Acta Chemica Scandinavica A 36 (1982) 779–781

Short Communication

A Small Angle Neutron Scattering Investigation on Aluminium Hydroxide

A. NØRLUND CHRISTENSEN,[a]
M. S. LEHMANN[b] and A. WRIGHT[b]

[a] Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark and [b] Institut Max von Laue – Paul Langevin, B.P. 156, F-38042 Grenoble Cedex, France

In the hydrolysis of aluminium solutions with bases, the polynuclear complex $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ is formed.[1] A small angle X-ray scattering investigation on hydrolyzed aluminium nitrate solutions with OH – Al ratios up to 2.25 showed the presence of a particle with a 4.3 Å radius of gyration in good agreement with that calculated for the polynuclear complex.[2] When the OH – Al ratio exceeds 2.7, an amorphous aluminium hydroxide gel is formed, and a small angle X-ray scattering investigation of the gel shows it to be polydisperse with particles of sizes from at least a few hundred Å to 25 Å or possibly less than 25 Å,[3,4] In a recent small angle neutron scattering investigation of the aging of iron(III) hydroxide gels it was found that the particle diameters were in the range 700 – 1000 Å, and all the systems investigated showed a clear polydispersity.[5] In order to study the early stages of the formation of a gel it was decided to make an on-line small angle neutron scattering experiment of the homogeneous hydrolysis of an aluminium solution with urea. In addition, the aging of aluminium hydroxide gels should be studied by small angle neutron scattering to compare the aging process with that of iron(III) hydroxide gels.

Hydrolysis of Me(III) solutions. In a previous investigation it was found that solutions of iron(III) nitrate on heating were hydrolyzed to α-Fe_2O_3.[6] The Me(III) solutions listed in Table 1 were sealed in thick-walled pyrex ampoules and kept at the indicated experimental conditions. By this treatment only the iron(III) solution and the indium(III) solution yielded solid products of hydrolyses. The solids were identified from Guinier photographs taken with a Guinier camera using Cu$K\alpha_1$ radiation.

Solutions of urea, NH_2CONH_2, in water can be used in a homogeneous hydrolysis of Me(III) solutions. When a solution of urea is heated to temperatures above 85 °C, NH_3 (and CO_2) is produced at a convenient rate for hydrolysis. Table 2 shows a selection of solutions of Me(III) salts hydrolyzed by urea in sealed pyrex ampouls at 94 °C. It is interesting to note the hydrolysis product of the iron(III) nitrate solution is crystalline α-FeOOH formed at low pH conditions in the solution, and that the product of hydrolysis of the aluminium nitrate solution is an amorphous gel.

Heat treatment of aluminium hydroxide gels. The gel of aluminium hydroxide was made from a 1 M solution of $Al_2(SO_4)_3.18H_2O$ (Merck) and a 3 M solution of NaOH (Merck). The base was added dropwise to the aluminium sulfate solution and pH was measured simultaneously with a Radiometer PHM 64 pH-meter. The precipitation was

Table 1. Hydrolysis of 1 M metal salt solutions at 180 °C for 6 h.

Solution of	pH before	pH after	Product
$Fe(NO_3)_3.6H_2O$	0.62	−0.22	α-Fe_2O_3
$In_2(SO_4)_3$	1.05	0.59	$InOHSO_4$
$Cr(NO_3)_3.9H_2O$	1.66	0.71	No solid
$Al(NO_3)_3.9H_2O$	1.70	1.60	No solid
$La(NO_3)_3.6H_2O$	4.57	4.62	No solid

Table 2. Hydrolysis of metal solutions with urea at 94 °C for 24 h. The solutions are 4.5 M with respect to urea and 0.75 M with respect to the metal ions.

Solution of	pH before	pH after	Product
$Fe(NO_3)_3.6H_2O$	1.87	7.24	α-FeOOH
$In_2(SO_4)_3$	2.39	6.94	$In(OH)_3$[a]
$Cr(NO_3)_3.9H_2O$	2.60	7.71	Gel
$Al(NO_3)_3.9H_2O$	2.70	7.90	Gel

[a] Contains $In(OH)_3$ and an unidentified compound.

0302-4377/82/090779-03$02.50

interrupted when pH of the solution was 4.77, and 15 ml samples of the aluminum hydroxide with the mother liquid were sealed in pyrex ampouls and kept at 94 °C for up to 24 h.

Small angle neutron scattering experiments. The small angle neutron scattering experiments were performed at the Institut Max von Laue – Paul Langevin in Grenoble with the instrument D11, using 10 Å neutrons and a sample detector distance of 20 m. The specimens were housed in cuvettes of quartz placed in a rack where a temperature of up to 100±0.5 °C could be obtained during the diffraction experiment. The scattered neutrons were measured with a two dimensional multi detector and the data reduction was performed as described previously.[5] The scattering curves show that the particles belong to a polydisperse size distribution, and a simple model has been used for analysis. This model has been developed for analysis of small angle scattering curves from colloidal systems.[7] At the present time, it is limited to describing scattering from spherical particles with a hard sphere exclusion potential exceeding the radius of the particle. Therefore, the interparticle interference effects can be described by including in the fit the effective volume fraction of the extended sphere. Cleary, the use of a spherical particle model to describe a gel system is a coarse approximation, but it is not possible at the present time to calculate the particle function for lower symmetry particles. The other parameters in the least-squares analysis were the particle size (S), the size distribution function (σ) and the intensity of forward scattering [$I(Q_o)$].

When a solution containing Al^{3+} ions and urea is heated to temperatures above 85 °C, pH of the solution will increase with time, and the faster the higher the temperature and the concentration of urea. At a pH value of approximately 6 a gel is

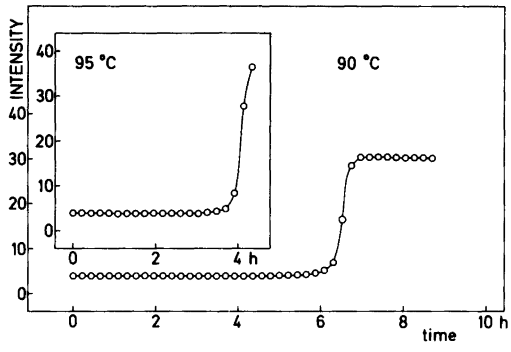

Fig. 1. Total scattering intensity of a solution that is 0.74 M Al^{3+} and 4.50 M urea *vs.* The formation of the gel results in an increase in the scattering intensity.

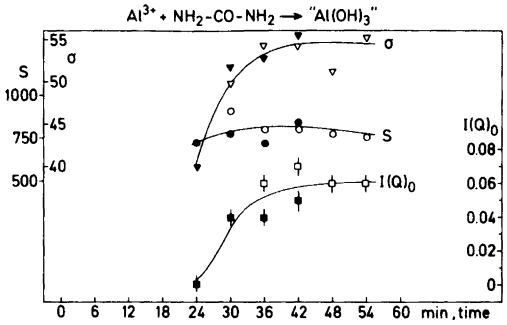

Fig. 2. $I(Q_o)$, S, and σ for gels of aluminium hydroxide formed by the hydrolysis of urea.

formed. At this pH value the dominant species is the $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ ion[8] and the formation of the gel is so fast that it has the character of a polymerization. Fig. 1 displays the total scattering (on an arbitrary scale) *vs.* time for a solution that was 0.74 M with respect to Al^{3+} and 4.50 M with respect to urea. After approximately 4 h at 95 °C or 6 h at 90 °C, the total scattering of the specimens increases and reaches a maximum value within 1 h. Fig. 2 shows $I(Q_o)$, the particle size, S, and the standard deviation of the size distribution function, σ, for gels of aluminium hydroxide formed by the hydrolysis with urea. The solutions were pre-heated for 6 h in a thermostat kept at 90 °C, and the diffraction experiments were then performed with the cuvettes at a temperature of 90 °C. It is interesting to note that the values, apparently, reach a constant maximum in the homogeneous hydrolysis process. Fig. 3 displays $I(Q_o)$, σ, and S for specimens of aluminium hydroxide gels aged at 94 °C for up to 24 h.

The measurements show that the polycondensation appears to be a two stage process. Within a narrow pH range the abrupt appearance of large particles is observed. There is no evidence of a small particle precursor. Within the time period of the experiment the particles do not grow significantly in size (Fig. 2). However, the growth in forward scattering observed for long time aging at room temperature or at elevated temperatures (Fig. 3) shows an increase in scattering contrast between particles and the solution which is interpreted as elimination of protons from the precipitate.

Whilst a moderately good fit to the scattering curves can be obtained without introduction of interparticle interference effects, the fit in the middle scattering range can be improved by using the volume fraction as a parameter in the least-squares analysis. However, we do not consider that the volume fraction so obtained is a reliable value in the

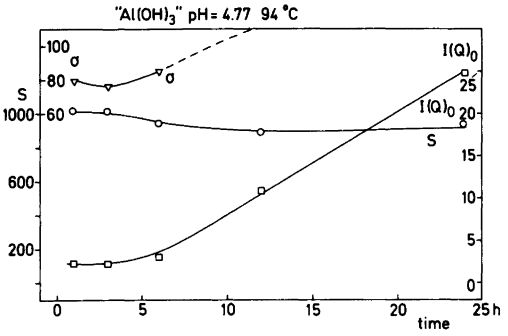

Fig. 3. $I(Q_o)$, S, and σ for gels of aluminium hydroxide aged at 94 °C for up to 24 h.

absence of a marked interference peak. It is equally likely that the use of spherical particles in the model is a poor approximation to the real particle scattering function in this range of Q. Small angle scattering patterns of silica gel show a shoulder in $I(Q)$ which can be interpreted according to a model of agglomerated spherical particles in which a dimer of two spheres in contact gives the best particle scattering function.[9] This model is consistent with a process in which independently formed particles stick together in contact without rearranging to form a more compact cluster. Further analysis of the iron(III) data [5] will be made to test this hypothesis.

Acknowledgements. The Danish Natural Science Research Council is acknowledged for financial support to one of us (ANC). We are indebted to Dr. H. Haesslin and R. Oberthür for the loan of the sample heater used in the scattering experiment.

1. Johansson, G. *Acta Chem. Scand. 14* (1960) 771.
2. Rausch, W. V. and Bale, H. D. *J. Chem. Phys. 40* (1964) 3391.
3. Bale, H. D. and Schmidt, P. W. *J. Chem. Phys. 62* (1958) 1179.
4. Bale, H. D. and Schmidt, P. W. *J. Chem. Phys. 31* (1959) 1612.
5. Christensen, A. N., Lehmann, M. S. and Wreight, A. *Acta Chem. Scand. A 37* (1983). *In press.*
6. Christensen, A. N., Convert, P. and Lehmann, M. S. *Acta Chem. Scand. A 34* (1980) 771.
7. Hanis, N. *Thesis.* Institut Laue–Langevin, Grenoble 1980.
8. Öhman, L.-O. and Forsling, W. *Acta Chem. Scand. A 35* (1981) 795.
9. Hayter, J. and Wright, A. *To be published.*

Received May 27, 1982.