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High-Resolution Solid-State ^{31}P NMR of Alkali Phosphates

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High-resolution solid-state ^{31}P NMR spectra have been measured for inorganic alkali phosphates with different condensations in the PO_4 units, and the isotropic chemical shift and anisotropy have been determined. The isotropic chemical shifts in alkali orthophosphates do not correlate directly with the cation size. The hydration effects have been carefully examined by means of a ^1H decoupling experiment and by the heat treatment of the materials, accompanied by thermogravimetric analysis. Hydration causes an upfield shift in Na_3PO_4, K_3PO_4, and $Na_4P_2O_7$, while it causes a downfield shift in Rb_3PO_4 and Cs_3PO_4. All the five peaks observed in the $K_4P_2O_7$ sample can be ascribed to anhydrous species; this is in contrast to the findings of previous works. The field-dependence experiments definitely demonstrate that the splittings in $K_4P_2O_7$ and $(KPO_3)_n$ are caused by inequivalent sites.

High-resolution solid-state NMR using magic-angle sample spinning (MAS)[1,2] has been used in a variety of fields recently.[3] Inorganic phosphates are constructed of PO_4 units, which are connected with each other by the sharing of their oxygen atoms. The PO_4 condensation can be expected to be identified by using ^{31}P MAS NMR, much as the SiO_4 condensation is identified by means of ^{29}Si MAS NMR.[4]

Several groups have studied ^{31}P MAS NMR in inorganic phosphates. Rothwell et al.[5] have studied some solid calcium phosphates as examples of mineralized tissues. Andrew et al.[6] and later Haubenreisser et al.[7] and Burlinson et al.[8] have studied sodium triphosphate. Grimmer and Haubenreisser[9] have reported the chemical shifts of PO_4 groups in potassium phosphates with different condensations. Duncan and Douglass[10] have studied several condensed phosphates. Mudrakovskii et al.[11] have measured the spectra of various I—IV-group orthophosphates and pyrophosphates. Turner et al.[12] have studied various orthophosphates and have tried to relate the chemical-shift values with some structural parameters. Prabhakar et al.[13] have measured the spectra of some sodium and potassium phosphates. As reviewed above, data on the ^{31}P MAS NMR spectra of alkali phosphates have been accumulated to some extent. However, the observed lines have not been assigned completely, and there remain some controversies in the assignments.

In the present work, we have measured the ^{31}P MAS NMR spectra of inorganic alkali phosphates and have determined the isotropic chemical shift and its anisotropy, being careful to take account of the effect of the hydration on the chemical-shift parameters. Since the aim of this paper is to present reliable data, we have attempted various measurements, such as ^1H dipolar decoupling and magnetic-field dependence, as well as the heat treatment of the materials.

Experimental

Materials. The materials were purchased from Nacalai Tesque, Inc. (Kyoto, Japan), unless otherwise noted. The $K_4P_2O_7$ was also obtained from the Aldrich Chemical Co. (Milwaukee, U. S. A.); the $Na_5P_3O_{10}$, from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and the $Rb_3PO_4 \cdot 4H_2O$ and $Cs_3PO_4 \cdot 2.4H_2O$, from the Soekawa Chemicals Co., Ltd. (Tokyo, Japan). The $Na_5P_3O_{10}$ and $K_5P_3O_{10}$ were also synthesized by heating mixtures of M_2HPO_4 and MH_2PO_4 (M=Na, K) at 550 °C.[14] The contents of water in the hydrated materials were checked by means of thermogravimetric analysis (TG). Their anhydrous samples were prepared by heating the hydrated phosphates at the evolution temperatures determined by TG. Three samples, $Na_6P_4O_{13}$, $(NaPO_3)_6$, and $(NaPO_3)_n$, are amorphous, as checked by powder X-ray diffraction.

NMR Measurements. The NMR spectra were measured mostly by the use of a Bruker MSL400 pulsed spectrometer, whose ^{31}P resonance frequency (ν_0) was 161.98 MHz. A JEOL FX200 pulsed spectrometer (ν_0=80.76 MHz) was also used to check the field dependence of the spectra. The probes were doubly tuned to ^{31}P and ^1H resonances, being capable of MAS (magic-angle sample spinning). The chemical shifts are given with respect to 85% H_3PO_4, with the higher-frequency side (i.e., the downfield side) being expressed as positive.

The ordinary single-pulse sequence was used. Typical measuring conditions were $\pi/4$ for the flip angle of the pulse and 10—20 s for the repetition time. A ^1H dipolar decoupling experiment was always performed to check the effect of the ^1H spins.

Since the ^{31}P nucleus has a large chemical-shift anisotropy in many cases, the isotropic peaks are accompanied by many spinning sidebands, especially in high magnetic fields such as used in this work. The isotropic peaks were identified by changing the spinning rate of the sample. The principal values of the chemical-shift tensor were evaluated from the intensities of the spinning sidebands by using the graphical method proposed by Herzfeld and Berger.[15] Q_n in the text denotes that the PO_4 unit shares n oxygen atoms with other PO_4 units. The accuracy of the isotropic chemical shift is about ±0.2 ppm, while that of the principal values of the shift tensor is about ±5 ppm.

Results and Discussion

Orthophosphates (Q_0). In orthophosphates, the PO_4 units are isolated from each other; they are denoted as Q_0. Some typical ^{31}P MAS NMR spectra

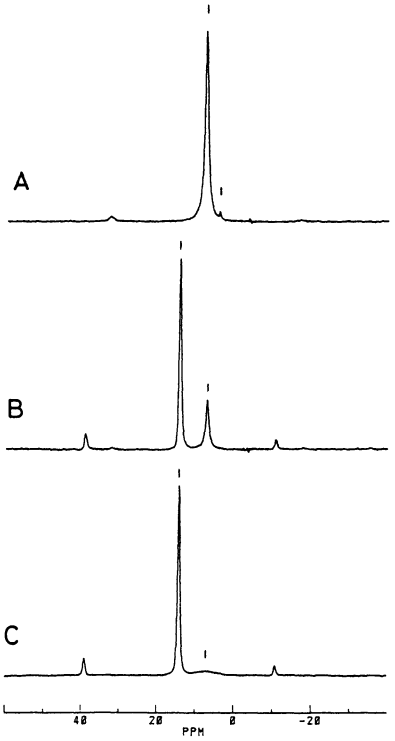

Fig. 1. ^{31}P MAS NMR spectra at ν_0=161.98 MHz of $Na_3PO_4 \cdot 10H_2O$ with ^1H dipolar decoupling (A) and its dehydrated sample with (B) and without (C) decoupling. Bars on top of the peak indicate the isotropic peaks.

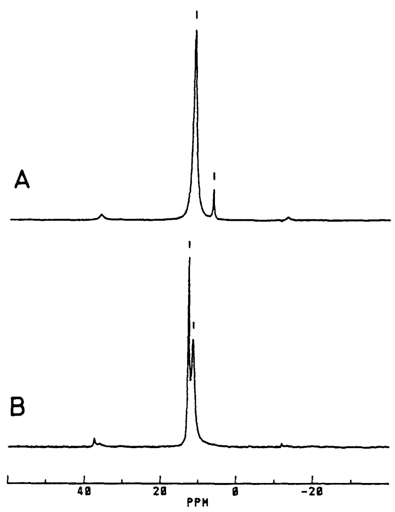

Fig. 2. ^{31}P MAS NMR spectra with ^1H dipolar decoupling of (A) $K_3PO_4 \cdot 3H_2O$ and (B) its dehydrated sample measured at ν_0=161.98 MHz. Bars on top of the peak indicate the isotropic peaks.

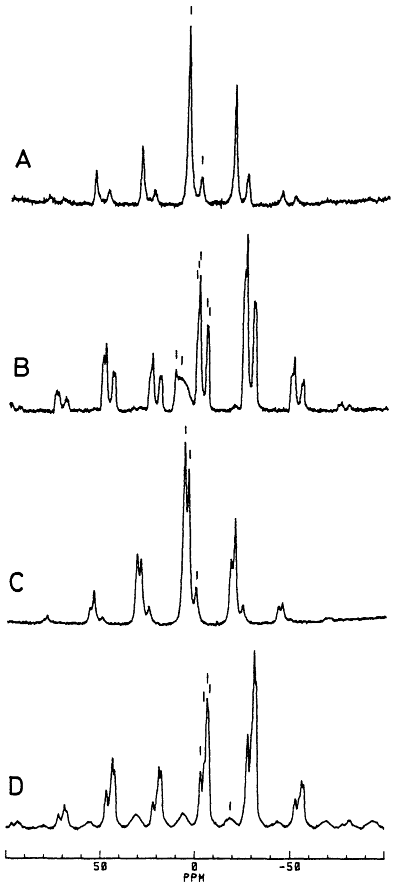

Fig. 3. ^{31}P MAS NMR spectra at ν_0=161.98 MHz of (A) $Rb_3PO_4 \cdot 4H_2O$ with decoupling, (B) its dehydrated sample without decoupling, (C) $Cs_3PO_4 \cdot 2.4H_2O$ with decoupling and (D) its dehydrated sample without decoupling. Bars on top of the peak indicate the isotropic peaks.

of alkali orthophosphates are shown in Figs. 1—3, while the parameters obtained are summarized in Table 1. Impurity peaks are usually omitted from the table if they can be identified. The procedures of the peak assignments will be described below, starting from the lightest cation.

Anhydrous Li_3PO_4 has an isotropic chemical shift of 10.8 ppm, and its tensor is almost isotropic (spectra are not shown).

$Na_3PO_4 \cdot 10H_2O$ has an isotropic chemical shift of 7.7 ppm (Fig. 1A). The thermogravimetric analysis indicates that this sample has the above composition rather than that of $Na_3PO_4 \cdot 12H_2O$ nominated by the supplier. This peak interacts with the ^1H spins in the hydrated water through the dipole-dipole interaction. Another, very small peak is observed at 4.0 ppm; it does not interact with the ^1H spins. This peak disappears after the heat treatment at 210 °C and might be ascribed to much-hydrated species. Heavy hydration is considered to enhance the motion of the PO_4 unit, which can make the time average of the dipole-dipole interaction zero. The sample dehydrated at 210 °C for 0.5 h has isotropic peaks at 14.0 and 6.7 ppm (Fig. 1B). The 14.0 ppm peak is free from the dipolar interaction with the ^1H spins, while the 6.7 ppm peak interacts with the ^1H spins, as is demonstrated in Fig. 1C. The 14.0 ppm peak can be ascribed to anhydrous Na_3PO_4, and the 6.7 ppm peak, to the rehydrated material, $Na_3PO_4 \cdot 10H_2O$.

$K_3PO_4 \cdot 3H_2O$ has an isotropic chemical shift of 11.3

Table 1. Orthophosphates (Q_0)$^{a)}$

Compound	δ_i ppm	δ_1 ppm	δ_2 ppm	δ_3 ppm	$\Delta\delta$ ppm	η	Ref.
Li_3PO_4	10.8	—	—	—	N$^{b)}$	NM$^{c)}$	This work
	10.8	—	—	—	NM	NM	12
	10.0	—	—	—	0	0	11
$Na_3PO_4\cdot 10H_2O$	7.7	—	—	—	N	NM	This work
$Na_3PO_4\cdot 12H_2O$	7.8	—	—	—	NM	NM	12
Na_3PO_4	14.0	—	—	—	N	NM	This work
	13.0	—	—	—	0	0	11
	13.7	—	—	—	NM	NM	13
$K_3PO_4\cdot 3H_2O$	11.3	—	—	—	N	NM	This work
K_3PO_4	12.5	—	—	—	N	NM	This work
	11.7	—	—	—	0	0	9
$Rb_3PO_4\cdot 4H_2O$	5.6	−25	−25	66	91	0	This work
	−1.2$^{d)}$	−49	−27	72	110	0.30	
$Rb_3PO_4$$^{e)}$	0.5 −0.2 −0.9	−41	−41	78	119	0	This work
	−5.2 −5.6	−45	−45	74	119	0	
$Cs_3PO_4\cdot 2.4H_2O$	6.3	—	—	—	NM$^{f)}$	NM	This work
	4.2	—	—	—	NM$^{f)}$	NM	
	−0.1$^{d)}$	−49	−5	54	81	0.81	
$Cs_3PO_4$$^{e)}$	−3.1 −5.1 −6.4 −7.1	−45	−45	71	116	0	This work

a) The following definitions are used; δ_i: isotropic shift, δ_1, δ_2, and δ_3: principal values of the shift tensor, $\Delta\delta$: shift anisotropy, and η: asymmetry factor in the shift tensor.

$$|\delta_3-\delta_i| \geqq |\delta_1-\delta_i| \geqq |\delta_2-\delta_i| \qquad \delta_i=(\delta_1+\delta_2+\delta_3)/3$$

$$\Delta\delta=\delta_3-(\delta_1+\delta_2)/2 \qquad \eta=(\delta_2-\delta_1)/(\delta_3-\delta_i)$$

b) Negative; its absolute value is less than 30 ppm. c) Not measured. d) Anhydrous species. e) Condensed phosphates might be present. f) Overlapping of the signals prevents accurate estimation.

ppm (Fig. 2A) which interacts with the ^{1}H spins. Another, small peak observed at 6.2 ppm might be ascribed to much-hydrated species, since it does not interact with ^{1}H and disappears after heat treatment at 300 °C. The sample dehydrated at 300 °C for 4.5 h has shifts of 12.5 and 11.3 ppm (Fig. 2B). The interaction with the ^{1}H spins is not found in the former peak, which can be ascribed to anhydrous K_3PO_4. On the other hand, the 11.3 ppm peak does interact with the ^{1}H spins and so can be ascribed to $K_3PO_4\cdot 3H_2O$.

The above orthophosphates and their hydrates have little anisotropy (less than 30 ppm). The obtained shift parameters agree very well with some of the literature data, as is shown in Table 1. The presence of the rehydrated species in the dehydrated samples suggests that the anhydrous compounds are easily hydrated to form $Na_3PO_4\cdot 10H_2O$ and $K_3PO_4\cdot 3H_2O$, while such partially hydrated species as $Na_3PO_4\cdot nH_2O$ (n=1—9) and $K_3PO_4\cdot mH_2O$ (m=1,2) are not stable.

The $Rb_3PO_4\cdot 4H_2O$ sample has two isotropic peaks, at 5.6 and −1.2 ppm (Fig. 3A). The former interacts with the ^{1}H spins, whereas the latter does not. This indicates that the 5.6 ppm peak can be ascribed to a hydrated species like $Rb_3PO_4\cdot 4H_2O$ and the −1.2 ppm peak, to anhydrous Rb_3PO_4. The sample dehydrated at 400 °C for 2 h has seven isotropic peaks (Fig. 3B), none of which interact with the ^{1}H spins. The peaks at 0.5, −0.2, −0.9, −5.2, and −5.6 ppm can be ascribed to Rb_3PO_4, and the other small peaks at 11.3 and ca.7 ppm, to impurities. The broad linewidth of the 7 ppm peak suggests that a small amount of the amorphous phase was created by the heat treatment.

The $Cs_3PO_4\cdot 2.4H_2O$ sample has three isotropic peaks (Fig. 3C). The 6.3 and 4.2 ppm peaks interact with the ^{1}H spins and can be ascribed to hydrated species. On the other hand, the −0.1 ppm peak does not interact with the ^{1}H spins and can be ascribed to anhydrous species. The sample dehydrated at 400 °C for 1.3 h has peaks at −3.1, −5.1, −6.4, −7.1, and −19 ppm (Fig. 3D). The peaks other than −19 ppm might be ascribed to Q_0, but the presence of the −19 ppm peak (Q_2) suggests that condensation was encouraged by the heat treatment. The broad linewidth of this peak suggests that an amorphous phase is formed.

In summary, the isotropic chemical shift does not correlate with the cation radius directly in alkali orthophosphates. Hydration causes upfield shifts in Na_3PO_4 and K_3PO_4, while it leads to downfield shifts in Rb_3PO_4 and Cs_3PO_4. The shift tensors are not isotropic in the orthophosphates with larger cation sizes.

The crystal structure of the hydrated compounds has been studied for $Na_3PO_4 \cdot 12H_2O$.[16] Water molecules coordinate to the Na^+ ion, forming octahedra centered on the Na^+ ion. The PO_4^{3-} ion interacts with the Na^+ ion indirectly through the hydrated water. Thus, the chemical shift of the hydrated compound approaches the value of a Na_3PO_4 aqueous solution ranging from 5.4 to 6.0 ppm.[17] Also, in the other hydrated orthophosphates, water molecules are considered to coordinate to the cations, approaching the shift values near to that of an aqueous solution.

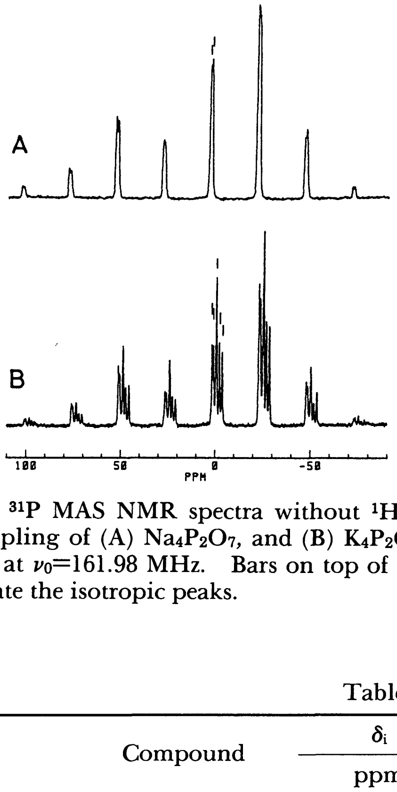

Fig. 4. ^{31}P MAS NMR spectra without ^1H dipolar decoupling of (A) $Na_4P_2O_7$, and (B) $K_4P_2O_7$, measured at ν_0=161.98 MHz. Bars on top of the peak indicate the isotropic peaks.

Pyrophosphates (Q_1-Q_1). Two PO_4 units are connected by sharing one oxygen atom in pyrophosphates. Figure 4 shows the spectra of pyrophosphates; the results are summarized in Table 2.

$Na_4P_2O_7$ has doublet peaks, whose isotropic chemical shifts were 3.0 and 2.2 ppm (Fig. 4A). No splitting was observed at the lower frequency of 80.76 MHz. Thus, the field-dependence measurement failed to elucidate the origin of the splitting. Duncan and Douglass[10] and Prabhakar et al.[13] have reported similar doublets. Duncan and Douglass[10] have interpreted, based on the X-ray diffraction study,[18] that this splitting is caused by inequivalent sites. The magnitudes of the splitting were found to be 1.2 ppm (100 Hz) at 81.015 MHz by Duncan and Douglass,[10] 1.1 ppm (130 Hz) at 121.495 MHz by Prabhakar et al.,[13] and 0.73 ppm (120 Hz) at 161.98 MHz by authors. The ^{31}P-^{31}P scalar coupling in solution is about 20 Hz,[17] much smaller than the observed splitting. Thus, we consider that the interpretation proposed by Duncan and Douglass is most reasonable. In other words, the two Q_1 units in the same Q_1-Q_1 group have different chemical shifts.

$Na_4P_2O_7 \cdot 10H_2O$ shows a similar splitting. The isotropic peaks are observed at −1.4 and −2.3 ppm. The two peaks show interaction with the ^1H spins, and the hydration causes an upfield shift in this compound. Water molecules take part in the sodium coordination, forming octahedra centered on the sodium cation.[19,20] The $P_2O_7^{4-}$ anion interacts with the octahedra through hydrogen bonds. Thus, the chemical shift of the hydrated compound approaches the value of the $Na_4P_2O_7$ aqueous solution (−5.5 to −7 ppm).[17]

On the other hand, five isotropic peaks are observed in $K_4P_2O_7$ (Fig. 4B). Their chemical shifts are 1.4, 0.7, −0.9, −2.5, and −4.0 ppm, and their intensity ratios are approximately 1 : 1 : 2 : 1 : 1. The field-

Table 2. Pyrophosphates (Q_1-Q_1)[a]

Compound	δ_i	δ_1	δ_2	δ_3	$\Delta\delta$	η	Ref.
	ppm	ppm	ppm	ppm	ppm		
$Na_4P_2O_7$	3.0, 2.2	−40	−40	89	129	0	This work
	2.4, 1.2	−37	−37	80	117	0	10
	2.1, 3.2	—	—	—	NM	NM	13
$Na_4P_2O_7 \cdot 10H_2O$	−1.4, −2.3	−38	−38	70	108	0	This work
$K_4P_2O_7$ -I	1.4	−43	−43	89	132	0	This work
	−4.0	−44	−44	77	121	0	
-II	0.7	−43	−43	87	130	0	
	−2.5	−40	−40	73	113	0	
-III	−0.9	−40	−40	78	118	0	
$K_4P_2O_7$	−0.3, −2.2[b] −2.4, −4.9[c]	—	—	—	126	0	9
$K_4P_2O_7$	0.9, 0.0[b] −1.8 −3.3, −4.8[c]	−43	−43	82	125	0	10

a) Symbols have the same meanings as in Table 1. b) Ascribed to $K_4P_2O_7$ according to the reference. c) Ascribed to $K_4P_2O_7 \cdot 3H_2O$ according to the reference.

dependence measurements definitely demonstrate that the five lines can be ascribed to inequivalent sites. The ^{1}H dipolar decoupling has no effect on the spectra, which indicates that no effective hydration takes place. None of the five lines change a position or intensity after heat treatment at 150 °C for 1 h. Therefore, all five lines can be ascribed to inequivalent sites in anhydrous $K_4P_2O_7$.

The sample obtained from Aldrich gives the same results as to the position, but the relative intensities of peaks differ from those in Nacalai's sample. Based on the principle that the intensity ratio of the peaks belonging to the same phase is constant, a detailed examination of the intensities suggests that three phases are mixed in these samples. The first phase has peaks at 1.4 and −4.0 ppm; the second, at 0.7 and −2.5 ppm, and the third, at −0.9 ppm. The Q_1 units in the same Q_1-Q_1 group have different chemical shifts in the first two phases, while they have the same chemical shift in the third phase.

On the other hand, Grimmer and Haubenreisser[9] have observed four lines— at −0.3, −2.2, −2.4, and −4.9 ppm. They tentatively ascribed the former two lines to anhydrous $K_4P_2O_7$, and the latter two, to $K_4P_2O_7 \cdot 3H_2O$. Duncan et al.[10] reported results similar to ours, but they ascribed their lines according to Grimmer and Haubenreisser,[9] except for the −1.8 ppm line. The above two groups gave the average parameters of anisotropy, probably because the lines were not well resolved. On the other hand, we can determine the anisotropy parameters of each line, since the lines are well separated.

Triphosphates (Q_1-Q_2-Q_1). Three PO_4 units are connected linearly in triphosphates. Figure 5 shows the spectra of triphosphates, and Table 3 summarizes the results.

Both the commercial and synthesized $Na_5P_3O_{10}$ samples have two isotropic peaks at 5.1 and −5.6 ppm; their intensities are 2.2 : 1 (Fig. 5A). The 5.1 ppm and the −5.6 ppm peaks can be ascribed to the end-chain (Q_1) and middle-chain (Q_2) PO_4 groups respectively.[6–8] The third sets of peaks, observed at 3.0 and 2.2 ppm, can be ascribed to the $Na_4P_2O_7$ contained as an impurity.

The synthesized $K_5P_3O_{10}$ sample has at least eight isotropic peaks— at 1.4, 0.3, −0.7, −2.7, −3.7, −16.3, −18.7, and −19.8 ppm (Figs. 5B and 5D). The three strong peaks can be ascribed to Q_1 (−0.7 and −3.7 ppm) and Q_2 (−18.7 ppm) in the Q_1-Q_2-Q_1 unit. The remaining, small peaks can be ascribed to other phases.

On the other hand, the commercial sample has at least six isotropic peaks— at 7.6, 6.8, −0.7, −3.5, −5.3, and −18.6 ppm (Figs. 5C and 5E). Upon the use of

Table 3. Triphosphates (Q_1-Q_2-Q_1)[a]

Compound	δ_i	δ_1	δ_2	δ_3	$\Delta\delta$	η	Q_n	Ref.
	ppm	ppm	ppm	ppm	ppm			
$Na_5P_3O_{10}$	5.1	−62	−32	109	156	0.29	Q_1	This work
	−5.6	79	24	−120	−172	0.48	Q_2	
$Na_5P_3O_{10}$	5.6	—	—	—	NM	NM	Q_1	6
	−6.2	—	—	—	NM	NM	Q_2	
$Na_5P_3O_{10}$-I	1.2	—	—	—	140	0.38	Q_1	7
	−8.0	—	—	—	−185	0.36	Q_2	
-II	4.6	—	—	—	159	0.29	Q_1	
	−6.6	—	—	—	−169	0.40	Q_2	
$Na_5P_3O_{10}$-II	4.0	−62	−37	113	163	0.23	Q_1	8
	−5.7	79	22	−118	−169	0.51	Q_2	
$K_5P_3O_{10}$ -I	−0.7	−64	−34	96	145	0.31	Q_1	This work
(Synth.)	−3.7	−70	−38	97	151	0.32	Q_1	
	−18.7	77	14	−147	−193	0.49	Q_2	
-II	1.4	—	—	—	NM	NM	Q_1	
	0.3	—	—	—	NM	NM	Q_1	
	−2.7	—	—	—	NM	NM	Q_1	
	−16.3	—	—	—	NM	NM	Q_2	
	−19.8	—	—	—	NM	NM	Q_2	
$K_5P_3O_{10}$	7.4[b]	−35	−21	77	105	0.20	Q_1	This work
(Commercial)	−0.7	−62	−38	98	148	0.24	Q_1	
	−3.5[c]	−67	−33	90	140	0.36	Q_1	
	−5.3[b]	−71	−17	72	116	0.70	Q_1	
	−18.6	79	13	−147	−193	0.51	Q_2	
$K_5P_3O_{10}$	−1.2 −4.2	—	—	—	146	0	Q_1	9
	−19.4	—	—	—	−191	0.38	Q_2	
$K_5P_3O_{10}$	−1.2	−55	−55	106	161	0	Q_1	10
	−4.0	−51	−51	90	141	0	Q_1	
	−19.5	75	16	−148	−194	0.46	Q_2	

a) Symbols have the same meanings as in Table 1. b) This peak might be ascribed to an impurity. c) This peak might be partly ascribed to an impurity.

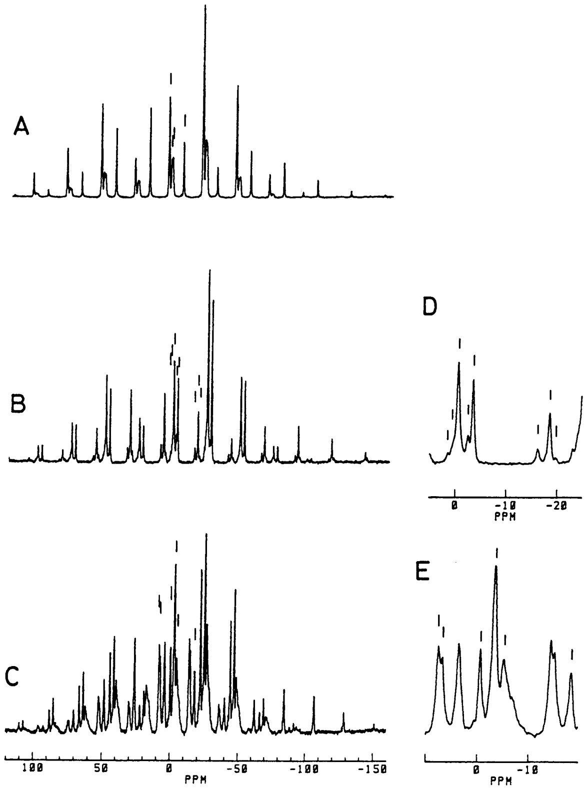

Fig. 5. ^{31}P MAS NMR spectra without ^{1}H dipolar decoupling of (A) $Na_5P_3O_{10}$ (commercial) (B) $K_5P_3O_{10}$ (synthesized), and (C) $K_5P_3O_{10}$ (commercial) measured at ν_0=161.98 MHz. (D) and (E) are expanded plots of the isotropic region of (B) and (C) respectively. Bars on top of the peak indicate the isotropic peaks.

^{1}H dipolar decoupling, the two peaks at 7.6 and 6.8 ppm collapse into one line, at 7.4 ppm, suggesting that the lines are split by the interaction with the ^{1}H spins. The field-dependence measurements demonstrate that the five peaks at 7.4, −0.7, −3.5, −5.3, and −18.6 ppm can be ascribed to inequivalent sites. The magnitudes and signs of the anisotropy suggest that the −18.6 ppm peak can be ascribed to Q_2, and the others, to Q_1. Heat treatment at 200 °C increased the intensities of the 7.4, −3.5, and −5.3 ppm peaks, while the others decreased relatively. This fact and the results on the synthesized sample lead to the following assignments. The −0.7, −3.5, and −18.6 ppm peaks are attributed to the triphosphate anion (Q_1-Q_2-Q_1). The two peaks at −3.5 and −5.3 ppm can be ascribed to Q_1 in the diphosphate anion (Q_1-Q_1), contained as an impurity. The −3.5 ppm peak consists of two components; thus, its intensity is strongest. However, the assignment of the 7.4 ppm peak is still ambiguous.

On the other hand, Grimmer and Haubenreisser[9] have reported the presence of three lines— at −1.2, −4.2, and −19.4 ppm. Duncan and Douglass[10] have reported similar results.

Tetraphosphates (Q_1-Q_2-Q_2-Q_1). Four PO_4 units are linearly linked in tetraphosphates. $Na_6P_4O_{13}$ has two isotropic signals, at 1.5 and −16.4 ppm (Fig. 6A and Table 4), which can be ascribed to Q_1 and Q_2 respectively. The X-ray diffraction results demonstrate that this sample is amorphous. Thus, the broad linewidth is produced by chemical-shift dispersion due to the disorderness in the amorphous material.

Metaphosphates (-Q_2-). In metaphosphates, many PO_4 units are linked by sharing two of the four oxygen atoms to form rings and chains. The spectra of the metaphosphates are shown in Fig. 6, while the shift parameters are summarized in Table 4.

$(NaPO_3)_n$ has an isotropic chemical shift of −19.9 ppm (Fig. 6B); it can be ascribed to the middle-chain PO_4 group (Q_2). A small peak was also observed at −6.2 ppm; it can be ascribed to the end-chain PO_4 group (Q_1). The linewidths are broad because of the amorphousness. Since the chemical-shift dispersion, which is the origin of the linewidth for this sample, is proportional to the static magnetic field (in Hz unit), lower-field measurements are useful in reducing the linewidth if the spinning rate of the sample is constant. The measurements at ν_0=80.76 MHz reveal the presence of the third, small components at about 1 ppm; they might be Q_1. The $(NaPO_3)_6$ sample shows similar results, as is shown in Table 4.

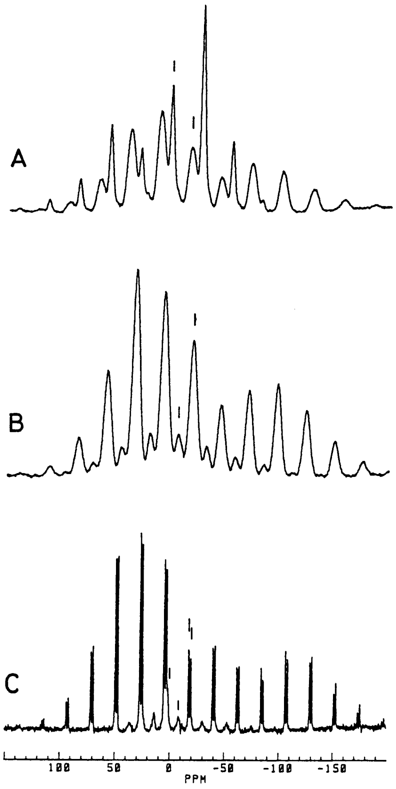

Fig. 6. ^{31}P MAS NMR spectra of (A) $Na_6P_4O_{13}$ and (B) $(NaPO_3)_n$ without ^{1}H dipolar decoupling and (C) $(KPO_3)_n$ with ^{1}H decoupling, measured at ν_0=161.98 MHz. Bars on top of the peak indicate the isotropic peaks.

Table 4. Tetraphosphates (Q_1-Q_2-Q_2-Q_1) and Metaphosphates (-Q_2-)[a)]

Compound	δ_i ppm	δ_1 ppm	δ_2 ppm	δ_3 ppm	$\Delta\delta$ ppm	η	Q_n	Ref.
$Na_6P_4O_{13}$	1.5	−47	−47	98	145	0	Q_1	This work
	−16.4	85	18	−152	−204	0.49	Q_2	
$(NaPO_3)_n$	1	—	—	—	NM	NM	Q_1	This work
	−6.2	—	—	—	NM	NM	Q_1	
	−19.9	85	20	−165	−218	0.45	Q_2	
$(NaPO_3)_6$	−6	—	—	—	NM	NM	Q_1	This work
	−19.6	87	19	−165	−218	0.47	Q_2	
$(NaPO_3)_n$	2	−45	−45	95	140	0	Q_1	10
	−19	90	13	−160	−212	0.55	Q_2	
$(NaPO_3)_n$	−15.6, −18.5 −19.9, −24.1 −26.8	—	—	—	NM	NM	Q_2	13
$(KPO_3)_n$	−17.9	88	33	−174	−235	0.35	Q_2	This work
	−19.8	88	34	−181	−242	0.33	Q_2	
$(KPO_3)_n$	−18.5, −20.7	—	—	—	−237	0.34	Q_2	9
$(KPO_3)_n$	−17.8, −19.8	—	—	—	NM	NM	Q_2	13

a) Symbols have the same meanings as in Table 1.

Duncan and Douglass[10)] have reported results similar to ours. Prabhakar et al.[13)] have reported five resonance lines— at −15.6, −18.5, −19.9, −24.1, and −26.8 ppm for $(NaPO_3)_n$. The lines were all ascribed to Q_2. Their sample is considered to be crystalline, in contrast to Duncan and Douglass's sample and to ours.

$(KPO_3)_n$ has two isotropic peaks, at −17.9 and −19.8 ppm (Fig. 6C), ascribed to the middle-chain (Q_2) group. The field-dependence experiments demonstrate that these two peaks are produced by two inequivalent sites. The X-ray diffraction study[21)] supports the presence of two inequivalent sites. Grimmer and Haubenreisser[9)] have reported the values of −18.5 and −20.7 ppm, while Prabhakar et al.[13)] have reported the values of −17.8 and −19.8 ppm. Some other peaks were observed which can be ascribed to impurities. The peak at 4.1 ppm interacts with the ^{1}H spins and vanishes after the sample has been heated at 260 °C; it can be ascribed to hydrated species. Three peaks developed in the course of the experiment— at 0.8, −10.4, and −22.6 ppm. They have negligible anisotropy and no interaction with the ^{1}H spins. Heat treatments of the sample could not reduce the intensities of these peaks. From the above observations, they can be ascribed to decomposed species formed by hydrolysis. By analogy with the solution data,[17)] the 0.8 ppm peak can be ascribed to Q_0; the −10.4 ppm peak, to Q_1, and the −22.6 ppm peak, to Q_2.

Summary

The ^{31}P chemical shift and its anisotropy in each Q_n species have been discussed previously.[6−13)] The present work generally confirms the previous results. An upfield shift in Q_n is observed as n increases. The Q_0 group in M_3PO_4 usually has an isotropic shift-tensor. On the other hand, the Q_1 group usually has an axially-symmetric tensor or an asymmetric factor lower than 0.3. The Q_2 group has a non-axially symmetric tensor with asymmetric factors between 0.3 and 0.6. The magnitudes of the anisotropy, $|\Delta\delta|$, are 100—160 and 170—240 ppm for the Q_1 and Q_2 respectively, while the signs of $\Delta\delta$ are opposite for the two groups.

In the present work, new data on the orthophosphates of Rb and Cs are presented. These orthophosphates have considerably greater magnitudes of anisotropy than the other orthophosphates. Although the data from Li to Cs have been collected, the isotropic chemical shift does not correlate directly with the cation size.

The hydration effects have been carefully examined by means of the ^{1}H decoupling experiment and heat treatment of the materials, accompanied by thermogravimetric analysis. The coexistence of Na_3PO_4 and $Na_3PO_4{\cdot}10H_2O$ demonstrates that the stable hydrate contains 10 H_2O in a quantity not less than 10. Similar phenomena are observed in K_3PO_4 and its hydrate, $K_3PO_4 \cdot 3H_2O$. Hydration causes upfield shifts in Na_3PO_4, K_3PO_4, and $Na_4P_2O_7$, while it causes downfield shifts in Rb_3PO_4 and Cs_3PO_4. Although previous works[9,10)] have suggested that two peaks in the spectra of $K_4P_2O_7$ are attributable to its hydrate, our experiment demonstrates that all five peaks can be ascribed to anhydrous $K_4P_2O_7$. In the hydrated compounds, water molecules coordinate to alkali cations, and the phosphate anions interact with the cations indirectly through the water molecules. This situation is similar to that in an aqueous solution; thus, the chemical shifts of the hydrated compounds approach the values in the aqueous solution.

The field-dependence experiment can clearly demonstrate whether the splitting is caused by inequivalent sites or by spin-spin coupling. The splittings in $K_4P_2O_7$ and $(KPO_3)_n$ are caused by inequivalent sites. The doublets in $Na_4P_2O_7$ and its hydrate are also considered to be caused by inequivalent sites, but no experimental evidence was obtained.

Finally, the present work has revealed that some materials contain coexisting phases and/or impurities. The ^1H decoupling experiment, the field-dependence measurements, and the heat treatment of the material can help very much in the confirmation of the impurity, as is demonstrated by the complicated spectra of commercial $K_5P_3O_{10}$.

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