Mixing Time Measured Using a Recyclable Electrochemically Generated Chromophore

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The phenomenon of mixing impacts nearly every aspect of the chemical processing world. Consequently, knowledge of mixing is crucial in the chemical industry to insure safety, product quality, and productivity. While the literature is replete with theory and examinations of factors that affect mixing phenomena, relatively few techniques have been developed to measure mixing time generically. Much of the work on mixing fluids has been reviewed (Harnby et al., 1985; Nagata, 1975).

Mixing time, as defined by Harnby et al. (1985), is the time measured from the point of addition until the contents of the vessel have reached some degree (typically 95%) of a steady-state condition. Logically, techniques developed to measure mixing time have employed some means to monitor the addition of a tracer to a stirred vessel. Solution conductivity was used early on by Biggs (1963) followed by many other investigators to monitor the addition of electrolyte to a mixing tank. The heat of neutralization has been used (Norwood and Metzner, 1960) as a means to follow the mixing rate of an acid injected into a stirred tank of base. Numerous investigators have used a fluorescence technique similar to the one described by Lee and Brodkey (1963) to monitor concentration fluctuations of an added fluorophore to a mixing vessel. Other optical methods, such as absorbance and chemiluminescence, have also been used to monitor mixing time (Harnby et al., 1985; Walker, 1987).

In general, all of these techniques have employed a probe-type measuring device whose active sensing volume is placed at a specified location (for example, behind a baffle and under the impeller) within the stirred vessel. As well, each experimental measurement would require an addition of the tracer species (electrolyte, fluorophore, and so on) to the vessel. Unless the vessel is emptied, the tracer is allowed to accumulate. The accumulation of tracer after several runs represents a continually diminishing signal-to-noise ratio since the measured response of the probe must distinguish newly added tracer over what has accumulated within the tank. This condition becomes even more problematic, when a large mixing vessel is used and the frequent emptying and refilling of the tank solution is very inconvenient and makes for inefficient data collection. This report describes a technique for measuring mixing time that circumvents the problem of tracer accumulation and diminishing signal-to-noise ratio and allows for efficient mixing studies.

Selection of Measurement Probe

While fluorescence has been more often selected as the optical method of choice for measurement of mixing time, should the burden of tracer accumulation be removed, the extra sensitivity provided by fluorescence over a simple optical absorbance technique becomes unnecessary. In this approach, we can use the entire dynamic range of the instrument for each experimental measurement. This approach removes the requirements of ultrahigh sensitivity and large linear working ranges to detect incremental additions of tracer. We have elected to use an off-the-shelf fiber optic colorimeter (Brinkmann PC801) which measures the % transmission of light (whose wave length is determined by interference filters) through a fixed volume of solution at the end of the fiber. In the work described here, a 2-cm path length was used (1-cm opening at the end of the probe). The use of the fiber-optic colorimeter allows for selective monitoring of various chromophores through simple selection of an appropriate wave-length filter.

Electrochemical Chromophore Generation

To avoid the tracer accumulation, an electrochemical scheme, which allows for reuse of starting reagents, has been developed. The scheme is based on the electrochemical generation of a chromophore (tri-iodide ion) from reagents present in the tank (potassium iodide) that is subsequently converted back to starting material upon addition of a chemical redox reagent (ascorbic acid). The approach is outlined in Figure 1. This cycle can be used to measure mixing time via optical absorbance and repeated many times, provided that the following conditions are met.

1. The electrogenerated chromophore has an absorption profile such that some distinct wave length can be used to monitor its presence selectively.
2. The chromophore, upon reaction with the added redox

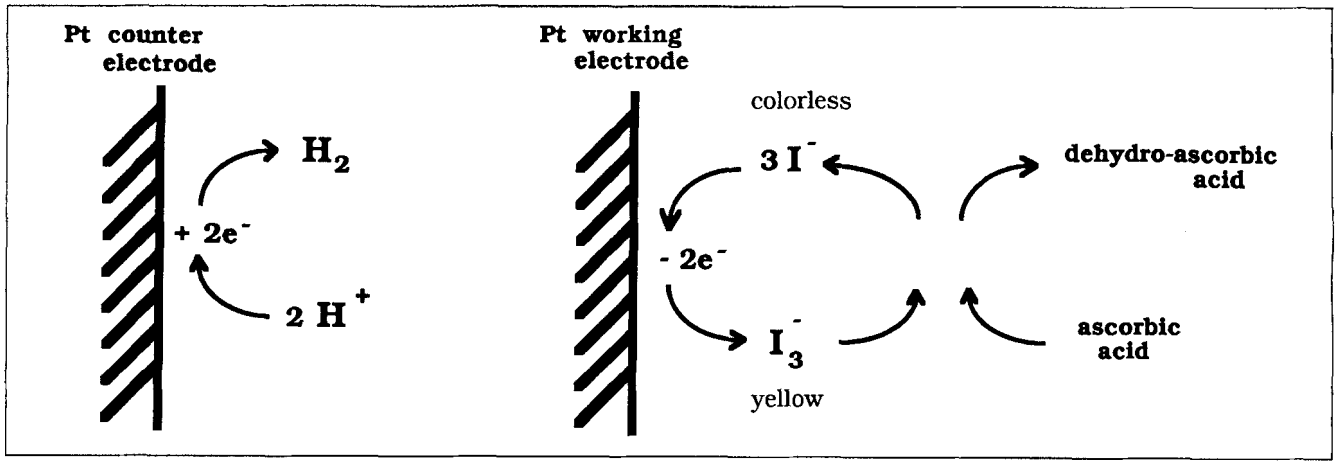

Figure 1. Electrogenerated chromophore/redox reagent scheme used for the measurement of mixing time.

reagent (indirect tracer), is converted back to the starting form from which it was electrochemically generated.

3. The kinetics of the redox reaction between the generated chromophore and the added redox reagent is fast enough to make mixing time the rate-limiting process.

4. The redox reagent, upon reaction with the chromophore, is converted irreversibly to a product that will not interfere with measurement of the chromophore or the successive electrogeneration of chromophore.

5. The counterelectrode reaction should not involve or pro-

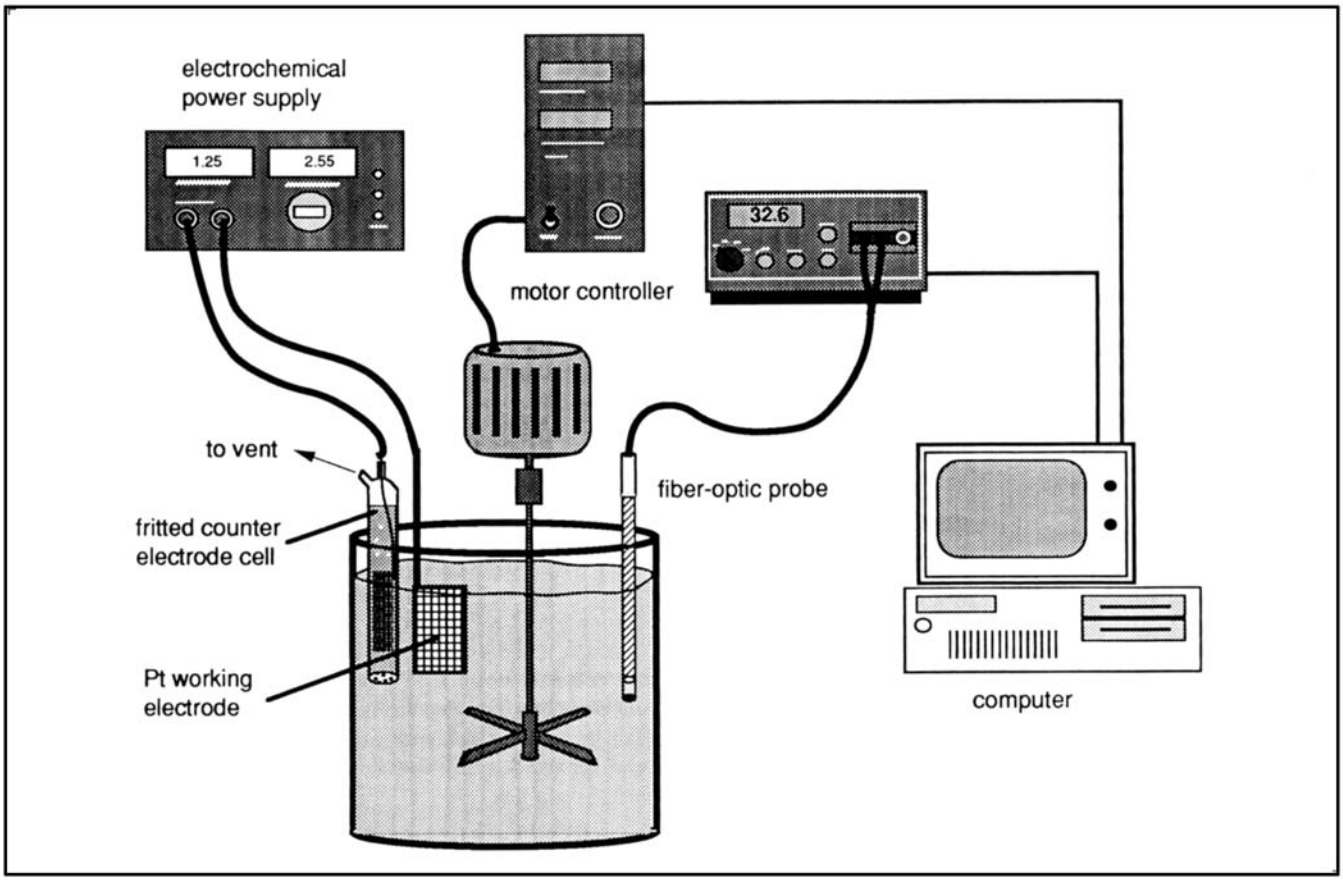

Figure 2. Typical experimental setup for measurement of mixing time using the fiber-optic monitoring of an electrochemically generated chromophore.

duce species that will interfere with the chromophore generation, or redox reaction between the chromophore and added redox reagent.

6. The working and counterelectrodes used should be inert to the electrochemical process involved and not affect other components of the solution or the fluid dynamics during the mixing time measurement.

The chromophore,tri-iodide, is electrochemically generated *in situ* by applying an oxidizing potential to a platinum electrode in a solution containing iodide ion. The tri-iodide appears yellow in aqueous solution. Starch is often used in conjunction with the tri-iodide ion to form an intensely colored complex to indicate its presence at very low concentrations in solution. The starch tri-iodide complex is dark blue. The iodine/iodide redox system has long been used as a volumetric method of analyzing reducing agents (Skoog and West, 1979). The reductant used in this case was ascorbic acid (Vitamin-C). This reductant was chosen to meet condition 4 listed above. Upon reaction with tri-iodide ion, the ascorbic acid is irreversibly converted to dehydroascorbic acid, while the tri-iodide is reduced back to iodide. Mixing time is measured by following the disappearance of tri-iodide in solution (with the fiber-optic probe) upon addition of ascorbic acid (which acts as an indirect tracer). In this way, the electrodes necessary for the production of the chromophore can be removed from the stirred solution during actual data acquisition, thus avoiding extraneous mixing effects their presence may cause.

A typical experimental setup is depicted in Figure 2. A platinum flag electrode (fabricated from platinum wire screen) is used for the production of tri-iodide ion. The necessary counterelectrode reaction is carried out in a separate fritted counterelectrode cell such as the one shown in Figure 2. The counterelectrode reaction in Figure 1 involves the conversion of hydrogen ion to hydrogen gas, which is subsequently vented from the cell. The potential drop between the working and counterelectrodes is minimized with a medium porous glass frit fitted to the counterelectrode cell. This avoids unnecessary contamination of the counterelectrode solution with the solution present in the tank. The electrochemical power supply used was a Hewlett Packard HP 6264B capable of delivering 0-20-V DC. The potential applied across the electrodes was typically 1.5-2.5-V DC. The current flow was typically 50-100 mA during the production of the chromophore.

The materials of construction for the reactor should be resistant to attack from acidic solutions (pH ~ 3). All wetted parts (except for the Pt electrodes) used for this work were either a quality stainless steel or glass.

Results and Discussion

To demonstrate the concept, an experimental setup such as the one depicted in Figure 2 was used. A 1-L vessel was used unbaffled. The fiber-optic probe is positioned to the area of interest within the vessel to measure mixing time. Multiple probe(s)/position(s) are feasible, however, for this demonstration; a single probe used was positioned near the vessel wall half-way up from the bottom of the vessel. The tri-iodide ion was generated until the absorbance at 450 nm as monitored by the probe was approximately a 40-50% transmittance. At this point, the electrodes are turned off and removed from the stirred vessel. The reductant (ascorbic acid) concentration was

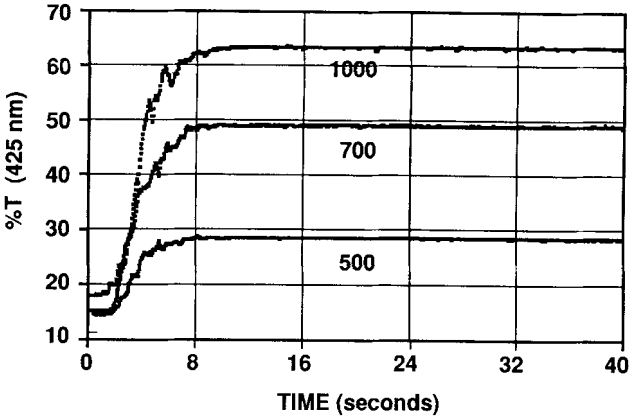

Figure 3. Mixing profiles generated for injections of 500, 700 and 1,000 μL of ascorbic acid solution under identical stirring conditions.

made so that a 1-mL addition to the 1-L stirred solution would completely consume the tri-iodide chromophore. The injection was performed with an electronic digital syringe that delivered the ascorbic acid in less than 2 s. The injections were made to the center of the vortex in the stirred vessel. The data acquisition used was a combined hardware/software package from National Instruments (LabView2) used with an Apple Macintosh IIcx microcomputer. The data acquisition system was triggered simultaneously with the start of the reagent addition.

A condition for measuring mixing time as stated previously is that the kinetics of the redox reaction between the electrochemically generated chromophore and the added redox reagent be fast such that the mixing time is the rate-limiting process. To test this, the mixing time profile was recorded for injections of 500, 700 and 1,000 μL of the stock ascorbic acid solution. In this experiment, the total amount of ascorbic acid injected was insufficient to remove completely the tri-iodide in the stirred tank. All conditions were identical for each injection (such as probe position and mixing speed). The mixing profiles are shown in Figure 3. Allowing for slight deviations in the time for reagent addition (between 1 and 2 for all injections), the mixing time was essentially identical regardless of the levels of ascorbic acid injected. In each case, a constant

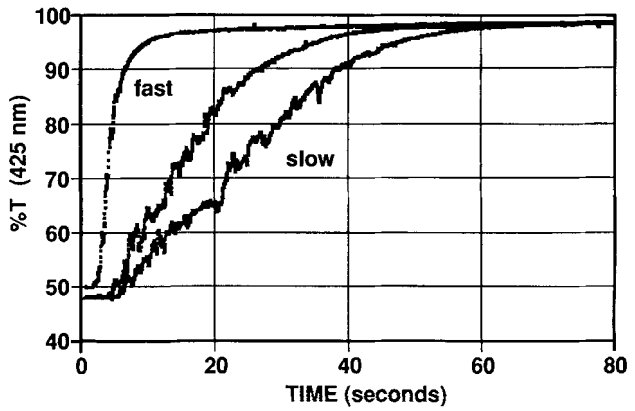

Figure 4. Mixing profiles generated for identical injections of 1,000 μL of ascorbic acid solution at three stirring rates.

percent transmittance level (steady state) was achieved in approximately 11 s after injection. As expected, for varying amounts of ascorbic acid injected, the steady-state signal as indicated by the percent transmission of the probe varies accordingly. Because the mixing time is essentially identical regardless of the levels of ascorbic acid injected, one can conclude that the reaction rate between the ascorbic acid and tri-iodide is fast enough to be limited by mixing time. Supportive of the apparent fast rate constant for the reduction of tri-iodide with ascorbic, a similar redox reaction involving the reduction of tri-iodide back to iodide has been examined (Rao and Mali, 1974). The reduction is reported to be quantitative with a rate constant of $1.51 \times 10^5\ M^{-1} \cdot s^{-1}$ at 25°C and is first-order with respect to tri-iodide.

Figure 4 shows three mixing profiles for which the only parameter to change was the stirring rate of the tank solution. The fast stir rate shows an efficient mixing profile (fast rise to steady state), while the slower stir rates decrease accordingly. It is also worth noting that the "structure" in the mixing profile is "real" and is indicative of the poor micromixing of the injected ascorbic acid. In all cases, the observed mixing time profiles the first-order response typical of mixing processes in stirred tanks with similar systems (Biggs, 1963). Similar curves can be obtainable, for example, should the probe position be changed. Even at a constant stirring speed, the mixing time measured behind a baffle would be considerably slower than that obtained directly below the vortex.

With regard to run-to-run precision, the mixing profiles generated for replicate injections of tracer were essentially identical when the injection time was smaller than the total mixing time. Significant deviations did exist for replicate measured mixing times, when the mixing times were on the same order of time as the injection time (that is, very rapidly stirred tanks). This can be avoided by utilizing an injection technique that consumes very little time to introduce the tracer into the stirred solution.

This method of utilizing an electrochemically generated chromophore with a fiber-optic probe to monitor mixing is ideal to determine the best combination of impeller types, baffle configurations, impeller speeds, and so on, where a large amount of experimental data needs to be collected. A simple change in the position of the fiber-optic probe would allow for comparison of mixing efficiencies at various locations throughout the stirred tank (for example, behind a baffle, near the surface, and under the impeller). Again, a major benefit of this approach is that for each measurement, essentially 100% of the dynamic range of the colorimeter can be used rather than assuring small increments of the range to allow for multiple measurement capability. This signal-to-noise ratio advantage may be necessary when one may wish to examine with greater detail the "structure" within a mixing profile.

It is interesting to note that when a starch indicator was used as an indicator for the tri-iodide ion (as in the case for volumetric iodometric titrations), the system is no longer suitable for use as a means of measuring mixing time. Apparently, the breakup of the starch-tri-iodide complex occurs slowly enough that the mixing time is no longer limiting. For visual impact of the demonstration, however, the starch indicator provides a much more pronounced color change (from dark purple to colorless) than when viewing the tri-iodide ion without starch (from yellow to colorless).

Acknowledgment

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