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XRD study of thermal stability of hydroxyl-aluminium chloride

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An XRD study of hydroxyl - aluminium chloride has been carried out at different temperatures in a dry atmosphere. It has been observed that solid hydroxyl-aluminium chloride, obtained from an aqueous solution by drying under very mild conditions, gives an XRD pattern characteristic of a crystalline material. The transition from crystalline to semi-crystalline state at temperatures above 80°C gives evidence of the role of coordinated water molecules and hydroxyl groups in building up the crystalline structure at lower temperatures. SEM pictures of hydroxyl-aluminium chloride dried under mild heating show platy habits.

Hydroxyl-aluminium chloride is one of the most versatile inorganic compounds, used as a formation stabilizer in the oil industry[1], as an anti-perspirant in pharmaceutical applications and as a flocculant or water clarifier in various chemical operations. Several workers[2,3] have proposed that hydroxyl-aluminium chloride has a hexagonal ring structure similar to fragments of $Al(OH)_3$ crystals. However, many recent studies based on ^{27}Al NMR have favoured the existence of a Keggin ion type structure[4]. This structure was originally proposed by Johanssen[5]. The structure contains a tetrahedral AlO_4^{4-} center, surrounded by twelve Al-O octahedra sharing edges and corners. Teagarden *et al.*[6] have tried to explain the structure by the use of XRD, ^{27}Al-NMR and IR. In an XRD study of hydroxyl-aluminium chloride made from samples where stereo-chemical coordination of metal ion is not distorted, the diffraction pattern of a crystalline material can be expected. Careful drying of the sample was therefore carried out under very mild heating at a temperature of 40 to 50°C. Solids thus obtained were hygroscopic in nature. XRD was consequently carried out in a very dry atmosphere of approximately 0% relative humidity.

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Experimental

Hydroxyl-aluminium chloride with a chemical composition $Al(OH)_{2.1}Cl_{0.9}$ was synthesized in the laboratory by reacting metallic Al with $AlCl_3.6H_2O$ solution in stoichiometric amounts. Products obtained were slowly dried at a temperature of 40 to 50°C. It was observed that finely ground hydroxyl-aluminium chloride is hygroscopic in nature. Therefore in every step, care was taken to avoid moisture pick up by the sample from atmosphere. The chemical formula $Al(OH)_{2.1}Cl_{0.9}$ can be rearranged to $AlO_4Al_{12}(OH)_{19.3}Cl_{11.7}$, which agrees with the structural formula proposed by Johannsen in 1960. The special sample holder for XRD study had the facility to maintain a desired atmosphere by circulation of different gases. In addition to this also heating facilities were present. Incident and diffracted X-rays were filtered through an X-Ray transparent polymer window. Dry air was continuously circulated through the sample holder. Silicon was mostly used as an internal standard. XRD was carried out with Siemens Kristalloflex diffractometer : Cu k_α (35 kV/20 mA) and a scan speed 0.01° (2θ)/sec. These products were gradually heated to 80°, 100°, 140°, 180°, 250° and 500°C. XRD patterns recorded after every stage of heating were aimed at determining the changes. Thermal analysis of hydroxyl-aluminium chloride was carried out with a Du-Pont thermogravimetric analysis system with a heating rate of 2°C/min under a continuous flow of dry air. IR spectroscopic study was carried out in a Perkin Elmer IR spectrometer with KBr pellets in the scanning range 4000 - 250 cm^{-1}. Due to high adsorption of moisture by hydroxyl-aluminium chloride, extreme care was taken during preparation of KBr pellets. Three samples of hydroxyl-aluminium chloride were taken for IR spectroscopic study: a sample obtained after very mild drying of hydroxyl-aluminium chloride aqueous solution, and a sample heated to 110 and 180°C, respectively. Scanning electron micrographs of samples obtained after mild drying, were taken in a Cambridge Stereoscan scanning electron microscope.

Results and discussion

XRD patterns of hydroxyl-aluminium chloride obtained at lower temperatures show clear diffractional peaks . This is in contrast to the pattern shown by Teagarden *et al.*[6], which can only be obtained after heat-

Table 1 — Unit cell data of hydroxyl -aluminium chloride
System = Triclinic P

a = 9.1155 Å, b = 11.50Å, c = 24.31Å,

$\alpha = 107.26°$, $\beta = 94.31°$, $\gamma = 105.517°$

Line number	d spacings (Å)		Indices	2 θ°		
	Observed	Calculated	*(h k l)*	Observed	Calculated	Difference
1	10.59	10.61	(0 1 0)	8.34	8.32	.015
2	8.79	8.78	(1 0 0)	10.06	10.06	.003
3	8.73	8.75	(0 1 1)	10.13	10.10	.025
4	8.24	8.23	(-1 0 1)	10.73	10.74	.015
5	7.93	7.94	(1 -1 1)	11.14	11.15	.009
6	6.99	6.98	(1 0 2)	12.66	12.66	.003
7	5.94	5.94	(-1 1 2)	14.9	14.9	.003
8	5.84	5.85	(0 -1 4)	15.10	15.13	.03
9	5.62	5.63	(1 1 1)	15.76	15.74	.017
10	5.20	5.20	(-1 -1 3)	17.03	17.02	.008
11	5.17	5.16	(-1 2 0)	17.12	17.14	.020
12	4.47	4.48	(-2 1 0)	19.82	19.77	.047
13	4.02	4.03	(-2 1 2)	22.08	22.04	.040
14	3.89	3.89	(1 2 1)	22.83	22.84	.014
15	3.73	3.73	(-2 2 1)	23.81	23.81	.003
16	3.69	3.69	(0 -3 2)	24.08	24.07	.003
17	3.45	3.45	(2 1 2)	25.82	25.81	.009
18	3.43	3.43	(-1 3 1)	25.99	25.97	.013
19	3.30	3.30	(-2 -1 4)	26.98	26.99	.007
20	3.25	3.25	(2 -3 3)	27.38	27.40	.014
21	3.02	3.03	(1 3 0)	29.52	29.53	.002
22	2.97	2.97	(-2 2 4)	30.07	30.05	.021
23	2.94	2.93	(2 2 1)	30.39	30.43	.04
24	2.73	2.73	(-1 3 4)	32.75	32.73	.017
25	2.56	2.56	(0 4 1)	34.95	35.10	.05
26	2.50	2.506	(-2 -3 1)	35.86	35.85	.01
27	2.49	2.49	(-2 -3 3)	35.95	35.92	.024
28	2.31	2.31	(-3 -2 3)	38.97	38.98	.004
29	2.19	2.18	(2 -5 1)	41.20	41.22	.012
30	2.06	2.06	(-4 0 4)	43.98	43.99	.004
31	1.98	1.98	(4 -4 1)	45.66	45.66	.005
32	1.94	1.94	(2 4 2)	46.66	46.66	.005
33	1.82	1.82	(5 -2 2)	50.16	50.16	.003
34	1.76	1.76	(5 0 0)	52.00	52.01	.01
35	1.69	1.68	(-5 2 4)	54.37	54.37	.003
36	1.67	1.67	(-1 6 3)	54.86	54.89	.03

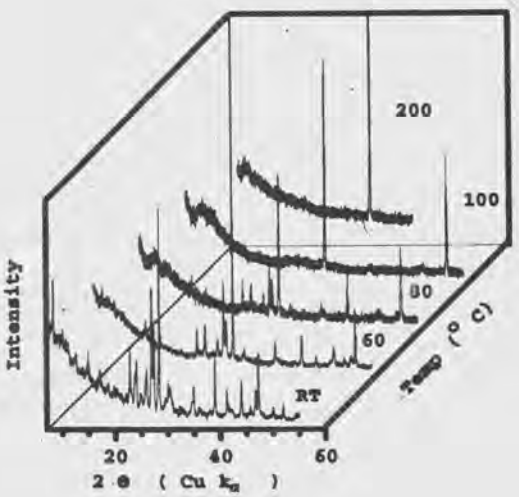

Fig. 1 - Comparative view of XRD patterns of hydroxyl-aluminium chloride obtained at different temperatures (RT = room temperature).

ing to a higher temperature (Fig. 1). This gives evidence for the transition to a less crystalline phase at temperatures above 80°C. This implies that an effective XRD study can only be carried out on powders which are the result of a very mild drying of hydroxyl-aluminium chloride aqueous solutions. Indexing of XRD patterns carried out at room temperature suggests a unit cell as given in Table 1. However out of thirty seven peaks selected, the indexed pattern could not include one peak at 32.25° 2θ (2.773Å) having a relative intensity I/I_o of 9.2 .

Thermogravimetric analysis results show that weight loss begins at a temperature of 80°C. The weight loss curve also shows an inflection at 160°C which is better seen on the derivative thermogravimetric pattern. The DTG pattern also shows another peak at 110°C. This two stepped weight loss, together with the IR patterns obtained after heating the sample at different temperatures, shows that coordinated water is completely lost ~ 160°C . The IR pattern of the sample obtained after heating to 160°C does not show the peak around 1600 cm^{-1}, corresponding to the bending vibration of coordinated water. The platy habits of dried

Fig. 2 - Scanning electron micrograph of hydroxyl-aluminium chloride.

samples of hydroxyl-aluminium chloride is given in SEM pictures (Fig. 2). Curling of the plates is due to dehydration during sample preparation under high vacuum for SEM.

Hydroxyl-aluminium chloride possesses a crystalline structure which undergoes a transition to a semi-crystalline state at a temperature above 80°C. Therefore, the sample preparation technique for hydroxyl-aluminium chloride is crucial for powder XRD, a rise of temperature above 80°C during this stage changes the crystallinity due to loss of coordinated water molecules which build up the crystalline structure. Indexing of powder XRD pattern of the compound obtained after drying at 40°C gives a unit cell with following cell parameters, system = Triclinic P, a= 9.1155Å, b = 11.50Å, c = 24.31Å, $\alpha = 107.26°$, $\beta = 94.313°$, $\gamma = 105.517°$.

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