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^{31}P NMR spectroscopic studies of the influence of the environment in the degradation process of the Graham's salt

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Abstract

The "Graham's salt" is a vitreous sodium polyphosphate with a general formula of $Na_{(n+2)}P_nO_{(3n+1)}$. It is used in the ceramics industry as a deflocculant additive in a matrix of sodium silicate with different SiO_2:Na_2O ratios. The influence of the environment in which the Graham's salt is usually placed on its degradation into smaller particles has been studied by ^{31}P NMR spectroscopy at several temperatures on solutions with 7% of Graham's salt in sodium silicate with Rw = 1.6, 2.0, 3.3, in sodium carbonate 0.15 M, in sodium hydroxide 0.10 M and 1.0 M and in water. The signals in the ^{31}P NMR spectra of Graham's salt in D_2O, depending on their chemical shift δ (ppm) and multiplicity, have been assigned to the different phosphorous atoms of the skeleton of the several polyphosphates that are present in the solution. The integration of these signals at different temperatures has enabled the collection of kinetic and thermodynamic data: kinetic constants k (s^{-1}), activation energy E_a, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Results indicate that the environment is a factor which favours the degradation of polyphosphates, since with increasing basicity of deflocculating solutions the rate of degradation is faster. White gel obtained as a final product of the degradation process of Graham's salt has been analyzed with ^{31}P NMR spectroscopic measurements identifying orthophosphate and pyrophosphate as the main final species of the degradation of Graham's salt.

Keywords: Spectroscopy (B); Lifetime (C); Silicate (D); Degradation of polyphosphates

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1. Introduction

Deflocculating systems are widely used to decrease viscosity of colloidal dispersions. Specifically their use is extensive in the ceramic industry [1,2] in which clay, at different stages of the industrial process, has to have specific rheological properties.

At present, deflocculants in the ceramic industry are made as a mixture of compounds [3,4]; to sodium silicate ($Na_2O{\cdot}nSiO_2$) [5] are added either organic polymers [6,7] as polyacrylates or inorganic polymers as polyphosphates or both of these. Many efforts have been made to understand colloidal processing of ceramics [8–10] and generally it is accepted that reduction in the viscosity of deflocculants is due to a combination of different factors:

(i) It introduces a counter-ion like Na^+ to the solution thus forming a rigid layer adjacent to the colloid (Stern layer) [11].
(ii) It increases the pH of the solution favouring a decrease of zeta potential in the colloid and the viscosity of suspension.
(iii) It allows complexation of divalent and trivalent flocculating cations [12,13] like Ca^{2+} or Al^{3+}.
(iv) A steric repulsion effect is introduced due to adsorption of deflocculant onto the surface of clay particles [14].

Sodium hexametaphosphate (SHMP) is an inorganic polyphosphate [15,16] known to be good in ceramic processing [17]. However, industrially, the compound used is a mixture of polyphosphates [18] known as "Graham's salt". This vitreous polyphosphate is obtained by fusion of NaH_2PO_4 at 700–800 °C for several hours followed by rapid cooling. It consists of linear chains of the unit $(NaPO_3)_x$ with two terminal groups (Na_2PO_4) and has the general formula $M_{(n+2)}P_nO_{(3n+1)}$. Characterization of this kind of compound depends on the ratio Na_2O:P_2O_5 present in the mixture.

Graham's salt is widely used in the ceramic industry mixed with a matrix of sodium silicate of different SiO_2:Na_2O ratios in a range of concentrations between 1% and 10% depending of

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the final casting slip properties and the type of clay used in the process.

It has been previously reported Graham's salt shows degradation into smaller polyphosphates [19] which do not show good deflocculating properties due to temperature and ageing.

The aim of this work is to establish the influence of the environment in which Graham's salt is usually placed on its degradation into smaller particles with poorer deflocculating properties. For this purpose ^{31}P NMR spectroscopic measurements at several temperatures have been made on solutions with 7% of Graham's salt in sodium silicate with Rw = 1.6, 2.0, 3.3, in sodium carbonate 0.15 M, in sodium hydroxide 0.10 M and 1.00 M and in water. Experiments have been carried out at different temperatures to obtain kinetic and thermodynamic data.

High degradation of 8% of Graham's salt in NASIL gave rise to a "colloidal suspension" due to the presence of low solubility phosphate anions. Complete dissolution of the precipitate was observed with gradual heating from room temperature. ^{31}P NMR spectroscopic measurements were carried out with the purpose of identifying precipitated and finally degraded species.

2. Experimental details

2.1. General methods

^{31}P NMR spectra at room or higher temperatures, in the range 20–85 °C were recorded on a Bruker ARX-300 spectrometer from D_2O solutions. Ethylenglycol patterns were used to calibrate different temperatures.

2.2. Materials

Sodium silicate in different Rw ratios SiO_2:Na_2O was provided by IQE (Industrias Químicas del Ebro). NASIL® 1.6, 2.0, 3.3. Sodium carbonate monohydrate (99.5%) used to prepare a 0.15 M solution was purchased from Sigma–Aldrich. Sodium hydroxide (<98%), used to prepare 0.1 M and 1 M solutions, was purchased from Panreac. The phosphorous salt was crystalline sodium polyphosphate known as Graham's salt and commonly designed as "hexametaphosphate" [20] in the USA. It was provided by Arkem.

2.3. Methods

2.3.1. Preparation of NMR samples

The NASIL/D_2O/Graham's salt relation used in solutions with the three ratios SiO_2:Na_2O; Rw = 1.6, 2.0 and 3.3 was 75/18/7 respectively. All solutions were prepared following the same experimental procedure. First most of the water from NASIL was removed with a vacuum pump and the volume evaporated was replaced with D_2O. Graham's salt dissolved in D_2O was added to the NASIL in the ratio indicated previously. The freshly prepared solutions were placed in silica NMR tubes and cooled to −30 °C to avoid any degradation of the Graham's salt in advance of the ^{31}P NMR experiments. Sodium carbonate solution was prepared by dissolving the appropriate amount of the salt to get the required concentration in a D_2O solution with 7% of SHMP. Sodium hydroxide solutions were prepared by dissolving the required amount to obtain concentrations of base 0.1 M and 1 M with 7% of SHMP. A 93/7 D_2O/SHMP solution was prepared by dissolving the salt in D_2O.

A solution of NASIL/D_2O/Graham's salt 75/17/8 was prepared, placed in a silica tube and heated for 15 h to 90 °C obtaining an almost complete degradation of the Graham salt. ^{31}P NMR experiments were then carried out at 20 °C, 40 °C, 50 °C and 60 °C. Thereafter the solution was again heated to 90 °C for 15 h to complete not only the degradation of the Graham salt but also the degradation of the shorter polyphosphates that contain 3 or more phosphorous atoms. The ^{31}P NMR measurements after the 30 h heating at 90 °C were made at 20 °C, 40 °C, 50 °C, 60 °C and 81 °C.

3. Results

3.1. ^{31}P NMR results

3.1.1. Thermodynamic and kinetic data

The signals in the ^{31}P NMR spectra of Graham's salt in D_2O, depending on their chemical shift δ (ppm) and multiplicity, can be assigned to the different phosphorous atoms of the skeleton of the several polyphosphates that are present in solution. The integration of these signals at different temperatures allows study of the kinetics of the degradation process.

Fig. 1 shows the ^{31}P NMR spectrum of a sample of NASIL 2.0/D_2O/Graham's salt 75/18/7 at an intermediate level of degradation. In this figure it is possible to assign all the representative peaks.

The singlet at 5.71 ppm (**a**) is due to the ^{a}P signal of the orthophosphate anion $(PO_4)^{3-}$ that is the smallest fragment in the breaking of the phosphate polymer and the final step in the complete degradation of the Graham's salt.

The two areas (**b**) and (**c**) in Fig. 1 are expanded respectively in Figs. 2 and 3 to carry out a detailed identification of the phosphorous atoms of the species that are present in the degradation process and also the rate.

Fig. 2 shows the (**b**) region of the ^{31}P NMR spectrum in which appear the signals due to the terminal phosphorous atoms of all polyphosphates. At −4.14 ppm appears a doublet due to the ^{c}P atoms of the tripolyphosphate anion $(P_3O_{10})^{5-}$. Another doublet centered at −4.08 ppm and partially overlapped with the previous signal is assigned to the terminal phosphorous atoms ^{e}P of polyphosphates with >3 phosphorous atoms. A partially overlapped singlet at −4.22 ppm corresponds to the two ^{b}P of pyrophosphate $(P_2O_7)^{4-}$.

Scheme 1 shows the assignation of the phosphorous atoms in the polyphosphate anions to the signals observed in the ^{31}P NMR spectrum.

Fig. 3 shows the region (**c**) of the ^{31}P NMR spectrum and the signals that appear in it correspond to the internal phosphorous atoms of the different polyphosphates anions. Each signal has been numbered from (**1**) to (**6**). The triplet signal (**1**), at