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Ion-Selective Membranes Involved in Pattern-Forming Processes

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The ability of simple inorganic reactions such as NaOH + $CuCl_2$, NaOH + $AgNO_3$, and $CuCl_2$ + $K_3[Fe(CN)_6]$ to form various complex precipitation patterns has recently been discovered. When the first reagent penetrates into a hydrogel by diffusion and reacts with the second reagent homogenized in the gel, a precipitate is built up that has two kinds of bordering surfaces with different properties. Our experimental results suggest that one of these surfaces is permeable, while the other one is an ion-selective membrane that restrains the diffusion of the first reagent's reacting ion, preventing the reactions from proceeding ahead of the membrane. The presence of an intermediary compound, the precursor of the precipitate, is observed in the front of the permeable surface.

Introduction

The formation of precipitate patterns in the wake of moving diffusion fronts has been widely studied in the past decades.[1] Special attention has been paid to Liesegang banding, in which one of the reagents, the outer electrolyte, penetrates into a hydrogel containing the inner electrolyte. When the experiments are conducted with certain simple inorganic reagents, a series of precipitate bands emerge in the gel behind the diffusion front of the outer electrolyte.[2−5] These reactions are seen as prototypes for the nucleation and growth of colloids. The investigations have also been motivated by the hope of obtaining a regular grid of precipitate sheets, with a wavelength on the order of micrometers.[6]

However, precipitation membranes or thin films were described more than a century ago. According to the experiments of Traube,[15] when a drop of copper sulfate solution is brought into contact with a drop of potassium ferrocyanide solution, a thin layer of reddish-brown copper−ferrocyanide precipitate forms at, and blankets, the entire boundary. After that, no further formation of precipitate occurs. Thus, the thin layer of precipitated material formed between the two drops of solutions has halted further passage to the other side of the copper ion as well as the ferrocyanide ion. By allowing the copper ferrocyanide precipitate to form within the wall of an unglazed porcelain cylinder, Pfeffer[16] transformed Traube's fragile layer of copper−ferrocyanide precipitate into a membrane strong enough to withstand not only routine handling but even unilateral application of mechanical pressure. This membrane was permeable to water, but not to sugar; therefore it was named a "semipermeable" membrane. However, as it was already emphasized by Nernst,[17] copper ferrocyanide membranes are permeable for several chemical substances, for example, nitrates, hydrochloric acid, and many pigments.

Recently, new precipitation reactions have been discovered that can yield a great variety of spatial patterns, observed previously only in more complex chemical systems.[7−10] Reactions such as NaOH + $CuCl_2$, NaOH + $AgNO_3$, and $CuCl_2$ + $K_3[Fe(CN)_6]$ were studied in a Liesegang-like setup, with the first reagent as the outer electrolyte, and the second one as the inner electrolyte homogenized in a hydrogel. When the reactions are run in gel columns, they are able to build up, among others, spirals and concentric cones of precipitate, called primary patterns. The first two reactions in PVA (poly(vinyl alcohol)) gel medium can also result in regular grids and sheets of precipitate with small wavelengths, even on the order of 10 μm, termed secondary patterns.[8]

By running the reactions in gel sheets, it is possible to follow how the basic building elements of the primary patterns emerge (Figure 1). The diffusion front of the outer electrolyte is followed by a sharp precipitation front. If some impurities or inhomogeneities are present on the gel surface or inside the gel, the precipitation may not start or may cease at these points. As the staggered precipitation front proceeds, these centers expand into wedgelike regions free of precipitate (Figure 1a). The reaction does not proceed on the oblique borders that separate the already formed precipitate from the wedgelike empty regions. These stationary surfaces are referred to as the passive borders, while the precipitation front segments as the active borders of the precipitate region. The shrinking precipitation front segments gradually vanish, and the lower limit of the precipitate will be a zigzag-shaped passive border (Figure 1b). Reactions such as NaOH + $AgNO_3$ and $CuCl_2$ + $K_3[Fe(CN)_6]$ running in gel layers thicker than about 1 mm stop at this point,[10] but in some others, like NaOH + $CuCl_2$, new precipitation fronts may develop later, at the top of the wedgelike empty regions.[7]

In this paper, experimental results are presented that clarify some main steps of the pattern-forming process. The passive borders turned out to be semipermeable (ion-selective) membranes. These membranes restrain the passage of those ions of the outer electrolyte that react with the inner electrolyte to build

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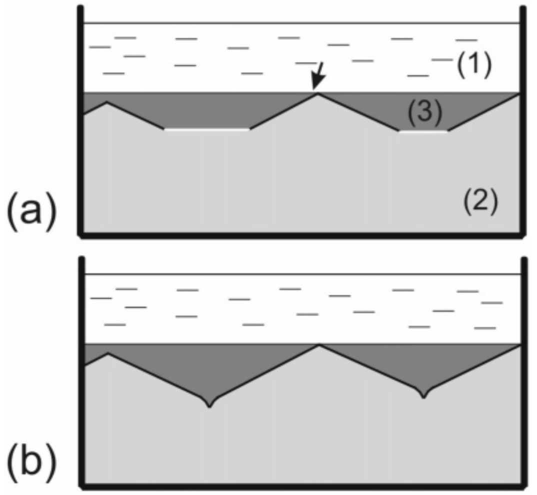

Figure 1. Formation of the basic building element of primary patterns in gel sheets. The outer electrolyte (1) penetrates into the gel containing the inner electrolyte (2), and precipitate (3) is forming. Passive borders are marked by black, while the active ones are marked with white lines. (a) Precipitate delimited by active and passive borders. Reactions are proceeding only on active borders. A point where precipitation did not start at all is denoted by an arrow. (b) The reactions ceased; the precipitate is delimited below by a continuous passive border.

up the precipitate. As a consequence, the reaction cannot proceed ahead of the passive borders. Because the active borders are permeable to these ions, they will cross these surfaces, and reactions will take place ahead of them. In the NaOH + $CuCl_2$ process, where the precipitation can restart ahead of the passive borders, these might be slightly leaking or may become damaged. Our results also confirmed that the reaction yields first a diffusive intermediary compound, which is supposed to be the precursor of the precipitate.

Note that computer simulations of mathematical models based on the above experimental findings reproduced the main features of pattern formation.[11]

Materials and Methods

Agarose gel (2% w/w) was prepared by adding agarose powder to high-purity water at room temperature. Solubilization was achieved by stirring the mixture for 1−2 min at 70−80 °C. The inner electrolyte concentration was set by adding an appropriate amount of concentrated inner electrolyte solution at 30−40 °C to 100 mL of agarose solution. The amount of the mixture was increased to 200 mL using high-purity water at 50−60 °C. After vigorous shaking, certain amounts of the above mixture were poured and allowed to cross-link in the experimental setup. Gelation took place when the mixtures were allowed to cool to room temperature, except when the inner electrolyte was $AgNO_3$. In the latter case, the process took a longer time, and at concentrations above 1 M, cross-linking did not take place at all.[10]

PVA gel was made as follows. 8.6% w/w PVA solution was prepared by adding PVA powder to high-purity water under continuous stirring at 70−80 °C for 4 h, and then it was allowed to cool to room temperature. The inner electrolyte concentration was set by adding to 100.0 mL of the resulting PVA solution an appropriate amount of concentrated inner electrolyte solution. The acidity and degree of cross-linking of the gel were set by adding 2.00 mL of 18.50% w/w HCl and 1.00 mL of 1.0 M glutaraldehyde to the above mixture. High-purity water was used to top off the solution to 200.0 mL. After a strong mixing, the air bubbles were driven out by ultrasonication for 10−20 s. Certain amounts of the mixtures were poured and allowed to cross-link in the experimental setup. The gelation took place in about 1−3 h.

The reactions were started by layering the outer electrolyte on the top of the gel (Figure 1). The chemicals used were as follows: agarose (SeaKen ultralow EEO), poly(vinyl alcohol) (Merck, Z.S.), glutaraldehyde (Merck, Z.S.), HCl (Carlo Erba, Z.S.), $AgNO_3$ (Reanal, A.R.), NaOH (Reanal, A.R.), $CuCl_2$ (Reanal, A.R.), and $K_3[Fe(CN)_6]$ (Merck, Z.S.).

Results

Long-Lasting pH Gradients Confirm the Restraining Properties of the Passive Borders. As mentioned previously, in the NaOH + $AgNO_3$ reaction, no precipitation takes place ahead of the passive borders, while in the NaOH + $CuCl_2$ system, the restarting of the precipitation is also delayed.

Because in the NaOH + $AgNO_3$ and NaOH + $CuCl_2$ systems the OH^- radical is the reacting ion of the outer electrolyte, it is plausible to assume that the precipitation ceases because the passive border restrains the crossing of the OH^- ions. To confirm this hypothesis, simultaneous measurements of pH on both sides of the passive border were performed in the following experimental setup. The gel containing the inner electrolyte was located between two 83 × 102 mm glass plates held 3 mm apart, the inner part of the first plate being covered by a polyethylene film. The outer electrolyte was layered on the gel (Figure 2a). In a certain stage of the experiment, after removing the outer electrolyte, the first plate could easily be taken away. By gently stripping the plastic foil, the surface of the gel could be revealed, and indicator paper was placed on the naked gel surface in such a manner that it touched both sides of the passive border. Drying of the gel is not significant in the time scale of the pH measurements (about 5 min).

In the case of the NaOH + $AgNO_3$ reaction, precipitation ceases after the passive border covers the entire lower surface of the precipitate. The pH measurement was performed about 14 h after the reaction stopped (Figure 2b). Because the pH did not equalize during this time, it is reasonable to assume that the passive border slows significantly the diffusion of the pH-determining ions. Note that in the course of the revealing, the passive border may have been damaged and the precipitation process can restart along it, but this has a minor effect on the results of the, relatively quick, pH measurements.

The NaOH + $CuCl_2$ reaction does not stop after the first complete layer of passive border is formed. The reason new precipitation fronts can arise below the passive borders is presently unknown; perhaps the passive borders are slightly leaky or are damaged at some points. In the first hour of the reaction, precipitation restarts along the passive borders in ca. 10 min. Approximately 3 h later, long segments of passive borders were present in the gel, and these remain free of precipitate for several hours. The pH measurements performed on this system showed as well that a pH gradient between the two sides of the passive border lasted at least for 4 h (Figure 2c).

Permeability of the Membranes: Conductance and Impedance Measurements. The above experiments indicated that the passive borders should restrain further passage of at least the pH-determining ions in the case of the NaOH + $AgNO_3$ system. It is plausible to assume that, in the case of the $CuCl_2$ + $K_3[Fe(CN)_6]$ system, the passage of copper ions is restricted by the passive border (visual observations also support this assumption).

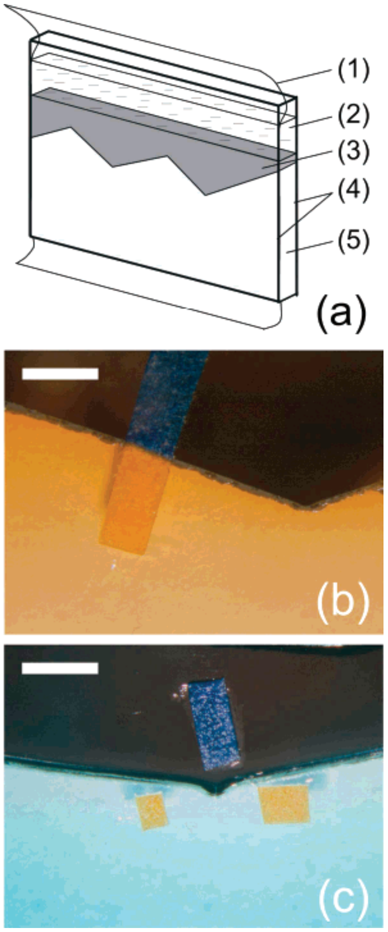

Figure 2. Measuring the pH difference between different sides of passive borders. The outer electrolyte is highly basic, while the inner electrolyte is slightly acidic. (a) Experimental setup: (1) polyethylene film, (2) outer electrolyte, (3) precipitate, (4) glass plates, and (5) gel containing the inner electrolyte. The investigated reactions were 8 M NaOH + 0.647 M $AgNO_3$ in agarose gel (b), as well as 4 M NaOH + 0.586 M $CuCl_2$ in agarose gel (c). The indicator paper has an orange color at slightly acidic, and a dark blue color at strongly basic pH. It is shown that the strongly basic NaOH solution impregnates the precipitate, but cannot pass the passive border that "protects" the gel region containing the inner electrolyte. Scale bars = 3 mm.

However, it is unclear at this point whether the passive borders are completely insulating membranes or restrain the diffusion of some kinds of ions only. Such questions can be answered by measuring the resistance (or conductance) of an appropriate gel segment with a passive border occupying the whole cross section of it: a high resistance indicates a completely insulating membrane; a low resistance indicates that some ions can cross the passive border.

For the electrochemical experiments, those chemical systems (NaOH + $AgNO_3$ and $CuCl_2$ + $K_3[Fe(CN)_6]$) were selected in which the reactions stop as the passive border covers the entire bottom part of the precipitate. The experimental setup for the electrochemical measurements was built up as follows. The gel column, having a height of about 2 cm, was located in a Petri dish of 5 cm diameter, made of transparent plastic. Special care was taken on the cleaning of the plastic Petri dish. The bottom of the dish contained a hole of 3 cm diameter. When the initial mixture was poured into the dish, the hole was closed with a polyethylene film. After the cross-linking took place, the film was removed, and the dish containing the gel was settled into a pot with larger diameter that contained an inner electrolyte solution with the same concentration as in the gel.

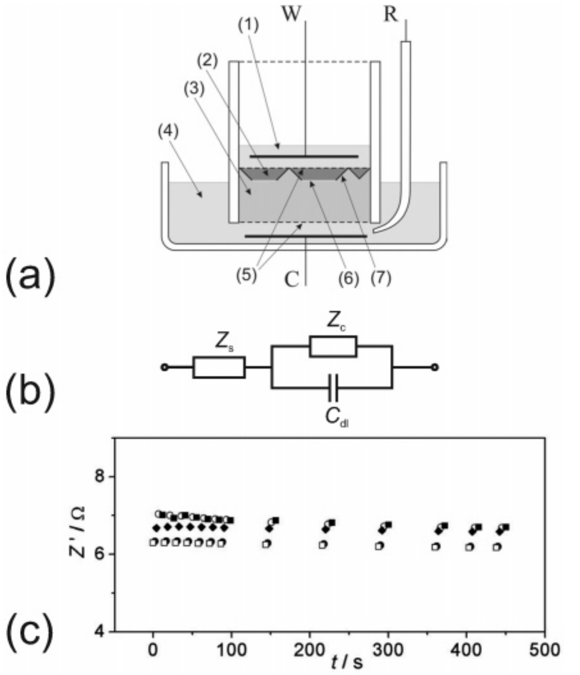

Figure 3. (a) Schematic picture of the experimental setup used for impedance measurements. W, working electrode; R, reference electrode; C, counter electrode. (1) Solution of the outer electrolyte, (2) precipitate, (3) gel containing the inner electrolyte, (4) solution of the inner electrolyte, (5) boundaries of the gel, (6) active border, (7) passive border. (b) Equivalent circuit representing the impedance of the system. C_{dl}, double-layer capacitance; Z_c, charge-transfer impedance; Z_s, the impedance corresponding to the conduction process. (c) Results of impedance measurements carried out at the equilibrium potential of the Cu working electrode on 2.93 M $CuCl_2$ + 0.12 M $K_3[Fe(CN)_6]$ system in agarose gel. Z', real part of the complex impedance at different frequencies: □, 10.09 kHz; ●, 788.5 Hz; ◆, 65.71 Hz; ○, 5.97 Hz; ■, 0.5 Hz. The duration of a single frequency scan was 14.4 s, and each impedance value is assigned to the time of the completion of the measurement at the corresponding frequency.

In Figure 3a, a typical experimental setup used for impedance measurements is shown. In most experiments, an electrochemical cell consisting of a working electrode (W), a counter electrode (C), and a reference electrode (R) connected to an Autolab PGSTAT 20 electrochemical system (potentiostat + FRA module) was used. However, in some cases, the reference electrode was directly connected to the counter electrode (to check the results also in the "two-electrode" mode). In the three-electrode arrangement, in the case of the $CuCl_2$ + $K_3[Fe(CN)_6]$ system, a disk-shaped copper plate with a diameter of 3 cm was used for the working electrode, a platinum disk was used for the counter electrode, and a saturated calomel electrode (SCE) served as a reference. Figure 3a shows that gel layers with and without the precipitate, the corresponding active and passive borders, and solution layers are located between the working electrode and the reference electrode.

Using the above setup, the "total" impedance of the system (the impedance of the working electrode + the impedance of the different layers, borders, and conducting phases between the working and the reference electrode) can be measured as a function of the frequency of a sinusoidal perturbing signal.[12−13] The equivalent circuit representing the impedance of the above system is presented in Figure 3b. According to this model, a charging current and a current corresponding to the "faradaic" processes at the working electrode pass the metal/solution interface, while the total current is conducted by the electrolyte in the adjoining phases. The impedance elements corresponding to these processes are the double-layer capacitance (C_{dl}), the charge-transfer impedance (Z_c), and the impedance of the conduction process (Z_s). In the most simple cases, Z_s and Z_c are pure ohmic resistances (R_s is the "solution resistance", and R_c is the "charge-transfer" or "polarization" resistance). On the basis of the above consideration, one can realize immediately that the resistance of the precipitate membranes is included in R_s in the equivalent circuit.

In Figure 3c are presented results of impedance measurements carried out at the equilibrium potential of the Cu working electrode. By repeating the frequency scans continuously (and sufficiently fast), the time evolution of the impedance after contacting the reacting solutions also could be followed. The frequency scans were started immediately after the outer electrolyte was layered on the top of the gel, and were finished when the passive border covered the entire lower surface of the precipitate. The impedance was measured during each scan at six discrete frequencies over a frequency range from $f = 0.5$ Hz to $f = 20$ kHz, applying a sinusoidal perturbing signal (amplitude: 10 mV). It can be seen that the Z' real parts of impedances are always relatively small ($<7\ \Omega$), and the values measured at $f = 10$ kHz and $f = 788.5$ Hz, which can be identified unequivocally with the R_s resistance of the solution and precipitation/gel phases between the working and the reference electrode, are practically independent of time during the evolution of the precipitation patterns in the gel.

We obtained similar results for the resistance of the system on the basis of polarization curves, as well. These measurements were performed when the reactions were over and the bottom passive border was complete.

The results of the electrochemical measurements indicate that, in the case of the $CuCl_2 + K_3[Fe(CN)_6]$ system, neither the borders nor the precipitation phases behind them are insulating. Similar results were also obtained for the $NaOH + AgNO_3$ system.

Microspectrophotometry Indicates the Presence of the Precipitate's Precursor Ahead of the Active Borders. In a previous work,[9] several arguments were listed supporting the hypothesis that the precipitate forms from a precursor referred to as the diffusive intermediary compound, that is present ahead of the active borders.

In this section, results of microspectrophotometric measurements are presented demonstrating the existence of a compound ahead of the active borders that is supposed to be the diffusive intermediary compound. Assuming that the passive borders halt the diffusion of the reacting ions contained by the outer electrolyte, the explanation of the spatial distribution of this compound becomes straightforward: the reagents can meet in high enough concentrations, and react, only ahead of the active borders.

Spectral absorption measurements were made from small areas at small spatial intervals across the active border. The measurements were performed with the $NaOH + CuCl_2$ reaction in PVA gel, because the hypothetical diffusive intermediary compound was assumed to have absorbance in the visible range.[14]

First, a gel layer of about 0.2 mm thickness was prepared between a microscope slide and a cover glass. This was achieved by putting some droplets of the initial mixture on the slide, covering it with a cover glass, and letting it cross-link in this setup. Between the slide and the cover glass, two splinters of a cover glass were placed as spacers. The reaction was started by placing some droplets of NaOH on an edge of the gel sheet. The droplet was covered by another cover glass to avoid its evaporation.

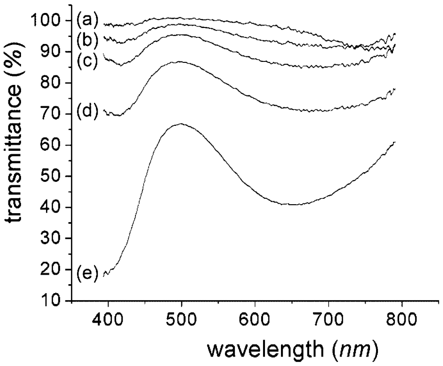

Figure 4. Microspectrophotometric measurements on 8 M $NaOH$ + 0.586 M $CuCl_2$ in PVA gel. Curve (a) represents the spectrum of regions far from the precipitation front, where the limit of the measuring beam was at 180 μm from the front itself. Here, only the inner electrolyte is present. Curves (b), (c), and (d) were measured closer to the precipitation front (75, 45, and 24 μm, respectively), where traces of a new material can be observed. Curve (e) is the spectrum of the blue-green precipitate in the wake of the precipitation front.

The measurement system consisted of an Olympus BHB compound microscope fitted with a camera port. The sample was mounted on the microscope stage and illuminated using standard bright field illumination. The sample was viewed with a 10× NA 0.25 Olympus PL10 objective which enabled the advancing precipitation front to be imaged via 10× eyepieces, one of which was fitted with a graticule. The ocular graticule allowed the user to determine the position on the preparation of the projected image of a 500 μm diameter fiber optic which was mounted in the center of the camera port. Light from a 50 μm diameter area of the precipitation front was thus collected by the fiber optic, which terminated in an Ocean Optics USB2000 miniature spectrometer. Spectral measurements were made in the range 400−800 nm, the data being recorded with Ocean Optics OOIBase32 software. Spectral measurements were made of the system dark current by occluding the fiber optic ("dark" measurements), a gel layer that does not contain the reagents, having the same thickness as the sample, (the "baseline"), as well as the sample itself. Absorbance data were calculated as the negative decadic logarithm of the spectral transmission, the latter being calculated at each wavelength as (sample-dark)/(baseline-dark).

Spectral absorbance measurements were started when the precipitation front (the active border of the precipitate region) was about 200 μm from the measuring light beam. At this point, only the spectra of the $CuCl_2$ could be observed (Figure 4). The front was approaching the measuring area at a speed of about 0.7 μm/s, and thus its distance from the beam decreased with time. The spectrum changed significantly when the distance decreased below about 80 μm. Although the spectrum is too simple for determining the character of the underlying chemical compound, it clearly indicates the presence of a compound that is different from the reagents. Here, we mention that no precipitation (formation of secondary patterns[8]) took place ahead of the active border.

As the front overtook the measuring light beam, the spectrum of the precipitate, having a blue-green color and assumed to be mainly $Cu(OH)_2$, could be recorded. This spectrum shows similarity with that measured ahead of the front. Note that 7−8 min after it has been formed, the blue-green precipitate decays in brown CuO, but this last step has no influence on the process of pattern formation.[8]

This experiment also confirmed the hypothesis that the bulk precipitate does not halt the diffusion of the outer electrolyte's reacting ion, and neither does the active border.

Other Experimental Findings. Two further experimental findings also support the tightly closed structure of the passive borders.

Dissolving by EDTA (ethylene-diamine-tetraacetate) the final CuO precipitate formed in the NaOH + $CuCl_2$ reaction in PVA gel, we could observe the trace of the passive borders even by the naked eye as opalescent surfaces. This indicates that the gel structure is getting damaged when the passive borders build up. In addition, when the reactions are over, the gel breaks more easily along the trace of the passive borders.

Consequences of damaging the passive border while the reaction is running were also examined. When the passive border was mechanically cut, or destroyed by a strong laser beam, new precipitation fronts started but soon were passivized, probably because the inhomogeneities generated during the damaging act as centers where new passive borders can start. When a small gel segment, crossed by a passive border, was replaced by a piece of gel containing only the inner electrolyte, a new precipitation front started at that region.

Discussion

In this paper, a series of experimental results were presented suggesting that the passive borders of the precipitated regions in the NaOH + $CuCl_2$, NaOH + $AgNO_3$, and $CuCl_2$ + $K_3[Fe(CN)_6]$ reactions running in a Liesegang-like setup are semipermeable (ion-selective) membranes, and precipitation is preceded by the formation of a precursor that is present ahead of the active borders. Although not all of the above chemical systems were subject to all of the three experiments presented above, their similar behavior allows the generalization of the results.

Our experimental results suggest that a class of precipitates, among others the copper−ferricyanide, can have two kinds of borders, one of them selectively restraining the passage of some ions, while the other border, as well as the bulk precipitate, does not prohibit diffusion. The microscopic structure of these borders is the subject of intensive research. These investigations have to reveal the mechanism of the ion-selectivity, as well as the reason the precipitation easily restarts ahead of the passive borders of the NaOH + $CuCl_2$ reaction. The results could lead to the practical applications of the precipitates formed in the reactions discussed above.

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