LETTERS

Spontaneous Formation of Cellular Chemical System that Sustains Itself far from Thermodynamic Equilibrium

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We report the observation of the spontaneous formation of a cellular structure in a simple inorganic system. The system is obtained by immersing a pellet of calcium and copper chlorides in an alkali solution containing sodium carbonate, sodium iodide, and hydrogen peroxide. The system produces a cell surrounded by a semipermeable membrane. Reactants diffuse and react inside the cell with copper ions serving as catalyst. The products diffuse out of the cell. The system sustains itself far from thermodynamic equilibrium.

Patterns in nature are formed spontaneously in systems which are exposed to energy and matter fluxes. These systems sustain themselves far from thermodynamic equilibria. In these systems, the temporal and spatial structures may appear spontaneously and complexity increases. Experimental studies of these patterns are conducted in chemical reactors where chemicals flow in, react, and flow out. In biological systems, membranes forming the cell separate the system from its surroundings. Chemicals diffuse in and react, and products diffuse out. These constitute examples of systems which are far from equilibrium. Here we report the spontaneous formation of a similar system.

A pellet of calcium chloride (the weight of the pellet is 0.20 g with a diameter of 6.0 mm. The pellet has been prepared using Perkin-Elmer press) immersed in a solution of 1.5 M of sodium carbonate produces a cell surrounded by a semipermeable membrane as shown in Figure 1. This membrane is transparent and elastic.[1,2] The omposition of the membrane may be described as $Ca_x(CO_3)_y(OH)_z(H_2O)_\nu$ and a detailed structure is still unknown. Because of osmotic pressure, water diffuses into the cell, and the cell grows, to about 1.0 cm in diameter. The
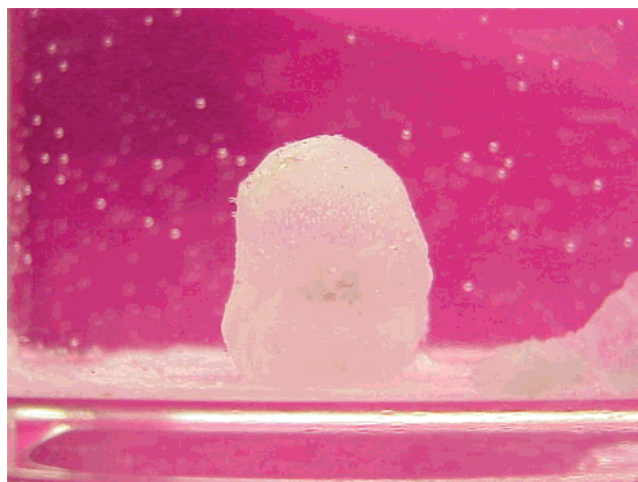
Figure 1. Formation of a membrane when a pellet of calcium chloride is submerged in a solution of 1.5 M of sodium carbonate. The weight of the pellet is 0.20 g with a diameter of 6.0 mm. The picture was taken 1 h after mixing all reagents. The pellet is dissolved and only a membrane surrounding the cell is visible.

cell may produce daughter cells that separate from the mother cell or may form a structure with many cells connected together.

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Figure 2. Formation of a membrane when a pellet of calcium chloride with copper chloride is submerged in a solution of 1.5 M of sodium carbonate containing hydrogen peroxide, sodium iodide, and starch. The weight of the pellet is 0.20 g with diameter of 6.0 mm. The pellet contains 7% copper(II) chloride. The initial concentrations of the reagents in the solution are the following: 0.08 M sodium iodide and 0.08 M hydrogen peroxide. 10 mL of 2% soluble starch solution was added to the solution. The total volume of the system is 250 mL. The violet "clouds" made by the complex of iodine with starch are visible. Copper causes the green color inside the cell. The picture was taken 10 min after mixing all reagents.
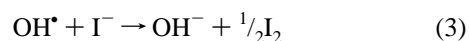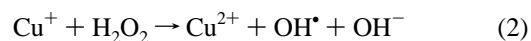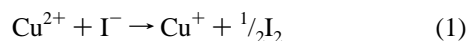
The detailed mechanism of cell growth is unknown. Only recently the initial studies on structures mechanism have been conducted.[3,4] Pictures taken by the Zeiss LSM 510 confocal microscope suggest that when the surface of the cell is broken under internal pressure, the solutions from inside and outside mix producing a new segment of membrane. It has been discovered that water and various small molecules may diffuse easily through the membrane, whereas large molecules, such as ferroin (the complex of iron(II) with 1,10-phenantroline) do not diffuse. The spontaneous formation of cells surrounded by a semipermeable membrane is a crucial step in the origin of life and until now it has only been studied in organic sytems.[5,6] Contrary to these studies, in the system reported here, a cell is formed by common inorganic components. The origin of life starting from inorganic compounds[7-9] as opposed to organic compounds[10,11] should receive increased attention.

If the calcium chloride is doped with copper(II) chloride and the solution also contains sodium iodide and hydrogen peroxide, then the semipermeable membrane is also formed as shown in Figure 2. In this case, we found iodine outside the cell. Starch was added to the initial solution to visualize the formation of iodine, a product of the reaction. If the pellet consists only of calcium chloride, then no iodine formation is observed. The mechanism of iodine formation appears to follow the following steps. The reactants, iodide ions and hydrogen peroxide, diffuse into the cell. They react inside the cell producing iodine and hydroxyl ions. The process is catalyzed by copper(II) ions inside the cell. The products diffuse out of the cell. We cannot also exclude that transport of the reagents and products occurs also due to convection. It is worth noting that the chemical reaction occurs only inside the cell. Elemental iodine is not produced if we form a precipitate by mixing solutions of copper(II) chloride and sodium carbonate and add into it proper amounts of solutions containing sodium iodide and hydrogen peroxide. Moreover, we have not observed the I_2 formation in those experiments when there was no cell formation. These observations support our assumption that iodine is formed inside the cell.
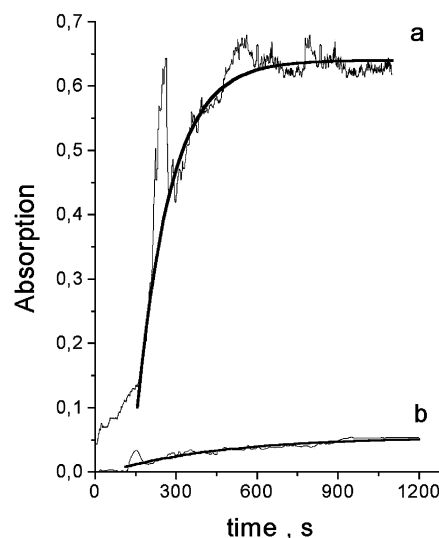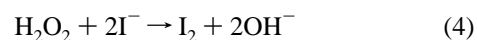

Figure 3. Kinetic curves showing the iodine formation. Recording started after addition of a solution. The initial concentrations of the reagents in the solution were as follows: (a) 0.17 M sodium iodide, 0.17 hydrogen peroxide, (b) 0.17 M sodium iodide. 1 mL of 2% soluble starch solution was added into the solution (volume 24 mL). Absorbance was measured by a CECIL CE2041 Spectrometer at the wavelength of 504 nm. Thin noisy curves represent experimental data. Thick smooth curves give their exponential approximation.

In the simplest way, the chemical transformations inside the cell are the following set of reactions:[12-17]

$$Cu^{2+} + I^- \rightarrow Cu^+ + {}^1\!/_2 I_2 \tag{1}$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + OH^\bullet + OH^- \tag{2}$$

$$OH^\bullet + I^- \rightarrow OH^- + {}^1\!/_2 I_2 \tag{3}$$

The net reaction is

$$H_2O_2 + 2I^- \rightarrow I_2 + 2OH^- \tag{4}$$

According to this mechanism, iodide ions and hydrogen peroxide diffuse into the cell. There, iodide ions interact with copper(II) ions producing elemental iodine and copper(I). Copper(I) reacts with hydrogen peroxide, recovering copper(II) and producing a hydroxyl radical and a hydroxyl anion. The hydroxyl radical reacts with iodide producing more iodine. Finally, iodine diffuses out of the cell. The actual process undoubtedly consists of a larger number of reactions and events leading to iodine production and cell growth. Among them, there are reactions releasing oxygen from hydrogen peroxide and reactions with oxygen catalyzed by copper(II),[15] iodine hydrolysis producing hypoiodous acid and it reactions,[18] and the iodide-catalyzed decomposition of hydrogen peroxide.[19] Details of the whole mechanism may be found elsewhere.[12-19] Particularly, it directly relates to the iodine clock reaction. However, there are two main reactions that are responsible for the whole process: the copper-(II) interaction with iodide and the copper(I) interaction with hydrogen peroxide.

Curve (a) in Figure 3 gives the kinetics for the iodine accumulation measured by the absorption at 504 nm due to the iodine complex with starch. The reaction is characterized by induction time before the appearance of a jump in absorption. The induction time corresponds to the growth and development of the cell. A part of the kinetic curve may be described by first-order kinetics.
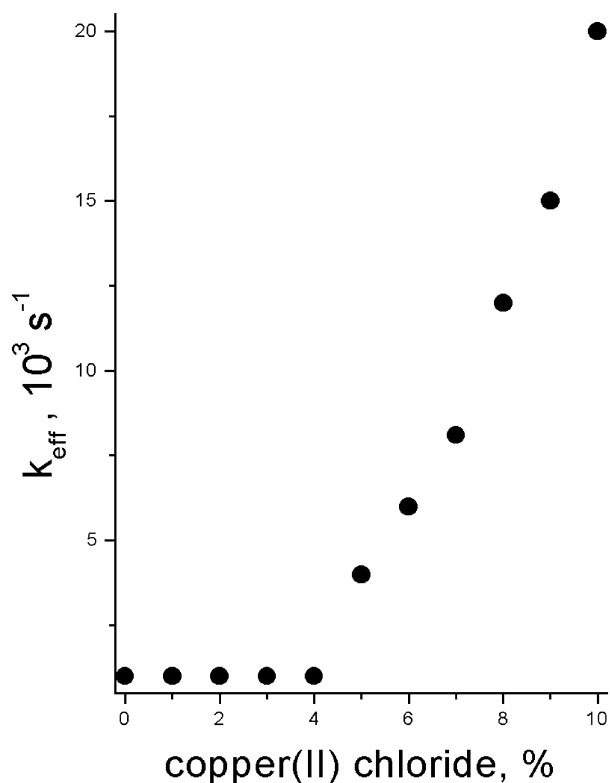
Figure 4. Dependence of the rate constant on a copper concentration in pellet. Experimental details are the same as indicated in Figure 3.

$C(t) \propto A(t) = A_\infty(1 - \exp(-k_{eff}t))$ where $C(t)$ gives the iodine concentration, A is the absorption at time t, and k_{eff} is an effective rate constant. The smooth curve (a) in Figure 3 gives an exponential approximation of the experimental data. Despite the noisy characteristics of the experimental points, the exponential curve gives a relatively good quantitative description. Therefore, the value of k_{eff} characterizes the rate of the chemical process.

As a comparison, curve b in Figure 3 gives the kinetic curve for the system without hydrogen peroxide. The rate of the process is much slower, and the final iodine concentration is an order of magnitude less, compared to the system with hydrogen peroxide. Therefore, atmospheric oxygen affects the system, leading to the production of iodine. However, the amount of iodine and the rate of its accumulation are negligible compared to the system containing H_2O_2.

According to the chemical reactions described, the value of k_{eff} would be expected to be proportional to the catalyst concentration. Therefore, the value of k_{eff} should increases with an increase of the copper content in the pellet. This agrees with the experimental results shown in Figure 4. These data indicate of the existence of a threshold for the copper(II) contamination in the pellet below which the rate of the iodine production is comparable to the system without hydrogen peroxide. Possibly, the appearance of such a threshold is a consequence of complex kinetics for the chemical process as well as for the cell growth.

Our studies show, for the first time, an example of the heterogeneous chemical composition that exhibits spontaneous formation of a cellular system that sustains far from thermodynamical equilibrium. We produced this system by submersing a pellet containing calcium and copper(II) chlorides into a sodium carbonate solution that also contains sodium iodide and hydrogen peroxide. Our chemical system is constructed from two subsystems: (1) a pellet containing calcium and copper chlorides submersed into a sodium carbonate solution producing a cell with a semipermeable membrane and (2) oxidation of iodide ions by hydrogen peroxide catalyzed by copper(II) ions. The evolution of the first subsystem produces a separate compartment in a chemically reactive medium in such a way that it creates a flux of reagents into the cell. The catalytic process occurs into the cell, and products diffuse outside. Therefore, the system maintains by itself the flux of energy and chemicals and is sustained far from thermodynamic equilibrium. This system may produce multicellular chemical structures, and separation of daughter cells form the mother cell has been observed. It is probable that a variety of inorganic systems could be constructed showing the same kind of behavior that we reported here. The spontaneous formation of cellular chemical systems that are sustained far from equilibrium may be an important step in understanding the possibility of the formation of different forms of life on other planets under other conditions.[20]

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