Buoyancy-driven instabilities induced by a neutralization reaction in immiscible fluids

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Abstract. Buoyancy-driven instabilities triggered by neutralization reaction in an immiscible two-layer system placed in a vertically oriented narrow cell were studied experimentally. The initial density of the layers was always set to exclude the development of the Rayleigh-Taylor instability. The problem was examined for the surface-inactive species, namely hydrochloric acid and sodium hydroxide, which allowed studying a convective instability development solely due to buoyancy-driven mechanisms, excluding Marangoni effects. We show that one of two global scenarios develops in the system right after the layers came into contact. These scenarios, called by us diffusion-controlled and convection-controlled, essentially differ in the prevailing mechanism of mass transfer and, therefore, in the rate of reaction-diffusion-convection processes. The authors introduce the nondimensional parameter, the value of which determines the border between the two scenarios in the regime map.

1. Introduction
The chemical reactions in a liquid media are essential in many natural phenomena and a significant number of technological processes. The reaction proceeding is accompanied by a variety of physical phenomena, as well as changes in the thermodynamic state of the system as a whole. The variations of the physico-chemical properties of a liquid media in the course of reaction, such as density, viscosity, thermal conductivity, and surface tension may result in a number of hydrodynamic instabilities, and as a result, the formation of convective flows, which are able to change essentially the intensity of the heat and mass transfer in the system. This in turn causes an increase in reaction rate and may even provoke a change of the nature of the reaction (e.g., from the frontal to the volume one). A second-order exothermic neutralization reaction has been actively used as a model reaction in many studies because of a comparatively simple, albeit nonlinear, kinetics. If two species are initially separated in space within a two-layer configuration, then this reaction can form a reaction front. The scenario for instability, developing in the vicinity of the front, essentially differs in immiscible and miscible systems of liquids. If the reaction occurs in a two-layer miscible system under gravity, then it may result in various buoyancy-
driven instabilities. In case a denser solution is initially placed above a less dense one or if an unstable density stratification near a reaction front is forming during reaction, then Rayleigh-Taylor instability develops. The difference between the diffusion rate of species results in a differential-diffusive instability. These instabilities result in formation of variety of convective patterns: irregular fingers [1], regular convective cells [2], and even shock-wave-like structures [3]. Completely different situation is observed in immiscible systems, where reagents are initially dissolved in two immiscible solvents. As a rule, one of the reactants can not penetrate through the interface between the immiscible phases and the reaction takes place only in one of the layers, where another reactant comes to through the interface due to diffusion. In this case, large concentration and temperature gradients, caused by diffusion processes and the reaction, form near the interface, which may result in interfacial instabilities due to Marangoni effect. However, in experimental studies, having to do with neutralization reaction, Marangoni instability either was not found out or was observed only in the very early stage with further fast decay [4-6]. The researchers observed that as a rule, the formation of irregular finger patterns or regular convective cells depended on the reactants used. In later theoretical studies [7, 8] it was shown that Marangoni mechanism can be suppressed by buoyancy-driven ones, but it may play important role in formation of surprisingly regular cell patterns found out in some experiments. Thus, the role of Marangoni mechanism in formation of convective patterns in immiscible systems is still under discussion which requires additional investigations. In this article, we consider the case of an immiscible two-layer system in which a neutralization reaction occurs. We simulate experimentally the situation where the development of Marangoni instability becomes impossible, but the conditions for buoyancy-driven instabilities remain. This becomes possible when using reagents, as well as the reaction product, which are not surface-active. We show that depending on the ratio of the initial reagent concentrations one of two global scenarios develops from the very beginning of the system's evolution. They essentially differ in the prevailing mechanism of mass transfer that in turn determines the reaction rate and the characteristic time of reaction processes. We propose the physical mechanism responsible for the observed phenomena and a dimensionless parameter, the value of which determines the development of one of the detected scenarios. In conclusion, we discuss the results comparing them with those obtained in previous studies.

2. Experimental setup and measuring techniques
The experiments were carried out in a vertically oriented rectangular cavity formed by two plane-parallel glass plates separated by a thin glass spacer that set the internal dimensions of the cavity: width b=5 cm, height a=10.0 cm, thickness h=0.12 cm. Before starting the experiment, a two-layer system of immiscible liquids with initially stable stratification was forming in the cavity, which excluded the development of the Rayleigh-Taylor instability. The lower layer consisted of an aqueous solution of sodium hydroxide with a concentration \( C_b \), the value of which could be set in the range from 0.1 to 6.0 M. The upper layer was formed by a solution of hydrochloric acid in pentanol with a concentration \( C_a \) being set in the range from 0.1 to 3.0 M. The aqueous solution was prepared on the basis of bidistilled water. The solutions were made by weighing each component using electronic balances (accuracy 0.01 g). Since water and pentanol are slightly soluble in each other, the solvents were mutually saturated before the solutions were prepared. Side glass plates bounding the cavity formed the cell of the Fizeau interferometer mounted using an autocollimation scheme. The use of the interferometer made it possible to observe in real time the spatial distribution of the refractive index caused by inhomogeneities in the concentration of solutes. In addition, the effect of entrainment of concentration isolines by a moving liquid, due to the smallness of the viscous time compared to the diffusion one (the Schmidt number \( Sc \sim 10^3 \)), also made it possible, in some cases, to use the interferograms to observe the structure of the convective flow and measure the velocity of the liquid. A universal acidity indicator was added to the lower layer, which allowed visualizing the spatial distribution of the reagents and the reaction product, as well as determining a position of the reaction
front. The temporal evolution of interferograms and pH distribution was recorded using a video camera with high spatiotemporal resolution. All experiments were performed at the temperature of (23±1) °C.

3. Results and discussion

The analysis of the experiments made with various initial concentrations of acid and base allows combining all the results into two general groups which differ in scenario of reaction-diffusion-convection processes developing in two-layer system just after the layers brought into contact. In the case of relatively small base concentrations, a number of relatively large plumes are formed below the interface, rapidly spreading downwards (Fig.1a).

![Interferograms and pH images](image)

**Figure 1.** Interferograms (left) and pH images (right) observed in the framework of convection-controlled regime at certain times after the layers were brought into contact: (a) – 70 s, (b) – 710 s, (c) – 1040 s. The initial concentration of acid and base is 0.5 M and 0.2 M, respectively.

At a certain depth, the value of which depends on the ratio of the initial reagent concentrations, the plumes stop. As a result, a horizontal row of convective cells with an almost flat lower boundary is formed in the lower layer (Fig.1b). The lower boundary of the cells shifts down as time goes, resulting in an increase in the vertical size of the convective structure. When the lower edge of the cells reaches the lower border of the cell, the reaction stops. The total duration of the reaction-diffusion-convection process depends significantly on the growth rate of the cell zone, and ranges from several minutes to several tens of minutes in different experiments. Hereinafter, we will call this mode of reaction convection-controlled (CC).

![Dependence of velocity](image)

**Figure 2.** Dependence of velocity of the lower cell boundary displacement on the initial base concentration for three different initial acid concentrations: 1 – 0.50 M, 2 – 0.83 M, 3 – 1.66 M. The concentrations in the abscissa axis marked with stars are the threshold concentrations of the base corresponding to the change of the regimes.
The velocity of the lower cell boundary displacement depends on the ratio of the initial concentrations of the reagents (Fig. 2). It can be seen that at a fixed base content in the lower layer, an increase in the acid concentration leads to an increase in the boundary velocity. On the contrary, at a fixed acid concentration in the upper layer, the cell boundary velocity decreases rapidly with increasing base concentration. Finally, the cells do not form above a certain threshold initial base concentration, which depends on the acid content in the upper layer, and the second of the detected global scenarios is implemented in the two-layer system. Within the second scenario, a stably stratified diffusion zone is formed below the interface (Fig. 3), the vertical size of which slowly increases with time. The analysis of the spatial distribution of pH (Fig. 3, right) shows that the acid does not penetrate the volume of the lower layer, and the reaction front is localized at the interface. In this case, the formation of the diffusion zone is due to the presence of a base concentration gradient that diffuses from the volume to the reaction front, as well as the gradient of the salt concentration that forms at the reaction front and diffuses into the volume of the lower layer. Since mass transfer near the reaction zone is mainly due to diffusion, the total reaction time within this scenario is tens of hours. Hereinafter, we will call this mode of reaction diffusion-controlled (DC). The regime map in coordinates of initial acid and base concentrations is shown in Fig. 4. It is clearly seen that each of the above described modes is implemented within a certain range of the parameters.

In order to understand the physical mechanisms behind the observed phenomena, consider the processes that occur near the interface. Since the base dissolved in the water phase can not penetrate into organic phase, where the acid is initially dissolved, the reaction takes place only in the lower layer where the acid comes to from the upper, organic, layer due to diffusion through the interface. In this case, the upper layer plays the role of passive reservoir, which provides the acid supply into the reaction zone, placed initially just beneath the interface. The further evolution of the system will depend on the final density of the reaction zone being formed during the reaction. If it is greater than that of the lower layer, then conditions for the development of the Rayleigh-Taylor instability arise in the lower layer. The convective structure in the form of plumes, which is characteristic for this type of instability, is observed in experiments made within the range of the parameters, corresponding to the CC regime. However, the plumes stop at a certain vertical coordinate, rather than spread unboundedly as it is typically in the case of the Rayleigh-Taylor instability. The pH distribution (Fig. 1, right) shows that the descending plumes contain an excess amount of acid remaining unreacted after the reaction. The acid residue reacts with the surrounding base, causing the plume density to decrease as they move. Plumes stop when their density becomes equal to the density of the base's solution. As a result, a horizontal row of convective cells is formed in the lower layer. In what follows, the lower border of the convective cells moves downwards as the base, containing in the lower layer, is consuming in the course of reaction.
If the density of the reaction zone is smaller than that of the lower layer, steady density stratification is settled in the entire lower layer from the very beginning of the process, which makes it impossible for a convective motion to develop. As a result, a supply of the reagents towards the reaction zone and removal of the salt away from it are provided only via diffusion. Later, this mutual diffusion of the base and the salt may result in development of a convective motion due to differential diffusion effects. Taking into account slower diffusion of the salt, we should expect the development of the double-diffusive instability. Indeed, the formation of the salt fingers, which are typical for this type of instability, can be easily visible in the images obtained within of DC regime (Fig.3).

\[ \text{Figure 4. Regime map. The symbols denote the parameters at which convection-controlled (open circles) or diffusion-controlled (closed circles) regimes were observed in experiments. The curves obtained from equation (3) taking into account acid's concentration in the organic (dashed line) or water (solid line) phase.} \]

The ratio of the density of the reaction zone \( \rho_{rz} \) to that of lower layer \( \rho_l \) can be calculated from existing initial concentrations of the reagents by the following equation

\[
\frac{\rho_{rz}}{\rho_l} = \frac{1 + \beta_s C_s + \beta_{res} C_{res}}{1 + \beta_b C_b}
\]

(1)

Here, \( \beta \) is the solutal expansion coefficient, \( C \) is the molar concentration, and the subscripts “s” and “b” denote the quantities relating to the salt and the base always dissolved in the lower layer, respectively.

The last term in the numerator of the equation (1) describes the contribution of the unreacted reagent to the density of the reaction zone. Since during the reaction, each molecule of one of the reagents reacts with one molecule of another reagent, in the case of non-equimolar solutions, i.e. when initial concentration of acid and that of base are not equal, a part of the molecules of that reagent whose concentration is initially greater remains unreacted in the reaction zone. \( \beta_{res} \) and \( C_{res} \) denote the solutal expansion coefficient and molar concentration of this residual reagent, respectively. Taking into account that the acid has always higher concentration within the reaction zone, the ratio of the densities can be calculated as follows

\[
\frac{\rho_{rz}}{\rho_l} = \frac{1 + \beta_s C_s + \beta_b (C_a - C_b)}{1 + \beta_b C_b}
\]

(2)
The condition $\hat{K}_\rho = 1$ determines the position of the boundary between the parameter areas where the CC mode ($\hat{K}_\rho > 1$) and DC mode ($\hat{K}_\rho < 1$) should realize in the experiment. The following ratio of the reagent concentrations, corresponding to this condition, can be obtained from equation (2)

$$\frac{C_b}{C_a} = \frac{\beta_a}{\beta_a - \beta_s + \beta_b} \approx 1.1$$

(3)

Figure 5. Dependence of acid concentration in water phase on its content in organic phase

In the last expression the following values of solutal expansion coefficients were taken for calculation:

$\beta_a = 0.018 \text{ L} \cdot \text{mol}^{-1}$, $\beta_b = 0.043 \text{ L} \cdot \text{mol}^{-1}$, $\beta_s = 0.041 \text{ L} \cdot \text{mol}^{-1}$. The curve, corresponding to expression (3), is plotted in the regimes map in Fig.4 (dotted line). We can see that the boundary between the regimes, being predicted by calculation, lies essentially lower than that obtained in the experiments. In our opinion the reason is connected with difference in acid content in organic and water phases. The concentration of hydrochloric acid is expected should be higher taking into account its higher solubility in water than in pentanol. Additional experiments were made to define real acid concentration in water phase. For that purpose, a small amount of water of 1 mL volume was added to 100 mL of acid solution in pentanol. Thus, large ratio of phase’s volumes is needed to keep a constant concentration of acid in pentanol during its diffusion into the water phase. After an equilibrium distribution of the acid between the phases has been reached the content of acid in water phase was measured by conductometry. Figure 5 presents the dependence of acid concentration in water phase on its content in organic phase. It is seen that the concentration of acid in water is three-four times higher than in pentanol. The curve, corresponding to the condition $\hat{K}_\rho = 1$, which was calculated taking into account the real acid concentration in water, is presented in Fig.4 (solid line). One can see that the curve well describes the experimental results, correctly predicting the location of the border between regions of different regimes existence. This fact confirms the correctness of the physical interpretation of the observed phenomena and the choice of a dimensionless governing parameter $\hat{K}_\rho$. 

4. Conclusions
In the paper, we present the results of experimental study of the reaction-diffusion-convection processes developing in the course of neutralization reaction taking place between a strong acid and a strong base which are initially dissolved in two immiscible solvents. Both reagents and reaction product are not surface-active which allowed studying a convective instability development solely due to buoyancy-driven mechanisms, excluding Marangoni effects. According to the analysis of the experimental observations we introduced the dimensionless parameter $\hat{K}_\rho$, equal to ratio of the density of the reaction zone to that of the lower layer, which acts as a bifurcation parameter that determines the occurrence of one of the two global scenarios from the very beginning of the system's evolution. These scenarios, found out by us in experiments, differ in the prevailing mechanism of mass transfer that in turn determines the rate of conversion of reagents and, accordingly, the characteristic time of reaction processes. In case $\hat{K}_\rho > 1$ the lower layer turns out to be unstably stratified which triggers the development of Rayleigh-Taylor instability. Intensive convective motion results in the reaction takes place in volume, rather than in frontal manner. As a result, the Rayleigh-Taylor instability develops in a limited space, not extending to the entire volume of the lower layer, which is atypical for this type of instability. In case $\hat{K}_\rho < 1$ a stable density stratification is settled in the whole lower layer from the very beginning, which makes the diffusion to be the only mass transfer mechanism at the initial stage. This fact results in the reaction proceeds in a frontal manner and characterizes by rather slow reagents conversion rate. The results of calculations, based on the nondimensional parameter, and the results, obtained in the experiments, are in good agreement with each other on the regime map, which supports the correctness of the physical interpretation of the observed phenomena.

In conclusion, it is worth to compare the results obtained in the present study with those reported previously for immiscible systems. First, we showed that various convective structures being observed in different previous studies can be formed solely by buoyancy-driven mechanisms and does not require Marangoni effect to be considered. Secondly, both irregular finger structures and regular convective cells, which were earlier found out separately in different reactive systems, can be obtained within one pair of reagents by variation of value of the dimensionless parameter introduced in the paper. Calculation of this parameter and plotting the regime maps allows any researcher to predict the regions of existence of different regimes in the problem parameter space.

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