The effect of electric field on the Liesegang ring

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The Liesegang pattern which develops in diffusion-precipitation systems has been intensively studied since the discovery. In earth sciences, it is well known as the banding structures in sedimentary rocks and the vesicle layering in solidified magma bodies. Recently we experimentally found that the pattern transition from the periodic banding precipitation pattern to the tree-like crystal aggregates pattern occurs as the agar concentration varies. In the present talk, we report the result of experiments under electric fields, which aim at understanding the effect of advection on the diffusion-precipitation system.

Agar solutions of KI and $Pb(NO_3)_2$ are prepared as plates (2cm x 8cm x 0.5cm). Agar plates of KI and of $Pb(NO_3)_2$ are contacted at 2cm wide side. The electric fields are applied at the ends by Pratinum electrodes (- at KI side and + at $Pb(NO_3)_2$ side). Concentrations of KI and $Pb(NO_3)_2$ are kept at constants 0.32mol/l and 0.01mol/l, respectively. Concentrations of agars are varied of 0.5 and 2.5wt%, and the field strengths are varied of 2, 5, 10, 20 V.

The precipitation patterns are structurally divided into two distinct regions in space of $Pb(NO_3)_2$) agar: near-region and far-region against KI agar. The propagation velocity of precipitation increases with the field strength, and approximately 0.7cm/hr at 10V. The change from the near-region to the far-region discontinuously occurs in space. In the near-region, quite narrow bands of precipitation are developed. The spacing of band (0.15 - 0.3mm in width) is constant regardless of distance from the contact and decreases with increasing the field strength. Each grain in precipitation bands is an irregular branching crystal. At higher agar concentration (2.5wt%), such a banding structure appears under all of field strengths, whereas at lower agar concentration (0.5wt%), it does only under higher field strength (10 and 20V). The spacing of band In the far-region, the banding structure with wider spacing by one order of magnitude than that in the near-region appears depending on the voltage and agar concentration.

Generally the spacing of band is controlled by the interplay between two competing effects: the supersaturation of PbI_2 monomer due to increase of I concentration, and the decrease of monomer concentration by the crystallization with diffusion. Let us dx as the band spacing, dt as the time interval of neighboring band formation, v as the propagation velocity of supersaturation and D as the diffusivity of monomer PbI_2. When the propagation length of supersaturation during dt exceeds the length scale of depletion of monomer, the next precipitation band occurs. Namely $v\,dt = (D\,dt)^{1/2}$ must hold. Then the band spacing $dx = v\,dt = D/v$ is derived. Values of $v=0.7cm/hr=2x10^{-6}$(m/s) and dx= 0.2mm at 10V yields the realistic value of $D=4 \times 10^{-10}$ (m^2/s) in agar solution. In the case of ordinary Liesegang ring without electric fields, the propagation velocity of supersaturation, v, is controlled only by the diffusion of I anion from KI agar and decreases with distance from the contact, so that the band spacing decreases with distance following the geometric progression.