

Chemoconvective structures driven by a neutralization reaction

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Abstract

The development of chemoconvective motion in the initial stationary and steadily stratified system of aqueous solutions of the reacting liquids is studied experimentally in the vertical Hele-Shaw cell under the neutralization reaction conditions. It was found that depending on the initial reactant concentration, there are two reaction modes (i) diffusive mode, in which the dominant mass transfer mechanism is diffusion and (ii) convective mode characterized by the formation of the intense convective motion and high rate of reaction. A physical model of the observed phenomenon and the dimensionless parameter, determining the type of the reaction regime have been proposed. Maps of reaction regimes for different “acid-base” pairs were built.

1 Introduction

In the last decades, considerable progress has been made in the area of chemohydrodynamics, which studies the heat/mass transfer processes, the mechanisms responsible for the onset of hydrodynamic instability and the structure and flow evolution in the system of reacting fluids. From the fundamental point of view these problems attract considerable attention as the examples of nonlinear systems, in which the spatial-temporal variations of physical properties of fluids described by the reaction-diffusion equations can give rise to hydrodynamic instability, affecting the intensity of the heat/mass transfer processes up to a change in the type of reaction.

The development of the reaction in miscible and immiscible fluids has quite different scenarios. In experimental studies [1, 2] the new effects produced by the interaction of the exothermic neutralization reaction with the liquid-liquid interface of the two-layer system, placed in the Hele-Shaw cell are described. It was shown that by changing reagents and their initial concentrations it is possible to obtain different types of convective structures — spontaneous spreading of convective finger-shaped structures [1], which is commonly observed in such systems and even the ideal periodic system of convective cells formed in the zone between the interface and the reaction front [2].

Essentially different situation is observed in the systems of miscible reacting fluids [3-5]. Because of the absence of the interface the only source of chemoconvective structures is the gravitational mechanisms of instability initiated by the formation

of local zones with unstable density stratification. The first reason for the occurrence of such zones is the reaction product, whose density can differ from that of the surrounding medium which can lead to the formation of the Rayleigh-Taylor (RT) instability. The second is the double diffusion (DD) instability caused by the difference in the diffusion rate between reactants and the reaction product. In both cases the development of instability can provoke the formation of irregular convective structures in the form of salt fingers travelling at both sides of the reaction front. However, our previous work [5] has revealed the existence of the structure, which is not common for miscible systems. It consists of *periodic* convective rolls localized within the stable transient zone between the reagent layers. The theoretical studies showed that the discovered type of instability (we called it concentration-dependent diffusion instability or CDD convection) can be classified as DD instability and its onset is the result of *concentration dependence* of the diffusion coefficient. Bibliographical retrieval has shown that although there has been a lot of relevant works in the literature, up to now no systematic investigation (neither experimental nor theoretical) of the stability problem has been undertaken for miscible reacting systems. The only exception is paper [4], in which an attempt has been made to develop a generalized approach to such systems. However, the correctness of their approach is doubtful. The objective of the present paper is to study experimentally the stability of a two-layer system of miscible reacting fluids in the context of the problem of neutralization reaction. Based on the results of experiments with several “acid-base” liquid systems carried out in a wide range of concentration we developed a unified approach to the description of such systems.

2 Experimental technique

The experiments were performed in a vertically oriented Hele-Shaw cell made by glass plates separated by an insert, which specified the inner dimensions of the cavity: 9.0 cm×2.4 cm×0.12 cm. The cell was filled with a two-layer system of miscible reacting fluids, which had steady density stratification. One of the layers was an aqueous solution of HNO₃ and the other was formed by an aqueous solution of LiOH, NaOH or KOH. The solution concentrations varied in the range of 1.0div 3.0 mol/l. The slots were cut in the walls of the cell along its midsection to fit in the sliding shutter separating the initial reagents. At the beginning of each experiment the cell was filled to half its volume with a denser fluid (depending on the reagent concentration this might be either an aqueous solution of the acid or one of the hydroxides), after which the shutter was slid into the place and the less dense solution was pored into the cuvette over the shutter. In order to start the reaction the shutter was slid out from the cell.

The Fizeau interferometer was used to visualize the refractive index distribution caused by changes in the concentration distribution of species and by heat generation due to reaction exothermicity. The maximum temperature increment recorded by a thermocouple probe near the reaction front was less than 1 K. Light-scattering particles were added to the solution to observe the patterns forming during the reaction. We also visualised the pH distribution by adding a small amount of the universal acid-base indicator to the solutions. All experiments were performed at

ambient temperature (23 ± 1)°C.

3 Results

The results of experiments showed that there are two basic regimens of the reaction evolution: diffusion and convection. In the first case after the withdrawal of the shutter the front of reaction becomes the site of the formation of a transient zone with a stable stratification, in which the reagent transport is accomplished solely by diffusion (Figure 1 a). With the passage of time, as the reaction proceeds further, the vertical dimension of the zone slowly increases. The characteristic time of the reaction process is comparable with the diffusion time evaluated throughout the height of the cuvette. In our experiments it ranged from a few hours up to several days, depending on the initial concentration of the reagents.

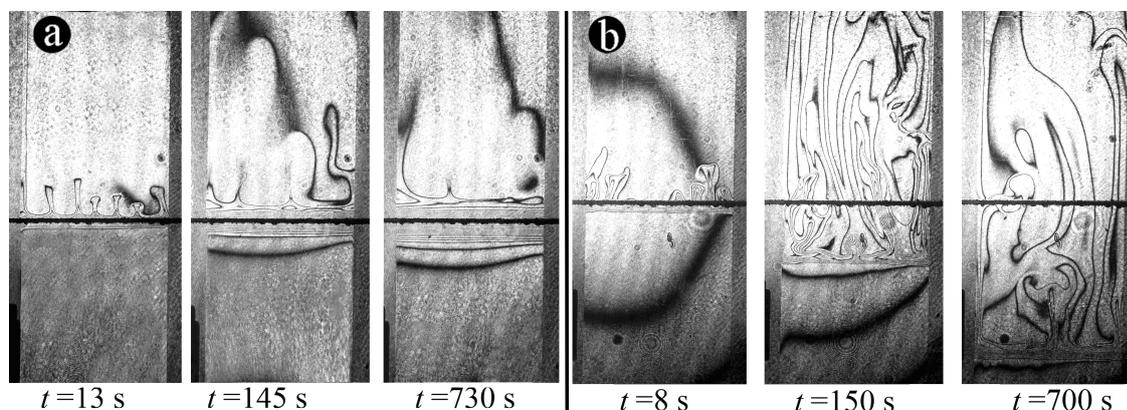


Figure 1: Time evolution of the reaction regimes. (a) Diffusive regime. The experiment is for HNO_3 ($C_a=1$ mol/l) and NaOH ($C_b=2$ mol/l); (b) Convective regime. The experiment is for HNO_3 ($C_a=1.5$ mol/l) and NaOH ($C_b=1.4$ mol/l)

In the case when the reaction proceeds in the convective regime, the withdrawal of the shutter leads to the formation of convective motion in the zone located above the reaction front. This motion develops in the form of rising plumes, which rapidly reach the upper boundary of the cell (Figure 1 b). As a result, an intensive fluid flow spreads throughout the upper layer. The reaction front moves downward rather quickly and reaches the lower boundary of the cell, after which the reaction ceases. The characteristic time of the reaction process ranged from 10 to 30 minutes depending on the initial reagent concentrations. It should be noted that all “acid-base” pairs used in our investigation followed the above mentioned reaction scenarios, no matter which of the reagents is present in the upper or lower layers.

The observed phenomena can be initiated by the following physical mechanisms. At the initial time, as soon as the reacting media come into contact, the diffusion of reagents into each other leads to the formation of a thin transient zone, which after completion of the reaction includes aqueous solutions of the reaction product and one of the reagents taken to excess. If the density of the transient zone is lower than the density of the upper layer, it rises due to the RT instability responsible for the generation of plumes observed in the experiment. This convective motion entrains

new portions of the upper reagent, which enter into the reaction forming another transient layer and the situation is repeated. Due to this fact, the upper layer becomes the zone of intensive convective motion, which continuously carries reagent in the reaction region and provides removal of the reaction product. If the density of the transient zone is higher than the density of the upper layer, the density stratification of the system becomes stable, which leads to the establishment of mechanical equilibrium in the system. As a result, the layers of the reagent solutions are found to be separated by a transient zone, which extends as the reaction goes further. Since in the absence of convective motion the transport of the reagents within the transient zone is accomplished by the diffusion processes, the rate of reaction turns to be a few orders of magnitude lower than in the convective regime.

To generalize the description of the evolution of the two-layer system we introduce a dimensionless parameter, representing the stability of the transient zone — $K_\rho = \rho_{dz}/\rho_u$, where ρ_{dz} is the transient zone density, ρ_u is the density of the upper layer of the reagent solution. The density of the transient zone can be calculated like $\rho_{dz} = \rho_s(C_s) + \rho_{res}(C_{res}) - \rho_0$, where ρ_s is the density of the solution of the resultant reaction product with the molar concentration C_s ; ρ_{res} is the density of the reagent solution with the molar concentration C_{res} , which was taken to excess and remains unreacted in the transient zone after completion of the reaction; ρ_0 is the density of the solvent (water in the examined case). The concentrations of the remaining reagent and the reaction product can be determined from the simple relations: $C_s = C_{min}/\delta_D$ and $C_{res} = (C_{max} - C_{min})/\delta_D$, where C_{min} and C_{max} are the maximal and minimal initial concentrations in the examined reagent pair, $\delta_D = D_{slow}/D_{fast} - 1$ is the parameter specified by the ratio of the diffusion coefficient D_{slow} of the “slower” reagent (slowly reacting substance) in the above pair to that of the “quicker” reagent (quickly reacting substance, D_{fast}). It is to be noted that the diffusion coefficients should be selected taking into account their dependence on the concentration.

The value of the obtained dimensionless parameter K_ρ specifies the system evolution. If $K_\rho < 1$, the reaction proceeds in the convective regime and in the opposite case when $K_\rho > 1$ it proceeds in the diffusive regime. The results of calculations were used to build the map of regimes of reaction evolution in the coordinates of initial reagent concentration. The map of reaction regimes for all used “acid-base” pairs are shown in Figure 2 a. The isopycnic line (depicted by a dashed line) divides the whole field of the map into two regions, in which the upper layer is generated by the solution of acid or base fluid of lower density. Coloured zones are zones, in which the reaction proceeds in the convective regime. For all other concentrations the reaction is governed by diffusion. The experiment results show good agreement with the results of computation, which supports the validity of the selected physical mechanism controlling the observed phenomenon and the adequacy of the dimensionless parameter. In Figure 2 b the same map is depicted in the $(C_a\beta_a, C_b\beta_b)$ parameter plane, where β_a and β_b are solutal expansion coefficients for acid and base, respectively. As it is evident from the figure, for the selected acid HNO_3 an increase in the ratio of the diffusion coefficients of the reagents ($D_{LiOH} < D_{NaOH} < D_{KOH}$) leads to the extension of the reagent concentration range, in which the reaction proceeds in the convective regime. Indeed, an increase in δ_D leads to a decrease in the con-

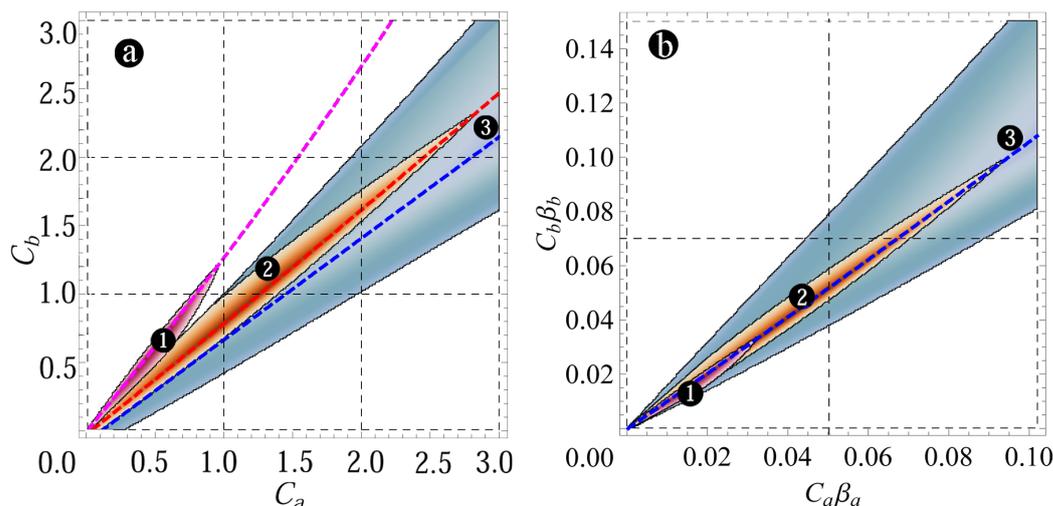


Figure 2: Maps of reaction regimes for the following systems of aqueous solutions: (1) $\text{HNO}_3\text{-LiOH}$, (2) $\text{HNO}_3\text{-NaOH}$, (3) $\text{HNO}_3\text{-KOH}$ in (a) $C_a - C_b$; (b) $C_a \beta_a - C_b \beta_b$. Colored regions are zones of the convective regime

concentrations of the reaction product and excess reactant in the transient zone after completion of the reaction and, consequently, to a decrease of the dimensionless parameter K_ρ . It should be noted that in a strict sense the zone of diffusive regime of the reaction evolution is not the region of mechanical equilibrium of the two-layer system. Inside this parameter region, the diffusion is just the prevailing mechanism of matter transfer in the vicinity of the reaction front, namely, inside the transient zone. However, in this case there is still a possibility for the development of convective motion due to the DD mechanism, but its intensity is generally low and has a rather weak effect on the mass transfer in the system. To substantiate this observation we investigated the propagation of the reaction front in different regimes of proceeding of the reaction. To our knowledge [6], in the case of purely diffusive mass transfer the propagation of the reaction front is governed by the following law: $x_f = C_f \sqrt{t}$, $C_f = \frac{C_a}{C_b} \sqrt{\frac{D_a}{D_b}} - 1$, where C_a and C_b are the concentrations, and D_a and D_b are the diffusion coefficients of the acid and base, respectively. It is seen that if $C_a = C_b$ and $D_a = D_b$, the position of the front does not vary with time. In other cases the front coordinate changes $\sim \sqrt{t}$. In this case, depending on the sign of the proportionality coefficient C_f , the front can move upward and downward. Figure 3 a, showing the map of regimes for the $\text{HNO}_3\text{-NaOH}$ pair, displays curves corresponding to $C_f = 0$, i.e., a change in the direction of the front propagation. Here also we indicate points, at which we measured the position of the reaction front as a function of time (Figure 3 b). Obtained dependencies for highlighted points are presented in Figure 3 b. It is seen that in the convective regime the reaction front propagates much quicker than in the diffusive regime, which is caused by the matter transport near the reaction front by the convective motion. In the range of parameters corresponding to the diffusive regime of reaction evolution the front moves as $x_f \propto t^{1/2}$. Crossing the curve C_f means that the reaction front reverses its direction. The above results show that in the region of diffusive regime of reaction

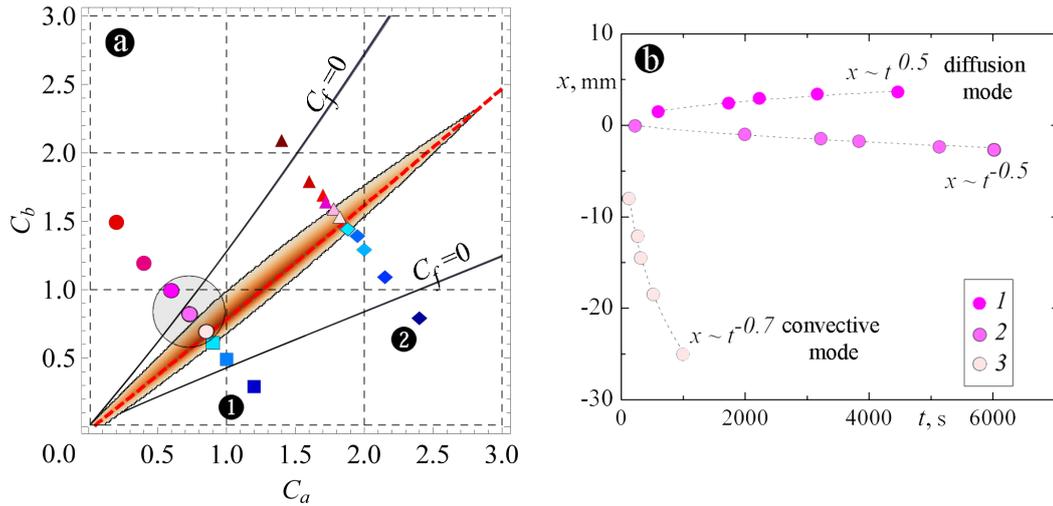


Figure 3: (a) The map of regimes for the HNO_3 - NaOH system with the indicated points for which experiments have been performed; (b) The position of the reaction front as a function of time for respective points in the (a)

evolution the transport of the reagents and reaction products is controlled by the diffusive mechanism, whereas weak movements of the fluid initiated by the double diffusion mechanism exert negligible effect on the mass transfer processes. Such a

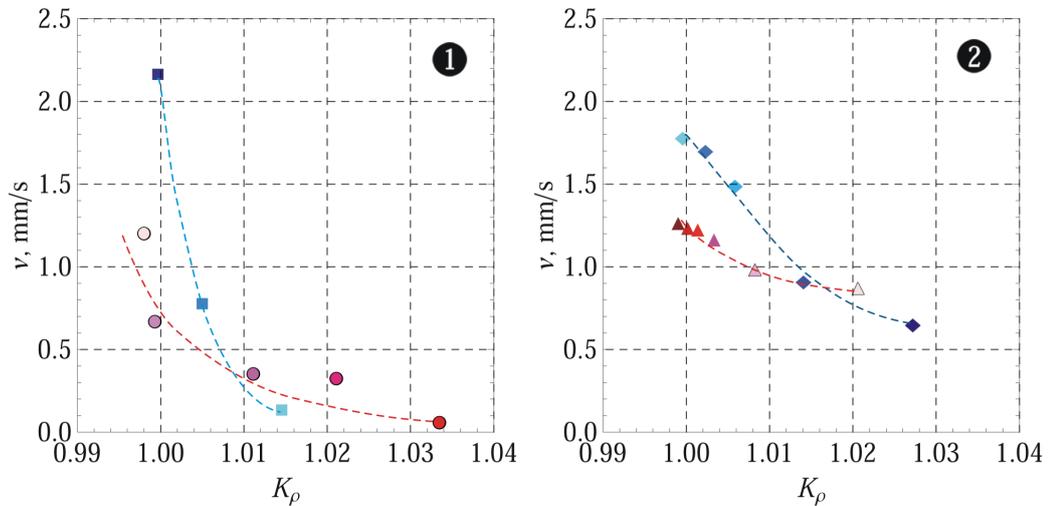


Figure 4: The velocity of plume rise at the initial instant of time as a function of dimensionless parameter K_ρ for experiments depicting in figure 3 a

conclusion can be drawn from the analysis of the plume rise velocity at the initial stage of the development of convective motion in the zone above the reaction front. The above parameter characterizes the intensity of arising convective motion. In figure 4 these dependences are plotted for reactions run at the parameters denoted in figure 3 a by symbols marked by numbers 1 and 2. It is seen that in crossing the boundary, corresponding to a change from the convective to diffusive regime, the intensity of the convective regime rapidly decreases up to zero values. In the range of parameters corresponding to a diffusive regime the experiment revealed a new

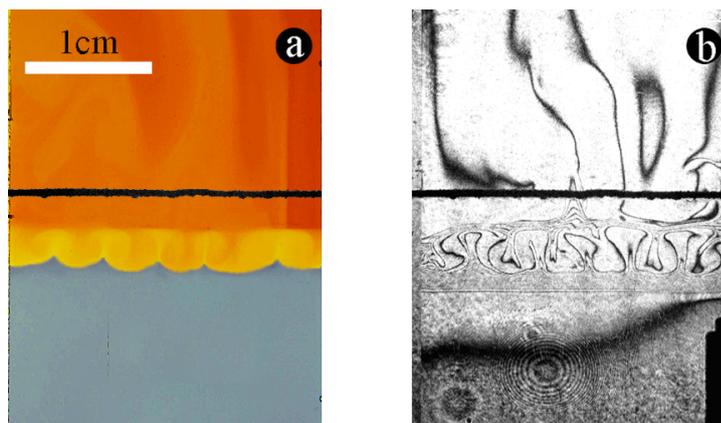


Figure 5: Localized convective structure. (a) pH distribution; (b) interferogram

type of instability, which can be qualified as another type of DD instability. The evolution of the system can be described as follows. The interaction of the reacting

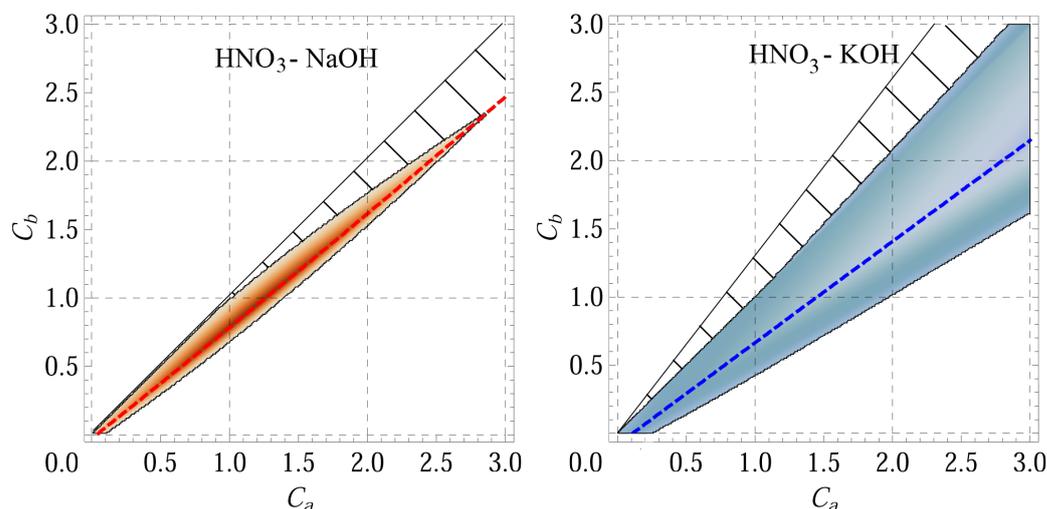


Figure 6: Maps of reaction regimes. CDD instability zones are dashed

layers immediately leads to the formation of a transient zone, inside which the reaction front is located. The transient zone remains immovable, whereas transport of the reagents and reaction products in the zone is accomplished by diffusion. As it has been mentioned above, the space above the transient zone is the region of the formation of a weak convective motion controlled by the DLC mechanism. A few minutes after the beginning of the experiment one can also observe the initiation of convective motion in the transient zone, yet in the form of a horizontal series of convective cells (Figure 5). The observed convective structure exists between two immovable sections of the transient zone, which is indicative of the formation of localized density “pocket” with unstable density stratification. The discovered structure exists for a few hours. With the lapse of time the size of the cells increases, while their number decreases. The cells remain in the transient zone, the vertical dimension of which also increases with time due to diffusion. The instability exists in a very narrow region on the map of reaction regimes. In figure 6, this is

dashed. It is seen that this type of instability is observed only at the one side from the isopycnic line (experiments where base is poured into the bottom layer). Such asymmetry along with the fact that the diffusion coefficient of acid is always higher than that of the base, also counts in favor of diffusion mechanism responsible for the initiation of CCD instability.

Acknowledgements

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