GRAVITY EFFECT ON THE FORMATION OF PERIODIC PRECIPITATION PATTERNS

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Dedicated to Professor Ľudovít Treindl on the occasion of his 70th birthday.

The effect of gravity on the formation of Liesegang patterns of $Ag_2Cr_2O_7$ in gelatin and that of PbI_2 in agar was investigated. Spatial arrangement of Liesegang bands was measured in the parallel and antiparallel orientation to the gravitational field in a single sample with all other parameters kept fixed. The experimental results are discussed in terms of the prenucleation theory of periodic precipitation.

Key words: Liesegang bands; Gravitational field; Spatial coefficients; Precipitation; Silver dichromate; Lead iodide; Gels; Colloids.

Formation of periodic precipitation patterns, known as the Liesegang phenomenon, has been the object of intensive study in the past[1]. After some decline of initial interest, the work in this field began to rise again, first of all due to the development of the non-linear irreversible thermodynamics. Besides the classic Liesegang experiment, *i.e.* the precipitation of potassium dichromate with silver nitrate in gelatin, some other reactants and gels, as well as non-gelatinous media, were studied[2,3]. The apparent similarity to geological textures and patterns in the plant and animal biology also stimulated the research[4]. The mechanism of the formation of Liesegang rings or bands is rather complex and involves several processes, namely the diffusion of the reactants, formation of colloid particles prior to precipitation, coagulation of the colloid and subsequent formation of a crystalline phase. Various theories of the Liesegang phenomenon have been published up to the present time. The most important theoretical assumption is that of supersaturation of silver chromate, introduced by Wilhelm Ostwald in his theory of periodic precipitation[5]. The supersaturation means that the Liesegang system is removed far from equilibrium which is the indispensable condition for the occurrence of the oscillations. A further condition for an oscillatory system can be also found in the process of formation of Liesegang patterns. It is the autocatalytic growth of colloidal particles during the coagulation of the nuclei[6]. The coagulated particles of the precipitate form a turbidity zone surrounding the ring system[7,8]. In some Liesegang systems the secondary structure is observed in which microscopically spaced bands of precipitate are superimposed on the visually observable primary bands[9,10]. The role of gravity in the formation of Liesegang patterns was investigated in the past by several authors but no unambiguous results were presented[7,11–13].

The aim of our work was to bring new experimental material on the effect of gravity in the classic Liesegang systems, potassium dichromate with silver nitrate in gelatin and potassium iodide with lead nitrate in agar, and to contribute to answering the question whether gravity does influence or not the formation of Liesegang bands.

EXPERIMENTAL

Liesegang bands of $Ag_2Cr_2O_7$ have been obtained with a solution of 0.017 M $K_2Cr_2O_7$ (p.a., Lachema Brno) in 10 wt.% gelatin (Gelatina animalis ČSL.3, Medika Bratislava). The gelatin was dialyzed before use. The solution with a weighed amount of gelatin was heated to 90 °C for approximately 30 min, then it was filtered and poured into tubes (150 × 5 mm) provided with a stopper on the bottom. The gel was left to set at room temperature, then cooled in a refrigerator to 6.5 °C. After cooling to reaction temperature, about 1 cm from the bottom part of the tube was cut off and the tube was immersed into a reservoir with approximately 0.6 ml of a concentrated solution of $AgNO_3$. At the same time, 0.2 ml of the nitrate was pipetted onto the top of the tube (Fig. 1). The tube was immediately placed in a refrigerator and left in the dark at 6.5 °C for 24 h. Under these conditions, a system of well defined sharp bands of primary and secondary structure was formed. In another series of experiments instead of gelatin agar was used (Agar, Medika Bratislava) with the concentration

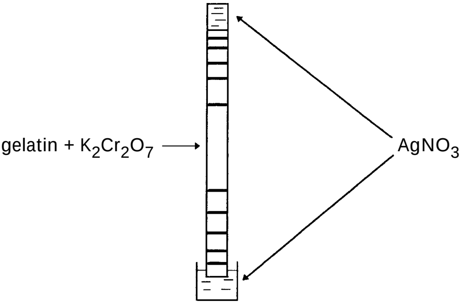

FIG. 1
Experimental arrangement for the evaluation of Liesegang bands in the parallel and antiparallel direction to the gravitational field

of 1 wt.%, the reactants being $Pb(NO_3)_2$ (saturated solution), and 0.012 M KI. Sharp bands of PbI_2 were formed, however, no secondary structure could be detected in this system. The spatial arrangement of Liesegang bands was measured by means of a travelling microscope (Abbé Komparator, Carl Zeiss Jena). Some tubes were photographed, the photographs were enlarged and the positions of bands were measured with a ruler.

RESULTS AND DISCUSSION

As stated in ref.[13], the main problem in providing the existence of a gravitational efect on Liesegang bands comes from the difficulty of performing reproducible experiments. A system far from equilibrium can be strongly affected by various internal and external factors. The present experimental arrangement provides equal conditions for the pattern formation in both parallel and antiparallel orientation of the gravitational field. For the evaluation of experiments the spacing law in the form (*1*) was used[7,14]:

$$x_N = x_0\, p^N \,, \qquad (1)$$

where x_N is the position of the N-th band, x_0 the initial position (the top and/or the bottom of the tube), and p is the spacing coefficient. From the logarithmic form of Eq. (*1*) a straight line can be obtained in the coordinates $\ln x_N = f(N)$. However, only first 6–7 bands lay on the straight line. The Jablczynski law (*2*) for the ratio of band distances x_N and x_{N-1} was also used:

$$x_N/x_{N-1} = \alpha \,, \qquad (2)$$

α being constant for most investigated Liesegang systems. Typical dependences of $\ln x$ on N for $Ag_2Cr_2O_7$ bands evaluated in both parallel and antiparallel directions to the gravitational field are presented in Fig. 2. The figure demonstrates that there is only little difference between the corresponding straight lines, the values of the spacing coeficients being 1.0202 for the parallel and 1.0144 for the antiparallel direction to the gravitational field, respectively. These values do not permit an unambiguous conclusion. The values of the spacing coefficients p as well as the values of α for the primary and secondary structure of $Ag_2Cr_2O_7$ Liesegang bands are summarized in Table I. It can be seen that the mean values of spacing coefficients indicate the effect of gravity. However, their differences for both directions to

TABLE I
Spacing coefficients p and the ratios $\alpha = x_N / x_{N-1}$ for the $Ag_2Cr_2O_7$ Liesegang bands evaluated in the parallel and antiparallel direction to the gravitational field; 10 wt.% of gelatin, 0.017 M $K_2Cr_2O_7$, saturated solution of $AgNO_3$, 6.5 °C

Experiment	p (parallel)	p (antiparallel)	α (parallel)	α (antiparallel)
		Primary structure		
1	1.0014 ± 0.0005	1.0015 ± 0.0002	1.0019 ± 0.0005	1.0018 ± 0.0005
2	1.0012 ± 0.0004	1.0019 ± 0.0006	1.0016 ± 0.0004	1.0019 ± 0.0006
3	1.0023 ± 0.0001	1.0035 ± 0.0002	1.0032 ± 0.0010	1.0037 ± 0.0010
4	1.0136 ± 0.0003	1.0185 ± 0.0005	1.0220 ± 0.0030	1.0240 ± 0.0020
5	1.0021 ± 0.0002	1.0023 ± 0.0001	1.0029 ± 0.0010	1.0030 ± 0.0008
		Secondary structure		
6	1.0090 ± 0.0048	1.0061 ± 0.0030	1.0070 ± 0.0022	1.0072 ± 0.0014
7	1.0046 ± 0.0004	1.0053 ± 0.0004	1.0076 ± 0.0021	1.0093 ± 0.0032
8	1.0044 ± 0.0009	1.0053 ± 0.0007	1.0060 ± 0.0016	1.0096 ± 0.0033

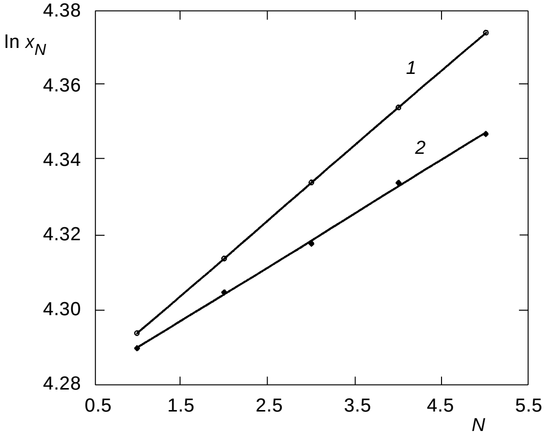

FIG. 2
ln x_N *vs* N plot according to Eq. (*1*): *1* parallel, *2* antiparallel direction to the gravitational field; 10 wt.% of gelatin, 0.017 M $K_2Cr_2O_7$, saturated solution of $AgNO_3$, 6.5 °C

the gravitational field are within the experimental error (experiments 3 and 4 are the exceptions). The primary and secondary structures show the same effect which is in favour of the opinion that the secondary structure is an integral part of the Liesegang phenomenon. The values of the spacing coefficients *p* for PbI_2 bands in agar in the parallel and antiparallel direction to the gravitational field are 1.0022 ± 0.0002 and 1.0027 ± 0.0006, respectively.

The effect of gravity on the formation of Liesegang bands is considered as a support of the postnucleation theory of periodic precipitation. According to this theory, the structure arises from a spatially continuous region of colloid in a long time after nucleation has occurred. The influence of gravity on the band locations assumes the existence of colloid particles of several hundred angströms in size[7]. Roughly estimated, the colloid particle in a Liesegang system consists of about 11 molecules of silver chromate[4]. The mass of such an aggregate is obviously too small to be influenced by the gravitational field to a measurable extent; hence, the negative result of the measurement of the gravity effect on Liesegang patterns does not necessarily imply rejection of the postnucleation theory.

A definitive conclusion about the absence and/or presence of the effect of gravity on periodic precipitation needs further work with other Liesegang systems besides the classical one.

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