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DIFFERENTIAL CALORIMETRIC STUDY OF THE POLYMER $Al_{13}O_4(OH)_{28}(H_2O)_8^{3+}$ AND AN AMORPHOUS ALUMINIUM TRIHYDROXIDE GEL IN AQUEOUS SOLUTION

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ABSTRACT

The enthalpy of formation at 298.15 K of the polymer $Al_{13}O_4(OH)_{28}(H_2O)_8^{3+}$ and an amorphous aluminium trihydroxide gel was studied using an original differential calorimetric method, already developed for adsorption experiments, and aluminium-27 NMR spectroscopy data. ΔH_f "Al_{13}" (298.15 K) $= -602 \pm 60.2$ kJ mole^{-1} and ΔH_f $Al(OH)_3$ (298.15 K) $= -51 \pm 5$ kJ mole^{-1}. Using theoretical values of ΔG_R "Al_{13}" and ΔG_R $Al(OH)_3$, we calculated ΔG_f "Al_{13}" (298.15 K) $= -13282$ kJ mole^{-1}; ΔS_f "Al_{13}" (298.15 K) $= +42.2$ kJ mole^{-1}; ΔG_f $Al(OH)_3$ (298.15 K) $= -782.5$ kJ mole^{-1}; and ΔS_f $Al(OH)_3$ (298.15 K) $= +2.4$ kJ mole^{-1}.

INTRODUCTION

Differential calorimetry is a direct method for measuring in situ the enthalpy of formation of aluminium hydroxo complexes. Combined with other experimental methods which allow assay of the different species, information necessary for calculating thermodynamic data is obtained. Calorimetry has been used for studying properties of alumina and sodium aluminate [1]. These experimental data are based on the decomposition of different precipitates (hydrargilite, bayerite...) in basic media. The enthalpies of precipitation of the different products, whatever their physicochemical nature, is about 460 J g^{-1} [1]. The transformation from amorphous to crystalline products is not energetically measurable [1]. The existing data [2–7] principally concern results in basic media or theoretical calculations,

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not taking into account the polymeric species intermediate between the solid and the monomers such as $Al(H_2O)_6^{3+}$. We have measured the enthalpy of formation at 298.15 K of the aluminium polymer $Al_{13}O_4(OH)_{28}(H_2O)_8^{3+}$ [8] in an acidic medium, and the enthalpy of formation of an amorphous precipitate at neutral pH. Measurement of the physicochemical composition of the different species at the end of the reaction was done using high-resolution aluminium-27 NMR in the Fourier transform mode following the method described previously [8].

EXPERIMENTAL METHOD

Calorimetric measurements of the enthalpy of formation were carried out using a Tian–Calvet microcalorimeter [1] with a differential device for the

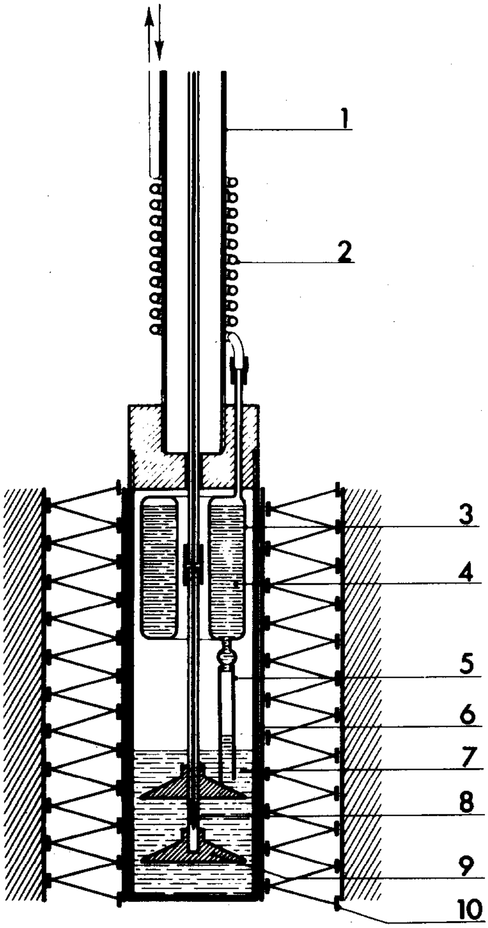

Fig. 1. Experimental differential calorimeter apparatus. 1, Glass tube; 2, copper coil; 3, glass reservoir; 4, poured solution; 5, thin tube; 6, cell; 7, solution; 8, 1 kΩ resistance; 9, agitator; 10, thermocouples.

introduction of the reagents, especially adapted to the experimental requirements (Fig. 1). The experimental procedure is as follows. The $AlCl \cdot 6\ H_2O$ solution (Merck), of concentration $0.5\ m\ l^{-1}$ is placed in the laboratory cell (7). The glass reservoir (3) contains the sodium hydroxide solution (Titrisol, Merck), the concentration of which depends on the neutralization ratio $r = (NaOH)/(Al_T)$ desired. The gaseous phase above the sodium hydroxide solution is placed in contact by a 1 m long copper coil (2) with a peristaltic pump located at the exterior of the calorimeter. In the glass reservoir of the reference cell is placed the same volume of sodium hydroxide. The reference cell (7) contains demineralized water (Millipore quality).

The two calorimetric systems attain thermal equilibrium in about 5 h. When the baseline is judged satisfactory the solvent-saturated air from the glass reservoir is continuously injected with a peristaltic pump (Gilson Minipuls) which allows a constant flow ($\sim 0.1\ cm^3\ min^{-1}$) into the two cells. The calorimetric experiments were repeated at least twice at 298.15 K. The concentrations of the species after reaction are measured using aluminium-27 NMR with a Brucker HX-90 spectrometer interfaced to a Nicolet 1080 computer [8]. The solutions prepared have the same concentration of total aluminium (Al_T) equal to $10^{-1}\ m\ l^{-1}$ and the neutralization ratios are $r = (NaOH)/(Al_T) = 1$, 1.5, 2, 2.1, 2.3, 2.5, and 3.

CHEMICAL REACTIONS

The chemical reactions are for r between 1 and 2.5

$$(13x + y)\ Al^{3+} + OH^- \rightarrow x\ Al_{13}O_4(OH)_{28}^{3+} + y\ Al(OH)_3 + (10x + y)\ H^+ \quad (1)$$

$$(13x + y)\ Al^{3+} + (32x + 3y)\ OH^- \rightarrow x\ Al_{13}O_4(OH)_{28}^{3+} + y\ Al(OH)_3 + 4\ H^+$$

where x and y vary with the neutralization ratio r during the partial hydrolysis of the aluminium chloride. The reaction corresponding to the neutralization ratio $r = 3$ is

$$Al^{3+} + 3\ OH^- \rightarrow Al(OH)_3 \quad (2)$$

The values of x and y are determined from the NMR measurements. The small vertical agitation (60 r.p.m.) obtained by two plateaux [9] in the two cells does not allow perfect homogenization of the sodium hydroxide in the aluminium chloride solution. Localized supersaturation exists with respect to the precipitated gel, dissolution of which is more or less rapid. In this case, the enthalpies measured in the two cells are:

In the laboratory cell

$$Q_1\ \text{exp} = Q_1(\text{polym.}) + Q_1(\text{dil. Al}) + Q_1(\text{gel}) - Q_1(\text{dissol. gel}) + Q(\text{agit.}) + Q_1(\text{dil. Na})$$

TABLE 1

NMR and calorimetric results of the hydrolysed aqueous solutions

$r=(\mathrm{NaOH})/(\mathrm{Al_T})$	% "$\mathrm{Al_{13}}$" by NMR	% Monomers by NMR	%Gel = 0.1 − $\mathrm{Al_{13}}$ + monomers	Q_{exp}(J)
1	19	62.4	18.6	−30.1
1.5	43.9	36.5	20	−47.6
2	44	18	38	−61
2.5	65	5	30	−70
3	0	0	100	−76.8

in the reference cell

$$Q_2 \exp = Q_1(\text{dil. Na}) + Q(\text{agit.})$$

$$Q \exp_{\mathrm{tot}} = Q_1 \exp - Q_2 \exp$$

$$= Q_1(\text{polym.}) + Q_1(\text{gel}) - Q_1(\text{dissol. gel}) + Q_1(\text{dil. Al})$$

where Q_1(polym.) = enthalpy of formation of the "$\mathrm{Al_{13}}$" polymer, Q_1(gel) = enthalpy of formation of gel, Q_1(dil. Al) = enthalpy of dilution of monomers, Q_1(dissol. gel) = enthalpy of dissolution of gel, Q(agit.) = enthalpy released by agitation, Q_1(dil. Na) = enthalpy of dilution of $\mathrm{Na^+}$ ion.

The experimental measurement depends on four data. The Q_1 (dil. Al) value is experimentally measured.

An $\mathrm{Al(OH)_3}$ precipitate is rapidly formed in the laboratory cell. The quantitative results (Table 1) allow calculation of the enthalpy of formation of the $\mathrm{Al_{13}O_4(OH)_{28}\,(H_2O)_8^{3+}}$ polymer after verifying that the value of the energy contribution of the dilution of $\mathrm{Al(H_2O)_6^{3+}}$ by a point by point experiment is negligible (1 J). In this case the reaction is

$$Q \exp = Q_1(\text{polym.}) + Q_1(\text{gel}) - Q_1(\text{dissol. gel})$$

RESULTS AND DISCUSSION

Supposing that the trihydroxide formed during the preneutralization is the same as that precipitated for $r=3$, we can then calculate the energy contribution of the precipitate formed for each preneutralized solution using the NMR results (Table 1). The enthalpy of formation of the "$\mathrm{Al_{13}}$" polymer is ΔH_{f} "$\mathrm{Al_{13}}$" (289.15 K) = -602 ± 60.2 kJ mole^{-1} for a molecular weight of 1035. The error of 10% comes mainly from the NMR experiments.

The experimental enthalpy of precipitation of $\mathrm{Al(OH)_3}$ in the solution of which the neutralization ratio is $r=3$, is $\Delta H_{\mathrm{f}}\mathrm{Al(OH)_3} = -51$ kJ mole^{-1}, with a molecular weight of 78.

The latter value is different from the literature data obtained by dissolution of a precipitate: $\Delta H_f = -35.88$ kJ mole^{-1}.

The experimental thermograms are similar, which seems to indicate that the "Al_{13}" polymer and the trihydroxide gel have similar structures. In fact, we know [9] that there is a structural correlation between the colloidal gel in solutions in which r is less than 2.5 and the "Al_{13}" polymer. In other words, the fresh colloidal gel is an association of "Al_{13}" polymers.

All the experimental curves of enthalpy vs. time correspond to exothermic reactions (Fig. 2) and have the same shape. Only the quantitative values of the total enthalpy increase with the neutralization ratio r from -30 J for $r = 1$ to -78.6 J for $r = 3$. The shapes of the thermograms (Figs. 3 and 4) show the complexity of the polymerization. The non-horizontality of the plateau is due to three simultaneous reactions; (i) the formation of "Al_{13}" polymer, (ii) formation of a precipitate composed of associated polymers (exothermic reactions), and (iii) dissolution of the precipitate (endothermic reaction) (Fig. 4). The return to the baseline after an ageing time of 5 h corresponds to slow kinetics of partial solubilization of the precipitate. If the hydrolysis reaction of the $Al(H_2O)_6^{3+}$ ion in the "Al_{13}" polymer were "complete" as can be obtained in solution with $r = 2$ under vigorous stirring [8], the thermogram would present a plateau, the extent of which would depend on the injection time and the sodium hydroxide concentration. Indeed there is a short plateau characteristic of a stationary state, corresponding to the continuous formation of the "Al_{13}" polymer outside of any

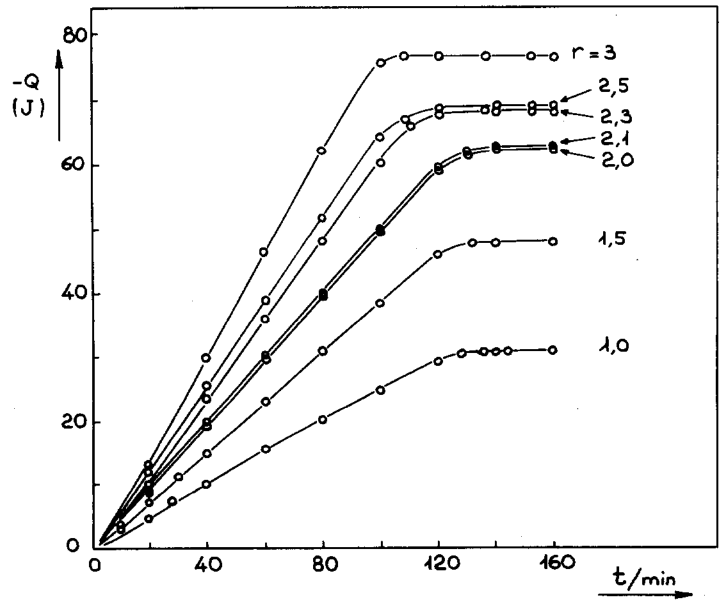

Fig. 2. Experimental integral heating curve vs. time.

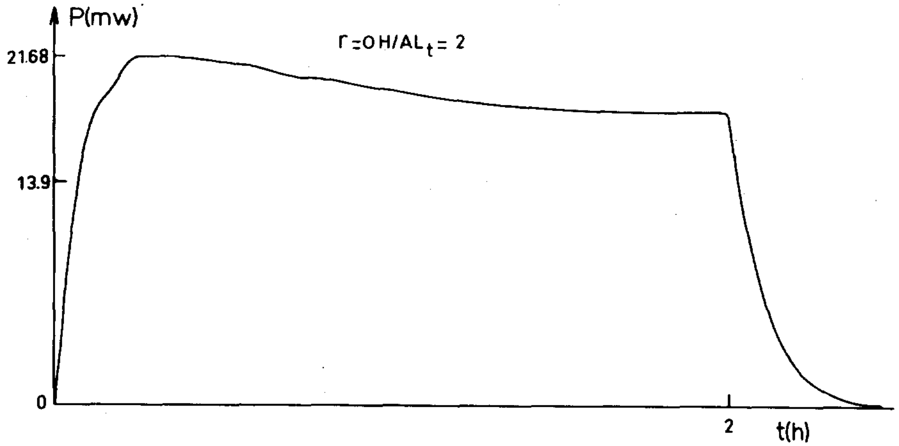

Fig. 3. Thermogram of the reaction corresponding to the preparation of the solution $r = 2$.

precipitation. Measurement of the time constant (corresponding to the release of half the total heat) is an interesting way of studying reaction kinetics and is particularly significant for similar chemical reactions. This time constant, calculated using experimental thermograms (Fig. 5), indicates that the kinetics of polymer formation is faster for $r = 2$ than for $r = 2.5$. At the end of the injection, a decrease in the calorimetric signal is observed. Usually the return to the baseline is exponential but in our experiments this is not always so, which confirms the fact that the reaction continues after the injection. This is true for solutions with $r = 1$ to $r = 2$ [Fig. 6(a)]. The return to exponential from $r = 2.3$ to $r = 3$ [Fig. 6(b)] means that the reaction has stopped when the injection of sodium hydroxide is stopped.

From the NMR results, computer calculation [8] and literature data, we

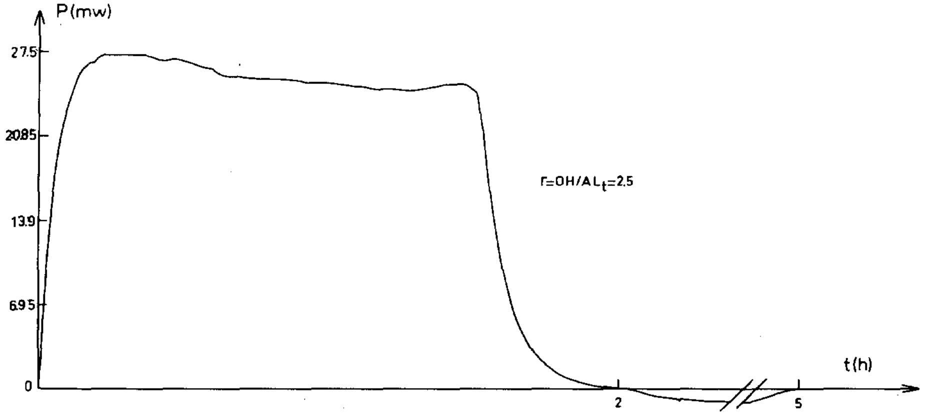

Fig. 4. Thermogram of the reaction corresponding to the preparation of the solution $r = 2.5$.

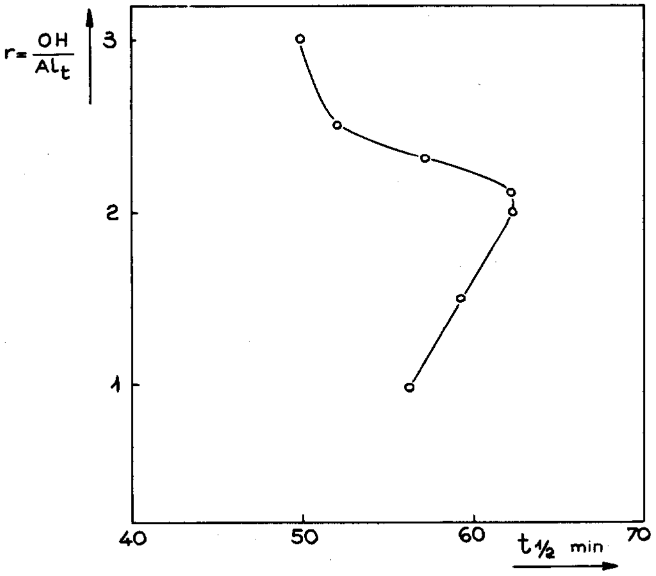

Fig. 5. Evolution of the time of half-reaction with the neutralization ratio *r*.

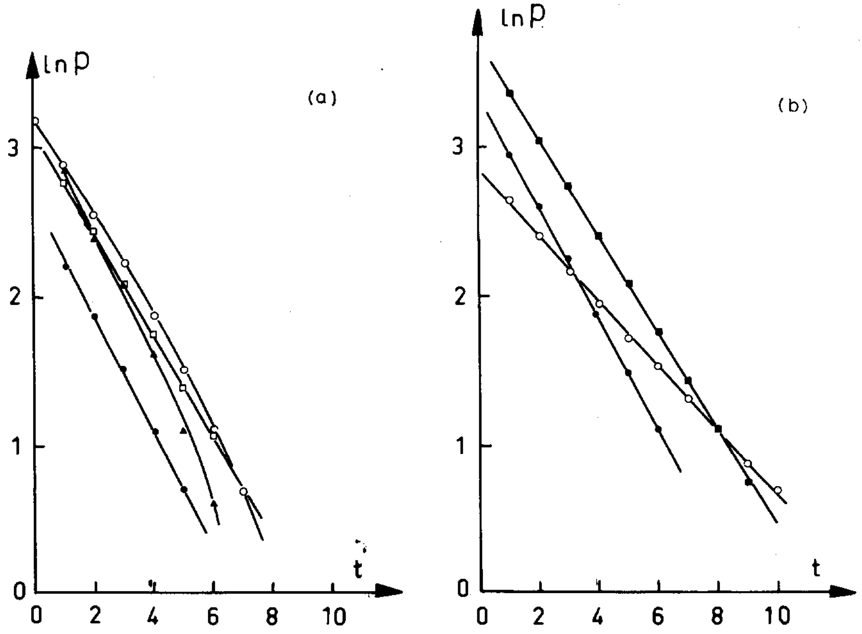

Fig. 6. Plot of the Naperian logarithm of the return to the baseline vs. time. (a) ●, $r = 1$; ○, $r = 1.5$; ▲, $r = 2$; □, $r = 2.1$. (b) ●, $r = 2.3$; ■, $r = 2.5$; ○, $r = 3$.

have calculated Gibbs energy of formation of the "Al_{13}" polymer and $Al(OH)_3$ as well as the entropy of formation at 298.15 K

$$\Delta G_r = -1{,}364 \log K_r = \Sigma \Delta G_{f\ \mathrm{reaction}} - \Sigma \Delta G_{f\ \mathrm{reactants}}$$

$$\Delta G_f = \Delta H_f - T\,\Delta S_f$$

where ΔG_r = Gibbs energy of reaction. K_r = equilibrium constant relative to equilibrium between Al^{3+} and "Al_{13}" and between Al^{3+} and $Al(OH)_3$, with K (polymer) = 10^{-105} [8] and K_s Al $(OH)_3 = 10^{-30.5}$ [7].

For the $Al_{13}O_4(OH)_{28}^{3+}$ polymer, $\Delta G_f = -13282.0$ kJ mole^{-1}; and $\Delta S_f = +42.5$ kJ mole^{-1}. For the amorphous $Al(OH)_3$ species, $\Delta G_f = -782.5$ kJ mole^{-1}; and $\Delta S_f = +2.4$ kJ/M.

CONCLUSION

The association of calorimetric measurements and aluminium-27 NMR data at 298.15 K has allowed calculation of the enthalpy of formation of the polymer $Al_{13}O_4(OH)_{28}(H_2O)_8^{3+}$ and a precipitate $Al(OH)_3$ at neutral pH: ΔH_f(polymer) = -602 ± 60.2 kJ mole^{-1}; and $\Delta H_f Al(OH)_3 = -51 \pm 5$ kJ mole^{-1}. From these experimental results and from potentiometric titration and NMR [8] we obtain values of ΔG_f and ΔS_f: ΔG_f(polymer) = -13282 kJ mole^{-1}; ΔS_f(polymer) = $+42.5$ kJ mole^{-1}; $\Delta G_f[Al(OH)_3] = -782.5$ kJ mole^{-1}; and $\Delta S_f[Al(OH)_3] = +2.4$ kJ mole^{-1}.

The main interest of these experiments arises from the experimental method itself, developed initially for studying the adsorption in aqueous media [10] and then applied here for studying the hydrolysis of the $Al(H_2O)_6^{3+}$ ion. The general form of the thermograms as a function of the neutralization ratio $r = (NaOH)/(Al_T)$ does not vary significantly. We therefore suppose that the precipitated gel for $r = 3$ has the same physicochemical nature as that obtained for $r \leqslant 2.5$. This assumption seems to be justified by comparison with the results obtained by small-angle X-ray scattering on gels at neutral pH [11,12] and with those obtained at pH $\leqslant 5$ [9], which led to the conclusion that there exist cylindrical or homogeneous platelets about 200–500 Å "long" and 15–60 Å "thick". It seems that the metastable phases preceding the precipitation of stable species is not energetic [1]. Nevertheless, the results concerning the enthalpy of formation of the $Al(OH)_3$ species are different from those of the literature. This fact may be due to the nature of the anion and the purity of the products. A systematic study is being carried out concerning the influence of anions (NO_3^-, SO_4^{2-}...) on the enthalpy of formation of the trihydroxide gel.

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