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

José M. Casas [a,*], María P. García [a], Manuel Sanz [a], Francisco Cacho [b], Jorge Pérez [b]

[a] Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza–C.S.I.C., E-50009 Zaragoza, Spain

[b] Departamento de Investigación y Desarrollo, Industrias Químicas del Ebro, E-50057 Zaragoza, Spain

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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

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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* Corresponding author. Tel.: +34 976 761182; fax: +34 976 761187.
E-mail address: casas@unizar.es (J.M. Casas).

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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

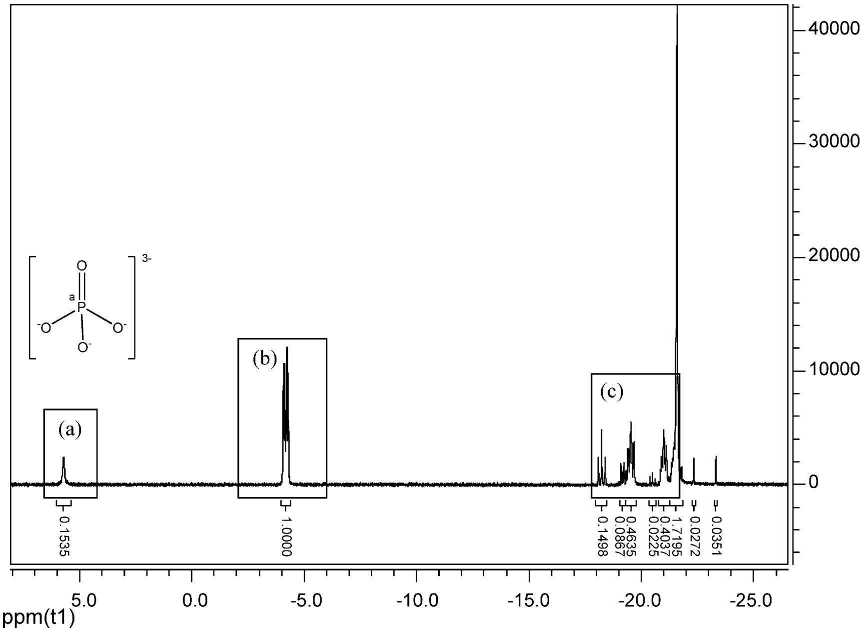


Fig. 1. ^{31}P NMR spectrum of a sample of NASIL 2.0/D_2O/Graham's salt with a relation of 75/18/7 in an intermediate level of degradation.

−18.23 ppm, corresponds to the central phosphorous atom of the tripolyphosphate anion designed as ^{d}P in Scheme 1. Signal (**2**), at −19.13 ppm, is assigned to the internal phosphorous atoms ^{f}P of the tetrapolyphosphate anion and signal (**3**) corresponds to the *n* phosphorous atoms ^{g}P of the polyphosphates containing five or more phosphorous atoms. At −20.49 ppm (**4**) appears the central ^{h}P of the pentapolyphosphate anion. At −20.89 ppm appears (**5**), that corresponds to phosphorous atoms ^{i}P of polyphosphates anions with six or more phosphorous atoms. Signal (**6**) at approximately −21.45 ppm is partially overlapped and corresponds to the phosphorous atoms ^{j}P of polyphosphates. Finally the intense broad signal at −21.62 ppm is due to the overlapping of the more internal phosphorous atoms of polyphosphates with eight or more phosphorous atoms.

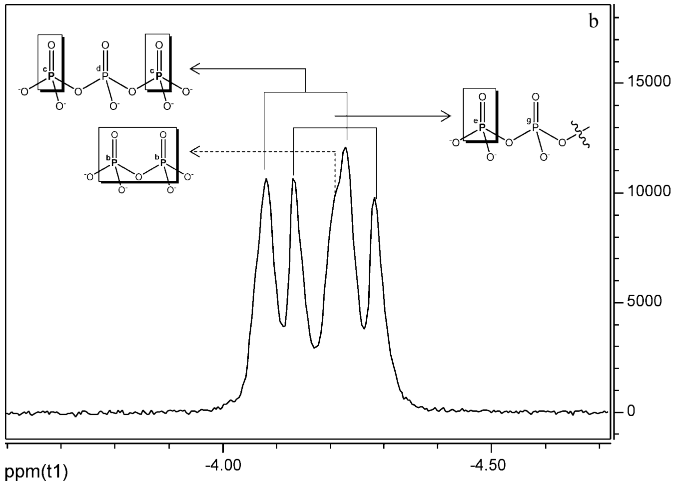


Fig. 2. Region (**b**) of the ^{31}P NMR spectrum in which appear the signals due to the terminal phosphorous atoms of all polyphosphates.

Experiments with Graham's salt at different temperatures were carried out to see the influence of the environment on the kinetics of degradation. The temperatures of the different ^{31}P NMR experiments are summarised in Table 1.

The degradation of Graham's salt is a first order kinetic process [11] with respect to the salt and then ln $C_o/C = kt$. C_o always corresponds in the ^{31}P NMR spectra with the addition of all integral values obtained. *C* is the value of the integral assigned to the main branch polyphosphates (s, −21.30 ppm). A subsequent plot of ln C_o/C versus *t* (s) gives a slope that matches with the kinetic constant *k* (s^{-1}) for the process. Time of the experiments was enough to collect sufficient points to make a good fit of the line. In Table 2 are collected the *k* (s^{-1}) parameters obtained at each temperature. Fig. 4 shows a plot of values of *k* (s^{-1}) collected.

As can be seen in Eq. (1), *k* parameters are required for a plot of ln *k* versus 1/*T*. The fit of points obtained gives a straight line of familiar form $y = mx + b$ where the slope $m = E_a/R$ (R = 8.314 J/mol K). From this value can be obtained the E_a (activation energy) parameter which is the energy that must be overcome in order for a chemical reaction to occur, the degradation process of Graham's salt in the present case.

$$\ln k = -\frac{E_a}{RT} + \ln A \qquad (1)$$

Thus this parameter gives information about the energy needed in the degradation process. All E_a parameters given in kJ/mol are collected in Table 3 and a graphic comparison between these values is shown in Fig. 5. Larger values of E_a show lower rate of degradation and the smaller values of E_a show faster rate of degradation.

The Eyring equation is a theoretical construct, based on a transition state model, which describes the temperature dependence of the reaction rate. From the Eyring equation

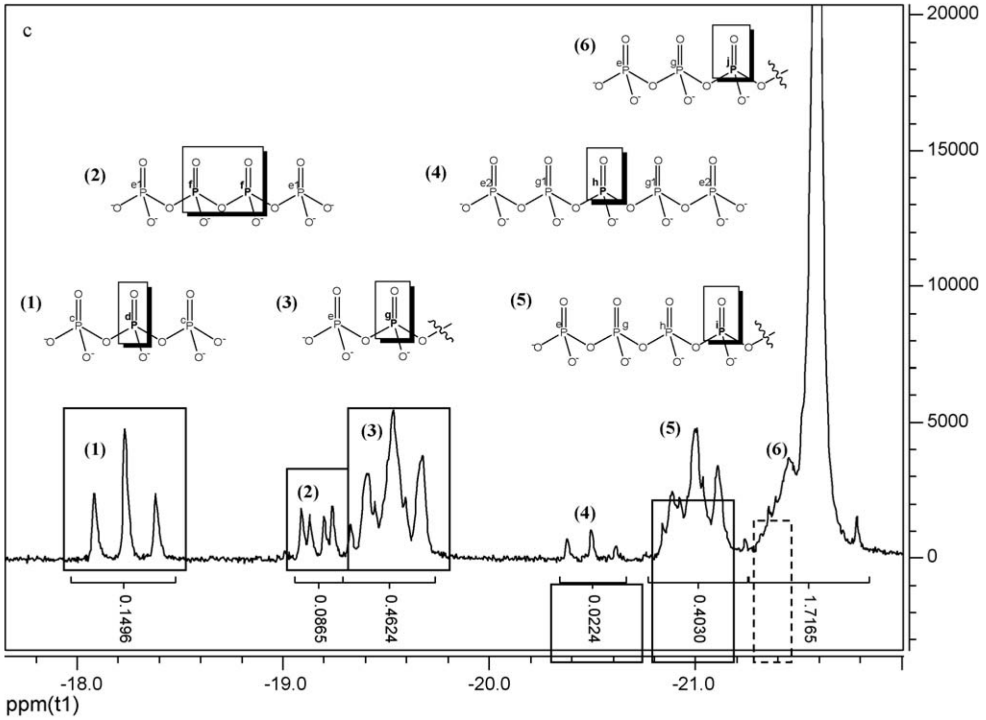


Fig. 3. Region **(c)** of the ^{31}P NMR spectrum in which appear the signals due to the internal phosphorous atoms of all polyphosphates.

Table 1
^{31}P NMR experiments carried out at different temperatures and environments.

Solutions	Temperatures (K)			
NASIL 1.6		315.4	326.2	337.0
NASIL 2.0		323.0	333.0	342.0
NASIL 3.3	337.0	343.0	351.5	358.5
NaOH 0.10 M	345.0	348.0	352.0	357.0
NaOH 1.0 M	315.0	321.5	326.0	331.0
Na_2CO_3 0.15 M		345.0	353.5	360.0
H_2O		345.0	354.0	361.0

(2) a plot of ln(k/T) versus 1/T produces a straight line of the form $y = mx + b$ where $m = -\Delta H^{\ddagger}/R$. $\Delta H^{\ddagger}$ can be calculated from the slope m of this line [21,22]:

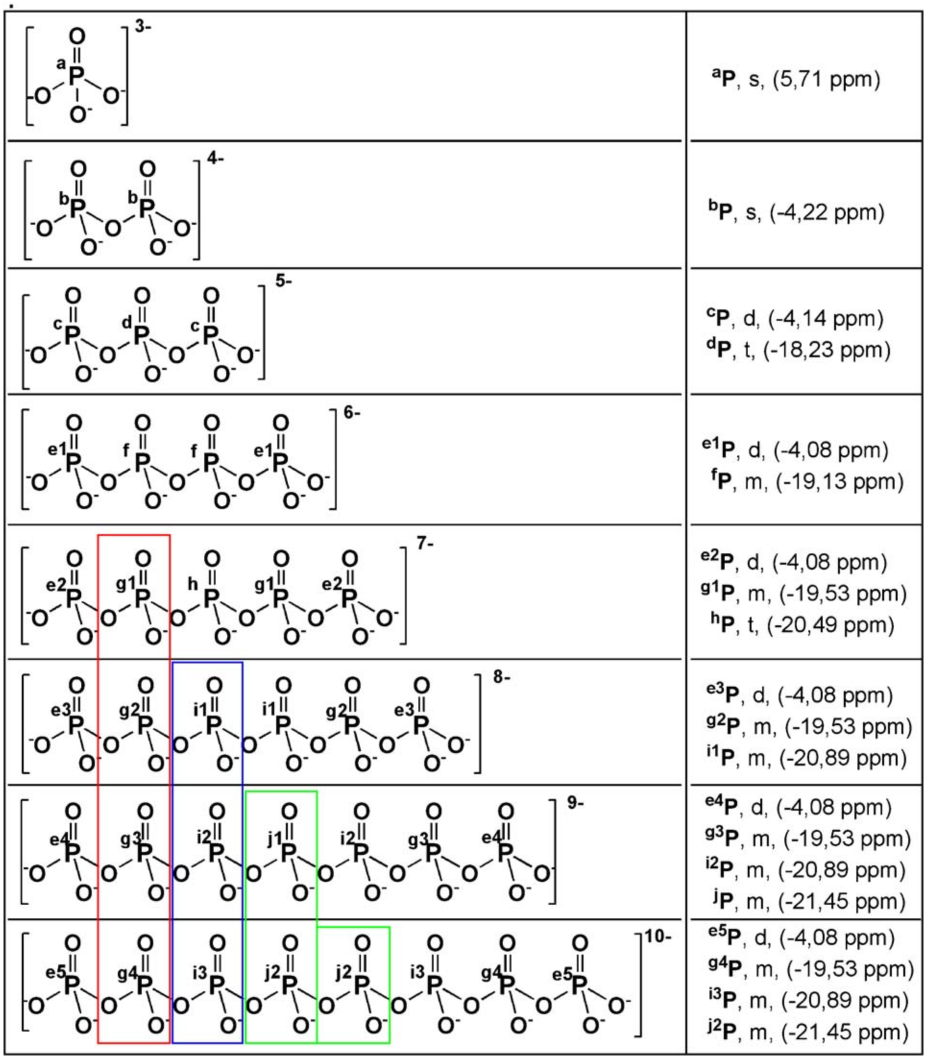
$$\ln\frac{k}{T} = -\frac{\Delta H^{\ddagger}}{R}\frac{1}{T} + \ln\frac{K_B}{h} + \frac{\Delta S^{\ddagger}}{R} \tag{2}$$

K_B is the Boltzmann's constant (1.381×10^{-23} J K^{-1}) and h is the Planck constant (6.626×10^{-34} J s). Moreover from the y-intercept it is possible to determine the $\Delta S^{\ddagger}$ according to Eq. (3).

$$y(x = 0) = \ln\frac{K_B}{h} + \frac{\Delta S^{\ddagger}}{R} \tag{3}$$

Table 2
Kinetic constants k (s^{-1}) obtained in ^{31}P NMR experiments at each temperature.

Solutions	k (s^{-1})			
NASIL 1.6	$k_{315.4}$ 9.3780×10^{-6}	$k_{326.2}$ 2.7630×10^{-5}	$k_{337.0}$ 6.3680×10^{-5}	
NASIL 2.0		$k_{323.0}$ 5.9246×10^{-6}	$k_{333.0}$ 4.1202×10^{-5}	$k_{342.0}$ 1.5861×10^{-5}
NASIL 3.3	$k_{337.0}$ 8.2983×10^{-6}	$k_{343.0}$ 1.7481×10^{-5}	$k_{351.5}$ 3.2012×10^{-5}	$k_{358.5}$ 6.5983×10^{-5}
NaOH 0.1 M	$k_{345.0}$ 9.1453×10^{-6}	$k_{348.0}$ 1.2028×10^{-5}	$k_{352.0}$ 2.0051×10^{-5}	$k_{357.0}$ 3.1960×10^{-5}
NaOH 1 M	$k_{315.0}$ 5.8820×10^{-6}	$k_{321.5}$ 1.0616×10^{-5}	$k_{326.0}$ 2.0189×10^{-5}	$k_{331.0}$ 3.0155 × 10−5
Na_2CO_3 0.15 M		$k_{345.0}$ 6.4160×10^{-6}	$k_{353.5}$ 1.8109×10^{-5}	$k_{360.0}$ 3.0997×10^{-5}
H_2O		$k_{345.0}$ 4.6076×10^{-6}	$k_{354.0}$ 1.7074×10^{-5}	$k_{361.0}$ 3.4616×10^{-5}



Scheme 1.

Thermodynamic parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are all collected in Table 4.

By simple inspection of the data collected it can be noted that temperature is the main factor which favours degradation of polyphosphates. The environment is also important since the experiments done at similar temperatures result in different values of k. With increasing basicity of deflocculating solutions the rate of degradation is faster as has been previously reported [23]. This can be linked to the parameter E_a and ΔH values obtained in this work: small values of E_a and ΔH imply a fast rate and large values of E_a and ΔH imply a slow rate. The kinetics of degradation can be described following the order:

$$\text{NASIL}\quad 1.6 > \text{NaOH}\quad 1\,\text{M} > \text{NASIL}\quad 2.0 >$$
$$\text{NASIL}\quad 3.3 > \text{NaOH}\quad 0.1\,\text{M} \sim \text{Na}_2\text{CO}_3\quad 0.15\,\text{M} > \text{H}_2\text{O}$$

This fact is very important since in the ceramic industry Graham's salt is mixed in a matrix of sodium silicate with a ratio Rw ranging 1.6–2.0 giving high basicity to the deflocculating systems. This situation can generate a reduction in the efficiency of the dispersant power of the system.

3.2. ^{31}P NMR results

3.2.1. Study of the final products of degradation

In the degradation process of Graham's salt is obtained a white gel that does not have deflocculant properties. To identify the species that are present in the gel we have carried out the degradation experiments in NMR tubes. The solution NASIL 1.6/D_2O/Graham's salt 75/18/7 was placed in a silica tube for 15 h at 90 °C and the white gel was obtained cooling at room temperature. The ^{31}P NMR experiments were carried out at 20 °C, 40 °C, 50 °C and 60 °C (Fig. 6). Subsequent heating of the sample for 15 h further was done to complete degradation and again ^{31}P NMR experiments were carried out at 20 °C, 40 °C, 50 °C, 60 °C and 81 °C (Fig. 7).

Orthophosphate (~6 ppm) and pyrophosphate (~−4 ppm) are the most significant signals indicating that they are the final products of the degradation. A weak triplet peak around −19 ppm confirmed the presence of a very small amount of tripolyphosphate. The other doublet signal corresponding to tripolyphosphate is overlapped by the pyrophosphate signal:

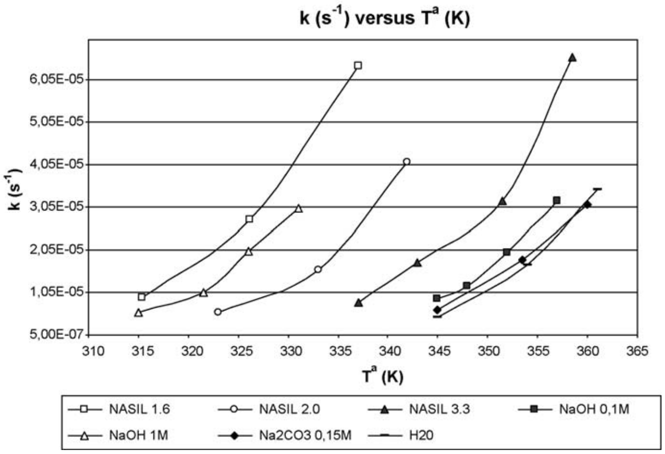


Fig. 4. Plot of k (s^{-1}) versus T (K).

Table 3
Activation energy E_a (kJ/mol) of the degradation process of Graham's salt obtained in different environments.

	E_a (kJ/mol)	Error E_a
NASIL 1.6	78.4	±4.3
NASIL 2.0	93.6	±3.5
NASIL 3.3	95.1	±6.3
NaOH 0.1 M	109.1	±4.9
NaOH 1 M	91.1	±6.6
Na_2CO_3 0.15 M	109.3	±10.1
H_2O	131.5	±11.4

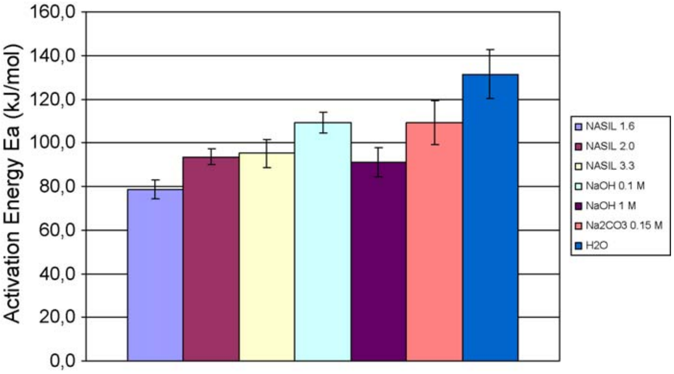


Fig. 5. Comparison of the activation energy E_a (kJ/mol) of the degradation process of Graham's salt obtained in different environments with their respective error bars.

[Integral $(P_2O_7)^{4-}$] – [Integral $(P_3O_{10})^{5-}/2$] = [Real value of $(P_2O_7)^{4-}$ Integral]. Results are shown in Table 5.

The presence of so small an amount of tripolyphosphate suggests its presence exclusively in solution so the tripolyphosphate integral is used as reference to establish the amount of the two other species related to it, orthophosphate and pyrophosphate, as a function of temperature. R_p is the quotient [$(PO_4)^{3-}$]/[Real value of integral $(P_2O_7)^{4-}$] and gives information about the relative concentration of both species and also about their ''relative'' solubility versus temperature as can be seen in Table 6.

Table 4
Thermodynamic parameter of $\Delta H^{\ddagger}$ in kJ/mol and $\Delta S^{\ddagger}$ in J/mol of the degradation process of Graham's salt obtained in different environments.

	$\Delta H^{\ddagger}$	Error $\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Error $\Delta S^{\ddagger}$
NASIL 1.6	−75.7	±4.3	−101	±13
NASIL 2.0	−90.8	±3.5	−65	±11
NASIL 3.3	−92.2	±6.3	−69	±21
NaOH 0.1 M	−106.2	±5.0	−35	±12
NaOH 1 M	−88.5	±6.6	−65	±17
Na_2CO_3 0.15 M	−106.4	±10.2	−37	±25
H_2O	−128.5	±11.4	25	±28

From 20 °C to 50 °C the R_p value indicates orthophosphate concentration increases in the solution. However from 50 °C to 81 °C the R_p value decreases and the pyrophosphate integral is higher in these spectra. Both facts show that the gel is formed by a mixture of orthophosphate/pyrophosphate which solubilises when the temperature increases. At low temperatures (20–50 °C) the most soluble part corresponds to orthophosphate, completely solubilised at 50 °C. From 50 °C until the gel is completely soluble R_p decreases so the pyrophosphate concentration in solution increases. The most soluble part of the gel is orthophosphate and the most insoluble is pyrophosphate; this justifies $R_{p_{20\,°C}} > R_{p_{60\,°C}}$.

The final species of the degradation of Graham's salt are mainly orthophosphate and pyrophosphate. The degradation process from pyrophosphate to orthophosphate is slower as can be observed in Figs. 4 and 5. On heating at 90 °C from 15 h to 30 h only 25% of pyrophosphate decomposes to orthophosphate. It is predicted that a longer period of degradation of Graham's salt will

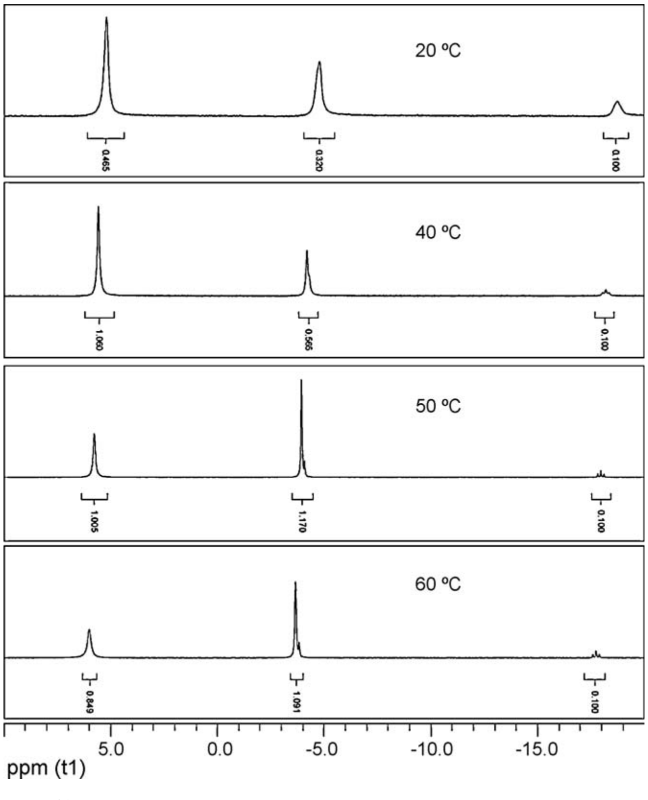


Fig. 6. ^{31}P NMR experiments carried out with the sample after 15 h at 90 °C. Temperatures of the experiments were 20 °C, 40 °C, 50 °C and 60 °C.

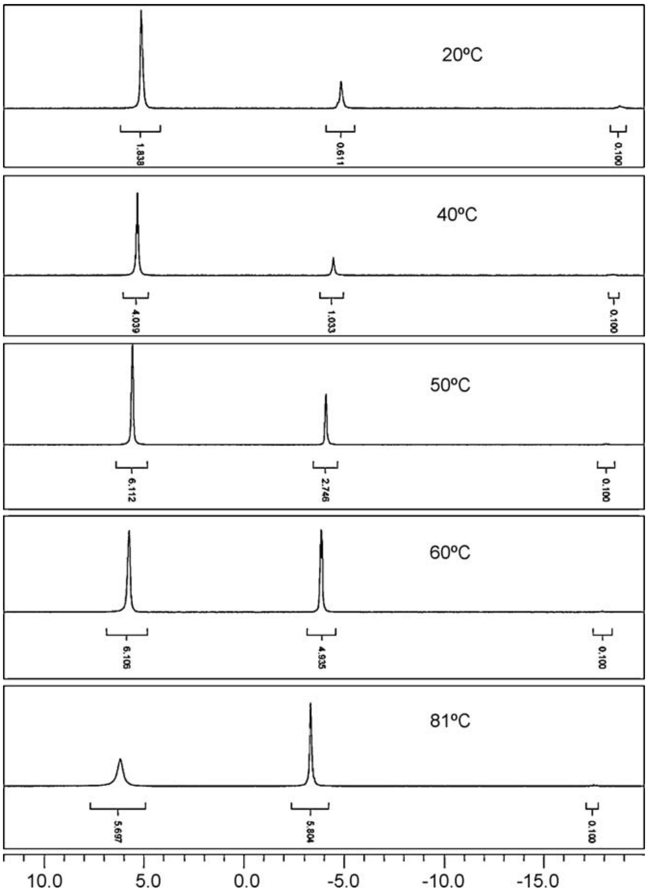


Fig. 7. ^{31}P NMR experiments carried out with the sample after 30 h at 90 °C. Temperatures of the experiments were 20 °C, 40 °C, 50 °C, 60 °C and 81 °C.

Table 5
Real value of $(P_2O_7)^{4-}$ Integral. (a) After 15 h at 90 °C. (b) After 30 h at 90 °C.

T (°C)	(a)	(b)
20	0.270	0.561
40	0.515	0.983
50	0.120	2.696
60	1.041	4.885
81		5.754

Table 6
Quotient R_p $[(PO_4)^{3-}]/[\text{Real value of integral } (P_2O_7)^{4-}]$ for 15 h and 30 h degradation of Graham's salt.

T (°C)	R_p after 15 h at 90 °C	R_p after 30 h at 90 °C
20	1.671	3.008
40	2.078	3.910
50	0.897	2.226
60	0.816	1.237
81		0.982

lead to orthophosphate as the only phosphorous containing species.

4. Conclusions

Previous studies have indicated that temperature is the main factor which favours degradation of polyphosphates into smaller phosphate anions without deflocculant properties. The ^{31}P NMR experiments, carried out in this article, show that the environment in which Graham's salt is dissolved is also important is this process. The results proved by increasing the basicity of deflocculating solutions the rate of degradation in Graham's salt was faster. Large values of the kinetic constant were obtained according to following order: NASIL 1.6 > NaOH 1 M > NASIL 2.0 > NASIL 3.3 > NaOH 0.1 M ~ Na_2CO_3 0.15 M > H_2O. This sequence matched up with increasing values of basicity from NASIL 1.6 to H_2O.

Moreover, small values of E_a and $\Delta H^{\ddagger}$ were obtained for those reactions with large values of k. Therefore, high basicity of solutions increases the ratio of degradation of larger polyphosphates in Graham's salt into smaller phosphate species. This fact is very important since in the ceramic industry Graham's salt is mixed in a matrix of sodium silicate with a ratio Rw ranging 1.6–2.0 giving high basicity to the deflocculating systems. This situation can generate a reduction in the efficiency of the dispersant power of the system since smaller polyphosphates have weaker deflocculant properties.

Further ^{31}P NMR experiments were carried out with objective of analysing the final species of the degradation of Graham's salt. This implies that orthophosphate and pyrophosphate are the main species of the gel generated after a prolongated heating of a sample of Graham's salt in a matrix of NASIL 1.6. Results indicate that the degradation process from pyrophosphate to orthophosphate was slower. It is predicted that a longer period of degradation of Graham's salt will lead to orthophosphate as the only phosphorous containing species.

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