NUCLEAR MAGNETIC RELAXATION IN PHOSPHATE AND POLYPHOSPHATE SOLUTIONS

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STELLINGEN

behorende bij het proefschrift van

H.S.KIELMAN

I

Chemische uitwisselingsprocessen bij lage en hoge pH geven een eenvoudiger verklaring voor de door Glasel gevonden relaxatie snelheden in biopolymeer oplossingen dan zijn fenomenologische regels.

J.A.Glasel,J.Am.Chem.Soc.92,375(1970).

J.J.van der Klink,J.Schriever en J.Leyte,Ber.Bunsenges. phys.Chem.78,369(1974).

II

Berekende ESR spektra van isoalloxazine kation radicalen met behulp van de door Müller et al. gegeven koppelingskonstanten zijn niet in overeenstemming met hun meetresultaten.

F.Müller,P.Hemmerich en A.Ehrenberg, Flavins and Flavoproteins (Ed.H.Kamin)p.107, University Park Press Butterworths, Baltimore and London (1971).

III

De bewering van Rösch en Ratner dat de systeem-bad wisselwerking in de lineaire response theorie niet in de dichtheids operator thuishoort is onjuist.

N.Rösch en M.A.Ratner,J.Chem.Phys.61,3344(1974)

IV

De uitspraak dat het optimale systeem om niet exponentiele relaxatie waar te nemen een methyl groep op een groot molekuul zou zijn, valt te betwijfelen.

L.G.Werbelow en A.G.Marshall,J.Magn.Res.11,299(1973).

V

Het is verwarrend dat chemische industrieën natrium polyfosfaat nog steeds aanduiden met de naam natrium metafosfaat.

E.Merck Darmstadt en Fluka A.G.

VI

Gezien de resultaten voor benzeen is het teleurstellend dat Doering en Moore in het lage energie elektron-impact energieverlies spektrum van pyridine onder grotere verstrooiingshoeken geen aandacht besteden aan een mogelijke verschuiving van het 5.0 eV maximum naar lagere elektron-excitatie energie.

J.P.Doering,J.Chem.Phys.51,2866(1969).

J.P.Doering en J.H.Moore,J.Chem.Phys.56,2176(1972).

VII

De beschrijving van optische aktiviteit door een tweede orde afhankelijkheid van een vibronische storing is niet volledig als slechts die elektrische en magnetische dipoolovergangsmomenten worden beschouwd, die in eerste orde afhangen van de storing.

O.E.Weigang Jr.,J.Chem.Phys.43,3609(1965).

R.T.Klingbiel en H.Eyring,J.Phys.Chem.74,4543(1970).

VIII

Het is te betreuren dat Navon en Lanir hun conclusie dat een belangrijk deel van de ^1H relaxatiesnelheid van azijnzuur het gevolg is van intermolekulaire dipool interactie met de eiwit protonen, niet op de gebruikelijke wijze hebben gecontroleerd door de relaxatie aan volledig gedeutereerd azijnzuur te meten.

G.Navon en A.Lanir,J.Magn.Res.8,144(1972).

IX

De stationsnaam aanduidingen op de perrons dienen niet evenwijdig aan, maar loodrecht op de rijrichting der treinen te worden geplaatst.

NUCLEAR MAGNETIC RELAXATION IN PHOSPHATE AND POLYPHOSPHATE SOLUTIONS

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PROEFSCHRIFT

ter verkrijging van de graad van Doctor
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op gezag van de Rector Magnificus Dr.A.E.Cohen,
Hoogleraar in de faculteit der letteren,
volgens besluit van het college van dekanen
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te klokke 16.15 uur

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HENDRIK SIMON KIELMAN

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Krips Repro B.V. Meppel

PROMOTOR: DR.J.C.LEYTE

Aan mijn ouders

Voor Liesbeth

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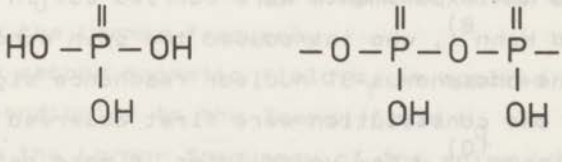
CHAPTER I

GENERAL INTRODUCTION

1.Purpose of investigation.

Nuclear magnetic resonance and more in particular nuclear magnetic relaxation studies on polyelectrolyte systems are relatively scarce although interesting information should be obtainable with this method of ionic and polyionic motion and the interaction between polyions and counterions. The systems selected for this work were aqueous solutions of sodium polyphosphates. The structure of the polyacid is seen in figure 1.1. This polyelectrolyte was studied for



$$\mathrm{HO{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}OH} \qquad \mathrm{{-}O{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}O{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}}$$

Figure 1.1 Structure of phosphoric acid (left) and two monomeric units of polyphosphoric acid (right).

several reasons. First of all there are two nuclei that can be observed here by NMR: Phosphorus-31 in the negatively charged ion and Sodium-23 as the positive counterion. Secondly the polyphosphates are easily prepared and they are very soluble in water. It is also possible to obtain solutions of the monomer(orthophosphate). A disadvantage that has to be mentioned is the hydrolysis that always occurs in the presence of water.

The orthophosphates and the polyphosphates are studied with a number of NMR techniques: pulsed NMR, Fourier transform spectroscopy and the pulsed field gradient method. This study can be classified into three major parts: the phosphorus-31 relaxation study in orthophosphate and in polyphosphate solutions, the sodium-23 study in polyphosphate solutions and the study of selfdiffusion coefficients in ortho- and polyphosphate solutions.

2.NMR methods.

The first nuclear magnetic resonance experiments in the condensed phase were realized by Purcell,Torrey and Pound1) and by Bloch,Hansen and Packard2) in 1946 using solid paraffin and water. In 1951 the idea of chemical shift was introduced by Arnold,Dharmatti and Packard3) on the spectrum of ethanol. The first commercial high resolution NMR spectrometer was sold by Varian Associates in 1953. The first theoretical articles on magnetization and relaxation were published by Bloch4) and Bloembergen5)6). The first pulsed NMR experiments were carried out in 1949 by Torrey7) and Hahn8), who introduced the spin echo. Chemical shifts of the phosphorus-31 nuclear resonance signal as a function of the constitution were first observed by Knight9) and by Dickinson10) a few years later. A more detailed study of phosphorus shifts in mainly organic samples has been carried out first by Gutowsky and McCall11). Later a large number of data was collected by van Wazer et al. and by Crutchfield et al.[12][13]. Since 1955 the number of articles concerning ^{31}P NMR has increased every year. However, the information about relaxation studies of phosphorus containing compounds is relatively small in relation to the number of high resolution spectra reported. Some relaxation studies of the phosphorus nuclei in these compounds are known, mostly in phosphorus halide molecules[14][15].

The NMR measurements can be divided into a number of different types of experiments:

1)Measurements in the frequency domain to obtain the high resolution spectra. This method will not be discussed.

2)Pulsed measurements in the time domain.

a)Relaxation experiments to obtain the longitudinal and the transversal relaxation rates.

b)Fourier transform measurements to obtain the frequency spectra and relaxation rates.

c)Spin echo experiments in the presence of a (time dependent)field gradient to obtain selfdiffusion coefficients.

a) Relaxation.

The classical equation of motion for a magnetic moment μ associated with an angular momentum $p=\gamma^{-1}\mu$ in an external magnetic field H_0 is

$$\frac{d\mu}{dt} = \mu \times \gamma H_0$$

which represents the motion of the magnetic moment precessing around the direction of the magnetic field H_0 with angular velocity $\omega_0=\gamma H_0$, γ being the gyromagnetic ratio and $\nu_0=\frac{\omega_0}{2\pi}=\frac{\gamma}{2\pi}H_0$ being the Larmor frequency.

When a second magnetic field H_1 is applied in the direction perpendicular to the Zeeman field H_0 and precessing with exactly the Larmor frequency of the spins, the spins start to precess around this H_1 field with frequency $\omega_1=\gamma H_1$ in the plane perpendicular to H_1. In pulsed nuclear magnetic resonance technique the radiofrequent field during the pulse is so intense, that all other interactions of the nuclear moment can be neglected. The time during which the H_1 field is present can be characterized by the angle over which the magnetization, representing the vectorsum of all spins, rotates from the original direction along the Zeeman field. For example, if the magnetization has turned into the plane perpendicular to the H_0 field the time τ during which H_1 is present is given by $\omega_1\tau = \gamma H_1 \tau = \frac{1}{2}\pi$ and called a 90^0 pulse. After such a pulse we have a nonequilibrium state in two respects. First there is a nonequilibrium state concerning the energy. The equilibrium distribution of the spin system is disturbed and after the pulse the magnetization returns to the state of equilibrium along the direction of H_0. This process has a characteristic time constant: T_1 ,the longitudinal or spin-lattice relaxation time. The second process is a consequence of the fact that all spins start simultaneously to precess around the H_0 field at the end of the pulse. This is not a state of maximum entropy. After the H_1 field is turned off the spins start to fan out and the entropy relaxes to its maximum (equilibrium) value. This process takes place with another time constant: T_2 ,the transversal or spin-spin relaxation time.

There are some other processes involved in studying the time dependence of the magnetization after a disturbance of the system. After a 90^0 pulse the magnetization disappears from the xy-plane (perpendicular to H_0 if we define the direction of the Zeeman field as the z-direction) by two processes: the transversal relaxation and the inhomogeneity of the Zeeman field. The inhomogeneity results in a slightly different frequency of the spins at different places in the sample tube. An additional process of selfdiffusion occurs; however the effect due to this process is generally small as concluded from exponential decay functions, while the selfdiffusion itself results in a nonexponential decay of the magnetization as a function of time. This phenomenon of selfdiffusion will be discussed in chapter VI.

The longitudinal relaxation rate T_1^{-1} is measured by a two pulse sequence. First a 180^0 pulse is applied to obtain a nonequilibrium state. The magnetization has turned to the -z direction. Some time later we apply a 90^0 pulse to detect in the xy-plane how far the magnetization has turned from the -z to the +z direction (equilibrium). This experiment is carried out for a number of different time intervals between the two pulses. The return to equilibrium is often given by the equation of Bloch[4]:

$$\frac{dM_z(t)}{dt} = - \frac{M_z(t)-M(0)}{T_1}$$

The transversal relaxation rate T_2^{-1} is measured by the spin echo method introduced by Hahn[8]. This method excludes the effect of field inhomogeneity. The magnetization is turned into the xy-plane by a 90^0 pulse. The spins start to fan out due to relaxation and other effects such as diffusion and inhomogeneity of the H_0 field. After a certain time t we apply a 180^0 pulse which reverses the inhomogeneity effect upon the magnetization but not the effects of relaxation and selfdiffusion. We neglect here the selfdiffusion. After this second pulse the spins start to fan backwards and at a time of 2t a spin echo is obtained. The amplitude of the spin echo will be the same as the amplitude of the magnetization after the first 90^0 pulse if no relaxation occurs. The spin echo amplitude decreases, due to transversal relaxation, as a function of time according to the second equation of Bloch[4]:

$$\frac{dM_{xy}(t)}{dt} = - \frac{M_{xy}(t)}{T_2}$$

b) Fourier transform measurements.

In this method a slightly different procedure is used.

The method of the measurements and all experimental details are given in chapter IV. The method is used in two ways. First to obtain from the time decay function after a 90^0 pulse the frequency spectrum and in the second place, in combination with a two pulse sequence as discussed above,to obtain relaxation rates of nuclei in one sample which are shifted with respect to each other. In a T_1 experiment the time decay function after the 90^0 pulse is transformed; in a T_2 experiment the second half of the spin echo is transformed into the frequency spectrum.

c) Selfdiffusion.

The measurements of the selfdiffusion coefficients are carried out in the presence of large time dependent field gradients. The method and the experimental information will be given in the last chapter.

The experimentally obtained relaxation rates are determined by the type of coupling of the nuclear moments with their molecular surroundings and the time dependence of the interaction. A spin I can be subject to several types of coupling with its environment, including other spins,describable by means of tensors, which are functions of the lattice parameters. Thus a bilinear coupling between two spins I and S ,i.e. dipolar interaction, can be written as $I.\hbar A.S$. A bilinear coupling between the applied field H and the spin I may be described by $H.\hbar A_s.I$,A_s being the chemical shift tensor. Such a coupling can be the result of an anisotropic shift of the Larmor frequency of the spin. For spins larger than ½ the coupling of electric field gradients with the quadrupole moment of the nucleus is a very important relaxation mechanism.The spin-rotation interaction is caused by the magnetic field at the position of the nucleus produced by the electrons and other nuclei in a molecule which have an angular velocity. The interaction is modulated as a result of the changes in angular velocity of the molecule associated with the thermal molecular motion in the liquid. A bilinear coupling different from the dipolar coupling between I and S can exist between an electronic and a nuclear spin if the electronic wavefunction has a non vanishing value at the position of the nucleus for different spins ($\nu_I \neq \nu_S$). The modulation can occur in two ways: either the coupling is time dependent by exchange or the other spin S has a relaxation time, due to some other mechanism than the coupling mentioned here, much shorter than the inverse of the frequency difference. Together with the scalar relaxation of the first kind due to chemical exchange, the chemical shift can be modulated and can become a mechanism of transversal relaxation. This is also an example of coupling of the spin with a fluctuating magnetic field.

All these couplings are the possible causes of the longitudinal and transversal relaxation of the nuclei under observation to their equilibrium state in the external Zeeman field after a disturbance. The relaxation rates following from all these couplings are discussed in chapter V concerning the quadrupolar relaxation (^{23}Na) and concerning the other mechanisms in chapter III (^{31}P).

3. NMR of phosphates and polyphosphates.

The investigation described in this thesis was restricted to mainly two nuclei: ^{31}P and ^{23}Na. Incidentally other nuclei were observed like ^{7}Li and ^{35}Cl. The measurements concerning the ^{23}Na nucleus were all carried out at a magnetic field of 14.09 kG and a frequency of 15.87 MHz. The resonance frequency of ^{31}P at that field is 24.29 MHz. Due to the fact that there exists a difference, in the systems described here, between the longitudinal and the transversal relaxation rates of ^{31}P, measurements were carried out at different frequencies.

The relaxation experiments as well as the selfdiffusion coefficient- and Fourier measurements were all done with a Varian Associates 14.09 kG magnet equiped with a magnet flux stabilizer. At the field of 14.09 kG we also used a Bruker NMR stabilizer B-SN 15. The pulsed NMR spectrometer used for all measurements was a Bruker B-KR 302 S16/60 MHz. This spectrometer was used with two power amplifiers for different frequency ranges and a Schomandl frequency synthesizer in order to perform measurements at all possible frequencies from 4 up to 60 MHz.

The registration took place by way of a Hewlett Packard storage oscilloscope and a time averaging procedure with a boxcar integrator, described elsewhere 16), in order to improve the signal to noise ratio. The signal of the nuclear magnetization close after the second pulse or at the maximum of the spin echo was automatically printed on paper tape and plotted on a semilogarithmic recorder. The slope of the line, drawn through the printed points, determines the relaxation rate. An example of such a relaxation rate measurement is given in figure 1.2.

The time decay function obtained in a Fourier transform experiment is stored in a Varian Associates C1024 time averaging computer (CAT). After the signal to noise ratio improvement procedure the time decay function was punched on paper tape via an interface and a Facit tape punch. The paper tape was used as the input to a Fourier transform computerprogram described in chapter IV.

The Fourier method was used for several purposes only concerning the phosphorus nucleus:

1)To obtain the phosphorus frequency spectrum to determine the degree of polymerization of polyphosphates.

2)To check the process of hydrolysis in aqueous polyphosphate solutions.

3)To obtain relaxation data of phosphorus nuclei with different chemical shifts in polyphosphate solutions.

The selfdiffusion measurements were only carried out at 14.09 kG as these coefficients are frequency independent and the signal to noise ratio improves at higher frequency. The experiments were done with a Bruker Feldgradienten-Einheit and field gradient coils at each side of the probehead in anti-Helmholtz configuration. Details of the procedure of the measurements are given in chapter VI.

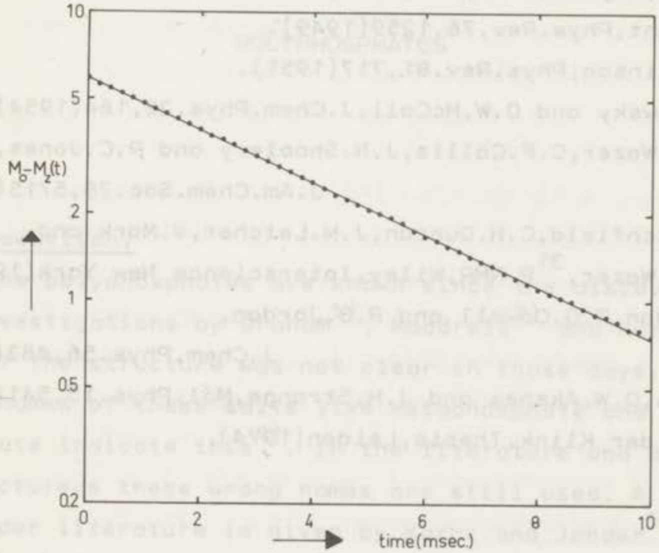


Figure 1.2 *Semilogarithmic plot of the decay of the longitudinal magnetization of* ^{23}*Na in an aqueous solution of 0.45 eq.*l^{-1} *NaPP(DP=34) + 0.05 eq.*l^{-1} *NaCl.* T_1^{-1}*=209 sec.*$^{-1}$ *,calculated from the slope.*

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CHAPTER II

POLYPHOSPHATES

1.Introduction.

The polyphosphates are known since the discovery and the investigations by Graham[1], Maddrell[2] and Kurrol[3]. However the structure was not clear in those days. The first names of these salts like metaphosphate and hexametaphosphate indicate this[4]. In the literature and also by manufacturers these wrong names are still used. A survey of the older literature is given by Karbe and Jander[5], who were the first to mention that the Graham salts consist of about fifty PO_3 groups. Other investigators also studied the structure of the polyphosphates[6] up to about 1953, when it was generally accepted that the polyphosphates consist of a string of PO_4 tetrahedrons with one common oxygen atom[7][8]. The differences, in the early days assumed to exist between Grahams, Maddrells and Kurrols salt, appeared only to be a difference in degree of polymerization. Nowadays one uses the name polyphosphate for the chain compound and the name metaphosphate for the cyclic compound.When the structure was no longer a point of discussion the most interesting features were extensively investigated: the hydrolysis behaviour[9)10)11)] and transport phenomena[12)13)] as a function of the degree of polymerization and neutralization. A large number of references exist in the literature especially by Thilo, van Wazer and Strauss. Concerning the hydrolysis it appeared that the branching points in the polyphosphates are very unstable[14)15)16)]. In relation to the behaviour of polyelectrolytes in water also a number of investigations was carried out concerning the polyion-counterion interaction upon the addition of salt[17)18)] and when there are divalent ions present in the solution[19)]. Studies of polyphosphates with the nuclear magnetic resonance technique were also carried out. A large number of data is collected by van Wazer[20)].

The phosphates and especially the polyphosphates are chemicals of universal application. One of the most important uses is in water treated with a phosphate glass to prevent the precipitation of Ca-salts. Nowadays there are other chemicals to prevent this and there is an increasing discussion going on about the polyphosphates in relation to the pollution of our environment[21)].

2.Preparation and fractionation.

The polyphosphates are polyelectrolytes of the following chemical constitution: $(MPO_3)_n.M_2O$ where M=Li,Na,K. A large number of studies has been performed on these polyphosphates (PP), especially before 1960, with all classical techniques. In later years also magnetic resonance studies are carried out; all high resolution spectra. A large amount of work has been reported on this subject until now.

In this magnetic relaxation study of the sodium polyphosphates the preparation, fractionation and determination of the degree of polymerization (DP) will be discussed, referring to the older literature.

The chemicals used in the measurements described in this thesis are the following.

All solutions of phosphoric acid in water were prepared from a stock of 85% phosphoric acid in water (E.Merck Darmstadt).
The solutions of deuterophosphoric acid were prepared from trideuterophosphoric acid (85%, min.99% D) (E.Merck).
In neutralizing these solutions KOH p.a. (titrisol), NaOH p.a. (titrisol) or NaOD p.a. (min.99% D) were used.

The sodium polyphosphates ($\alpha=1$) with a large number of different degrees of polymerization were made of several sources.
Sodium dihydroorthophosphate was from E.Merck Darmstadt.
Sodium tripolyphosphate from Alfa Inorganics USA.
Sodium hexametaphosphate, $(NaPO_3)_{12-13}.Na_2O$, from Fluka A.G. (The degree of polymerization was estimated by viscosity and FT NMR measurements and found to be 24 ± 2.)
Sodium metaphosphate, $(NaPO_3)_x$, from E.Merck.
(The degree of polymerization was estimated by the same methods and found to be 34 ± 2.)
The polyphosphoric acid solutions were prepared from:

1) $(NaPO_3)_n$ and the cationic exchanger Amberlite H(E.Merck).
2) "meta-Phosphorsaure p.a. Stangen zur Analyse $(HPO_3)_n$". (E.Merck).

   The degree of polymerization appeared to be about 20 and the degree of neutralization 0.6.

The polyphosphates were made by heating the starting material sodium dihydroorthophosphate(or polyphosphate with a lower degree of polymerization) in a platinum crucible at 900°C for at least 24 hours. Then after quickly cooling the polyphosphate glass we estimated the loss of weight for the

Table I. Fractionation of NaPP (DP=34) obtained from E.Merck (sodium metaphosphate).

Original solution: 102 g NaPP in 1 l H_2O.

added acetone (ml)	weight after freeze drying (g)	water content (%)	DP (visc.)
145	11.4	11.0	52
20	16.1	10.8	43
20	12.3	10.6	38
20	9.8	11.2	33
30	11.1	11.2	28
50	8.1	11.0	25
100	8.4	11.1	22
250	9.0	10.9	19

total: 86.2

Table II. Fractionation of NaPP obtained from NaH_2PO_4 after heating at $900^{0}C$ for 40 hours.

Original solution: 49 g NaPP in 750 ml H_2O.

added acetone (ml)	weight after freeze drying (g)	water content (%)	DP (visc.)
100	11.3	10.5	338
25	17.8	11.0	198
25	8.4	11.1	112
50	5.7	11.6	61
100	4.3	10.8	52

total: 47.5

following reaction:

$$n\ NaH_2PO_4 \longrightarrow (NaPO_3)_n + n\ H_2O$$

This loss was always within 2% of the theoretical value. The cooling procedure was carried out quickly for two reasons: 1) To obtain relatively high DP's.

2) To prevent water absorption.

The glass was solved in water and different quantities of acetone were added in a separatory funnel. When, after separation, the two solutions were clear, the NaPP-fraction was put in a round bottomed flask, some water added and freeze dried. Two most important examples are given in table I and II.

A number of Mark-Houwink relations are known for sodium polyphosphates in water:

1) $[\eta] = 1.76 \times 10^{-5}\ M$ in 0.035 N NaBr at 25.0 °C 22).
2) $[\eta] = 0.65 \times 10^{-4}\ M^{0.69}$ in 0.35 N NaBr at 25.0 °C 23).
3) $[\eta] = 4.94 \times 10^{-4}\ M^{0.50}$ in 0.415 N NaBr at 25.0 °C 23).

with M = viscosity average molecular weight.

$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c}$ η_{sp} = specific viscosity.
c = concentration(g/100ml).

The first relation holds for molecular weights from 7400 up to 20.000 (DP≈70-200). The second and third relation can be used for molecular weights above 70.000. In most cases we used the first equation in our experiments. The viscosities were measured for at least four concentrations with an Ostwald viscosimeter at 25.0 °C. The results are shown in figure 2.1. For the NaPP (DP=338) we also see a linear relationship and here it is assumed that the relation 1) still holds. For molecular weights lower than 7400 the results of the viscosity measurements are compared with the number average molecular weights determined from the Fourier

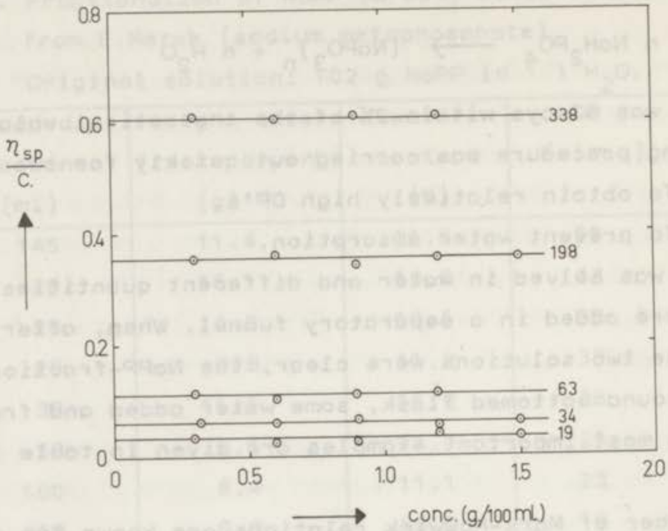


Figure 2.1 *Reduced viscosity of sodium polyphosphates in 0.035 eq.l.$^{-1}$ NaBr solutions in water at 25.0°C against concentration (g/100 ml). The numbers indicate the estimated degree of polymerization.*

transform ^{31}P NMR spectra. The areas (A) under the absorption bands of P_{middle} and P_{end} give the number average DP24):

$$DP = 2\,\frac{A(P_{middle}) + A(P_{end})}{A(P_{end})}$$

The results are shown in figure 2.2. The line gives the theoretical dependence for monodisperse polyphosphate ions and the measured data for the fractionated samples suggest a rather narrow distribution.

The viscosity measurements were performed on NaPP samples in aqueous solutions of NaBr. As the solutions of the NaPP were freeze dried before, no hydrolysis of the branching points will occur during these measurements. As the DP measurements were taken after the freeze drying

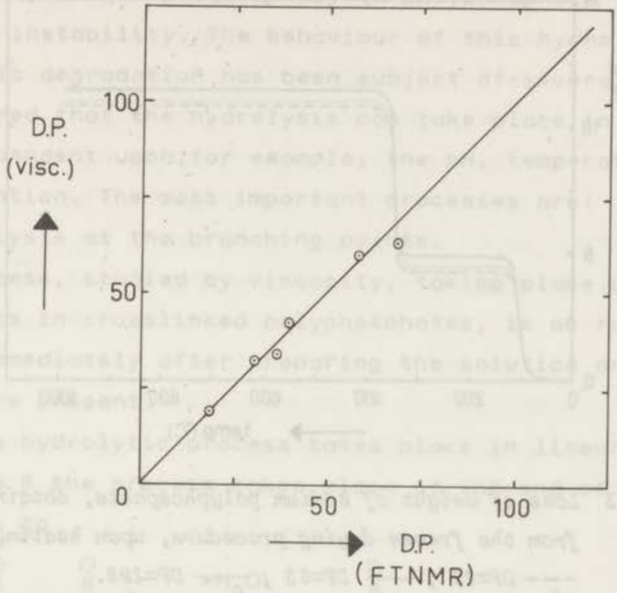


Figure 2.2 Comparison of the degree of polymerization estimated by viscosity and by Fourier transform measurements.

procedure a decrease of the DP, which occurs during this procedure, has not to be taken into account. Measurements of the viscosity of the solutions two days after the first measurements gave the same results. Pfanstiel and Iler[25)] carried out a number of viscosity measurements on potassium metaphosphate as a function of the K:P ratio. The viscosity seems to be greatly influenced by small changes in this ratio. As a result of the good agreement of the viscosity measurements and the Fourier transform NMR measurements, the influence of the Na:P ratio on the viscosity has not been studied.

An important value that has been to be known before the viscosity measurements can be done is the water content. By the freeze drying procedure some water remains in the NaPP. This water was estimated by weight-loss on heating

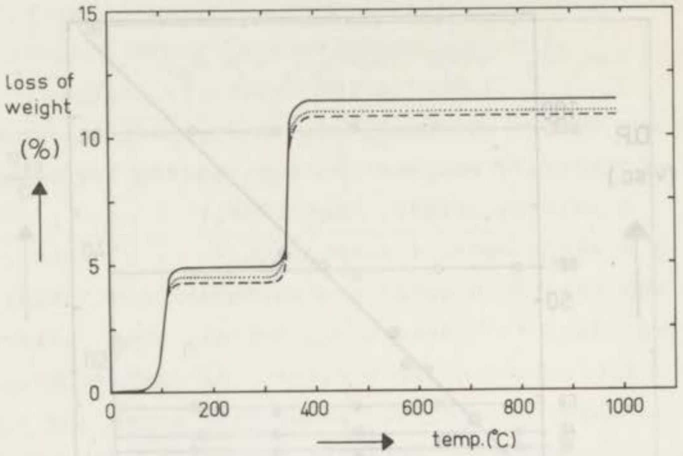


Figure 2.3 Loss of weight of sodium polyphosphate, obtained from the freeze drying procedure, upon heating.
- - - DP=28 ; ——— DP=63 ; ········ DP=198.

with a Differential Temperature Analyser. The water was present in two forms, as can be seen in figure 2.3. The amount of crystal water of 7% evaporating at 350°C comes close to one water molecule for two PO_3-groups. A possible explanation may be that one water molecule is (strongly) bound by H-bridges with two neighbouring P=O bonds. The other amount of water of about 4½% was dependent on the vacuum obtained at the freeze drying operation. This amount of water is adsorbed as the result of hygroscopic properties and the evaporating temperature of 100°C suggests no special bond between this water and the polyphosphates. To obtain the water content, the polyphosphates need not to be heated above 450°C.

In addition to the above mentioned methods some other methods are used to obtain the DP:

1)Endgroup titration of polyphosphoric acid with NaOH.

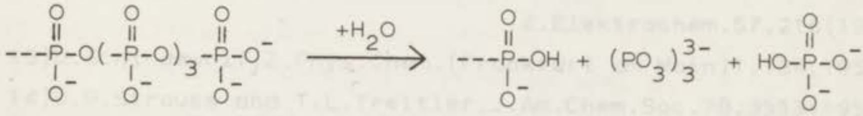
2)Determination of the ^{23}Na relaxation rate$^{26)}$.

Another important property of polyphosphate solutions is their instability. The behaviour of this hydrolysis or hydrolytic degradation has been subject of several studies. It appeared that the hydrolysis can take place in several ways, dependent upon, for example, the pH, temperature and concentration. The most important processes are:

1) hydrolysis at the branching points.

This process, studied by viscosity, taking place at branching points in crosslinked polyphosphates, is so rapid that almost immediately after preparing the solution only linear chains are present.

2) a slow hydrolytic process takes place in linear chains. At pH=7 à 8 the process takes place at the end of the chain according to



$$\text{---}\overset{O}{\underset{O^-}{P}}-O(-\overset{O}{\underset{O^-}{P}}-O)_3-\overset{O}{\underset{O^-}{P}}-O^- \xrightarrow{+H_2O} \text{---}\overset{O}{\underset{O^-}{P}}-OH + (PO_3)_3^{3-} + HO-\overset{O}{\underset{O^-}{P}}-O^-$$

where ortho- and trimetaphosphate are formed9).

At lower pH the process also takes place in the middle of the chain where there is always orthophosphate formed. This slower hydrolytic process takes place at pH > 6 with such a low speed that within a week at room temperature no orthophosphate can be detected. An excellent method to show the presence of orthophosphate in polyphosphate solutions is by the ^{31}P NMR spectrum, as the ^{31}P in orthophosphate is shifted from the ^{31}P in polyphosphates.

The measurements on polyphosphate solutions at full neutralization were all carried out within a week after the solutions were prepared. At lower degree of neutralization the measurements were performed within one day after the solutions were made. No hydrolysis was detected in these cases by the Fourier transform method, described in chapter IV. After keeping a solution at room temperature (20°C) for one month or for a longer period, hydrolysis could be detected as shown in figure 4.1. In chapter IV and V the relaxation of ^{31}P and ^{23}Na is discussed in polyphosphoric acid solutions. Commercial polyphosphoric acid of a low degree of neutralization is, as a result of the instability, not available. In order to obtain polyphosphoric acid with a high DP (>60) and a low α we treated sodium polyphosphate (DP=63) with Amberlite(H form) and obtained HPP with an α value of 0.01 or less. This value was estimated by titration with sodium hydroxyde in combination with the ^{31}P frequency spectrum to check for the effect of hydrolysis. The concentration was also estimated by Fourier transformation of the time decay function using an internal standard of known concentration (NaH_2PO_4).

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CHAPTER III

RELAXATION OF PHOSPHORUS-31 IN PHOSPHORIC ACID AND ORTHOPHOSPHATE SOLUTIONS

1. Introduction.

There exists in the literature a large number of NMR data concerning the phosphorus nucleus. Chemical shifts, coupling constants and relaxation rates are known of many organic and inorganic compounds. From all these data it appears that the relaxation behaviour of this nucleus is very complicated, and the relaxation rates, both longitudinal and transversal, are difficult to predict. To illustrate this we see that in different cases almost all relaxation mechanisms occur. Only quadrupole relaxation can be excluded due to the fact that $I(^{31}P)=\frac{1}{2}$.

In phosphorus halide compounds like PCl_3 1) and PBr_3 2)3) the relaxation is complicated and has been described by a contribution of three relaxation mechanisms: scalar coupling dipole-dipole interaction and anisotropic chemical shift. In a number of articles it is shown that spin-rotation interaction can give important contributions to the relaxation rates 4). Dale and Hobbs 5) studied the relaxation rates of

^{31}P in some organic and inorganic compounds and they also found more than one relaxation mechanism to contribute to the phosphorus relaxation.

In relation to phosphoric acid and orthophosphates a few NMR studies are known, mainly concerning the chemical shift and the determination of coupling constants.Jones and Katritzky[6)] measured the shift in phosphoric acid as a function of the degree of neutralization; our measurements gave the same results within experimental error. Also ^{31}P coupling constants are known in the literature in many cases concerning P-H coupling constants and the isotopic effects in replacing H by D in organic molecules where the proton is directly attached to the phosphorus[7)]. From the known P-(O-)H coupling constants it appears that these constants are usually smaller than approximately 200 Hz.[8)]. Relaxation data of ^{31}P in phosphoric acid and phosphates are, as far as we know, not mentioned in the literature except some uncertain data by Dale and Hobbs[5)]. They also mentioned that there might be a contribution from scalar interaction in the relaxation as a result of chemical exchange in a 85% phosphoric acid solution in water, but due to the uncertainty of the data they were not able to give a more detailed treatment.

A qualitative and quantitative study of the ^{31}P relaxation in molecules where the phosphorus nucleus is tetrahedrally surrounded by four oxygen atoms should give interesting information on the structure and behaviour of phosphates and phosphoric acid in aqueous solutions. It can be extended to meta- and polyphosphates and finally it may be helpful in solving problems in biological systems where the ^{31}P nucleus plays an important role, for instance in ADP and ATP.

Concerning orthophosphoric acid and orthophosphates a number of articles appeared discussing the nature of the aqueous solutions[9)10)11)12)]. The behaviour of anion trans-

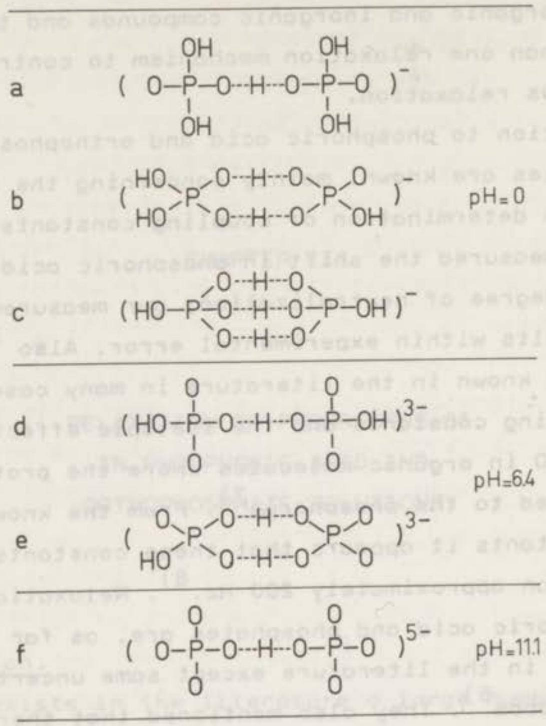

Figure 3.1 Some structures of complex ions in phosphate solutions. a) by Selvaratnam[9] b)c)d) by Childs[11] e)f) this thesis.

ference numbers and conductances of phosphoric acid cannot be explained by hydrogen jumps between the anions $H_2PO_4^-$ and H_3PO_4 as in HCl. These anomalies are explained by the existence of triple ions[9]. The same explanation is given for the fact that the degree of dissociation calculated from conductance or EMF in H_3PO_4 passes through a minimum at about 1 mole.l.$^{-1}$ [13]. The formation of hydrogen bonded $H_2PO_4^-.H_3PO_4$ ions in the solid state seems also probable since stable salts of the formula $MH_2PO_4H_3PO_4$ have been isolated[14]. Selvaratnam and Spiro[9] suggested that evidence for the existence of triple ions should be forthcoming from spectroscopic data, but their trials were inconclusive. Although a number of authors agree with each other about the existence of these triple or complex ions the structure of the ions remains a source of discussion. Figure 3.1 shows some examples of complex ions as suggested by Selvaratnam[9)] and Childs[11)] and some added by us.

2. Relaxation mechanisms.

When observing the ^{31}P nucleus by NMR relaxation we should know the possibilities concerning the contributions of the relaxation mechanisms to the relaxation rates. Therefore we will present a short discussion of the mechanisms and give the resulting equations ,referring for the derivations of these equations to the general NMR literature. Mechanisms that in general can give a contribution to the relaxation rate are the following:

1) Relaxation through dipolar coupling (DD).
   a) between like spins
   b) between unlike spins
2) Relaxation through spin-rotation interaction (SR).
3) Relaxation through anisotropic chemical shift (ACS).
4) Relaxation through scalar spin-spin coupling (SC).
   a) by chemical exchange
   b) by fast relaxation of the other spin
5) Relaxation through modulation of the chemical shift (MCS).

1) The formulas for the relaxation rates in the case of dipolar coupling are given by Abragam[15)]:

a) for like spins(I)

$$T_1^{-1}(DD) = \frac{3}{2}\gamma_I^4\hbar^2 I(I+1)(J^1(\omega_I)+J^2(2\omega_I)) \qquad (1)$$

$$T_2^{-1}(DD) = \frac{3}{2}\gamma_I^4\hbar^2 I(I+1)(\frac{1}{4}J^0(0)+\frac{5}{2}J^1(\omega_I)+\frac{1}{4}J^2(2\omega_I)) \qquad (2)$$

b) for unlike spins the relaxation rates of spin I due to interaction with spin S are:

$$T_{1II}^{-1}(DD)=\gamma_I^2\gamma_S^2\hbar^2 S(S+1)\left(\frac{1}{12}J^0(\omega_I-\omega_S)+\frac{3}{2}J^1(\omega_I)+\frac{3}{4}J^2(\omega_I+\omega_S)\right) \quad (3)$$

$$T_{1IS}^{-1}(DD)=\gamma_I^2\gamma_S^2\hbar^2 I(I+1)\left(-\frac{1}{12}J^0(\omega_I-\omega_S)+\frac{3}{4}J^2(\omega_I+\omega_S)\right) \quad (4)$$

$$T_{2I}^{-1}(DD)=\gamma_I^2\gamma_S^2\hbar^2 S(S+1)\left(\frac{1}{6}J^0(0)+\frac{1}{24}J^0(\omega_I-\omega_S)+\frac{3}{4}J^1(\omega_I)+\frac{3}{2}J^1(\omega_S)+\frac{3}{8}J^2(\omega_I+\omega_S)\right) \quad (5)$$

with $\omega_I=2\pi\nu_I$ ν_I=resonance frequency of spin I
$\omega_S=2\pi\nu_S$ ν_S=resonance frequency of spin S
γ =gyromagnetic ratio
$\hbar$ =reduced constant of Planck

The spectral density functions in the case of isotropic random rotation are:

$$J^0(\omega)=\frac{24}{15}\cdot\frac{1}{r^6}\cdot\frac{\tau_c}{(1+\omega^2\tau_c^2)} \quad (6)$$

$$J^1(\omega)=\frac{4}{15}\cdot\frac{1}{r^6}\cdot\frac{\tau_c}{(1+\omega^2\tau_c^2)} \quad (7)$$

$$J^2(\omega)=\frac{16}{15}\cdot\frac{1}{r^6}\cdot\frac{\tau_c}{(1+\omega^2\tau_c^2)} \quad (8)$$

r =distance between the two nuclei
τ_c =rotational correlation time

In orthophosphate solutions the relaxation through dipolar coupling between like spins can only take place between two nuclei in different molecules. The distance between the two phosphorus atoms is very large, even in the complex structures suggested in figure 3.1. A contribution to the observed relaxation rate cannot be expected from this mechanism. A contribution to the relaxation rate of ^{31}P from the dipolar coupling between unlike spins is possible from the coupling between P and H. For instance, assuming a P-H distance of 2.1 Å, which is rather short, and a correlation time of

10^{-10} sec. we calculate $T_{2I}^{-1}(DD)=0.22$ sec^{-1}. Relatively long correlation times are needed to contribute significantly, mainly to the transversal relaxation rate.

2) The contribution of the spin-rotation interaction will not be considered in relation to the ^{31}P relaxation in phosphates for several reasons. This mechanism mainly occurs in non-hydrogen bonded liquids and gases of small molecules. Most important is the contribution of this mechanism to the relaxation rate as a function of temperature. For a spherical molecule, undergoing isotropic Brownian motion we have[1)16)]:

$$T_1^{-1}(SR)=\frac{2}{3}\cdot\frac{I_\circ kT}{\hbar^2}c^2\tau_{SR} \qquad (9)$$

$I_\circ$= moment of inertia of the molecule.

$c^2=2c_\perp^2+c_\parallel^2$, $c_\perp$ and $c_\parallel$ being the components of the diagonalized spin-rotation interaction tensor.

τ_{SR}=correlation time for the molecular angular velocity.

The relaxation rate due to spin-rotation interaction increases with increasing temperature, a behaviour opposite to all other mechanisms. As mentioned in the experimental section this temperature dependence of the relaxation rates was never observed here.

3) The relaxation through anisotropic chemical shift is a result of the anisotropy of the tensor coupling of the applied field H_0 and the spin I. The relaxation rates as a result of this mechanism are under the assumption of cylindrical symmetry of the chemical shift tensor:

$$T_1^{-1}(ACS)=\frac{6}{20}\omega_I^2\delta^2\frac{\tau_c}{1+\omega_I^2\tau_c^2} \qquad (10)$$

$$T_2^{-1}(ACS)=\frac{1}{20}\omega_I^2\delta^2\left(4\tau_c+\frac{3\tau_c}{1+\omega_I^2\tau_c^2}\right) \qquad (11)$$

with δ=axial component of the chemical shift tensor in the frame of the molecule.

The longitudinal and transversal relaxation rates will increase with increasing frequency. It has to be noted that in ordinary electrolyte solutions at room temperature the narrowing limit condition will be fulfilled ($\omega_I\tau_c \ll 1$). In that case:

$$T_1^{-1}(ACS) = \frac{6}{20}\omega_I^2\delta^2\tau_c \quad (12) \qquad \text{and} \qquad T_2^{-1}(ACS) = \frac{7}{6}T_1^{-1}(ACS) \quad (13)$$

4) The mechanism of relaxation through scalar spin-spin coupling becomes important if a) the exchange time τ_e is shorter than the reciprocal coupling constant or shift between the two sites in which the nucleus can reside. The multiplet structure disappears and a single resonance line is observed; b) the other nucleus has a relaxation time short in relation to the inverse frequency difference. This includes relaxation rates as a result of dissolved oxygen or paramagnetic impurities. The equations for the relaxation rates of spin I due to time dependent scalar coupling with spin S are (case a):

$$T_1^{-1}(SC) = \frac{2}{3}A^2S(S+1)\frac{\tau_e}{1+(\omega_I-\omega_S)^2\tau_e^2} \quad (14)$$

$$T_2^{-1}(SC) = \frac{1}{3}A^2S(S+1)\left(\tau_e + \frac{\tau_e}{1+(\omega_I-\omega_S)^2\tau_e^2}\right) \quad (15)$$

with $A=\gamma_I\gamma_S J$ and J= reduced coupling constant.

If $(\omega_I-\omega_S)\tau_e \gg 1$: $\quad T_2^{-1}(SC) = \frac{1}{3}A^2S(S+1)\tau_e \quad (16)$

The relaxation formulas for the scalar coupling of the second kind look similar to those above if τ_e is replaced by the relaxation time of the spin S.

5) Relaxation through modulation of the chemical shift seldom appears to be important in the literature up to now, but it could provide a contribution to the transversal relaxation rate in the case that chemical exchange is present. Equations for the relaxation rate in the presence of chemical exchange for a two site model were derived by Wennerström 17). These

rates are:

$$T_1^{-1}(\mathrm{MCS}) = 0 \tag{17}$$

$$T_2^{-1}(\mathrm{MCS}) = p_A p_B \Delta\omega^2 \tau_e \tag{18}$$

for the equilibrium $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$ with $\Delta\omega\tau_e \ll 1$

$p_{A,B}$ = equilibrium population of fraction A,B

$\Delta\omega$ = shift between the nucleus in site A and B

τ_e = exchange time between the two sites

$$\tau_e = \frac{p_A}{k_1} = \frac{p_B}{k_{-1}} \quad \text{where } k = \text{reaction rate.} \tag{19}$$

3.Results and discussion.

A number of relaxation time measurements was carried out (both longitudinal and transversal) on the ^{31}P nucleus in orthophosphate solutions as a function of temperature,concentration,degree of neutralization and Larmor frequency. The most interesting results are shown in the figures in this chapter. Figure 3.2 shows the relaxation rates in orthophosphoric acid as a function of the pH. Two maxima are observed; at pH=6.4 and at pH=11.1. In these pH regions the chemical shift changes fast as a function of pH relative to other pH values[18)]. At pH=6.4 the amount of $H_2PO_4^-$ ions is about equal to the amount of $HPO_4^=$ ions.At pH=11.1:conc.$HPO_4^=$ =conc.$PO_4^\equiv$. Figure 3.3 shows the relaxation rates in deuterophosphoric acid partly neutralized by NaOD in heavy water. In fact all protons are replaced by deuterons. We also observe two maxima at pD=6.0 and pD=10.7. These observed pD values (meter readings) are in agreement with literature data: $(\mathrm{pH})_{\mathrm{obs.}} = (\mathrm{pD})_{\mathrm{obs.}} + 0.4$ [19)]. The relaxation rates in the figures 3.2 and 3.3 differ greatly. In both figures we have a T_1-T_2 difference,so a frequency dependence of the relaxation rates can be expected. Replacing in all solutions sodium by

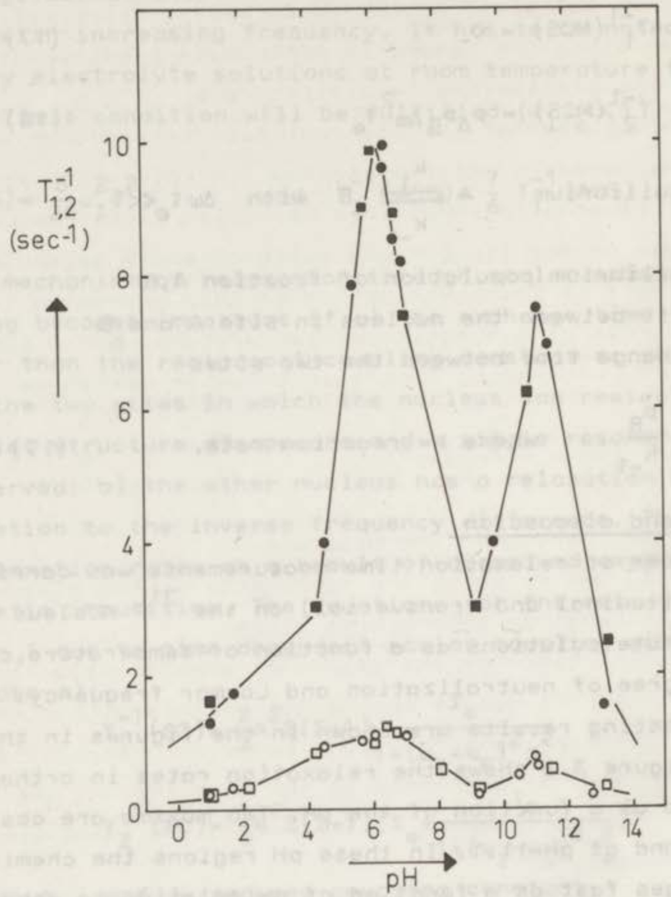

Figure 3.2 *Relaxation rates of* ^{31}P *in aqueous solutions of mixtures of NaOH and* H_3PO_4 *or KOH and* H_3PO_4 *at constant* ^{31}P *concentration(1.00 mole.l*$^{-1}$*) at* $25^{o}C$ *and 24.29 MHz as a function of pH.*

□ : T_1^{-1} *of mixture with potassium*
■ : T_2^{-1} *of mixture with potassium*
○ : T_1^{-1} *of mixture with sodium*
● : T_2^{-1} *of mixture with sodium*

The lines are drawn to show the relaxation rates as a function of the pH more clearly.

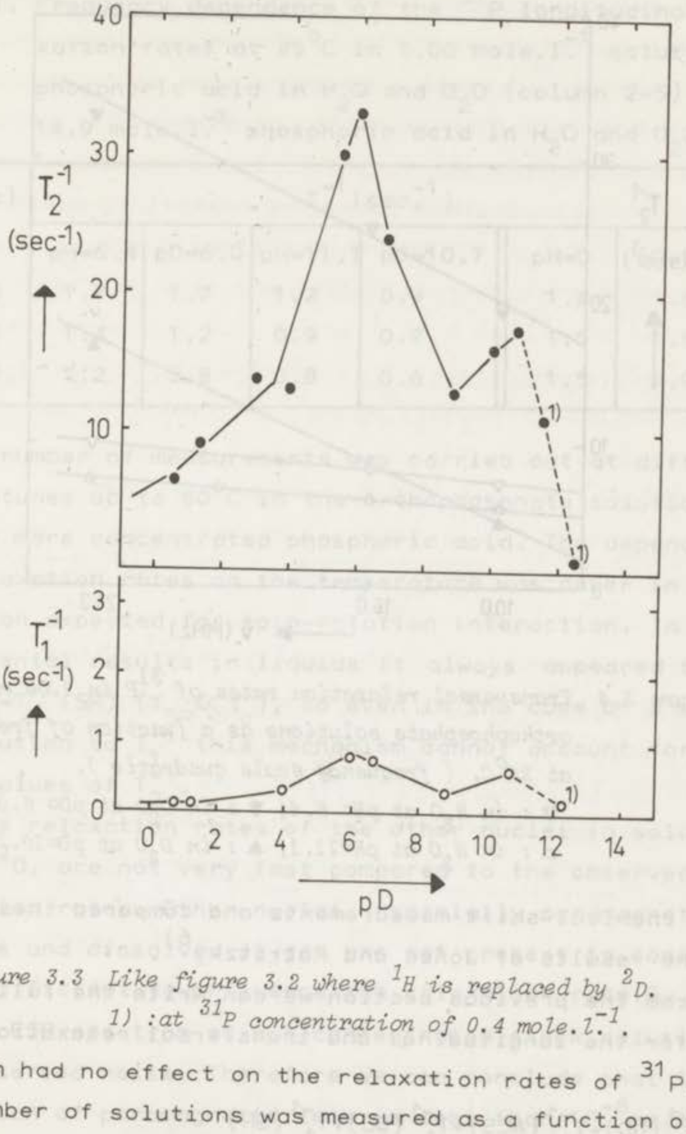

Figure 3.3 Like figure 3.2 where ^1H *is replaced by* ^2D.
1) *:at* ^{31}P *concentration of 0.4 mole.l*$^{-1}$.

potassium had no effect on the relaxation rates of ^{31}P. A large number of solutions was measured as a function of the pH with sodium hydroxyde and potassium hydroxyde as neutralizing agent for the phosphoric acid. The mentioned frequency dependence is shown in figure 3.4 and in table I for the solutions where the relaxation rates are highest (pH=6.4 and pH=11.1 respectively pD=6.0 and pD=10.7). In order to check the correct values for the degree of neutralization we per-

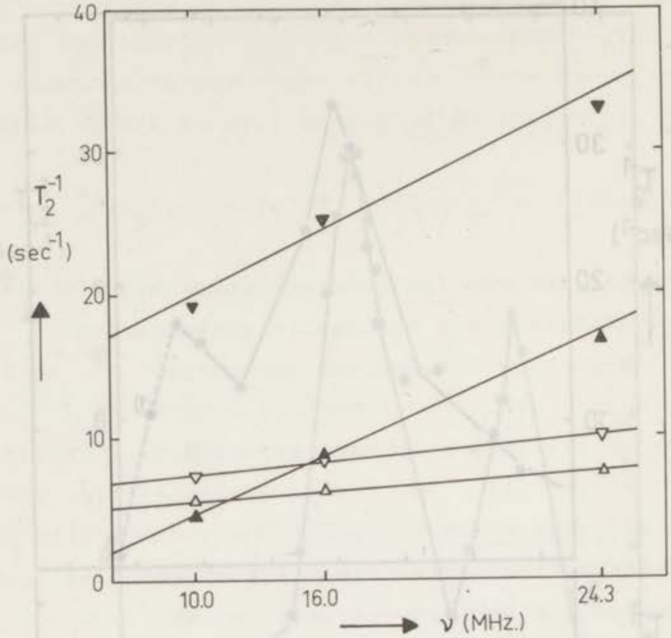

Figure 3.4 Transversal relaxation rates of ^{31}P in 1.00 mole.l.$^{-1}$ orthophosphate solutions as a function of frequency at 25^{o}C. (frequency scale quadratic).
▽ : in H_2O at pH= 6.4; ▼ : in D_2O at pD= 6.0
△ : in H_2O at pH=11.1; ▲ : in D_2O at pD=10.7

formed chemical shift measurements and compared these data with the results of Jones and Katritzky$^{6)}$.

From the previous section we can write the full expressions for the longitudinal and transversal relaxation rates:

$$T_1^{-1}=T_1^{-1}(DD)+T_1^{-1}(ACS)+T_1^{-1}(SC)+T_1^{-1}(SR) \quad (20)$$

$$T_2^{-1}=T_2^{-1}(DD)+T_2^{-1}(ACS)+T_2^{-1}(SC)+T_2^{-1}(SR)+T_2^{-1}(MCS) \quad (21)$$

Considering qualitatively the possible relaxation mechanisms and the results obtained in the aqueous orthophosphate solutions some simplifications can be made.

Table I. Frequency dependence of the ^{31}P longitudinal relaxation rates at 25°C in 1.00 mole.l.$^{-1}$ solutions of phosphoric acid in H_2O and D_2O (column 2-5) and in 14.9 mole.l.$^{-1}$ phosphoric acid in H_2O and D_2O (6-7).

ν (MHz)	T_1^{-1} (sec.$^{-1}$)					
	pH=6.4	pD=6.0	pH=11.1	pD=10.7	pH=0	pD=0
10.00	1.7	1.7	1.2	0.9	1.4	1.6
16.00	1.4	1.2	0.9	0.7	1.5	1.8
24.29	1.2	0.8	0.8	0.6	1.5	1.9

A number of measurements was carried out at different temperatures up to 80°C in the orthophosphate solutions and also in more concentrated phosphoric acid. The dependence of the relaxation rates on the temperature was never in the direction expected for spin-rotation interaction. In many experimental results in liquids it always appeared that $T_2^{-1}(SR)=T_1^{-1}(SR)$ ($\tau_{SR} \ll \tau_c$), so even in the case of a small SR contribution to T_1^{-1} this mechanism cannot account for the large values of T_2^{-1}.

The relaxation rates of the other nuclei in solution, ^1H and ^2D, are not very fast compared to the observed ^{31}P relaxation rates. Other nuclei, especially paramagnetic impurities and dissolved oxygen are not present in concentrations sufficient to influence the relaxation rate. By measuring the ESR spectrum of our concentrated stock solutions we only observed noise. Therefore we can conclude that the concentration of paramagnetic ions is less than 10^{-6} eq.l.$^{-1}$. So, scalar interaction of the second kind will be absent.

As pointed out before the P-P dipole-dipole interaction will not be important due to the large distance between the atoms. From the relaxation data obtained in H and D containing solutions we observe that dipolar interaction between P and H(D) can be excluded as the transversal relaxation rates in the deuterated solutions are much faster than in the proton containing solutions. Only in the longitudinal relaxation rate of the ^{31}P nucleus in the proton solutions there can be a P-H dipole-dipole contribution which is small as the longitudinal relaxation rate in the deuterated solutions is about the same. In describing the relaxation rates at pH=6.4 and pH=11.1 in our case it follows that:

$$T_1^{-1} = T_1^{-1}(SC)+T_1^{-1}(ACS)+T_1^{-1}(DD)$$

$$= \frac{2}{3}\gamma_I^2\gamma_S^2 J^2 S(S+1)\frac{\tau_e}{1+(\omega_I-\omega_S)^2\tau_e^2} + \frac{6}{20}\omega_I^2\delta^2\frac{\tau_c}{1+\omega_I^2\tau_c^2} + T_1^{-1}(DD) \quad (22)$$

$$T_2^{-1} = T_2^{-1}(SC)+T_2^{-1}(ACS)+T_2^{-1}(MCS)+T_2^{-1}(DD)$$

$$= \frac{1}{3}\gamma_I^2\gamma_S^2 J^2 S(S+1)\left(\tau_e+\frac{\tau_e}{1+(\omega_I-\omega_S)^2\tau_e^2}\right) + \frac{1}{20}\omega_I^2\delta^2\left(4\tau_c+\frac{3\tau_c}{1+\omega_I^2\tau_c^2}\right)+$$

$$+ p_A p_B \Delta\omega^2\tau_e + T_2^{-1}(DD) \quad (23)$$

For the low viscosity solutions studied here the rotational correlation time τ_c will be short ($<10^{-9}$ sec.). The narrowing limit condition will be fulfilled in considering DD and ACS interactions.

$$T_1^{-1} = \frac{2}{3}\gamma_I^2\gamma_S^2 J^2 S(S+1)\frac{\tau_e}{1+(\omega_I-\omega_S)^2\tau_e^2} + \frac{6}{20}\omega_I^2\delta^2\tau_c + T_1^{-1}(DD) \quad (24)$$

$$T_2^{-1} = \frac{1}{3}\gamma_I^2\gamma_S^2 J^2 S(S+1)\left(\tau_e+\frac{\tau_e}{1+(\omega_I-\omega_S)^2\tau_e^2}\right) + \frac{7}{20}\omega_I^2\delta^2\tau_c +$$

$$+p_A p_B\Delta\omega^2\tau_e + T_2^{-1}(DD)$$

$$= \frac{1}{3}\gamma_I^2\gamma_S^2 J^2 S(S+1)\tau_e + \frac{1}{2}T_1^{-1}(SC) + \frac{7}{6}T_1^{-1}(ACS) +$$

$$+p_A p_B\Delta\omega^2\tau_e + T_1^{-1}(DD) \quad (25)$$

As $T_2^{-1} \gtrsim 10T_1^{-1}$:

$$T_2^{-1} = \frac{1}{3}\gamma_I^2\gamma_S^2 J^2 S(S+1)\tau_e + p_A p_B\Delta\omega^2\tau_e \quad (26)$$

A more quantitative treatment of the longitudinal relaxation rates seems not possible as a result of relatively small changes due to the small frequency range that could be studied here and the resulting small experimental accuracy. As only two relaxation mechanisms contribute significantly to the transversal relaxation rate we can separate the contribution of the scalar interaction and the modulation of the chemical shift as only the latter is frequency dependent.

By carrying out Carr Purcell spin echo experiments in the Gill Meiboom modification in the orthophosphate solutions at pH=6.4(pD=6.0) and pH=11.1(pD=10.7) and in the concentrated phosphoric acid solutions we can conclude, from the fact that the experimentally found T_2 is independent of the pulse spacing down to 10 µsec., that $\tau_e<10^{-5}$ sec.[20]. On the other hand the T_1-T_2 difference suggests that a $\tau_e>10^{-8}$ sec. plays an important role in the relaxation behaviour. From literature data it is known that proton exchange occurs in phosphate solutions and that the rate constant is high ($k=1.45\times10^{+9}$ mole.$^{-1}$ l.sec.$^{-1}$ at 25°C)[21]. Considering this and the small coupling constant of P-(O-)H in the orthophosphate group it is concluded that proton exchange between the water molecules and an orthophosphate ion is a process that does not contribute significantly to the relaxation rates. This process can only give a contribution if the rate constant is much lower at the pH values discussed here. It was pointed out in the introduction that there is proof for the existence of complex ions. The P-(O-)H(D) coupling constants, the ^{31}P chemical shift and the lifetime of the complex ions are unknown. The existence of these complex ions may be the source of the fast phosphorus relaxation at the pH values where these ions seem most probable or stable. From the predicted τ_e value of $10^{-8}<\tau_e<10^{-5}$ the coupling constant of P-H in these complexes must be large (order of 1 kHz) to cause the observed relaxation rates.

Concerning the chemical shift it must be concluded from the contribution of this mechanism to the relaxation rates that a relatively large chemical shift must be present at pH=6.4 and pH=11.1. In the average chemical shift, measured in orthophosphate solutions as a function of the pH no large variations are observed[6)18)], so these shifts must be present at each pH value. That the modulation of the chemical shift becomes important as a relaxation mechanism may be the result of larger modulation or exchange times at the pH values discussed here relative to other pH values.

The transversal relaxation rates consist of two contributions: one is constant (SC) and one is quadratic with frequency (MCS). Assuming a two state model and assuming that the reduced coupling constants J and the chemical shifts are the same in the ordinary and the deuterated solutions, the isotopic effect on τ_e for the scalar coupling and the modulation of the chemical shift can be estimated. Comparing only solutions in H_2O and D_2O where the concentrations of the proton containing phosphate ions are equal to the concentrations of the deuterium containing phosphate ions we can express $\tau_e(D_2O)$ in τ_D, in the same way as $\tau_e(H_2O)$ in τ_H, where τ_D and τ_H are assumed to be the lifetimes of either of the two states.

$$\frac{T^{-1}_{2D}(SC)}{T^{-1}_{2H}(SC)} = \frac{2A_D^2\tau_D}{\frac{3}{4}A_H^2\tau_H} \quad \text{and} \quad \frac{T^{-1}_{2D}(MCS)}{T^{-1}_{2H}(MCS)} = \frac{\tau_D}{\tau_H} \qquad (27)$$

A_H and A_D being the P-(O-)H and P-(O-)D root mean squared coupling constants.

From the intercepts and the slopes of the lines in figure 3.4 the following isotopic effects are calculated:

pH (pD)	SC	MCS
6.4 (6.0)	$(6.2)^2$	5.5
11.1 (10.7)	5.9	5.8

A possible explanation for these isotopic effects concerning the scalar coupling may be the existence of different complex ions at the different pH values studied. The structures e and f in figure 3.1 are consistent with the estimated values, assuming an isotopic effect of

$$\frac{\tau_D}{\tau_H} = \frac{k_H}{k_D} = 5.8 \pm 0.4$$

for the formation of one O--H(D) bridge in a complex ion. The isotopic effect of the frequency dependent part of the relaxation rates suggests that the rate determining process in the modulation of the chemical shift is different from that in the scalar coupling. The results indicate that here only one H-bridge is involved.

That a value of 5.8 for this isotopic effect seems reasonable is shown below in the general case of the kinetic isotopic effect in a proton(deuterium) exchange reaction. The isotopic effect for a reaction of the type

$$XOH + OX \rightleftharpoons XO{-}{-}{-}H{-}{-}{-}OX$$

$$XOD + OX \rightleftharpoons XO{-}{-}{-}D{-}{-}{-}OX$$

is $\frac{k_H}{k_D} = \exp((E_D - E_H)/kT)$ (28)

where E is the difference between zero-point energies of the activated complex and the initial particles[22)]. Usually values from 4 - 10 are found.

The relaxation rates in phosphoric acid were measured as a function of frequency at several concentrations. The results of the frequency dependent measurements at very high concentrations are shown in figure 3.5. Here a correction was made to the T_2^{-1} values for a contribution from anisotropic chemical shift which should be present as concluded from the longitudinal relaxation rates shown in Table I (pH=0). Elmore et al.[13)] calculated the distribution of species in phosphoric acid solutions. The amount of complex ions increases with concentration and at high concentration some

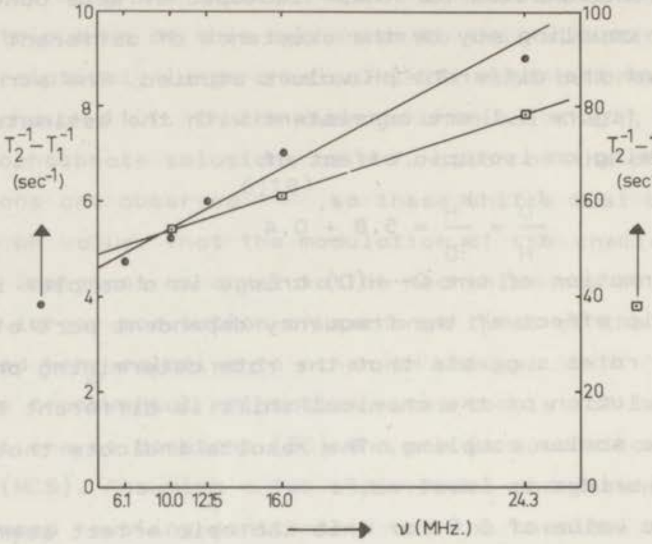

Figure 3.5 ^{31}P *relaxation rates as a function of frequency in concentrated phosphoric acid and deuterophosphoric acid. Conc.* $^{31}P = 14.9$ *mole.l.*$^{-1}$ *; temperature : 25*^{o}*C.* ⊙ *: H ;* ⊡ *: D; frequency scale quadratic.*

influence of proton(deuterium) exchange on the transversal relaxation rate may be expected. At ^{31}P concentrations higher than 6 mole.l.$^{-1}$ the isotopic effects can be calculated in the same way and with the same assumptions as decribed above for the orthophosphate solutions from the experimental relaxation rates in phosphoric acid and deuterophosphoric acid. The isotopic effect that was found for the frequency dependent part (MCS) was 6.0 ± 0.5 ; for the scalar coupling a value of $(5.6 \pm 0.3)^3$ was calculated.

At lower concentrations the isotopic effect seemed to decrease for the scalar coupling and to increase for the modulation of the chemical shift, however exact data could not be determined accurately due to the small variation of the relaxation rates with frequency at relatively low concentrations and in the second place due to the instability of the magnetic field (H_0) over periods longer than 12 hours. This long time was necessary due to the small T_1^{-1} values.

At high concentrations where the complex ions are supposed to be present in considerable amounts the isotopic effects of MCS and SC are quite different. In the case of scalar coupling this value seems consistent with the existence of a complex ion with a structure like c in figure 3.1. Concerning the isotopic effect of the MCS the same conclusions as drawn above in the case of the orthophosphate solutions are also valid here.

Although the relaxation mechanisms have now been identified experimentally, including the isotopic effects on the rate constants, an interpretation in terms of molecular processes is still uncertain. Due to the complicated nature of the solutions, several fast exchanging species are present, a quantitative description of the relaxation rates as a function of the rate constants of defined chemical reactions is at this moment impossible.

Further indications for the complex formation can be obtained from measurements of the ^{23}Na relaxation rate in phosphoric acid solutions as a function of the pH. These results are shown in figure 3.6. The sodium relaxation rates are somewhat faster than expected at some pH values when we assume that the rates show a quadratic dependence on the charge of the counterion(phosphate) as suggested by Versmold[23]. For $\alpha=1.0$, $\alpha=2.0$ and $\alpha=3.0$ this assumption agrees well with the experimental data ($\alpha \equiv [Na] / [P]$). However at $\alpha=1.5$ and $\alpha=2.5$ the rates are considerably higher which may be due to the complex formation of the phosphate ions, as the rates increase linearly with concentration and quadratic with the charge of the anions.

The measurements of the selfdiffusion coefficients of

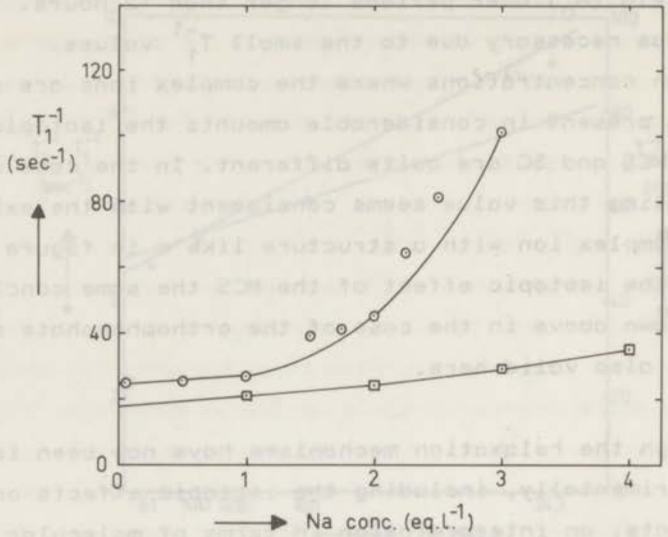

Figure 3.6 ^{23}*Na relaxation rates of NaOH at 15.87 MHz and 25°C as a function of concentration.*
⊡ : *in* H_2O ; ⊙ : *in 1.00 mole.l.*$^{-1}$ H_3PO_4.

the phosphate ions in orthophosphate solutions as a function of the pH (charge of the anion) as mentioned in chapter VI figure 6.5 also give some indications of the complex formation at pH=6.4 and pH=11.1.

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CHAPTER IV

RELAXATION OF PHOSPHORUS-31
IN POLYPHOSPHATE SOLUTIONS

1. The Fourier transform method.

With the nuclear magnetic resonance technique we can distinguish between different types of phosphate (PO_4) groups in the frequency domain[1)2)]:

1) Phosphate groups with no neighbouring group (orthophosphates and phosphoric acid): P_o. The shift relative to 85% H_3PO_4 is 0--6 p.p.m. dependent on the pH.
2) Phosphate groups with one neighbouring group (pyrophosphates and the end groups in polyphosphates): P_e. The shift relative to 85% H_3PO_4 is 5-12 p.p.m. dependent on the pH and chainlength.
3) Phosphate groups with two neighbouring groups (metaphosphates and the middle groups in polyphosphates): P_m. The shift relative to 85% H_3PO_4 is 20-24 p.p.m. dependent on the pH and chainlength.
4) Phosphate groups with three neighbouring groups (branching points in polyphosphates). Due to the fast hydrolysis these groups do not show up in this investigation.

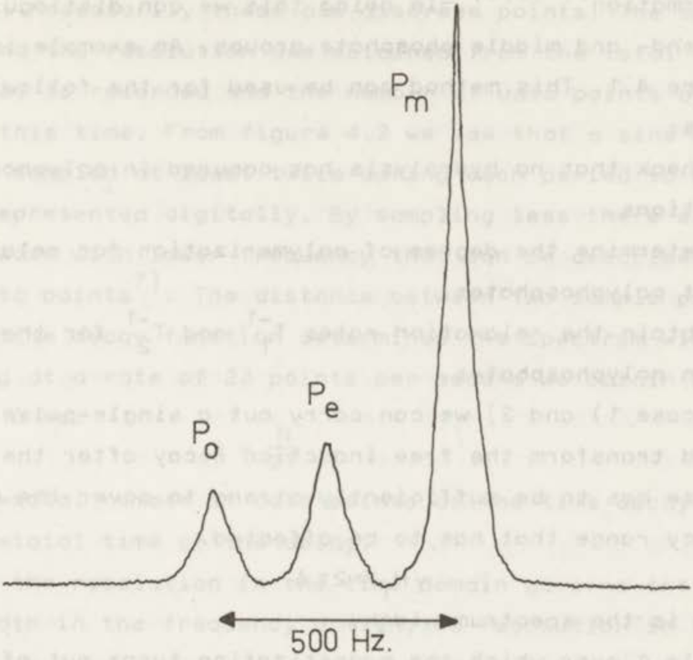


Figure 4.1 ^{31}*P FTNMR spectrum of a partly hydrolysed polyphosphate at 24.29 MHz.* P_o *: orthophosphate ;* P_e *: end groups ;* P_m *: middle groups.*

In systems with only one ^{31}P resonance signal the longitudinal and transversal relaxation times can be obtained by a pulse experiment. For a T_1 measurement a $180^o-\tau-90^o$ pulse sequence is used and the magnetization after the second pulse is observed as a function of τ; for T_2 we need a $90^o-\tau-180^o-\tau$-echo sequence and observe the amplitude of the spin echo as a function of τ. This can be done for orthophosphate and polyphosphate ($DP \geq 60$) solutions, for instance. However when we have a multiline spectrum due to different types of phosphate groups, we cannot distinguish in pulse experiments between different groups. In order to separate the resonance signals of different phosphate groups we must transform the time decay function into the frequency spectrum by a Fourier transformation[3)4)5)6)]. In doing this we can distinguish ortho-, end- and middle phosphate groups. An example is given in figure 4.1. This method can be used for the following purposes:

1) To check that no hydrolysis has occured in polyphosphate solutions.
2) To determine the degree of polymerization for relatively short polyphosphates.
3) To obtain the relaxation rates T_1^{-1} and T_2^{-1} for the P_e and P_m in polyphosphates.

In the case 1) and 2) we can carry out a single-pulse experiment and transform the free induction decay after the pulse. The pulse has to be sufficiently strong to cover the whole frequency range that has to be affected.

$$\gamma H_1 \gg 2\pi\Delta \qquad (1)$$

where Δ is the spectrum width.

The angle θ over which the magnetization turns out of the H_0-direction is given by: $\theta = \gamma H_1 t$ (2)

where t is the duration of the pulse. To ensure phase coherence after a 90° pulse this pulse should be sufficiently short: $t(90^\circ) \ll \frac{1}{4\Delta}$ (3)

In the case of 3) we must carry out a two pulse sequence. For the T_1 measurement ($180^\circ - \tau - 90^\circ$) we obtain as a function of τ a number of partially relaxed free induction decays after the 90°-pulse. After Fourier transformation of these decays we can separately measure the intensities of the absorption lines in the spectrum for different types of phosphate groups as a function of τ. For the T_2 measurements ($90^\circ - \tau - 180^\circ - \tau -$ echo) the same method is used, only here the second half of the spin echo is transformed into the frequency spectrum. In practical experiments we have to consider the resolution and the width of the spectrum that can be obtained in the frequency domain. The data of the free induction decay are recorded digitally during a certain period of time. Necessarily these are discrete points. The spectrum width and the resolution are obtained from the total time the decay is recorded and the number of data points obtained during this time. From figure 4.2 we see that a sine wave must be sampled at least twice during each period to be properly represented digitally. By sampling less there exists a sine wave with lower frequency that can be described by the same data points$^{7)}$. The distance between two sample points of the time decay function determines the spectrum width. Sampling at a rate of 2Δ points per second we obtain a spectrum of Δ Hz:

$$\Delta = \frac{N}{2T} \tag{4}$$

where N=total number of data points of the time decay function

T=total time of the decay.

Just as the resolution in the time domain governs the spectrum width in the frequency domain, the resolution in the

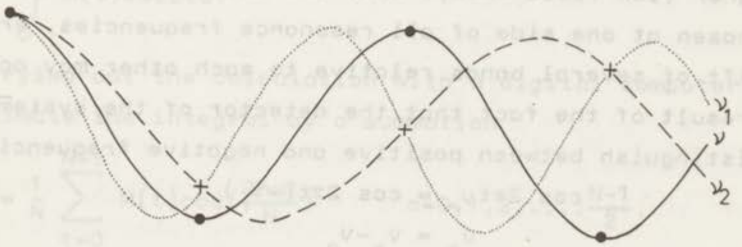


Figure 4.2 Illustration of the digitising procedure.

• These points can be described by a (co)sine wave function represented by the solid line, with a lowest frequency of two points each period.

+ These points are described by two wave functions: ······· with a frequency $\nu_1 > \nu$ and by --- with $\nu_2 < \nu$. In the FT-technique the wave function represented by ······· is folded back around frequency ν, resulting in the wave function represented by --- due to $\nu_1 - \nu = \nu - \nu_2$.

frequency domain (R) is determined by the total decay time.

$$R = \frac{1}{T} \qquad (5)$$

In our case, using a Varian Associates time averaging computer C-1024, we collected 1024 data points in a total time of 100 msec.. The obtained spectrum has a resolution of 10 Hz and a width of 5120 Hz. From the original 1024 points we obtain 512 as a cosine transform function (absorption spectrum). As the shifts of the phosphorus nuclei at 24 MHz are not larger than about 1000 Hz the spectrum width covers all the absorption lines.

Due to the inhomogeneity of the Zeeman field all the absorption bands are much wider than the resolution. The only choice that still has to be made is that of the carrier frequency (ν_o). This must be done in such a way that all the absorption bands are between this carrier frequency and a frequency ($\nu_o+\Delta$) or ($\nu_o-\Delta$). So the carrier frequency can be chosen lower than all signal frequencies (high field lock) or higher (low field lock). When the carrier frequency is not chosen at one side of all resonance frequencies, errors in shift of several bands relative to each other may occur as a result of the fact that the detector of the system can not distinguish between positive and negative frequencies:

$$\cos 2\pi t\nu_r = \cos 2\pi t(-\nu_r) \qquad (6)$$

$$\nu_r = \nu_s - \nu_o$$

ν_s = resonance frequency of signal.

This phenomenon is called "Folding".

As a result of the digitising procedure folding can also occur at the frequency determined by the spectrum width $\nu_o+\Delta$ if $\nu_s > \nu_o+\Delta$. This is also illustrated in figure 4.2. The data points (+) can be represented by two sine waves with frequencies $(\nu_o+\Delta) + (\nu_s-(\nu_o+\Delta))$ and

$$(\nu_o+\Delta) + (\nu_o+\Delta-\nu_s)$$

These folding errors should be avoided.

As mentioned before, we used a time averaging computer(CAT).

To improve the signal to noise ratio, 200 time decay functions were added in most experiments. This also provides a constant phase error, as explained below.

The Fourier transformation is given by

$$M(\omega) = \int_{-\infty}^{+\infty} M(t)e^{-i\omega t}dt \qquad (7)$$

for the transformation into the frequency domain where $M(\omega)$ represents the spectrum and $M(t)$ the time decay function. In our case $M(\omega)=0$ for $\omega<\omega_o$ where $\omega_o=2\pi\nu_o$; ν_o=carrier freq.
$M(t)=0$ for $t<0$.

So

$$M(\omega) = \int_0^{\infty} M(t)e^{-i\omega t}dt \qquad (8)$$

As we are only interested in the absorption spectrum we can calculate the cosine transform

$$M(\omega) = \int_0^{\infty} M(t)\cos\omega t dt \qquad (9)$$

By carrying out the calculation with a digital computer we approximate the integral by a summation

$$M_n(\omega) = \frac{1}{N}\sum_{t=0}^{N-1} M(t)\cos(\frac{2n\omega t}{N}) \qquad n=0,1,2,\ldots,\frac{N-1}{2}. \qquad (10)$$

with N= total number of data in the time domain.

However in practice we invariably obtain a mixture of sine and cosine transform due to phase errors. Phase errors can occur as a result of the following causes:

1) a wrong radiofrequency phase in the time domain.
2) by not starting the digitising at t=0.
3) missing point(s) at the beginning of the stored time decay function.
4) as a result of the fact that the trigger of the pulse spectrometer is given somewhat later in time than the

trigger of the first point of the CAT.

The Fourier transform for one absorption band with a frequency equal to the carrier frequency is given by

$$M(\omega) = \int_0^\infty M_o e^{-t/T^{\dagger}} \cos\omega t \, dt \tag{11}$$

where M_o = magnetization at $t=0$

$T^{\dagger}$ = time constant determined by the field inhomogeneity, assuming this time decay function to be exponential (Lorentzian field distribution).

For one absorption band with a shift δ (Hz) relative to the carrier frequency we have

$$M(\omega) = \int_0^\infty M_o e^{-t/T^{\dagger}} \cos 2\pi\delta t \cos\omega t \, dt \tag{12}$$

A wrong radiofrequency phase $e^{-i\phi}$ causes a frequency independent phase error. As the time decay function was always on an oscilloscope before Fourier transformation this error was always corrected before the calculation : $e^{-i\phi}=1$ (13)

The phase errors caused by 2)3) and 4) are of the same kind. The starting point of the time decay function should be represented by $t+\Delta t$ instead of t where Δt= time delay between starting point of the time decay and $t=0$.

$$M(\omega) = \int_0^\infty M_o e^{-(t+\Delta t)/T^{\dagger}} \cos 2\pi\delta(t+\Delta t) \cos\omega t \, dt \tag{14}$$

$$= M_o e^{-\Delta t/T^{\dagger}} \int_0^\infty e^{-t/T^{\dagger}} \cos 2\pi\delta(t+\Delta t) \cos\omega t \, dt \tag{15}$$

As a result of the fact that the time decay starts somewhere between the starting point of the CAT and the time the second point is sampled (t_1), Δt will be

$$0 \leqslant \Delta t \leqslant t_1 \tag{16}$$

In our case $t_1 = \frac{T}{N} \approx 10^{-4}$ sec.

The time between all points in the decay function is always constant. By adding at least 200 times the decay function to itself we obtain an average value of the time delay $\Delta t = \frac{1}{2} t_1 \approx 50$ μsec. Assuming that in the decay function the exponent does not change during a time t_1, we replace

$$\cos 2\pi\delta(t+\Delta t) \text{ by } \frac{1}{2\Delta t}\int_{-\Delta t}^{+\Delta t} \cos(2\pi\delta(t+\Delta t+t'))dt' \qquad (17)$$

The phase error as a result of the last causes 2)3) and 4) will, in the frequency spectrum, be dependent on the frequency δ. The calculated cosine transform can now be represented by

$$M(\omega) = \frac{1}{2\Delta t} M_0 e^{-\Delta t/T^{+}} \int_0^\infty e^{-t/T^{+}} \left(\int_{-\Delta t}^{+\Delta t} \cos 2\pi\delta(t+\Delta t+t')dt' \right) \cos\omega t \, dt \qquad (18)$$

with $\Delta t = 50$ μsec.

In a relaxation experiment we calculate a number of spectra as a function of the time τ, by replacing in equation (18) M_0 by:

a) in a T_1 experiment: $M_0(1-2e^{-\tau/T_1})$.

b) in a T_2 experiment: $M_0 e^{-\tau/T_2}$.

Calculating the integrals of equation (18) for this cosine transform results in[8]:

$M(\omega) = C.\sin Y(\cos Y.A - \sin Y.D)$ (19)

with $C = \text{constant} = f(M_0, \tau, T_1(T_2), \Delta t)$

$Y = 2\pi\delta\Delta t$

$A = \text{absorption curve} = T^{+}/(1+(\delta-\nu)^2 T^{+2})$ (20)

$D = \text{dispersion curve} = (\delta-\nu)T^{+2}/(1+(\delta-\nu)^2 T^{+2})$ (21)

with T^{+} = time constant determined by the inhomogeneity of the Zeeman field.

Figure 4.3 gives a measured cosine transform without phase correction and the calculated cosine transform with equation (19).

As a result of the fact that the carrier frequency is

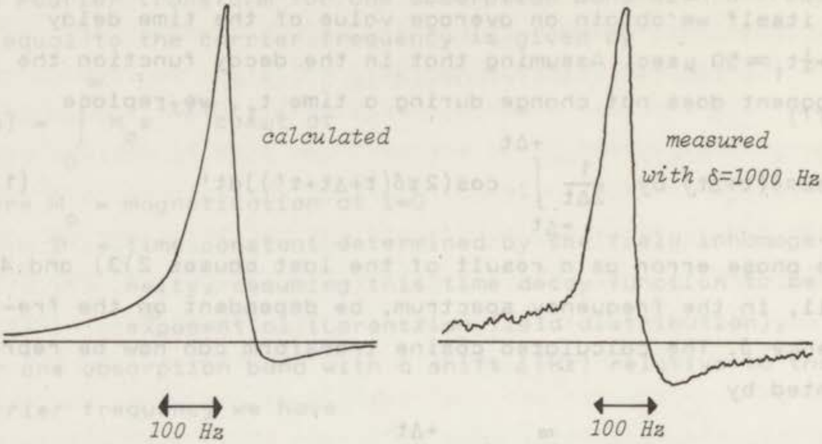


Figure 4.3 Illustration of a measured absorption band without phase correction and a calculated absorption band according to equation (19) with $\delta=1000$ *Hz,* $T^{-1}=50$ *Hz and* $\Delta t=50$ *µsec.*

not changed during one experiment, the phase errors are always the same in one point in the frequency spectrum. In carrying out relaxation measurements it is not strictly necessary to correct the phase errors. However a phase correction is needed when we use the spectrum to determine the degree of polymerization of polyphosphates.

In the computer program this phase correction is always carried out in order to get somewhat higher intensities of the absorption bands.

2. The computer program.

The decay of the magnetization as a function of time, with the correct RF phase detection as seen on an oscilloscope, was stored in a Varian C 1024 CAT. The signal to noise ratio was improved by detecting at least 200 times. This was also done for other reasons as mentioned before. This time decay function, translated into 1024 points at equal time intervals, was punched via an interface unit[9)] on paper tape which was the program input. The program was built up of the following sections: 1) Read in; 2) Fourier transformation; 3) Phase correction; 4) Plotting the spectra. All sections were written in Fortran H.

The paper tape input contains the data and the channel numbers. The data are translated into reals necessary for the Fourier transformation. The channel numbers are used to check for missing data; if so these data are added. At the end of this checking section we have 1024 reals without errors.

To carry out the Fourier transformation of the digitised time decay function into a cosine transform (absorption spectrum) and a sine transform (dispersion spectrum) the method of Cooley and Tukey[10)] was used, known as Fast Fourier Transform (FFT). The advantage of this method is that the whole calculation can be carried out within the data locations necessary to store the original time decay data. So the number of memory locations needed is relatively small. The disadvantage is that the transform can only be carried out for 2^N data ($N = 1,2,\ldots$), however in our case we always used $N=10$. In our program the subroutines HARM and RHARM from the IBM Subroutines Library[11)] were used. After the transformation we have the cosine and the sine transform, both with phase errors as explained before.

The third step is the phase correction, carried out because of the errors arising from the digitising. The transforms are mixed in such a way that these errors disappear and the only spectrum we are interested in, the absorption one, results: e.g.(criterion: maximum area)

$$c_i = a_i \cos(i\pi/n) + b_i \sin(i\pi/n) \qquad i=1,\ldots,n$$

c_i = correct cosine transform.

a_i = cosine transform with phase error.

b_i = sine transform with phase error.

The last step in the program is the plot section. The cosine transform is plotted as a function of frequency calculated from the time scale of the original decay. For each spectrum this scale factor was plotted also.

The program was carried out on a IBM 370/158 computer and the plots were drawn on a Calcomp plotter at the Centraal Rekeninstituut of the University.

Figure 4^a and 4^b show a typical time decay function and the FT spectra resulting from such a decay. Figure 4^c shows a semi-logarithmic plot of the intensities of the absorption bands of figure 4^b.

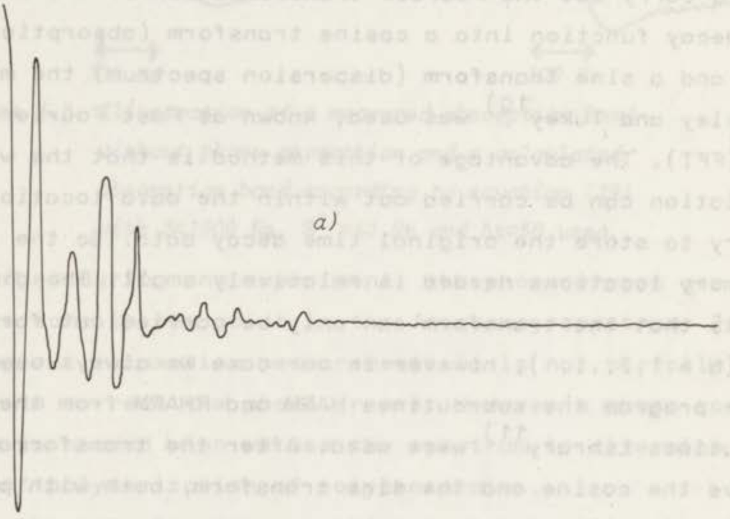
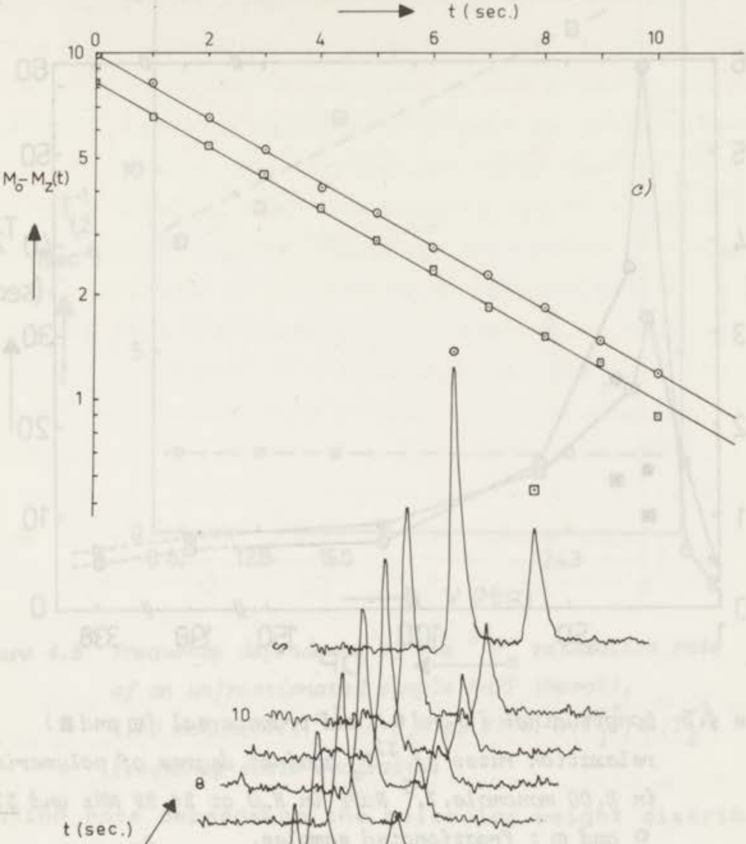


Figure 4.4 a) First 200 points of the time decay function after a 90^o pulse of 0.33 mole.$l.^{-1}$ $Na_5P_3O_{10}$ in H_2O at 24.29 MHz and 27^oC.(Total decay time 100 msec.,1024 points)
b) Longitudinal relaxation of ^{31}P in the same solution. Each spectrum is obtained after FT of the time decay function after the 90^o pulse in a 180^o-t-90^o sequence as a function of t(sec.). ⊡ : P_m ; ⊙ : P_e.
c) Magnetization, obtained from the amplitudes of the absorption bands of figure b), plotted against t. Observed relaxation rate of ^{31}P : 0.21 sec^{-1}.


t (sec.)
0
2
4
6
8
10
10
5
2
1
M_o- M_z(t)
c)
t (sec.)
10
8
6
4
2
0
b)
0
500
1000
1500
freq.(Hz)

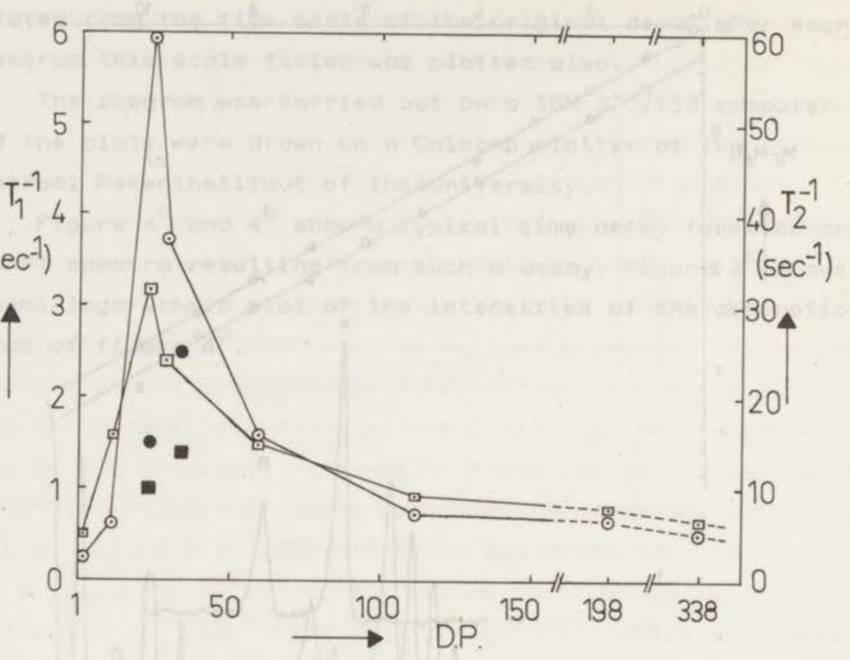


Figure 4.5 *Longitudinal (⊙ and ●) and transversal (⊡ and ■) relaxation rates of* $^{31}P_m$ *against degree of polymerization in 2.00 monomole.*l^{-1} *NaPP in* H_2O *at 24.29 MHz and 27°C.*

⊙ *and* ⊡ *: fractionated samples.*

● *and* ■ *: unfractionated samples (Fluka and Merck Ch.II)*

3. Results and discussion.

As a result of the rather complicated relaxation behaviour of phosphorus-31 in orthophosphate solutions the investigation of the relaxation in polyphosphates will be limited here to some preliminary measurements and some qualitative conclusions about the relaxation mechanisms.

From the measurements, some of which are shown in figure 4.5, 4.6 and 4.7 we can see the following:

1) The relaxation rate depends on the degree of polymerization with a maximum at about DP=25. Consequently the rela-

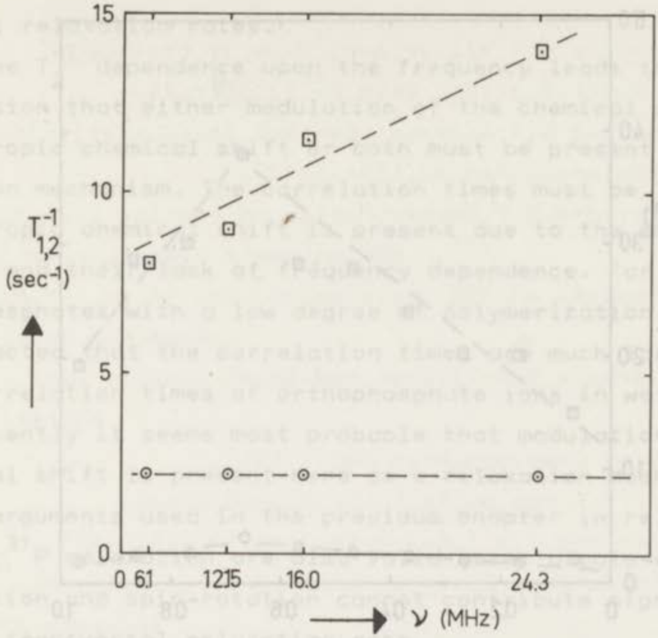


Figure 4.6 *Frequency dependence of the* $^{31}P_m$ *relaxation rate of an unfractionated sample NaPP (Merck), 2.00 monomole.l.*$^{-1}$ *in* H_2O *at* 27^oC. ⊙:T_1^{-1}; ⊡:T_2^{-1}. *Frequency scale quadratic.*

xation rate depends on the molecular weight distribution.

2) Only one T_1^{-1} value is observed for the middle and end phosphorus, while different T_2^{-1} values are seen.
3) The relaxation rates are not frequency independent; the transversal relaxation rate increases with increasing frequency.
4) The relaxation rate depends on the degree of neutralization with a maximum at $\alpha \approx 0.6$.

From these few measurements we can say something about the relaxation of ^{31}P in polyphosphate solutions. Roughly speaking the relaxation rates are of the same order as in orthophosphates. The fact that the transversal relaxation rates are somewhat larger and the longitudinal rates are of the same order of magnitude may be due to some larger corre-

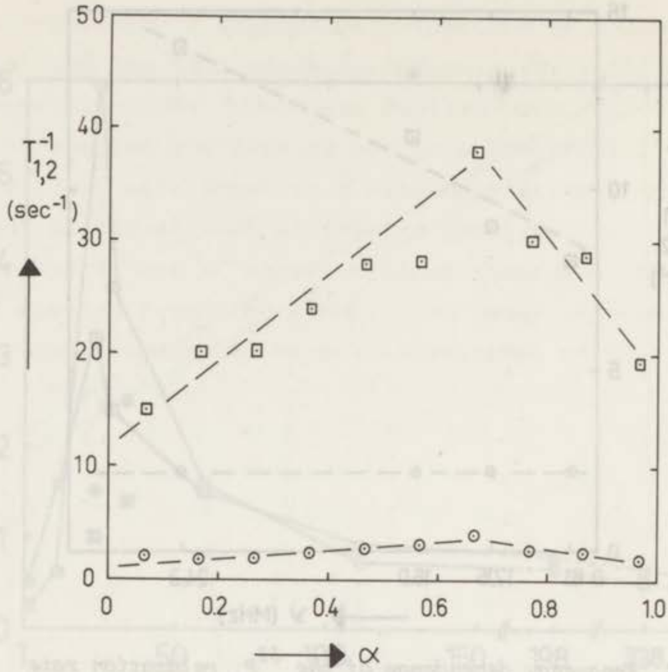


Figure 4.7 Relaxation behaviour of $^{31}P_m$ *in NaPP (DP=63) as a function of the degree of neutralization at 24.29 MHz and 27°C. Conc.P =0.30 monomole.l.*$^{-1}$ *.* ⊙ *:*T_1^{-1} *;* ⊡ *:*T_2^{-1} *.*

lation times involved here. Like in orthophosphate solutions there exists a maximum as a function of the pH. Internal hydrogen bonds between neighbouring PO_3 groups may be the cause of this effect.

The relaxation rates of the P(in end groups) and the P(in middle groups) are different. This is observed in all Fourier transform measurements for the transversal relaxation rate. However in all measurements one T_1 value is observed. This suggests that the process of spin-diffusion occurs$^{12)13)}$. This spin flip mechanism from slow relaxing P nuclei to faster relaxing P nuclei (sinks) should occur here with such a speed that it influences only the longitudinal relaxation rates.

The T_2^{-1} dependence upon the frequency leads to the conclusion that either modulation of the chemical shift or anisotropic chemical shift or both must be present as a relaxation mechanism. The correlation times must be long if anisotropic chemical shift is present due to the small T_1^{-1} values and their lack of frequency dependence. For sodium polyphosphates with a low degree of polymerization it cannot be expected that the correlation times are much larger than the correlation times of orthophosphate ions in water. Consequently it seems most probable that modulation of the chemical shift is present here as a relaxation mechanism. Other arguments used in the previous chapter in relation to the ^{31}P relaxation are also valid here: dipole-dipole relaxation and spin-rotation cannot contribute significantly to the transversal relaxation rate.

To explain the relaxation rates of both P_m and P_e quantitatively, much more experimental results with the Fourier transform method are needed,especially as a function of the degree of polymerization, degree of neutralization and the Larmor frequency, while all these measurements should be carried out in H_2O and D_2O as solvents.

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CHAPTER V

RELAXATION OF SODIUM-23 IN POLYPHOSPHATE SOLUTIONS

1.Abstract.

Nuclear magnetic relaxation of counterions in polyelectrolyte solutions should in principle yield interesting information on polyion-counterion interactions. For example the relaxation behaviour of the sodium ion is governed by the interaction of the nuclear quadrupole moment with the electric field gradient at the site of the nucleus. A study of the relaxation rate of ^{23}Na ions in the presence of negatively charged macroions should therefore contribute to our knowledge of the details of the behaviour of counterions in these systems. Expressions for the relaxation rates of these ions were recently developed for aqueous solutions of infinitely long polyelectrolytes.

As relatively short polyions are easily prepared we first examined the relaxation rates in H_2O and D_2O as a function of the degree of polymerization. It is found that for DP>60 the polyions can be assumed to be infinitely long as far as the counterion relaxation is concerned.

Secondly we examined the relaxation rates as a function of the degree of neutralization and using the ion condensation concept the average distance of the condensed counterions to the polyion was calculated to be 3.0 Å. Thirdly the relaxation rates of ^{23}Na in mixtures of polyphosphates and sodium chloride in aqueous solution were measured and using again the ion condensation concept we calculated e.g. with a two state model the distance of the sodium ions to the polyion chain at the point of salting out. This appeared to be 2.1 Å which seems a reasonable value compared to literature data of the Na-O distance in solid polyphosphates. In the last part of this chapter a comparison is made between the binding of sodium, lithium and potassium ions to the polyphosphate chain in salt free solutions.

2.Relaxation as a function of the degree of polymerization.

We wish to report some results obtained on aqueous solutions of sodium polyphosphates (NaPP) with samples of different degree of polymerization (DP).

Some sodium polyphosphates were prepared by heating sodium dihydroorthophosphate in a platinum crucible for 40 hr at 900°C. The resulting $(NaPO_3)_n$ glass is very soluble in water. The polyphosphates of different degree of polymerization were obtained by solubility fractionation of the aqueous solution with acetone by the method of van Wazer[1)]. Some other polyphosphates were made by the same fractionation method of 10% aqueous solutions of commercially obtained sodium metaphosphate (E.Merck,Darmstadt). All the fractions were freeze dried. The samples contained about 11% water. The DP was found by viscosity measurements in 0.035 N NaBr solutions with an Ostwald viscosimeter[2)].

The nuclear magnetic relaxation rates described in the first part of this chapter were measured at 26°C in 15 mm diameter tubes at a frequency of 16 MHz with a Bruker

B-KR 302S 16/60 MHz pulsed NMR spectrometer (all other measurements were carried out in 10 mm diameter tubes). All the NMR measurements were carried out within a few days after making the solutions of the sodium polyphosphates to exclude the influence of hydrolysis of the polyphosphates[3]. The measurements of the longitudinal relaxation time (T_1) were performed with a 180°-τ-90° pulse sequence at different τ's. For a number of cases the transversal relaxation time (T_2) was measured by the standard spin-echo technique, and was always found equal to T_1 within experimental error. The accuracy of all T_1 measurements is estimated to be 5%.

As a reference point for the investigation of the macromolecular systems, we first determined the ^{23}Na relaxation rate in aqueous NaH_2PO_4 solutions. The results are given in Table I and it is concluded that the longitudinal relaxation time is of the same order as has been found in other sodium salt solutions[4)5)6)].

In solutions of NaPP (degree of polymerization: 34) the relaxation rate is increased by about one order of magnitude as may be seen by comparing the results shown in figure 5.1 with the experimental values for the NaH_2PO_4 solutions in Table I.

Now, according to Hertz, et al.,[7)] the field gradient at the nucleus contains contributions from the surrounding water molecules and all other ions. Therefore, if ion condensation[8)9)10)] occurs an increase in the relaxation rate is to be expected. From the fact that T_1 and T_2 are equal in these solutions it is seen that the correlation time for the field gradient is very short ($<10^{-9}$ sec) and this directly confirms the conclusion of Schindewolf[11)12)] based on potentiometric and transport results, that the sodium ions do not reside for any appreciable time on given sites on the polyelectrolyte, even though ion condensation occurs.

As, in theoretical work on polyelectrolytes, the con-

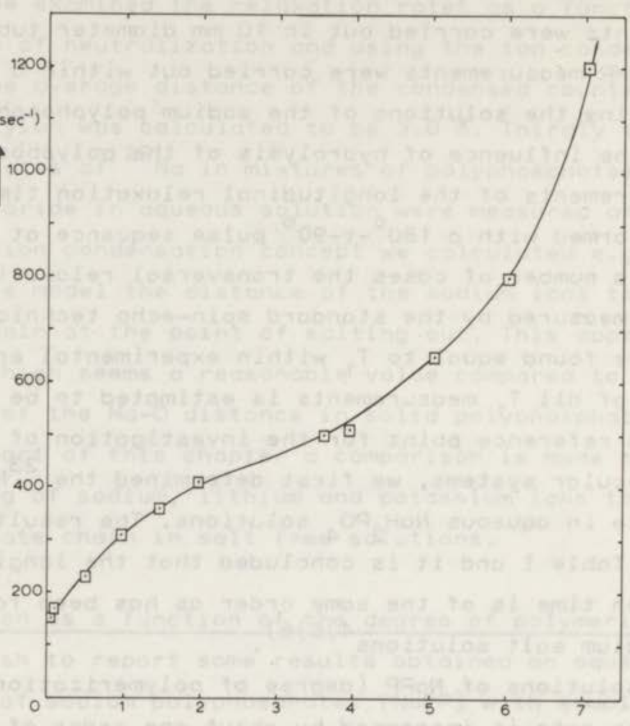

Figure 5.1 Concentration dependence of ^{23}Na relaxation rate in aqueous NaPP solutions of NaPP sample with DP=34.

Table I. ^{23}Na relaxation rate in aqueous solutions of sodium dihydroorthophosphate.

conc. (eq.l^{-1})	T_1^{-1} (sec^{-1})
0.0	17.5 (extrapol.)$^{5)}$
1.00	28
2.01	39
3.00	51

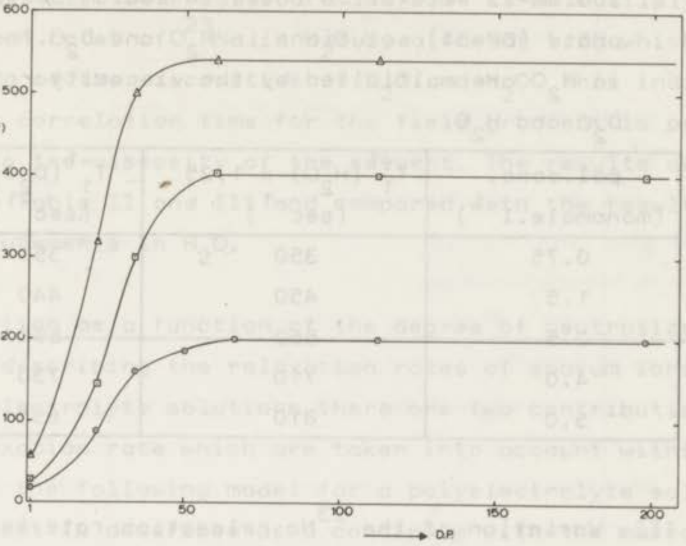

Figure 5.2 Variation of ^{23}*Na relaxation rate with DP at several polymer concentrations in aqueous solutions:* ⊙ *=0.089 eq.*$l.^{-1}$*;* ⊡ *=0.89 eq.*$l.^{-1}$*;* △ *=3.50 eq.*$l.^{-1}$*.*

cept of infinitely long charged rods is used, it is of interest to investigate what degree of polymerization is effectively infinite from the point of view of the counterions or, in other words, at what chain length do the properties of the counterions become independent of this length.

In figure 5.2 it is shown that at a degree of polymerization of about 60 a steep initial increase of T_1^{-1} as a function of the DP levels off sharply. This is observed for concentrations up to 3.50 eq.$l.^{-1}$. For solutions of NaPP with a degree of polymerization of 338 we still found the same values for T_1^{-1} as for samples with a DP=198.

We also performed measurements of the ^{23}Na relaxation rates in D_2O. The same concentrations and temperature were used. All the data give similar results as a function of concentration and of the degree of polymerization. Qualitatively the behaviour is analogous to the results in H_2O and

Table II. Sodium-23 relaxation rates in sodium polyphosphate (DP=34) solutions in H_2O and D_2O. The values in H_2O are multiplied by the viscosity ratio of D_2O and H_2O.

pol.conc. (monomole.l^{-1})	T_1^{-1} (H_2O) × 1.25 (sec^{-1})	T_1^{-1} (D_2O) (sec^{-1})
0.75	350	350
1.5	450	440
2.5	560	550
4.0	710	730
5.0	810	850

Table III. Variation of the ^{23}Na relaxation rate in sodium polyphosphate solutions with DP at two concentrations in D_2O. The data are compared with the measurements in H_2O, multiplied by the D_2O-H_2O viscosity ratio.

Na conc. (eq.l^{-1})	DP	T_1^{-1} (D_2O) (sec^{-1})	T_1^{-1} (H_2O) × 1.25 (sec^{-1})
0.089	1	24	24
	22	110	110
	34	200	190
	60	240	245
	112	245	250
	198	250	250
	338	245	250
0.89	1	34	34
	22	185	185
	34	370	370
	60	480	490
	112	480	500
	198	480	500
	338	480	500

quantitatively the results are the same if we multiply the relaxation rates of ^{23}Na in H_2O by a factor 1.25 which is the ratio of the viscosities of D_2O and H_2O. This indicates that the correlation time for the field gradient is proportional to the viscosity of the solvent. The results are shown in Table II and III and compared with the results of the measurements in H_2O.

3.Relaxation as a function of the degree of neutralization.

In describing the relaxation rates of sodium ions($I=\frac{3}{2}$) in polyelectrolyte solutions there are two contributions to the relaxation rate which are taken into account within the scope of the following model for a polyelectrolyte solution. The solvent is described as a continuum with the macroscopic properties (viscosity and dielectric constant) of water. The counterions are represented by point charges and the polyion is represented as an infinitely long rigid rod with an uniform negative charge density. The system can be described either by the Poisson-Boltzmann theory or the ion condensation model. The polyion plus counterion system is supposed to have cylindrical symmetry. In this system the Na^+ ion under study moves through the solvent on an equipotential surface of the total charge distribution of polyion and counterions. The relaxation rate of the ^{23}Na ions in these solutions can then be described by two contributions: one which is assumed to be caused by the water dipoles and one which has its origin in the presence of the poly- and the counterions.

The theoretical expression describing the relaxation rate of sodium-23 in polyelectrolyte solutions as a function of the degree of neutralization has recently been published$^{13)14)}$ and this expression will be applied to the results obtained on sodium polyphosphate solutions.
From reference 13) we have:

$$T_1^{-1} = C_d + \frac{1}{30}\left(\varepsilon P(1-\gamma_\infty)\frac{eQ}{\hbar}\right)^2 \frac{1}{D}\langle E_r^2\rangle_r \qquad (1)$$

where value(c.g.s.)

ε = dielectric constant of the medium

P = polarization factor 0.5[15]

$1-\gamma_\infty$ = shielding correction 5.8[16]

e = electron charge 4.80×10^{-10}

Q = quadrupole moment 0.15×10^{-24} [17]

$\hbar$ = constant of Planck divided by 2π 1.05×10^{-27}

D = selfdiffusion coefficient 5×10^{-6} [18][19]

$\langle E_r^2\rangle_r$ = radial averaged mean squared electric field.

C_d = contribution to the relaxation rate due to the solvent molecules in the presence of the polyions.

Using the ion condensation concept described by Manning[8] we see at low charge densities ($\lambda<1$) the contribution of the polyion to the relaxation rate will be small. For higher charge densities a fraction $(\lambda-1)/\lambda$ of the counterions condenses on the line charge: resides at an average distance d. The charge density parameter λ, used in this context is:

$$\lambda = \alpha \frac{e^2}{\varepsilon bkT} \qquad (2)$$

where α = degree of ionization ; pH measurements indicated that for $\alpha > 0.15$ the degree of ionization $\approx$ degree of neutralization.

b = intercharge distance at full neutralization.

k = constant of Boltzmann.

T = absolute temperature.

In polyphosphate solutions we have: $b = 2.6 \times 10^{-8}$ cm [20][21]

$\lambda = 2.85\,\alpha$ [22]

The other counterions are free to move in the solution and contribute little to the relaxation rate. For $\lambda>1$, the mean squared electric field is given by :

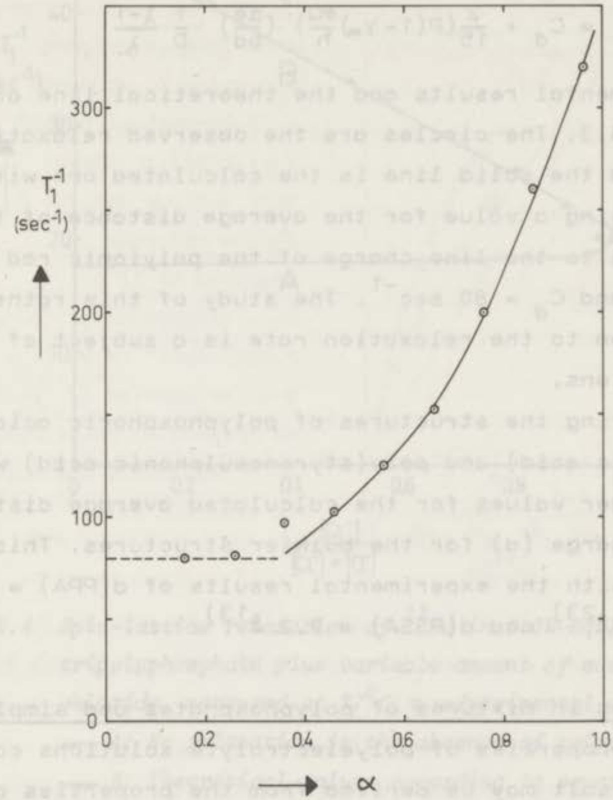

Figure 5.3 *Spin-lattice relaxation of ^{23}Na in 0.30 monomole.l.$^{-1}$ polyphosphoric acid (DP=63) as a function of the degree of neutralization, measured at 27^{o}C.*
⊙ : experimental results.
--- : assumed constant value for the contribution of the water dipoles to the observed relaxation rate.
—— : water contribution plus the ion cloud contribution according to equation (4).

$$\langle E_r^2 \rangle_r = \left(\frac{2\alpha e}{\varepsilon b d}\right)^2 \cdot \frac{\lambda-1}{\lambda} \tag{3}$$

So

$$T_1^{-1} = C_d + \frac{2}{15}\left(P(1-\gamma_\infty)\frac{eQ}{\hbar}\right)^2 \cdot \left(\frac{\alpha e}{bd}\right)^2 \cdot \frac{1}{D} \cdot \frac{\lambda-1}{\lambda} \tag{4}$$

The experimental results and the theoretical line are shown in figure 5.3. The circles are the observed relaxation rates of ^{23}Na and the solid line is the calculated one with formula (4) using a value for the average distance of the counterions to the line charge of the polyionic rod of d = 3.0 Å and C_d = 80 sec^{-1}. The study of this rather high contribution to the relaxation rate is a subject of future investigations.

Comparing the structures of polyphosphoric acid, poly(acrylic acid) and poly(styrenesulphonic acid) we should expect larger values for the calculated average distances to the line charge (d) for the bulkier structures. This is in agreement with the experimental results of d(PPA) = 3.0 Å, d(PAA) = 5 Å[23] and d(PSSA) = 9.2 Å[13].

4.Relaxation in mixtures of polyphosphates and simple salt.

Many properties of polyelectrolyte solutions containing simple salt may be derived from the properties of salt free solutions on the one hand and those of the simple electrolyte solutions on the other hand by the application of additivity rules. In a number of cases the observed relaxation rate can be described by the additivity rule[24][25]:

$$T_1^{-1} = p_A T_A^{-1} + p_B T_B^{-1} \tag{5}$$

where in the case of a mixture of sodium phosphate and sodium chloride:

$$p_B = \frac{\text{conc. Cl}^-}{\text{conc. Na}^+}$$

$$p_A = 1 - p_B$$

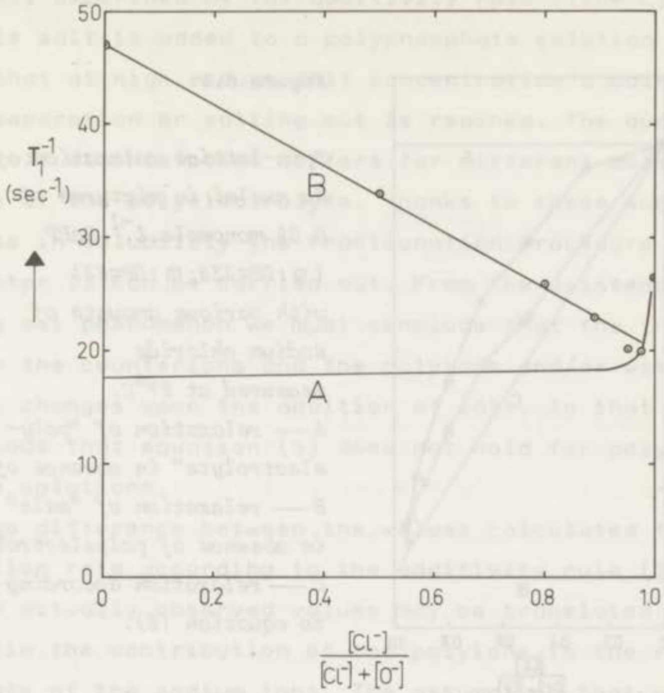

Figure 5.4 Spin-lattice relaxation of ^{23}Na in 0.05 eq.l.$^{-1}$ tripolyphosphate plus variable amount of sodium-chloride, measured at 27°C. ⊙:experimental values.

— A: Na relaxation in the absence of tripolyphosphate.

— B: Theoretical values according to equation (5).

$T_A^{-1} = T_{1A}^{-1} = T_{2A}^{-1}$ = relaxation rate of the sodium ions in the absence of sodium chloride.

$T_B^{-1} = T_{1B}^{-1} = T_{2B}^{-1}$ = relaxation rate of the sodium ions in the absence of sodium phosphate.

This is equivalent to the introduction of a two state model for the counterions in the case when the exchange time between these two states is very fast in comparison with the relaxation times T_A and T_B. This is the case, as we conclude from the exponential decay observed for all measurements. An example is shown in figure 1.2 for a mixture of $(NaPO_3)_{34}$ and NaCl. Measurements have been carried out for mixtures

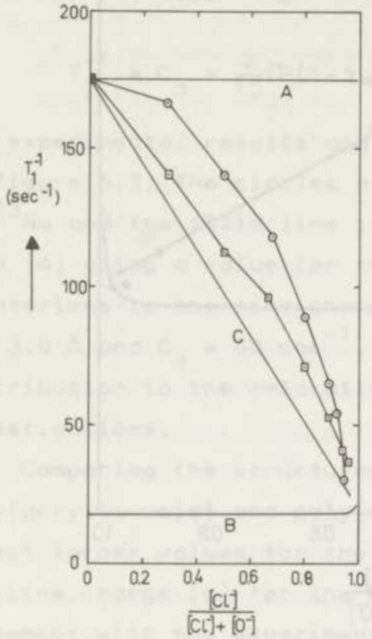

Figure 5.5

Spin-lattice relaxation of Na nuclei in mixtures of 0.05 monomole.l.$^{-1}$ NaPP (⊙:DP=338; ⊡:DP=63) with various amounts of sodium chloride measured at 27°C.
A — relaxation of "polyelectrolyte" in absence of salt.
B — relaxation of "salt" in absence of polyelectrolyte.
C — relaxation according to equation (5).

of sodium tripolyphosphate and sodium chloride and the results are shown in figure 5.4, where it is seen that the observed data are well described by formula (5).

The same type of measurements have been carried out in mixtures of sodium polyphosphates and sodium chloride. In figure 5.5 we show a number of measurements with two polyphosphate samples of different degree of polymerization (63 and 338), both in the region of molecular weights where the sodium relaxation rate is independent of chain length in salt free solutions. From the line A in figure 5.5 , representing the sodium relaxation rate of the counterions of the polyphosphate in the absence of salt, and B, representing the sodium relaxation rate of NaCl solutions without polyelectrolyte5) , we calculate the line C with formula (5). It is seen that the observed relaxation rates are not very well described by the additivity rule (line C). When a simple salt is added to a polyphosphate solution it is known that at high enough salt concentration a point of phase separation or salting out is reached. The quantity of added salt at this point differs for different molecular weights of the polyelectrolyte. Thanks to these subtle differences in solubility the fractionation procedure described in chapter II can be carried out. From the existence of the salting out phenomenon we must conclude that the interaction between the counterions and the polyions and/or with the solvent changes upon the addition of salt. In that case it is obvious that equation (5) does not hold for polyelectrolyte solutions.

The difference between the values calculated for the relaxation rate according to the additivity rule (line C) and the actually observed values may be translated into a change in the contribution of the polyions to the relaxation rate of the sodium ions. The assumption that only this contribution to the relaxation rate of the sodium ion changes is based on the following facts:

a) The polyions together with an equivalent number of counterions are salted out at high simple salt concentration, while the salt stays in solution.
   No ^{35}Cl resonance signal could be detected in the precipitated phase.
b) The sodium relaxation in NaCl solutions is almost independent of concentration, if compared to the observed values[5)]. A slight increase in concentration does not materially change the contribution of T_B^{-1} in formula (5).
c) In the concentration range used we do not observe a change in the ^{35}Cl relaxation rates of the added NaCl in the polyelectrolyte solutions relative to a solution without this polyelectrolyte, where the changes of the ^{35}Cl relaxation rate as a function of concentration in

aqueous solutions of NaCl are about three times larger than the changes of the ^{23}Na relaxation rate[5)26)]. So, describing the difference in calculated and observed values entirely as a result of changes in the contribution of the polyions we rewrite formula (5) into

$$T_1^{-1} = p_A(T_A^{-1})' + p_B T_B^{-1} \qquad (6)$$

and calculate new values for the polyion contribution to the relaxation rate of the sodium ions upon the addition of NaCl. After substracting the estimated constant contribution of the water dipoles (C_d) from the calculated value according to equation (6) and the "theoretical" value, represented by the line C in figure 5.5 where it is assumed that there is no interaction between the polyions and the simple salt ions,we can calculate the ratio of these values. This ratio is plotted in figure 5.6. We note that of course the ratio of these relaxation rates for two mixtures with polyphosphates of different DP is equal in two points:

1) without added salt

2) at the point of salting out.

The relaxation rate of ^{23}Na ions in the precipitated phase was 2200 sec^{-1}. This value was estimated from the time decay function after a 90° pulse and it was found also that, with an accuracy of about 20%, $T_1 = T_2$.

The difference in the lines in figure 5.6 corresponding to the different DP's is due to the change of the solubility product of the NaPP as a function of DP. This phenomenon is not independent of the DP over the whole range. However we can compare the contribution of the polyions to the relaxation rates of ^{23}Na at these two points. From the value of λ in salt free solutions it was seen that 65% of the sodium ions are condensed on the chain[27)]. In the precipitated phase just the compensating number of counterions is present, while there are 4-5 water molecules

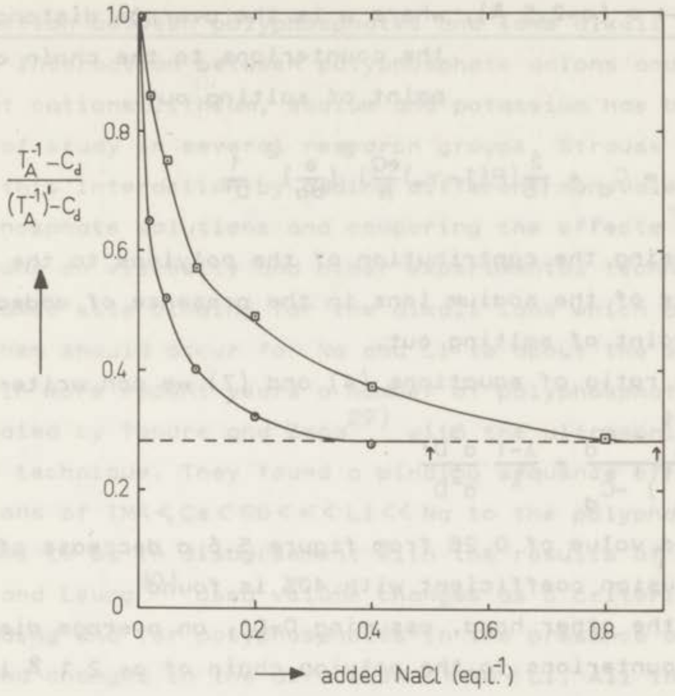

Figure 5.6 Ratio of the polyion contributions to the ^{23}Na relaxation rates without and with correction (eq.(4) and (7)) as a function of the amount of added salt. ⊙:DP=338; ⊡:DP=63. --- Limiting value at the point of phase separation(↑).

per monomeric unit. This was roughly verified by NMR intensity measurements on the ^{31}P and ^{23}Na nuclei. At the point of salting out the degree of neutralization has not changed (α=1).

In solid sodium polyphosphates values for the distance (a) of the sodium nucleus to the chain are known [20)21)]: a= 2.3-2.5 Å. Assuming all other constants, except D, will not change upon the addition of salt we can rewrite equation (4) due to:

1) $\alpha = 1$
2) $(\lambda-1)/\lambda \longrightarrow 1$
3) $D \longrightarrow D'$

4) d $\longrightarrow$ a (a=2.5 Å), where a is the average distance of the counterions to the chain at the point of salting out.

$$(T_A^{-1})' = C_d + \frac{2}{15}\left(P(1-\gamma_\infty)\frac{eQ}{\hbar}\right)^2 \cdot \left(\frac{e}{ba}\right)^2 \cdot \frac{1}{D'} \qquad (7)$$

$(T_A^{-1})'$ being the contribution of the polyions to the relaxation rate of the sodium ions in the presence of added NaCl at the point of salting out.

From the ratio of equations (4) and (7) we can write:

$$\frac{T_A^{-1} - C_d}{(T_A^{-1})' - C_d} = \frac{\lambda-1}{\lambda} \cdot \frac{a^2 D'}{d^2 D} \qquad (8)$$

Reading a value of 0.28 from figure 5.6 a decrease of the selfdiffusion coefficient with 40% is found.

On the other hand, assuming D=D', an average distance of the counterions to the polyion chain of a= 2.1 Å is calculated.

Although the applicability of the ion condensation model should be seriously doubted here, the results in polyphosphate solutions are quite satisfactory. Upon the addition of NaCl a simple two state model can be used, although the polyion contributions to the relaxation rates are not independent of the amount of added salt. This was not mentioned in reference 13), which probably was a result of the fact that this effect here was smaller due to the smaller contributions of the polyion (PAA) to the relaxation rates of the sodium ions. It is also suggested here that the assumption of Manning[8)] that the number of condensed counterions does not change upon the addition of a mono-monovalent salt does not hold at concentrations as used in this investigation ($>10^{-3}$ eq.l^{-1}.).

5. Interaction between polyphosphates and some alkali ions.

The interaction between polyphosphate anions and the univalent cations lithium, sodium and potassium has been a subject of study in several research groups. Strauss et al.[28)] studied this interaction by adding different monovalent salts to polyphosphate solutions and comparing the effects of the alkali ions on viscosity and other experimental techniques. They assumed site binding for the alkali ions which according to them should occur for Na and Li to about the same extend. In more recent years a number of polyphosphates have been studied by Tondre and Zana[29)] with the ultrasonic absorption technique. They found a binding sequence of the alkali ions of TMA < Cs < Rb < K < Li << Na to the polyphosphates. This seems to be in disagreement with the results of Strauss. Strauss and Leung[30)] used volume changes as a criterion for site binding and for polyphosphates in the presence of salt they found changes in the direction K < Na < Li. All the above mentioned measurements were performed on polyphosphate solutions containing salt (alkali bromides or chlorides). Concerning the potassium and the lithium ions the above mentioned sequence seems in contradiction with a remark of Gregor[31)]. He mentioned some observations of Scatchard that "the binding sequence of the alkali metal cations favored potassium with the monobasic phosphates but lithium as the negative charge increased to the dibasic and tribasic phosphate anions".

The difference in solubility between the different alkali polyphosphates is remarkable. Sodium polyphosphate is very soluble in water up to concentrations of 8 monomole.l^{-1}. Potassium polyphosphate with the same DP is much less soluble, while lithium polyphosphate is also far less soluble than NaPP. However solutions of lithium polyphosphates of 0.4 monomole.l^{-1} can be prepared. The precipitation behaviour is also different in comparing the Na, Li and K salts. While LiPP and NaPP are precipitated as gels upon the addition of salt (NaCl) or acetone, the KPP precipitate is semi-crystalline[28).

In the last part of this chapter we will discuss the results of our relaxation experiments on the ^{23}Na and ^{7}Li nuclei at 15.87 and 23.31 MHz in aqueous solutions of polyphosphate without the addition of simple salt. Sodium polyphosphate was treated with the cationic exchanger Amberlite H. The obtained polyphosphoric acid was immediately neutralized to full neutralization (α=1) with two bases in different ratios. The following combinations were used: NaOH+LiOH ; NaOH+KOH and LiOH+KOH . The relaxation rates of ^{23}Na and ^{7}Li were measured in (Na+Li)PP where $f_{Na}+f_{Li}=1$ with $f_{Na}=[Na]/([Na]+[Li])$ and $[Na]+[Li]=[PO_3]$ in an aqueous solution of 0.30 monomole.l^{-1} (PO_3).

The sodium relaxation rates are shown in figure 5.7, while the lithium relaxation rates were found to be : $T_1^{-1} = T_2^{-1} = 1.68 \pm 0.08$ sec^{-1} and they are constant over the whole range of Na:Li ratios. These relaxation rates are about 30 times faster than the rates in normal electrolyte solutions in water, like LiCl[32)33). The sodium relaxation rates were also measured in the same way in (Na+K)PP at 0.44 monomole.l^{-1} in aqueous solution and a larger decrease of the relaxation rate was observed with increasing amount of potassium ions in comparison with the (Na+Li)PP solutions. This is also shown in figure 5.7.

In general the lithium relaxation is determined by contributions of two relaxation mechanisms: dipolar interaction with the surrounding protons of the water molecules and quadrupolar interaction (due to the fact that I_{Li}= Li-spin= $\frac{3}{2}$) with the field gradient at the site of the nucleus[32)33). By measuring the lithium relaxation rates in H_2O and D_2O we can discriminate between these two mechanisms

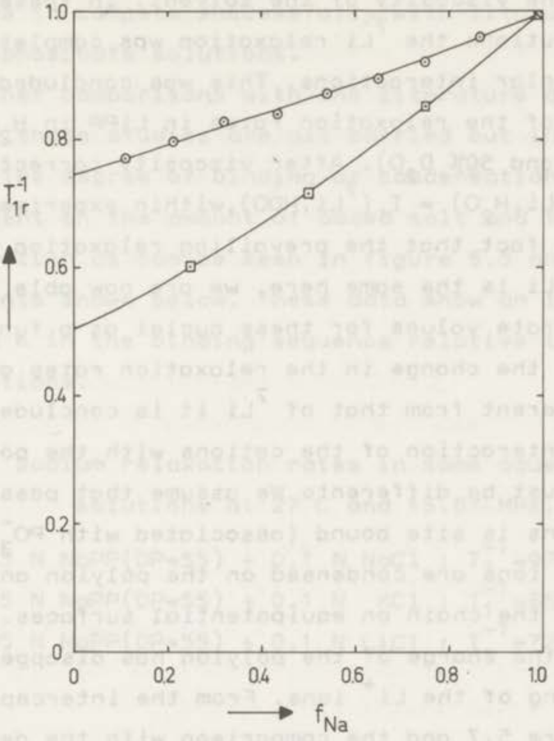

Figure 5.7 *Relative relaxation rates of* ^{23}*Na at* 27^{o}*C and 15.87 MHz in aqueous solutions of polyphosphates (DP=55) as a function of the fraction* Na^{+} *ions.*

⊙ *fully neutralized with Na and Li.*

Pol.conc.=0.30 monomole.l^{-1} . $T_1^{-1}(f_{Na}=1)=250$ sec^{-1}.

⊡ *fully neutralized with Na and K.*

Pol.conc.=0.44 monomole.l^{-1} . $T_1^{-1}(f_{Na}=1)=321$ sec^{-1}.

The solid lines represent parts of the line as calculated in figure 5.3 fitted to the measured relaxation rates.

as the dipolar contribution will almost disappear in heavy-water solutions and the quadrupolar contribution will only change with the viscosity of the solvent. In these polyphosphate solutions the ^{7}Li relaxation was completely governed by quadrupolar interactions. This was concluded from measurements of the relaxation rates in LiPP in H_2O and in HDO (50% H_2O and 50% D_2O). After viscosity correction (1.12) we found $T_1(^7\text{Li},H_2O) = T_1(^7\text{Li},\text{HDO})$,within experimental error.

From the fact that the prevailing relaxation mechanism of ^{23}Na and ^{7}Li is the same here, we are now able to compare the relative rate values for these nuclei as a function of $f_{Na}=1-f_{Li}$. As the change in the relaxation rates of ^{23}Na is quite different from that of ^{7}Li it is concluded that the type of interaction of the cations with the polyphosphate chain must be different. We assume that possibly part of the Li^+ ions is site bound (associated with PO_3^- groups), while the Na^+ ions are condensed on the polyion and are free to move along the chain on equipotential surfaces. In that case part of the charge of the polyion has disappeared only through binding of the Li^+ ions. From the intercept at $f_{Na}=0$ in figure 5.7 and the comparison with the decrease of the relaxation rate in figure 5.3, the amount of site bound Li ions is estimated to be 15%. A roughly constant percentage of the lithium ions site bound to the polyion chain seems then consistent with the observed constant relaxation rate over the whole range of Na:Li ratios.

Potassium decreases the ^{23}Na relaxation rate just as the Li ions do and it seems to compete even more successfully with sodium in the interaction with the polyphosphates as can be concluded from figure 5.7. That the potassium ions are more associated with the polyphosphate chain than the lithium ions in salt free solutions is confirmed by the Li relaxation rate measurements in (Li+K)PP in aqueous solutions with a polyion concentration of 0.15 monomole.l^{-1}.

Upon increasing the K:Li ratio, the lithium relaxation rate decreases from 0.79 sec^{-1} to 0.63 sec^{-1}. Therefore, potassium seems to compete successfully with lithium in salt free polyphosphate solutions.

Further comparisons with the literature data are difficult as these studies are all carried out in the presence of salt. The degree of binding or condensation seems strongly dependent on the amount of added salt and the degree of polymerization as can be seen in figure 5.5 and in the measurements shown below. These data show an interchange of Li and K in the binding sequence relative to the salt free solutions.

Sodium relaxation rates in some aqueous
solutions at 27°C and 15.87 MHz.

0.05 N NaPP(DP=55) + 0.1 N NaCl : T_1^{-1} =97 sec^{-1} .
0.05 N NaPP(DP=55) + 0.1 N KCl : T_1^{-1} =86 sec^{-1} .
0.05 N NaPP(DP=55) + 0.1 N LiCl : T_1^{-1} =72 sec^{-1} .

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CHAPTER VI

SELFDIFFUSION OF PHOSPHATE AND POLYPHOSPHATE ANIONS IN AQUEOUS SOLUTIONS

1. Abstract.

Selfdiffusion coefficients of phosphate and polyphosphate anions were measured at 25°C with the method of the NMR spin echo technique using a time dependent field gradient and observing the ^{31}P nucleus. Selfdiffusion measurements in phosphoric acid were carried out as a function of concentration and temperature. The radius of the phosphoric acid molecule was estimated at 3.2 ± 0.4 Å.

Using the theory of Brownian motion of ellipsoids for the selfdiffusion coefficients, the polyphosphate anions with varying length can satisfactorily be represented as ellipsoids with constant minor axis and a major one varying with the degree of polymerization. It is suggested that previous results obtained with optical methods in concentration gradients yield diffusion coefficients largely determined by the mobility of the counterions.

2. Introduction.

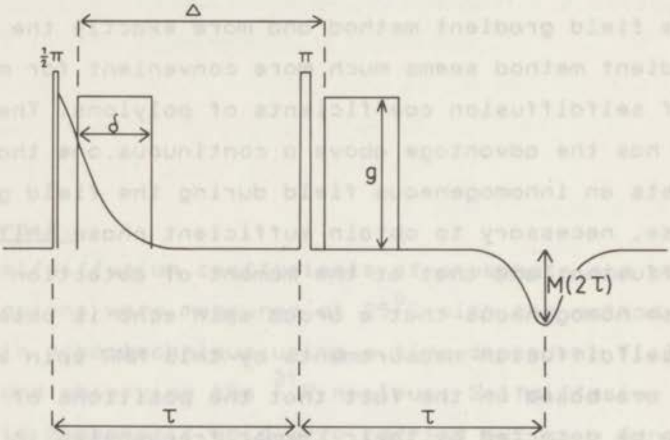
To study the motion of (poly)ions in aqueous solutions two methods can be distinguished. In one, not in thermodynamical equilibrium, the diffusion of the salt is studied as a function of time in a cell with a concentration or temperature gradient. The other method, in thermodynamical equilibrium, yields the selfdiffusion data of the ions. These may be determined in several ways; examples are the tracer method, the field gradient nuclear magnetic resonance method and light scattering. In the study of polyelectrolyte solutions the tracer method has been used successfully for the study of the counterions$^{1)}$. For polyions this method seems less attractive considering the preparative requirements. The field gradient method and more exactly the pulsed field gradient method seems much more convenient for measurements of selfdiffusion coefficients of polyions. The pulsed method has the advantage above a continuous one that there exists an inhomogeneous field during the field gradient pulse, necessary to obtain sufficient phase shift due to selfdiffusion, and that at the moment of detection the field is so homogeneous that a broad spin echo is observed.

The selfdiffusion measurements by this NMR spin echo technique are based on the fact that the positions of the nuclei can be detected by their Larmor frequencies in a spatially dependent magnetic field. The diffusional motion of a nucleus through the magnetic field causes a change in Larmor frequency. The total effect of all spins is a randomization of the frequencies, resulting in a loss of transversal magnetization, which is observed by a decreasing amplitude of the spin echo.

This method has been used for the phosphorus nucleus in phosphoric acid, sodium phosphate and sodium polyphosphate solutions in water.

3. The experiment.

A more extensive description of the theoretical background is given in the original literature 2)3)4) and in reference 5). Here we will only describe the principle and the actual experiment. The experiment is carried out as shown in figure 6.1. The echo amplitude is dependent on transversal relaxation and selfdiffusion effects. As the time between the 90° pulse and the 180° pulse is held constant, relaxation effects can be ignored. The spin echo amplitude depends on the loss of transversal magnetization as a result of diffusion during the time between the two field gradient pulses. The amplitude of the spin echo is



$$\ln \frac{M(2\tau,g)}{M(2\tau,0)} = -D.(\gamma g\delta)^2.\Delta$$

Figure 6.1 Scheme of the spin echo experiment to obtain selfdiffusion coefficients.
δ = length of gradient pulse g.
τ = time between 90° pulse and 180° pulse.
Δ = time between the two gradient pulses.

observed as a function of the intensity of the gradient pulses while the length of these pulses is held constant during an experiment.

If we consider a large number of nuclei with non-zero spin in a perfectly homogeneous magnetic field (H_0) along the z axis they will precess with the Larmor frequency

$$\omega_0(z) = \gamma H_0(z) \tag{1}$$

If, after the first 90° pulse, a gradient pulse is applied, an inhomogeneous field in the direction of the Zeeman field during a time δ, the frequency of the spins at the location z_1 is

$$\omega_0(z_1) = \gamma(H_0 + gz_1) \tag{2}$$

where g = gradient.

The phase shift during this time is

$$\phi(z_1) = \gamma g z_1 \delta \tag{3}$$

After the 180° pulse we apply a second gradient pulse of equal length and intensity. The frequency of the spins at the location z_2 is

$$\omega_0(z_2) = \gamma(H_0 - gz_2) \tag{4}$$

The phase shift due to this second gradient pulse is

$$\phi(z_2) = -\gamma g z_2 \delta \tag{5}$$

The total phase shift due to both gradient pulses is

$$\phi(z) = \gamma g \delta z \qquad \text{with } z = z_1 - z_2 \tag{6}$$

If the spins do not move during the time Δ, the phase shift caused by the first gradient pulse is precisely corrected by the second one. However if the spins move through the solution there will be a net phase shift due to the selfdiffusion of these spins (and the molecules related with them) in the z direction. We assume the dimensions of the sample volume large in relation to the displacement z in a time Δ. In a spin echo experiment this phase shift is detected by a change in the spin echo amplitude. Neglecting relaxation effects the decrease of the magnetization at a time 2τ is only influenced by the probability P of displacement z during a time Δ. The magnitude of the magnetization after the second gradient pulse is given by

$$M(\gamma g\delta,\Delta) = M(0)\int_{-\infty}^{+\infty} P(z,\Delta)e^{-i\gamma g\delta z}\,dz \qquad (7)$$

Assuming P is an even function of z and writing $k=\gamma g\delta$ it follows

$$M(k,\Delta) = M(0)\int_{-\infty}^{+\infty} P(z,\Delta)\cos(kz)\,dz \qquad (8)$$

Assuming $P(z,\Delta)$ to obey the second law of Fick

$$\frac{\partial P(z,\Delta)}{\partial \Delta} = D.\frac{\partial^2 P(z,\Delta)}{\partial z^2} \qquad (9)$$

one has 5): $\frac{\partial M(k,\Delta)}{\partial \Delta} = -Dk^2 M(k,\Delta)$ (10)

This is the same equation as given by Stejskal and Tanner 3)4) and shown below figure 6.1.

In our experiments we used a commercial pulsed NMR spectrometer and a pulsed field gradient unit (Bruker). In practice it is rather difficult to generate a second gradient pulse exactly equal to the first one 6). The result of this inequality is a deformed or attenuated echo. The amplitude of the second gradient pulse was therefore always corrected in such a way that at a given first gradient pulse a maximum echo amplitude was obtained. The details of the construction of the probehead can be found in reference 5). The experimental settings are as follows:

Coil factor	14 G.cm^{-1}.A^{-1}.
Length of gradient pulse	1.6- 4.0 msec.
Experimental repeat time	1 - 5 sec.
Gradient current	5 - 20 A.
Time between gradient pulses	10 - 20 msec.

The gradient pulses are long enough relative to rise and fall times at beginning and end to describe them as rectangular. These pulses are proportional to the current according to

$$g = \alpha I \tag{11}$$

where the gradient current I is monitored by meter reading and the constant α has to be found by measuring the decrease of the magnetization of a sample with well known selfdiffusion coefficient D. For this purpose we used the measurements of ^{22}Na in NaCl solutions in water at 25^{o}C by the tracer method 7). We performed selfdiffusion measurements on two nuclei: ^{23}Na and ^{31}P at respectively 15.87 and 24.29 MHz. Some selfdiffusion data on sodium are found in Table I.

Experimentally we estimated errors of about 10% in all D values. This was concluded from duplo measurements and the accuracy of the estimation of the spin echo amplitudes. These errors are drawn in the figures 6.3, 6.4, 6.5 and 6.8. An example of a typical measurement is given in figure 6.2. The materials used in the experiments in this chapter were all made as described in the literature 8)9)10) and in chap-

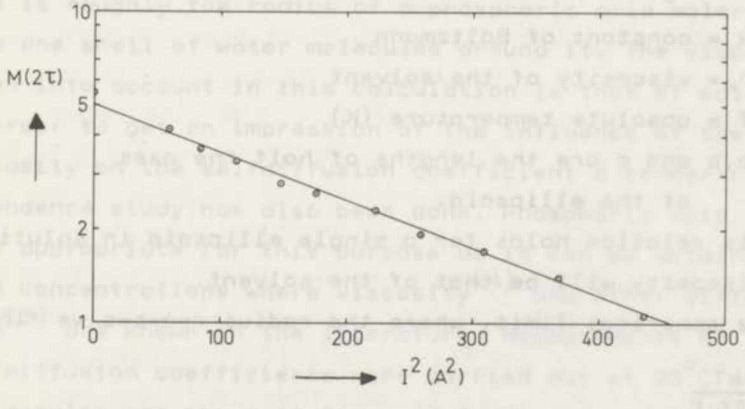


Figure 6.2 Example of a measurement, showing the exponential decrease of the echo amplitude as a function of I^2 *for 3.00 mole.l.*$^{-1}$ *phosphoric acid at 25*^{o}*C.*

Table I. Selfdiffusion coefficients of sodium ions in some aqueous solutions at 25°C.

	conc. (eq.l^{-1}.)	D (10^{-6} $cm^2 sec^{-1}$)
NaH_2PO_4	1.01	7.9
$Na_5P_3O_{10}$	1.67	11
NaCl	1.00	12
NaCl	2.18	11.17 (ref.7))
NaCl	3.00	10

ter II. In order to relate our selfdiffusion data to those found in the literature we used NaCl p.a. (E.Merck).

4.Results and discussion.

About fourty years ago Perrin 11)12) described the Brownian motion of an ellipsoid in solution and calculated the translational diffusion coefficient of this ellipsoid as a function of the length of the three half axes:

$$D = \frac{kT}{12\pi\eta_\circ} \int_0^\infty \frac{ds}{\sqrt{(a^2+s)(b^2+s)(c^2+s)}} \qquad (12)$$

with k = constant of Boltzmann

$\eta_\circ$ = viscosity of the solvent

T = absolute temperature (K)

a,b and c are the lengths of half the axes of the ellipsoid.

As this relation holds for a single ellipsoid in solution the viscosity will be that of the solvent.

In the spherical limit, where the radius r=a=b=c we find

$$D = \frac{kT}{6\pi\eta_\circ r} \qquad (13)$$

which is the same relation as found by Stokes and Einstein:

$$f = 6\pi\eta_\circ r \qquad (14)$$

$$Df = kT \qquad (15)$$

Table II. Selfdiffusion data of 1.00 mole.l^{-1} phosphoric acid in H_2O as a function of temperature.

T (K)	D (10^{-6} $cm^2 sec^{-1}$)	η_o [13)] (cP)	$\frac{kT}{6\pi\eta_o D}$ (Å)
278	4.1	1.52	3.3
283	5.5	1.31	2.8
288	6.9	1.14	2.9
293	6.8	1.01	3.1
298	7.0	0.89	2.9
303	8.7	0.80	3.2
308	8.7	0.72	3.6
313	10.9	0.66	3.2
			r = 3.2 ± 0.4

This spherical model has been applied to the measured selfdiffusion coefficients of phosphoric acid. From the measurements of 1.00 mole.l^{-1} H_3PO_4 in water as a function of temperature, as shown in Table II, we see the molecules can be represented by a sphere with a radius of 3.2 ± 0.4 Å. This is roughly the radius of a phosphoric acid molecule with one shell of water molecules around it. The viscosity taken into account in this calculation is that of water. In order to get an impression of the influence of the macroviscosity on the selfdiffusion coefficient a concentration dependence study has also been done. Phosphoric acid is very appropriate for this purpose as it can be obtained at high concentrations where viscosity[14)] and other diffusion data[15)] are known in the literature. Measurements of the selfdiffusion coefficients were carried out at 25°C and the results are shown in figure 6.3. We can conclude that over the concentration range from 0.5 mole.l^{-1} to 15 mole.l^{-1} the selfdiffusion coefficient changes linearly with the reciprocal viscosity of the solution. The difference in

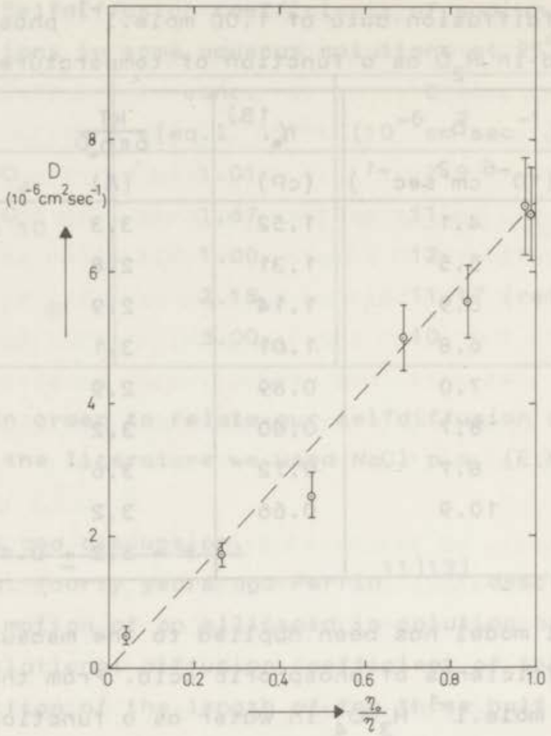


Figure 6.3 Selfdiffusion coefficients of phosphoric acid at 25°C against reciprocal viscosity relative to water.

viscosity between a solution of 1.00 mole.l^{-1} phosphoric acid in water and an infinitely dilute solution is very small, keeping in mind the accuracy of the measurement. This is in agreement with the fact that the observed selfdiffusion data do not change much below a concentration of 1.0 mole.l^{-1}. So, as we have about 50 moles of water to one mole of phosphoric acid, we describe the diffusion of the P nuclei with the viscosity of water. At relatively high concentrations the selfdiffusion could be influenced by some complex formation, mentioned elsewhere. That this is not seen in figure 6.3 could be the result of the fact that the accuracy of the measurements is too low to detect this. In figure 6.4 we show data by Edwards and Huffmann[15)] mea-

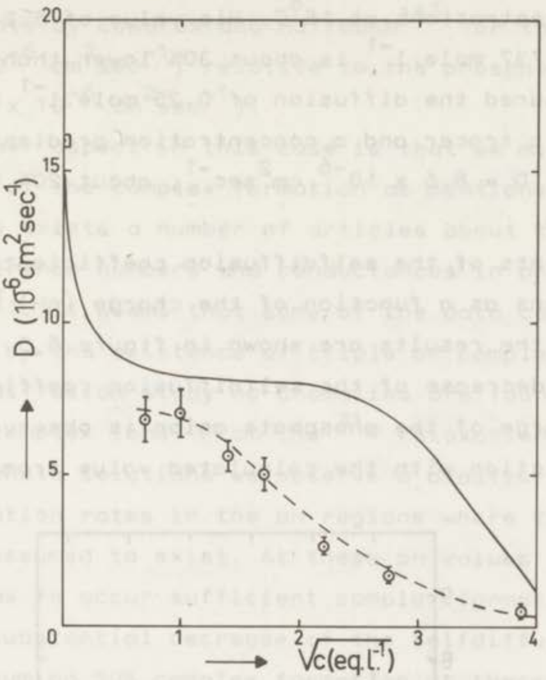


Figure 6.4 Diffusion and selfdiffusion coefficients of phosphoric acid at 25°C. ⊡ *:Nernst limiting diffusion coefficient.*
—— *: Diffusion data by Edwards and Huffmann.*
⊙ *: Observed selfdiffusion data.*
--- *: This line represents the same dependence as the line in figure 6.3.*

sured in a Gouy diffusiometer at 25°C in a concentration gradient. We plotted our selfdiffusion data in the same figure. Remarkable differences occur especially in the concentration range above 2 mole.l^{-1} and in very dilute solutions. An extrapolation to the Nernst limiting value mentioned in reference 15) seems not possible. The radius calculated by these authors for the diffusing phosphoric acid molecule of 3.41 Å however seems a very reasonable value. The tracer method has also been used. For example, Rolfe[16)] estimated the selfdiffusion coefficient at a number of concentrations at 18°C. His value of 5.2×10^{-6} $cm^2 sec^{-1}$ at 0.737 $mole.l^{-1}$ is about 30% lower than our value. Walker 17) measured the diffusion of 0.25 $mole.l^{-1}$ $H_3{}^{32}PO_4$ into H_2O with a tracer and a concentration gradient and found at 20°C: $D = 8.6 \times 10^{-6}$ $cm^2 sec^{-1}$, about 20% higher than our value.

Measurements of the selfdiffusion coefficients of the phosphate anions as a function of the charge (pH) were also performed and the results are shown in figure 6.5. In the first place a decrease of the selfdiffusion coefficient with increasing charge of the phosphate anion is observed, which is in contradiction with the calculated value from diffusion

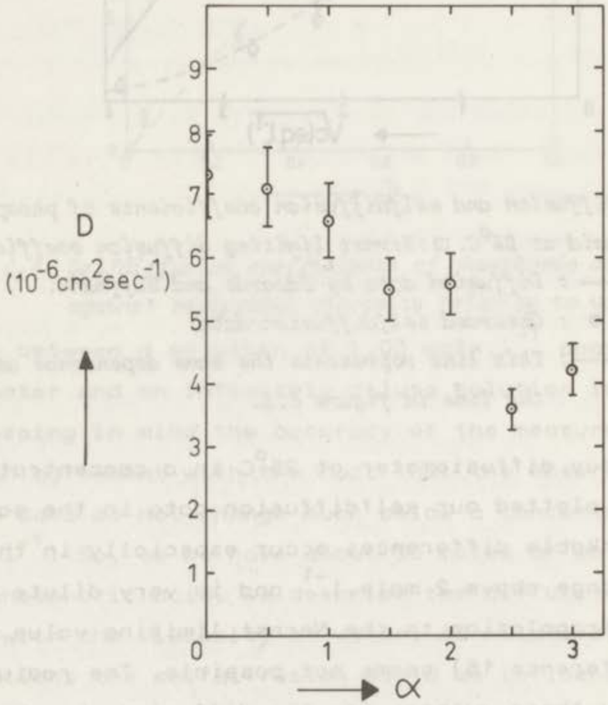


Figure 6.5 Selfdiffusion data of phosphoric acid neutralized by NaOH at 29°C as a function of the degree of neutralization ([Na]/[P]). acid conc.=0.5 $mole.l^{-1}$

measurements by Edwards and Huffmann[15)] for the $H_2PO_4^-$ anion ($8.76 \times 10^{-6}\ cm^2 sec^{-1}$) relative to the phosphoric acid molecule ($7.6 \times 10^{-6}\ cm^2 sec^{-1}$).

Another aspect in this case is that we might find some influence of the complex formation as mentioned in chapter III. There exists a number of articles about the behaviour of transference numbers and conductances in phosphate solutions[18)19)]. It seems that some of the data can only be explained by the existence of triple or complex ions. In this selfdiffusion study no anomalies are found with respect to these complex ions. From the ^{31}P relaxation data in orthophosphate solutions we observe a drastic increase of the relaxation rates in the pH regions where these complex ions are assumed to exist. At these pH values (6.4 and 11.1) there seems to occur sufficient complex formation[19)] to effect a substantial decrease of the selfdiffusion coefficient. Assuming 50% complex formation at these pH values ($\alpha=1.5$ and $\alpha=2.5$) and a value for l equal to $2r$ we calculate according to equation (17) a decrease of D with 12% relative to a sphere with radius r. The measured values are shown in figure 6.5. By drawing a line through the points at $\alpha=0.0$, 0.5, 1.0, 2.0 and 3.0 we observe the experimental values at $\alpha=1.5$ and at $\alpha=2.5$ to be about 10% to 20% lower, which may be due to the complex formation.

As the polyphosphates are relatively easy to prepare over a wide range of degrees of polymerization (DP) we are able to test the applicability of the formulas derived by Perrin. Assuming we can describe the polyphosphates as ellipsoids of revolution, with equal minor axes and a major axis varying with the DP, moving in water we can write

$$D = \frac{kT}{12\pi\eta_0} \int_0^\infty \frac{ds}{(r^2+s)\sqrt{(c^2+s)}} \qquad (16)$$

where a=b=r=radius of the ellipsoid of revolution.

If c>r

$$D = \frac{kT}{6\pi\eta_o r}\cdot f(p) \tag{17}$$

with
$$f(p)= \frac{\ln(p+\sqrt{(p^2-1)})}{\sqrt{(p^2-1)}} \tag{18}$$

and
$$p = \frac{c}{r} \tag{19}$$

Describing the polyion as a sequence of PO_4 tetrahedrons linked together linearly we write

$$p \approx 1 + \frac{(n-1)l}{2r} \tag{20}$$

with n = degree of polymerization

l = length of a monomeric unit.

This is illustrated by figure 6.6.

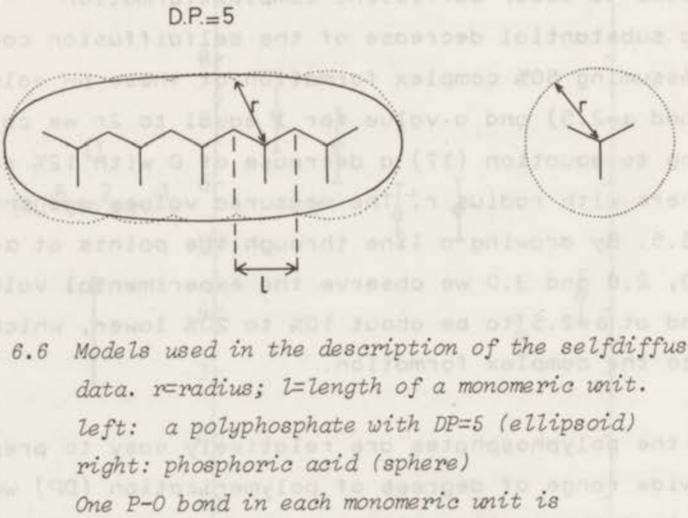


Figure 6.6 Models used in the description of the selfdiffusion data. r=radius; l=length of a monomeric unit.
left: a polyphosphate with DP=5 (ellipsoid)
right: phosphoric acid (sphere)
One P-O bond in each monomeric unit is perpendicular to the plane of drawing.

Using values for the length of a monomeric unit and the radius of the ellipsoid we can calculate the selfdiffusion coefficients. The measured and the calculated data are presented in figure 6.7 and 6.8. The calculated values of D as a function of f(p) or DP are shown as a solid line.

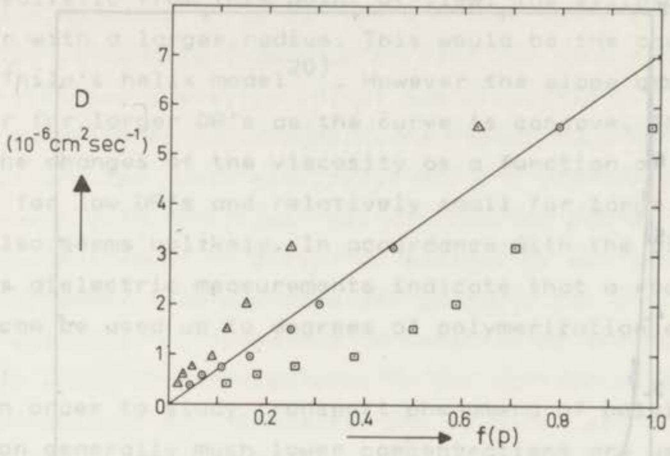


Figure 6.7 Selfdiffusion coefficients of the polyion in 1.00 ± 0.02 monomole.l.$^{-1}$ NaPP against f(p).

△ : Observed values plotted with $l=2r$.

⊙ : Observed values plotted with $l=0.8r$.

⊡ : Observed values plotted with $l=0.2r$.

— Calculated translational diffusion coefficients of ellipsoids with constant radius(r) and $l=0.8r$.

The radius of the ellipsoid used is the same one as found for the monomeric phosphoric acid: 3.2 Å. The length of one monomeric unit, a PO_4 tetrahedron, is calculated from the P-O bond length of 1.60 Å and the tetrahedral angle. So, in the formulas (17), (18) and (20) we used $r=3.2$ Å and $l=2.6$ Å. As the radius is held constant the line in figure 6.7 presents a linear relationship. The lines in figure 6.7 and in figure 6.8 represent the same dependence of the selfdiffusion coefficient upon the DP. The observed selfdiffusion coefficients are also presented for some other p values, resulting in a non-linear relationship between D and f(p). The line drawn was constructed under the assumption that the polyions can be described as ellipsoids of revolution with varying length, calculated from molecular bond lengths

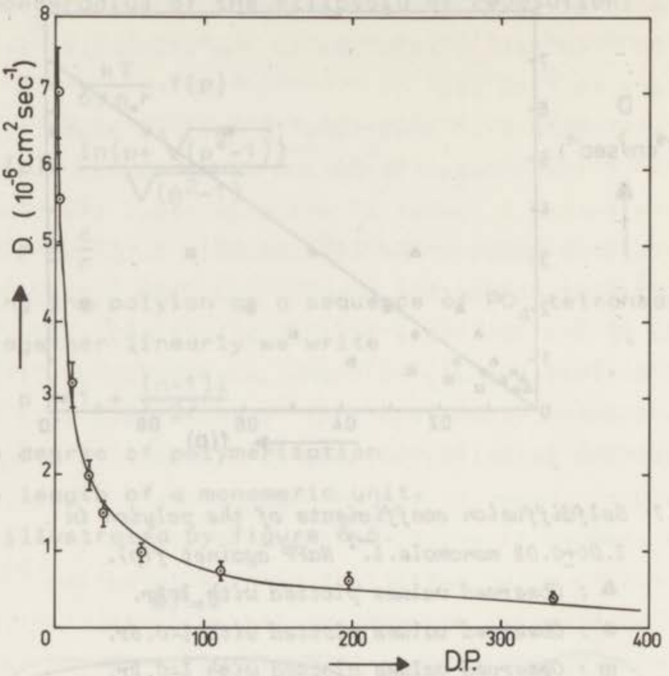


Figure 6.8 Selfdiffusion coefficients of the polyions in 1.00±0.02 monomole.l.$^{-1}$ NaPP as a function of the DP. ⊙ : Observed values.
— Calculated values with constant radius and l=0.8r.

and angles. It is surprising how well the calculated line fits to the observed data, considering the relatively high concentration of the solutions (1.00 monomole.l^{-1}). Although it is possible to describe the selfdiffusion coefficients with other combinations of radius, monomeric length and viscosity, none of these variables can be held constant in describing all the experimental selfdiffusion coefficients in the range of DP's from 1 to 350. This can be seen in figure 6.7. The line one can draw through the triangles seems not very probable from geometric considerations. The radius should in that case be even smaller than the proposed one here. The line one can draw through the squares seems more realistic from this point of view. The ellipsoids are shorter with a larger radius. This would be the case in using Thilo's helix model[20]. However the slope becomes smaller for larger DP's as the curve is concave. This means that the changes of the viscosity as a function of DP are larger for low DP's and relatively small for large DP's. This also seems unlikely. In accordance with the present results dielectric measurements indicate that a rodlike model can be used up to degrees of polymerization of about 200[21].

In order to study transport phenomena of polyions in solution generally much lower concentrations are used. In this work the rather bad signal to noise ratio did not permit us to obtain selfdiffusion coefficients via the phosphorus nucleus at lower monomer concentration. In spite of this some remarks in relation to other diffusion and selfdiffusion measurements of these systems can be made. Several measurements of diffusion coefficients obtained by a concentration gradient method are known in the literature. Comparing our measured selfdiffusion data of the polyion in fully neutralized sodium polyphosphates we see remarkable differences with other studies. Kern[22] estimated in a concentration gradient the diffusion of potassium polyphosphates (DP=6300) and found coefficients of 4.3-6.6 × 10^{-6} $cm^2 sec^{-1}$. These values seem to be more influenced by the counterions than the polyions if we compare the values with ^{23}Na and ^{31}P selfdiffusion data. The same remarks can be made for the measurements performed by Katchman and Smith[23]. These coefficients are also much to high to describe the polyion diffusion. The values are probably largely determined by the diffusion of the small counterions. The authors themselves mentioned this possibility. Malmgren[24] also did measurements on polyphosphates with optical methods. He found for concentrations of 0.05 monomole.l^{-1} diffusion coefficients of 0.15-0.06 × 10^{-6} $cm^2 sec^{-1}$ where DP = 2800-23000. These data are more in agreement with ours, although comparison is difficult due to the different concentrations used and the much larger chainlengths. Large differences both qualitatively and quantitatively occur between our measurements and non-equilibrium results. Partly these differences are due to cations diffusing in their concentration gradient and dragging the polyions with them. The same type of results is obtained by Schriever in comparing the selfdiffusion coefficient of poly(methacrylic acid) determined by ^1H resonance in D_2O solutions as a function of the degree of neutralization and the diffusion data obtained by Kern[25)26)]. It can be concluded that the measurements in a concentration gradient are not very suitable for studying polyion diffusion. The results for the polyphosphates are surprisingly simple, considering the relatively high concentrations in describing them as rigid ellipsoids with constant radius. We conclude therefore that the polyphosphate ions behave at full neutralization as extended particles in solution.

One of the most interesting measurements would have been the selfdiffusion data of the ^{23}Na counterions. However the very fast transversal relaxation rates of these counterions results in an echo too small to detect at time 2τ, as it is necessary that τ is long enough to observe a significant decrease of the spin echo as a function of the intensity of the gradient pulses to obtain a selfdiffusion coefficient with sufficient accuracy.

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CONCLUDING REMARKS

In chapter III and IV experimental results on phosphorus relaxation have been presented. From the analysis of these results it appeared that scalar interaction and modulation of the chemical shift are the most important relaxation mechanisms for the transversal magnetization. Scalar interaction, anisotropic chemical shift and in some cases dipole-dipole interaction are the main contributions to the longitudinal relaxation. As a result of the small frequency range that could be investigated no full quantitative analysis could be presented. An investigation of a larger frequency range may be helpful in obtaining more accurate values for the exchange time, the coupling constants in the complex ions and the chemical shifts that play a role. In relatively concentrated solutions, where there are more ^{1}H and ^{2}D nuclei participating in these reactions than at lower concentrations, the ^{1}H and ^{2}D relaxation rates must be influenced by for instance the scalar coupling between these nuclei and phosphorus. In this case and also at lower concentrations double resonance experiments may be helpful in distinguishing between the several relaxation mechanisms that play a role in these interactions[1)].

Before going into the investigations of the phosphorus relaxation in polyphosphates,or in the first place pyrophosphate, trimeta- and tripolyphosphate, it is seen from the preliminary measurements in chapter IV that a better insight in the quantitative contributions from the possible relaxation mechanisms should be obtained from the suggested investigations of orthophosphates. As the amount of the complex ions is probably strongly concentration dependent, measurements at very low concentrations should also yield information on this subject.

In polyphosphates we have the additional process of spin-diffusion, which complicates a description of the observed relaxation rates even more. However it may be interesting to study the phosphorus relaxation in polyphosphate solutions upon the addition of univalent and divalent ions. It is suggested in the literature that the divalent ions are really site bound to the polyphosphate chain. If a proton exchange process is the dominant chemical process responsible for the relaxation, decrease of the relaxation rates has to be expected from an increasing amount of binding counterions. If an investigation of the relaxation rates of ^{31}P in polyphosphate solutions is carried out this should include a variation of the following parameters: degree of polymerization, including the distribution, degree of neutralization, concentration, nature of counterions and Larmor frequency. The ^{31}P relaxation rates of the end and middle phosphate groups will in general be different, therefore the Fourier transform method must be used.

The selfdiffusion coefficients of the phosphorus nucleus in the polyphosphate ions give interesting information about the mobility and the shape of the particles in solution. Thilo$^{2)}$ assumed, from the hydrolysis behaviour, that the conformation of the polyphosphates in solution is a certain type of helix. It is shown in the last chapter that our selfdiffusion data can be described assuming essentially a rigid rod model represented by an elongated ellipsoid. The model suggested by Thilo cannot be fitted for the range of degrees of polymerization studied here with acceptable values for the radius and the monomeric length. Strauss$^{3)}$ uses a random coil model for the polyions, but his measurements are always in the presence of simple salt. Measurements of selfdiffusion coefficients as a function of the amount of alkali chlorides present should yield interesting information concerning the shape of the polyion. In our salt free polyphosphate solutions, the rigid rod model seems also satisfactory in describing the relaxation rates of the sodium counterions. In comparing the alkali ions, the nature of the binding or association of Na and Li seems to be different. In the presence of salt the binding sequence concerning Li and K seems opposite if compared with salt free solutions. As the counterion condensation is strongly dependent upon the degree of polymerization these measurements only indicate that complicated processes are playing a role here and that an extensive investigation of counterion relaxation as a function of salt concentration, degree of polymerization and in mixtures with several alkali ions is needed to obtain a more detailed picture of polyion-counterion interaction. The study with divalent ions should also give information on this subject.

Clearly the study of the selfdiffusion coefficients of the counterions, especially Li, in polyphosphate solutions with and without the addition of simple salt should yield interesting results.

Some investigations of polyphosphate solutions are described here, however much additional work has to be done to obtain a better understanding of the relaxation of P, Na and Li nuclei and of the interaction between polyphosphate and counterions in aqueous solutions.

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SUMMARY

In this thesis an attempt is made to study the polyion-counterion interaction in sodium polyphosphate solutions by nuclear magnetic relaxation and selfdiffusion. The nuclei used for this purpose are mainly sodium-23 and phosphorus-31. In chapter I a general introduction is given of the nuclear magnetic relaxation method. In chapter II the preparation and some properties of the polyphosphates are described. This includes the determination of the degree of polymerization.As a consequence of the fact that the relaxation behaviour of the phosphorus nucleus is complicated, relaxation rates of this nucleus are studied in orthophosphate solutions in chapter III. It can be concluded that scalar coupling and modulation of the chemical shift are the main relaxation mechanisms for the transversal relaxation rate. Due to the large isotopic effects that are found, it seems that these rates can only be explained by assuming the existence of complex ions. The phosphorus relaxation in polyphosphate solutions seems to be determined by the same relaxation mechanisms. An additional process is that of spin-diffusion which should be present as concluded from the Fourier transform spectra. This method is discussed together with some preliminary measurements in chapter IV. In chapter V the relaxation of the counterions, sodium and in a few cases lithium, is discussed as a function of the degree of polymerization and the degree of neutralization, and for mixtures with simple salt and different cations. By using the ion condensation concept rather small values are calculated for the average distance to the polyion chain. In comparing Li and Na the binding appeared to be of a different nature.

In the last chapter the selfdiffusion coefficients of the phosphate and polyphosphate anions in aqueous solutions

are discussed. An ellipsoid model is proposed for the polyphosphate ions and a reasonable description of the measured data is obtained. A comparison is made with published diffusion and selfdiffusion coefficients of phosphate and polyphosphate anions in aqueous solution.

SAMENVATTING

In dit proefschrift wordt een poging gedaan om de polyion-tegenion interactie in natrium polyfosfaat oplossingen te onderzoeken door middel van metingen van kernspin relaxatie snelheden en zelfdiffusie coefficienten. De kernen die voor dit doel zijn gebruikt zijn hoofdzakelijk fosfor-31 en natrium-23. Een algemene inleiding betreffende de magnetische relaxatie wordt gegeven in hoofdstuk I. In hoofdstuk II worden de polyfosfaten behandeld, inclusief de bereiding en de bepaling van de polymerisatiegraad. Ten gevolge van het feit dat het relaxatiegedrag van de fosfor kern ingewikkeld is, is dit gedrag eerst bestudeerd in orthofosfaat oplossingen, beschreven in hoofdstuk III. In deze oplossingen blijken modulatie van de chemische verschuiving en scalaire koppeling de belangrijkste mechanismen te zijn voor de transversale relaxatie. Het bestaan van complexe ionen is in overeenstemming met de gevonden grote isotoop effekten. De relaxatie van de fosfor kern in polyfosfaten lijkt door dezelfde mechanismen bepaald te worden. Tevens speelt het spin-diffusie proces een rol, zoals uit de Fourier spectra geconcludeerd kan worden. De relaxatie van ^{31}P in polyfosfaten wordt beschreven in hoofdstuk IV. In hoofdstuk V wordt de relaxatie van de tegenionen, Na en in een aantal gevallen Li, besproken als functie van de polymerisatiegraad, neutralisatiegraad en in mengsels met verschillende kationen en hoeveelheden toegevoegd zout. Tamelijk kleine afstanden worden berekend voor de gemiddelde afstand van het tegenion tot de polyion keten met behulp van het ion condensatie model. De aard van de binding lijkt voor Li anders dan voor Na.

In het laatste hoofdstuk worden de zelfdiffusie coefficienten van fosfaat en polyfosfaat ionen in water beschreven. Een omwentelingsellipsoide geeft een goede beschrijving van de gemeten waarden voor de polyfosfaat ionen. Een vergelijking wordt gemaakt tussen een aantal gepubliceerde diffusie en zelfdiffusie coefficienten van fosfaat en polyfosfaat ionen en de hier beschreven resultaten.

Op verzoek van de Faculteit der Wiskunde en Natuurwetenschappen volgt hier een kort overzicht van mijn academische studie.

Na het behalen van het einddiploma HBS-B aan de Dalton HBS te Rotterdam in 1964 en enkele jaren studie aan de Technische Hogeschool te Delft (Scheikundige Technologie) werd in 1967 begonnen met de studie in de Scheikunde aan de Rijksuniversiteit te Leiden. Het kandidaatsexamen,S4, werd in mei 1969 afgelegd. De doctoraalstudie met als hoofdvak fysische chemie, bijvak numerieke wiskunde en derde richting theoretische organische chemie stond onder leiding van de hoogleraren Dr.M.Mandel, Dr.A.J.Staverman, Dr.G.Zoutendijk en Dr.L.J.Oosterhoff en de lector Dr.J.C.Leyte. Het doctoraal examen werd in mei 1971 afgelegd.

Hierna werd begonnen met een onderzoek op het gebied van de kernspin resonantie. In januari 1972 werd een aanvang gemaakt met het in dit proefschrift beschreven onderzoek.

Vanaf juni 1971 was ik verbonden aan het fysisch chemisch praktikum; tot 1 januari 1974 als doctoraal assistent, daarna als wetenschappelijk medewerker.

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