ORIGINAL CONTRIBUTION

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Pattern forming precipitation in gels due to coupling of chemical reactions with diffusion

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Abstract Precipitate-forming chemical reactions have been studied in chemically cross-linked poly(vinyl alcohol) gel medium. One of the reactive components was incorporated into the gel, the other was allowed to diffuse into it. Depending on the experimental conditions the reaction-diffusion process often results in patterns of different type. Experiments performed in tubes and in thin layers were carried out in order to investigate the effects of various factors (cross-linking density, swelling degree as well as the concentrations of the outer and inner electrolytes) on the morphologies of the precipitate patterns. It was found that precipitation occurs not only in the Liesegang bands, but also between bands. Beside Liesegang-type structures, tree-like patterns have been observed, showing a characteristic periodicity in the density profile obtained by digitalized image analyses.

Key words Poly(vinyl-alcohol) gel medium – Liesegang bands – cross-linking density

Introduction

Reactive systems in which one (or all) of the reactants are transported by diffusion often result in pattern formation. This reaction-diffusion process may include material deposition which can occur intermittently in terms of time or space or both [1–4].

In general, two fundamental time scales characterize the diffusion-reaction systems: the diffusion time and reaction time. If the reaction time is much shorter than the diffusion time, the process is diffusion limited. In such cases the whole process often results in pattern formation [5]. A good example of such a diffusion-limited reaction is the so-called Liesegang phenomenon, when an electrolyte (outer electrolyte) diffuses into a gel containing another electrolyte (inner electrolyte) and the reaction of these two diffusing materials forms an insoluble product. In these systems under certain conditions formation of rhythmic pattern (bands or rings) of precipitate can be observed [6, 7]. The pattern is macroscopic, so it is visible by naked

eye. The primary function of the gel is to prevent convection and sedimentation, thus the diffusion mechanism becomes effective. It is to be mentioned that Liesegang pattern formation can also occur in the absence of a gel [8].

For laboratory research in most of the cases gelatin-, agar-, starch- or silica gels were used. The mentioned gels have no accurately known composition or structure and generally they are contaminated by undesirable impurities. This might be the reason why the same chemical reaction can result in quite different pattern formation in different samples of the same gel, or in different gels. This means that either the gel structure or impurities can produce influence on the precipitation process. According to our knowledge no systematic studies on the role of the gel in the Liesegang phenomenon have been reported.

The main purpose of the present work therefore was to investigate the pattern forming precipitation of different salts, performing experiments with the aid of chemically crosslinked poly(vinyl-alcohol) (PVA) gels.

Poly(vinyl-alcohol) hydrogels without permanent crosslinks have already been applied for studying the Liesegang ring formation [12, 13]. In our paper chemically crosslinked PVA was used and the effect of crosslinking density as well as the polymer concentration was studied. Beside the gel parameters the influence of crystal form as well as solubility of the precipitate were also investigated. By applying crosslinked PVA as gel medium for the experiments, one obtains several advantages. PVA is a neutral, water-soluble synthetic polymer which can be conveniently chemically crosslinked by glutaric aldehyde [13, 14]. On the basis of stoichiometry of gel-forming reaction it is possible to vary the degree of crosslinking density in a wide range. Due to the permanent connection between the chains, no gel-sol transition can occur when increasing the temperature, therefore the effect of latter can be investigated as well.

Theoretical backgrounds

The formation of rhythmic pattern of precipitate has induced numerous experimental and theoretical works. Many theories are based on the assumption that the periodic band or ring formation is due to two main independent processes [1, 2]:

1) two electrolytes should diffuse into each other at the same time;
2) at a point where the product of their concentrations reaches a critical value, precipitation occurs.

If the experiments are carried out in a one-dimensional arrangement (say a tube in x direction) and if the reaction time is negligibly small in comparison with the diffusion time, then the position of the advancing diffusion front obeys Fick's law:

$$x = k\sqrt{2Dt} , \tag{1}$$

where t is the time D is the diffusion coefficient of the outer reactant, k is a constant, called front factor. One can rewrite Eq. (1) by taking into account the position of first, x_1, second, x_2, and n^{th}, x_n, ring measured from the diffusion boundary developing in time t_1, t_2, and t_n respectively. From a practical point of view, x is considered as distance measured from the advancing interface layer, that is, the position of precipitate/gel surface.

$$x_1:x_2:....:x_n = t_1^{1/2}:t_2^{1/2}:....:t_n^{1/2} . \tag{2}$$

Equations (1) and (2) are often regarded as the time law for the formation of rings or bands.

Another important information is the spacing of bands, that is, how the position of the $(n + 1)^{th}$ band can be related to that of the nth band. This relation has been derived by Jablczynsky on the basis of thermodynamical arguments [9] and was supported by many experimental reports [1, 2, 9–11, 15–19].

$$x_{n+1} = Px_n , \tag{3}$$

where P is defined as the spacing coefficient.

Similar relation can be derived for the thickness of the bands Δx_n [10]:

$$\Delta x_{n+1} = C\Delta x_n , \tag{4}$$

where C represents a proportionality factor.

It is to be mentioned that there are several experimental results which cannot be interpreted with the aid of a simple Fickian diffusion equation. A modern approach is provided by Flicker and Ross, based on non-linear reaction-diffusion equations and on the nucleation kinetics leading to chemical instabilities [8].

Experimental part

Preparation of the gels

We have realized our experiments in chemically crosslinked poly(vinyl-alcohol) (PVA) gels. The gels were prepared by crosslinking primary PVA chains with glutaric aldehyde (GDA) in aqueous solution [12–14]. Commercial PVA (Merck 821038) and solution of 25 wt % GDA (Merck) were used. This polymer can be characterized by an acetate content of less than 2 mol % and by a number average molecular mass of 72 000.

The initial polymer concentration, C_p as well as the crosslinking density were altered. This latter means the ratio of monomer unit (VA) to the crosslinking agent (GDA). This ratio [VA]/[GDA], called degree of cross-linking (DC) was varied between 50 and 400.

In order to study the precipitation in swollen networks, one of the reactants was mixed with the polymer solution containing the crosslinking agent. Then, slow gelation process was induced by decreasing the pH of the system by nitric acid (Carlo Erba). The gelling solution was poured into glass tubes or onto glass plates. The size of the tubes as well as that of the plates were also varied. At pH = 2 the gelling process took place within 5–7 h. After completion of the network formation, the gels were brought into contact with the reactant allowing it to diffuse into the gel.

The gels are characterized by the polymer concentration/degree of crosslinking. Symbols like "6/100" mean that the polymer concentration, C_p equals to 6 wt % and the ratio [VA]/[GDA] is 100.

The experiments reported here were carried out at room temperature.

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Chemical reactions studied

Since our intention was to investigate the effects of various factors (such as crystal growth, solubility of precipitates, complex formation) on the pattern formation, we have studied several chemical reactions. These are the following:

(A)

1. $MgCl_2 + 2NH_4OH = \underline{Mg(OH)_2} + 2NH_4Cl$
2. $MgCl_2 + 2NaOH = \underline{Mg(OH)_2} + 2NaCl$
3. $CdSO_4 + 2NaOH = \underline{Cd(OH)_2} + Na_2SO_4$
4. $CoCl_2 + 2NaOH = \underline{Co(OH)_2} + 2NaCl$
5. $CaCl_2 + K_2SO_4 = \underline{CaSO_4} + 2KCl$
6. $Pb(NO_3)_2 + 2NaCl = \underline{PbCl_2} + 2NaNO_3$

(B)

1. $Cr(NO_3)_3 + 3NaOH = \underline{Cr(OH)_3} + 3NaNO_3$
$\underline{Cr(OH)_3} + NaOH = Na[\underline{Cr(OH)_4}]$
2. $HgCl_2 + 2KI = \underline{HgI_2} + 2KCl$
$\underline{HgI_2} + 2KI = K_2[\underline{HgI_4}]$

In reactions listed in group A a weakly soluble salt is produced, which is not able to redissolve in the excess of the diffusing reactant. The concentration of the diffusing electrolyte was in every case much greater than that of the inner electrolyte incorporated in the gel.

In reactions mentioned in group B, the weakly water soluble reaction product can redissolve in the surplus of the outer electrolyte due to complex formation.

All of the sparingly water soluble precipitates we studied were crystalline. Sometimes the crystals are visible (e.g., $PbCl_2$), but in many cases they are too small to be visible to the naked eye, that is, the precipitate is micro crystalline (e.g., $Mg(OH)_2$).

Experimental setup

In order to obtain Liesegang patterns, several experiments were performed in glass tubes containing the swollen network, and in gel layers.

The length and the diameter of the glass tubes were varied. The maximal length was 220 cm, the minimal 20 cm. The diameter was between 1 and 5 cm. The reactant solution was used to fill the space above the gel and the diffusion was allowed to take place downwards. To prevent evaporation the tubes were sealed. Position of bands x_n measured from the surface of gel as well as the formation time t_n of each band have been determined by photographic and video-techniques. Gel films of different thicknesses were also used. The bottom of the layers, together with a glass plate holding them was immersed in a solution allowing the diffusion to proceed upwards. To avoid evaporation of gel liquid and to minimize deforma-

tion of the gel – in some cases – paraffin oil was poured upon the water solution. So the upper $\sim 90\%$ of the gel layer was under paraffin oil, while the bottom 10% was in contact with water solution. The thin gel medium enabled us to investigate the microscopic structure of precipitate bands and that of the aggregates between subsequent zones. Silica gel layers, used for chromatographic purposes, were also applied.

The experiments were realized in a thermostat which controlled the temperature within $\pm 0.2\,°C$.

Experimental results

Precipitation of $Mg(OH)_2$ in PVA gels

It turned out that the crosslinked PVA-gel is an excellent medium for studying the Liesegang phenomenon [14, 15]. Depending on the conditions and on the nature of the precipitate, one can obtain periodic precipitation where the distance between two neighboring precipitate bands varies from 0.1 mm to 400–500 mm. It is worth to mention that – according to the best of our knowledge – no such long distance between two subsequent bands has been published as yet.

Figure 1 shows a typical experimental setup. When comparing Figs. 1a and 1b, one may observe significant differences. The distance between two adjacent bands is strongly influenced by the nature of the outer electrolyte. In the case of NH_4OH this distance falls in the order of centimeters, whereas for NaOH the spacing between neighboring bands is within the magnitude of millimeters.

Fig. 1 Liesegang bands formed from $Mg(OH)_2$ precipitates in testtubes a) Gel: 2.84/300, inner electrolyte: 0.20 M $MgCl_2$, outer electrolyte: 14.7 M NH_4OH b) Gel: 4/300, inner electrolyte: 0.01 M $MgCl_2$, outer electrolyte: 0.35 M NaOH
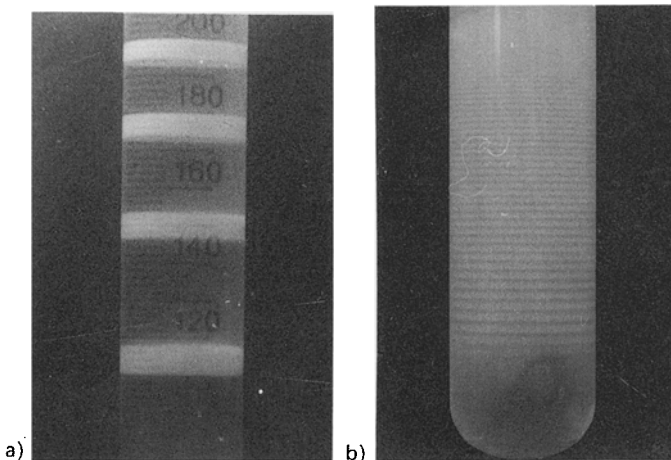
This basic difference may be attributed to the different dissociation constant of NH_4OH and NaOH. It must be mentioned that by variation of inner and outer concentrations of electrolytes as well as the polymer concentration and crosslinking density, we were not able to increase or decrease the distance between two adjacent bands significantly. We found closely packed bands for reactions A2, A4, and B1, whereas looser bands were obtained for A1, A3, and A5.

On the basis of Fig. 1, it is obvious that one can determine the position of bands with a rather high precision. Figure 2 shows the dependence of position of the n-th band on the time as well as the reaction front position x_f against time. The reaction front was visualized by using phenolphtalein indicator in the inner electrolyte to show the extension of OH^- ions in time. On the basis of data, one may conclude that both x_n and x_f obeys the relation given by Eq. (1). In order to establish whether the periodic pattern formation of $Mg(OH)_2$ precipitate is controlled by the diffusion mechanism, the spacing of bands has been investigated. The geometric law expressed by Eq. (3) can be written as follows:

$$x_n = x_0 P^n \tag{5}$$

or

$$\ln x_n = \ln x_0 + n \ln P . \tag{6}$$

Here x_n is the distance of nth band from the gel surface, x_0 is a characteristic constant.

In Figs. 3 and 4 experimental data are plotted according to Eq. (6). One can see that within the experimental accuracy the agreement is rather good. Many systems can be described by Eqs. (5) or (6). From the slope the spacing coefficient P from the intercept, the value of x_0 can be deduced. These data obtained by linear least square fitting
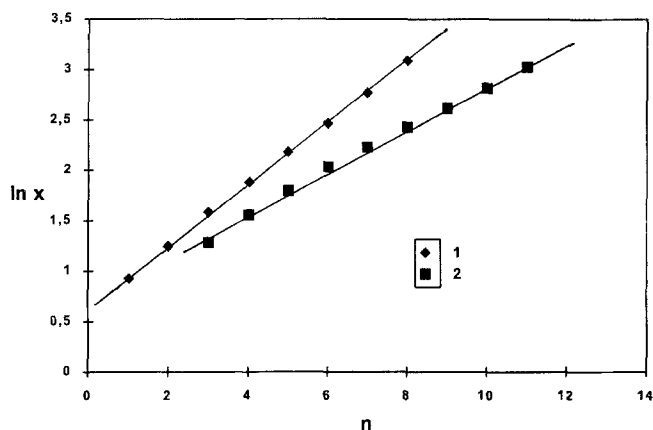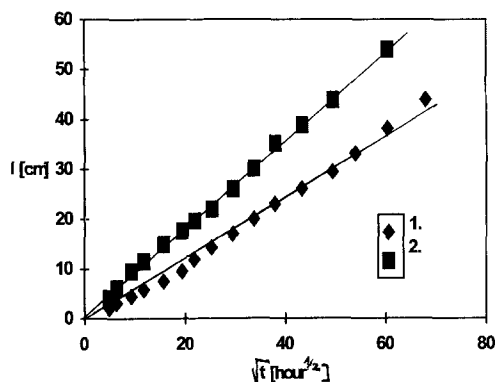

Fig. 3 Verifications of the spacing law. Gel: 2.84/300 outer electrolyte: 14.7 M NH_4OH Symbols: ♦ inner electrolyte: 0.2 M $MgCl_2$, $P = 1.84$; ■ inner electrolyte: 0.08 M $MgCl_2$, $P = 1.26$
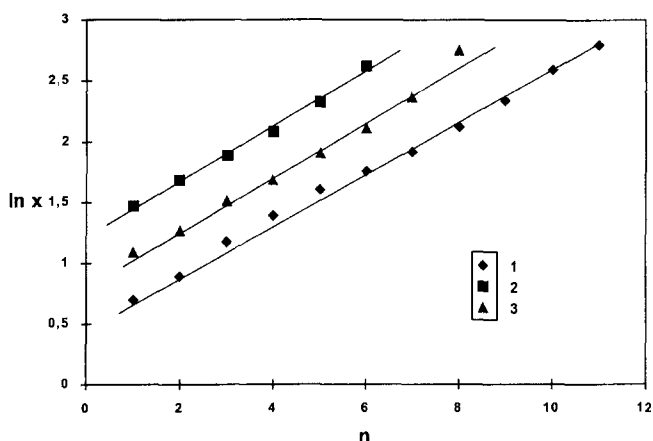

Fig. 4 Verification of the spacing law. Gel: 3.5/300 inner electrolyte; 0.1 M $MgCl_2$ Symbols: ♦ outer electrolyte: 14.7 M NH_4OH $P = 1.25$; ■ outer electrolyte: 13.0 M NH_4OH $P = 1.25$; △ outer electrolyte: 11.0 M NH_4OH $P = 1.25$

Fig. 2 Verification of time law for $Mg(OH)_2$ precipitate formation. Gel: 4/300, inner electrolyte: 0.1 M $MgCl_2$ outer electrolyte: 14.7 M NH_4OH Symbols: ■ precipitate, ♦ OH^- ions

as well as the concentrations of inner and outer electrolytes are summarized in Tables 1–4.

The influence of polymer concentration and degree of crosslinking on the spacing coefficient

In order to first establish the effect of polymer concentration on the periodic precipitation of $Mg(OH)_2$, gel samples with identical crosslinking density were prepared. The degree of crosslinking [VA]/[GDA] = 300 was kept constant, whereas the polymer concentration was varied between 2.5 wt % and 5.5 wt %. The results of two experimental series are shown in Table 1. On the basis of data it is obvious that the spacing coefficient seems not to be

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Table I The influence of the polymer concentration on the spacing coefficient (P). Parameters: [VA]/[GDA] = 300. Outer electrolyte: NH_4OH; Inner electrolyte: $MgCl_2$

Gel	Inner electrolyte concentration ($MgCl_2$)	Outer electrolyte concentration (NH_4OH)	x_0	P	x_1
2.5/300	0.08 M	14.7 M	2.52	1.23	3.09
3.5/300	0.08 M	14.7 M	2.23	1.21	2.69
4.5/300	0.08 M	14.7 M	2.23	1.21	2.69
5.5/300	0.08 M	14.7 M	2.40	1.19	2.85
3.0/300	0.05 M	14.7 M	1.56	1.17	1.82
4.0/300	0.05 M	14.7 M	1.75	1.18	2.06
5.0/300	0.05 M	14.7 M	1.79	1.16	2.07

Table II The effect of crosslinking density on the spacing coefficient. Outer electrolyte: NH_4OH; Inner electrolyte: $MgCl_2$

Gel	Inner electrolyte concentration ($MgCl_2$)	Outer electrolyte concentration n (NH_4OH)	x_0	P	x_1
4.0/50	0.08 M	14.7 M	no band, ring formed		
4.0/150	0.08 M	14.7 M	1.81	1.18	2.13
4.0/250	0.08 M	14.7 M	1.71	1.19	2.03
4.0/400	0.08 M	14.7 M	1.70	1.20	23.04

Table III The effect of concentration of the outer electrolyte (NH_4OH) on the spacing coefficient and on x_0. The composition of gel: 3.5/300. The concentration of inner electrolyte ($MgCl_2$):0.1 M

Concentration of NH_4OH in the gel [M]	Spacing coefficient (P)	x_0	x_1
2.9	only one band		
3.0	2.01	0.42	0.84
5.0	1.46	1.17	1.70
7.0	1.35	1.01	1.36
9.0	1.27	1.21	1.53
11.0	1.25	2.29	2.86
13.0	1.25	3.46	4.32
14.7	1.23	1.67	2.05

Table IV The influence of inner electrolyte on P and x_0. The gel 3/300. The concentration of outer electrolyte (NH_4OH):14.7. M

Concentration of $MgCl_2$ in the gel [M]	Spacing coefficient (P)	x_0	x_1
0.005	continuous precipitate	continuous precipitate	
0.01	spiral	spiral	
0.05	1.21	2.01	2.43
0.08	1.26	1.70	2.14
0.2	1.84	0.23	0.42

significantly influenced by polymer content. Within the experimental accuracy P remains constant when changing the polymer concentration. For x_0 no definite dependence can be established. When the inner electrolyte concentration equals to 0.08 M, x_0 was found to be decreased with increasing polymer concentration, whereas at 0.05 M concentration x_0 increases with increasing polymer content. In connection with these results we have to mention that in several papers the spacing coefficient was found to be inversely proportional to the concentration of the gel medium [16–18]. It was assumed, that with increasing polymer content the diffusion coefficient of the species is decreased. Another reason may be due to the adsorption (or selective solvatation) of some ions on the polymer chains. Our experimental results tell us that neither the influence of polymer concentration on the diffusion coefficients nor adsorption occurring between sol particles and PVA play significant roles in structure formation.

We have prepared several gels by varying the degree of crosslinking in the range of 50–400. In these experiments the amount of polymer in the swollen gel was kept constant (4 wt %). We have found that the spacing coefficient slightly increases when the ratio [VA]/[GDA] increases. This finding is demonstrated in Table 2.

It is worth mentioning that at high degree of crosslinking (gel: 4/50), no bands, but rather rings developed. This is probably due to network elasticity. The larger the amount of GDA, the stronger the gels, and as a consequence, the highest elasticity resistance takes place against precipitate

formation. This idea is supported by other experimental evidence concerning the band thickness. With increasing crosslinking density the width of bands significantly decreases and above a certain value, bands no longer form. As shown in Fig. 7 instead of bands, rings develop. This results are in agreement with those reported by Matsuzawa et al. [12] with increasing degree of crosslinking x_0 also increases.

The effect of inner and outer electrolyte concentration on the spacing coefficient of $Mg(OH)_2$

The concentration of inner and outer electrolyte produces strong influence both on P and x_0. The spacing coefficient was found to increase by decreasing the concentration of the outer electrolyte and by increasing the concentration of the inner electrolyte. These dependences are shown in Tables 3 and 4.

According to Wagner [19] and Matalon and Packter [20], the spacing coefficient can be theoretically related to both inner and outer concentrations. It was predicted that P is inversely proportional to both kinds of electrolyte concentrations:

$$P = \frac{a}{C} + b ,\qquad (7)$$

where a and b are characteristic constants and C stands for both inner-, and outer electrolyte concentrations, respectively. In Fig. 5 we have plotted the spacing coefficient against the reciprocal concentration of outer electrolytes. Our experimental results on $Mg(OH)_2$ precipitates do not entirely support the validity of Wagner–Matalon–Packter relation given by Eq. (7). This latter seems to be valid only at large outer electrolyte concentrations. At smaller concentrations positive deviation from the Wagner–Matalon–Packter relation can be observed. We found that Eq. (7) does not hold for the dependence of spacing coefficient on the concentration of inner electrolyte.

It is worth to mention that spacing coefficients obtained for the precipitation of $Mg(OH)_2$ in crosslinked PVA gels are much larger than those reported by others [1, 2]. As can be seen in Tables 1–4, P was found to be between 1.16 and 2.01. In the literature the characteristic value of P lays between 1.05 and 1.2.

Another important information which is characteristic for the Liesegang pattern formation is the thickness of bands. It has been assumed that the thickness can be expressed similarly to the Eq. (6), that is,

$$\ln(\Delta x_n) = \ln(\Delta x_0) + n \ln P ,\qquad (8)$$

where Δx_n represents the width of nth band and Δx_0 and P are constants. Figure 6 shows the dependence of Δx_n on n for some representative experiments. It seems that Eq. (8) does not hold for our experiments. No simple relation has been found in order to describe the dependence of band thickness on various parameters. As a general rule, one may conclude that thickness of bands increases with band number. Especially the last band was found to be much bulkien (see Fig. 7).

Much less is understood about x_0. Since it has no simple physical meaning, instead of x_0, the position of the first band $x_1 = Px_0$ is discussed. It can be seen in Tables 1–4 that x_1 is influenced by all the parameters varied. On the basis of experimental data, one can arrive at the following conclusions:

The effect of C_p on x_1 cannot be formulated in a simple way. Both increasing and decreasing behavior have been found.

Fig. 5 The spacing coefficient against the reciprocal concentration of outer electrolyte (NH_4OH) Gel: 3.5/300, inner electrolyte: 0.1 M $MgCl_2$
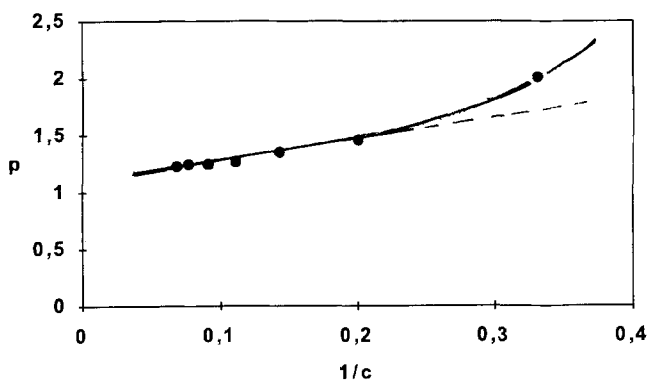
Fig. 6 Dependence of the width of the Liesegang bands as a function of n. (Δx is given in mm.) Gel: 2.84/300 inner electrolyte: 0.05 M $MgCl_2$, outer electrolyte: 14.7 M NH_4OH

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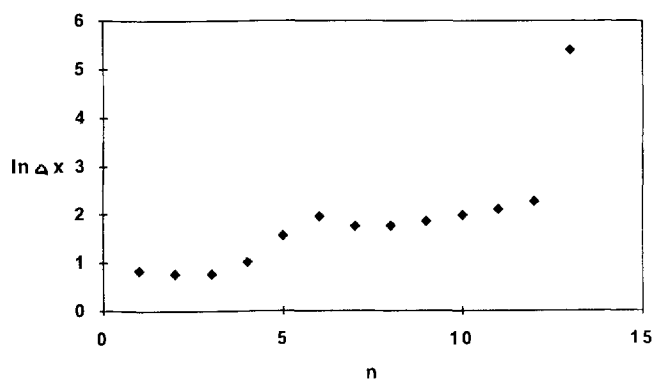
As the concentration of outer electrolyte is decreased, as a consequence, x_1 decreases.

With increasing the concentration of inner electrolyte x_1 was found to decrease.

The position of the first band was found to be not far from the gel/liquid interface if the network is loosely cross-linked, the concentration of inner electrolyte is high and that of the outer electrolyte is low.

Unusual morphologies

Very often miscellaneous forms come into existence. In case of highly crosslinked gels instead of compact bands, rings develop. It was also found that bands that were formed far from the gel surface are deformed.

The different shapes – observed by us – are shown in Fig. 7. Bands, rings, spheres, spirals can be seen. The

Fig. 7 Different precipitate morphologies observed at $Mg(OH)_2$ precipitate
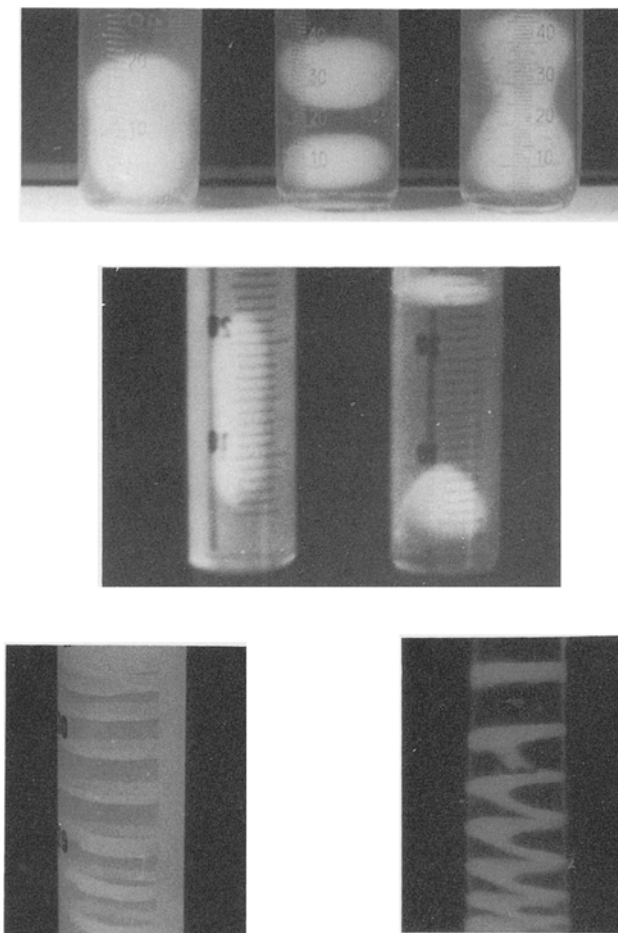
formation of such morphologies cannot be interpreted on the basis of present knowledge on Liesegang phenomena.

We have found systems for which the Jablczynsky's spacing law could not be applied. Figure 8 shows the dependence of $\ln x_n$ on n_x according to Eq. (6). This figure evidences that no simple power law describes the position of bands. It seems that the Liesegang pattern can be described by two sets of parameters. The position of the first six bands can be characterized by $P_1 = 1.36$ and $x_0 = 0.74$, whereas $P_2 = 1.19$ and $x_0 = 1.74$ belong to the remaining seven bands. The origin of this effect is the subject of our further studies.
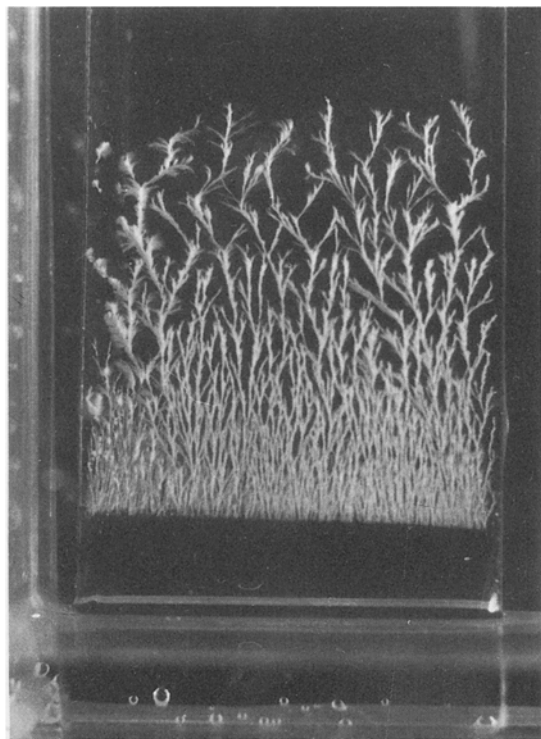
Precipitation – in thin layers

Several Liesegang-type experiments were realized in gel films. Thin films of crosslinked PVA containing the inner electrolyte were prepared on glass plates. The thickness of gels was varied between 0.5–2 mm. A part of the film was immersed in the solution of the outer electrolyte and as a result of this, the diffusion took place vertically upwards. It must be mentioned that no definite effect of layer thickness on the developing patterns could be observed. Depending on the experimental conditions, a great variety of patterns could be observed in this two-dimensional arrangement. In case of $Mg(OH)_2$ precipitate one obtains the expected Liesegang stripes. This is not the case for $PbCl_2$ where instead of stripes a tree-like structure develops. This highly ramified pattern reminds us of that obtained by simulation of diffusion-limited deposition [21] as shown in Fig. 9. The tree-like morphology of $PbCl_2$ precipitate emphasizes the strong influence of crystal structure on the final pattern.

$PbCl_2$ forms small needle-shaped crystals with a length of about 1–2 mm. These crystals are arranged along con-

Fig. 8 Liesegang-pattern which can be characterized by two spacing coefficients. Gel: 4/250; $P_1 = 1.36$, $P_2 = 1.19$; inner electrolyte: 0.08 M $MgCl_2$; outer electrolyte: 14.7 M NH_4OH
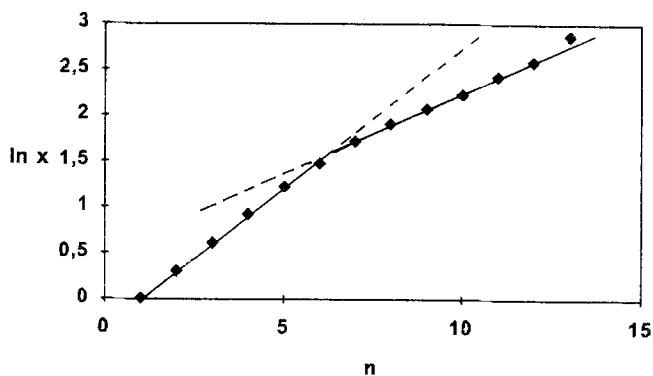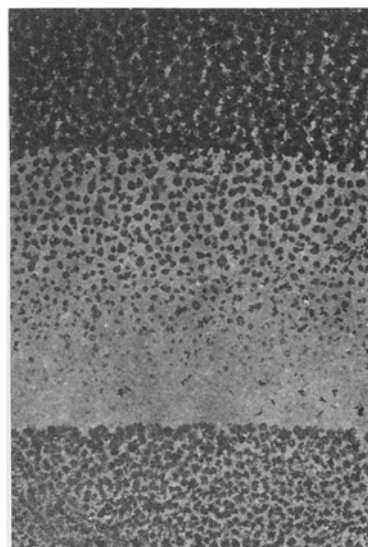
tinuous line resulting in tree-like patterns, as shown in Figs. 9 and 10. In these figures, one observes no "empty zones" between adjacent bands, but rather continuous lines developing from the bottom of the gel layer upwards.

Fig. 11 Liesegang patterns developed in this silica layers. inner electrolyte: 0.2 M KI, outer electrolyte: 0.15 M HgCl₂

Fig. 9 Tree-like precipitation pattern of PbCl₂ in thin PVA film. Gel: 3.5/250 inner electrolyte: 0.03 M Pb(NO₃)₂, outer electrolyte: 1.5 M NaCl

Fig. 10 Periodic tree-like morphology of PbCl₂ in PVA film. Gel: 3.5/250 inner electrolyte: 0.03 M Pb(NO₃)₂, outer electrolyte: 1.0 M NaCl

Depending on the experimental conditions (on the concentration of inner and outer electrolytes), several tree-like patterns have been observed. Figure 10 shows such a pattern in which the Liesegang-type periodicity can be seen. At this precipitation the growth process abruptly ceases at certain distances and only a small part of branches start to grow again. These survivors propagate forward and from them many new branches grow. As a result, the concentration of deposits (PbCl₂) as a function of displacement has several maxima. This behaviour recalls the Liesegang phenomena.

We have made several experiments in thin silica layers, too. These layers are usually used for advantageous purposes, but we applied them as gels swollen by one of the electrolytes and then immersed into to other one. The main advantage of these experiments is that we can study the internal structure of precipitate zones and the spaces between subsequent stripes by light microscope. Figure 11 shows the Liesegang-pattern of HgI₂ precipate. It may be seen that precipitation occurs not only in bands but also between neighboring stripes.

Conclusions

Gels of chemically crosslinked PVA chains are an excellent medium for studying the pattern forming precipitation in reaction-diffusion systems.

It was found that PVA concentration has only a negligible effect on the spacing coefficient, contrast with other gelling materials.

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By variation of the crosslinking density, the restriction of precipitation due to network elasticity can also be investigated. In the case of high elastic resistance, no bands, but rather rings developed. The appearance of other miscellaneous forms has been promoted by strong gels.

Two basically different morphologies, Liesegang band formation and tree-like precipitation have been observed. On the basis of internal structure of Liesegang precipitates, obtained on thin silica layers, it may be established that precipitate deposition occurs not only in the bands, but also between them. In the case of tree-like precipitation, the fractal-like structure involves a periodicity of the Liesegang type under certain conditions.

Beside static precipitate patterns reported in this paper, a dynamic phenomenon has been observed. This will be reported in one of our forthcoming papers. Then, the experimental results will be interpreted on the basis of computer simulation.

References

1. Henisch KH (1991) Periodic Precipitation, Pergamon Press
2. Henisch HK (1988) Crystals in Gels and Liesegang Rings Cambridge University Press, New York
3. Winfree AT (1988) The Geometry of Biological Time, Biomathematics Vol. 8. Springer-Verlag, Heidelberg
4. Turing A (1952) Philos Trans R Soc B37:237
5. Keller JB, Rubinow SI (1981) J Chem Phys, 74(9):5000
6. Liesegang RE (1896) Naturwiss Wochenschr, 11:353
7. Liesegang RE (1896) Photog Arch 21:221
8. Flicker M, Ross J (1974) J Chem Phys 60(9):3458
9. Jablczynski K (1923) Bull Soc Chim Fr 33:1592
10. Chopard B, Luthi P, Droz M (1994) Phys Rev Lett 72:1384
11. Mueller KF (1984) Science 225:1027
12. Matsuzawa S, Hondo Y, Kawanchi Y, Kume M, Yamaura K, Tanigami T, Ogasawara K (1987) Colloid and Polymer Science, 265:810
13. Horkay F, Zrínyi M (1986) J Macromol Sci, B25(3):307
14. Zrínyi M, Gálfi L, Smidróczki E, Rácz Z, Horkay F (1991) J Phys Chem, 95:1618
15. Kárpáti-Smidróczki E, Büki A, Zrínyi M (1993) Makromol Chem, Macromol Symp 227
16. Buzágh A, Fraknoy V (1973) Kolloid Zeitschrift 150:99
17. Gnanam FD, Krishnan S, Ramasamy P, Laddha GS (1980) J Colloid and Interface Sci, 73(1):193
18. Ambrose S, Kanniah N, Gnanam FD, Ramasamy P (1982) Crystal Res and Technol 17(3):299
19. Wagner C (1950) J Colloid Sci 5:85
20. Matalon R, Packter A (1955) J Colloid Sci, 10:46
21. Vicsek T, Fractal Growth Phenomena, World Scientific London, 1989