# Direct observation of a crossover from heterogeneous traveling wave to Liesegang pattern formation

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a part of this stabilization is offset by the exchange repulsion that arises between the central ion pair and the neighboring ions. However, the repulsion has been shown above to be attenuated rapidly at a distance longer than 2.6 Å. The electrostatic interaction between ion pairs should be less significant in a covalent structure. Thus, interactions with environment are suggested to be another important source of stabilizing an ion-pair electron configuration.

**Conclusion**

From the discussion presented above, it is suggested that hydrocarbon ion pairs are more likely to be in a certain locally symmetric structure in which the HOMO (or high-lying occupied MOs) of an anion and the LUMO (or low-lying unoccupied MOs) of the cation do not overlap at the center of interactions. Large substituent groups may be useful in preventing a cation and an anioin by steric hindrance from forming an $sp^3$ addition product. Substituents will lower the HOMO level of an anion and elevate the LUMO level of a cation by conjugation to favor ion pair structures. Ion-pair structures will be stabilized if a system has electron-transferred configurations that yield large matrix elements with the lowest ion-pair electron configuration and close in energy.

The stability of anions may be discussed in a similar manner. A stable anion $CF_3^-$, for instance, has a large negative $\lambda_{oc}$ and the $CF_3^- - C_3H_3^+$ system in $C_{3v}$ symmetry has been shown to give a lower energy for $\Phi_0$ than for $\Phi(HOMO$ of $CF_3^- \rightarrow LUMO$ of $C_3H_3^+)$ for a range of $R = 2.2–2.9$ Å.

In the actual systems, cations and anions bear large substituent groups, and therefore a number of MOs come into play in interactions being spaced closely with each other. To analyze interactions around reactive sites and hopefully to design cations and anions of a desired reactive trend, we should focus our attention on the local characteristics of chemical interactions. A way of looking at interactions by means of paired interacting orbitals in the MO calculations for the composite interacting systems and a method of generating the occupied or unoccupied reactive orbitals for isolated cationic and anionic species will provide convenient tools for such purposes.

# Direct Observation of a Crossover from Heterogeneous Traveling Wave to Liesegang Pattern Formation

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A study of Liesegang band formation is presented with emphasis on the dependence of the precipitation pattern on its solubility. The formation of $Cr(OH)_3$ precipitate has been studied by diffusing NaOH into chemically cross-linked poly(vinyl alcohol) gel containing $Cr(NO_3)_3$. The precipitate can sparingly redissolve in the surplus of NaOH. The formation, together with the dissolution of the precipitate, coupled with diffusion leads to a propagating band, instead of a final static pattern. A crossover from traveling band to Liesegang pattern formation has been also observed. A model, based on reaction–diffusion phenomenon, allows us to correlate the band movement with various kinetic and chemical processes.

**Introduction**

Periodic precipitation[1,2,5] and oscillations[3] are the most frequently studied examples of chemical pattern formation due to the coupling of reaction with diffusion.[2,4]

When an electrolyte diffuses into a gel containing another electrolyte, the formation of rhythmic pattern of precipitate is known as the Liesegang phenomenon.[1,5] A weakly soluble salt is formed as a result of diffusion and a chemical reaction that yields precipitates in the form of bands parallel to the front of the diffusing electrolyte. The nature of precipitation does not play an important role in the onset mechanism. The gel may influence some structural details, but is is not essential for pattern formation. It prevents convection and sedimentation of the solid phase.

In 1952 Turing proposed a chemical basis for the stationary space periodic concentration patterns.[2] The Liesegang band formation may be considered as a possible physical example of the Turing phenomenon. Another extensively investigated example of chemical pattern formation is the oscillatory Belousov–Zhabotinskii reaction, which exhibits spatial inhomogeneities that can lead to the formation of static and dynamic patterns of immense complexity. Besides the stationary space periodic concentration patterns, chemical wave propagation presents one of the most

interesting phenomena.[3,7–9] A number of phenomenological observations and measurements on the kinematic properties have been collected and discussed theoretically in some detail.[3] An important distinction must be made between the chemical waves and Liesegang band formation. The patterns envisioned by Turing were stationary structures, not moving waves. Thus Turing's ideas seem to be irrelevant to the Belousov–Zhabotinskii reactions. Although the mechanism of pattern formation is thought to be completely different if one consider the heterogeneous Liesegang band formation and homogeneous steady chemical waves, from the phenomenological point of view, both can result in very similar stationary periodic structures. A certain similarity between the

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two phenomena has been emphasized by Flicker and Ross.[6] Up to now, traveling waves have been found to occur for homogeneous systems only.[3,7,8]

This paper presents a direct observation of a heterogeneous traveling wave. A crossover from moving prcipitate band to Liesegang pattern formation is also evidenced. A model is introduced to interpret some of the experimental results.

## Experimental Section

*Materials and Sample Preparation.* We have studied the formation of white chromium hydroxide precipitate, by diffusion of sodium hydroxide (Reanal, Hungary) into chemically cross-linked poly(vinyl alcohol) (Merck, FRG) gel containing chromium nitrate (Reachim, USSR).

The following reaction occurs when the spatially separated reactants come into contact:

$$Cr^{3+} + 3OH^- = Cr(OH)_3 \tag{I}$$

The $Cr(OH)_3$ precipitate can, to some extent, redissolve in the surplus of NaOH, providing soluble material of green color:

$$Cr(OH)_3 + OH^- = [Cr(OH)_4]^- \tag{II}$$
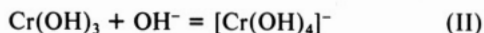
The highly swollen poly(vinyl alcohol) (PVA) gels were prepared by cross-linking of PVA chains with glutardialdehyde (GDA) (Merck, FRG) in aqueous solution, containing dissolved $Cr(NO_3)$, at 298 K according to a previously described method.[13] In all cases, the ratio of monomer unit of PVA [VA] to the cross-linking agent GDA was kept constant: [VA]:[GDA] = 242:1. The cross-linking reaction was catalyzed by nitric acid (Carlo Erba, Italy), providing pH = 1.

It is important to mention that, due to the presence of catalyst, partial neutralization of NaOH takes place parallel to reactions I and II. The aqueous solution of PVA, GDA, $Cr(NO_3)_3$, and $HNO_3$ was stirred, and then it was poured into sealed glass tubes. The gelling process usually took 3–4 h. After the completion of gelation, NaOH solution was used to fill the space above the gel. The ratio of the liquid and gel phases was always kept constant. The tubes were sealed and allowed to stand undisturbed at 300 K in a thermostat for several days. The concentration of $Cr(NO_3)_3$ in the gel phase varied between 5 and 125 mmol/dm$^3$. The concentration of NaOH solution diffusing into the gel was altered between 0.03 and 2.77 mol/dm$^3$. The polymer content of PVA gel was, in every case, 3.2 mass %. It must be mentioned that the experimental setup did not allow us to maintain the constancy of the boundary conditions. A small change in the NaOH concentration above the gel took place as a result of diffusion.

*Experimental Results.* A zone of reaction occurs at the interface when reactants come into contact by diffusion. The penetration of NaOH into the gel containing $Cr(NO_3)_3$ results in a sharp boundary interface of $Cr(OH)_3$ precipitate. This sharp boundary layer propagates throughout the gel. At the beginning of the experiment, due to the moving reaction front, the width of white band, containing $Cr(OH)_3$ precipitate, gradually increases up to a certain value and then remains constant. The surprising result is that instead of a Liesegang pattern, a dynamical system develops. After a certain time, one observes not only advancing but also receding boundary surface of precipitate. This latter is probably due to the redissolution of $Cr(OH)_3$ in the surplus of NaOH, which continuously diffuses into the gel. The precipitate band redissolves on one side and grows on the other; thus for the observer it seems to be moving. The advancing boundary layer corresponds to the $Cr(NO_3)_3/Cr(OH)_3$, while the receding one corresponds to the $Cr(OH)_3/Na[Cr(OH)_4]$ interface.

The formation and redissolution of precipitate coupled with diffusion leads to a propagating band, instead of a static Liesegang pattern. This phenomenon was predicted by Henisch[1,11] when Fick's diffusion equation or reagents in gels was solved by numerical methods. The thickness of the moving band was found to be constant within experimental error (Table I). The propagating spatial inhomogeneity in the concentration of intermediate

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**TABLE I: Dependence of the Width of the Traveling Band on the Concentration of $Cr(NO_3)_3$ Electrolyte in the Gel**

| $[Cr(NO_3)]/mmol/dm^3$ | $[NaOH]/mol/dm^3$ | $d/mm$ |
|---|---|---|
| 10 | 2.0 | no band[a] |
| 40 | 2.0 | 4.7 |
| 80 | 2.0 | 3.8 |
| 125 | 2.0 | 2.1 |

[a] A traveling band with increasing width can be observed only the first day. Then it disappears and a continuous zone moves toward.
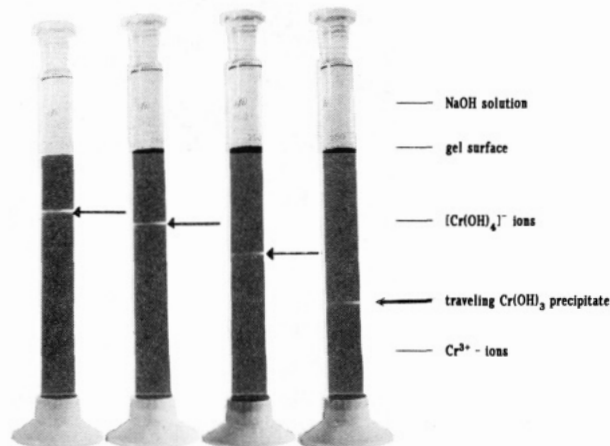


**Figure 1.** Traveling band of $Cr(OH)_3$ precipitate in PVA gel seen at different times: from left to right 2nd, 3th, 6th, and 12th day. The arrow indicates the temporary position of the moving precipitate band. $[Cr(NO_3)_3] = 0.10$ mol/dm$^3$, $[NaOH] = 2.00$ mol/dm$^3$.

species $Cr(OH)_3$ can be considered as a heterogeneous traveling wave.

Figure 1 shows the simplest experimental setup with the propagating $Cr(OH)_3$ band. It is worth mentioning that the stability of traveling concentration wave is maintained during the process investigated. When the band approaches roughly two-thirds of the gel column, it often disappears. In most cases, the moving bands have passed more than 10 cm before coming to an end. It is noted that the longest distance that a heterogeneous traveling wave passed was 130 cm. We have measured the position of the propagating band as a function of time. The velocity of the band turned out to be not constant as in the case of homogeneous traveling wave.[3] The propagation of $Cr(OH)_3$ band keeps on slowing down until it disappears. There is reason to suppose that, if the chemical reaction is much faster than the diffusion itself (the sharp boundary is usually thought to be the manifestation of this assumption[10]), then the boundary interface moves into the gel according to the simple relation

$$\xi^2 = const \times t \tag{1}$$

where $\xi$ represents the distance of advancing boundary layer measured from the surface of the gel at time, $t$.

In Figure 2 $\xi^2$ is plotted against $t$ for some representative experiments. It seems that only a certain range can be approximated by the $\xi^2 \sim t$ law.

Taking into consideration that at least three chemical reactions take place, each coupled with diffusion, it is doubtful whether such a simple solution of the problem hitherto considered can be given. In addition to the chemical complexity, the influence of finite dimension effect, as well as the continuous change in the boundary conditions, is also felt.

It is important to mention that the velocity of moving bands was found not to depend on the direction; that is, gravitational effects can be excluded.

We have found that both $Cr(NO_3)_3$ and NaOH concentrations affect the speed of the traveling band. However, no simple dependence can be reported. In most cases an increase in $Cr(NO_3)_3$ concentration results in slower movement. The sharpness of boundary layers seems to be slightly influenced by the concentration of $Cr^{3+}$ ions in the gel. The width of the bands definitely
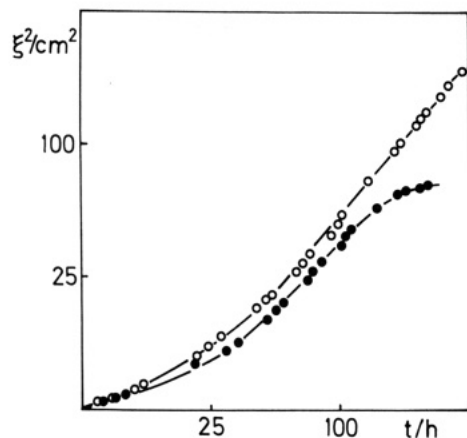
**Figure 2**. Square of displacement of bands as a function of time: (O) [Cr(NO$_3$)$_3$] = 80 mmol/dm$^3$, [NaOH] = 2.00 mol/dm$^3$; (●) [Cr(NO$_3$)$_3$] = 125 mmol/dm$^3$, [NaOH] = 2.00 mol/dm$^3$.
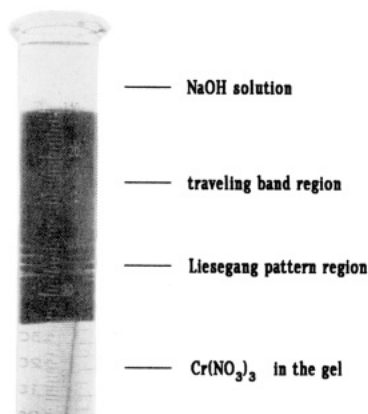


**Figure 3**. Liesegang band region of a representative sample. [Cr(NO$_3$)$_3$] = 30 mmol/dm$^3$, [NaOH] = 0.75 mol/dm$^3$.

decreases when the Cr(NO$_3$)$_3$ concentration is increased in the gel. This dependence is given in Table I.

One of our most important findings is that, at certain concentrations of Cr(NO$_3$)$_3$, not only a heterogeneous traveling wave but also a Liesegang pattern develops. At the beginning of the experiment a band of Cr(OH)$_3$ precipitate begins to move. After a certain distance (~4.5 cm) the band comes to an end. This process took roughly 4$^1/_2$ days. After another 4 days a continuous zone propagated, ~1.5 cm long. Then a Liesegang pattern started to develop. In the Liesegang region definite primary precipitation patterns can be seen. Figure 3 shows a photograph from the Liesegang band region of a representative system.

## Analytical Formulation of the Problem

The phenomenon can be described by a set of reaction–diffusion equations.[12] The most important equations are the following:

$$\frac{\partial a}{\partial t} = D_a \nabla^2 a - 3k_1 a^3 b - k_2 a - k_3 ac + k_4 e \quad (2a)$$

$$\frac{\partial b}{\partial t} = D_b \nabla^2 b - k_1 a^3 b \quad (2b)$$

$$\frac{\partial d}{\partial t} = k_1 a^3 b - k_2 a + k_4 e \quad (2c)$$

$$\frac{\partial e}{\partial t} = k_2 a - k_4 e \quad (2d)$$

$a$, $b$, $c$, and $e$ are the concentrations of ions OH$^-$, Cr$^{3+}$, H$^+$, and [Cr(OH)$_4$]$^-$ in the gel phase and $d$ represents the quantity of Cr(OH)$_3$ precipitate. $D$ stands for the diffusion coefficient and $k$ for reaction rate. The index specifies the component or the process. $k_1$ and $k_2$ may be functions of a precipitation threshold and a redissolution threshold, respectively. These functions can, in principle, simulate the conplicated nucleation processes as well.

Eq 2a tells us that the concentration of OH$^-$ ions ($a$) can change as a result of diffusion, chemical reactions given by eq I and II, and neutralization of catalyst (HNO$_3$) by NaOH. The change in the Cr$^{3+}$ ion concentration ($b$) comes from diffusion as well as consumption by eq 1. The quantity of Cr(OH)$_3$ ($d$) may increase as a consequence of reaction I and may decrease due to redissolution (eq II). The precipitate and the [Cr(OH)$_4$] ions cannot diffuse. The latter is trapped by the PVA chains. As a result of this, a large increase in the elastic modulus can be observed for those part of the gel where these ions form.

On the basis of the numerical solution of eqs 2a–d the following general statements can be made. The precipitate solubility ($k_2$) plays an important role as far as traveling wave formation is considered. The necessary condition to achieve a propagating band is to have highly soluble precipitate. In this case only one band forms which travels from the gel/liquid interface into the bulk. It must be mentioned that our result differs from that of Henisch[11] who found that a highly structured ring system advances and the entire tube gets filled almost uniformly with the precipitate. This difference may be due to the different formulation of the problems considered here. In the case of a less soluble precipitate, the Liesegang pattern can be reproduced. It must also be mentioned that, apart from the solubility parameter, the ratio of initial concentrations of $a$ and $b$, $a_0/b_0$, plays a decisive role. If there is a sufficient amount of solute ($a$) in the gel, the solubility factor is effective and high solubility favors traveling band formation. If the solute $a$ becomes exhausted, then a Liesegang pattern can be obtained again. When the ratio $a_0/b_0$ is intermediate, one obtains a traveling band in the beginning, and then, due to the consumption of component a, the propagating band stops and a Liesegang pattern begins to develop.

A full description of the calculation with the aid of parameters obtained from experimental measurements and detailed results will be the subject of a later paper.

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