EFFECT OF CALCIUM, SODIUM AND CHLORIDE IONS ON THE GROWTH OF IMOGOLITE TUBES AS MEASUED BY GEL FORMING PROPERTY

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ABSTRACT

To examine the effect of coexisting salts on the yield and gel forming property of synthetic imogolite, neutralized solutions of $Si(OH)_4$ and $AlCl_3$ with added NaCl and $CaCl_2$ were heated at 96°C. X-ray diffraction (XRD) on the freeze-dried products showed that the yield of imogolite decreased as the salt concentration increased. The gel volume determined by alkalinization and centrifugation of the heated sols approximately paralleled the intensity of imogolite peaks in XRD. The examination of the relationship between the ion concentrations and the gel volume showed that the gel forming property was solely determined by the chloride ion concentration and the accompanying cations had little effect under the present experimental conditions.

Key words: Gel, Imogolite, Synthesis

INTRODUCTION

Gel and sheet forming properties of imogolite suggest that it has a wide range of applicability as discussed by Farmer et al. (1983). In addition, imogolite is gaining increasing attention as a material for shape-selective catalysts (Imamura et al., 1996) and inorganic liquid crystal (Sonin, 1998).

Imogolite can be synthesized fairly easily by heating partially neutralized dilute solutions of monosilicic acid and aluminum salts (Wada et al., 1979) but increasing concentration of the starting solution leads to a serious decrease in its yield (Farmer and Fraser, 1978). Syntheses of imogolite from various inorganic and organic Al and Si compounds showed that the type and concentration of coexisting anion are critical factors affecting the development of imogolite structure. In general, an anion forming more stable complex with aluminum ion is more detrimental to the imogolite formation (Farmer and Fraser, 1978).

Farmer and Fraser (1978) achieved the higher imogolite yield using tetraethoxysilane and aluminum-s-butoxide and perchloric acid as starting materials. Other methods using inorganic Si and Al sources are still needed to supply imogolite at low cost. Before starting synthetic experiments for new efficient methods, it seems needed to have information about the effect of coexisting cations on the growth of imogolite because it is important to select

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the source of Si and the type of alkali for neutralization. Henmi and Matsue (1998) examined the effect of coexisting alkali and alkaline earth metal cations on the imogolite formation and reported that the products from Ca- and Mg-system gave a weaker X-ray diffraction (XRD) peak at about 2 nm than those from Na- and K-system. They concluded that the presence of the divalent cations is unfavorable for the development of tubular structural units of imogolite. Since the XRD peak arises from the bundles of the structural units, it does not necessarily parallel the gel forming property, which is important in some industrial applications (Farmer et al., 1983).

In the present study a series of syntheses were carried out following Henmi and Matsue (1998) and the products were characterized by gel volume measurement as well as by X-ray diffraction.

MATERIALS AND METHODS

A stock monosilicic acid solution was prepared by passing a 2 mmol L^{-1} Na_4SiO_4 solution through a column of H-saturated cation exchange resin. The Si concentration of the obtained solution was 1.90 mmol L^{-1}.

In a 2 L volumetric flask, 1.4 L of the monosilicic acid solution and 48 mL of a 0.1 mol L^{-1} $AlCl_3$ solution were placed and diluted with distilled water to the volume. To this solution, 107.52 mL of 0.1072 mol L^{-1} NaOH was added at a rate of 0.25 mL min^{-1}. The NaOH was delivered by a peristaltic pump through a Tygon® tube inserted into the solution and the solution was stirred vigorously by a magnetic stirrer. The final Si and Al concentrations of the prepared starting sol were 1.26 mmol L^{-1} and 2.28 mmol L^{-1}, respectively, and the degree of neutralization, OH/Al molar ratio, was 2.40.

To examine the effect of coexisting cation species, 45 mL portions of the starting sol were placed in 50-mL glass centrifuge tubes, each of NaCl and $CaCl_2$ was added at several different levels, and heated at 96°C with reflux condensers in an aluminum-block heater. Major ion concentrations of the salt-added solution are listed in Table 1. After heating for 120 h, the solutions were cooled down to the room temperature. An appropriate amount of each heated sol was diluted with distilled water to give the total Al concentration of 2 mmol L^{-1}. Ten mL portion of the diluted sol was placed in a graduated centrifuge tube, mixed with 1 mL of a 1.4 mol L^{-1} ammonium water, and centrifuged for 10 min at 2000 rpm. The volume of the settled gel was read and recorded. To assist identification of the gel-solution boundary, a small amount of chromatographic silica powder was put in the tube to cover the surface of the gel bed.

The remaining sols were dialyzed against distilled water until the AgCl reaction in the dialyzate became negative. A drop from each sol was dried on a microgrid and examined in an electron microscope and the remaining sols were freeze-dried. X-ray diffractograms were recorded on the dried products packed in glass holders.

To check the reproducibility, another series of synthetic experiments were carried out with addition of NaCl, KCl, $MgCl_2$ and $CaCl_2$ and the gel volume was measured in a similar way.

RESULTS AND DISCUSSION

The starting sol remained clear with no visible precipitate during NaOH addition and the final pH was 4.5. The addition of the salts did not affect the pH of the sol.

Addition of salt and heating did not affect the appearance of the sols and all the sols remained clear throughout the treatment. The pH of the sols, on the other hand, dropped significantly during heating. The pH values measured after cooling were 3.7 for the sol without salt addition and 3.8–3.9 for the sols of the highest chloride concentration. There was no significant difference in the pH among the sols that received NaCl and $CaCl_2$.

Fig. 1 shows the XRD patterns of the freeze-dried products from the NaCl and $CaCl_2$ systems. the product from the sol without additional salt showed broad peaks at around 2.1, 0.84, and 0.6 nm. Slight differences in d-spacings between the present product and those by Henmi and Matsue (1998) may be due to the difference in relative humidity. The intensities of these peaks decreased as the salt concentration increased and almost unidentifiable for the products from the sols having the salt concentration >50 mmol L^{-1} for the NaCl system and >30 mmol L^{-1} for the $CaCl_2$ system. The electron microscopy showed that the major product from the sol without salt addition was fibrous imogolite with trace mount of fine granules resembling allophane (not shown). The proportion of the granules increased as the salt content increased in both the NaCl and $CaCl_2$ systems.
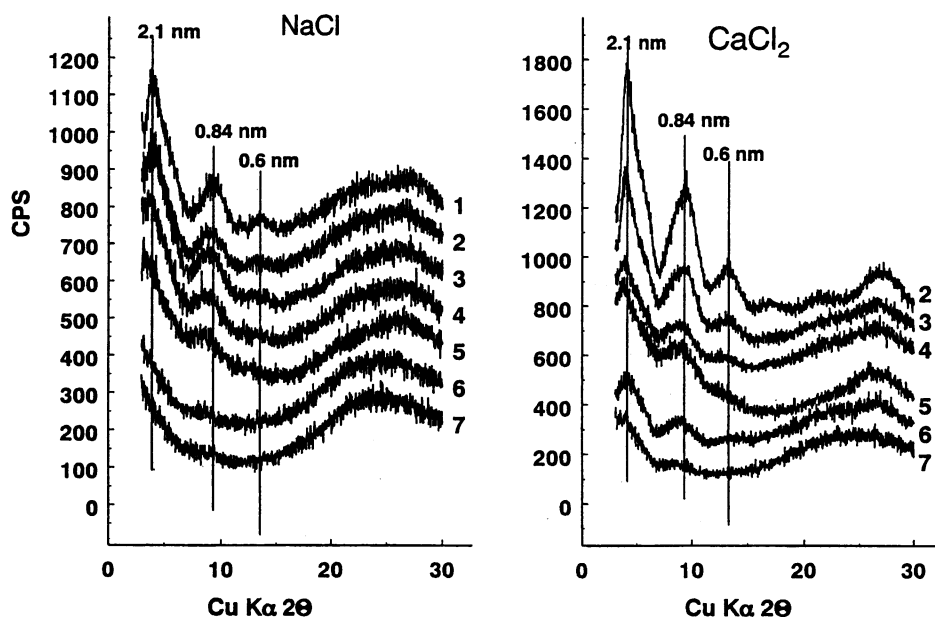

FIG. 1. XRD patterns of the freeze-dried products. The numbers correspond to the batch number indicated in Table 1. The products from the batches #8 to #10 showed no peaks and they are omitted.

Imogolite fibers were hardly detectable in the products from the sols having Cl^- concentration > 50 mmol L^{-1}.

On alkalinization with ammonium water, the products formed in the sols flocculated and settled to form clear gel by centrifugation. The gel from the sol without salt addition was almost transparent and the gel-supernatant boundary was invisible, indicating that the major product was fibrous imogolite and it flocculated to form bulky gel occluding much water. The gel volume measured with the aid of silica powder placed on the gel surface was 2.70 mL (Table 1), which is comparable with the value reported by Farmer and Fraser (1978). Since the possible byproducts including allophane do not form such a bulky gel and the addition of salt after the heat treatment did not affect the flocculated gel volume significantly the determined gel volume can be a measure of the development of long structural units of imogolite.

The values of the gel volume determined for the heated sols are listed in Table 1 together with the major ion concentrations. The coefficient of variation of the measured gel volume determined for some selected samples were $< 7.4\%$. For the NaCl system, the gel volume decreased as the concentration increased up to about 50 mmol L^{-1} and was nearly constant above that. For the $CaCl_2$ system, on the other hand, the gel volume was far below 0.5 mL when the $CaCl_2$ concentration was 22.2 mmol L^{-1}. The trend observed for the gel volume roughly paralleled that for the intensity of XRD peaks as shown in Fig. 1.

Although these experimental results suggest that foreign soluble salts hamper the elongation of the structural units of imogolite the contribution of individual ions is not clear. To get insight into the relative detrimental effect of Na^+, Ca^{2+} and Cl^- ions, the measured gel volume was plotted against the Cl^- concentration that was common to the both systems (Fig. 2-a). As readily seen, the plots for NaCl and $CaCl_2$ systems almost

TABLE 1.   Major ion composition of the starting sols and the gel volume determined on the heated sols

#	Added salts						
	NaCl			CaCl₂			
	[Na⁺]	[Cl⁻]	Gel volume*	[Na⁺]	[Ca²⁺]	[Cl⁻]	Gel volume*
	—mmol L^{-1}—		mL	————mmol L^{-1}————			mL
1	5.5	6.8	2.70	5.5	0	6.8	2.70
2	11.0	12.3	2.80	5.5	2.8	12.3	3.20
3	16.5	17.9	2.65	5.5	5.6	17.9	2.35
4	27.7	29.1	1.95	5.5	11.1	29.1	1.85
5	38.8	40.2	1.45	5.5	16.7	40.2	1.45
6	49.9	51.3	0.15	5.5	22.2	51.3	0.38
7	61.0	62.4	0.13	5.5	27.8	62.4	0.25
8	72.1	73.5	0.12	5.5	33.3	73.5	0.13
9	83.2	84.6	0.10	5.5	38.9	84.6	0.13
10	94.3	95.7	0.08	5.5	44.4	95.7	0.10

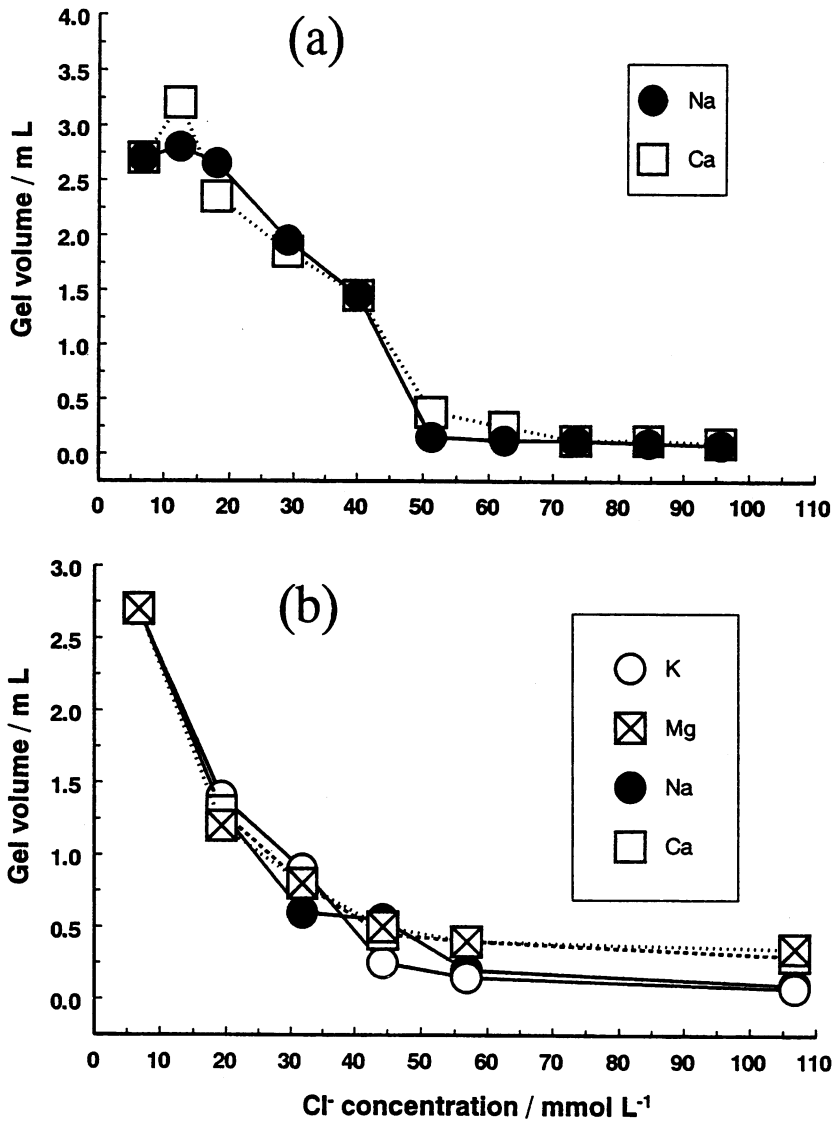* for the method of determination, see text.

FIG. 2.   (a) The relationships between the gel volume and the Cl⁻ concentration in NaCl-
and CaCl$_2$-added system. (b) The relationships between the gel volume and the Cl⁻
concentration in NaCl-, KCl-, MgCl$_2$- and CaCl$_2$-added systems prepared from a
separate starting sol.

coincided, suggesting that the major detrimental ion was Cl^- and the accompanying cations had little effect on the elongation of imogolite tubes.

To confirm this hypothesis, the gel volume measured in a separate series of synthetic experiments with added NaCl, KCl, $CaCl_2$ and $MgCl_2$ was also plotted against the Cl^- concentration in Fig. 2-b. The plots for the four systems, again, overlapped, indicating that the major ionic species that hamper the development of imogolite tubes was Cl^-. The critical Cl^- concentration estimated from the former series of the experiment was about 50 mmol L^{-1} and that from the latter was also around 50 mmol L^{-1}. However, the gel volume at the corresponding Cl^- concentrations below 50 mmol L^{-1} differed significantly between the two series of syntheses. Additional syntheses gave yet another values of the gel volume in the concentration range of 10–50 mol L^{-1} (not shown).

Since the reproducibility of the gel volume measurement was excellent with the largest coefficient of variation of 7.4%, it is not likely that the difference arose from the uncertainty in the measurement of the gel volume. In addition, the gel volume measured by the present method was approximately proportional to the imogolite concentration, at least for a particular imogolite sol. This was demonstrated by the plot of the gel volume against imogolite concentration determined for a series of diluted imogolite sol (Fig. 3).

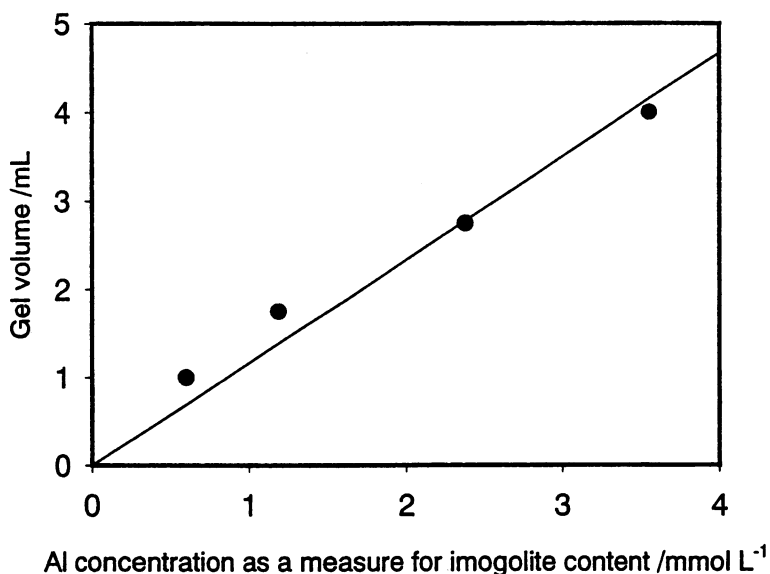Compilation of these experimental results suggests that the ion that is detrimental to the

FIG. 3.   The relationship between the imogolite concentration and the gel volume. A series of imogolite sol with different concentration was prepared by diluting a synthetic imogolite concentrate. Total Al concentration was used as a measure of imogolite concentration. One mmol L^{-1} of Al corresponds to about 150 mg imogolite/L.

imogolite formation is Cl^- but the development of the imogolite tubes very sensitively depends on the structure of precursors formed during neutralization of the starting mixed solutions. The results of the present experiments also suggest that alkalis other than NaOH can be used for neutralizing the starting Al^{3+}-silicic acid mixtures. The use of $CaCO_3$, for example, would be beneficial for homogeneous neutralization of the starting solution because it dissolves rather slowly in weakly acidic solutions generating CO_2. It is proven that the use of solid carbonate is advantageous for homogeneous neutralization of $FeCl_3$ solutions (Ryu and Wada, 1999).

Henmi and Matsue (1998) carried out a basically the same synthetic experiment. They measured the peak intensities of the XRD pattern of the products and found that the approximate critical concentrations of NaCl and $CaCl_2$ for imogolite formation were around 150 and 30 mmol L^{-1}, respectively. They also reported that the critical concentration from the KCl system was close to that of NaCl system and those for $CaCl_2$ and $MgCl_2$ systems were similar (Henmi and Matsue, 1998). On the basis of their observation they concluded that divalent alkaline earth metal cations are more detrimental to the growth of imogolite tubes than monovalent alkaline metal cations. Since the Cl^- concentration in a 150 mmol L^{-1} NaCl concentration is much higher than that in a 30 mmol L^{-1} $CaCl_2$ solution, their interpretation of their own experimental data is not unreasonable.

The conclusion on the effect of cations on the imogolite formation to be drawn from the results of the present study is different from that by Henmi and Matsue (1998). However, it should be noted that the criteria used in these studies were different, i.e., the peak intensity in XRD in Henmi and Matsue (1998) and the gel volume in the present study.

It is almost accepted that the intensity of a characteristic peak in XRD of a crystalline mineral can be used as a measure of its quantity, which is the principle on which many methods for quantitative determination of minerals are based. For imogolite it is not unquestionable to apply the same principle because the major XRD peaks arise from the rather weak association of individual structural units. It has been recognized that the major peaks are markedly intensified by heating at around 100°C due to the removal of molecular water intervening the intra-tubular spaces (Wada and Yoshinaga, 1969). These suggest that the factors like tube length and the presence of allophane may also influence the mode of arrangement of the units and in turn the XRD peaks. The product from the batch having Ca concentration of 2.8 mmol L^{-1} gave sharper diffraction peaks than the corresponding product from the NaCl system (Fig. 1). It is more probable that the sharper peaks arose from the better association of the structural units during freeze-drying than that trace amount of Ca^{2+} favored the growth of imogolite.

Similarly the gel volume cannot be a universal measure of the quantity of imogolite in a strict sense. Although Fig. 3 shows that the gel volume is nearly proportional to the imogolite concentration for a particular imogolite sol, it is highly probable that a concentrated imogolite sol containing short structural units and a dilute sol of long units may give the same gel volume. It would be naive to claim that the gel volume is the measure of the imogolite content for any imogolite-containing sol.

The studies by Farmer and Fraser (1978) and Henmi and Matsue (1989) as well as the

present study clearly show that the presence of salts at very high concentrations is extremely unfavorable for imogolite formation. However, it is difficult to draw the general conclusion about the effect of individual ions on the development of fibrous structural units of imogolite. Additional studies with a reliable method for quantifying imogolite seem needed.

Another research problem that was revealed in the present study is how the method and extent of neutralization affect the development of imogolite. Two plots in Fig. 2-a and four plots in Fig. 2-b suggest that separately prepared starting sols gave significantly different imogolite yield even if the same procedure was followed. Since the starting sols were prepared by injecting fairly concentrated NaOH in to mixed dilute $AlCl_3$-$Si(OH)_4$ solutions, excessive hydrolysis of Al^{3+} may have occurred locally depending on the stirring condition. Thus, the average structure of the precursors formed during neutralization may differ significantly from one batch to another, resulting in different imogolite yield. Similarly the degree of neutralization, the OH/Al ratio, would affect the structure of precursors. The OH/Al ratio employed by Henmi and Matsue (1998) was 2.0 while it was 2.4 in the present experiment. The observed difference in the effect of cations on the imogolite yield may have arisen from some difference in structure of precursors.

In spite of these uncertainties, the conclusion of the present study that the coexisting cations exert little effect on the gel forming properties of imogolite from starting sols having an OH/Al of 2.4 is valuable for development of new efficient synthetic methods. Because, the higher OH/Al ratios are preferable in terms of efficient use of raw materials and the gel forming property is important in possible applications such as a reversible support for solid in suspension (Farmer et al., 1983). As already discussed, solid calcium carbonate may be used for neutralizing starting solutions. According to the experience of authors, the homogeneous neutralization of the starting solution is one of the crucial factors for better imogolite yield. This is the reason why slow addition of NaOH was employed in many syntheses (Wada et al., 1979; Henmi nad Matsue, 1998). For relatively dilute starting solutions, the slow drop wise addition of NaOH works well (Wada et a., 1979). However the homogeneous neutralization becomes increasingly difficult as the concentration of starting mixture and NaOH solution are increased. Instantaneous addition of solid calcium carbonate to concentrated starting mixtures followed by desaltation and heating deserves further study.

ACKNOWLEDGMENTS

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