Diffusion of a reagent from a slowly rising droplet with accompanying surface chemical reaction

M O Denisova\textsuperscript{1, 2} and K G Kostarev\textsuperscript{1, 2}

\textsuperscript{1}Perm National Research Polytechnic University, Komsomolsky Pr. 29, 614990 Perm, Russia
\textsuperscript{2}Institute of Continuous Media Mechanics UB RAS, st. A. Koroleva 1, Perm, 614013.

E-mail: mod@icmm.ru, kostarev@icmm.ru

Abstract. The development of neutralization reaction during the reagent diffusion from an insoluble drop, slowly floating up in a quiescent chemically active liquid, was studied experimentally. The droplet is located in a narrow vertical gap, which causes it to take the form of a short horizontal cylinder with a free lateral surface and flat end faces. The latter circumstance allows using an interferometer to visualize the structure of the fields of reagent concentration in the droplet and the resultant products in the environment and to trace their evolution. To display the specific features of the observed phenomena, we also investigated the diffusion of a reagent from a motionless drop in a chemically active medium and diffusion of a reagent from a drop floating up in a chemically neutral liquid.

Introduction
The modern stage of production development is primarily associated with the introduction of high technologies. In the context of chemistry, this implies the replacement of large-size cyclical reactors with continuously-operated flow reactors. The latter have significantly smaller dimensions, demonstrate the efficient operation and allow low-tonnage batch production [1-3]. However, unlike the previous types of reactors, they require not only the knowledge of the specific character of chemical processes, but also a deep understanding and considering the physical conditions of the reaction [4]. The operating principle of one of these reactors is the extraction of the reagent from droplets moving upwards through a chemically active liquid. It is clear that an increase in the efficiency of such a reactor is directly related to the study of mass transfer between the droplet and the surrounding medium associated with a change in their density due to the diffusion of a reagent and synthesis of reaction products, as well as the non-isothermal nature of this process. The movement of the droplet is an additional complicating factor.

Experiment
In our work, the study of mass transfer was carried out experimentally by visualizing the concentration fields and flow structures generated during the diffusion of acetic acid from an insoluble droplet of a mixture of benzene and chlorobenzene into an aqueous solution of sodium hydroxide NaOH. Direct
contact of the acid and base molecules led to a neutralization reaction accompanied by the formation of water and water-soluble salts (in our case, sodium acetate). Water and aqueous solutions were insoluble in a droplet of benzene-chlorobenzene mixture; therefore, the reaction took place on the outer surface of the droplet. The drop floated up in a flat vertical Hele-Shaw cell with a gap of 1.2 mm and had the shape of a short horizontal cylinder with parallel end surfaces, which made it possible to use optical methods, in particular, the interferometric methods (Fig. 1). It is to be noted that shifting of one interference fringe to another corresponds to a change in the concentration of acid in the benzene mixture by 0.019 mol/L.

To simplify the problem, we considered the case of low initial acid concentrations of $C_0$ in the droplet, so the diffusion of acid occurs without the development of capillary motion (due to the threshold nature of the Marangoni convection [5]). Another simplification was introduced by equalizing the initial densities of the mixture of benzenes and acetic acid. In this case, all changes in the density of the mixture were only due to the effect of contraction [6], which, in the selected system of liquids, led to a very small increase in the density of the mixture during the diffusion of acid. Due to the absence of the Marangoni convection and weak buoyancy convection, the initial concentration of acid in the center of the droplet remained constant during its formation.

Figure 1. Experimental setup: (a) cuvette: 1 - hollow needle (removed after creating a drop); 2 - the drop of the mixture; 3 - plane-parallel glasses; (b) interferometer: 1 - helium-neon laser; 2 - folding mirror; 3 - micro lens; 4 - translucent mirror, 5 - collimator objective; 6 - external resonator with a cuvette, 7 - digital video camera

The experiment, studying the process of mass transfer between the drop and the surrounding medium, was divided into three parts, which allowed successful determination of its features specific to (I) the development of a reaction on the surface of a motionless drop, (II) the diffusion of the reagent from the drop into a chemically neutral medium (aqueous solution of chloride sodium NaCl), (III) the rising drop with the chemical reaction proceeding on its surface. Note that the velocity of the droplet motion is about 0.1 mm/s.

Results

Figure 2 shows three series of interferograms, describing the evolution of the concentration fields of acetic acid in the drop under the above-specified conditions. Note that during the diffusion of acid into an aqueous solution of sodium hydroxide, the droplet is kept motionless only when the densities of both media are close (Fig. 2, a-c), otherwise, the droplet starts to move (Fig. 2, g-i). Sodium chloride prevents the wetting of the cell walls with a mixture of benzenes; therefore, the droplet floats up at an arbitrarily small density difference (Fig. 2, d-f). In the case of a chemical reaction, the ascending torches are formed by both products of the reaction, while the descending torches are formed by sodium acetate only, which
has had time to dissolve in a sodium hydroxide solution. For a droplet floating up in a chemically neutral medium (Fig. 2, d–f), the descending torch is formed by acetic acid dissolved in the aqueous solution of sodium chloride. Note that the initial concentration of sodium chloride is selected in such a way that its density is equal to that of the acetic acid. However, in the process of acid absorption, its density becomes higher due to the effect of contraction, which leads to the formation of a torch.

As for the droplet itself, the common features of all examined situations is the formation of unstable stratification of the mixture density in its upper part due to acid diffusion into the surrounding medium. At the same time, the mixture, which has lost acid during mass transfer through the lateral surface of the droplet, moves downward, generating a descending near-wall flow. In turn, this flow is responsible for the rise of the central part of the drop with an invariable initial concentration of acid. The rising central part “props up” the unstable zone of stratification, which later causes a slow movement of this stratification downward (Fig. 2, b–c) or to a fall of concentration “fingers” (Fig. 2, e, h).

Note that all rising drops share a common trait – the formation of a zone with a small concentration difference in the lower part of the drop (Fig. 2, f, i) as a result of accelerated downward drift of the depleted mixture due to the motion of the interphase boundary. Moreover, the appearance of an interlayer of surrounding solution between the end surfaces of the droplet and the walls of the Hele-Shaw cell strongly intensifies the mass transfer between the droplet and the surrounding liquid, as evidenced by the enlargement of both the descending (Fig. 2, f, i) and the ascending torches in the event of reaction (Fig. 2, i). Figure 3 shows the evolution of the distribution of the acetic acid concentration along the vertical diameter of the drop in the cases of neutralization reaction evolving on the surface of motionless (a) and floating (b) drops (the initial concentration of acid in the droplet was chosen as the dimensioning unit). It is clearly seen that for a motionless drop, the distribution for a rather long time remains symmetrical with respect to the center of the drop, and all changes occur on its periphery. This can be explained both by a slight increase in the density of the mixture near the interface during the diffusion of acid and by local heating of the near-boundary region as a result of the progress of chemical reaction on the outer surface of the droplet. Note that the thermal contribution to a change in the density of the reaction mixture under normal conditions is very small (~ 5–7% of the total change [7]), but for the selected system of liquids, it compensates to a great extent for the increase in density due to a decrease in the acid concentration.

In the case of a rising drop, a change in concentration occurs much faster. There is also a rapid expansion of the lower zone with low concentration gradients accompanied by the displacement of the diffusion zone into the central part of the drop. However, the rate of development of this process is much lower than in the case of acid diffusion from a floating drop into a chemically neutral liquid (see Fig. 2). Apparently, as in the above situation, heat generated during the reaction reduces the average density of the upper part of the droplet.

The conclusions drawn from the discussion of Figures 2-3 are confirmed by the results of studying the time dependence of the acid concentration in the center of the droplet in the initial period of time, when the mass flow from the droplet is most intense (Fig. 4, a). It is clearly seen that the initial segment of the concentration vs time curve in all examined cases has the form close to a linear one. A pair-wise comparison of curves 1 and 3, and 4 and 2 shows that the appearance of a liquid layer between the end surfaces of the rising drop and the walls of the cell results in a more than a twofold increase in the intensity of mass transfer between the drop and the surrounding medium both during the reaction and diffusion of acid in chemically neutral medium. The movement of the droplet itself contributes to the acceleration of mass transfer due to the renewal of the composition of the solution in the interlayer region. And what is more, the displacement of the zone of maximum concentration from the center of the rising drop to the region of the boundary layer also leads to an increase in the interfacial concentration gradient and, accordingly, to an increase in the mass transfer rate.
Figure 2. Evolution of the concentration field of the acetic acid during its diffusion: (I) from the motionless droplet into the NaOH solution with $C_{01} = 0.87 \text{ mol/L}$ (vertical drop diameter $D_0 = 8.2 \text{ mm}$); (II) from the floating droplet into the NaCl solution with $C_{02} = 1.29 \text{ mol/L}$, $D_0 = 6.9 \text{ mm}$; (III) from the floating droplet into the NaOH solution with $C_{01} = 0.87 \text{ mol/L}$, $D_0 = 9.8 \text{ mm}$). The initial concentration of acid in the droplets is $C_0 = 0.87 \text{ mol/L}$. Time elapsed since the completion of the drop formation $t$, s: (a) $1$; (b) $30$; (c) $88$; (d) $28$; (e) $66$; (f) $2$; (g) $26$; (h) $26$; (i) $83$.

Figure 3. Acetic acid concentration distribution along the vertical diameter of the droplet in the presence of a reaction on its surface at different instants of time. $C_0 = 0.87 \text{ mol/L}$, $C_{01} = 0.87 \text{ mol/L}$: (a) from the motionless drop with $D_0 = 8.2 \text{ mm}$; $t$, s: $1 - 66$; $2 - 107$; $3 - 136$; (b) from the rising drop with $D_0 = 7.2 \text{ mm}$, $t$, s: $1 - 35$; $2 - 68$; $3 - 103$; $4 - 136$.
At the same time, the mass flow from a droplet floating up in a chemically neutral medium (curve 2) proves to be more intense than in the case of a rising droplet with a reaction progressing at its surface (curve 3). The reason is the generation of heat during the reaction, which "slows down" the descending flow near the interface of the drop and, consequently, the motion in the center of the drop.

Figure 4. (a) Time variation of the acetic acid concentration in the center of four droplets of similar size ($D_0 \approx 7.0$ mm) with $C_{01} = 0.87$ mol/L: the first drop with the reaction progressing at its surface is motionless (curve 1), the other is in motion in chemically neutral medium (curve 2), the third while floating up reacts with the surrounding medium (curve 3), the fourth remains stationary during the diffusion of acid into water (curve 4, [8]); (b) Time variation of the concentration of acetic acid in the center of rising drops with $C_{01} = 0.87$ mol/L, reacting with the surrounding medium and having different initial diameters $D_0$, mm: 1 – 9.8; 2 – 6.2; 3 – 4.2; 4 – 3.8

Another manifestation of the effect of heat generation is the inverse dependence of the intensity of mass transfer on the size of the reacting droplet (Fig. 4, b). This can be explained by the fact that the mass transfer is proportional to the rate of droplet rise, which is inversely proportional to the droplet radius. Indeed, the heat generation and, hence, the buoyancy force are proportional to the area of the lateral surface of the droplet and, consequently are proportional to its radius, whereas the friction force, which prevents the droplet movement, is proportional to the area of the end surface of the droplet and, accordingly, to the square of the radius.

Conclusion
A series of experiments conducted in this study allowed receiving information on the structure and evolution of the reagent concentration field both in the volume of the droplet and in its vicinity. The diffusion of acid from a motionless or slowly rising drop has been studied. The role of the development of a chemical reaction on its surface is estimated. It was shown that even a weak motion of a drop significantly affects the structure of the concentration field. The study of the evolution of the concentration distribution in the drop revealed the mechanism of the effect of heat release on the dynamics of mass transfer between the drop and the environment. It was found that the rate of mass transfer increases with the decreasing size of the reacting droplet. It should be noted that the results obtained are quantitative and, accordingly, can be used to verify the theoretical models of heat and mass transfer and numerical calculations.
Acknowledgments
The study was supported by Russian Science Foundation, grant No.19-11-00133.

References
1. Wiles Ch, Watts P 2012 *Green Chem.* **14** 38–54
2. Plutschack M, Pieber B, Gilmore K, Seeberger P 2017 *Chem. Rev.* **117** 11796–11893
3. Fitzpatrick D, Ley S 2018 *Tetrahedron* **74** 3087–3100
4. Ermakov S A, Ermakov A A, Chupakhin O N, Vaissov D V 2001 *Chem. Eng. Sci.* **84** 321–324
5. Birikh R V, Denisova M O, Kostarev K G 2015 *Fluid Dyn* **50** 361–370
6. Kostarev K G, Torokhova S V 2020 *Microgravity Sci Tec* **32** 507–512
7. Bratsun D, Kostarev K, Mizev A, Mosheva E 2015 *Phys. Rev. E* **92** 011003
8. Denisova M O, Oshmarina M V 2020 *Bull Phys. PSU* **4** 12–19 (In Russian)