Effect of Bulk Natural Convection on Chemical Processes Studied in a Tight Polymer Gel Reactor Composed of Polysaccharide Network and a Large Excess of Water

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The effect of bulk natural convection on various chemical processes was investigated in a tight polysaccharide gel reactor composed of a few percent polysaccharide and excess water. It was elucidated that molecular self-diffusion coefficient ($D\,\text{cm}^2\,\text{s}^{-1}$) in the gel is the same as in liquid water, but bulk natural convection is entirely prohibited making the molecular transport in these gels remarkably slower than in liquid water. Three-dimensional (3D) diffusion of $\text{Ru(bpy)}_3{}^{2+}$ in a tight 0.125 wt % agarose gel took place only by molecular self-diffusion since bulk natural convection is prohibited, and the diffusion length agreed well with the theoretical 3-dimensional (3-D) self-diffusion length calculated from D. 2D diffusion of thionine in a polysaccharide gel also agreed well with the theoretical 2-D self-diffusion length showing also the absence of bulk natural convection. The chemical processes in the tight gel reactor in relevance to natural convection effects are discussed in terms of the time scale of the chemical process and the corresponding self-diffusion length of the reactants. For short time scale processes (ns to s) such as photochemical and electrochemical reactions, the process was not affected by bulk natural convection, but for a longer time scale (0.1 to 10 h) the effect of bulk natural convection was large.

Chemical reactions are usually carried out in a liquid or gas phase. They can also be carried out in a solid phase, but then the diffusion of the reactants is suppressed or entirely prohibited, which often makes the reaction different from that in a solution. The present authors have found that, in a tight polysaccharide gel involving a large amount of water, i.e., in a tight gel composed of a small amount of polysaccharide and a large amount of water, the molecular self-diffusion coefficient (a parameter independent of any convection) is almost the same as in liquid water.[1] Various reactions including photochemical[2] and electrochemical[1,3,4] reactions took place in this gel similarly as in an aqueous solution. We have proposed that this polysaccharide gel involving a large amount of water inside is an interesting gel reactor for new chemistry.[1] However, the detailed characteristics of this tight polymer gel as a reactor have been open to further investigations. We have further found that bulk natural convection does not take place in these polysaccharide gels because of the macroscopic solid state of the materials.[5]

In a liquid or gas phase a molecule is transported by convection (forced convection and bulk natural convection) as well as by its molecular self-diffusion. Forced convection takes place under stirring or flow of the medium and bulk natural convection takes place due to the presence of gravity. The rate of molecular self-diffusion is determined by the size of the molecule and the viscosity of the medium, and is expressed by the diffusion coefficient D ($\text{cm}^2\,\text{s}^{-1}$), that is independent of any convection, i.e. D is an intrinsic parameter. When comparing the degree of molecular transport distance by the convections and the self-diffusion, convections contribute much more to the transport distance of molecules in the whole liquid or gas phase than self-diffusion. For instance, when a dye aqueous solution is added to water in the absence of forced convection (assuming that the volume is $10\,\text{cm} \times 10\,\text{cm} \times 10\,\text{cm}$) where bulk natural convection does exist (bulk natural convection exists always in a liquid on our earth due to the presence of gravity), the dye molecules are transported quickly into the water becoming a homogeneous solution even in the slowest case within nearly half an hour mainly due to the natural convection. However, if bulk natural convection does not exist at all, the dye can diffuse only by self-diffusion, and then its diffusion distance after 40 min, for instance, is only 3.8 mm according to theoretical calculation based on eq 2 (later shown) when assuming the diffusion coefficient (D) of the dye is $1 \times 10^{-5}\,\text{cm}^2\,\text{s}^{-1}$. However, it is not understood in general how forced and natural convection are important for a molecule to be transported in a liquid or gas phase. It is an interesting and important subject to investigate the effect of bulk natural convection on chemical processes as well as the degree of molecular diffusion (transport) by discriminating the self-diffusion from bulk natural convection. However, it has been impossible to discriminate molecular self-diffusion from bulk natural convection on the earth since natural convection always takes place in a liquid or gas phase due to the presence of gravity, different from cosmic space where natural convection does not occur due to the absence of gravity. Prohibition of natural convection is important for crystal growth for which convection hinders large and good crystal growth by disturbing substrate concentration gradients above the growing crystal surface. For this reason cosmic space has been attracting atten-

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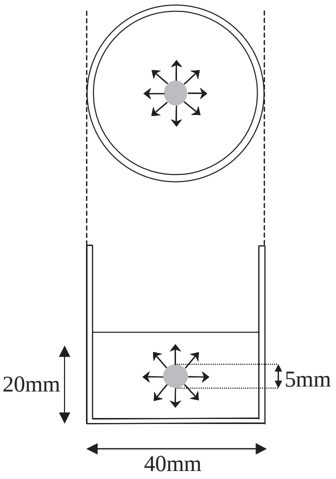


Figure 1. The cell and the size of the gel to investigate molecular diffusion in a polysaccharide gel containing a large excess of water.

tion to obtain ideal crystals or good molecular mixtures where natural convection does not exist due to the absence of gravity.

In the present paper we have investigated and discussed the characteristics of a tight polysaccharide gel involving a large excess of water as a reactor wherein bulk natural convection is entirely prohibited,[5] and the effect of natural convection on chemical processes will be discussed in terms of the time scale of the process.

Experimental

Materials. Agarose (**1**) (extra pure grade) was purchased from Acros Organics Co., Ltd. and κ-carrageenan (**2**) (extra pure grade) from Wako Pure Chemical Ind. Ltd. The purest grade reagents were used without further purification. Tris(2,2′-bipyridine)ruthenium(II) dichloride was purchased from Aldrich Co., Ltd., and used as received. Thionine (**3**) was from Tokyo Kasei Co., Ltd.

Measurements. Cyclic voltammograms were measured by the following instruments: (HA-301 potentiostat, HB-104 function generator from HOKUTO DENKO Co., Ltd., and RW-21 X-Y recorder from RIKADENKI KOGYO Co., Ltd.). An indium tin oxide (ITO, resistance $10\,\Omega\,\mathrm{cm}^{-2}$) working, a platinum counter, and Ag–AgCl reference electrodes were used.

In order to measure three-dimensional molecular diffusion in a tight polysaccharide gel containing a large excess of water, a disk shape (diameter 40 mm and height 20 mm) polysaccharide gel containing a large excess of water was prepared by dissolving a small amount of polysaccharide in pure water on a hot plate at about 90 °C, and then by cooling the hot solution in a glass cell (Figure 1).[5] Before complete gelation of the polysaccharide, air was injected from a syringe to make a round air bubble (diameter 5.0 mm) in the center of the solid, and then the polysaccharide was cooled down to room temperature (25 °C). The air bubble made in the tight gel was filled with a 66 µL aqueous solution of 5 mM $\mathrm{Ru(bpy)_3}^{2+}$ and 0.1 M KNO_3 by injecting the solution by syringe, and then the diffusion of the dye was observed from above the gel.

To measure two-dimensional molecular diffusion, a polysaccharide gel film was prepared (size 40 mm × 40 mm × 2 mm thickness) by pouring a hot aqueous solution of the polysaccharide into a mold made of poly(methyl methacrylate) plate, and then by cooling to room temperature. A disk shape hole (diameter 10 mm and thickness 2 mm) was made at the center of the film by removing a part of the polysaccharide, the hole was filled with an aqueous solution of 5 mM thionine, and then the diffusion length of the thionine was observed from above (Figure 2).

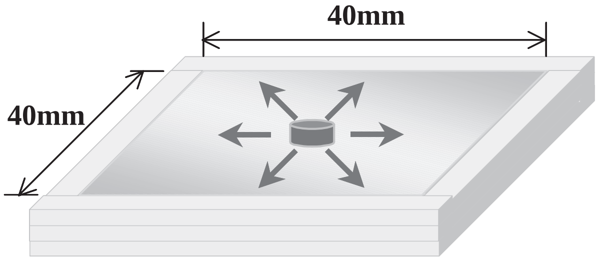


Figure 2. The cell to investigate two-dimensional molecular diffusion in a polysaccharide gel. Thickness of gel, 2 mm. The hole in the center of the gel film wherein an aqueous solution of a dye was filled, is a disk shape with 10 mm diameter and 2 mm height.

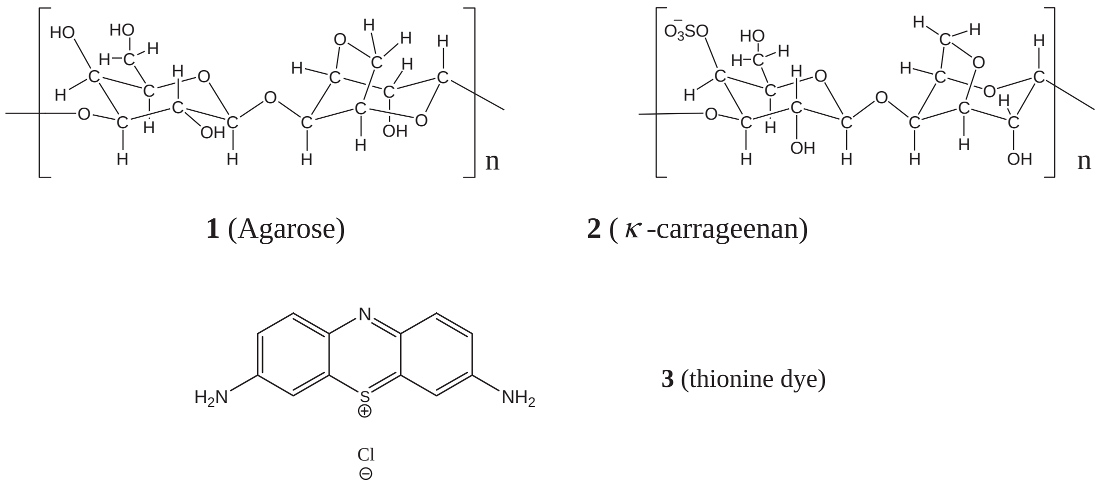
The relative hardness of the polysaccharide solid was measured by a hardness meter (Ttype 00 and E2) from TECLOCK Co. after preparing a block of polysaccharide solid (diameter 41 mm and height 16 mm).

All measurements were carried out at 25 °C.

Crystal Growth. A tight $24\,\mathrm{cm}^3$ of 0.4 wt % κ-carrageenan gel containing a large excess of water was prepared as mentioned above in a cylindrical glass tube (diameter 37 mm), and then a $50\,\mathrm{cm}^3$ hot and saturated aqueous solution of sodium tartaric acid (a sample received from Kishida Kagaku Co., Ltd.) was poured onto the gel. The κ-carrageenan gel floated on the aqueous phase by this procedure. As a poor solvent 40 mL of acetone was poured onto the gel, and the whole mixture was left at room temperature (25 °C). After cooling to room temperature large needle crystals started to grow in the gel phase. After one week the crystals were separated and washed with pure water. As a reference experiment, sodium tartaric acid was crystallized from water by a conventional procedure. The commercially available crystals were also tested by X-ray single-crystal analysis in addition to the crystal sample grown in the κ-carrageenan gel by using a single crystal X-ray structure analyzer, Rikadenki RASA-7R.

Results and Discussion

The materials used in this paper are shown in Chart 1. It has been known that polysaccharides make a tight and elastic gel containing a large excess of water (designated as solid/water) by forming a three-dimensional network structure of single, double, or sometimes triple helical main chains in nanometer scale orders.[6,7] The hardness of the gel has not been reported except in our recent reports.[4] The hardness of the polysaccharide gel (from 1 to 3 wt %) containing a large excess of water is shown in Figure 3. Below 1 wt % polysaccharide concentration the gel was so soft that the hardness could not be measured by the present hardness meter. Agarose formed harder gel than κ-carrageenan. κ-Carrageenan formed a tight gel in the presence of cations such as K^+ due to the binding of the chains having pendant sulfonate anionic groups with the K^+. The hardness increased with the increase in the polysaccharide concentration. To compare the hardness with conventional materials; a conventional rubber eraser gave the hardness of 83.0. Therefore, when roughly describing, the hardness of a 3 wt % agarose gel was about half of a rubber eraser, meaning that it is a tight gel.



1 (Agarose)

2 (*κ*-carrageenan)

3 (thionine dye)

Chart 1.

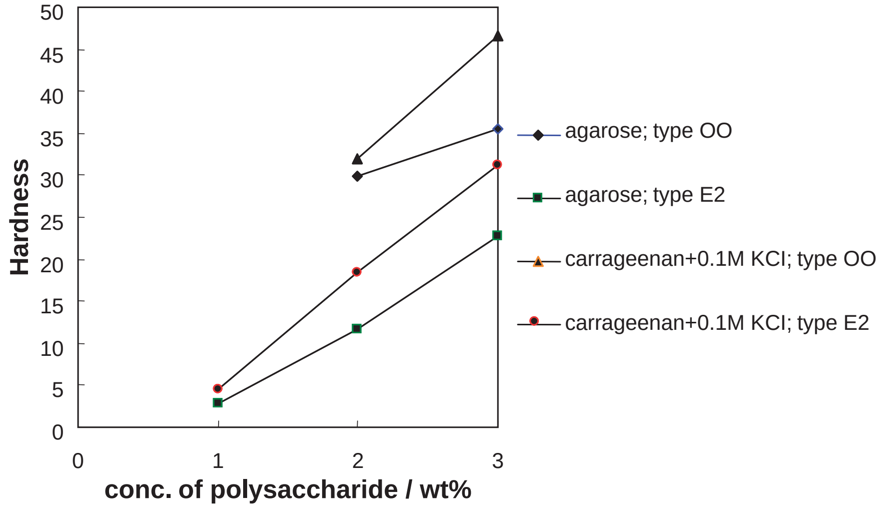


Figure 3. Hardness (arbitrary unit) of polysaccharide gels against its concentration. As a reference, a conventional rubber eraser gave a hardness of 83.0 by the hardness meter, type 00.

As reported earlier, in these tight and elastic polysaccharide gels containing a large excess of water, molecular self-diffusion coefficient ($D\,\mathrm{cm^2\,s^{-1}}$) is almost the same as in a liquid water.[1–4] Ionic conductivity in these gels by the salts such as KCl, KNO_3, KI, CsCl, and $CaCl_2$ was almost the same as in liquid water.[4] Further investigation showed an interesting and important fact that natural convection is prohibited in these gels, so that molecules are transported very slowly only by self-diffusion (coefficient) in contrast to the rapid transport of molecules in an aqueous solution where natural (or forced) convection contributes much to the molecular transport.[5]

We have proposed and proved that this tight polysaccharide gel involving excess water can be used as a solid medium for electrochemistry the same as liquid water.[1,3,4] For electrochemical measurements natural convection is usually neglected since we can not exclude natural convection on the earth. However, since natural convection makes transport of molecules very rapid as mentioned above, the effect of natural convection on electrochemical process should be investigated. This task has so far been impossible to achieve, but the present polysaccharide gel medium can provide a good medium for this investigation since self-diffusion coefficient of molecules is in principle the same as in a liquid but bulk natural convection is entirely prohibited.

The molecular self-diffusion coefficient can be determined electrochemically by cyclic voltammogram (CV) using the Randles–Sevcik equation (eq 1);[8,9]

$$i_\mathrm{p} = (2.69 \times 10^5)An^{3/2}D^{1/2}C_0 v^{1/2} \tag{1}$$

where i_p is peak current (A), A electrode area ($\mathrm{cm^2}$), n number of electron for the reaction, D intrinsic self diffusion coefficient $\mathrm{cm^2\,s^{-1}}$ that is independent of convection effect, C_0 initial concentration of redox compound in $\mathrm{mol\,cm^{-3}}$, and v scan rate ($\mathrm{mV\,s^{-1}}$).

In this treatment, if the peak current of the CV is proportional to the square root of scan rate ($v^{1/2}$), the process is regarded as diffusion-controlled. In this eq 1 it is assumed that molecules are provided to the electrode surface only by self-diffusion without any convection forming an ordered concentration gradient on the electrode surface. In order to clarify the issue if bulk natural convection does not affect the concentration gradient on the electrode surface, the diffusion length of

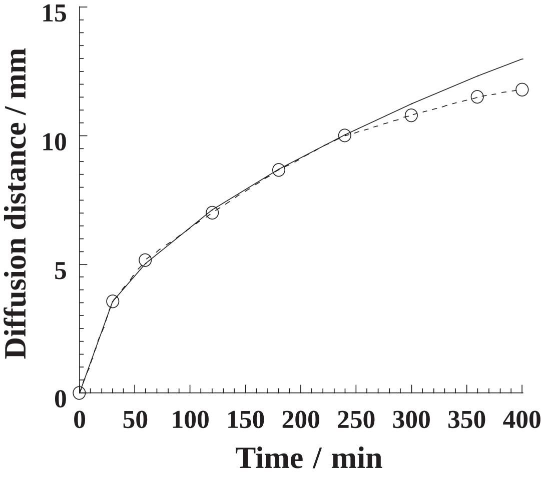


Figure 4. Three-dimensional diffusion distance of Ru(bpy)$_3{}^{2+}$ against time in a tight 0.125 wt % agarose gel (○). Solid line, theoretical curve based on self-diffusion (eq 2).

$\mathrm{Ru(bpy)_3}^{2+}$ was measured in a polysaccharide gel as follows.

Three-dimensional self-diffusion of 5 mM $\mathrm{Ru(bpy)_3}^{2+}$ was investigated with the cell (Figure 1) in an agarose (**2**) gel involving a large excess of water by varying the agarose concentration. The diffusion length of the complex against time is plotted in Figures 4 (in a 0.125 wt % agarose gel) and 5 (in a 0.025 wt % agarose gel). In these figures the theoretical curves for the diffusion distance (d cm) taking place by self-diffusion calculated by eq 2 is shown, where D is the self-diffusion coefficient of the molecule (cm^2 s^{-1}) and t is time (s).

$$d = (6Dt)^{1/2} \tag{2}$$

For the calculation of the transport distance by eq 2 in Figures 4 and 5, the self-diffusion coefficient (D) of the 5 mM $\mathrm{Ru(bpy)_3}^{2+}$ was measured by cyclic voltammogram based on eq 1. The CV as well as the D value of $\mathrm{Ru(bpy)_3}^{2+}$ obtained by eq 1 in both the 0.025 and 0.125 wt % agarose gels were the same as in an aqueous solution (where bulk natural convection exists, see Ref. 5) giving a D value of 1.17×10^{-5} cm^2 s^{-1}, exhibiting that bulk natural convection does not influence the D value. It should also be added here that another important aspect is that the agarose chains do not prohibit the molecular diffusion, because the D values were the same for all the 0, 0.025, and 0.125 wt % agarose concentrations. On the other hand, Ushida et al. reported interesting results about the time scale effect on the diffusion of molecules in a hyaluronan aqueous solution, that the observed diffusion constant (D) should depend on the observation time.[10] This behavior can be interpreted by the different average diffusion distance during the time scale, which is caused most probably by the hindrance by the hyaluronan chains in the solution. In our present case, however, such dependence of D on time scale (therefore on diffusion distance) is unnecessary to consider due to the obtained D values that are independent of polysaccharide concentrations.

In addition to this, as shown in Figures 4 and 5 molecular transport distance in the 0.025 wt % gel is much longer than that in the 0.125 wt % gel meaning that bulk natural convection exists in the former lower concentration gel. In spite of this however, the measured D values were the same for both the solids also exhibiting clearly that for the electrochemical D value measurement according to eq 1, bulk natural convection has no influence. It should be noted that in pure water the actual diffusion of the complex was so rapid due to the existence of natural convection that the liquid phase became homogeneous within 40 min after the Ru complex solution was injected into the center of the same shape liquid water. However, in the agarose gel the diffusion of the Ru complex was remarkably slow as shown in Figures 4 and 5. The diffusion length in the 0.125 wt % agarose gel agreed well with the theoretical self-diffusion length of the complex calculated by eq 2 (Figure 4) indicating clearly that the molecule diffuses only by self-diffusion. In lower concentration of agarose (0.025 wt %, Figure 5), a deviation was observed from eq 2 showing that a partial contribution of natural convection exists for molecular transport since the gel material was rather soft. In this case the contribution of convection was estimated from Figure 5 to be roughly 22% showing a moderate contribution of the natural convection to the transport of molecules in the soft gel that has a small degree of liquid character.

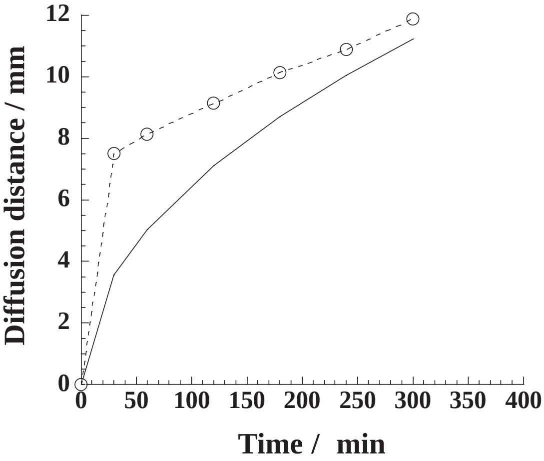


Figure 5. Three-dimensional diffusion distance of Ru(bpy)$_3{}^{2+}$ against time in a soft 0.025 wt % agarose gel (○). Solid line, theoretical curve based on self-diffusion (eq 2).

We have reported before three-dimensional diffusion of thionine in a 0.5 wt % agarose,[5] where the diffusion of the dye took place only by self-diffusion. Two-dimensional diffusion of thionine in a 2 wt % agarose was now investigated by using the cell of Figure 2. As shown in Figure 6, the diffusion length (d) agreed well with the calculated value based on the eq 3 that is the equation for the two-dimensional self-diffusion.

$$d = (4Dt)^{1/2} \tag{3}$$

For this calculation the D value of 4.98×10^{-6} cm^2 s^{-1} measured electrochemically in a 2 wt % agarose gel was used.[5]

It is now of importance and interest to discuss the effect of the present tight polysaccharide gel reactor for various chemical processes. Until now it has been difficult to experimentally investigate the effect of natural convection on reaction kinetics. For this purpose one problem exists in using polysaccharide gel, that is, a gel involving all the reactants should be pre-

Table 1. Characteristics of a Tight Polysaccharide Gel Reactor Involving a Large Excess of Water Depending on the Time Scale of the Chemical Process in Relevance to Natural Convection Effect

Chemical process	Time scale	3D Self-diffusion length during the time scale when $D \approx 10^{-5}\,\mathrm{cm^2\,s^{-1}}$	Ratio of the process in gel/liquid	Effect of natural convection	Ref
Photochemical electron transfer	≈ns–μs	≈1–100 nm	1/1	None	11
Electrochemical process	≈s	≈100 μm	1/1	None	3, 4
2nd-order reaction (Coloration of dye)	≈0.1 h	≈1.5 mm	≈1/2	Large	12, 13
Molecular diffusion in a medium	≈10 h	≈1.5 cm	≈1/10	Remarkable	5 and present paper

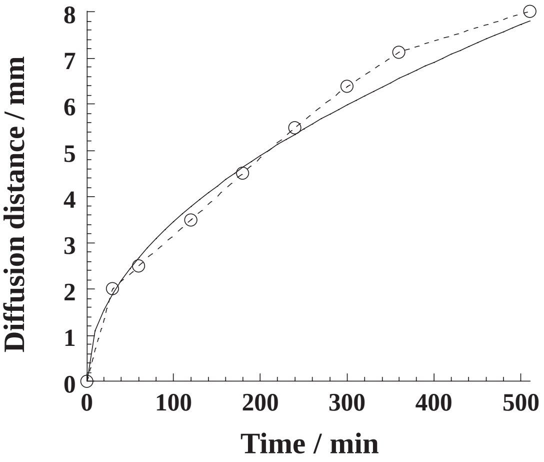


Figure 6. Two-dimensional diffusion of thionine in a 2 wt % agarose gel. Solid line, theoretical curve based on self-diffusion (eq 2).

pared at first, and then the reaction should be initiated by some stimulation such as light irradiation or electrochemical potential application. We have tried to study and discuss this aspect as follows, and the results of the difference of the chemical process in the gel and in the liquid are summarized in Table 1 including our recent results reported earlier, in conjunction with the time scale of the chemical processes.

For the photochemical reactions, we have already studied the electron transfer from the photoexcited $\mathrm{Ru(bpy)_3}^{2+}$ to 1,1′-dimethyl-4,4′-dipyridinium dichloride (methyl viologen) in polysaccharide gels, and found that the electron transfer in the agarose gel takes place the same as in pure water by a dynamic quenching mechanism giving almost the same rate constants ($10^8\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ order of magnitude) both in the gel and in liquid water.[11] This result means that bulk natural convection does not influence this photoinduced electron transfer probably because the event is a very rapid one taking place within the lifetime of the photoexcited sensitizer (about 600 ns in water).

In electrochemical reactions the time scale for the event is much longer than the above photochemical process. It has not been investigated yet how bulk natural convection affects or does not affect electrochemical processes taking place on an electrode surface; usually such bulk natural convection factors are neglected. As mentioned above the electrochemical reaction takes place in the gel the same as in liquid water giving the same D values meaning that bulk natural convection does not influence the electrochemical events.

When the time scale for chemical reactions is much longer, a large effect of bulk convection is observed. We have reported that UV-light induced coloration of Fluoran dye takes place in the presence of acid generator in an agarose gel film containing excess 2-propanol leading to fabrication of a film capable of visualizing UV irradiation.[12,13] In this case the time scale of the coloration reaction was the order, absorbance increase of 0.1 per 0.1 h.[13] The rate constant of the coloration (k_C, reaction of Fluoran with a proton to give colored dye in the agarose solid) was 1/1.8 of that in a 2-propanol solution demonstrating an accelerating effect by bulk natural convection on the reaction. Therefore, when the time scale is the order, ns to s (photoexcited state reaction and electrochemical reactions), the process is not affected by natural convection. However, when the time scale is around 0.1 h (conventional bimolecular reaction), a large accelerating effect of convection appears, and in the time scale of 1 to 10 h (transport of molecules in the medium), the process is remarkably affected by bulk natural convection.

For chemical reactions activation energy and/or frequency factors are controlling factors. The effect of the gel reactor in longer time scales than around one second must be due to the decrease of the frequency factor coming from the lack of bulk natural convection.

In recent years crystal growth in solid phases such as biomaterials, gels, and polymers has been attracting a great deal of attention.[14,15] Star-shaped calcite ($\mathrm{CaCO_3}$) crystals have been found to be formed in agarose gels (1 wt %) different from typical rhombohedral calcite crystals.[15] In that work an agarose gel (1 wt %) containing $\mathrm{CaCl_2}$ was soaked in an aqueous solution of $\mathrm{Na_2CO_3}$ so that the $\mathrm{CO_3}^{2-}$ ions diffuse into the gel to form $\mathrm{CaCO_3}$ crystals. The reason for the star-shaped calcite crystal formation was inferred to be due to the slow diffusion of $\mathrm{CO_3}^{2-}$ ions from the outer liquid water phase into the gels. It might be true that the diffusion of the carbonate ions from the outer liquid water phase into the gel should be slow. On the other hand, bulk natural convection factors should also be taken into account for crystal growth in gel matrixes. Bulk natural convection disturbs the concentration gradient of sol-

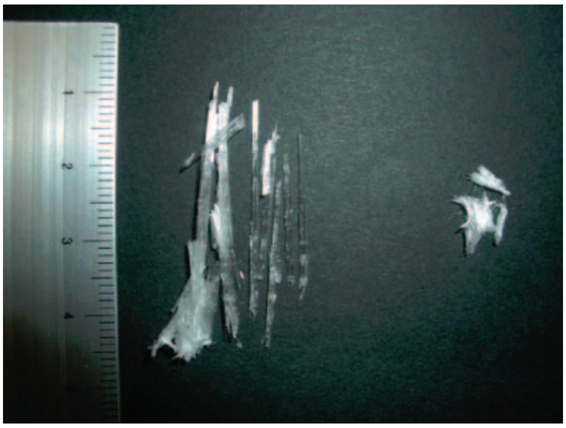


Figure 7. Crystals of sodium tartaric acid obtained in a 0.4 wt % κ-carrageenan gel (left) and in an aqueous solution (right).

utes above the surface of growing crystals, which hinders ideal crystal growth. In the absence of convection the solute concentration gradient above a growing crystal is not disturbed, which allows slow solute supply and therefore slow crystal growth to form high quality single crystals (or crystals with different structure), as carried out in cosmic space where natural convection does not exist due to the absence of gravity. As clearly shown in the present paper the tight polysaccharide gel containing a large excess of water can also provide such conditions where bulk natural convection is entirely prohibited.

The objective of the present paper is to report and discuss the characteristics of the polysaccharide gels as a chemical reactor, but since crystal growth is important in relevance to chemical processes, one experiment has been performed on crystal growth in a polysaccharide gel, and the result is reported here. It was remarkable that in a 0.4 wt % κ-carrageenan gel containing a large excess of water, very large crystals (3 cm long) of sodium tartaric acid were successfully obtained (Figure 7 left). As a reference experiment, sodium tartaric acid was recrystallized from an aqueous solution by a conventional procedure resulting in only small needle single crystals (a few mm size, Figure 7 right). The most probable interpretation would be that the absence of bulk natural convection in the solid induced such a large crystal growth. The crystals grown in an aqueous solution were not good enough for single-crystal analysis. To evaluate the quality of the single crystal, the analysis of the crystals by X-ray was carried out, showing a much lower R value for the crystals grown in the agarose gel ($R = 0.027$) than that for the commercially available crystals ($R = 0.049$), exhibiting unambiguously much better single crystals growth in the tight gel most probably due to the absence of bulk natural convection.

To conclude, the characteristics of tight polysaccharide network gels involving a large excess of water were investigated as a solid-state reactor and discussed. The characteristics were discussed in terms of the time scale of the chemical processes in relevance to the effect of bulk natural convection. In chemical processes with ns to s timescale, the chemical process in the gel took place the same as in liquid water, in the processes over 0.1 h the process was affected to some extent by bulk natural convection, and for processes with a time scale longer than around 1 to 10 h the effect of bulk natural convection was remarkable.

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References

1 M. Kaneko, N. Mochizuki, K. Suzuki, H. Shiroishi, K. Ishikawa, *Chem. Lett.* **2002**, 530.

2 T. Shoji, N. Katakura, N. Mochizuki, H. Shiroishi, M. Kaneko, *J. Photochem. Photobiol.* **2004**, *161*, 119.

3 H. Ueno, M. Kaneko, *J. Electroanal. Chem.* **2004**, *568*, 87.

4 H. Ueno, Y. Endo, Y. Kaburagi, M. Kaneko, *J. Electroanal. Chem.* **2004**, *570*, 95.

5 M. Kaneko, N. Gokan, K. Takato, *Chem. Lett.* **2004**, *33*, 686.

6 *Gel Handbook*, ed. by Y. Osada, K. Kajiwara, NTS, Tokyo, **1997**.

7 H. Saitô, Y. Yoshioka, M. Yokoi, J. Yamada, *Biopolymers* **1990**, *29*, 1689.

8 J. E. B. Randles, *Trans. Faraday Soc.* **1948**, *44*, 327.

9 A. Sevcik, *Collect. Czech. Chem. Commun.* **1948**, *13*, 349.

10 A. Masuda, K. Ushida, H. Koshino, K. Yamashita, T. Kluge, *J. Am. Chem. Soc.* **2001**, *123*, 11468.

11 K. Suzuki, H. Shiroishi, M. Hoshino, M. Kaneko, *J. Phys. Chem. A* **2003**, *107*, 5523.

12 Y. Kaburagi, S. Tokita, M. Kaneko, *Chem. Lett.* **2003**, *32*, 888.

13 K. Takato, Y. Kaburagi, Y. Kurimura, S. Tokita, T. Noguchi, M. Kaneko, *J. Photochem. Photobiol.* **2004**, *163*, 271.

14 S. Mann, *Angew. Chem., Int. Ed.* **2000**, *39*, 3392.

15 D. Yang, L. Qi, J. Ma, *Chem. Commun.* **2003**, 1180.