

# Equilibrium and Structural Studies of Silicon(IV) and Aluminium(III) in Aqueous Solution. 8. A Potentiometric Study of Aluminium(III) Salicylates and Aluminium(III) Hydroxo Salicylates in 0.6 M Na(Cl)

LARS-OLOF ÖHMAN and STAFFAN SJÖBERG

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Equilibria between aluminium(III), salicylic acid (2-hydroxy-benzoic acid,  $H_2L$ ) and  $OH^-$  were studied in 0.6 M Na(Cl) medium at 25 °C. The measurements were performed as emf titrations (glass electrode) within the limits  $2 \leq -\lg [H^+] \leq 9$ ;  $0.0005 \leq B \leq 0.01$  M;  $0.006 \leq C \leq 0.015$  M and  $0.6 \leq C/B \leq 30$  ( $B$  and  $C$  stand for the total concentrations of aluminium(III) and salicylic acid, respectively). All data can be explained with the following species (tentative structures) and corresponding equilibrium constants:  $AlL^+$ ,  $\lg \beta_{-2,1,1} = -3.052 \pm 0.005$ ;  $AlL_2^-$ ,  $\lg \beta_{-4,1,2} = -8.391 \pm 0.011$ ;  $Al(OH)L_2^{2-}$ ,  $\lg \beta_{-5,1,2} = -15.99 \pm 0.024$  and  $Al(OH)_2L_2^{3-}$ ,  $\lg \beta_{-6,1,2} = -25.31 \pm 0.11$ . The standard deviations are  $3\sigma(\lg \beta_{p,q,r})$ . The carboxylic acid dissociation constant  $H_2L \rightleftharpoons HL^- + H^+$  was studied in separate titrations and it is found to be  $\lg \beta_{1,0,1} = -2.724 \pm 0.001$ . Data were analyzed with the least squares computer program LETAGROPVRID. In some solubility models with kaolinite as solid phase, the strength of complexation is compared to the complex formation in the gallic acid system, reported in earlier papers of this series.

The ability of Si(IV)<sup>1,2</sup> and Al(III)<sup>3-6</sup> to form aqueous complexes with ligand types occurring in natural waters is under extensive study. The most important classes of these ligand types are the high molecular weight organic material called humic and fulvic acids. By different degradation techniques, several types of probable complex formation sites in the humic and fulvic acids have

been revealed and one of them, *i.e.* the *o*-diphenolic binding site, has been studied in preceding papers of this series.<sup>3,5,6</sup> Other often quoted model ligand types for the humic substances are the 2-hydroxybenzoic acid derivatives. The complex formation of the simplest of these derivatives, *i.e.* salicylic acid, to  $Al^{3+}$  has, according to Stability Constants,<sup>7,8</sup> been the subject of one earlier investigation.<sup>9</sup> However, as that work is based on a very restricted number of data, especially in neutral and alkaline solutions, we have found it important to perform a careful and unbiased reinvestigation of this system.

## EXPERIMENTAL

*Chemicals and analysis.* Sodium salicylate ( $NaC_7H_5O_3$ , NaHL) (Merck *p.a.*) was used without further purification after drying. Stock solutions were prepared by dissolving NaHL in water and the  $HL^-$  content determined potentiometrically. The titrated amount was in full agreement (within 0.1 %) with that expected from the weighed amount. All other solutions were prepared and analyzed as described elsewhere.<sup>3</sup>

*Apparatus.* The automatic system for precise emf titrations, the thermostat and the electrodes was described elsewhere.<sup>3</sup> The coulometer was the same as in Part 2 of this series.<sup>1</sup>

## METHOD

The present investigation was carried out as a series of titrations at 25 °C in a constant ionic medium of 0.6 M Na(Cl). In the titrations, the free hydrogen ion concentration,  $h$ , was varied either by means of coulometric generated  $\text{OH}^-$  or by  $\text{H}^+$ -solution and  $h$  was measured with a glass electrode. As the carboxylic  $pK_a$  for salicylic acid is too low to permit the customary procedure in calibrating the electrode (*cf.* Ref. 3) the following titration procedure was used: to  $V_o$  ml of  $\approx 3$  mM HCl in 0.6 M Na(Cl) approximately ten successive coulometric additions with intervening emf recordings were made until the solution was nearly neutralized. Then,  $V_T$  ml of  $\text{HL}^-$  or  $\text{Al}^{3+}/\text{HL}^-$ -solution was added and the titration continued. With this procedure, the electrode calibration can be evaluated as a mean of several measurements within the titration and in our opinion that gives a more accurate calibration than using separate solutions of known  $\text{H}^+$  concentration.

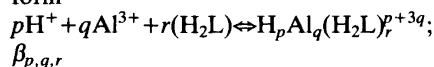
The carboxylic acidity constant of salicylic acid was determined in separate titrations within the concentration range 0.002–0.015 M. No attempts were made to evaluate the phenolic acidity constant as this would require the use of a hydrogen electrode.

During the three component titrations, the ratio between the total concentration of aluminium,  $B$ , and salicylic acid,  $C$ , was held constant. The measurements were performed within the limits  $2 \leq -\lg h \leq 9$ ;  $0.0005 \leq B \leq 0.01$  M and  $0.006 \leq C \leq 0.015$  M, covering the  $C/B$  ratios: 0.6, 1.5, 5, 7.5, 10, 15 and 30. At  $C/B \leq 7.5$  the available  $-\lg h$  range was restricted to an upper limit due to the formation of a white precipitate. To test reproducibility and reversibility of equilibria, both forward (increasing  $-\lg h$ ) and backward (decreasing  $-\lg h$ ) titrations were performed. To obtain more data points in the most interesting areas some dilution experiments (titrations with pure medium solution) were also performed.

**Data treatment.** The equilibria which must be considered in the present study can be divided into three groups:

- (i) the binary salicylic acid equilibrium  
 $\text{H}_2\text{L} \rightleftharpoons \text{HL}^- + \text{H}^+$ ;  $\beta_{-1,0,1}$
- (ii) the hydrolytic equilibria of  $\text{Al}^{3+}$   
 $p\text{H}^+ + q\text{Al}^{3+} \rightleftharpoons \text{H}_p\text{Al}_q^{p+3q}$ ;  $\beta_{p,q,0}$

(iii) three-component equilibria of the general form



In other parts of this series,<sup>4,6</sup> where experiments were also performed in 0.6 M Na(Cl) medium at 25 °C, we have shown that the following main hydrolytic complexes with corresponding equilibrium constants are:  $\text{Al}(\text{OH})_2^+$  ( $\lg \beta_{-1,1,0} = -5.52$ );  $\text{Al}_3(\text{OH})_4^{5+}$  ( $\lg \beta_{-4,3,0} = -13.57$ );  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$  ( $\lg \beta_{-32,13,0} = -109.2$ ) and  $\text{Al}(\text{OH})_4^-$  ( $\lg \beta_{-4,1,0} = -23.46$ ).

In the evaluation of the three-component experimental data, the binary complex models (*i* and *ii*) were considered as known and all effects above this level treated as being caused by ternary species. The mathematical analysis of data was performed with the least squares computer program LETAGROPVRID<sup>10</sup> (version ETITR<sup>11,12</sup>).  $pqr$ -triplets and corresponding equilibrium constants that “best” fit the experimental data were determined by minimizing the error squares sum  $U = \sum (H_{\text{calc}} - H)^2$ . The standard deviations  $\sigma(H)$ ,  $\sigma(\beta_{pqr})$  and  $3\sigma(\lg \beta_{pqr})$ , obtained in the LETAGROP calculations, were defined and calculated according to Sillén.<sup>13,14</sup> The computations were performed on a CD CYBER 730 computer.

## DATA, CALCULATIONS AND RESULTS

The data used to evaluate the carboxylic acidity constant of salicylic acid comprises 6 titrations with 129 experimental points. The analysis ended at  $\sigma(H) = 0.01$  mM giving  $\lg(\beta_{-1,0,1} \pm 3\sigma) = -2.724 \pm 0.001$ . Effects due to the formation of dimeric species, reported to occur in solutions of higher  $\text{H}_2\text{L}$  concentrations,<sup>15</sup> were not observed.

The mathematical analysis of the three component data, comprising 15 titrations with 431 experimental points, was started by making a Bjerrum plot  $\bar{n}(\lg [L^{-2}])$ . The plot is shown in Fig. 1. This figure shows that the data for  $\bar{n} \leq 2$  obviously could be explained by the formation of  $\text{AlL}^+$  and  $\text{AlL}_2^-$ . For  $\bar{n} \geq 2$ , however,  $\bar{n}$  is dependent of  $B$  and  $C$  and does not attain any limiting value within the investigated area. This is a clear indication that some ternary hydroxo complex and/or some Al(III) hydrolysis product ( $\text{Al}(\text{OH})_4^-$ ) are formed in appreciable amounts.

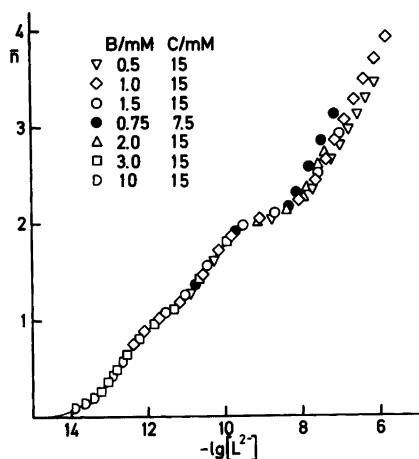


Fig. 1. A part of the experimental data plotted as curves  $\bar{n}(\lg [L^{2-}])$  for  $C/B$  ratios 1.5, 5, 7.5, 10, 15 and 30. In the calculation, the value  $\lg k_2 = -13.1$ , obtained for the second acidity constant of  $H_2L$  by Havelková *et al.*,<sup>9</sup> has been used. The chosen value affects the scale on the x-axis, but not the shape of the  $\bar{n}$  curves. Full drawn curve was calculated with  $\lg \beta_{-211}$  and  $\lg \beta_{-412}$  according to Table 1.

As a consequence, the data was divided into two parts, one with points with  $\bar{n} < 2$  and the other with  $\bar{n} > 2$ . The assumption of two mononuclear complexes at  $\bar{n} < 2$  was confirmed

when a LETAGROP calculation was performed on these data. The calculation ended at  $\sigma(H) = 0.04$  mM giving  $\lg \beta_{-2,1,1} = -3.051 \pm 0.005$  and  $\lg \beta_{-4,1,2} = -8.398 \pm 0.015$  ( $p, q, r$ -notations according to iii).

The analysis of data with  $\bar{n} > 2$  was performed as a  $p, q, r$ -analysis (systematic testing of different  $p, q, r$ -complexes) with the simple hypothesis that only one new complex  $H_p Al_q (H_2L)_r^{p+3q}$  was present. The criteria for "best fit" was thereby the magnitude of the error squares sum  $U = \Sigma (H_{\text{calc}} - H)^2$ . The result of this analysis is given in Fig. 2 and it is seen that the lowest value of  $U$  ( $U = 0.33$ ) was obtained for the complex  $H_5 Al (H_2L)_2^{2-}$  with  $\lg \beta_{-5,1,2} = -15.99 \pm 0.04$ . The complex  $AlL_3^{3-} (H_6 Al (H_2L)_3^{3-})$ , which is the major alkaline species in our earlier investigated  $Al^{3+}$ -*o*-diphenolic systems, only gives the second best fit ( $U = 0.45$ ;  $\lg \beta_{-6,1,3} = -16.71 \pm 0.05$ ) in this system. A detailed examination of the residuals obtained with either of these two species reveal that the difference between them occurs mainly as a concentration dependence difference at  $7 \leq -\lg h \leq 8$  and that the former species ( $H_5 Al (H_2L)_2^{2-}$ ) yield a much better fit to the experimental data in this area. It is also found that minor systematic deviations remain for  $-\lg h \geq 8$ . These effects at high  $-\lg h$  could be explained (with either of the complexes above) assuming that a complex  $H_6 Al (H_2L)_2^{3-}$  was formed. In a final attempt to determine whether

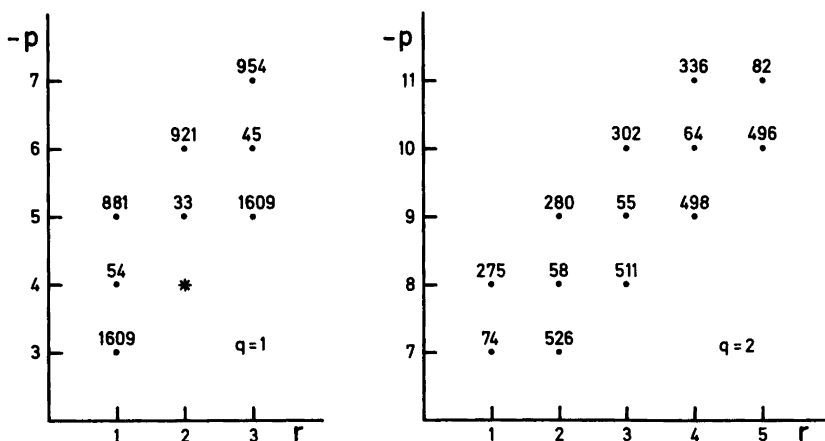


Fig. 2. Result of a  $pqr$ -analysis for data with  $\bar{n} \geq 2$ . The figures give the error squares sums  $U_H(pr)_q \times 10^2$  assuming one new complex. In the calculations, aluminium hydrolysis and the complexes  $(-2,1,1)$  and  $(-4,1,2)$  (marked with an asterisk in the left diagram) have been assumed to be known. The calculations are based on 108 experimental points giving  $U_H(00)_0 = 1609 \times 10^{-2}$ .

**Table 1.** Proposed binary and ternary complexes in the three-component system  $\text{Al}^{3+}$ - $\text{OH}^-$ -salicylic acid. The formation constants are related according to the reaction  $\text{pH}^+ + q\text{Al}^{3+} + r\text{H}_2\text{L} \rightleftharpoons \text{H}_p\text{Al}_q(\text{H}_2\text{L})_r^{+3q}$ , where  $\text{H}_2\text{L}$  stands for salicylic acid.

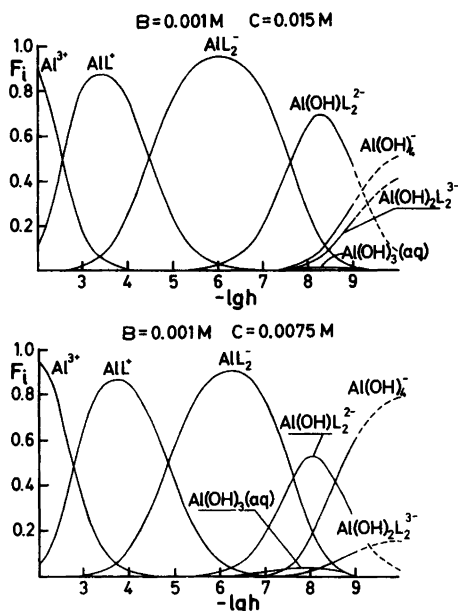
| No. of titr./<br>No. of points | $p q r$ | Proposed<br>formula                     | $\lg(\beta_{pqr} \pm 3\sigma)$ |
|--------------------------------|---------|---|--------------------------------|
| 6/129                          | -1 0 1  | $\text{HL}^-$                           | $-2.724 \pm 0.001$             |
| 15/431                         | -2 1 1  | $\text{AIL}^+$                          | $-3.052 \pm 0.005$             |
|                                | -4 1 2  | $\text{AIL}_2^-$                        | $-8.391 \pm 0.011$             |
|                                | -5 1 2  | $\text{Al}(\text{OH})\text{L}_2^{2-}$   | $-15.99 \pm 0.024$             |
|                                | -6 1 2  | $\text{Al}(\text{OH})_2\text{L}_2^{3-}$ | $-25.31 \pm 0.11$              |

the dominating species in neutral solutions was  $\text{H}_5\text{Al}(\text{H}_2\text{L})_2^{2-}$  or  $\text{H}_6\text{Al}(\text{H}_2\text{L})_3^{3-}$ , the formation constants for both these species were covaried. It turned out that while the formation constant for (-5,1,2) changed only moderately (a change with 0.09 lg-units) the complex (-6,1,3) was practically eliminated (a change in  $\lg \beta$  from -16.71 to -17.52). In an analogous calculation with (-5,1,2) and the third best species, (-4,1,1), the

(-4,1,1) species was rejected. Thus, our final proposal for the complexation at  $\bar{n} \geq 2$  is given by the species  $\text{H}_5\text{Al}(\text{H}_2\text{L})_2^{2-}$  and  $\text{H}_6\text{Al}(\text{H}_2\text{L})_3^{3-}$ .

The result of the final calculation, performed on the whole data, is given in Table 1. This calculation ended at  $\sigma(H) = 0.04$  mM indicating a good fit to experimental data.

In order to visualize the amounts of the different species, we have used the computer program SOLGASWATER<sup>16</sup> equipped with plotting procedures, to calculate some distribution diagrams. These are presented in Fig. 3.



**Fig. 3.** Distribution diagrams  $F_i(\lg h)_{B,C} \cdot F_i$  is defined as the ratio between aluminium(III) in a species and total aluminium(III). The calculations have been performed using the computer program SOLGASWATER with constants given in Table 1.

## DISCUSSION

The present investigation gives evidence for the formation of four mononuclear aluminium-salicylate complexes. Of these, we believe that the two species occurring at low  $-\lg h$  (-2,1,1)<sup>+</sup> and (-4,1,2)<sup>-</sup>, are chelates where the carboxylate and the phenolic group in salicylic acid coordinate to  $\text{Al}^{3+}$  and that these complexes actually could be written  $\text{AIL}^+$  and  $\text{AIL}_2^-$ , respectively. Concerning the two hydrolyzed species, (-5,1,2)<sup>2-</sup> and (-6,1,2)<sup>3-</sup>, we are of the opinion that these should be written  $\text{Al}(\text{OH})\text{L}_2^{2-}$  and  $\text{Al}(\text{OH})_2\text{L}_2^{3-}$ , thus being hydrolysis products of the hexacoordinated species  $\text{AIL}_2^-$ , i.e.  $\text{Al}(\text{H}_2\text{O})_2\text{L}_2^-$ . The acidity constants of  $\text{Al}(\text{H}_2\text{O})_2\text{L}_2^-$ , expressed as  $\text{p}K_a$ -values, are equal to 7.60 and 9.32. Corresponding values for the first acidity constant in the *o*-diphenol systems pyrocatechol<sup>17</sup> and 1,2-dihydroxynaphthalene-4-sulfonate<sup>6</sup> are 8.01 and 8.04, respectively. These values are significantly higher and it seems as if the carboxylate group in the salicylate ion has caused an increase in the acidity of coordinated

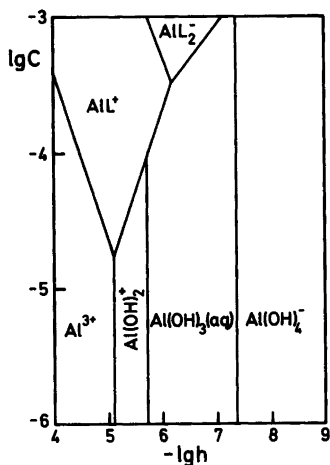


Fig. 4. Diagram showing predominating Al-species. In the calculations kaolinite was equilibrated with solutions of different compositions. The dissolution of kaolinite also yields small amounts of gibbsite,  $\text{Al}(\text{OH})_3$ . Formation constants for kaolinite, amorphous  $\text{SiO}_2$  and gibbsite are according to Helgeson.<sup>18</sup>

water molecules. This is probably due to the higher electron demand within a carboxylate group compared with a phenolic oxygen.

When our present results are compared with Havelková's,<sup>9</sup> we find a fair agreement in acidic solution (they reported  $\lg \beta_{-2,1,1} = -3.1$  and  $\lg \beta_{-4,1,2} = -8.8$ ) while, in neutral and alkaline solution, they propose the single complex  $\text{AlL}_3^{3-}$  with  $\lg \beta_{-6,1,3} = -18.3$ . Probably, their data was

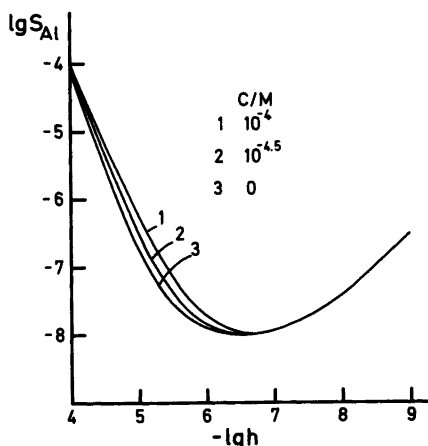


Fig. 5. The solubility of kaolinite,  $S_{\text{Al}}$ , with  $C=0$ , 30 and 100  $\mu\text{M}$ , respectively.

too limited to permit a detailed and unbiased analysis in this area.

In the evaluation of data in alkaline solution, we used an equilibrium constant for the aluminate ion which differs from the literature value by 0.24 logarithmic units. This constant was determined in Part 7<sup>6</sup> of our series. As appreciable amounts of  $\text{Al}(\text{OH})_4^-$  also form in this system (cf. Fig. 3) we found it valuable to covary the formation constants for  $\text{Al}(\text{OH})_4^-$  and  $\text{Al}(\text{OH})_2\text{L}_2^{3-}$ . The constant values did not change significantly ( $\lg \beta_{-4,1,0} = -23.52 \pm 0.16$ ;  $\lg \beta_{-6,1,2} = -25.24 \pm 0.23$ ) but large standard deviations, due to the close connection between the species, were obtained. Thus, a confirmation of the modified stability constant for  $\text{Al}(\text{OH})_4^-$  was obtained.

The main purpose of our work is to evaluate the complexation ability of different types of ligands towards Si(IV) and Al(III). In an attempt to show the significance of different  $\text{Al}^{3+}$ -salicylates in a natural water, the clay-mineral kaolinite,  $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$ , was equilibrated with solutions of different salicylate contents. In Fig. 4, a predominance area diagram shows that  $\text{AlL}^+$  and  $\text{AlL}_2^-$  both predominate in neutral and slightly acidic solutions. This implies that the solubility of kaolinite increases in the presence of salicylate ions. The magnitude of this increase is shown in Fig. 5 for different values of  $C$ . At  $-\lg h$  5 and 6

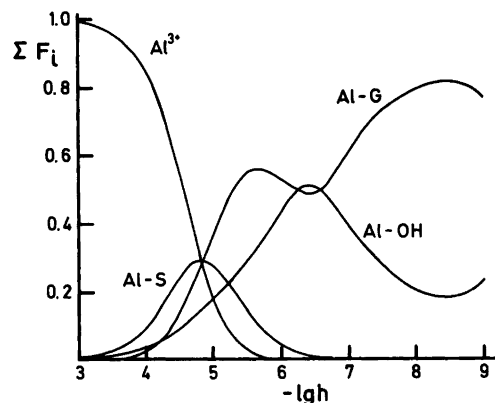


Fig. 6. Diagram showing the sum of distribution coefficients,  $\Sigma F_i$ , for Al-gallates (Al-G), Al-salicylates (Al-S), Al-hydrolysis (Al-OH) as well as  $F_{\text{Al}^{3+}}$ . The total concentration of gallic acid is equal to that for salicylic acid (30  $\mu\text{M}$ ) and kaolinite is the stable solid phase. Possible occurrence of mixed Al-S-G complexes have not been taken into consideration as no data for such species are known.

the solubility has increased by factors 1.8 and 1.1, respectively, ( $C=30 \mu\text{M}$ ), while with  $-\lg h \geq 6.5$  there is no increase. In order to compare the stability of the complexes formed in this system with the  $\text{Al}^{3+}$ -*o*-diphenolic complexes, we performed a model calculation where kaolinite was equilibrated with equal amounts of salicylic acid and gallic acid. The result of this calculation (Fig. 6) is that, except for the most acidic solutions, the  $\text{Al}^{3+}$ -*o*-diphenolic complexes dominate largely. In fact, in order to obtain equal amounts of Al-gallate and Al-salicylate complexes at  $-\lg h=6$ , the amount of salicylic acid has to be 8 times larger than the amount of gallic acid. Although actual values of the concentrations of these ligands in natural waters have not been determined, it is most likely that the *o*-diphenols are of at least the same importance as the 2-hydroxy-benzoic acid derivatives in discussing speciation and concentration of dissolved aluminium in a natural water. To compare the phenolic and carboxylate binding sites in a completely fair manner, emf investigations of the systems  $\text{Al}^{3+}$ -OH<sup>-</sup>-1,2-dihydroxybenzene (pyrocatechol) and  $\text{Al}^{3+}$ -OH<sup>-</sup>-benzene-1,2-dicarboxylic acid (phthalic acid) are now in progress.

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