

AN EXTENDED TECHNIQUE FOR PREDICTING THE MIXING TIMES OF HIGH-VISCOSITY LIQUID IN A MIXER —MIXING SYSTEMS WITH MOLECULAR DIFFUSION AND REACTION OF SOLUTES—

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Key Words: Mixing, Mixing Time, High-Viscosity Liquid, Molecular Diffusion, Reaction, Cycle Time Distribution

This paper presents an extended technique for predicting the mixing time of high-viscosity liquids in a mixer. The molecular diffusion and reaction between solutes each dissolved in the liquids are analyzed during the mixing. Concentration profiles are obtained by solving simultaneously the diffusion and reaction differential equation and a model equation representing the decrease of scale of segregation with time. The calculated mixing time is predicted as the elapsed time until the local maximum concentrations of the solute become less than a chosen criterion of mixing. Mixing experiments were carried out with helical screw/draft tube mixers and helical ribbon-impeller mixers filled with corn syrups prepared at various viscosities. The chemical reactions were the reduction of I_2 to $2I^-$ in the presence of either $Na_2S_2O_3$ or Na_2HPO_4 . It was found that the predicted mixing times were in fairly good agreement with those determined experimentally. The mixing time was found to depend mainly on the reaction rate of reactants as well as the operational conditions of the mixer.

Introduction

In liquid mixing operations carried out in many industries including the chemical industry, it is quite important to estimate the elapsed time from starting the stirrer until a chosen criterion of mixing is achieved. This information is necessary for evaluating the performance of a mixing device and also for conducting the mixing operation effectively. This elapsed time may be called the mixing time, which means the reaction time during which mechanical agitation is carried out. Many investigations for predicting the mixing time of high-viscosity liquid mixing systems in a batch mixer have been reported during the last few decades.^{3,4,9,13)}

The enormous number of mixing systems currently in use in industry makes the prediction of mixing times difficult. It is known in general that many solutes dissolved in high-viscosity liquid do not diffuse easily. The mutual molecular diffusion and reaction between solutes in bulk liquid are considered to be the important factors in determining the mixing time in a mixing system with reaction. From this point of view, the authors previously reported techniques for predicting the mixing time of mixing systems with and without molecular diffusion of solute in the liquid.^{11,12)}

Following these, the technique for predicting the mixing time in systems in which molecular diffusion and reaction between solutes in the mixture are occurring is investigated in the present work. In this technique, the well-known diffusion and reaction differential equation and a model equation representing the decrease of the scale of segregation with time are solved simultaneously. Prior to prediction of the mixing time, the diffusion coefficients of the reactants in the bulk liquid, the orders and rate constant of reaction in the reaction system, and the cycle time distribution of the liquid in the mixer must be determined. From concentration distributions calculated from these equations, the mixing time is predicted as the elapsed time until the local maximum concentrations of the tracer solute become less than a chosen criterion of mixing.

Mixing experiments were carried out in helical screw/draft tube mixers and helical ribbon-impeller mixers using corn syrup with various viscosities. The chemical reactions were the reduction of I_2 to $2I^-$ in the presence of either $Na_2S_2O_3$ or Na_2HPO_4 , using starch as indicator. The mixing time was determined experimentally as the elapsed time until the color of I_2 in the liquid just disappeared through reaction. The mixing times predicted by the proposed technique are compared with those determined experimentally. We also compared the mixing times for these reaction systems with those for the systems with molecular

* Received July 6, 1989. Correspondence concerning this article should be addressed to F. Saito.

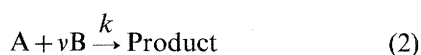
diffusion of solute reported in the previous paper.¹²⁾

1. Technique for Prediction of Mixing Time

The technique assumes a liquid medium containing a 'tracer' chemical species A at concentration c_A , in the form of a stretching and contracting lamina with nearly uniform conditions in planes parallel to the laminae, and bounded on both sides by wider laminae containing a chemical species B of uniform concentration c_B . The well-known diffusion and reaction differential equation expressing the variation of concentration with time takes the following form.¹⁾

$$\frac{\partial c}{\partial t} = \mathcal{D} \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) - \left(v_x \frac{\partial c}{\partial x} + v_y \frac{\partial c}{\partial y} + v_z \frac{\partial c}{\partial z} \right) - R \quad (1)$$

where \mathcal{D} is the coefficient of diffusion, t the time, v the velocity of liquid, R the term of reaction and x, y, z are the axes of Cartesian coordinates. If the chemical reaction between the two species A and B with the orders m, n and the reaction rate constant k progresses in the liquid as shown by Eq. (2) and the scale of segregation in the mixture is assumed to be minimum in the x direction, the differential equation can be simplified as Eq. (3).



$$\left. \begin{aligned} \frac{\partial c_A}{\partial t} &= \mathcal{D}_A \left(\frac{\partial^2 c_A}{\partial x^2} \right) - v_x \left(\frac{\partial c_A}{\partial x} \right) - k c_A^m c_B^n \\ \frac{\partial c_B}{\partial t} &= \mathcal{D}_B \left(\frac{\partial^2 c_B}{\partial x^2} \right) - v_x \left(\frac{\partial c_B}{\partial x} \right) - \nu k c_A^m c_B^{n-1} \end{aligned} \right\} \quad (3)$$

In Eq. (2), ν is the chemical equivalent coefficient of reaction. Equation (3) is still represented by the Eulerian coordinates. Introducing the nondimensional distance, X , defined as Eq. (4) in order to represent it by Lagrangian coordinates, and the nondimensional concentration, C , defined as Eq. (5), Eq. (3) is rewritten as Eq. (6).

$$X = \frac{x}{L(t)} \quad 0 \leq X \leq 1 \quad (4)$$

$$C = \frac{c_i - \bar{c}}{c_o - \bar{c}} \quad (5)$$

$$\left. \begin{aligned} \frac{\partial C_A}{\partial t} &= \left(\frac{\mathcal{D}_A}{L(t)^2} \right) \left(\frac{\partial^2 C_A}{\partial X^2} \right) - k c_{A_o}^{m-1} c_{B_o}^n C_A^m C_B^n \\ \frac{\partial C_B}{\partial t} &= \left(\frac{\mathcal{D}_B}{L(t)^2} \right) \left(\frac{\partial^2 C_B}{\partial X^2} \right) - \nu k c_{A_o}^m c_{B_o}^{n-1} C_A^m C_B^{n-1} \end{aligned} \right\} \quad (6)$$

where $L(t)$ is the statistical representative length in the X direction between the maximum and minimum

concentrations of species A and/or B in the mixture. $L(t)$ decreases gradually with time. When the shear rate of the liquid in the flow field is already known, such as in a stationary vessel with rotating coaxial cylinder, $L(t)$ is expressed theoretically.^{7,8)} For ordinary mixers such as a helical ribbon-impeller mixer, Eq. (7) has been proposed from the statistical point of view.¹⁰⁾

$$L(t) = L_o \exp(-\alpha_r t) \quad (7)$$

where L_o is the representative length of convective flow path of the liquid in a mixer and α_r is the probability of inflow of liquid element per unit time, which can be obtained by applying the concept of stochastic processes to the cycle time distribution.¹¹⁾ In such cases, the nondimensional concentrations of each reactant at any position of X can be calculated from Eqs. (6) and (7) with an aid of the initial and boundary conditions, given by Eqs. (8) and (9), by the finite difference method. Initial conditions ($t=0$):

$$\left. \begin{aligned} C_A &= 1, \quad C_B = 0 & \text{at } 0 \leq X \leq b \\ C_A &= 0, \quad C_B = 1 & \text{at } b \leq X \leq 1 \end{aligned} \right\} \quad (8)$$

Boundary condition ($t > 0$):

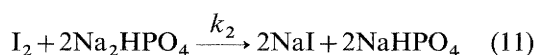
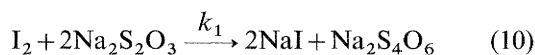
$$\frac{\partial C_A}{\partial X} = \frac{\partial C_B}{\partial X} = 0 \quad \text{at } X = 0, 1 \quad (9)$$

In Eq. (8), b is equivalent to the volume fraction of tracer liquid to mother liquid in a mixer. From the variation of calculated concentration distributions in the X direction with time, the calculated mixing time is predicted as the elapsed time until the local maximum concentrations of the tracer solutes are no more than 5%^{6,7)} in the nondimensional concentration of the mixture (refer to Fig. 2).

2. Experimental

Mixing devices used in this work were helical screw/draft tube mixers (the ratio of impeller diameter, d , to vessel diameter, D , was kept constant at 0.67) and helical ribbon-impeller mixers ($d/D = 0.86$). The two types of mixer were scaled to geometrical similarity in four steps. The vessel diameters ranged from 75 mm to 200 mm. The detailed geometry of these mixers is the same as that used in the previous work.^{11,12)}

Corn syrups, which are regarded as Newtonian liquids in the range of laminar flow, having viscosities between $\mu = 0.3$ and $1.6 \text{ Pa} \cdot \text{s}$ at 291 K were prepared as the bulk liquids. The reactants were iodine (I_2) as species A, and either sodium thiosulphate ($Na_2S_2O_3$) or monohydrogen disodium phosphate (Na_2HPO_4) as species B; they were each dissolved in the bulk liquid. The reaction equations are as follows.



The orders and rate constants of reaction for these reaction systems were determined experimentally by the stopped-flow method,²⁾ using a spectrophotometer. Both m and n have the value of 1, and k_1 and k_2 are respectively 5.80×10^8 l/mol/s and 1.2×10^2 l/mol/s for the two reaction systems. Thus a fast reaction system (I_2 - $\text{Na}_2\text{S}_2\text{O}_3$) and a relatively slow reaction system (I_2 - Na_2HPO_4) were employed in this work. In the mixing experiments, the initial amount of $\text{Na}_2\text{S}_2\text{O}_3$ or Na_2HPO_4 to that of I_2 was fixed respectively at four or eight times in chemical equivalent at the complete mixing state. The initial amounts of the two reactants were set in this way because the mixing times determined experimentally were known to become constant when the initial amount of either $\text{Na}_2\text{S}_2\text{O}_3$ or Na_2HPO_4 to that of I_2 is more than three times the chemical equivalent.⁶⁾ The concentration of the iodine solution (tracer liquid) was 1.33×10^{-2} mol/l, and the concentrations of $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2HPO_4 solutions (mother liquids) were 2.66×10^{-3} mol/l and 5.32×10^{-3} mol/l respectively. The volume ratio of tracer liquid to mother liquid was kept constant at (1/40). The coefficients of diffusion of $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2HPO_4 in corn syrups of different viscosities were determined by the Moiré fringe method.⁵⁾ The diffusion coefficient for I_2 in the liquid was determined by the visualisation method using a camera, as in the previous work.^{11,12)} Figure 1 shows the variation of the coefficients of diffusion of solutes with viscosity of the liquid. The reason why the diffusion coefficient of I_2 in the liquid is much smaller than those for $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2HPO_4 may be association of I_2 and corn syrup.

The experimental procedures for the helical screw/draft tube mixers and then helical ribbon-impeller mixers are the same as those presented in the previous papers.^{11,12)} The mixing completion state was judged by taking photographs at suitable time intervals in addition to direct observation through the vessel. The criterion of mixing in the experiment was that the colour of tracer liquid in the whole vessel should just have disappeared. The elapsed time, from starting the stirrer until the colour just vanished, was measured several times under the same experimental conditions. The data for cycle times of the liquid in the mixers and the value of L_0 in Eq. (7) for the mixers refer to the previous paper.^{11,12)}

3. Results

Figure 2 shows the variation of the calculated

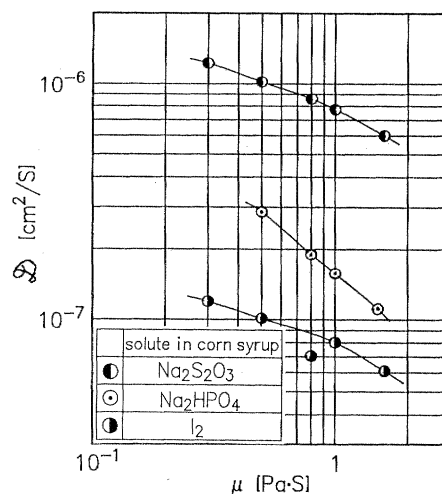


Fig. 1. Variation of coefficient of diffusion of solute in liquid with its viscosity

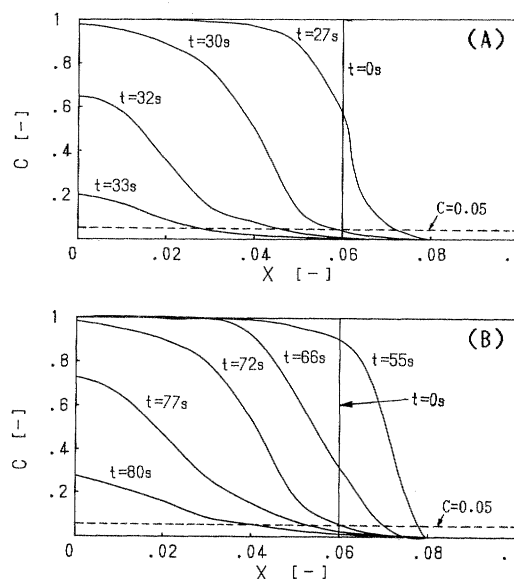


Fig. 2. Nondimensional concentration distributions for liquid of $\mu = 0.5$ Pa·s in helical ribbon-impeller mixer of $D = 0.2$ m at $N = 1.0$ s⁻¹: (A), $\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$ (B), $\text{I}_2 + 2\text{Na}_2\text{HPO}_4 \rightarrow 2\text{NaI} + \text{NaHPO}_4$

nondimensional concentration distributions of the tracer solute in the different reaction systems in the bulk liquid with $\mu = 0.5$ Pa·s, using the helical ribbon impeller mixer of $D = 20$ mm at impeller rotational speed $N = 1.0$ s⁻¹. From these distributions for the I_2 - $\text{Na}_2\text{S}_2\text{O}_3$ reaction system, it was found that the local maximum concentration (at $X = 0$) decreased rapidly with time. The calculated nondimensional concentration distributions for the slow reaction system were found to change slowly with time.

Figure 3 shows the progressive mixing processes of the liquid of $\mu = 1.0$ Pa·s with reaction for the different reaction systems in the helical ribbon-impeller mixer of $D = 0.2$ m at $N = 1.0$ s⁻¹. As can be seen from these photographs, decolorization of tracer in the fast

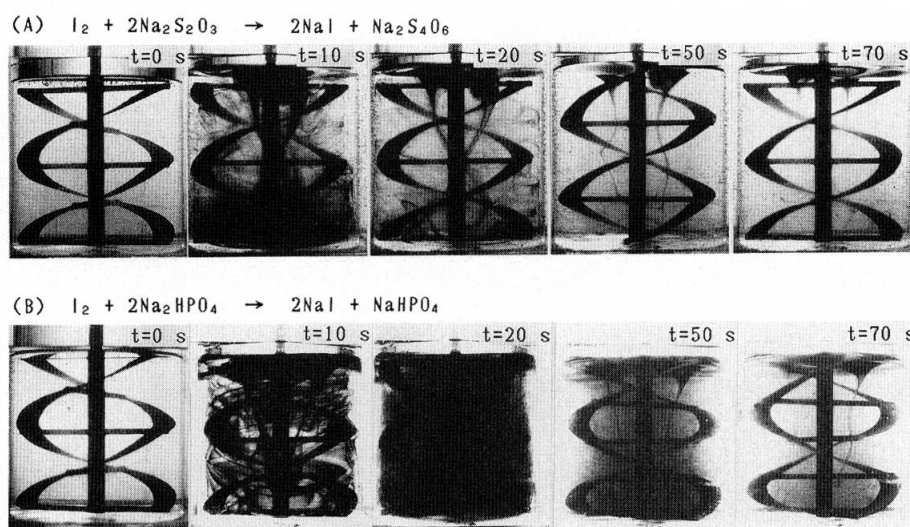


Fig. 3. Progressive mixing processes for liquid of $\mu = 1.0 \text{ Pa} \cdot \text{s}$ in helical-ribbon impeller mixer of $D = 0.2 \text{ m}$ at $N = 1.0 \text{ s}^{-1}$: (A), $I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$; (B), $I_2 + 2Na_2HPO_4 \rightarrow 2NaI + NaHPO_4$

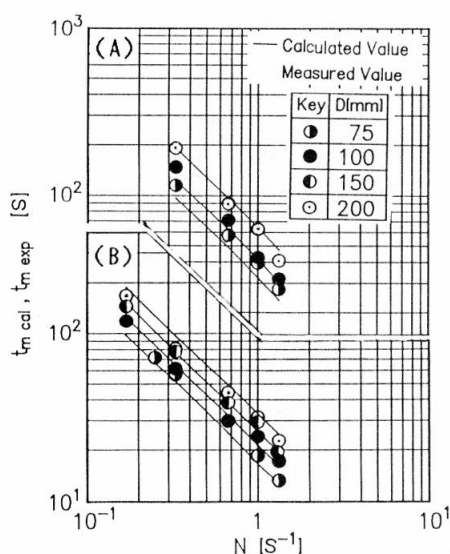


Fig. 4. Variation of mixing time with rotational speed of impeller for I_2 and $Na_2S_2O_3$ reaction system: (A), helical-screw/draft tube mixers, liquid; $\mu = 0.3 \text{ Pa} \cdot \text{s}$; (B), helical ribbon-impeller mixers, liquid; $\mu = 0.5 \text{ Pa} \cdot \text{s}$

reaction system proceeded smoothly, comparable to mechanical agitation, while decolorization in the slow reaction system took place slowly. It seems that the reaction for the fast reaction system occurs immediately on the boundary layer of two liquids, at which the mutual diffusion of reactants in the liquid takes place. For the slow reaction system, though the reaction seems to occur on that layer, the contraction and stretching of liquid by the impeller come to an end before the reaction is attained.

Figure 4 shows the relation between the mixing time, t_m , and the rotational speed of impeller, N , for the fast reaction system in the different types of mixers. In Fig. 4, the calculated values are represented by solid lines and the experimental values by circles with

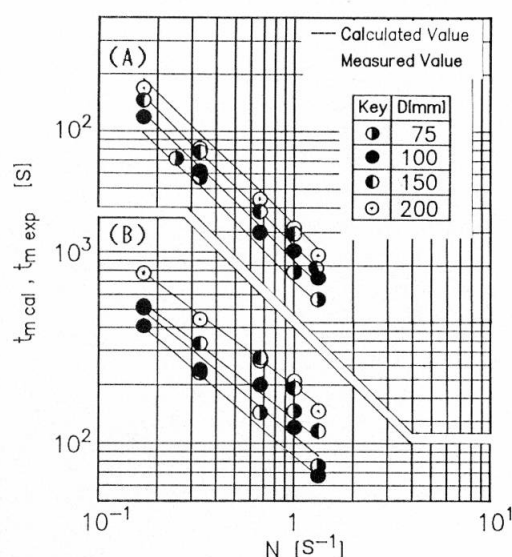


Fig. 5. Variation of mixing time with rotational speed of impeller for liquid of $\mu = 0.5 \text{ Pa} \cdot \text{s}$ in helical ribbon-impeller mixers: (A) $I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$; (B), $I_2 + 2Na_2HPO_4 \rightarrow 2NaI + NaHPO_4$

various markings. From Fig. 4 the calculated mixing time, $t_{m \text{ cal}}$, was found to be in fairly good agreement with the experimental value, $t_{m \text{ exp}}$. Furthermore, $t_{m \text{ cal}}$ was found to increase with increase of scale of the mixer, because the larger the mixer scale, the smaller was the value of α_r for the mixers used in this work.¹¹⁾

Figure 5 shows the relation between t_m and N for the various reaction systems in the helical ribbon-impeller mixers, each scaled to geometrical similarity. As can be seen from this figure, $t_{m \text{ cal}}$ is in fairly good agreement with $t_{m \text{ exp}}$. Moreover, t_m for the fast reaction system is found to be much shorter than that for the slow reaction system. This may be due to the difference in reaction rate constant rather than in diffusional coefficient of solutes.

Figure 6 shows a comparison of the nondimensional mixing times determined experimentally, $(Nt_m)_{exp}$, with those calculated for the various reaction systems in the helical ribbon-impeller mixers. From Fig. 6, the two are found to be in good agreement within the scatter of the experimental results. The relative error of the calculated values to the experimental value under each experimental conditions, $\sum (|t_{mcal} - t_{mexp}|/t_{mexp})/Z$, was less than about $\pm 8\%$.

Figure 7 shows the relation between (Nt_m) and Reynolds number $Re (= \rho ND^2/\mu)$, using the liquid of $\mu = 0.5 \text{ Pa}\cdot\text{s}$ in the helical ribbon-impeller mixers according to the reaction rate. The data of (Nt_m) for the mixing system with molecular diffusion of solute, which are the same as those in the previous paper,¹²⁾ are also indicated in this figure. Comparing (Nt_m) for the two reaction systems, these values for the slow reaction system were larger than those for the fast reaction system. Furthermore, (Nt_m) for the slow reaction system increased slightly with increase of Re . For the fast reaction system, each value of (Nt_m) was kept nearly constant over the experimental range of Re in spite of the difference in size of the mixers. It is considered that, for the slow reaction system, the partial mixing rate by the reaction on the boundary layer of two liquids is slower than that by mechanical agitation. In the early stage of mixing, the tracer liquid is spread over the whole region of the liquid in the mixer. After this stage, the color of tracer liquid gradually disappeared.

For the fast reaction system, the reaction is considered to proceed promptly on the boundary layer of two liquids as soon as the mutual diffusion of reactants in the liquid takes place there. The values of (Nt_m) for the diffusional mixing system were smaller than those for the slow reaction system, yet (Nt_m) values for the diffusional mixing system were larger than those for the fast reaction system. This implies that (Nt_m) for a fast reaction system is smaller than that for a diffusional mixing system when partial mixing by reaction for a fast reaction system proceeds faster than that by mechanical agitation. Therefore, the factors governing the mixing rate as indicated by (Nt_m) may be a reaction rate constant and diffusion coefficients of solutes in a mixing system with reaction as well as the operational conditions of the mixer.

Conclusion

A technique for predicting the mixing time of a high-viscosity Newtonian liquid mixing system, in which molecular diffusion and reaction between solutes in the mixture is occurring, is presented. This technique is based on a combination of the differential diffusion and reaction equation with the model equation. The diffusion coefficients, the orders and

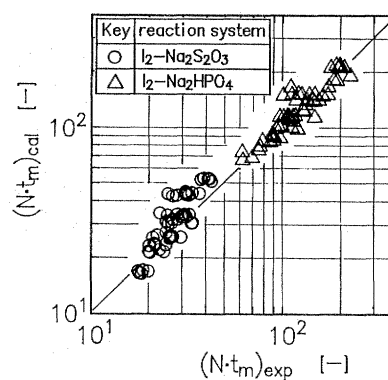


Fig. 6. Comparison of $(Nt_m)_{cal}$ with $(Nt_m)_{exp}$ for different reaction systems

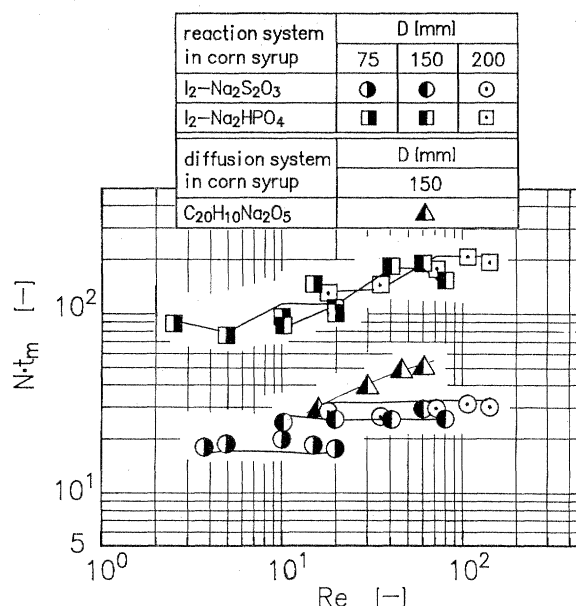


Fig. 7. Variation of (Nt_m) with Re for different mixing systems

rate constant of reaction in a reaction system and the cycle time distribution of liquid in a mixer must be determined prior to the calculation of concentration of solutes. Mixing experiments were carried out with helical screw/draft tube mixers and helical ribbon-impeller mixers filled with corn syrups of various viscosities to dissolve the reactants. Two kinds of reaction system with different reaction rates were used in this work.

It was found that the mixing time for the reaction mixing systems can be predicted by using the proposed technique. The nondimensional mixing time for the relatively slow reaction system was found to be larger than that for the fast reaction system. The former increased slightly with increase in the Reynolds number, while the latter was independent of the Reynolds number. It was concluded that the mixing time depends on the reaction and diffusion characteristics of the solute(s) dissolved in the liquid and on the Reynolds number.

Acknowledgment

The authors are grateful to Mr. Tsuyoshi Ohhinata for his assistance in this work and to Mr. Shigeru Nishioka, director of Satake Chemical Equipment Mfg., Ltd., for supplying the mixing impellers.

Nomenclature

A, B	= reactants	
b	= volume ratio of tracer liquid to bulk liquid	[—]
C	= nondimensional concentration defined by Eq. (5)	[—]
c	= concentration	[mol/l]
d	= impeller diameter	[mm]
D	= inner diameter of vessel	[mm]
\mathcal{D}	= coefficient of diffusion	[cm ² /s]
k	= rate constant of reaction	[l/mol/s]
L(t)	= scale of segregation	[mm]
L ₀	= representative length of convectional flow path	[mm]
m,n	= orders of reaction	[—]
N	= rotational speed of impeller	[s ⁻¹]
Re	= Reynolds number defined by $(\rho Nd^2/\mu)$	[—]
t	= time	[s]
t _m	= mixing time	[s]
X	= nondimensional distance defined by Eq. (4)	[—]
x	= distance	[mm]
Z	= number of measurement of mixing time	[—]
α_r	= probability of inflow of liquid element per unit time	[s ⁻¹]
μ	= viscosity	[Pa·s]
ν	= stoichiometric coefficient	[—]
ρ	= density	[kg/m ³]

<Subscripts>

A, B	= reactants
cal	= calculated
exp	= experimental
i	= arbitrary, inner
0	= initial, outer

<Superscript>

“—”	= mean
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