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NMR STUDIES ON THE COMPLEXATION OF ALUMINIUM ION WITH INORGANIC LIGANDS IN CROSSLINKED POLYSACCHARIDE GEL

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Abstract—Complexation equilibria of aluminium ion with phosphinate, thiocyanate and sulphate anions in uncharged polysaccharide gels with different degrees of crosslinking have been investigated by using ^{27}Al NMR spectroscopy. Stability constants of these 1 : 1 complexes in the gel phase were compared with those in an aqueous solution. The constants for Al^{3+}–$PH_2O_2^-$ and –SO_4^{2-} systems increased in the order: aqueous solution < Sephadex G-15 < Sephadex G-10. The enhancement in the stability was larger for the Al^{3+}–SO_4^{2-} system. On the other hand, the order for $AlSCN^{2+}$ was reversed. These results are interpreted in terms of a low dielectric constant in the gel phase and a "hydrophobic interaction" between the anions and the gel matrix.

Gel chromatographic separations of various inorganic compounds using Sephadex gels have been carried out by several workers.[1–3] Gregorio *et al.*[4] and Deguchi *et al.*[5] demonstrated that simple inorganic anions such as iodide, perchlorate and thiocyanate ions are adsorbed onto the Sephadex gel. They suggested that the adsorption of these anions can be attributed to a certain interaction (so-called "hydrophobic interaction") between the anions and the gel matrix. The adsorption occurs reversibly and reaches equilibrium in a relatively short time. Some chromatographic application of this phenomenon was also achieved. Yoshimura *et al.*[6] have separated successive complexes of chromium(III) with thiocyanate using Sephadex gels. The chromium(III)–thiocyanate complexes have different affinities with the gel matrix. Kura *et al.*[7] have separated Zn^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+} in the thiocyanate media using Sephadex G-15 gel as a kind of anion exchanger in the thiocyanate form. The distribution coefficients of these metal ions must depend upon the complexibility in the gel phase.

Concerning the chemical reactivity of ions, the gel internal phase can be regarded as a heterogeneous polysaccharide solution. The knowledge on the complexation in the gel phase must be important in both applied and academic research. However, little information is available on the complexation of ions sorbed into the gel. We have been studying the complexation equilibria in crosslinked polymer gels by using spectroscopic techniques such as electronic[8] and NMR spectroscopies.[9,10] In particular, NMR is an effective method for analyses of complexation equilibria in the heterogeneous media. In a previous paper,[10] we reported the study on protonation equilibria of oxoanions within Sephadex gels. The protonation constants in the gel phases were always larger than those in the corresponding aqueous solution and became larger in accordance with an increase in the degree of crosslinking.

In this study, we have investigated the complexation of aluminium ion with simple inorganic ligands, such as phosphinate (hypophosphite), thiocyanate and sulphate anions, in the uncharged polysaccharide gels by using ^{27}Al NMR spectroscopy. It was found that the complexibility in the gel phase is different from that in the corresponding aqueous solution. Stabilities of the complexes in each medium depend upon the hydration ability of the ligands.

EXPERIMENTAL

Chemicals

All chemicals were of commercially available reagent grade and used without purification. Deionized and distilled water was used throughout. Uncharged polysaccharide gels with different degrees of crosslinking, Sephadex G-10 and G-15 (Pharmacia, Uppsala, Sweden) were used.

Samples for NMR measurements

A 5 mmol dm^{-3} $Al(NO_3)_3$ solution containing 8 mmol dm^{-3} $NaPH_2O_2$ [pH 1.1–1.5, $I = 0.1$ ($NaNO_3$)], 0.5 mol dm^{-3} NaSCN (pH 2.5), or 0.5 mol dm^{-3} Na_2SO_4 (pH 2.0) was prepared. The pH of the solution was adjusted to a value of pH 1.1–2.5 with a small amount of HNO_3 solution in order to avoid the formation of aluminium hydroxo complexes. An appropriate amount of Sephadex gel (e.g. 1.2 g for G-10 and 1.0 g for G-15) was equilibrated with 20 cm^3 of the solution in a stoppered test tube at room temperature for 3–6 h. The gel beads immersed in the solution were packed into a 10 mm I.D. NMR sample tube with a small amount of equilibrium solution and allowed to settle to a height of *ca* 4.5 cm.

NMR measurements

The NMR spectra were recorded on a JEOL JNM-GX 400 spectrometer with a 10 mm multinuclear probe at temperature of 22.5(±1)°C. ^{31}P NMR spectra were recorded at 161.9 MHz. Standard NMR parameters were as follows: a flip angle of *ca* 90° (20.0 μs), pulse repetition time 3 s and spectral width *ca* 6500 Hz. The chemical shifts were reported with respect to 85% H_3PO_4 as an external reference. ^{27}Al NMR spectra were recorded at 104.2 MHz. The NMR parameters were typically: flip angle *ca* 70° (20.0 μs), pulse repetition time 0.66 s and spectral width 25,000 Hz. The chemical shifts were reported with respect to 0.1 mol dm^{-3} $Al(NO_3)_3$ solution containing 0.1 mol dm^{-3} HNO_3 as an external reference. NMR spectra for the gel phase were recorded in the same way as described in a previous work.[10]

Determination of ionic concentrations in a gel phase

A Sephadex gel bed was simply divided into three regions: the gel internal solution, the gel skeleton and the interstitial solution. In the previous work, the volume fractions of these regions in an NMR sample tube were evaluated by using ^{31}P and ^{17}O NMR signal intensities (Table 1 in Ref. 10). These values were also utilized in this study to analyse complexation equilibria in the gel phase. The net volume of the gel phase, which was taken as the volume of the gel internal solution, was calculated from the bed volume and the volume fraction of the gel internal solution. The concentration of the species in the gel phase was expressed in mol dm^{-3}, as in the ordinary expression for a solution.

The concentration of $PH_2O_2^-$ in the Sephadex gel phase was estimated from the concentration in the equilibrium solution, ^{31}P NMR signal intensities of the species in the bed, and the volume fractions.[9] Corrections were made for a protonation of the anion in the gel phase using protonation constants reported in a previous work.[10] Concentrations of SCN^- and SO_4^{2-} in the Sephadex gel phase were determined by column operations. The gel beads were packed into a column and equilibrated with 0.5 mol dm^{-3} NaSCN or 0.5 mol dm^{-3} Na_2SO_4 solution. Then, the anion in the gel bed was eluted with water and the total amount of the species in the effluent was determined. In order to estimate the net amount in the gel phase, the contribution of the anion from the interstitial solution to the obtained value was eliminated using the concentration in the external solution and the volume of the interstitial solution, where the volume was calculated from the apparent bed volume and the volume fraction of the interstitial solution. The concentration of the anion in the gel phase was evaluated from the net amount and the volume of the gel internal solution.

RESULTS AND DISCUSSION

Concentration of ligand in the gel phase

^{31}P NMR spectrum for the Sephadex G-10 bed with a solution [$I = 0.1$ ($NaNO_3$), pH 1.4] containing 5 mmol dm^{-3} $Al(NO_3)_3$ and 8 mmol dm^{-3} $NaPH_2O_2$ is shown in Fig. 1. Three sets of triplet signals were observed separately. Assignment of the signals was made using the changes of respective peak intensities that occurred with changes of the interstitial solution of the gel bed. The lowest field triplet signal (a) was assigned to the free and protonated phosphinate in the gel phase, the second lowest one (b) to the species in the interstitial solution, and the highest one (c) to $AlPH_2O_2^{2+}$ in both the gel phase and the interstitial solution. The signal intensities of peaks (a) and (b) were used for determination of the concentration of $PH_2O_2^-$ in the gel phase.

The concentrations of SCN^- and SO_4^{2-} in the

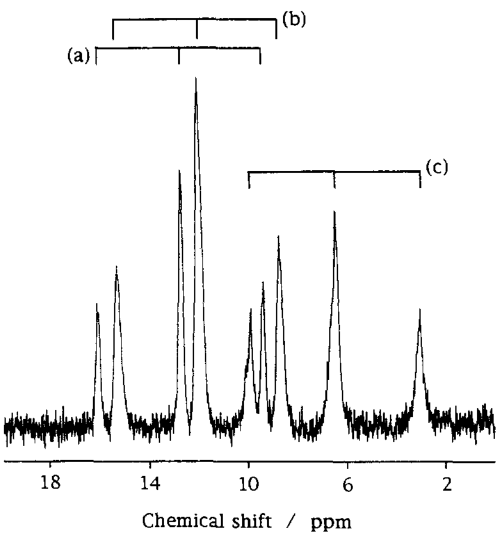

Fig. 1. ^{31}P NMR spectrum for the Sephadex G-10 bed with a solution [$I = 0.1$ ($NaNO_3$), pH 1.4] containing 5 mmol dm^{-3} $Al(NO_3)_3$ and 8 mmol dm^{-3} $NaPH_2O_2$. (a) HPH_2O_2 and $PH_2O_2^-$ in the gel phase, (b) HPH_2O_2 and $PH_2O_2^-$ in the external solution and (c) $AlPH_2O_2^{2+}$ in the bed.

Sephadex gel phase were determined by the column operations (see Experimental).

The ratios of the anion concentration in the gel phase to that in the external solution ($[\bar{L}]/[L]$) are summarized in Table 1. The affinity of these anions for the gel phase increases in the order: $SO_4^{2-} < PH_2O_2^- < SCN^-$. This order is in good agreement with literature data.[4–6] The more hydrophobic the anion, the more strongly adsorbed onto the gel phase, mainly because of hydrophobic interactions between the anion and the gel matrix. On the other hand, the more hydrophilic the anion, the more readily it is excluded from the gel phase.

It was found that the Sephadex G-10 has a maximum of 5.6 μeq g^{-1} ionic groups. Such a concentration of the impurity ionic groups would not lead to any significant errors for equilibrium analyses in the gel phase, and Donnan equilibria driven by the ionic groups were ignored at the ionic strengths investigated.

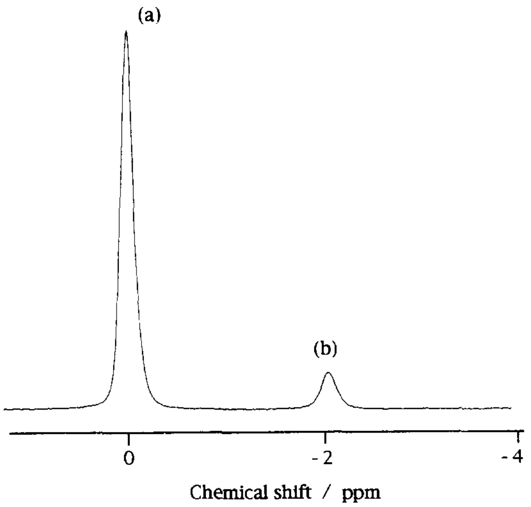

Fig. 2. ^{27}Al NMR spectrum for the Sephadex G-10 bed with a solution [$I = 0.1$ ($NaNO_3$), pH 1.4] containing 5 mmol dm^{-3} $Al(NO_3)_3$ and 8 mmol dm^{-3} $NaPH_2O_2$. (a) Al^{3+} and (b) $AlPH_2O_2^{2+}$ in the bed.

^{27}Al *NMR spectrum for the Sephadex gel bed*

^{27}Al NMR spectrum for a Sephadex G-10 bed with a solution [$I = 0.1$ ($NaNO_3$), pH 1.4] containing 5 mmol dm^{-3} $Al(NO_3)_3$ and 8 mmol dm^{-3} $NaPH_2O_2$ is shown in Fig. 2. The 1 : 1 complex was only formed under this condition. Since the ligand exchange rate of the complex is sufficiently low relative to the NMR time-scale, the NMR signals were observed independently for different species. The signals at 0 and -2.1 ppm were assigned to Al^{3+} and $AlPH_2O_2^{2+}$, respectively. The spectrum for the gel bed contained signals for both the gel phase and the interstitial solution, and the signals were not observed separately for each phase. Therefore, the net NMR spectrum for the gel phase was obtained by subtracting the spectrum for the interstitial solution from that for the gel bed.

Furthermore, ^{27}Al NMR spectrum for the gel bed with a 5 mmol dm^{-3} $Al(NO_3)_3$ solution containing 0.5 mol dm^{-3} NaSCN or 0.5 mol dm^{-3} Na_2SO_4 was recorded (spectra not shown). The signals of $AlSCN^{2+}$ and $AlSO_4^+$ appeared at -4.7 and -3.1 ppm for each spectrum besides the signal of Al^{3+}.

Table 1. The ratio of anion concentration in the Sephadex gel phase to that in the external solution

Sephadex	$[\overline{PH_2O_2^-}]/[PH_2O_2^-]$	$[\overline{SCN^-}]/[SCN^-]$	$[\overline{SO_4^{2-}}]/[SO_4^{2-}]$
G-10	0.684	1.96	0.446
G-15	1.01	1.84	0.557

The net NMR spectra for the gel phase were obtained in the same procedure for the Al^{3+}–$PH_2O_2^-$ system.

Stability constants of aluminium complexes in the gel phase

For the purpose of comparing complexibilities in a Sephadex gel phase and in an aqueous solution, the stability constants of $AlPH_2O_2^{2+}$, $AlSCN^{2+}$ and $AlSO_4^+$ complexes in the gel phase were evaluated from the net ^{27}Al NMR signal intensities and the free ligand concentrations. The constants of these complexes in aqueous solutions, in which the total concentrations of each ionic species were equal to those in the gel phase, were also determined by ^{27}Al NMR. Stability constants obtained are given in Table 2. The stability constants in the gel phase are different from those in the corresponding aqueous solution, and the order of the stabilities in each medium differs among these complex systems.

For Al^{3+}–$PH_2O_2^-$ and Al^{3+}–SO_4^{2-} systems, stabilities of 1 : 1 complexes increased in the order: aqueous solution < Sephadex G-15 < Sephadex G-10. The higher complexibility in the gel phase would be attributed to a low dielectric constant due to the presence of polysaccharide skeleton. Ishikawa *et al.*[11] reported the dielectric constant in a Sephadex G-25 gel to be 67. The stability constant in the gel phase increased with an increase in the degree of crosslinking, namely, with a decrease in the dielectric constant. The enhancement in the complexibility is notable for the system with multivalent ions, that is, for the Al^{3+}–SO_4^{2-} system.

Table 2. Stability constants of 1:1 aluminium complexes in the Sephadex gel phase and the corresponding aqueous solution

Medium	$AlPH_2O_2^{2+}$	$AlSCN^{2+}$	$AlSO_4^+$
Sephadex G-10	2.8×10^2	0.08	0.63
Sephadex G-15	2.2×10^2	0.19	0.44
Solution	1.7×10^2	0.47	0.22

Metal–thiocyanate complexes are adsorbed onto Sephadex gels.[6,7] However, the phenomena can never mean the higher stability of the complex in the gel phase compared with that in the equilibrium solution. The stability of $AlSCN^{2+}$ decreased in the order: aqueous solution > Sephadex G-15 > Sephadex G-10. The lower complexibility in the gel phase may be ascribed to a hydrophobic interaction between SCN^- and the gel matrix, the interaction which weakens the activity of the anion. The higher the degree of crosslinking, the stronger the hydrophobic interaction: thus the complexation decreases.

Above all, the polysaccharide gel has complexation inhibiting and enhancing effects that depend upon the hydration ability of the ligand.

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REFERENCES

1. S. Ohashi, N. Yoza and Y. Ueno, *J. Chromatogr.* 1966, **24**, 300.
2. P. A. Neddermeyer and L. B. Rogers, *Anal. Chem.* 1969, **41**, 94.
3. K. Ujimoto, I. Ando, T. Yoshimura, K. Suzuki and H. Kurihara, *J. Chromatogr.* 1980, **190**, 161.
4. V. D. Gregorioi and M. Sinibaldi, *J. Chromatogr.* 1976, **129**, 407.
5. T. Deguchi, A. Hisanaga and H. Nagai, *J. Chromatogr.* 1977, **133**, 173.
6. K. Yoshimura and T. Tarutani, *J. Chromatogr.* 1982, **237**, 89.
7. G. Kura, A. Koyama and T. Tarutani, *J. Chromatogr.* 1977, **144**, 245.
8. H. Waki and Y. Miyazaki, *Polyhedron* 1989, **8**, 859.
9. Y. Miyazaki and H. Waki, *Polyhedron* 1992, **11**, 3031.
10. Y. Miyazaki and H. Waki, *J. Chem. Soc., Faraday Trans.* 1993, **89**, 3925.
11. A. Ishikawa, T. Hanai and N. Koizumi, *Bull. Inst. Chem. Res.* 1984, **62**, 251.