# Molecular Reactor for Solution Chemistry

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It was for the first time demonstrated that in a tight and stable solid made of polysaccharides such as carrageenan and agarose containing water, electrochemical and photochemical reactions can take place the same as in pure water.


Chemical reactions can take place in a solid, but in such case the reactants do not diffuse at all or move only slightly, so that chemical reactions in a solid are usually entirely different from those in a pure liquid. If chemical reactions can occur in a stable and tight solid the same as in a pure liquid, it leads to new and wide applications such as chemical reactors, microreactors, electrochemical/photochemical sensors, microanalysis, combinatorial chemistry, Laboratory on chips, etc. We have now succeeded in preparing tight and stable solids from polysaccharides containing a large excess water by carefully choosing the conditions, and found that electrochemical and photochemical reactions in these solids can take place the same as in pure water. As for the polysaccharide, κ-carrageenan[1] (**1**) and agarose[2] (**2**) were used.

1 (κ-carrageenan)   **2 (agarose)**
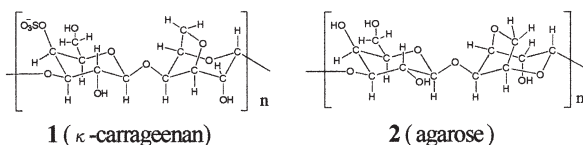
Electrochemical behavior of redox molecules in thin polymer films and gels coated on an electrode has been investigated,[1,3–12] but they have been studied in the presence of outer electrolyte solution except the report[9] that uses microelectrode in the absence of outer electrolyte solution. The diffusion coefficient (D) of the redox substrate in these films or solids coated on an electrode has usually been very small.[3–12] Entirely solid state voltammogram by using a conventional three electrodes system has not been achieved yet. We have succeeded in achieving electrochemical reactions in a tight solid made of polysaccharide and water. In this solid very conventional electrochemical reaction and measurement could be performed using a normal three electrodes system the same as in pure water without any outer water phase and vessel, and the electrochemical reactivity was the same as in pure water.

Four weight percent κ-carrageenan powder (purchased from Wako pure chemical Ind. Ltd.) was put in pure water, heated on a hot plate, and then irradiated very carefully by a high frequency wave (2.45 GHz) in an electric oven to entirely solubilize the material. Application of high frequency wave was important to prepare high concentration solid materials more than 2 wt%. After cooling the clear solution to room temperature under ambient conditions, a tight, elastic and clear solid was obtained. Agarose powder (from Acros Organics) gave a similar solid as the carrageenan by the same way. The solids are tight and elastic when the content is over about 1 wt% for agarose and over 2 wt% for carageenan.

In preparing a 1 wt% agarose/water (4 ml) solution, tris(2,2'-bipyridine)ruthenium(II) dichloride (Ru(bpy)$_3{}^{2+}$) and KNO$_3$ were added in the water so as to have their concentration 1 mmol dm^{-3} and 0.1 mol dm^{-3}, respectively, and the mixture was heated and cooled the same way as the above. In a viscous state of the mixture before entire cooling, transparent indium tin oxide (ITO) working, platinum counter, and Ag-AgCl reference electrodes were soaked in the solution, and the mixture was solidified by cooling to room temperature. Cyclic voltammogram (CV) was measured for this solid, and is shown in Figure 1.
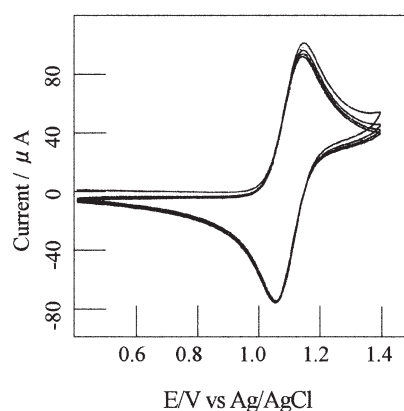

Figure 1. Solid-state cyclic voltammogram of Ru(bpy)$_3{}^{2+}$ (1 mmol dm^{-3}) in a 2 wt% agarose/water solid containing 0.1 mol dm^{-3} KNO$_3$ electrolyte without any outer water phase and vessel. Scan rate, 20 mV s^{-1}.

The voltammogram in the solid shows almost the same feature as in a liquid water including redox potential, peak separation, and peak currents. The solid was so stable and self-standing that CV could be measured without any outer cell or vessel after being taken off from the vessel used for the preparation of the solid. Diffusion coefficients (D) of the Ru complex in a 1 wt% agarose solid (agarose/water = 1/99) as well as in water containing the same 0.1 mol dm^{-3} KNO$_3$ were estimated from the peak currents of the CV. The D value in the solid (5.88 × 10^{-6} cm^2 s^{-1}) was the same order of magnitude as in a liquid water (4.28 × 10^{-6} cm^2 s^{-1}). Similar results were obtained also for the carrageenan solid. In a Nafion film (Nafion is a sulfonated perfluoroalkyl polymer from Du Pont Co. Ltd.) containing adsorbed Ru(bpy)$_3{}^{2+}$ in the water phase in the hydrophilic column (water is present in a ca. 20 vol% hydrophilic column of the Nafion[8]) coated on an ITO electrode and soaked in a 0.1 mol dm^{-3} KNO$_3$ aqueous solution, D was 10^{-10} cm^2 s^{-1}, four orders magnitude lower than that in the above agarose and carrageenan solids.

To further investigate chemical reaction in the solid, electron transfer from a photoexcited state Ru(bpy)$_3{}^{2+}$ to methylviologen

(MV^{2+}) was investigated in the polysaccharide solid containing a large excess water. Electron transfer from a photoexcited $Ru(bpy)_3^{2+}$ to MV^{2+} in a dry solid matrix was first reported by one of the present authors by adsorbing the compounds on a cellulose sheet,[13] and the mechanism of such electron transfer in a dry polymer solid phase has later been established to be a static one in which the reaction components do not move at all for the electron transfer to occur.[14,15] Now in a 2 wt% carrageenan/water solid containing both $Ru(bpy)_3^{2+}$ (50 μmol dm^{-3}) and MV^{2+} (from 50 to 400 μmol dm^{-3}), electron transfer from the photoexcited $Ru(bpy)_3^{2+}$ to MV^{2+} was investigated under irradiation with the wavelength of 453 nm (λ_{max}) at 25 °C. The visible absorption and emission spectra of the $Ru(bpy)_3^{2+}$ (λ_{max} 453 nm and emission max E_{max} 627 nm) were the same as in a pure water. The Stern-Volmer plots[14,15] of the relative emission intensity (I_0/I, where I_0 is the emission intensity at 627 nm without MV^{2+} and I with MV^{2+}) from the photoexcited Ru complex as well as relative emission lifetime (τ_0/τ) (measured by a single photon counting apparatus, τ_0 being the lifetime without MV^{2+}) in the carrageenan solid are shown in Figure 2.
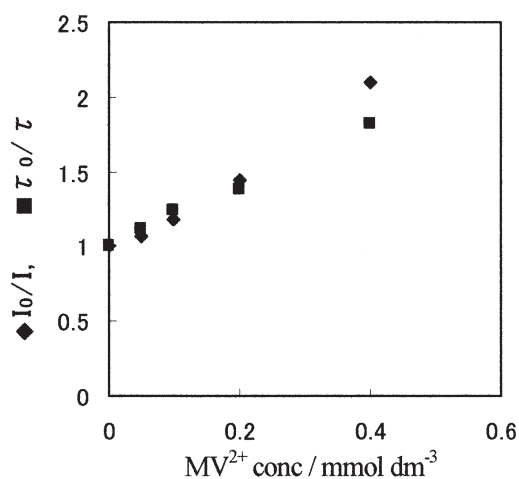
Figure 2. Stern-Volmer plots of the relative emission intensity (◆) and lifetime (■) against MV^{2+} concentration for the electron transfer quenching of the photoexcited $Ru(bpy)_3^{2+}$ by MV^{2+} in a 2 wt% carrageenan/water solid (1 × 1 × 3 cm size).

Both the plots of I_0/I and τ_0/τ fell on almost the same line showing that the electron transfer takes place by a dynamic mechanism[14,15] in which the molecules at first diffuse and react after collision. The second order rate constant of the electron transfer obtained by dividing the slope of the plots of Fig. 2 by

τ_0 (447 ns), 4.54×10^9 dm^3 mol^{-1}s^{-1}, is almost a diffusion-controlled value. On the contrary, a static mechanism took place in both dry and wet Nafion films containing adsorbed $Ru(bpy)_3^{2+}$ and MV^{2+} for which the Stern-Volmer plots based on τ_0/τ gave no slope.

To conclude, tight and stable solids could be prepared from polysaccharides and water, and chemical reactions including electrochemical and photochemical ones could be carried out in these solids the same as in pure water, which offers a new concept of solution chemistry taking place in solids. Since any outer flask or vessel is not needed for this solid state reaction, we call this material a molecular reactor. In addition to its usage for conventional chemical reactions, application to microscale reactors would be promising.

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