INTERACTION BETWEEN FLUID MIXING AND CHEMICAL REACTION - EFFECT OF NON-UNIFORM CHAOTIC MIXING ON CONCENTRATION DISTRIBUTION FOR PERIODICAL REACTION SYSTEM

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Abstract. Mixing time and pattern in the impeller-agitated vessel were investigated at various mixing Reynolds numbers (Re) by use of two chemical reactions: ordinary decolorizing experiment with iodine and sodium thiosulfate and Belousov-Zhabotinskii (BZ) periodical reaction experiment. The periodical steady color-variation in BZ reaction system remained after the sufficient time required for the complete decolorization. The sequential spatial color-patterns obtained in steady periodical variation process were similar to the transitional color patterns observed in the decolorization process. The color-patterns obtained in BZ periodical reaction were consistent with the outline of partially mixing regions where the exchange of substance is relatively slow in the vessel and they depended on Re. The phase of periodical concentration oscillation in each partially mixing region was shifted with one another in spite of the same period of oscillation. Whether the period and/or phase synchronize or not in each partially mixing region would depend on the relative speed between the exchange of substance and the synchronization of periodical oscillation of concentration there.

Keywords: Mixing; Mixing Time; Visualisation; Fluid Mechanics; Nonlinear Dynamics; Periodical Reaction

1. INTRODUCTION

Mixing in stirred tank reactors in a wide variety of tank sizes and impeller shapes has been often utilized to homogenize different substances and to conduct chemical reactions in industrial chemical processes. Recently in various industrial processes, a wide range of operation for stirred tank is required depending on purposes and conditions. “Mixing time” is essential as one of index to evaluate the mixing process in stirred tank experimentally. Various techniques for measuring mixing time have been used such as coloration, decolorization, measurements of electric conductivity and temperature, and so on. Coloration is most simple technique to observe the mixing state in a whole tank, while it has a few demerits: it is difficult to detect the mixing state in a central part of stirred tank and the required time for complete mixing. Measurement of electric conductivity [1] enables us to detect delicate time variation of conductivity, but only local information for mixing near the sensor of conductivity can be obtained. Measurement of temperature has also demerits that only local information for mixing near thermocouples can be obtained, which is similar to measurement of electric conductivity. There are additional problems such as the variation of fluid property due to temperature change and thermal insulation for the measurement of temperature. It is expected that tomography [2] can compensate these demerits for other techniques efficiently in future, while its low resolution and high cost remain the key issue for
the evaluation of mixing state. Decolorization enables us to observe easily the difference of mixing state at every position in stirred tank. In the case of decolorization, it is easy to determine the completion time of mixing because the termination of decolorization is directly equivalent to the completion time of mixing (For detail, see the section 2.3). Consequently, decolorization is generally used as a simple method for the measurement of mixing time. In the case of the visualization using chemical reactions such as decolorization, however, the relation between the rate of chemical reaction and that of convective mixing is quite important.

Based on general mixing theory, the completion time for mixing should be defined as the time that is required to homogenize the concentration of each fluid component all over the place in the system. In above general techniques for the measurement of mixing time, fluid is judged to mixed completely at the time that its concentration, conductivity, and temperature are homogenized in stirred tank. The properties such as concentration, conductivity, and temperature are considered to have one-to-one relationship with substance quantity of fluid component (that is, concentration). Hence, it is reasonable to use these properties as an index to evaluate mixing state. On the other hand, there are unique cases containing fluid properties that are not one-to-one relationship with concentration. For example, in the periodical vibrational system by Belousov-Zhabotinskii (BZ) reaction, fluid has not only the property of concentration but also the properties of period and/or phase of concentration oscillations, which depend on the dynamical mode of reaction and do not have simple relationships with the concentration. In this case, it is inadequate to judge the mixing completion based on only the homogeneity of concentration of each component in stirred tank. In addition, final pattern by convective mixing would potentially depend on only the structure of flow field. For example, under low mixing Reynolds number (Re) conditions, the presence of segregated mixing regions from the chaotic mixing regions (CMR) in the form of toroidal vortices above and below an impeller, which is called as “isolated mixing region (IMR)” [3, 4], is well known. Material exchange by diffusion is dominant at the interface between CMR and IMR. In this case, even if the decolorization (homogenization of concentration) in the whole region of stirred tank, IMR must remain there essentially. Hence, it is necessary to evaluate mixing degree based on not only the homogeneity of concentration but also various index.

The present study focused attention on reconsidering the traditional concept of mixing that was based on the homogeneity of concentration. In the present study, required time for complete mixing and mixing patterns containing “partially mixing regions” such as IMR in CMR were investigated by use of two chemical reactions: conventional decolorizing reaction (with iodine and sodium thiosulfate) and periodical oscillating reaction (BZ reaction). Based on experimental results, the body of matter that was mixed by impeller agitation and the correspondence between chemical reaction and convection were discussed with the view of “fluid-informatic” engineering. In addition, the availability of periodical reaction for the visualization of partially mixing regions was briefly discussed.

2. EXPERIMENTAL SECTION

2.1 Materials

In the present study, we used several chemical materials (research grade) as follows: research grade sodium thiosulfate (Na2S2O3, anhydrous, mole fraction purity 0.950), potassium iodine (KI, mole fraction purity 0.995), iodine (I2, mole fraction purity 0.998), starch (hydrsoluble), saccharose (hydrsoluble), sulfuric acid (H2SO4, 0.001 mol/m3), malonic acid (CH2(COOH)2, mole fraction purity of 0.98), sodium bromate (NaBrO3), and ferroin ([Fe(phen)3]SO4, 25 mol/m3). All of them except for NaBrO3 (Sigma-Aldrich) and [Fe(phen)3]SO4 (MERCK) were obtained from the Wako Pure Chemical Industries, Ltd. and were used without further purifications. In addition, deionized water was produced using water-manufacturing equipment made by Nihon Millipore K. K.
2.2. Apparatus

The experimental apparatus in the present study consisted of the acrylic cylindrical vessel (handcrafted), two-paddled agitating impellers (handcrafted), agitating motors (HEIDON, BL-600), syringe pump (HARVARD, PHD-2000), digital video camera (NAC., MLX-ST706), and temperature control system (AS ONE, LTB-400). The diameter of vessel \( D \) was 44 mm. To reduce photographic distortion and control the temperature inside vessel, the vessel was immersed into a square vessel of acrylic resin where the thermostated water was circulated. In the present study, two-bladed paddle impeller was adopted, which was the simplest among various impellers. The diameter \( d \), length \( l \), and thickness of impeller were 22 \( (d/D = 0.5) \), 4.5 \( (l/D = ~0.1) \), and 1.5 mm, respectively. One of impeller blades was fabricated so that the tracer fluid could be injected into the vessel from the tip of the impeller blade. The diameter of impeller shaft was 4 mm. The impeller was installed on the centerline at a distance \( h \) of 22 mm from the bottom of the vessel, which was half the height of impeller \( (h/D = 0.5) \). The working fluid was poured to the height of 44 mm in advance, which was equivalent to the diameter of vessel \( (H/D = 1.0) \). The viscosity \( (\mu) \) and density \( (\rho) \) of fluid used in the present study were measured by cone-plate type viscometer (Tokyo Keiki Co., Ltd., VISCONIC ELD) and pycnometer, respectively. Based on these data, in the present study, the mixing Reynolds number defined as \( Re = \rho n r^2 / \mu \) was controlled under condition of \( 50 < Re < 2000 \). Experimental temperature was measured by a Pt resistance thermometer (Thermoprobe Inc., TL-1A). The uncertainty of temperature and viscosity were 0.06 K and 1 \%, respectively.

2.3. Procedures

2.3.1. Decolorization.

In this method, a redox reaction of I\(_2\) with Na\(_2\)S\(_2\)O\(_3\) was utilized to study a mixing state and pattern. First of all, water solution of saccharose was prepared at the concentration of 13 mass% as a working fluid. The viscosity and density of 13 mass% saccharose solution was \~2.3 \( \text{mPa}\cdot\text{s} \) and \~1054 \( \text{kg/m}^3 \) at 278.15 K, respectively. Then, appropriate quantities of I\(_2\) were dissolved in saccharose solution with the help of KI and this solution was black-colored by dissolution of starch (iodo-starch reaction). The necessary quantity of this solution was set in the vessel. After that, an agitating motor was operated at desired rotating speed \( (\text{rpm}) \) that was suitable for the desired \( Re \). After fluid field reached a cyclostationary state in the agitated vessel, the Na\(_2\)S\(_2\)O\(_3\)-saccharose solution prepared at a desired concentration was injected to the vessel from the position of \( r = 22 \text{ mm} \) and \( z = 33 \text{ mm} \). The injecting quantity and rate of Na\(_2\)S\(_2\)O\(_3\)-saccharose solution were about 1.2 times as large as the equivalent amount of I\(_2\) and 5.0 \( \text{cm}^3/\text{min.} \), respectively, which was based on the previous report [5]. The convective-mixing region was decolorized by redox reaction, while immiscible region was stood out in bold relief as poor mixing regions. Consequently, mixing patterns were obtained in the agitated vessel. The experimental images were recorded by use of digital video camera. In addition, the time needed for complete decolorization (generally regarded as the time for complete mixing) was determined.

2.3.2. BZ periodical reaction.

BZ reaction is well known as a periodical reaction that metal-ion oxidation and reduction alternately arise in the system and then its concentration changes autonomously and periodically. Figure 1(a) shows the limit-cyclic closed orbit of BZ reaction where \( x \)- and \( y \)-axes stand for the concentration of Br\(^-\) and ferrin ([Fe(phen)]\(_3\))\(^{3+}\), respectively [6]. Wherever the initial state locates in this concentration-phase plane, the trajectory of concentration always come close to the limit cycle after the transitional state. In Figure 1(a), the arrows stand for the direction of migration of concentration phase points. Figure 1(b) shows time variation of concentration of Br\(^-\), [Fe(phen)]\(_3\))\(^{3+}\), and HBrO\(_2\) on the limit cycle. The color of
solution is dark red at initial state, while it becomes blue under the conditions of high concentration of $[\text{Fe(phen)}_3]^3+$. Therefore, the color of solution changes from dark red to blue for a short time. In general, the periodical color variation keeps up for several hours. As shown in Table 1, the solution A and B were prepared at desired concentrations and equal volume (33 cm$^3$). At first, the solution B was injected into the vessel and the system was kept static. Then, the solution A was put in the vessel rapidly. Just after that, the contents were preliminarily agitated at the rotation speed of 250 rpm for fifteen minutes (pre-mixing process, $Re = 883$). Then, the agitation speed was set at a given constant value and the mixing pattern was visualized. For the first several minutes after the pre-mixing process, the transient state occurs, where anomalous spatiotemporal pattern of concentration oscillation is observed. After that, the periodical steady color variation is repeated for a few hours, while the configuration and period of stationary color variation depend on $Re$ conditions. In BZ reaction experiments, $t$ is defined as the time measured after the pre-mixing process. The system temperature in the vessel was kept constant at 278.15 K. The viscosity and density of agitating fluid obtained by mixing solution A and B was $\sim 2.4$ mPa•s and $\sim 1051$ kg/m$^3$ at 278.15 K, respectively. In this case, the color of solution periodically and alternately changed from dark red (derived from $[\text{Fe(phen)}_3]^2+$) to blue (derived from $[\text{Fe(phen)}_3]^3+$). The sequential digital images of color change pattern were taken with a digital video camera.

Incidentally, it has been already confirmed that with or without pre-mixing process and initial setup of agitating fluids (for example, the injecting amount and/or position of decolorizing fluid, the setting turn of fluids (for detail, please see fluids A and B in Table 1) for the BZ reaction, and so on) would not affect the experimental results obtained in the present study. That is, the mixing time and color-variation patterns have intrinsic significance in the system.

![Figure 1](image1.png)

**Figure 1.** Limit-cycle trajectory in Oregonator model (a) (the arrows represent the direction of motion of concentration phase points); Temporal change of concentration of three ionic species in BZ reaction: (a)Br$^-$, (b)$[\text{Fe(phen)}_3]^3+$, and (c) HBrO$_2$ (b).

| Table 1. Details on the concentration of aqueous solutions used in BZ reaction. |
|----------------------------------|----------------------------------|
| Solution A                      | Solution B                      |
| NaBrO$_3$                       | CH$_3$(COOH)$_2$                |
| $6.00 \times 10^2$ mol/m$^3$    | $2.00 \times 10^2$ mol/m$^3$    |
| H$_2$SO$_4$                     | [Fe(II)(phen)$_3$]$^{2+}$      |
| $2.00 \times 10^2$ mol/m$^3$    | $1.92$ mol/m$^3$               |
|                                  | H$_2$SO$_4$                     |
|                                  | $2.00 \times 10^2$ mol/m$^3$    |

3. RESULTS & DISCUSSION

Figure 2 shows the typical images of time variation on mixing patterns in the agitated vessels under various $Re$ conditions by use of decolorizing and BZ periodical reaction. At $Re = 117$ (Figure 2(a)), as you can see in the top region of vessel, decolorizing proceeds from near the vessel wall ($t = 22$ s), and then decolorizing gradually expands near the shaft. In this
case, decolorizing proceeds in the region except for the center of vortices of secondary discharged-flow (above and below an impeller), which is called as IMR [3, 4]. Long after that ($t = 459$ s), decolorizing also proceeds in the bottom region of vessel. Fluid exchange between top and bottom regions is performed at only the limited region that locates near the vessel wall. That is, fluid particles are difficult to get across both top and bottom regions and consequently mixing action through both regions remains weak despite relatively high $Re$. Finally, at $t = 1032$ s, IMR region is completely decolorized, which is generally defined as the required time for complete homogeneous mixing. In the BZ reaction system ($t = 1513 - 2247$ s), on the other hand, the following periodical color variation is repeated in the stationary state as follows: the whole system is dark red $\rightarrow$ the bottom region turns blue and dark red toroidal IMR region appears inside that $\rightarrow$ the bottom region turns dark red, while the top region turns blue and dark red toroidal IMR region appears inside that $\rightarrow$ the whole system returns dark red $\rightarrow \cdots$. On the other hand, as aforementioned, the required time for complete decolorization is at most $t = 1032$ s at the same $Re$. That is, interestingly, the periodical steady color-variation in BZ reaction system remains even if the time required for the complete decolorization (that is, ordinary mixing time) is passed over. Under this condition ($Re = 117$), the period of color variation is $T = 167$ s. The sequential spatial color-patterns obtained in periodical variation process are similar to the transitional color patterns observed in the decolorization process until the complete decolorization.

At $Re = 780$ (Figure 2(b)), unlike the low $Re$ case, decolorizing proceeds rapidly and uniformly ($t = 10$ s) in the whole system except for the small region around impeller shaft, which is generally called as “forced vortex zone”. This indicates that the mixing between forced vortex zone and ambient fluid is relatively slow. At $t = 41$ s, the whole region containing forced vortex zone is completely decolorized. In BZ reaction system ($t = 660 - 2660$ s), the periodical steady color variation is repeated for a few hours after the transient state and the period of color variation is $T = 468$ s. The time for the completion of transient state ($t = 41$ s) is almost close to that of complete decolorization at the same $Re$. As you can see, the following periodical color variation is repeated in the stationary state as follows: the whole system is dark red $\rightarrow$ the system except for the small region around impeller shaft (forced vortex zone) becomes blue $\rightarrow$ the whole system becomes blue $\rightarrow$ the whole system returns dark red $\rightarrow \cdots$. Hence, as in the cases with the other $Re$, the sequential spatial color-patterns obtained in periodical variation process are similar to the transitional color patterns observed in the decolorization process.

Figure 2(c) shows the color-pattern diagrams corresponding to these experimental images at various $Re$ (= 117 and 780). In Figure 2(c), the region of A and A’ stands for the well (chaotic) mixing region, while the region of B and B’ does the poor mixing region (partially mixing region) such as toroidal IMR and forced vortex zone. Hence, the mixing rate of substances is fast in the region of A and A’, while that is relatively slow in the region of B and B’. The exchange rate of substances between the well and bad mixing regions (that is, between A and B or A’ and B’) is relatively slow compared with the mixing rate of each one region. As a result, the partially mixing region inevitably appears and remains in the vessel. In addition, although both regions of A and A’ are well mixing region and consequently the exchange of substances in each region is efficient, the exchange rate of substances between the region of A and A’ is relatively slow. This is because the fluid exchange between top and bottom region in the impeller-agitated vessel is performed not near the impeller blade but through only narrow route around the stagnation point near the vessel wall, where the discharge flow from the impeller impacts [7]. In the decolorizing experiment, the spatial color-patterns shown in Figure 2(c) appear at the transient state until the complete decolorization. On the other hand, in the BZ reaction experiment, these spatial color-patterns are observed steadily and periodically after the mixing of substances are completed. This may be derived from the existence of some partially mixing regions in the vessel, where the
exchange rate of substances is slow. In each partially mixing region, the period and phase of color variation are synchronized and uniformized, while they cannot be synchronized completely between other partially mixing regions because of slow exchange rate of substances. In the present study, these result in the phase gap of periodical color variation and its retention.

Figure 2. The experimental images obtained from the decolorizing experiment and the BZ reaction experiment; (a) $Re = 117$ and (b) $Re = 780$. Panel (c) shows the color-pattern diagrams corresponding to these experimental images.

4. CONCLUSION

In the present study, mixing time and pattern in the impeller-agitated vessel were evaluated by means of two chemical reactions: ordinary decolorizing experiment (with iodine and sodium thiosulfate) and BZ periodical reaction experiment at various $Re$. The periodical steady color-variation in BZ reaction system remains after the time required for the complete decolorization (that is, ordinary mixing time) is passed over. The sequential spatial color-patterns obtained in steady periodical variation process are similar to the transitional color-patterns observed in the decolorization process until the complete decolorization. The color-patterns obtained in BZ periodical reaction are consistent with the outline of partially mixing regions where the exchange of substance is relatively slow in the vessel and they depend on $Re$. The phase of periodical concentration oscillation in each partially mixing region is shifted with one another in spite of the same period of oscillation. The relative speed between the exchange of substance and the synchronization of periodical oscillation of concentration dominates the probability of phase synchronization between partially mixing regions that have oscillation patterns containing phase gap.

5. REFERENCES