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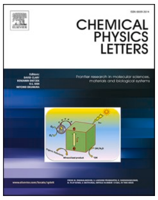

Propagation behavior of silver hydroxide precipitate bands

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ABSTRACT

When sodium hydroxide diffuses in a gel medium containing silver nitrate, silver hydroxide precipitates and forms a white band in a narrow glass tube. The silver hydroxide precipitate changes to brown silver oxide due to its instability in excess diffusing electrolyte. As a result, and in contrast to the Liesegang ring phenomenon, in which a series of bands forms, the whole AgOH band propagates via formation due to precipitation and disappearance due to conversion to the more thermodynamic stable Ag_2O. The dynamics of the propagating silver hydroxide band exhibits a power law behavior for the distance traveled and the velocity with time. The effect of changing the gelatin percentage on the occurrence and the width of the band were investigated and showed a linearly increasing width as a function of gel percentage until a specific gel percentage. The dependence of the formation of the precipitates on the local concentration of NaOH confirms that the mechanism of the AgOH band formation is diffusion regulated.

1. Introduction

The spontaneous formation of solid-phase dynamic patterns driven far from equilibrium has been the subject of interest of new research after the extensive work done in fluid mechanics [1–4]. Regularity in solid-phase systems arises in the spatial distribution of matter, or the temporal response of the solid to external stimuli, including the initial concentrations of electrolytes, the nature of the medium, applied electric fields, or temperature [5–7].

The phenomenon of solid particles moving in a stagnant gelatin or agar phase containing an inner electrolyte occurs when a precipitation reaction is coupled with redissolution as an outer electrolyte diffuses into the gelatin/agar medium. In some systems, the precipitate band or stratum of bands propagates, because once formed, it is dissolved in the presence of excess outer electrolyte, and another precipitate forms ahead of the reaction front. Many systems, including $Al(OH)_3/[Al(OH)_4]^-$, $Co(OH)_2/[Co(NH_3)_6]^{2+}$, $HgI_2/[HgI_4]^{2-}$ as the precipitate/dissolved ion systems, have been studied [8–10]. These systems differ from the one studied in this paper by the fact that for the silver nitrate-sodium hydroxide system, precipitation of AgOH is followed by the formation of the more stable solid Ag_2O rather than redissolution or formation of a complex in solution as diffusion proceeds. The current study also paves the way for pH-controlled growth of Ag_2O nanoparticles, which possess oxidant [11,12] and electrical [13] properties.

In aqueous solution, when silver nitrate is mixed with sodium hydroxide, an acid base-reaction takes place, since the silver ions in water are in the form of the aqua complex $[Ag(H_2O)_4]^+$, which can donate a proton to the hydroxide ion and thus act as a weak Bronsted acid.

$$[Ag(H_2O)_4]^+ \text{ (aq)} + OH^- \text{ (aq)} \rightleftharpoons AgOH \text{ (s)} + 4\, H_2O\text{(l)} \tag{1}$$

The pH of the aqueous solution of silver nitrate can be calculated from the formula for the pH of weak acids $pH = \frac{1}{2}(pK_a - \log c)$, where K_a is the acid dissociation constant of $[Ag(H_2O)_4]^+$ ($pK_a = 11.7$) and c is the initial concentration of silver nitrate. The precipitation of AgOH will start when the pH of the mixture is approximately one order of magnitude greater than the pH of the silver nitrate solution. After the precipitation proceeds, and as the pH increases, the white AgOH spontaneously yields the thermodynamically more stable brown silver oxide Ag_2O [11,14,15].

$$2\, AgOH \text{ (s)} \rightarrow Ag_2O \text{ (s)} + H_2O\text{(l)} \tag{2}$$

Thus, the overall reaction that takes place in an aqueous medium upon mixing silver nitrate with sodium hydroxide is.

$$2\, [Ag(H_2O)_4]^+ \text{ (aq)} + 2\, OH^- \text{ (aq)} \rightarrow Ag_2O \text{ (s)} + 9\, H_2O \text{ (l)} \tag{3}$$

Under normal conditions the reaction is fast, and the brown Ag_2O precipitate forms directly. However, in this study the large excess of OH^-

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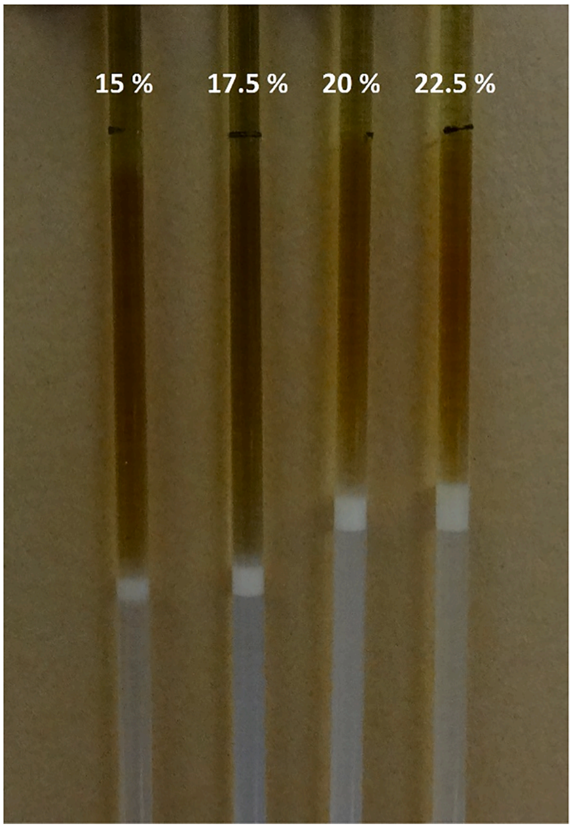

Fig. 1. White AgOH bands formed by the diffusion of the outer electrolyte NaOH solution through the inner gelified $AgNO_3$ solution for different gel percentages. The inner diameter of the tube is 0.30 cm. Picture taken 105.0 h after the start of the diffusion.

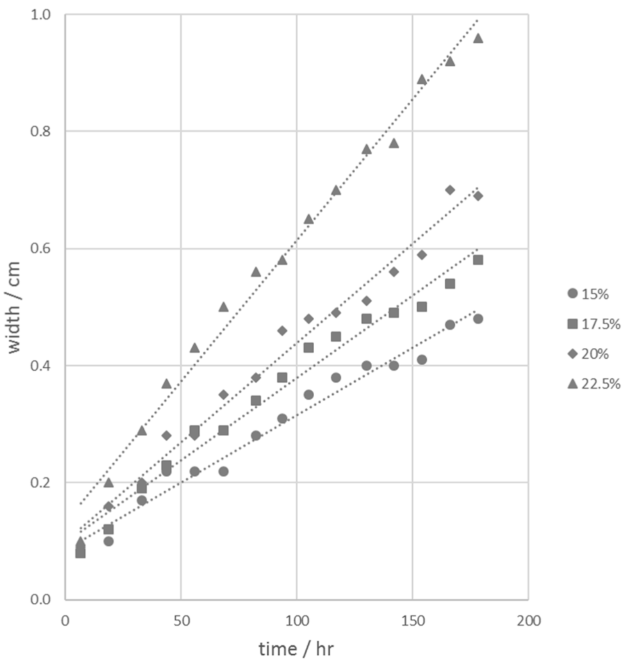

Fig. 2. The width of the AgOH precipitate band in the $AgNO_3$/NaOH system as a function of time for experiments with 15%, 17.5%, 20%, and 22.5% gel percent. The error bars are smaller than the size of the symbols.

ions diffuses into an aqueous gel matrix in which Ag^+ ions are homogeneously distributed. The encounter between the ions is slowed by diffusion, and an isolated white AgOH precipitate band is formed first at the reaction front. Then as the hydroxide ion concentration increases with time, the band propagates vertically, and the more stable brown Ag_2O forms at the upper edge of the band. The macroscopic propagation of the AgOH precipitation band serves as a visual measure of the dynamics of the processes taking place. Our results show that the propagation is characterized by scaling laws, and the band propagation is proportional to the square root of time. In what follows, we also explain the effects of the gel percentage and the local concentration of the hydroxide ions on the band appearance and propagation.

2. Experimental

Gel solutions of silver nitrate were prepared by dissolving the desired amounts of reagent grade $AgNO_3$ and gelatin powder (Sigma Aldrich) in distilled water. The gel solutions were heated and stirred until they became homogeneous. The following two sets of gelatin and silver nitrate solutions were prepared; *Set A*: 10%, 12.5%, 15%, 17.5%, 20%, 22.5%, 25%, and 27.5% gelatin with 0.02 M $AgNO_3$, and *Set B*: 20% gelatin with 0.01 M, 0.02 M, 0.03 M, 0.04 M, 0.05 M, and 0.06 M $AgNO_3$. Each solution was used to fill 15 cm of a 20 cm glass tubes of 0.3 cm inner diameter. A set of three tubes was prepared for each gel percent as a reproducibility check. The solutions in the glass tubes were then left to gel overnight at room temperature and in the dark to avoid the photoreduction of silver ions [16]. On the second day, the upper level of the gelled silver nitrate (inner electrolyte) solutions in the tubes were marked and sodium hydroxide NaOH (outer electrolyte) solutions were added to fill the empty upper 5 cm in the glass tubes. 1.6 M NaOH solution was added to the tubes of *Set A*; and 1 M, 2 M, 3 M, and 4 M NaOH solutions were added to the tubes of *Set B* for each $AgNO_3$ concentration. Then tubes were covered and placed in the dark. The instant at which sodium hydroxide touched the inner electrolyte solution marked the beginning of the experiment. The diffusion of the outer electrolyte solution into the inner electrolyte was left to proceed, and distance measurements were regularly taken.

3. Results

For *Set A* experiments, at gel percentages less than 15%, no bands were formed during the first days after the addition of NaOH and the start of the experiment. Later very thin bands appeared, but it was difficult to measure their width. At gel percentages above 22.5%, the thin bands that formed initially disappeared after about a day, and the propagation of the brown Ag_2O continued down the tube.

For experiments with gel percentages 15%, 17.5%, 20%, and 22.5%, as the outer sodium hydroxide electrolyte solution diffuses into the gel medium containing the silver ions, the white silver hydroxide AgOH precipitate forms because of its low solubility product constant ($K_{sp} = 1.52 \times 10^{-8}$) [17]. Then, as the diffusion of the outer electrolyte continues, creating an excess of OH^- ions, the unstable AgOH precipitate changes to brown Ag_2O [11,18]. This concomitant AgOH band formation by precipitation at the reaction front and then its change to Ag_2O at the band top lead to the propagation of the band down the tube with time. Fig. 1 shows the horizontal silver hydroxide white bands and the brown silver oxide above the bands for 15%, 17.5%, 20%, and 22.5% gelatin after four days from the start of the experiments.

The variations of the band width and the distance of the band front (d_f) and rear (d_r) from the outer/inner electrolyte interface with time for the 15%, 17.5%, 20%, and 22.5% gelatin experiments are shown in Figs. 2 and 3, respectively. The velocity of the AgOH precipitation (V_1) and that of the conversion to Ag_2O (V_2) are then calculated as the slope of the tangent to the curve in the $d_f(t)$ and $d_r(t)$ plots, respectively. The variations of V_1 and V_2 with time are presented in Fig. 4.

For *Set B* experiments, the AgOH white band was observed for 0.02

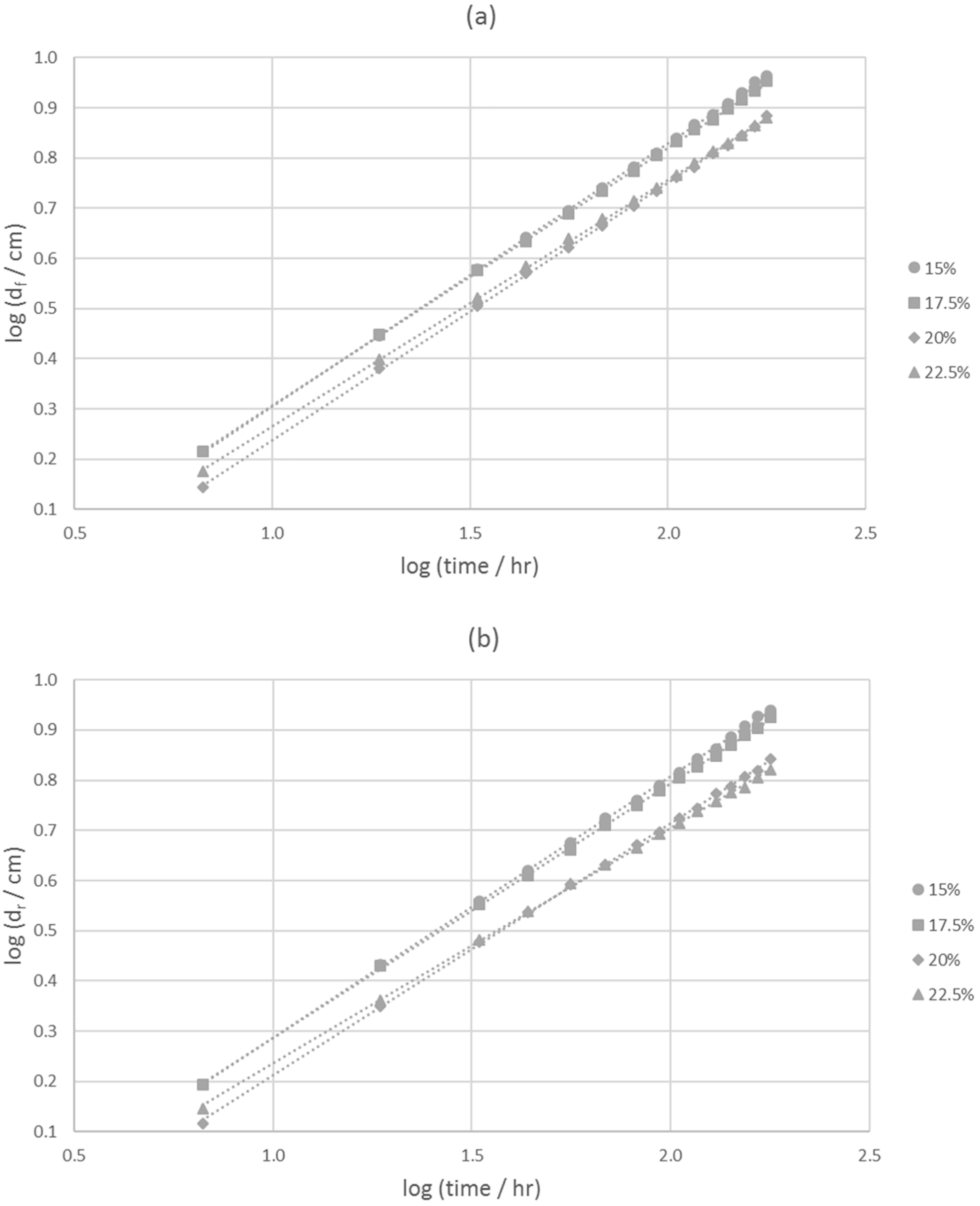

Fig. 3. Plots exhibiting scaling laws for the propagation of AgOH precipitate band for different gel percentages. (a) The variation of the distance of the band front from the outer/inner electrolyte interface (d_f) versus time in a log–log plot. (b) The variation of the the distance of the band rear from the outer/inner electrolyte interface (d_r) versus time in a log–log plot. The error bars are smaller than the size of the symbols.

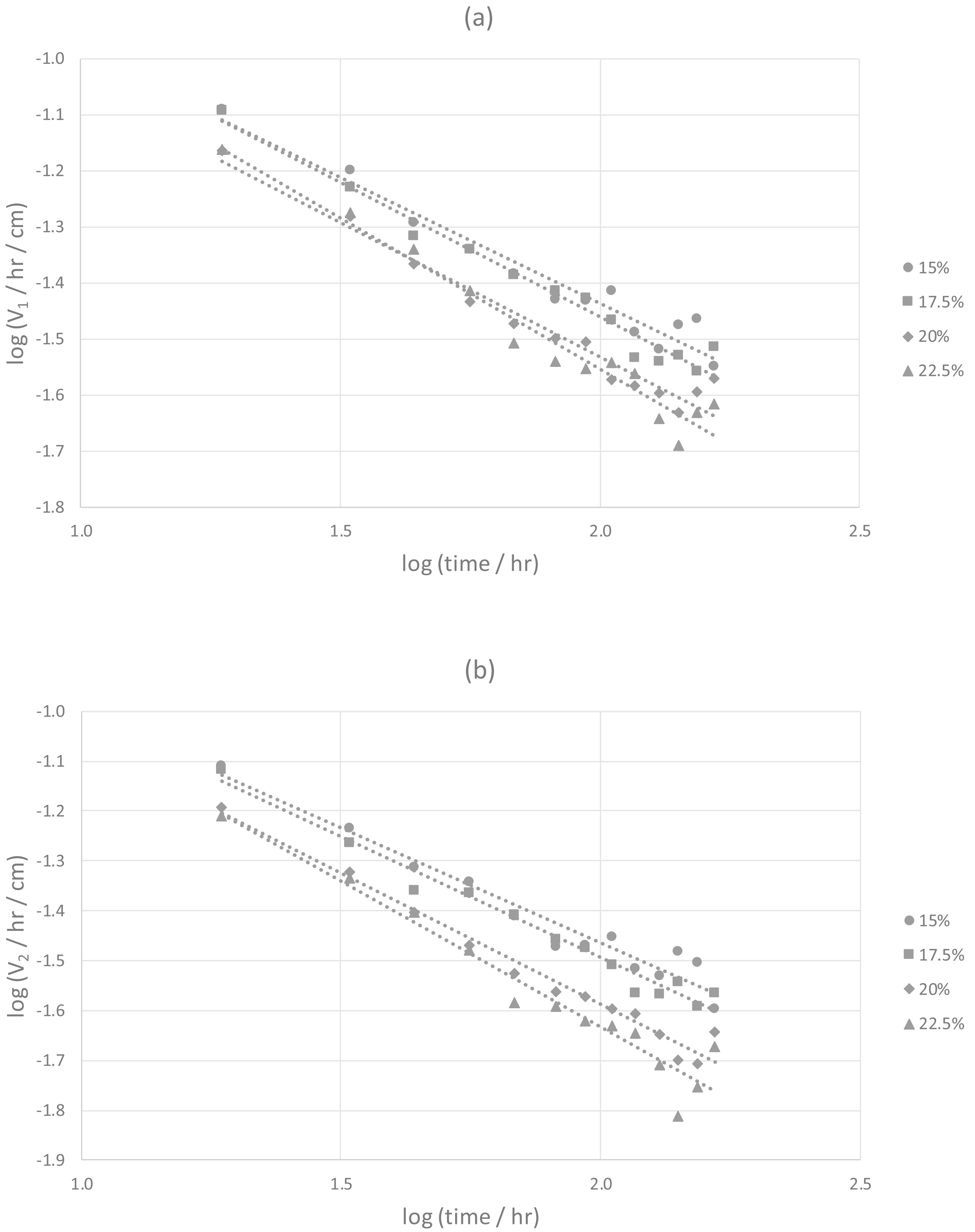

Fig. 4. Plots exhibiting scaling laws for the propagation of AgOH precipitate band for different gel percentages. (a) The variation of the velocity of AgOH precipitation (V_1) versus time in a log–log plot. (b) The variation of the velocity of conversion of AgOH to Ag_2O (V_2) versus time in a log–log plot. The error bars are smaller than the size of the symbols.

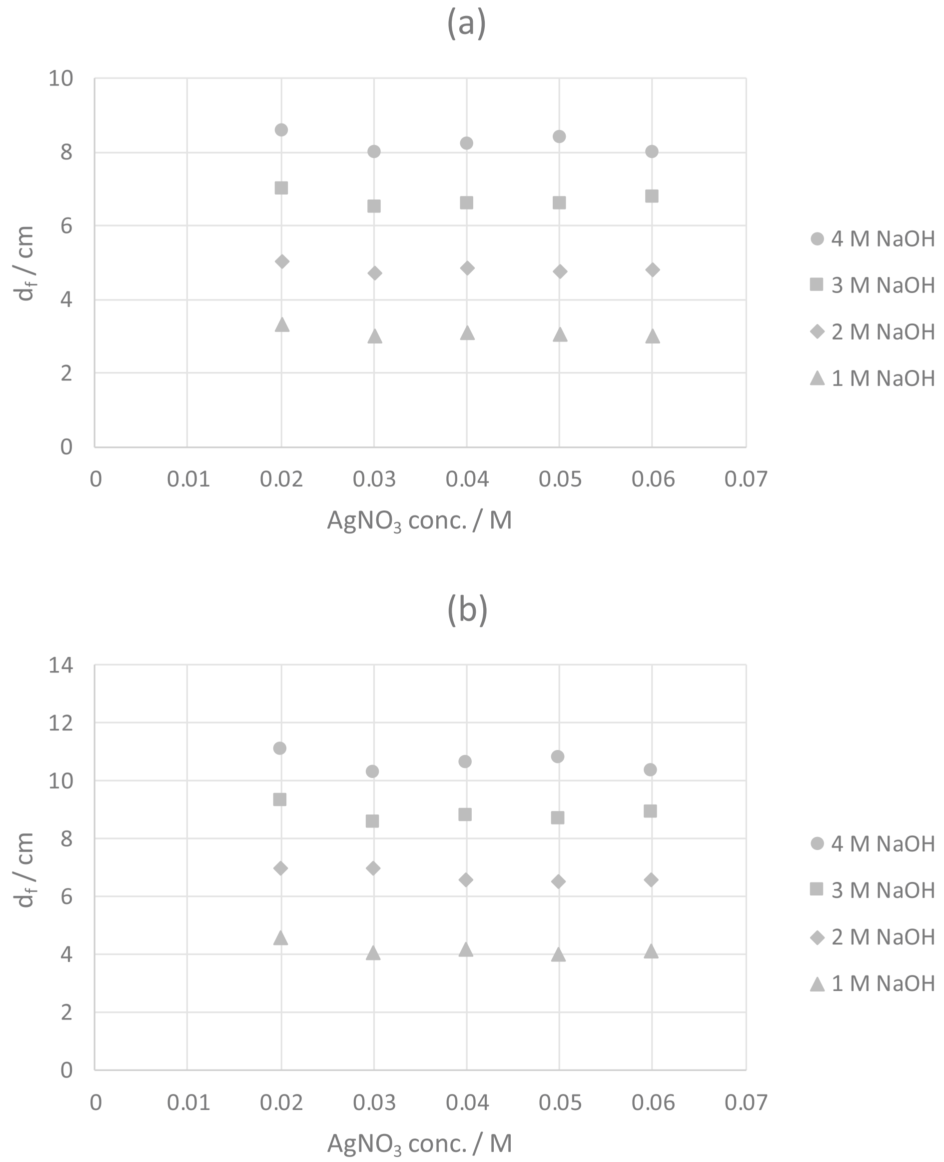

Fig. 5. The variation of d_f, the distance traveled by the reaction front, with the concentration of $AgNO_3$ for 1 M, 2 M, 3 M, and 4 M NaOH at two fixed times (a) 36.5 hr and (b) 63.5 hr. The gelatin percentage is 20%. The error bars are smaller than the size of the symbols.

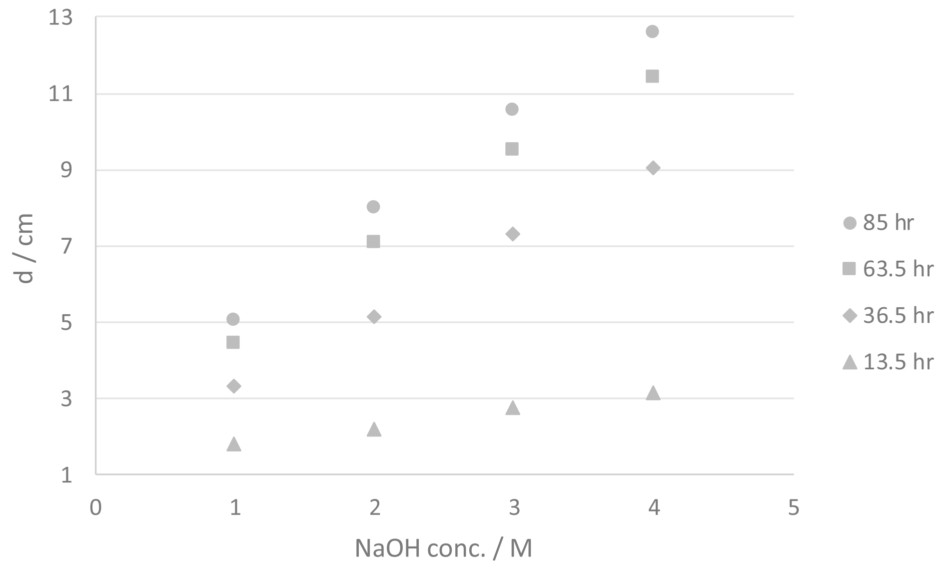

Fig. 6. The variation of d, the distance traveled by the reaction front, with the concentration of NaOH at four fixed times. The gelatin percentage is 20% and the $AgNO_3$ concentration is 0.01 M. The error bars are smaller than the size of the symbols.

Table 1
The values of power law exponent for the dependence of d_f, d_r, V_1, and V_2 on time.

Power law exponent	Distance and velocity	15% gel	17.5% gel	20% gel	22.5% gel
α	d_f	0.524	0.514	0.512	0.491
	d_r	0.521	0.508	0.503	0.470
β	V_1	−0.45	−0.48	−0.48	−0.54
	V_2	−0.46	−0.48	−0.53	−0.59

M, 0.03 M, 0.04 M, 0.05 M, and 0.06 M $AgNO_3$ concentrations. The distance traveled by the band front d_f from the interface was measured and Fig. 5 shows the variation of d_f with the concentration of silver nitrate for 1 M, 2 M, 3 M, and 4 M NaOH concentrations at two selected times. On the other hand, the white AgOH band was not detected for the 0.01 M $AgNO_3$ experiments at any of the NaOH concentrations used. Silver hydroxide was directly converted to silver oxide and the distance d traveled by Ag_2O from the reaction front is plotted as a function of the NaOH concentration in Fig. 6 at four selected times.

4. Discussion

The width of the silver hydroxide precipitate band at a given instant increases with the gelatin percentage, as seen in Fig. 2. This effect may result from the internal branched structure of the gelatin, which is denser at higher gel percentages, leading to a faster nucleation rate and larger number of small crystals dispersed in the polymer matrix [19–21]. This more rapid nucleation of AgOH precipitate coupled with the slower diffusion of NaOH at higher gelatin percentages produces the observed trend in band width. However, at the highest gel percentages, 25% and 27.5%, although the rate of nucleation of silver hydroxide is fast, yet AgOH forms close to the interface and changes readily to Ag_2O. This explains why at early times a thin AgOH band forms which later disappears and the change to Ag_2O takes over. On the other hand, at 10% and 12.5% gel percentages, fewer nuclei are formed, and the diffusion of excess hydroxide ions is fast, thus hindering the formation of an AgOH band except at longer times, when the local concentration of the hydroxide ions becomes smaller.

To determine the temporal evolution of the band front and the band rear, we investigated the distance of the band front from the outer/inner electrolyte interface (d_f) and the distance of the band rear from the outer/inner electrolyte interface (d_r) as functions of time. Fig. 3 (a) and (b) show d_f and d_r monotonically increasing with time for experiments with 15%, 17.5%, 20%, and 22.5% gelatin. As expected, the distance traveled at any instant decreases with increasing gel percent. In addition, both $d_f(t)$ and $d_r(t)$ are proportional to t^α with α close to 0.5 for all gel percentages, Table 1. This square root time dependence of the vertical propagation of the band suggests that the rates of formation of both AgOH and Ag_2O are controlled by diffusion [22].

The temporal variation of the velocity of AgOH precipitation (V_1) and that of the conversion to Ag_2O (V_2) are shown in Fig. 4. Both velocities V_1 and V_2 decrease with time as the pattern moves away from the interface and they also exhibit a scaling law, $V(t) \propto t^\beta$, with β close to −0.5, Table 1. Table 2 presents a summary of the rates of the processes and the resulting relationship between V_1 and V_2 for band appearance at

Table 2
Relative relationships between processes for band occurrence for experiments with 10%, 12.5%, 15%, 17.5%, 20%, 22.5%, 25%, and 27.5% gelatin percentages at early and later times.

Gelatin percentage	10% and 12.5%	15% and 17.5%	20% and 22.5%	25% and 27.5%
OH^- ion diffusion rate	Very fast	Fast	Slow	Very slow
AgOH nucleation rate	Very slow away from the interface	Slow nucleation	Fast nucleation	Very fast nucleation close to the interface
Early times	$V_1 < V_2$	$V_1 > V_2$	$V_1 > V_2$	$V_1 > V_2$
Later times	$V_1 > V_2$	$V_1 > V_2$	$V_1 > V_2$	$V_1 < V_2$
Band formation	Band forms only at later times when the diffusion of OH^- becomes slower	Narrow band forms away from the interface	Thick band forms close to the interface	Band forms only at early times then the conversion to Ag_2O takes over

early and late times for the entire span of the gelatin percentages studied.

The relative temporal variation of the velocities V_1 and V_2 directly affects the dependence of the band width on the time since it is this repetitive AgOH precipitation/conversion to Ag_2O cycle that yields the behavior observed in Fig. 2. Table 1 shows that the velocity of conversion V_2 is decreasing faster with time than the velocity of precipitation V_1, which leads to the increase of the band width away from the interface as time advances. This result of a linearly increasing width with time differs from experimental findings on other chemical systems [8,23] and theoretical studies [24,25], which showed a constant width with time or an exponential behavior.

The effect of the local concentrations of Ag^+ and OH^- ions on the rates of formation of AgOH and Ag_2O was further investigated by varying the initial concentrations of the inner and outer electrolytes at a fixed gelatin percentage. Fig. 5 shows that the distance d_f of the AgOH band front from the interface is almost independent of the local concentration of Ag^+ ions and is largely dependent on the concentration of the outer diffusing electrolyte NaOH. In addition, for the experiments with 0.01 M $AgNO_3$ where no AgOH bands were observed, the distance d of the Ag_2O reaction front from the interface shows a direct dependence on the concentration of the outer diffusing electrolyte NaOH, Fig. 6. These findings emphasize the role of the local concentration of the hydroxide ion, as the main factor in determining the evolution of the pattern. At a fixed gelatin percentage, the local concentration of NaOH increases with its initial concentration due to an increased gradient along the experimental tubes. And the dependence of the formation of AgOH and Ag_2O on the local concentration of OH^- ions unrelatedly to the local concentration of Ag^+ ions confirms that the mechanism of the AgOH band propagation is diffusion regulated.

Finally, such band propagation so far has no well-established experimental laws for its propagating precipitation process similar to the time law and width law of the well-known Liesegang phenomenon [26–28].

5. Conclusion

The diffusion of hydroxide ions into a gel medium containing silver ions generates a single migrating precipitate band due to the instability of the precipitate AgOH formed in the presence of excess hydroxide ions. The migration process is characterized by a square root dependence on time of the distance of the band front and band rear from the outer/inner electrolyte interface, suggesting that the behavior is governed by diffusion. In addition, the width of the band increases with time and varies with the gelatin percentage. The local concentration of the hydroxide ions plays the major role in the evolution of the pattern.

Data availability statement

The data that support the findings of this study are available from the authors upon request.

CRediT authorship contribution statement

Layla Badr: Methodology, Validation, Formal analysis, Writing – original draft. **Irving Epstein:** Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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