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NUCLEAR MAGNETIC RELAXATION OF ^{23}Na AND ^{7}Li IONS IN POLYPHOSPHATE SOLUTIONS

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Nuclear magnetic relaxation rates of ^{23}Na and ^{7}Li have been measured in aqueous polyphosphate solutions. The Li^+-polyion interaction is shown to be qualitatively different from the Na^+-polyion interaction. This is concluded from the relaxation studies on Li-polyphosphate/Na-polyphosphate mixtures and from the dependence of the relaxation rates on the polymer-charge.

1. Introduction

A large number of studies has been performed on the polyphosphates (PP), especially before 1960, with classical techniques. In later years also magnetic resonance studies of the high resolution spectra of the ^{31}P nucleus have been carried out. 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. In our previous paper [1,2], we reported the dependence of the ^{23}Na relaxation in polyphosphates on the molecular weight of the polymer. It was shown that for degrees of polymerization above 60 the relaxation rate is constant. This sets a lower limit to the applicability of the rigid rod polyelectrolyte model in the study of polyion-counterion interaction. A recently developed theory for quadrupolar relaxation of counterions in polyelectrolyte solutions [3,4] opens the possibility of a more quantitative study of the polyphosphate systems.

2. Experimental

The polyphosphates were prepared 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 25 hr. Then, after quickly cooling the polyphosphate glass, we estimated the loss of weight for the following reaction:

$$n\mathrm{NaH_2PO_4} \rightarrow (\mathrm{NaPO_3})_n + n\mathrm{H_2O}\ .$$

This loss was always within 2% of the theoretical value. The cooling procedure was carried out quickly to obtain relatively high degrees of polymerization. The glass was dissolved 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 placed in a round bottomed flask some water was added and finally the solution was freeze dried. All DP's were determined by viscosity measurements. The viscosities were measured for at least four concentrations with an Ostwald viscosimeter at 25.0°C in aqueous solutions of 0.035 N NaBr [1,2]. For molecular weights lower than 7400 the results of the viscosity measurements were compared with the number average molecular weights determined from the Fourier transform ^{31}P NMR spectra. The areas (A) under the absorption of P_{middle} and P_{end} give the number average DP:

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

The relaxation experiments were all carried out with a Varian Associates 14.09 kG magnet equipped with a magnet flux 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 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, 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.

All the NMR measurements were carried out within a few days after preparation of the solutions of the sodium polyphosphates to exclude the influence of hydrolysis of the polyphosphates [5]. The measurements of the longitudinal relaxation time (T_1) were performed with a 180° – τ – 90° pulse sequence. For a number of cases the transversal relaxation time (T_2) was measured by the standard spin-echo technique and was always found to equal T_1 within experimental error. The accuracy of all T_1 measurements is estimated to be 5%. The relaxation rate measurements were all carried out in 10 mm diameter tubes at one frequency as in all cases $T_1 = T_2$. The frequency for ^{23}Na was 15.87 MHz and for ^{7}Li: 23.31 MHz, while all measurements were carried out at 27°C.

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 ^{23}Na in polyelectrolyte solutions as a function of the degree of neutralization has recently been published [3,4] and this expression will be applied to the results obtained on sodium polyphosphate solutions. From ref. [3] we have:

$$T_1^{-1} = C_{\mathrm{d}} + \frac{1}{30}\left(\epsilon P(1-\gamma_\infty)\frac{eQ}{\hbar}\right)^2 \frac{1}{D}\langle E_{\mathrm{r}}^2\rangle_{\mathrm{r}} \qquad (1)$$

where

ϵ	= dielectric constant of the medium	
P	= polarization factor	0.5 [6]
$1-\gamma_\infty$	= shielding correction	5.8 [7]
e	= electron charge	4.80×10^{-10} e.s.u.
Q	= quadrupole moment	0.15×10^{-24} cm^2 [8]
D	= selfdiffusion coefficient	5×10^{-6} cm^2 s^{-1} [9,10]
$\langle E_{\mathrm{r}}^2\rangle_{\mathrm{r}}$	= 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 [11] at low charge densities ($\lambda < 1$) the contribution of the polyion to the relaxation rate will be less important. 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:

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

where

α = degree of ionization: pH measurements indicated that for $\alpha > 0.15$ the degree of ionization ≈ degree of neutralization at concentrations as used in this study

b = intercharge distance at full neutralization

k = Boltzmann constant

T = absolute temperature.

In polyphosphate solutions we have: $b = 2.6 \times 10^{-8}$ cm [12]; $\lambda = 2.85\,\alpha$ [13].

The counterions which are not condensed 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:

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

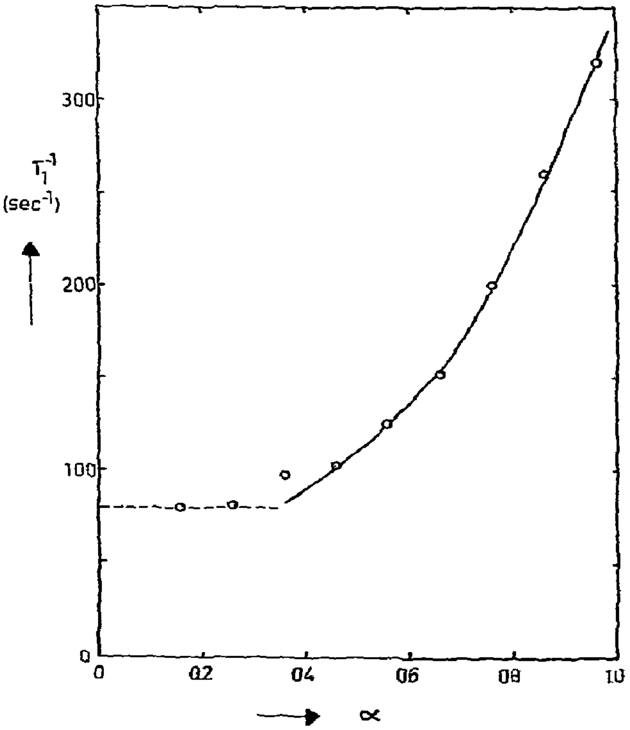

Fig. 1. Spin-lattice relaxation of ^{23}Na in 0.30 monomole ℓ$^{-1}$ polyphosphoric acid (DP ≈ 63) as a function of the degree of neutralization, measured at 27°C. ⊖: Experimental results. – – –: Assumed constant value for the contribution of the water dipoles to the observed relaxation rate. ——: Water contribution plus the ion cloud contribution according to eq. (4).

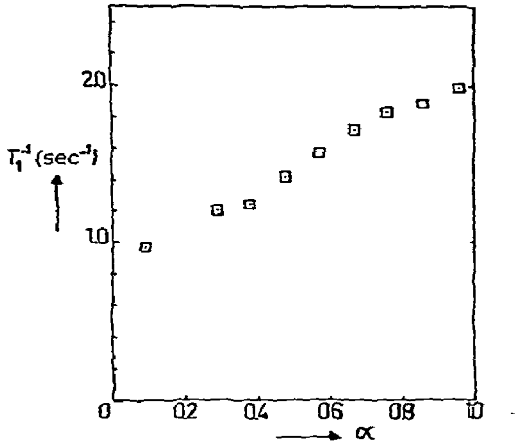

Fig. 2. Relaxation rates of ^{7}Li ions in aqueous polyphosphates solutionns as a function of the degree of neutralization. Concentration polyphosphate: 0.30 monomole/ℓ; DP = 300; measured at 27°C and 23.31 MHz.

Therefore [3]

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

The experimental results and the theoretical line are shown in fig. 1. 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 investigation.

Comparing the structures of polyphosphoric acid, poly(acrylic acid) and poly(stryrenesulphonic 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 [14] and d(PSSA) = 9.2 Å [4,25].

The sodium relaxation rates are 4 to 15 times faster in polyphosphate solutions than in ordinary salt solutions. The lithium relaxation rates were also measured as a function of the degree of neutralization and it appeared that the α dependence is quite different. The rates are completely determined by quadrupolar interaction (this was checked by replacing all protons in the solution by deuterons) and are 15 to 40 times faster than the rates in aqueous LiCl-solutions of the same concentration. The α dependence is less steep and seems linear rather than quadratic as a function of the degree of neutralization, as shown in fig. 2.

This is essentially different from the behaviour of ^{23}Na, both in polyphosphate and in polyacrylate [3] solutions.

This indicates that a different type of interaction, *not accounted for in the model, is involved in the* Li-polyphosphate solutions.

3.1. ^{7}Li and ^{23}Na relaxation in mixtures of LiPP and NaPP

The different interaction of the Li ions with the polyphosphates should show up in the ^{23}Na relaxation rate in mixtures of LiPP and NaPP. If, for example, part of the Li ions are site-bound, be it on a time scale which is short with respect to the reciprocal Larmor frequency involved (as $T_1 = T_2$), the Na relaxation rate should be lowered in comparison with the NaPP solution due to the disappearance of part of the polyion charge.

We have therefore obtained the ^{23}Na and ^{7}Li relaxation rates at 15.87 MHz and 23.31 MHz respectively, in aqueous solutions of polyphosphate. To gain an impression of the K-polyion interaction the experiments were extended to mixtures with KPP, although the K relaxation rate itself could not the measured.

Sodium polyphosphate was treated with the cationic exchanger Amberlite H. The obtained polyphosphoric acid was immediately neutralized to full neutralization ($\alpha = 1$) 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 fig. 3, while the lithium relaxation rates were found to be: $T_1^{-1} = T_2^{-1} = 1.68 \pm 0.08$ s^{-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 [15, 16]. 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 fig. 3.

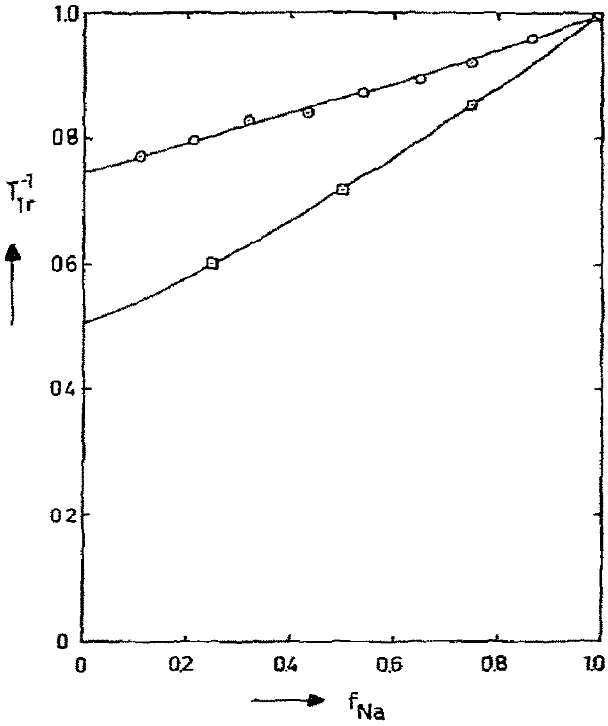

Fig. 3. Relative relaxation rates of ^{23}Na at 27°C and 15.87 MHz in aqueous solutions of polyphosphates (DP = 55) as a function of the fraction Na$^+$ ions. ⊖: Fully neutralized with Na and Li. Polymer conc. = 0.30 monomole ℓ^{-1}. $T_1^{-1}(f_{Na} = 1) = 250$ s^{-1}. ⊟: Fully neutralized with Na and K. Polymer conc. = 0.44 monomole ℓ^{-1}. $T_1^{-1}(f_{Na} = 1) = 321$ s^{-1}.

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 interactions with the field gradient at the site of the nucleus [15,16]. By measuring the lithium relaxation rates in H_2O and D_2O we can discriminate between these two mechanisms 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. We found $T_1(^{7}\mathrm{Li}, H_2O) = T_1(^{7}\mathrm{Li}, \mathrm{HDO})\,(\eta(H_2O)/\eta(\mathrm{HDO}))$, 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 confirmed that the type of interaction of the cations with the polyphosphate chain must be different. Probably 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 through binding of the Li^+ ions. From the intercept at $f_{Na} = 0$ in fig. 3 and the comparison with the decrease of the relaxation rate in fig. 1 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 concluded from fig. 3. 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 0.25 monomole ℓ^{-1}.

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

3.2. Relaxation in mixtures of polyphosphates and simple salt

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. [17] studied this interaction by adding different monovalent salts to polyphosphate solutions and comparing the effects of the alkali ions on viscosity and other physical properties. 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 [18] with the ultrasonic absorption technique. They found a binding sequence of the alkali ions of $TMA < Cs < Rb < K < Li \ll Na$ to the polyphosphates. This seems to be in disagreement with the results of Strauss. Strauss and Leung [19] 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).

We have therefore undertaken an investigation of the counterions relaxation rates in polyphosphate solutions in the presence of salt.

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 behavior 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 [17].

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 [20,21]:

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

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

$$p_B = \frac{\text{conc. Cl}^-}{\text{conc. Na}^+}\,, \qquad p_A = 1 - p_B\,,$$

$T_A^{-1} = T_{1A}^{-1} = T_{2A}^{-1}$ = 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 in very short 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.

Measurements have been carried out for mixtures

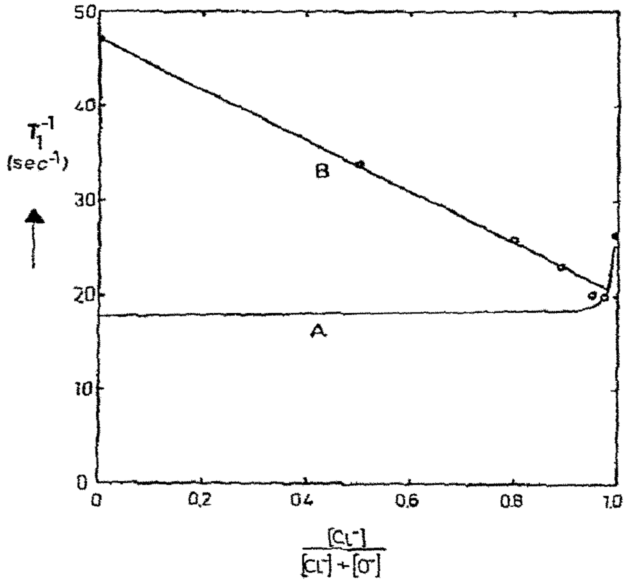

Fig. 4. Spin-lattice relaxation of ^{23}Na in 0.05 eq ℓ^{-1} tripolyphosphate plus variable amount of sodium-chloride, measured at 27°C. ⊙: Experimental values —— A: Na relaxation in the absence of tripolyphosphate. —— B: Theoretical values according to eq. (5).

of sodium tripolyphosphate and sodium chloride and the results are shown in fig. 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 mixture of sodium polyphosphates and sodium chloride. In fig. 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 fig. 5 indicating 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 polyelectrolyte [22], we calculate the line C with formula (5). It is seen that the observed relaxationrates 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. 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 eq. (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.

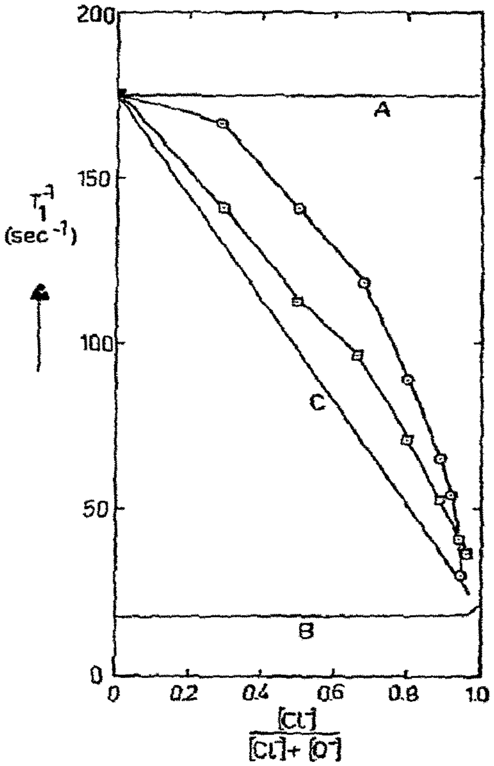

Fig. 5. Spin-lattice relaxation of Na nuclei in mixtures of 0.05 monomole ℓ^{-1} NaPP (⊙: DP = 338; ⊡: DP = 63) with various amount of sodium chloride measured at 27°C.
A —— relaxation of "polyelectrolyte" in absence of salt.
B —— relaxation of "salt" in absence of polyelectrolyte.
C —— relaxation according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

(b) The sodium relaxation in NaCl solutions is almost independent of concentration, if compared to the observed values [22]. 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 [22,23]. So, describing the difference in calculated and observed values entirely as a result of changes in the contribution of the polyions we write 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 ion upon the addition of NaCl. After substracting the estimated constant contribution of the water dipoles (C_d) from the calculated value according to eq. (6) and the "theoretical" value, represented by the line C in fig. 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 fig. 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.

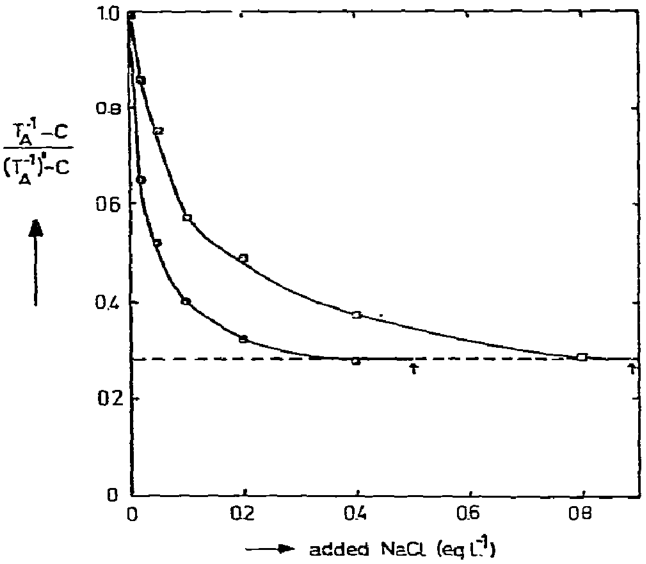

Fig. 6. Ratio of the polyion contribution to the ^{23}Na relaxation rates without and with correction (eqs. (4) and (7)) as a function of the amount of added salt. ⊖: DP = 338; ⊟: DP = 63. —.-— Limiting value at the point of phase separation (↑).

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

The difference in the lines in fig. 6 corresponding to the different DP's is due to the change of the solubility product of the NaPP as a function of DP. From the value of λ in salt free solutions it was seen that 65% of the sodium ions are condensed on the chain [24]. In the precipitated phase just the compensating number of counterions in present, while there are 4–5 water molecules per monomeric unit. This was roughly verified by NMR intensity measurements on the ^{31}P and ^{23}Na nuclei. It will therefore be assumed that at the point of salting out exactly the equivalent number of counterions is associated with the polyion.

In solid sodium polyphosphates values for the distance (a) of the sodium nucleus to the chain are known [12]: $a = 2.3 - 2.5$ 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) $(\lambda - 1)/\lambda \to 1$;

(3) $D \to D'$;

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

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

$(T_A^{-1})'$ 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 eqs. (4) and (7) we can write:

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

Reading a value of 0.28 from fig. 6 a decrease of the selfdiffusion coefficient with 40% is found.

Table 1
^{7}Li relaxation rates in mixtures of LiPP and LiCl at 27°C and 23.31 MHz in aqueous solution

LiPP (DP = 300) pol. conc. (monomole ℓ^{-1})	LiCl salt conc. (eq. ℓ^{-1})	pol. fraction P_p	salt frac. P_a	Li relax. without pol. [a),b),c)]	T_1^{-1} (s^{-1}) obs.	calc. Li relax. of pol. fract. (s^{-1})
0.05	1.50	0.032	0.968	0.060	0.165	3.3
0.05	3.00	0.016	0.984	0.068	0.148	5.1
0.05	4.50	0.011	0.989	0.078	0.152	6.8
0.05	6.00	0.0083	0.9917	0.092	0.181	10.8
0.05	6.75	0.0074	0.9926	0.098	0.179	11.0 [d)]

[a)] Ref. [15].
[b)] Ref. [16].
[c)] Our measurements were in agreement with [a)] and [b)].
[d)] Point of salting out.

On the other hand, assuming $D = D'$, an average distance of the counterions to the polyion chain of $a = 2.1$ Å is calculated. The behaviour of the lithium relaxation rate was also observed in fully neutralized lithium polyphosphate with increasing amounts of lithium chloride until the point of phase separation was reached. The data are shown in table 1.

In all measurements a single exponential decay of the magnetization as a function of time was observed, so exchange between the polyion- and the chloride-"atmosphere" must be fast in relation to the relaxation rates.

In this case, adding LiCl to LiPP, the amount of simple salt that must be added in order to reach the point of phase separation is much higher than in the case of adding NaCl to NaPP at the same polyphosphate concentration.

From the observed relaxation rates and the known concentrations of polyphosphate and chloride the relaxation rates of the lithium ions "in the absence of lithium chloride" can formally be calculated according to eq. (5)

$$T_A^{-1} = \frac{T_1^{-1} - P_B T_B^{-1}}{P_A} \qquad (9)$$

where Na$^+$ should be replaced by Li$^+$ in the definition of P_A, P_B, T_A^{-1} and T_B^{-1}.

The calculated values in table 1 and fig. 7 clearly demonstrate the dependence of T_A^{-1} on the salt concentration. A simple additivity relation with a polyelectrolyte contribution which is independent of the amount of added salt does not hold therefore in this case.

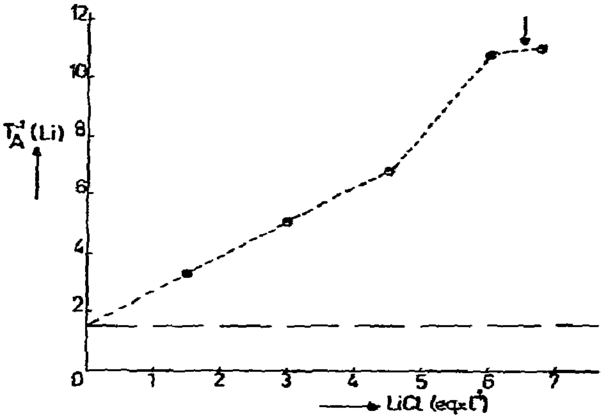

Fig. 7. Calculated polyion contribution to the relaxation rate as a function of the amount of added salt (see also table 1).

At the point of salting out the relaxation rate of the lithium ions "bound" to the polyphosphate chain has increased from about 1.8 s^{-1} to 11.0 s^{-1}. Now a comparison with the previously mentioned lithium measurements can be made. From the decrease of the sodium relaxation rate as shown in fig. 3 the amount of "site-bound" Li-ions was found to be 15%.

If it is assumed that, at the point of salting out, the polyphosphate chain is completely occupied with Li-ions (100% association), we may again calculate the amount of site-bound Li-ions in the saltfree polyphosphate solutions. Taking the fraction of Li-ions bound to the polyphosphate to be proportional to the ^{7}Li-relaxation rate, the constant rate of 1.68 s^{-1} in the saltfree solutions indicates 15% of the Li-ions to be bound. This is therefore in accordance with the conclusion drawn from the ^{23}Na relaxation rate in the

LiPP/NaPP mixtures. These data confirm the difference in the nature of the interaction of lithium and sodium ions respectively with polyphosphate anions in aqueous solutions.

Although the applicability of the ion condensation model should be doubted here, the results in polyphosphate solutions are quite interesting. Upon the addition of NaCl a simple two state model can be used, although the polyion contribution to the relaxation rate is not independent of the amount of added salt.

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