A Medium Wherein Molecular Diffusion Takes Place the Same as in a Liquid but Convection is Prohibited

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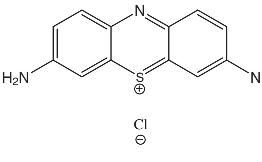
Polysacchride solids involving excess water were proposed as media wherein molecular diffusion takes place as in a liquid water, but convection is prohibited.

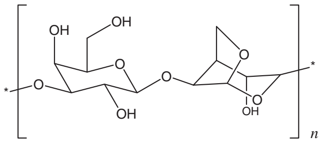
In a liquid or gas phase a molecule diffuses both by self-diffusion and convection when there exists no other disturbing factor such as stirring or flow of the medium. Between the self-diffusion and convection, convection contributes much more to the transport of molecules in the whole liquid or gas phase than self-diffusion (vide infra). However, it is not recognized in general how convection is important for a molecule to move throughout the liquid or gas phase. It is an important and interesting research subject to investigate the degree of molecular diffusion (movement) by discriminating the self-diffusion and bulk convection. However, it has been impossible to discriminate self-diffusion and convection since convection always take place on the earth due to the presence of gravity except the cosmic space where convection does not occur due to the absence of gravity. Prohibition of convection is also important for crystal growth for which convection prohibits large and good crystal growth by disturbing concentration gradient near the growing crystal surface. On this reason cosmic space has been attracting attention to obtain ideal crystals where convection does not take place due to the absence of gravity.

We have found that, in a polysaccharide solid involving excess water, molecular diffusion can take place the same as in a liquid water.[1] Various reactions including photochemical[2] and electrochemical[1] reactions can take place in this solid the same as in an aqueous solution. In this solid molecules can diffuse freely as in liquid water, but we have now found that bulk convection does not take place because of the macroscopic solid state of the material. Convection always takes place in a liquid or gas phase on the earth because of the gravity, and so can be prohibited only in the cosmic space. If convection can be prohibited on the earth, it would lead to new basic science, chemical reactions, as well as applications to such as crystal growth. In this letter we will report the interesting results of molecular diffusion in a polysaccahride solid involving excess water wherein convection does not take place.

3-D self-diffusion of thionine dye (**1**) was investigated in an agarose (**2**) solid involving excess water.



1 (thionine dye)



2 (agarose)

A disk shape (diameter 40 mm and height 20 mm) agarose solid (2 wt %) containing excess water was prepared by dissolving agarose in water on a hot plate at about 90 °C, and then by cooling the hot solution down to room temperature (25 °C) in a glass cell (Figure 1).

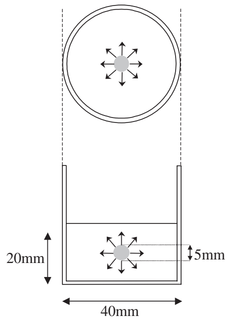


Figure 1. The cell and the size of the solid to investigate diffusion of thionine dye in the solid containing excess water.

The 2 wt % agarose solid was tight and elastic, the hardness being almost the same as a brick cheese and one third of a conventional rubber eraser. An air was injected from a syringe to make a round air bubble (diameter 5.0 mm) in the center of the hot solution before cooling, and after the cooling the bubble was filled with an aqueous solution of 5.0 m·mol·dm^{-3} thionine by using a syringe. 3-D diffusion of the thionine was observed from the top of the cell, and the diffusion distance was plotted against time at 25 °C (Figure 2). As a reference, the same thionine solution was injected by a syringe in the middle of the same shape liquid water (as in Figure 1) in the absence of any stirring and flow, and the diffusion of the thionine was observed.

In the liquid water the injected thionine became homogeneous in the water within 40 min, while in the agarose solid its diffusion was remarkably slow as shown in the Figure 2.

The diffusion length of a substance (d cm) in a gas or liquid phase in the absence of any other driving forces such as convection and flow of the liquid or gas is represented by the equation (1), where D is the diffusion coefficient (cm^2 s^{-1}) of the substance and t is time (s).

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

The D values of thionine in a 2 wt % agarose solid and in an aqueous solution were determined by cyclic voltammograms (as for the method see the reference[1]) to be 4.98×10^{-6} cm^2 s^{-1} (in the 2 wt % agarose solid) and 2.21×10^{-6} cm^2 s^{-1} (in aqueous solution). The electrochemical measurement of the diffusion coefficient is based on the self-diffusion of a molecule onto the electrode surface, so that conventional convection does not affect the D value obtained. The diffusion coefficient in the solid was even larger than that in water showing that self-diffusion of thionine should take place in the agarose solid the same as

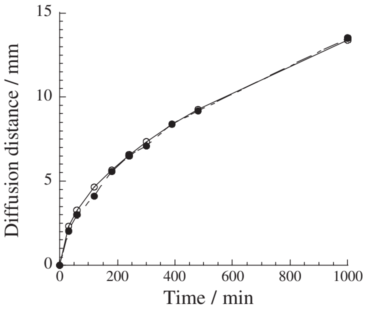
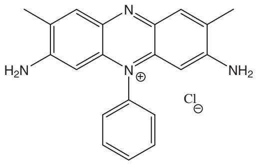


Figure 2. Diffusion distance of thionine against time in agarose solid. (-○-)Theoretical value of diffusion distance of thionine by self-diffusion according to Eq 1. (●) Observed diffusion distance of thionine in agarose solid. In a pure liquid water thionine became homogeneous within 40 min in a reference experiment under the similar conditions.

or even quicker than in a liquid water if only self-diffusion contributes to the diffusion. However, as it was mentioned in the Figure 2 the diffusion of thionine in a liquid water was much quicker than that in the agarose solid. The experimental diffusion distance of thionine in the solid as shown in Figure 2 was in good agreement with the calculated value (shown by a solid curve) based on self-diffusion, that is, only self-diffusion contributes to the transport of thionine. These results show evidently that in the agarose solid convection is almost entirely prohibited. It should also be noted that for diffusion of solutes in a liquid, contribution of convection is extremely larger than self-diffusion.

In recent years crystal growth in solid phases such as biomaterials, gels, and polymers is attracting a great deal of attention.[3,4] Star-shaped calcite ($CaCO_3$) crystals have been found to be formed in agarose gels (1 wt %) different from the typical rhombohedral calcite crystals.[4] In that work an agarose gel (1 wt %) containing $CaCl_2$ was soaked in an aqueous solution of Na_2CO_3 so that the CO_3^{2-} ions diffuse into the gel to form $CaCO_3$ crystal. The reason for the star-shaped calcite crystal formation was inferred to be due to the slow diffusion of CO_3^{2-} ions from the outer liquid water phase into the gels. In a sense it is true that the diffusion of the carbonate ions from the outer liquid water phase into the gel should be slow. On the other hand convection factor should also be taken into account for crystal growth in matrixes. Convection disturbs the concentration gradient of solutes above a growing crystal surface, 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, as carried out in the cosmic space where convection does not take place due to the absence of gravity. As clearly shown in the present paper the polysaccharide solid containing excess water can also provide such conditions where bulk convection does not take place.

In order to investigate the degree of contribution of convection on the diffusion distance, the diffusion of tolusafranine (**3**) was measured in various concentrations of agarose.



3 (tolusafranie)

Above 0.5 wt % agarose concentration conditions the diffusion length again agreed well with the value calculated by Eq 1, i.e., with the value in the absence of convection. However, in a 0.1 wt % agarose soft gel, a small contribution of convection existed making the diffusion length 22% larger than the value clalculated by the Eq 1.

Thus, tight polysaccharide media containing excess water are proposed wherein only self-diffusion of solutes can take place and convection is prohibited.

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