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

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Key Words: Mixing, High Viscosity Liquid, Mixing Time, Shear Deformation, Cycle Time Distribution, Diffusion Coefficient

This paper presents a technique for predicting the mixing time in a high-viscosity liquid mixing system where molecular diffusion is occurring in the mixture. In the technique, the diffusion differential equation and the model equation representing the decrease in scale of segregation with time are solved simultaneously. However, prior to prediction of the mixing time, the diffusion coefficient of the solute in the bulk liquid and the cycle time distribution of liquid in a mixer must be determined. From the concentration profile obtained by the technique proposed in this work, the macroscopic mixing time is predicted as the elapsed time until the local maximum concentrations of the solute become less than a chosen arbitrary criterion of mixing. Mixing experiments were carried out for helical screw/draft tube mixers and helical ribbon impeller mixers using corn syrup and PVA solutions of various viscosities. The mixing time was determined experimentally as the elapsed time until the segregation of tracer becomes uniform. The predicted mixing times were in good agreement with those determined experimentally.

Introduction

Mixing in high-viscosity liquid mixers is a common operation in the chemical and polymer industries, one of the main purposes being chemical reaction and mass transfer. In such processes, prediction of the mixing time of several kinds of miscible liquids in a batch mixer is very important for the evaluation of the mixing characteristics of the mixer, and thus for the prediction of optimum operational conditions. From this point of view, several investigations of mixing time prediction for high-viscosity liquid mixing systems in the laminar-flow region have been reported.\textsuperscript{5,3,12,13,14,18,21} We also have reported a technique for predicting the mixing time of mixing systems with negligible diffusion of solute in bulk liquid in a mixer.\textsuperscript{20} However, there are few investigations on the technique for predicting the mixing time in systems in which both molecular diffusion of solute in bulk liquid and shear deformation contribute to the liquid mixing. The mechanism of mixing in systems where molecular diffusion of solute in bulk liquid is occurring is different from that in systems with negligible diffusion of solute in the liquid.\textsuperscript{7,11} Furthermore, the criteria of mixedness in the each mixing system are also different. Although the diffusion rate of solute in most high-viscosity liquids is quite slow, it is important for clarifying the mixing mechanisms that the effect of diffusion of solute on mixing of the liquid in a mixer be studied. Thus the technique for predicting mixing times in systems with molecular diffusion of solute is investigated in this paper. This technique combines the well-known diffusion differential equation with a model equation representing the decrease of scale of segregation with time.\textsuperscript{16,19} It is necessary to determine the coefficient of diffusion of solute in bulk liquid and the cycle time distribution of the liquid in a mixer in advance for use in calculating the concentration of tracer solute in the liquid when applying this technique. The macroscopic mixing time is predicted as the elapsed time until the local maximum concentrations of the tracer solute reach a chosen arbitrary criterion of mixedness. In this paper, the calculated mixing times predicted by the proposed technique are compared with those determined experimentally.

2. Technique for Prediction of Mixing Time

The technique assumes a fluid medium containing a "tracer" chemical species A at concentration $c$ 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 without any chemical species. The mass balance equation is obtained by taking the molecular diffusion of solute, $D$, in conventional flow into consideration, and the well-known diffusion differential equation

\begin{equation}
\frac{\partial c}{\partial t} = D \nabla^2 c
\end{equation}
expressing the variation of concentration with time takes the following form.\(^{11}\)

\[
\frac{\partial c}{\partial t} = \mathcal{D}(c^3 c/\partial x^2 + c^2 c/\partial y^2 + c^2 c/\partial z^2) \\
- (v_x \partial c/\partial x + v_y \partial c/\partial y + v_z \partial c/\partial z)
\]  

(1)

where \(\mathcal{D}\) is the coefficient of diffusion of solute, \(t\) is the time, \(v\) is the velocity of liquid, and \(x, y, z\) are the axes of three-dimensional coordinates. Taking the \(x\) and \(z\) axes as the shrinkage directions and the \(y\) axis as the elongation direction, Eq. (1) can be simplified as Eq. (2) when the width of segregation in the \(x\)-direction is much smaller than that in the \(z\)-direction.

\[
\frac{\partial c}{\partial t} = \mathcal{D}(c^3 c/\partial x^2) - v_z \partial c/\partial x
\]  

(2)

Introducing the nondimensional distance, \(X\), defined by Eq. (3) and the nondimensional concentration, \(C\), defined by \(C = (c - \bar{c})/(c_0 - \bar{c})\), and taking the Lagrangian observation, Eq. (2) is rewritten as Eq. (4):

\[
X = x/L(t)
\]  

(3)

\[
\frac{\partial C}{\partial t} = (\mathcal{D}/L(t)^2)\frac{c^2}{\partial X^2}
\]  

(4)

where \(L(t)\) is the statistical representative length in the \(X\)-direction between the maximum and minimum concentrations of solute in the mixture. This value decreases gradually with time. Eq. (5) has been proposed from the statistical point of view.\(^{16,17,19}\)

\[
L(t) = L_0 \exp(-\alpha_t t)
\]  

(5)

In Eq. (5), \(L_0\) is the representative length of conventional flow path of the liquid in a mixer, and \(\alpha_t\) 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.\(^{20}\) Under the initial and boundary conditions as given by Eqs. (6) and (7), Eq. (8) can be solved analytically. Initial conditions \((t = 0):\)

\[
\begin{align*}
C &= 1, \quad X = 0 \\
\frac{\partial C}{\partial X} &= -\bar{c}/(c_0 - \bar{c}), \quad X = 1
\end{align*}
\]  

(6)

Boundary conditions:

\[
\begin{align*}
C &= 0, \quad t = \infty, \quad 0 \leq X \leq 1 \\
\frac{\partial C}{\partial X} &= 0, \quad t = 0, \quad X = 0, \quad X = 1
\end{align*}
\]  

(7)

\[
C = (2/\pi) \sum_{k = 0}^{\infty} \left\{ \left( 1 - (-1)^k \right)/k \right\}
\times \left[ \exp \left\{ -\mathcal{D} k^2 \pi^2 t/(4b^2 L(t)^2) \right\} \right]
\times \sin \left[ k\pi (X + b)/2b \right] \quad 0 \leq x \leq b
\]

\[
C = \left\{2\bar{c}/(c \bar{c} - c_0)\right\} \sum_{k = 0}^{\infty} \left\{ \left( 1 - (-1)^k \right)/k \right\}
\times \left[ \exp \left\{ -\mathcal{D} k^2 \pi^2 t/\left( 4(1-b)^2 L(t)^2 \right) \right\} \right]
\times \sin \left[ k\pi (X - b)/(2(1-b)) \right] \quad b \leq X \leq 1
\]  

(8)

In Eq. (8), \(b\) is the volume fraction of tracer liquid to bulk fluid and \(k\) is a positive integer. From the calculated concentration distribution in the \(X\)-direction, the macroscopic mixing time is predicted as the elapsed time until the local maximum concentrations of the tracer solute are no more than 4% of the mean concentration of the mixture at complete mixing. This is the chosen arbitrary criterion of mixing.\(^{5,6}\)

3. Experimental Apparatus and Procedure

Two kinds of mixing devices as shown in Fig. 1 were used in this work. They were helical screw/draft tube mixers and helical ribbon impeller mixers of three sizes, from \(D = 70\) mm to 200 mm vessel diameter. Each was made of transparent acrylic resin except for the impeller. The dimensions of component parts of each mixer are tabulated in Table 1.

Corn syrup and PVA aqueous solutions, which are regarded as Newtonian fluids in the laminar-flow region with viscosities between 0.35 and 1.5 Pa·s at 291 K, were prepared. Two solutes were prepared for this experiment. They were potassium chloride, KCl, and fluorescein sodium, \(C_{20}H_{10}Na_2O_5\). The con-
Table 1. Dimensions of component parts of mixers
(a) Helical screw/draft tube mixer

<table>
<thead>
<tr>
<th>D [mm]</th>
<th>D' [mm]</th>
<th>d [mm]</th>
<th>H [mm]</th>
<th>H' [mm]</th>
<th>h [mm]</th>
<th>D1 [-]</th>
</tr>
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<td>137</td>
<td>133</td>
<td>300</td>
<td>200</td>
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</table>

(b) Helical ribbon impeller mixer

<table>
<thead>
<tr>
<th>D [mm]</th>
<th>d [mm]</th>
<th>H [mm]</th>
<th>h [mm]</th>
<th>h' [mm]</th>
<th>w [mm]</th>
<th>D1 [-]</th>
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<td></td>
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<tr>
<td>150</td>
<td>131</td>
<td>163</td>
<td>142</td>
<td>18</td>
<td>2.00</td>
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</table>

Centrations of KCl in corn syrup were $2.5 \times 10^{-4}$ mol/l in the bulk liquid and $10^{-2}$ mol/l in the tracer liquid. The concentration range was such that the output signal from the electric probe used in this experiment was proportional to the concentration of KCl in the corn syrup. The concentration of \( C_{20}H_{10}Na_2O_5 \) in the PVA aqueous solution was $10^{-4}$ mol/l in the tracer liquid. The coefficient of diffusion of KCl in the corn syrup was determined by the electrical conductivity method.\(^6\)\(^9\) The diffusion coefficient for \( C_{20}H_{10}Na_2O_5 \) in the PVA aqueous solution was determined by a visualization method using a camera. In this method, a small cell (cross-sectional area = 30 mm $\times$ 20 mm, depth = 60 mm) made of transparent acrylic resin was used. The boundary line at which the two liquids contact in the cell was easily observed by directing light having a wave length of 5100Å through a 0.3-mm slit in the side of the cell. Therefore, by making visible the boundary line in a film at adequate time intervals, the coefficient of diffusion of \( C_{20}H_{10}Na_2O_5 \) in the PVA aqueous solution could be obtained. Figure 2 shows the variation of the coefficient of diffusion with viscosity of the bulk liquid. The diffusion coefficient of \( C_{20}H_{10}Na_2O_5 \) in the PVA aqueous solution was much higher than that of KCl in the corn syrup. The discrepancy may be due mainly to the association between the solute and the liquid and the molecular weight ratio of the solute to the liquid.\(^2\)

The cycle time of the liquid in the mixer was determined by using short waste-cotton fibre as a tracer. For the helical screw/draft tube mixer, the reference cross section for the axial flow direction was chosen at half the depth of liquid in the mixer (see Fig. 1). The reference section for the circumferential flow direction was chosen at the vertical plane including the rotating axis of the impeller. The liquid outside the draft tube flows upward perpendicularly; inside the draft tube it flows downward while rotating around the impeller shaft. As the rotating flow inside the draft tube is considered by the cycle time in the axial flow direction, the measurement of the cycle time in the circumferential direction is therefore omitted. For the helical ribbon impeller mixer, the reference cross section for the axial flow direction was chosen at (H/4) from the bottom of the vessel, and another reference section for the circumferential flow direction was chosen in the same plane as that for the helical screw/draft tube mixer (see Fig. 1). In the plane, the liquid flows downward near the axis and upward near the wall. The number of cycle times measured in each experimental condition ranged from 300 to 500. The cycle time distributions in the axial and circumferential flow directions were obtained separately for PVA aqueous solution and corn syrup in the each mixer. From the cycle time distribution curve, \( \tau \) can be determined.\(^2\)\(^0\) The value of \( L_0 \) in Eq. (5) can be obtained from Eq. (9).\(^2\)\(^0\)

\[
L_0 = 2H: \text{helical screw/draft tube mixer} \\
L_0 = 2[H(H + (nD/2))]^{1/2}; \text{helical ribbon impeller mixer}
\]

Mixing experiments for the PVA aqueous solution-C\( \text{\(C_{20}H_{10}Na_2O_5\)} \) mixing system were carried out, using the two types of mixer. The experimental procedure and the criterion of mixing were the same as those for the corn syrup-C\( \text{\(C_{20}H_{10}Na_2O_5\)} \) system described in the previous paper.\(^2\)\(^0\) To confirm the applicability of this technique, the mixing experiments were carried out using the corn syrup-KCl system in the helical ribbon impeller mixer of \( D = 150 \) mm vessel diameter. The mixing processes were analysed by using an electrical conductivity method.\(^6\) The mixing procedure was the same as that for the PVA aqueous solution-C\( \text{\(C_{20}H_{10}Na_2O_5\)} \) system. The concentration change of the liquids was followed by electrodes set in the liquid surface and by the wall near the bottom of the mixer. In this case the criterion chosen was the same as that used in the calculation.
4. Results

4.1 Prediction of mixing time

1) Helical screw/draft tube mixer The relation between \( \alpha \) and \( n \) for the three mixers, each scaled to geometrical similarity, is shown in Fig. 3. It shows that \( \alpha \) is proportional to \( n \) in the scope of these experiments. Furthermore, it is found that the relation between \( \alpha \) and \( n \) may be independent of the viscosity of the solution covered in this work. Consequently, the nondimensional concentration distribution of the mixing system in the mixer can be calculated by the technique mentioned above. Figure 4 shows the variation of the calculated nondimensional concentration distribution in the \( X \)-direction with time for the mixer of \( D = 100 \) mm. From the distributions as shown in Fig. 4, \( t_m \) can be determined as the time required until the nondimensional concentration of the liquid reaches the criterion of mixedness.

2) Helical ribbon impeller mixer The relation between \( \alpha \) and \( n \) shows the same trend as that for the helical screw/draft tube mixers. Therefore, \( t_m \) of the mixing systems in the mixer can be calculated by using the proposed technique.

4.2 Measurement of mixing time

1) Helical screw/draft tube mixer In Fig. 5(a), a series of photographs shows the progression of mixing of the tracer liquid through PVA aqueous solution of \( \mu = 1.0 \text{ Pa}\cdot\text{s} \) in the mixer of \( D = 100 \text{ mm} \) at an impeller rotational speed of \( n = 0.5 \text{ s}^{-1} \) on the \( x-y \) plane in Eq. (1). In these photographs, the measuring region of the segregation scale is from 40 mm to 50 mm from the liquid surface outside the draft tube. The values of "t" beside each photograph are elapsed times from the start of mixing. The scale of tracer in the \( x \)-direction is always much thinner than that in the \( z \)-direction. As can be seen from these photographs, the scale of segregation of tracer liquid decreases with elapsed time. From Fig. 5(a), \( t_m \) required until the tracer liquid spread over the whole region of the solutions in the mixer can be determined experimentally. Figure 6 shows the relation between the experimental and calculated mixing times, \( t_{\text{mexp}} \), \( t_{\text{mcal}} \), and \( n \), with the viscosity of solution and the inner diameter of the mixer as parameters. As can be seen from Fig. 6, \( t_{\text{mcal}} \) agreed well with \( t_{\text{mexp}} \) in the range of these experiments. Also, the values \( t_{\text{mexp}} \) and \( t_{\text{mcal}} \) were found to increase slightly with increasing liquid viscosity. This result may be due to the dependency of the coefficient of diffusion of solute upon the liquid viscosity. Furthermore, \( (n t_m) \) was found to remain constant in the scope of these experiments. This result is similar to that in the same range of Reynolds number obtained by previous researchers. \(^{2,3,12,13,14,18,21} \) A comparison of \( (n t_m)_{\text{exp}} \) with \( (n t_m)_{\text{cal}} \) is shown in Fig. 7. The two are in good agreement within the scatter of the experimental results. The coefficient of variation of the calculated values with that found by experiment was below about \( \pm 8\% \).

2) Helical ribbon impeller mixer A series of photographs showing the progression of mixing of the tracer liquid through PVA aqueous solution of \( \mu = 1.0 \text{ Pa}\cdot\text{s} \) in the helical ribbon impeller mixer of \( D = 100 \text{ mm} \) at \( n = 0.5 \text{ s}^{-1} \) is shown in Fig. 5(b). In these photographs, the measuring region of the segregation scale is from 40 mm to 50 mm from the liquid surface. The result shows a similar trend to that shown in Fig. 5(a). Figure 8 shows the response curve of the concentration of KCl in corn syrup in the mixer. From Fig. 8, \( t_m \) can be determined experimentally by setting the criterion of mixing in the experiment. Figure 9 shows the relationship between \( t_{\text{mexp}} \), \( t_{\text{mcal}} \), and \( n \) with parameters of the solution viscosity and the inner diameter of the mixer. The relationship shows a similar trend to that obtained for the helical
screw/draft tube mixer. Figure 10 shows a comparison of $(n_{t_w})_{exp}$ with $(n_{t_w})_{cal}$. It can be seen that $(n_{t_w})_{cal}$ agrees quite well with $(n_{t_w})_{exp}$ within the scatter of the experimental results. The coefficient of variation was

**Fig. 5.** Photographs of progressive process of mixing pattern at the observing area
(a) Helical screw/draft tube mixer
(b) Helical ribbon impeller mixer

**Fig. 6.** Variation of $t_w$ with $n$ for helical screw/draft tube mixers (PVA aque. solu.-C$_{20}$H$_{10}$Na$_2$O$_4$)

**Fig. 7.** Comparison of $(n_{t_w})_{cal}$ with $(n_{t_w})_{exp}$ for the helical screw/draft tube mixers (PVA aque. solu.-C$_{20}$H$_{10}$Na$_2$O$_4$)

**Fig. 8.** Schematic signal pattern of concentration change of KCl in corn syrup

**Fig. 9.** Variation of $t_w$ with $n$ for helical ribbon impeller mixers
(a) PVA aque. solu.-C$_{20}$H$_{10}$Na$_2$O$_4$
(b) Corn syrup-KCl

**Fig. 10.** Comparison of $(n_{t_w})_{cal}$ with $(n_{t_w})_{exp}$ for helical ribbon impeller mixers
below approximately ±9%.

Conclusion

A technique for predicting the mixing time of high-viscosity Newtonian liquid mixing systems, in which molecular diffusion of solute in the mixture is occurring, is presented. In this technique, the well-known diffusion differential equation and a model equation representing the decrease of scale of segregation with time are solved simultaneously. The diffusion coefficient of solute in bulk liquid and the cycle time distribution of liquid in the mixer must be determined prior to the calculation of solute concentration. It was found that the mixing time in the mixing systems for the helical screw/draft tube and helical ribbon impeller mixers can be predicted precisely by using this proposed technique.

The technique may be useful in predicting the mixing times of diffusing systems in a batch mixer where a component is dissolved in a high-viscosity liquid.

Acknowledgement

The authors are grateful to Shigeru Nishioka, director of Satake Chemical Equipment MFG., Ltd., for supplying the mixing impellers.

Nomenclature

\[ b = \text{volume ratio of tracer liquid to bulk fluid} \]  
\[ C = \text{nondimensional concentration} \]  
\[ c = \text{concentration} \]  
\[ D = \text{inner diameter of vessel} \]  
\[ D_0 = \text{inner diameter of reference vessel} \]  
\[ D' = \text{inner diameter of draft tube} \]  
\[ D_i = \text{scale-up ratio defined by } (D/D_0) \]  
\[ d = \text{diameter of impeller} \]  
\[ H = \text{height of liquid} \]  
\[ h = \text{height of impeller} \]  
\[ k = \text{positive integer} \]  
\[ L_0 = \text{representative length of flow path} \]  
\[ L(t) = \text{representative length between center of concentration profile of tracer liquid and that of bulk fluid} \]  
\[ n = \text{rotational speed of impeller} \]  
\[ n(t_0) = \text{nondimensional mixing time} \]  
\[ t = \text{time} \]  
\[ t_m = \text{mixing time} \]  
\[ u = \text{flow velocity of liquid} \]  
\[ w = \text{width of blade} \]  
\[ X = \text{nondimensional distance defined by } x/L(t) \]  
\[ x, y, z = \text{axes of three-dimensional coordinates} \]  
\[ \varepsilon = \text{probability of inflow of liquid element per unit time} \]  
\[ \mu = \text{viscosity of liquid} \]  
\[ \text{cal} = \text{calculated value} \]  
\[ \text{exp} = \text{experimented value} \]  
\[ i = \text{arbitrary location and time} \]  
\[ o = \text{initial} \]  
\[ x, y, z = \text{axes of three-dimensional coordinates} \]  
\[ 1, 2 = \text{axial and circumferential flow directions} \]  
\[ ^- = \text{arithmetic mean} \]

Literature Cited