 1 : 1 curve, which cannot be understood if soluble complexes are formed; for complex formation is favoured by excess of the ligand and a higher amount of Al would have remained in solution if the complexes were soluble. X-ray analysis of the white precipitate showed that it was quite a different compound from some Al-hydroxide. It was well crystallized. The equilibrium solutions had Cl- and Na-ion concentrations exactly equal to those used in the experiments. Hence, an uncharged complex compound, AlOHZ, or compounds such as $AlOH(HZ)_2$ or $Al(OH)_2HZ$ have been formed. The authors are inclined to assume the formation of AlOHZ as the most probable one. Elaborating on this idea, they calculated from the experimental data the solubility product:

$$K_{so} = a_{Al} \times a_{OH} \times a_Z \ ,$$

assuming that the concentration of the dissolved AlOHZ-complex is negligible small as compared

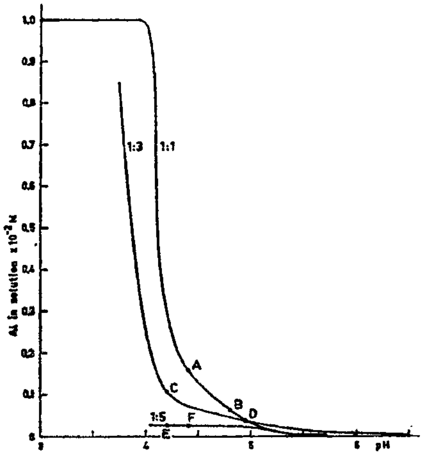

FIG. 5
Relation between total aluminium in solution and pH (the notation at the curves have the same meaning as in FIG. 2 and 3)

with the Al-ion concentrations. The points A, B, C, D, E and F of the curves of FIG. 5 were chosen for the calculations. The following relations were used:

$$c_Z = \frac{c_{\text{acid in solution}}}{\beta_H}, \text{ where } \beta_H = 1 + \frac{a_H f_Z}{f_{HZ} K_2} + \frac{a_H^2 f_Z}{K_1 K_2}$$

$$c_{HZ} = \frac{a_H f_Z \, c_{\text{acid in solution}}}{K_2 \, \beta_H \, f_{HZ}}$$

$$c_{AlOH} = \frac{10^{-5.05} \times a_{Al}}{a_H \times f_{AlOH}} \quad , \quad c_{Al(OH)_2} = \frac{10^{-4.71} \times f_{AlOH} \times c_{AlOH}}{a_H \, f_{Al(OH)_2}}$$

$$c_{\text{Al in solution}} = c_{Al} + c_{AlOH} + c_{Al(OH)_2}$$

$$3c_{Al} + 2c_{AlOH} + c_{Al(OH)_2} + c_{Na} + c_H = c_{Cl} + c_{HZ} + 2c_Z + c_{OH}$$

In this way it is possible to calculate a_{Al} and a_Z, if the ionic strength of the equilibrium solution can be determined. This is possible by assuming that the ionic strength is predominantly determined by the concentrations of chloride, sodium, pHBA and aluminium in solution. The activity coefficients can then be calculated when using the values given by KIELLAND (1937) for the parameter a_i. The results for the points mentioned are, — log K_{so} = 20.83, 20.84, 20.87, 20.75, 21.14 and 20.63 respectively, *viz.* essentially constant. The value of the solubility product is therefore: (0.15 ± 0.02) $\times 10^{-20}$. The results are strong indications that the precipitate has the assumed composition. Drying at 130° C reveals that 2 molecules of crystal water are present (determined loss of weight: 16.4 %; theoretically: 16.5 %). The theoretical C-content of the compound would then be: 38.9 %. Oxidation of the substance with $K_2Cr_2O_7$ + conc. H_2SO_4 and the subsequent spectrophotometric determination of the formed Cr^{3+}-ions (being a measure for the C-amount) resulted in a C-content of 39.2 %. It seems fairly certain, therefore, that the composition of the compound is $AlOHZ.2H_2O$. However, this has still to be verified by a complete elemental analysis.