

# Effect of the universal acid-base indicator on the formation of the concentration-dependent diffusion instability

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**Abstract.** The effect of the universal acid-base indicator on the pattern formation and mass transfer in a two-layer system composed of two reactive miscible liquids in a vertical Hele-Shaw cell is studied experimentally. The reaction we study is a neutralization one. It turns out that the presence of the indicator leads to a change in the spatio-temporal characteristics of the system and even in the mass transfer mechanism near the reaction front—from diffusive to convective. The conditions, where the universal indicator does not affect the reaction and can be used as a visualizing mean, are reported.

## 1. Introduction

Different types of indicators are used to visualize chemical composition of the reactive system in different fields of chemohydrodynamics increasingly often [1-4]. Particularly, various acid-base indicators are utilized in studies on the neutralization reaction in a two-layer system in order to visualize spatial distribution of reagents. Usually, physical parameters (viscosity, density, diffusivity) of an indicator and reagents are different. Hence, the use of an indicator may result in appearance of additional driving forces of convection and even gives rise to the pattern formation in the system.

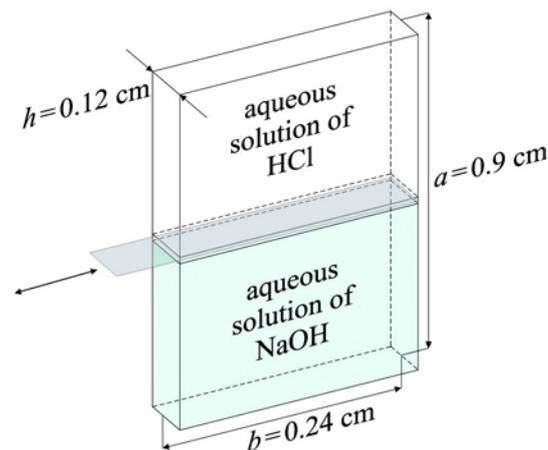
There are several studies on how the indicator affects buoyancy-driven instability of the acid-base front. In [5] it was demonstrated both numerically and experimentally, that an indicator can affect the instability scenarios by changing the density profile of the system. An attempt to determine the conditions, under which the indicators do not have a significant impact on the system and can be used as a visualizing mean, was made in [6]. The authors examined the neutralization reaction between aqueous solutions of hydrochloric acid and bromocresol green, which acts as a base. They reported the change in the scenario of instability development due to concentration variation of reactants. In [7] the neutralization reaction between the aqueous solutions of hydrochloric acid and sodium hydroxide with a dissolved color indicator was studied. In some cases the employed indicator was bromothymol blue, in other it was phenolphthalein. The authors reported that chemically reacting flows are drastically changed depending on the type of *pH* indicator. In [8] the same group of researchers repeated the experiment, but they added aqueous solution of ethanol to the base containing bromothymol blue. They showed that the predominant mechanism of mass transfer at the reaction front changes from diffusive to convective depending on the mass fraction of ethanol. There are also interesting series of studies where the reaction is caused by a droplet containing the *pH* indicator bromothymol blue that falls dropwise into an aqueous alkaline solution [9-10]. Authors investigated the short-term transport processes across the interface, including the fingering instability of the reaction front.



In our previous work [11], we showed that the dependence of the diffusion coefficients of the reactants on their concentration in a two-layer reactive system leads to the formation of a periodic cellular convective structure localized within the reactive zone; we called it the concentration-dependent diffusion instability (henceforth CDD instability). For visualization of emerging convective structures we used the acid-base universal indicator. We supposed that the indicator concentrations we used were sufficiently small and did not influence the reaction. However, the above-mentioned investigations raise the question whether the indicator we used could lead us to misleading results. In this regard, here we focus on the detailed study of the effect of the universal indicator on the onset of CDD instability and mass transfer processes near the reaction front in a miscible two-layer system composed of aqueous solutions of NaOH and HCl.

## 2. Experiment

The experiments were performed in a vertically oriented Hele-Shaw cell. The cell was made of two glass plates separated by a thin gap of 0.12 cm (figure 1). The reaction under consideration was the neutralization of hydrochloric acid by sodium hydroxide. The standard enthalpy change for this reaction is  $\Delta H = -57$  kJ/mol. Molar concentrations of acid and base aqueous solutions were  $C_a = 0.7$  mol/l and  $C_b = 0.5$  mol/l, respectively. Such concentrations were chosen due to the fact that CDD instability in HCl/NaOH system is observed at certain ratio of initial concentrations, specifically  $C_a/C_b = 1.4$  [11].



**Figure 1.** Sketch of the two-layer miscible system filling a vertical Hele-Shaw cell.

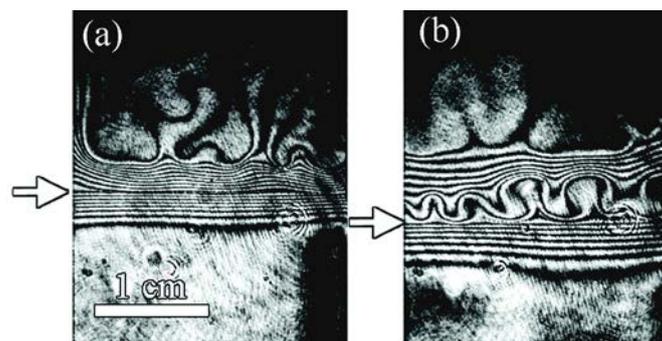
In order to provide an initially flat horizontal interface between the reagents, we used special thin plastic shutter that was separating solutions before their contact. At first, a lower layer was filled with NaOH solution, then the solution was tightly covered by the shutter, and then an upper layer was filled with HCl solution. After that, the shutter was carefully taken out of the cell, the reactants were brought into contact, and the reaction started.

Fizeau interferometer was used to visualize the refractive index field. In order to visualize the space distribution of the reagents and the reaction product, we used the universal indicator. An advantage of the universal indicator is that it provides an image with a distinct boundary between the reagents and the reaction product. Note that the universal indicator is a combination of several indicators (thymol blue, methyl orange, bromothymol blue, phenolphthalein, tropaeolin OO, bromocresol green, and bromocresol purple), that display colors at  $pH$  values inside the certain transition range. That is why the universal indicator displays color changes over a wide  $pH$  value range from 1 to 10. Colors from yellow to red indicate an acidic solution, colors from light to dark blue indicate bases, and green color indicates that a solution is neutral. The indicator was prepared on the basis of the aqueous solution of ethanol with mass concentration  $w = 80\%$ . The initial concentration and density of the indicator were

$2 \times 10^{-4}$  M and  $0.849 \text{ g/cm}^3$ , respectively. To provide high-contrast images of pH distribution, the Hele-Shaw cell was illuminated by white-light toroidal lamp. Experiments were recorded by digital camera with high spatio-temporal resolution. All experiments were performed at room temperature ( $24 \pm 1^\circ\text{C}$ ).

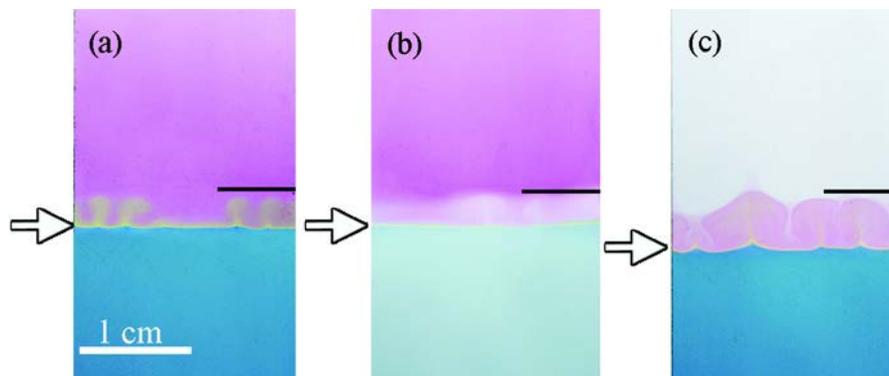
### 3. Results and discussions

At first, we would like to describe the typical experiment without any indicator. When reactants come into contact, the transition zone originates between them where the reagents are supplied towards the reaction front only due to diffusion mechanism, which substantially increases the duration of the reaction and leads to low rate of the reaction front propagation, which is approximately  $v = 10^{-4} \text{ cm/s}$  (see figure 4). Then, the occurrence of a depleted layer located above the diffusion zone gives rise to the formation of plumes which results in the development of weak buoyancy-driven convection in the entire upper layer, while the area below the diffusion zone remains motionless. After certain time (in our experiment, it was approximately 480 seconds), the fluid flow in the form of a horizontal array of convective cells is formed within the diffusion zone just above the reaction front. The convective cells structure exists between two parts of immobile fluid with stable density stratification, which indicates the occurrence of inflection on the density profile and consequently the formation of a localized density “pocket” with unstable density stratification. The refractive index distribution which reflects the density distribution in this experiment is presented in figure 2. A more detailed description of the formation mechanism of CDD instability can be found in [11].



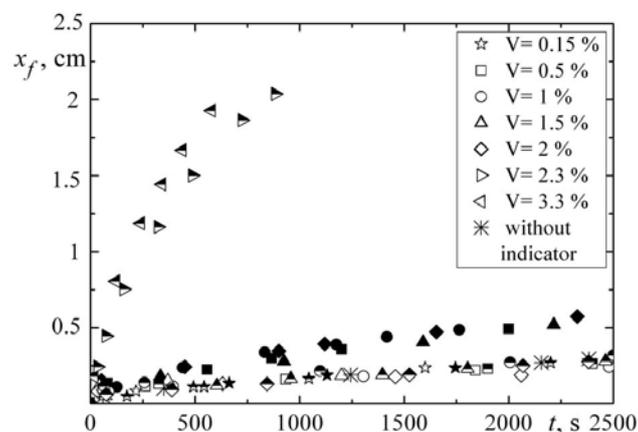
**Figure 2.** Interference images showing the development of CDD instability in experiment without indicator. The arrows indicate the reaction front position,  $x_f$  observed at (a) 400 s, (b) 1300 s after the aqueous solutions were brought into contact.

In order to investigate the influence of the universal indicator, three different situations were considered: (i) the universal indicator was dissolved in both layers, (ii) the indicator was dissolved only in the upper layer with acid, (iii) the indicator was dissolved only in the lower layer, containing the base. The indicator was dissolved in the solutions of reagents prior to the beginning of the experiments. The range of the volume concentration of the dissolved indicator is  $V = (0.15 \div 3.3)\%$ . Convective patterns observed at 2000 second for the experiments with different conditions are presented in figure 3. All images clearly demonstrate the appearance of the localized cellular structure. The purple downstreams indicates the acid entrained by the flow. The yellow upstreams enriching with salt points out on that the reaction occurs at the lower edge of the cellular structure, where the reaction front is.



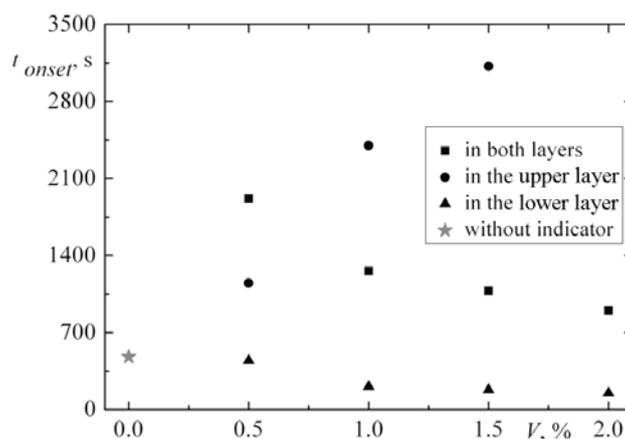
**Figure 3.** Chemoconvective patterns observed in the system with the universal indicator dissolved (a) in each layer; (b) in the upper layer, (c) in the lower layer. Volume concentration of the indicator is  $V = 1.5\%$ . The arrows indicate the reaction front position,  $x_f$ . Black line: initial contact line. (Colored online).

Comparison of the temporal evolution of the reaction front in the system with and without the indicator is shown in figure 4. It is interesting to note that in the case, where the volume concentration of indicator is  $V = 0.15\%$ , the reaction front rate is the same as in the experiment without the indicator, no matter in which layer the indicator was dissolved. An increase in the indicator concentration (up to  $V = 2\%$ ) does not essentially affect the front rate when it is dissolved in both layers or only in the layer with acid (in the figure they are indicated as half shaded and white symbols, respectively), but, as it will be shown later, it drastically changed the onset time of the instability. However, if the indicator is added only to the lower layer (black symbols), the front propagation rate noticeably increases. The addition of the indicator with concentration  $V > 2\%$  to both layers results in completely different reaction scenario. The CDD instability observed previously is not forming. Instead, in the upper layer of the system containing acid, an intense convective motion develops, which magnifies the mass transfer near the reaction front, leading to a significant increase in the front propagation rate. Thus, the addition of even such low indicator concentrations leads to a change in the mass transfer mechanism from diffusive to convective.



**Figure 4.** Temporal evolution of the reaction front position. Half shaded, shaded, and open symbols indicate experiments when the indicator is dissolved in both layers, in the lower layer, and in the upper layer, respectively.

In figure 5 the dependence of the onset time of CDD instability on the volume concentration of the dissolved indicator is presented. The experiment showed that the presence of the indicator in both or only in the upper layer always leads to delay of the instability development, whereas its addition only to the lower layer always reduces the instability onset time,  $t_{onset}$ . By varying the indicator concentrations and selecting the layer in which it will be dissolved, it is possible to approach the results obtained in the experiment in the absence of the indicator.



**Figure 5.** CDD instability onset time versus volume concentration of the dissolved indicator.

Such a behavior may be explained as follows. Due to low density of the indicator solution, the density of the layer in which the indicator is dissolved decreases. Thus, in experiments with indicator on the upper layer the system becomes more stable. Specifically, the density difference, which triggers the formation of the density pocket inside the reaction area, is smaller than the density difference forming in the experiment without indicator. Therefore, the time required for the density pocket formation, due to which the CDD instability develops, increases. It explains the observed delay in the formation of convective structure. Moreover, the greater the concentration of the indicator the more stable the system becomes. Experimental results show that the predominant mechanism of mass transfer near the reaction front is diffusion; therefore, the front propagation rate as shown above is almost the same as in the experiment without indicator.

In the reverse case, where the indicator is dissolved only in the lower layer, the value of the density difference that triggers the formation of the density pocket inside the reaction area becomes bigger. Thus, the onset time of CDD instability is almost the same as in the experiment without indicator. An increase of the indicator concentration further destabilizes the reaction area. Hence, the time required for the formation of the density pocket decreases. The main mechanism of mass transfer near the reaction front is also diffusion. However, due to the fact that CDD instability onsets earlier, the mass transfer near the reaction front is more intense than in the experiments without indicator; therefore, the front propagation rate is noticeably higher.

The presence of the indicator in both layers leads to a symmetrical change in their physical parameters, i.e., the value of the density pocket should not differ from its value in the experiment without indicator. That is why in this case, the front propagation rate coincides with the one observed without indicator. However, an increase of indicator concentration ( $V > 2\%$ ) triggers completely different scenario of the reaction. When reagents come into contact, a convective motion in the form of rising plumes develops above the reaction front. Formed plumes quite quickly reach the upper boundary of the cell. As a result, buoyancy-driven convection develops in the entire upper layer, but in contrast to the experiment without indicator, it is more intense. In this way, an intense convective motion that continuously supplies the fresh reagent to the reaction area and performs a removal of the

reaction product is formed above the reaction front. Constant refreshment of the reactive layer is fast enough, which leads to the rapid propagation of the reaction front until it reaches the lower boundary of the cell. The rate of the reaction front plotted in figure 4 is approximately  $v = 10^{-3}$  cm/s.

#### 4. Conclusions

In the experimental study of the effect of the universal indicator on the process of instability formation, the conditions, where the universal indicator does not make a significant impact on the system and can be used as a visualizing mean, are found. It is shown that the volume concentrations of the indicator  $V < 0.2\%$  does not affect the onset time of CDD instability, nor the mass transfer near the reaction front. Despite the fact that such indicator concentrations are negligible, it is enough to have a good visualization.

#### 5. Acknowledgments

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