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Multicomponent convection in the chlorite–tetrathionate reaction

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Abstract

The effect of chemical composition on the density fingering arising in the acid-catalyzed reaction of chlorite and tetrathionate ions is investigated experimentally. The increase in the concentration of reactants increases the region of convective instability observed in the reaction for both upward and downward propagating fronts. The increase of hydroxide ion concentration, however, stabilizes the downward propagating fronts and destabilizes the upward propagating fronts allowing multicomponent convection to dominate the pattern formation for certain chemical composition. The density fingering is also analyzed quantitatively by determining the dispersion curves and their characteristics describing the initial evolution of the pattern formation.

1. Introduction

Pattern formation arising from the interaction of reaction and transport processes are abound in nature. In chemical systems the simplest structures are propagating reaction–diffusion fronts, which may be altered by the macroscopic motion of the fluid [1]. Enhanced front velocities and cellular structure formation have been observed in numerous reaction [2–4]. If the solution with higher density lies on top of that with lower density in a sufficiently wide reaction vessel, the buoyant forces enhance the mixing of the reactants and products leading to higher front velocities in that direction [1]. This then results in a convectively unstable planar front: in thin tubes near the onset of convection first asymmetric [5] then symmetric structures develop on increasing the tube diameter due to the convection rolls of the fluid motion. In the opposite direction, however, convection does not arise and therefore, the usual reaction-diffusion fronts are observed. This phenomenon was categorized by Pojman et al. [6,7] as simple convection. In most circumstances heat evolution from exothermic reactions cannot be neglected. The local increase in temperature results in the thermal expansion of the solution, which may yield an overall density change opposite to that of pure solutal density change. This leads to the phenomenon multicomponent convection where front propagation in both direction differs from pure reaction–diffusion fronts [8,9].

The chlorite oxidation of tetrathionate is an acid-catalyzed reaction in slight chlorite excess [10]

$$7\mathrm{ClO_2^-} + 2\mathrm{S_4O_6^{2-}} + 6\mathrm{H_2O} = 7\mathrm{Cl^-} + 8\mathrm{SO_4^{2-}} + 12\mathrm{H^+} \quad (1)$$

with an empirical rate law of

$$r = -\frac{1}{7}\frac{\mathrm{d}[\mathrm{ClO_2^-}]}{\mathrm{d}t} = k[\mathrm{ClO_2^-}][\mathrm{S_4O_6^{2-}}][\mathrm{H^+}]^2. \quad (2)$$

The reaction can serve as a model for studying convective instabilities since in pure reaction–diffusion fronts a two-variable model based on Eq. (2) describes the experimental observations almost quantitatively both in closed [11–13] and open systems [14]. Under the conditions applied earlier [4], density increases in the course of the reaction leading to convectively stable upward and unstable downward propagating fronts. In wide and narrow cells (so-called Hele-Shaw cells [15]) the initially planar downward propagating front loses stability resulting in a cellular structure because of the buoyant forces arising due to the isothermal density change. The reaction is highly exothermic [4] and it has been shown that for thicker cells the heat removal becomes important [16], since besides leading to density fingering for

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upward propagating fronts, it also affects the instability of the downward propagating front. This type of multicomponent convection has been observed qualitatively in numerous reactions [7–9], detailed quantitative study, however, has not been carried out.

With the increasing number of theoretical works on the hydrodynamics of reacting interfaces [17,18], there is a great need for experimental studies providing data comparable to simulations [4,19,20]. Our aim is therefore, to describe quantitatively how the change in the chemical composition affects the convective instability observed in the chlorite–tetrathionate reaction which may also serve as a basis for numerical modelling of density fingering in this and similar systems [21,22].

2. Experimental

Reagent-grade chemicals (Sigma, Aldrich, Reanal) were used throughout the work, except for $NaClO_2$ (Aldrich, Tech.), which was recrystallized twice as described previously [11]. The solution with composition in Table 1 was mixed and injected into a Hele-Shaw cell of $16 \times 12 \times 0.104$ cm with Plexiglas walls at temperature 25 ± 1 °C. Planar fronts were initiated electrochemically by applying a 2–6 V potential difference between a pair of thin Pt-wire electrodes (0.4 mm in diameter) for 2–3 s. The traveling fronts were monitored through an appropriate cut-off filter – to enhance contrast between reacted and fresh solutions – by a monochrome CCD camera connected to an MVdelta imaging card. Frames of 768×576 pixels were digitized in 0.6–3 s intervals and processed by applying standard imaging procedures.

The densities of the reactant and the product solutions were measured by a digital density-meter (AP Paar DMA 58) within 10^{-5} g/cm^3 precision at 25 °C. The density change due to thermal expansion was calculated from the temperature profiles measured in a separate set of experiments. A thin thermocouple was placed in the solution and the temperature was measured as the front passed the thermocouple. The maxima of the temperature rise was in the range of 0.5–1.0 K on decreasing the initial concentration of hydroxide and 0.2–0.8 K on increasing the initial concentrations of potassium tetrathionate and sodium chlorite. The dispersion curves describing the initial evolution of the pattern formation were determined as described previously [4].

Table 1
Composition of reactant solution

$[K_2S_4O_6]$/mM	2.5–7.5
$[NaClO_2]$/mM	10–30
[NaOH]/mM	1–25
[Congo red]/mM	0.574

3. Results and discussion

Pure reaction–diffusion fronts of the chlorite oxidation of tetrathionate can be described by a two-variable model based on the empirical rate law of Eq. (2) valid only for a slight chlorite excess [11]. The ratio of the initial concentrations of chlorite to tetrathionate is therefore, kept constant and were set to 4.0 in the experiments. On increasing the initial concentration of the reactants with constant $[NaOH]_0$, the densities of both reactant and product solutions increase with increasing difference between them as shown in Fig. 1. The linear dependence illustrates that the solutions are dilute, the partial molar volumes are constant and additivity for the molar densities in the modelling can be applied [21]. Fig. 2 clearly illustrates that the region of instability for the downward propagating fronts increase on increasing the initial concentration of the reactants. At higher concentrations, the patterns appear earlier and the average wavelength decreases from 4.5 to 3.4 mm. The linear evolution of density fingering is quantitatively analyzed by determining the dispersion curves shown in Fig. 3. Increasing the initial concentration of potassium tetrathionate from 2.50 to 3.75 mM leads to an initial pattern where both the growth rate and the wave number of the most unstable mode increase. The further

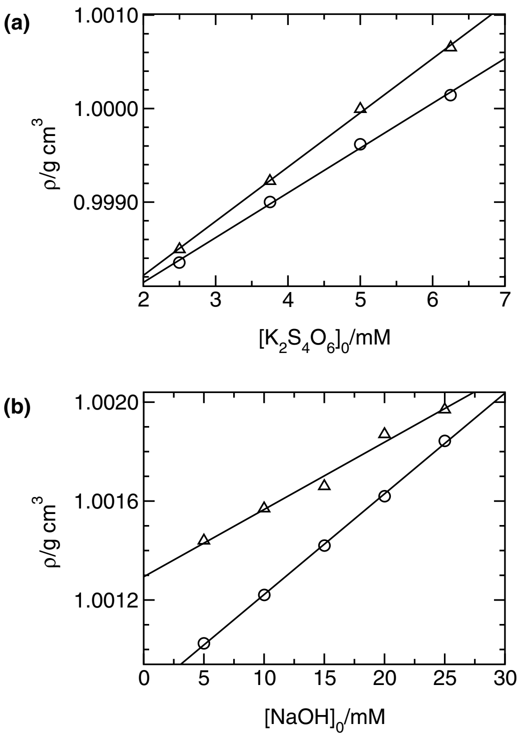

Fig. 1. The density of the reactant (○) and the product (△) at 25 °C as the function of the initial concentration of potassium tetrathionate with $[NaOH]_0 = 1$ mM (a) and as the function of the initial concentration of sodium hydroxide with $[K_2S_4O_6]_0 = 7.5$ mM (b) and $[NaClO_2]_0/[K_2S_4O_6]_0 = 4$.

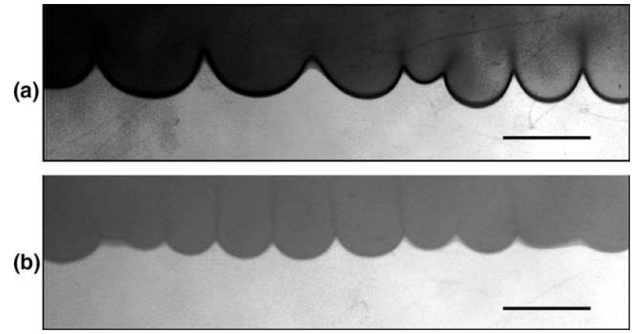

Fig. 2. Images of fronts propagating downwards for $[K_2S_4O_6]_0 = 3.75$ mM at $t = 90$ s (a) and for $[K_2S_4O_6]_0 = 6.25$ mM at $t = 51.6$ s (b). Darker regions represent the denser product solution and lighter the reactant. The black bar corresponds to 5 mm.

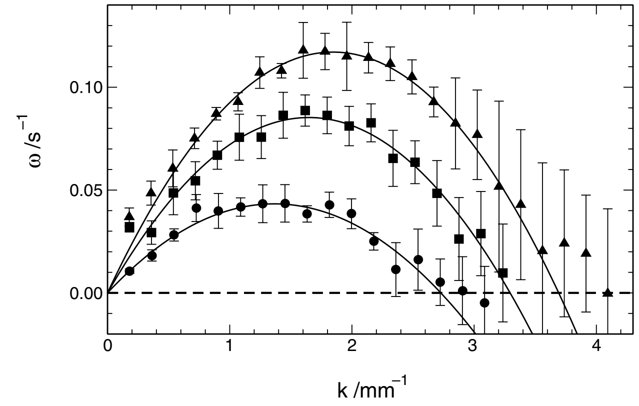

Fig. 3. Dispersion curves for $[K_2S_4O_6]_0 = 2.50$ mM (●), $[K_2S_4O_6]_0 = 3.75$ mM (■), and $[K_2S_4O_6]_0 = 6.25$ mM (▲) with $[NaClO_2]_0/[K_2S_4O_6]_0 = 4$ and $[NaOH]_0 = 1$ mM. The solid lines correspond to the fitted parabolas with zero origin to determine the fastest growing mode.

increase in the concentration, however, yields an increase in the growth rate only with an almost constant wave number of 1.9 mm^{-1} for the most unstable mode. This is in good agreement with the average wavelength observed. The increasing thermal contribution to the density change across the front leads to the destabilization of the upward traveling fronts only at the highest concentrations applied ($[K_2S_4O_6]_0 > 7.5$ mM).

Hydroxide ions are originally added to the reactants to suppress self-initiation and therefore, are responsible for the quick removal of the autocatalyst. Our experiments show that the amount of hydroxide ions present in the reactant mixture is an additional parameter controlling the behavior of the propagating front: the increase of the initial concentration from 5 to 20 mM not only significantly decreases the velocity of front propagation from 0.19 ± 0.01 to 0.09 ± 0.01 mm/s but also decreases the density change between the reactants and products as shown in Fig. 1. The additional heat elaborated by the neutralization is only 4% of the heat of the autocatalytic reaction, therefore, it would have negligible contribution to the thermal expansion of the solution in the adiabatic limit. This overall yields a decrease in the instability of downward propagating fronts and in the stability of upward propagating fronts which is confirmed by the observed behavior shown in Fig. 4. The convectively unstable regime for the upward propagating fronts slightly increases while the downward propagating fronts are significantly stabilized resulting in slowly evolving cells with an average wavelength of 4.9 mm.

At the highest initial concentration of NaOH applied, the instability of upward propagating front becomes sufficiently strong for the appearance of plumes shown in Fig. 5. The dynamics of the patterns clearly illustrates the effect of local increase in temperature giving rise to a locally lighter product which buoyantly rises quickly at first. As the solution cools down locally, the product becomes heavier and therefore drops in the lighter surrounding reactant solution (see Fig. 5f). New plumes then form along the flat segments of the front, and the cycle is repeated over again as the front propagates, which is a typical pattern formation arising as a result of multicomponent convection [1].

The two-variable model in its original form can only be applied for low reactant concentrations where simple convection is observed. The temperature profile may be approximated by a step function at the location of the front. For higher reactant concentrations where multicomponent convection appears, the model should be augmented with the energy balance equation. The incorporation of sodium hydroxide concentration as an additional parameter requires that the dissociation of water should be included in the chemistry as well. Since it is a fast equilibrium with respect to the autocatalytic step, the final model will also have two variables de-

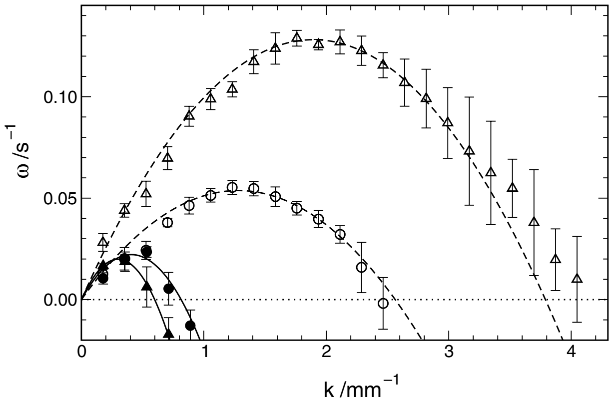

Fig. 4. Dispersion curves for downward and upward propagating fronts with $[K_2S_4O_6]_0 = 7.5$ mM, $[NaClO_2]_0 = 30.0$ mM and $[NaOH]_0 = 5$ mM (▲) for upward and (△) for downward propagating fronts and $[NaOH]_0 = 20$ mM (●) for upward and (○) for downward propagating fronts.

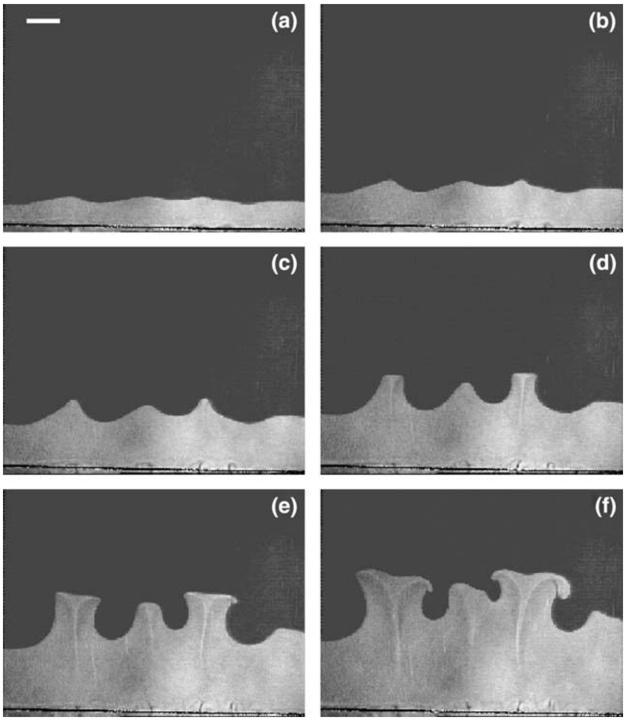

Fig. 5. The spatiotemporal pattern formation observed in the system with $[K_2S_4O_6]_0 = 7.5$ mM, $[NaClO_2]_0 = 30$ mM and $[NaOH]_0 = 25$ mM at $\Delta t = 60$ s. The white bar corresponds to 1 cm. Darker regions represent the reactant while the lighter regions the product solution.

scribing the chemical species, similarly to the application of fast reversible binding for hydrogen ions in previous studies of the reaction [12].

Finally, we can conclude that in the chlorite oxidation of tetrathionate there are two essential chemical control parameters: the initial concentration of the reactants and that of sodium hydroxide. Increasing the former raises both the solutal density change and the exothermicity of the reaction, which results in an expanding region of instability for the downward propagating fronts and at higher concentrations for the upward traveling fronts as well. On the other hand, increasing the initial concentration of sodium hydroxide lowers the solutal density change and has negligible contribution to the heat released, which has an opposite effect on the stability of fronts with respect to their direction at sufficiently high concentrations of reactants. The characteristics of the initially formed patterns are governed by the determined dispersion curves, which quantitatively describe the changes brought about by the variation of the concentration of the key species.

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