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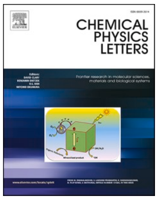

Research paper

Ionizing radiation induced reaction in nanoclay hydrogel

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ABSTRACT

Reactions induced by ionizing radiation in LAPONITE-XLG nanoclay hydrogel were investigated and compared with those in alkaline aqueous solutions using ns-pulse radiolysis. The LAPONITE concentration did not affect the decay rate of hydrated electrons in 1 and 2 wt% hydrogel. The scavenging of hydrated electrons by pyridine was examined in 2 wt% hydrogel, and was consistent with the reaction in aqueous solution. The absence of a “cage-effect” or adsorption effect for pyridine or pyridinium was found. This suggests that LAPONITE behaves as an inert material on condition that solute adsorption does not occur.

1. Introduction

LAPONITE®, a nanoclay (NC) material, is a synthetic inorganic compound composed of layered silicates (hectorite: $Na_{0.7}^{+}[(Si_8Mg_{5.5}Li_{0.3}O_{20}(OH)_4]^{0.7-}$). LAPONITE is known to form a colorless, clear, and stable gel in water with unusual rheological properties [1]. This hydrogel structure and its unique properties could be described as having a “house of cards” structure due to the disc-shaped particles of LAPONITE. This hydrogel has thixotropic features and can undergo reversible gelation. In addition, the gel has excellent suspension properties and adsorption abilities for organic molecules. Because of these properties, LAPONITE is widely used in various applications, including paints, cosmetics, and pharmaceuticals as hydrogel- or film-forming agent [2–5]. The wide applicability of nanoclays makes them suitable for use in a variety of environments and they would therefore be expected to be exposed to heat and light, or could be exposed to the ionizing radiation. An understanding of the fundamental reaction properties of hydrogels to enable the safe use of nanoclay materials in various environments is thus important. In addition, these hydrogels are also known to have limited ability to diffuse a solute due to the cage effect or adsorption of the solute on the clay material. Therefore, a fundamental understanding of hydrogels as a reaction field is of equal importance.

A recently reported application of LAPONITE hydrogel is as a three-dimensional dosimeter [6–19]. These dosimeters play a major role in the verification of three-dimensional radiotherapy treatment plans [20–22]. Because the LAPONITE hydrogel is stable and can maintain its spatial distribution, the 3D dose can be memorized by the hydrogel. Reports on these 3D dosimeter applications using hydrogels indicate that the products of chemical reactions induced by ionizing radiation remain at the site that was irradiated. Inorganic nanoclays are not regarded to affect chemical reactions induced by ionizing radiation because they are considered to be an inert silicate-like glass. Some clay materials like montmorillonite colloid solution [23,24], bentonite [25], saponite [24], and beidellite [24] are examined with water under colloidal, swelled or suspension conditions. These reports focus on ionizing radiation products and their yields because the reports consider nuclear waste storage by deep geological disposal. Therefore, radiation-induced reactions in LAPONITE hydrogels which composed much less clay like 2 wt% have not yet been investigated. Hydrogel condition can be limiting fluid properties and need to be clarified from the fundamentals. As mentioned above, hydrogel condition has unique situation and it is interesting if direct observation of their three-dimensional structure was made. However, hydrogel which composed of water and small amount of nano-size clay cannot be observed recent advance microscopic technique like electron microscopes which need observation under vacuum or X-ray computed tomography which had not had enough resolution. Therefore, we believe it is valuable to evaluate how reaction undergoes in the hydrogel conditions.

When the LAPONITE hydrogel was used in a three-dimensional dosimeter, the spatial distribution of the dose, which is a history of ionizing radiation irradiation, maintains at least for 9 days for Fricke gel [11] and more than 73 days for radio-fluorogenic gel dosimeters [12]. Therefore, these dosimeters show diffusionless feature after the

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irradiation, and therefore the hydrogel itself has enough stability over the time. However, it is still not clear whether the "diffusionless" feature comes from the chemical reaction process or the process after the chemical reaction. Therefore, it is reasonable to examine reaction kinetics in the LAPONITE hydrogel.

In this study, the cage effect as well as confinement effect, and solute adsorption effect were examined for ionization-induced chemical reactions. We observed hydrated electrons (e^-_{hyd}) in the hydrogel, and the use of pyridine (Py) as a scavenger of these electrons was examined in the LAPONITE hydrogel in comparison with water. The pulse radiolysis technique with an electron beam was selected as the most suitable method to investigate these reactions, because a high-energy electron beam makes it possible to provide homogeneous irradiation throughout the beam path [26–28]. This technique is appropriate to study the chemical reactions induced by ionizing radiation in the nanoclay-based hydrogel, which is composed of a liquid solution and swollen solid silicate clay.

2. Experimental

A nanoclay gel sample was prepared using 2 wt% nanoclay (LAPONITE-XLG; BYK) with ion-exchange water. Pyridine (FUJIFILM Wako Pure Chemical Industries) was used as received, and was chosen as the scavenging reagent for the hydrated electrons because the reaction between pyridine and these electrons is well-established [29–33]. Moreover, pyridine is one of the components of the nanoclay radiofluorogenic gel (NC-RFG) dosimeter, which has a unique and high-performance dose response [7–9,12–16,18]. The role of pyridine in the NC-RFG dosimeter was denoted as being that of a dispersing agent. However, pyridine is expected to play a greater role. The NC-RFG dosimeter was regarded as an example of application condition which composed of 2 wt% LAPONITE nano clay, 1 μM of dye, 100 mM of pyridine, 1 mM of $Fe_2(SO_4)_3$ and water [8]. Therefore, the simplified sample concentrations were use for the pulse radiolysis experiments. Deoxygenation was performed by bubbling argon into a glove box for 1 h. The prepared gel was poured into a quartz cuvette (10 mm × 10 mm) and sealed with a copper film in a glove box. The sealed samples were agitated using a rotation/revolution vacuum mixer for 1 min at 1200 rpm/600 rpm at atmospheric pressure using a special jig for a quartz cuvette (V-mini300, EME Corp.) to obtain homogeneous and bubble-free samples. The resultant gel samples were colorless and clear with no observable bubbles. The procedure to prepare other samples was reported in detail elsewhere [29–33]. The gel samples were equilibrated to 293 ± 2 K for one day. The density of 2.0 wt% NC-gel was determined as 1.0086 g/dm^3 by a density meter (DMA35, Anton Paar) at 296 ± 1 K. The water sample without any additive and alkaline water samples were prepared with ion-exchange water. NaOH (Nacalai Tesque) was used as a base to adjust the pH to 10.0 for alkaliene water sample. Prior to the measurements, both samples were placed in a quartz cuvette with silicon septa and deoxygenated by bubbling argon. The hydrogen ion concentrations (pH) were measured using a pH meter (AS-pH-11, AS ONE by Horiba) at 298 ± 1 K.

All the obtained hydrogel samples were colorless and transparent. However, fluidity varied according to the LAPONITE concentrations. The simplest series of the samples for the density measurement sample which composed of water and various concentration of LAPONITE can be good examples: At 1 wt% of LAPONITE hydrogel, the hydrogel is viscous but can possible to pore like liquid. At 2 wt%, the hydrogel loses fluidity and jelly like form. It is still possible to change its form by tilting but hard to flow. At 3 wt%, the hydrogel forms a stiff jelly but easy to scoop by a spatula. Therefore, deoxygenation by argon bubbling was safely appliable up to 2 wt%. Thus, pulse radiolysis experiments were conducted for 1 and 2 wt% samples. All samples with and without solutes had no separated water, no inhomogeneous part like supernatant fluid and no stickiness. As far as handling samples, all the samples were homogeneous.

The typical shape and size of a primary nanoparticle of LAPONITE XLG is thin disks with a diameter of 25 nm and thickness of 0.92 nm as shown in Fig. 1. It is known to form the "house of cards" structure of the nanoclay hydrogel, attached to the positively charged disc edge and negatively charged planar disc surface. The concentration of the nanoclay was proportionally related to the density up to 3.6 wt% (Fig. S1, Appendix). Therefore, the size of the nanoclay network depends on the concentration of the nanoclay in the hydrogel. The volume ratio of the sample can be understood as follows: the nanoclay occupies only 0.8 vol % from the density of the sample and the density of LAPONITE (2.53 g/dm^3) [1] without taking into consideration the swelling for the 2 wt% nanoclay hydrogel sample. The real structure or conformation of the primary particles of the LAPONITE has not been reported. It was not possible to determine the volume of the confined water space among the nanoclay networks. The molar concentration of the primary particle can be estimated as 29.3 μM for 2 wt% hydrogel without other solute, beside the molar concentration water is about 55.39 M at 298 K. It is interesting that the hydrogel was formed at low concentration of nanoclay particles though the softness of the hydrogel depended on the concentration of nanoclay.

The pulse radiolysis experiments were conducted using a 26 MeV electron pulse (8 ns FWHM pulse duration) generated by the electron linear accelerator (linac) at the Research Laboratory for Quantum Beam Science at SANKEN, Osaka University. A Xe flash lamp (LH-SA3H with LB-5L and SA-200F, Nisshin Electronic) was used as the monitoring light source, and the time course was recorded on an oscilloscope and detected using a Si photodiode (S1722-02, Hamamatsu) with a preamplifier (DHPVA-201, FEMTO Messtechnik GmbH). The experimental setup was previously described in detail [34,35]. The typical dose of the electron beam was 70 Gy/pulse for water (10 mm, 298 K), as evaluated by the reported molar absorption coefficient of hydrated electrons [36].

3. Results and discussion

The irradiation of water with ionizing radiation produces hydrated electrons [37,38] with a maximum absorption wavelength of 720 nm [39]. Fig. 2 shows the time expansion of the hydrated electrons in deoxygenated water (no additive, pH 7; pH 10 controlled by NaOH) and the hydrogel consisting of 1 and 2 wt% LAPONITE in the deoxygenated condition. The rate at which the hydrated electrons decay in the hydrogel samples was lower than that in pure water (pH7) because the LAPONITE nanoclay rendered the solution alkaline. In an alkaline aqueous solution, the recombination reaction of the hydrated electrons (Eq. (2)) was suppressed, which resulted in a longer lifetime (water pH 10 trace in Fig. 2) because the concentration of the counterpart of the

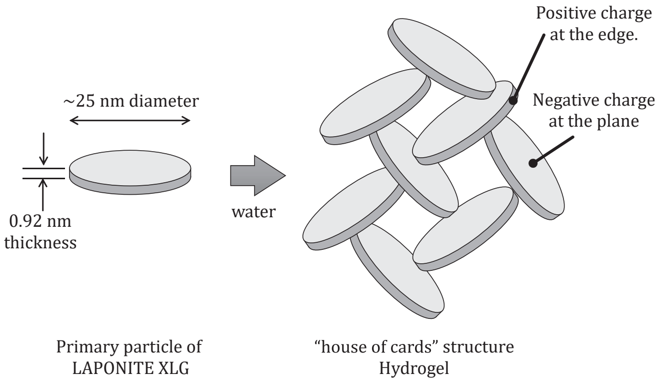

Fig. 1. The disc shape primary particle of LAPONITE XLG and the house of cards structure of the hydrogel. The house of cards structure believed to composed by the Coulomb interaction of the positive charge at the edge of the disc and the negative charge on the plane of the disc.

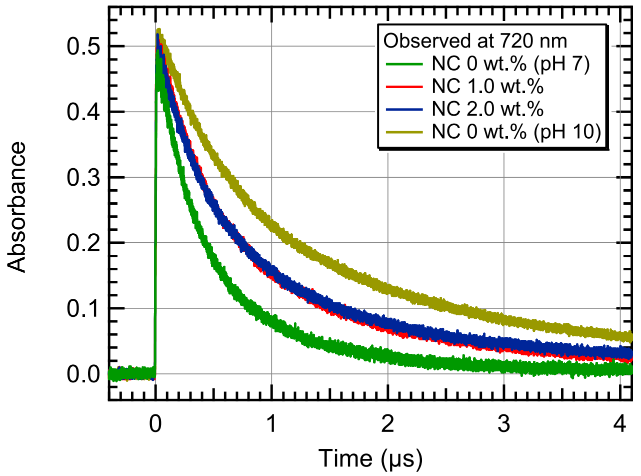

Fig. 2. Absorbance as a function of time of the hydrated electrons in LAPONITE hydrogel (NC 1.0 and 2.0 wt%), water (NC 0 wt%, no additive, pH 7) and alkaline water (NC 0 wt%, NaOH, pH 10) observed at 720 nm.

recombination reaction, H_3O^+, is significantly low under alkaline conditions (Eq. (3)) following the formation of hydronium ions of hole species (Eq. (1)). As a result, the hydrated electrons are consumed by hydroxyl radicals ($^\bullet OH$, Eq. (4)) or hydrogen atoms ($^\bullet H$, Eq. (5)). The difference of the observed decay between the hydrogel samples and pH 10 water sample may indicates lower effective concentration of OH^- for the hydrogel samples caused by the Coulomb interaction between positive charge of nanoclay and OH^-. It may also be possible to consider the weak cage effect of the hydrogel as the reason for the faster decay. However, it is difficult to determine the reason of observed differences. The main reactions of the hydrated electrons in alkaline water are summarized as follows [40]:

$$H_2O^{\bullet +} + H_2O \rightarrow H_3O^+ + {}^\bullet OH \tag{1}$$

$$e^-_{hyd} + H_3O^+ \rightarrow {}^\bullet H + H_2O \tag{2}$$

$$H_3O^+ + OH^- \rightarrow 2H_2O \tag{3}$$

$$e^-_{hyd} + {}^\bullet OH \rightarrow OH^- \tag{4}$$

$$e^-_{hyd} + {}^\bullet H\ (+\ H_2O) \rightarrow H_2 + OH^- \tag{5}$$

Noteworthy is that the decay rate does not depend on the LAPONITE concentration, as shown in Fig. 2. At concentrations of 1 wt%, the hydrogel maintains its fluidity. However, at 2 wt%, the hydrogel loses its fluidity and forms a relatively stable jelly in response to gentle external stimulation such as when tilting the sample cell. The correspondence between the decay kinetics of 1 and 2 wt% hydrogels indicates that the decay of the hydrated electrons is independent of gel formation or the coexistence of the nanoclay. Based on these results, it can be concluded that the hydrated electrons did not undergo a chemical reaction with the nanoclay.

Reportedly, the confinement of water in structures with a size of the order of nanometers significantly increases the initial yield of hydrated electrons for a controlled porous glass (CPG) plate with a pore size of 1 nm, as determined by ns-pulse radiolysis [41]. Here, the CPG is composed of almost pure silica. In addition, the hydrated electrons decayed much faster in the CPG with 1-nm pores. On the other hand, in the CPG with 57-nm pores, the decay kinetics of the hydrated electron was equivalent to those of bulk water, in which the electrons were not confined as in the CPG. This observation can be explained by the excitation and ionization of the CPG, which results in a high yield of hydrated electrons. In our case, for the LAPONITE hydrogel system, the yield of hydrated electrons was slightly higher than that in pure water, but no significant increase was observed, as shown in Fig. 2. This is a reasonable finding because the LAPONITE system contained only 2 wt% of solid material. This indicates that it is mostly the water molecules that are ionized. Regarding the difference in the observed kinetics between CPGs with 1-nm and 57-nm pores, physical confinement reportedly enhances the probability of reactive species encountering each other in the 1 nm case. This means that the agreement between the reaction kinetics in the 57-nm pores and bulk water indicates that 57 nm is sufficiently large such that the physical limitation for the reaction of the hydrated electron no longer plays a role. LAPONITE is understood to have a structure comprising thin disks with a diameter of 25 nm and thickness of 0.92 nm as the primary physical shape of the nanoparticles, which form a "house of cards" type structure in the hydrogel. Should the capsules formed by the "house of cards" structure in the water be sufficiently small to show the confinement effect, the decay kinetics would undergo accelerated decay. However, the experimental results neither revealed such fast decay nor any dependence of the nanoclay concentration on the decay kinetics, as shown in Fig. 2. Based thereupon, the decay kinetics of the hydrated electrons was concluded to be unaffected by the confinement or cage effect.

The transient absorption spectra of the aqueous pyridine solutions are shown in Fig. S2. The well-known absorption band of the hydrated electrons (e^-_{hyd}) was observed at approximately 720 nm immediately after irradiation with the electron beam. Relatively long-lived transient absorption bands were observed at approximately 480 nm. This transient can be assigned to OH-adducted pyridine [33,42].

The pyridine solution was alkaline because the pK_a of pyridine is reported to be 5.23 [43] (Eq. (6)). The LAPONITE-XLG hydrogel is also an alkaline solution with a measured pH of 10.0 for 2 wt% LAPONITE hydrogel. Therefore, the experimental conditions were alkaline for both the hydrogel and aqueous solutions thereof, except for pure water. Pyridine or the pyridinium cation (PyH^+) scavenges the hydrated electrons (Eq. (7), Eq. (8)), and a dihydropyridinyl radical ($C5H6N^\bullet$) or OH adduct product is formed on pyridine ($Py\text{-}OH^\bullet$) (Eq. (9)). Based on a previous study and our experimental results, pyridine-related reactions induced by ionizing radiation in aqueous solutions of pyridine can be understood as follows [33]:

$$Py + H_2O \rightleftarrows PyH^+ + OH^- \tag{6}$$

$$Py + e^-_{hyd} \rightarrow C5H6N^\bullet + OH^- \tag{7}$$

$$PyH^+ + e^-_{hyd} \rightarrow Py + H^\bullet \tag{8}$$

$$Py + {}^\bullet OH \rightarrow Py\text{-}OH^\bullet \tag{9}$$

The results of the scavenging experiments on hydrated electrons by pyridine in the hydrogel under other conditions are shown in Fig. 3 and summarized in Table 1. As shown in Fig. 3(b) and the table, the scavenging rate constants (K_Q) did not differ significantly from each other. In other words, pyridine scavenges hydrated electrons even in the hydrogel, just as in the aqueous or bulk solution. Thus, the "cage-effect" was not found to exist for the scavenging reaction of the hydrated electrons by pyridine in the 2 wt% LAPONITE hydrogel. It is also noted that the absence of a difference between the solution with and without NaOH indicates that the scavenging reaction has no effect regardless of the presence of pyridinium.

LAPONITE can adsorb solutes via Coulomb interactions in the hydrogel. Had the solute been adsorbed, the apparent concentration of the free solution would have been expected to decrease. However, the experimental results shown in Fig. 3(b) indicate that no dilution effect was observed for the hydrogel sample. Therefore, the results of the scavenging experiments indicate that the adsorption of pyridine or pyridinium was negligible under the present experimental conditions.

As mentioned in introduction, dosimeters composed of LAPONITE hydrogel have spatial stability and diffusionless feature. On the contrary, scavenging reaction of the hydrated electron by pyridine in the hydrogel showed diffusion limited reaction just the same as the reaction

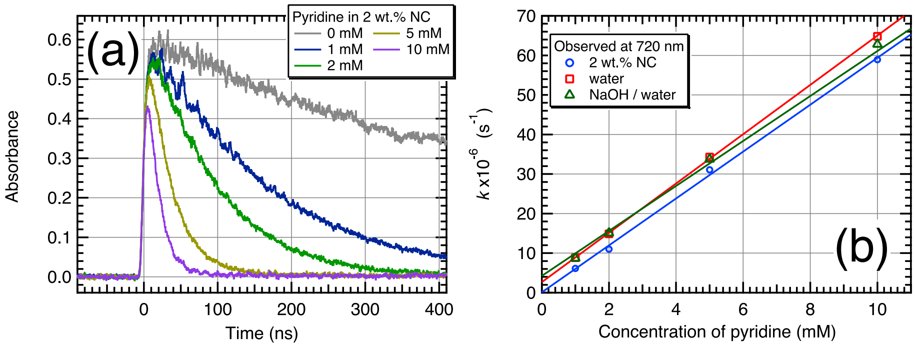

Fig. 3. Quenching effect of pyridine on hydrated electrons at 720 nm (a) and Stern-Volmer plot (b).

Table 1
Scavenging rate (K_Q) of hydrated electrons by pyridine.

Sample	$K_Q \times 10^{-9}$ / $M^{-1}s^{-1}$	Amount of NC	NaOH / M	pH
Py/water	6.23 ± 0.06	(none)	0	7.5 ± 0.1*
Py/NaOH/ water	5.68 ± 0.10	(none)	1×10^{-5}	9.8 ± 0.1*
Py/NC/water	5.93 ± 0.17	2 wt%	0	9.7 ~ 10.0**

* 10 mM solutions were repetitively measured.
** pH values of 0, 1, 2, 5, and 10 mM pyridine in the hydrogel were measured to be 10.0, 9.9, 9.8, 9.7, and 9.7, respectively.

in aqueous solutions. As seen in the above, LAPONITE itself had no contribution to the reaction kinetics in the present reaction system. Therefore, it is safely concluded that the ionizing radiation induced reaction in the hydrogel do undergoes diffusion just as it does in aqueous solution. Thus, the reported diffusionless feature of the hydrogel dosimeters expected to be originated from the adsorption of reaction product(s) on the nanoclays after reaction at least for the radiofluorogenic gel dosimeters, and not to be originated from the limited diffusion in the hydrogels.

4. Conclusion

In this paper, we reported the experimental observation of a reaction induced by ionizing radiation in LAPONITE-XLG nanoclay hydrogel compared to that in alkaline aqueous solution by ns-pulse radiolysis. The yield of hydrated electrons for both the 1 and 2 wt% nanoclay hydrogel was not dependent on the LAPONITE concentration. In addition, the reaction kinetics of the hydrated electrons in the hydrogel was not affected by confinement. The scavenging of hydrated electrons by pyridine was examined in 2 wt% hydrogel. The reactions of pyridine in the hydrogel were the same as those in aqueous solution. This led to the conclusion that the "cage-effect" of the hydrogel and the effect of the adsorption on pyridine or pyridinium was not observed for the present reaction system because the concentration dependence of the apparent decay rate constants of the hydrated electrons in the hydrogel was consistent and well overlapped with that in the aqueous solution. Thus, LAPONITE can act as an inert material, similar to quartz glass, as long as solute adsorption does not occur at least the concentrations of LAPONITE were less than 2 wt%.

CRediT authorship contribution statement

Masao Gohdo: Writing – review & editing, Writing – original draft, Visualization, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Takuya Maeyama:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cplett.2024.141656.

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