Helicoidal precipitation patterns in silica and agarose gels

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ABSTRACT

Helicoidal patterns grown in agarose and silica gels were studied using reaction–diffusion–precipitation processes with components $CuCl_2/K_2CrO_4$. We measured the probability P_H of the emergence of helicoids as the internal surface area of the gels was varied by changing the concentration for agarose and by modifying pH for silica. In addition, the effects of mixing the two gels were also investigated. Our main result is that the surface area effects parallel the effects of noise, namely increasing the surface area initially enhances the formation of helicoids but further increase leads to downturn in P_H due to proliferation of random patterns.

1. Introduction

Helical structures can be observed in a wide variety of natural and man-made systems [1–9]. Their emergence from a homogeneous background is a basic and rather complex problem due to the symmetry breaking that takes place at the initial stages of their evolution. Interest in chiral morphology, however, comes also from engineering applications since chirality is known to affect the physical properties of materials [10]. In particular, understanding and controlling helical structures are expected to be relevant in developing bottom-up fabrication techniques using nonlinear chemical kinetics [11,12].

Recently, we carried out a series of experimental and theoretical studies [9,13,14] in order to clarify how helices were formed in Liesegang-type setups where pattern emerged in the wake of a reaction–diffusion front [15,16]. We found that the formation of helical and helicoidal patterns was reproducible but had a probabilistic aspect. Namely, for a given set of experimental parameters, there was a well-defined probability for the helical pattern to emerge. The dependence of the probability on the initial concentration of the inner- and outer electrolytes, and on the size of the system was measured and compared successfully with a theory [9]. The theory suggested that the helices emerged from a complex interplay among the unstable precipitation modes, the motion of the reaction front, and the noise in the system. Unfortunately, the noise is not easily accessible in experiments although the probability depends sensitively on it. For example, changing

temperature is not a practical way of changing the noise amplitude since it simultaneously changes a number of important parameters (diffusion constants, reaction rates, precipitation thresholds, etc.) and the delineation of the various effects is practically impossible. The present work grew out of our attempts to overcome this problem and implement controlled noise by changing the properties of the gel.

In general, the gel is considered as an inert background in the theoretical treatments of Liesegang-type experiments [17–21]. At the same time, it is known that changing the concentration or the chemical composition of the gel leads to patterns with distinct spacing- and width laws and, frequently, to qualitatively different precipitation phenomena [22–24]. The simplest rationalization of these effects is that the gel provides a network of quenched impurities acting as nucleation centers [25]. Then the internal surface of the gel defines the density of nucleation centers (larger surface area corresponding to larger density of nucleation centers) which governs the general nucleation rate in the system. This view suggests that the internal surface area is roughly proportional to a noise-amplitude: the larger it is the larger is the probability of a nucleation event.

In order to see the effects resulting from internal surface area changes, we examined helicoidal patterns in agarose and silica gels and varied the internal surface area by changing the gel concentration in agarose gel and by varying the pH in the silica gel [26–28]. We measured the trends in the probability of the emergence of helices and found that they were in agreement with the interpretation that the internal surface acts as an effective noise inducing nucleation. We also searched for ways of maximizing the yield of helices by mixing agarose and silica gels, and the maximum value

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of 90% yield was obtained at 0.5% agarose concentration. The mixing results, however, do not readily submit to a simple interpretation in terms of an effective noise.

2. Experimental

Agarose gel was prepared by addition of a prescribed amount of agarose powder (Type1, Sigma Aldrich) to a 0.01 M solution of K_2CrO_4 (Merck). The mixture was heated to 90 °C under continuous stirring until a homogenous solution was obtained. The resulting solution was then poured into test tubes for 3 h.

We prepared silica gel by the following method. A solution was prepared from sodium metasilicate (Merck) and potassium chromate (Merck) in such way that the obtained solution had relative density of 1.03 and the concentration of potassium chromate was 0.01 M. Gelation was induced by decreasing the pH of the solution by adding HCl drop by drop. We also prepared mixed silica–agarose gel with various amounts of agarose by adding hot agarose gel solution to the silica gel prior the polymerization. We poured these solutions in test tubes and kept them undisturbed for 24 h till the gelation process was completed.

After gelation process we gently poured the solution of copper (II) chloride (Merck, 0.5 M) on the top of the gel. The test tubes were closed and kept undisturbed apart from visually observing the appearance of the precipitation pattern. The experiments were carried out at room temperature (27 ± 0.3 °C).

3. Results and discussion

3.1. Comparison of helicoidal patterns in agrose and silica gel

Experimental results displayed in Figure 1a indicate that helicoidal patterns are formed not only in agarose as shown previously [9] but also in silica gel. In order to investigate the effect of the internal surface area, we changed the gel concentration in agarose gel and the pH of the silica gel. In agarose, the internal surface of the gel can be considered to be proportional to the gel
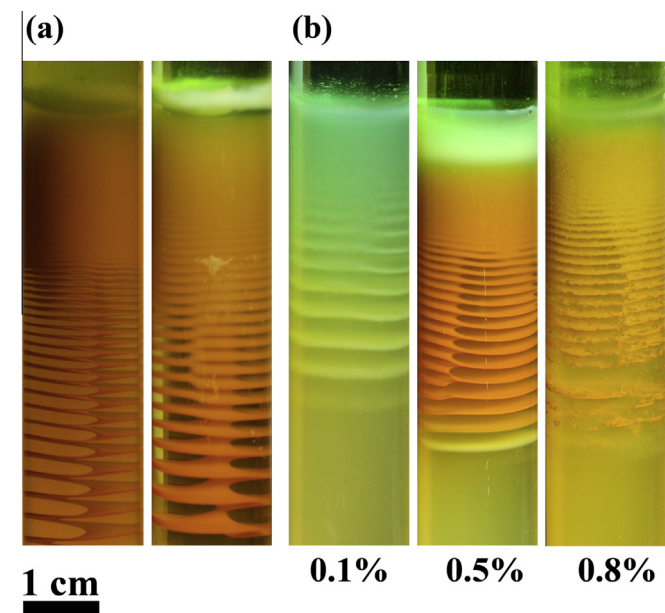

Figure 1. Precipitation patterns in agarose, silica and mixed silica–agarose gels. (a) Helicoids in agarose gel (1%; left) and in silica gel (pH = 7; right). (b) Patterns in mixed silica–agarose gels (pH = 7), numbers below the test tubes indicate the amount of agarose in silica gels. The concentration of the outer ($CuCl_2$) and inner (K_2CrO_4) electrolytes were 0.5 M and 0.01 M, respectively.

concentration [26,27]. On the other hand, in silica gel, acidity (pH) affects the pore size and the internal surface area, and the internal surface area is proportional to 1/pH [28,29]. Changing these two parameters gives a simple and experimentally controllable way to 'fine-tune' the gel property in these two chemically different gels. In agarose gel we found that the probability (P_H) of the emergence of single helicoids has a maximum ($P_H = 0.6$) at gel concentration of 0.75%, meanwhile the probability of Liesegang patterns decreases, parallel with this, the probability of distorted helicoids decreases, with increasing gel concentration (Figure 2a). In case of silica gel we have also maximum probability of getting helices ($P_H = 0.5$) at pH 7. This probability decreases rapidly at lower and higher pH (Figure 2b).

We can now discuss how to fit our experimental findings into a theoretical framework. The theory of helix formation in the wake of a front combines the properties of moving reaction front with the dynamics of the generation of precipitation pattern through pre- and post nucleation processes [9,14]. Technically, reaction–diffusion equations provide the source for the phase separation described by the Cahn–Hilliard equation with noise added [9,21,30–32]. This theory has been successful in reproducing the established regularities of Liesegang patters, and it also provided guidance in developing methods of controlling patterns by external fields and boundary conditions [21,33,34]. As far as the gel is concerned in precipitation systems, the usual argument is that the gel just prevents the convection of solutions and the sedimentation of precipitate. However, recent works [22–24] have shown transparently that the gel has a strong influence on pattern formation in agreement with the present experiments.

Introducing gels in the theories is highly nontrivial and we know only a few attempts in this direction [24,35]. Basically, the gel provides internal interfaces where the nucleation threshold is lowered [25]. Thus internal surfaces facilitate nucleation in the same way as increasing noise helps crossing thresholds in the nucleation processes. Assuming that parallels may be drawn between the effects of internal surfaces and noise, we can shortcut the theoretical difficulties, and interpret our experiments in terms of earlier results relating the probability of the emergence of the helices, P_H, to the amplitude of the noise η [9]. As can be seen in Figure 3b of [9], P_H is negligible in the $\eta \to 0$ limit (Liesegang bands dominate; $P_L \approx 1$), it increases with η to a point that $P_H > P_L$, and then P_H declines because more complicated (distorted chiral and random) structures take over. As we can see in Figure 2, the same sequence of changes in P_H occurs in the present experiments if only the noise is replaced by internal surface areas (appropriately interpreted through concentration of the agarose or 1/pH in case of silica). The above arguments are of course phenomenological and their validity could be judged only by developing of a more precise theoretical approach.

3.2. Effect of 'chemical impurity' in a mixed gel medium

One of the interesting aspect of the control and engineering of precipitation patterns is the variation of the purity (chemical composition) of the supporting medium. To our knowledge, there are only a few experimental papers where the effect of the gel composition/impurity on the morphology of patterns was investigated [22–24]. We carried out experiments in a mixed silica–agarose gel media containing various amounts of agarose in order to maximize the probability of the emergence of helicoids. Our experiments show that introducing the other gel can dramatically affect the formation of helicoids (Figures 1b and 2c). Increasing amount of agarose increases the probability of the emergence of helicoids up to 0.9, which means that helicoids practically appear with certainty. Further increase of the amount of agarose results in a decrease of P_H, however, it is still a high value (0.5).
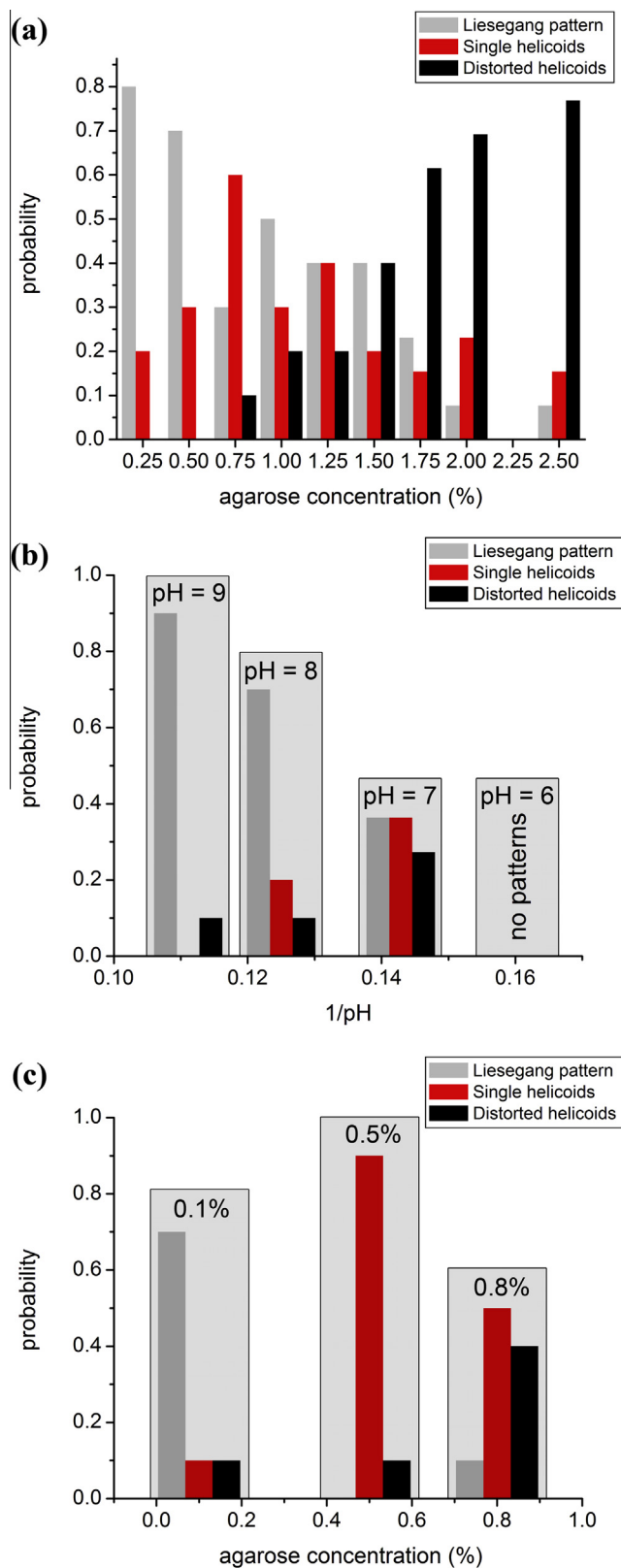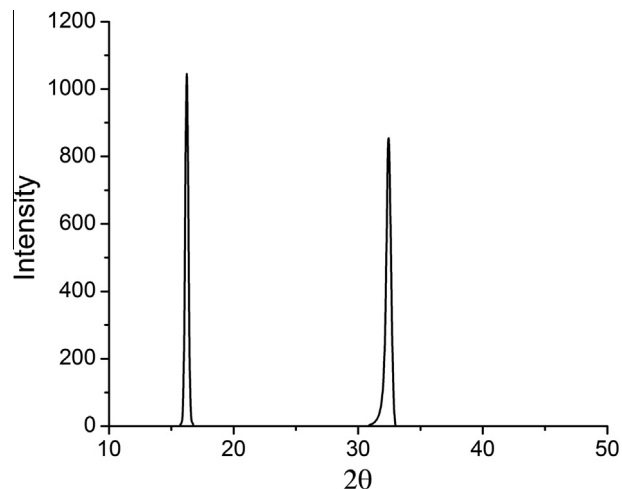
Figure 3. Powder XRD spectrum of precipitate particles collected from precipitation bands in silica gel. The wavelength of the X-ray was 1.5406 Å and the line broadening at half the maximum intensity was 0.29° and 0.42° for the first (2Θ = 16.23°) and second (2Θ = 32.39°) peak, respectively.

Explanation of this finding based on experimental and theoretical assumptions is problematic due to lack of the knowledge on physical and chemical properties of hybrid and mixed gels.

3.3. Scale of the building blocks

An interesting question related to helix formation is at what scale the symmetry breaking occurs. A lower limit of this scale is the size of the particles in the precipitate. In a previous study [13], we showed that, in agarose gel, the bulk precipitate of copper dichromate consists of ~1 μm particles (spherulites). Here we wanted to gather information on building blocks of the precipitate in silica gel. Therefore, we collected and dried solids from the helicoidal band regions and used powder XRD measurements to determine the particle size. The powdered sample was mounted on the sample holder and the XRD data were measured in a 2Θ range from 10° to 80° in steps of 0.1°. We found the presence of crystals containing copper from the positions and intensities of the diffraction peaks (Figure 3). We estimated the average size of the crystallite (d) from the line broadening using the Scherrer equation, $d = \frac{0.9\lambda}{\beta\cos\Theta}$, where λ is the X-ray wavelength (which was 1.5406 Å) and β is the line broadening at half the maximum intensity (which were 0.29° and 0.42° for the first and second peak, respectively). We obtained the order of few tens of nanometers (~25 nm) for the average particle size. This is markedly different from the scale of the spherulites (~1 μm) observed in agarose gel [13]. We should emphasize, however, that the scale found above sets only a lower limit for the scale of the emergence of chirality.

4. Conclusion

We investigated the formation of helicoidal precipitation patterns in silica and agarose gel by varying the internal surface area of the gel through its concentration and pH. The probability of the emergence of helices in agarose and silica gel were found to follow similar trends with the maximum probability occurring at intermediate internal surface areas. We also found that the probability may be significantly increased (P_{H} = 0.9) by mixing silica and agarose in an appropriate ratio. These results strongly suggest that the

Figure 2. Dependence of the probability of the emergence of Liesegang patterns (obtained from 10 experiments for each set of parameters), single helicoids and distorted helicoids in agarose gel where the agarose concentration was varied (a), in silica gel with the pH changed (b) and in mixed silica–agarose gel, where the agarose concentration was varied (c).

properties of the gel media on pattern formation are highly relevant in understanding the process.

Our XRD experiments revealed the presence of particles of the size of ~20–30 nm in the precipitation bands of the silica gel. This finding suggests that the supporting media may have a more pronounced effect on particle size than it has been believed, and nanoparticles with various sizes can be produced in this novel way using reaction–diffusion processes.

Acknowledgments

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